

INNOVATIVE APPROACHES FOR NANOCELLULOSE FUNCTIONALISATION

Ву

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Declaration

I, Hassan Ahmad, hereby declare that the work in this dissertation was carried out in accordance with the requirements of the University's Regulations and Code of Practice for Research Degree Programmes and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

SIGNED: Hassan DATE: 25-10-2019

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Abstract

Nanocellulose (NC) composite derivatives are a class of materials with many advantageous properties that can be exploited for various industrial applications. This is especially pertinent considering the mandate to adopt bio-based technologies as alternatives to environmentally damaging materials in current commercial products. However, the utilisation of nanocellulose is currently limited by several factors including the cost of production, harmful chemicals and pollutants produced via its production process, lack of research into the capacity for nanocellulose functionalisation and the characteristics of such derivatives, poor mechanical properties of nanocellulose composites, the high hydrophilicity and high thermal conductivity. This thesis describes novel approaches to overcome the stated limitations by detailing the characteristics and mechanisms involved in the production of high performing nanocellulose based composites. The thesis outlines: (I) A unique TEMPO-free oxidation method for achieving a transformed nanocellulose and the mechanism for in-situ grafting of alien nanoparticle substrates; (II) A chlorine-free bleaching alternative for nanocellulose production and the commercial applicability of the developed nanocellulose via adoption into pulp paper packaging and films; (III) the applicability of nanocellulose as an aerogel composite across different aspects including the optimal production process (for example, shear rates) and constituent ratios with polyvinyl alcohol (PVA); (IV) The effect of the oxidation treatment on the mechanical properties of cellulose-based aerogels; (V) the properties of NC-PVA aerogel crosslinked with water-soluble coupling agents, where a nine-fold and three-fold enhancement in storage modulus and strength were achieved respectively; (VI) the properties of cellulose aerogels functionalised with graphene oxide. Overall this thesis paves the way for the commercialisation of novel functionalised nanocellulose materials.

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Table of Contents

Declaration	I
Abstract	II
Acknowledgement	III
List of Figures	VII
List of Tables and Equations	Х
List of Abbreviations	XI
Chapter 1 Introduction	1
1.1 Introduction	1
1.2 Aims of research	
1.3 Specific objectives	
1.4 Outline of thesis	4
1.5 Novelty of research programme	8
1.5.1 Research significance	8
1.5.2 Contributions to the research community	8
Chapter 2 Literature review	10
	10
2.2 Nanocellulose: Types and properties	10
2.2.1 Nanocellulose via the top-down approach	10
2.2.2 Nanocellulose via the bottom-up approach	12
2.2.3 Nanocellulose properties	13
2.2.4 Mechanical and thermal properties	14
2.2.5 Liquid crystallinity and optical properties	16
2.3 Fabrication of nanocellulose	18
2.3.1 Mechanical fabrication	19
2.3.2 Production of cellulose nanocomposites	19
2.3.3 Modified cellulose and polymer aerogels	22
2.4 Applications of nanocellulose and its polymer hanocomposites	22
2.4.1 Incorporation and performance of nanocenulose in construction	20
2.4.2 Other notable applications of nanocentriose incorporation	50 27
2.5 d Granhene and Granhene Ovide	32 37
2.5.1 Graphene and Graphene Oxide	52
2.5.2 Graphene derivatives as a catalyst support	μΛ
2.5.5 Graphene derivatives as a catalyst support	44
2.5.4 CO do a catalyst minimum and a	47
	52
Chapter 3 Methodology	53
3.1 Introduction	53
3.2 Materials	53
3.2.1 Cellulose	53
3.2.2 Polyvinyl Alcohol and Polyethylene Oxide	53
3.2.3 Chemicals	54
3.2.4 Graphite (inorganic filler)	54
3.2.5 Crosslinkers	54
3.2.6 Deionised water	55
3.3 IVIETNOOS	55
3.3.1 Preparation of stock suspensions.	55
3.3.2 Preparing mixed suspensions and treeze-casting	59
3.3.5 Lyophilisation (freeze-arying)	61
5.5.4 Alien hanoparticle incorporation into hanocellulose	01

	62
3.4 Characterisation and testing	63
3.4.1 Physical properties	63
3.4.2 Mechanical properties	66
3.4.3 Analytical techniques	67
3.4.4 Microstructure characterisation	69
3.4.5 Wettability	71
Chapter 4 Morphological and chemical transformation of nanocellulose to enable successive	alien
nanoparticle in-situ grafting	72
4.1 Introduction	72
4.2 Experimental work	73
4.3 Results and discussion	73
4.3.1 Morphology of oxidised cellulose sol-gels	73
4.3.2 Analytical and morphological study of treated cellulose gels	76
4.3.3 Influence of oxidation on the crystal structure of nanocellulose	77
4.3.4 Effect of copper nanoparticle incorporation on nanocellulose	82
4.4 Conclusion	84
Chapter 5 Functionalised nanocellulose as functional additives and films	85
5.1 Introduction	85
5.2 Experimental work	85
5.3 Results and discussion	85
5.3.1 Nanocellulose as coatings and as additives for paper stock preparation.	85
5.3.2 Unveiling a totally chlorine-free nanocellulose additive alternative	88
5.3.3 Investigating nanocellulose films as a notential alternative to polyethene lini	ing of
disposable cups	95
5.4 Conclusion	106
Chanter 6 Ontimisation of cellulose-PVA aerogel content	107
6.1 Introduction	107
6.2 Evnerimental work	107
6.3 Results and discussion	107
6.3.1 Investigation of PVA aerogel morphology and mechanical property	107
6.3.2 Effect of high shear mixing on NC-DVA suspensions and aerogel mechanical property	107
0.5.2 Effect of high shear mixing of Ne+ VA suspensions and deroger mechanical property	(I I I I
6.3.3 Effect of NC content on NC-PVA served morphology	113
6.3.3 Effect of NC content on NC-PVA aerogel morphology 6.3.4 Effect of NC content on NC-PVA aerogel mechanical property and thermal condu	113 ctivity
6.3.3 Effect of NC content on NC-PVA aerogel morphology 6.3.4 Effect of NC content on NC-PVA aerogel mechanical property and thermal condu	113 ctivity 114
 6.3.3 Effect of NC content on NC-PVA aerogel morphology 6.3.4 Effect of NC content on NC-PVA aerogel mechanical property and thermal condu 6.4 Conclusion 	113 ctivity 114 116
 6.3.3 Effect of NC content on NC-PVA aerogel morphology 6.3.4 Effect of NC content on NC-PVA aerogel mechanical property and thermal condu 6.4 Conclusion 	113 ctivity 114 116 118
 6.3.3 Effect of NC content on NC-PVA aerogel morphology 6.3.4 Effect of NC content on NC-PVA aerogel mechanical property and thermal condu 6.4 Conclusion Chapter 7 Cellulose aerogel composites via Tempo-free oxidation 7.1 Introduction 	113 ctivity 114 116 118 118
 6.3.3 Effect of NC content on NC-PVA aerogel morphology 6.3.4 Effect of NC content on NC-PVA aerogel mechanical property and thermal condu 6.4 Conclusion Chapter 7 Cellulose aerogel composites via Tempo-free oxidation	113 ctivity 114 116 118 118 118
 6.3.3 Effect of NC content on NC-PVA aerogel morphology 6.3.4 Effect of NC content on NC-PVA aerogel mechanical property and thermal condu 6.4 Conclusion Chapter 7 Cellulose aerogel composites via Tempo-free oxidation	113 ctivity 114 116 118 118 118 118
 6.3.3 Effect of NC content on NC-PVA aerogel morphology	113 ctivity 114 116 118 118 118 119 119
 6.3.3 Effect of NC content on NC-PVA aerogel morphology	113 ctivity 114 118 118 118 118 119 119 120
 6.3.3 Effect of NC content on NC-PVA aerogel morphology	113 ctivity 114 118 118 118 119 119 120 122
 6.3.3 Effect of NC content on NC-PVA aerogel morphology	113 ctivity 114 118 118 118 119 119 120 122 123
 6.3.3 Effect of NC content on NC-PVA aerogel morphology	113 ctivity 114 118 118 118 118 119 120 122 123 125
 6.3.3 Effect of NC content on NC-PVA aerogel morphology	113 ctivity 114 118 118 118 119 120 122 123 125
 6.3.3 Effect of NC content on NC-PVA aerogel morphology	113 ctivity 114 118 118 118 118 119 120 122 123 125 2 and 126
 6.3.3 Effect of NC content on NC-PVA aerogel morphology	113 ctivity 114 118 118 118 119 120 122 122 123 125 126 126
 6.3.3 Effect of NC content on NC-PVA aerogel morphology	113 ctivity 114 118 118 118 118 119 119 120 122 123 125 2 and 126 126 127

8.3 Results and discussion	127
8.3.1 Functional groups of crosslinked NC aerogels	127
8.3.2 Reaction mechanisms of NC-PVA coupling	131
8.3.3 Morphology of aerogel composites	133
8.3.4 Compressive property of cellulose-PVA aerogels	135
8.3.5 Influence of crosslinkers on the basal spacing of NC-PVA aerogels	138
8.4 Conclusion	139
Chapter 9 Robustness of graphene oxide amalgamated cellulosic aerogel composites	140
9.1 Introduction	140
9.2 Experimental work	140
9.3 Results and discussion	141
9.3.1 Purity of GO	141
9.3.2 Interaction of GO with NC as aerogel composites via low shear mixing	144
9.3.3 Strengthening NC-GO composites with glyoxal via high-shear mixing	148
9.4 Conclusion	152
Chapter 10 Final appraisals	154
10.1 Summary of the research	154
10.2 Major conclusions	154
10.3 Future work	157
References	159
Appendix	191

List of Figures

Figure 1.1 Thesis layout7
Figure 2.1 Visual comparison via SEM/TEM images12
Figure 2.2 Various processing routes to achieving nanocellulose particles [44]14
Figure 2.3 Method routes to isolate nanocellulose fibrils and crystals
Figure 2.4 Processing routes to achieving aerogels and foams from nanocellulose [78]21
Figure 2.5 Potential application areas of different types of nanocelluloses based on their specific structure-properties relationships [127]
Figure 2.6 3D bio-printed cartilage structures using Nanocellulose (left) and other applications where nanocellulose can be incorporated (right) [44,170]
Figure 2.7 GO dispersed in water and 13 organic solvents (a), AFM image of GO sheets deposited onto a mica substrate (b) and UV-vis absorption spectra (c)
Figure 2.8 Photovoltaic device structure (a) and corresponding energy level diagram between the top (AI) and bottom (ITO) electrode (b)
Figure 2.9 A 50 μm aperture partially covered by graphene and its bilayer. The line scan profile shows the intensity of the transmitted white light along the yellow line
Figure 2.10 Schematic view of various metal clusters adsorbed on a stretched graphene sheet 45
Figure 2.11 Proposed structural models of GO,
Figure 2.12 GO model, demonstrating various oxygen functional group types distributed across aromatic regions (a) and graphite oxidation methods
Figure 3.1 Chemical monomer structure of cellulose53
Figure 3.2 Chemical monomer structure of polyvinyl alcohol54
Figure 3.3 Chemical structure of (a) glyoxal, (b) vinyltrimethoxysilane, (c) (3-Aminopropyl) triethoxysilane
Figure 3.4 Process of NC purification (a) Sigma 6k15 500 ml centrifuge flask displaying the salty water before decanting
Figure 3.5 (a) schematic of the tempo-free NC fabrication process; (b) TEM micrographs of the NFC network with the graphs in bi and bii corresponding to the width of the fibrils; (c) TEM micrograph of NCC; (d) size distribution of NC analysed by intensity
Figure 3.6 Schematic illustration of GO production via modified Hummer's method
Figure 3.7 Stock suspension of PVA59
Figure 3.8 Procedure of producing aerogels (a) mixed NC-PVA suspensions poured in aluminium moulds and being weighed using tray
Figure 3.9 Phase diagram of water61
Figure 3.10 Copper incorporated solutions and freeze dryer used to lyophilise the Eppendorf's of each sample for characterisation
Figure 3.11 Displays the production of recycled paper through (a) the Axform Dynamic Sheet Former, (b) Axform Press, (c) Axform Dryer and (d) the final 100 gsm paper sheets with varied nanocellulose dosages

Figure 3.12 NanoSight LM10 Microscope and schematic illustration of NanoSight operation
Figure 3.13 TA Fox 200 instrument and schematic illustration of thermal conductivity operation 64
Figure 3.14 Displays (a) Emtec fibre potential analyser on the left and Emtec charge analysing system on the right, (b) L&W burst strength tester and (c) L&W Bendsten porosity tester
Figure 3.15 Aerogels cut to cuboid specimens using a diamond band saw and compression testing using Instron 5900 series
Figure 3.16 Displays (a) Lloyd LRX tensile strength tester, (b) Messmer TMI sample puncher and (c) L&W compressive strength tester67
Figure 3.17 Perkin Elmer machine and schematic illustration of the ATR-FTIR mechanism
Figure 3.18 X-ray diffractometer Bruker machine69
Figure 3.19 Renishaw inVia Raman microscope and schematic illustration of Raman scattering 69
Figure 3.20 Displays (a) Polaron-SC7640 Sputter Coater, (b) Agar Turbo Carbon Coater, (c) Zeiss Supra 35VP SEM with an EDX attachment and (d) JEOL JEM-2100F TEM70
Figure 3.21 Displays (a) drop shape contact angle analyser and (b) contact angle classification 71
Figure 4.1 Comparative visual analysis of MCU and MCT via TEM micrographs of (a) MCU particles and (b) MCT particles; SEM images of (c) an MCT sheet layer and (d) MCU particles;
Figure 4.2 XRD spectra comparing MCU with MCT. The theoretical pattern of 90% cellulose Iβ + 10% cellulose II was also constructed using the cellulose II pattern from the ICDD database to signify its similarity to the MCT curve
Figure 4.3 FTIR spectra displaying (a) the overall peaks of MCU, MCT, MCU-Cu and MCT-Cu, (b) convoluted curves of MCU to highlight the peaks in the OH and double bond regions against the structure of cellulose Iβ,
Figure 4.4 EDX images showing (a) nanoparticle on the surface of MCU (Inlens detector), (b) nanoparticles (bright spots) on the sample holder substrate (Inlens detector)
Figure 4.5 Raman spectra analysis of Cu nanoparticles on MCU against MCT84
Figure 5.1 Comparative results of NFC (green) and NCC (blue) against blank paper sheet as control, displaying (a) burst index and (b) porosity index
Figure 5.2 Brown paper sheets coated with NC and SEM micrograph displaying stained NC to differentiate between NC coat and uncoated region
Figure 5.3 Relationship between hypochlorous acid (HOCl) and hypochlorite ion (OCl ⁻) at various pH values (which is inversely proportional to the ORP)
Figure 5.4 Comparative results of zeta potential and particle charge detection against anionic blank paper sheet as control
Figure 5.5 Comparative mechanical and physical property results of NC additives against retention aid additive, displaying (a) tensile strength index, (b) compressive strength index, (c) burst strength index and (d) air permeability index
Figure 5.6 Displays (a) NFC films at increasing NFC wt% concentration and (b) 0.4 wt% NFC film treated at varying drying conditions
Figure 5.7 Compares the transparency of NFC-LDPE compositions to the pure LDPE film
Figure 5.8 SEM surface micrographs of (a) a 0.4 wt% NFC film treated at 70 °C, (b) NFC-LDPE 90-10% film and (c) NFC-GPTMS film

Figure 5.9 DSC-TGA graphs of (a) pure LDPE, (b) pure NFC, (c) NFC-GPTMS 98-2%, (d) NFC-LDPE 90- 10%, (e) NFC-LDPE 80-20%, (f) NFC-LDPE 70-30%, (g) NFC-LDPE 60-40%, (h) NFC-LDPE 50-50% and (i) NFC-LDPE 90-10% modified with GPTMS
Figure 5.10 Moisture absorption comparison between the varied compositions
Figure 6.1 SEM micrograph of PVA aerogel and inset enlargements of the three distinct morphologies Dendritic morphological zone (DMZ), interstitial morphological zone (IMZ), and lamellar morphological zone (LMZ)
Figure 6.2 Compressive stress-strain plot of PVA aerogel and corresponding SEM cross-section of PVA microstructure to scrutinise the morphological zones' effect on the mechanical property 111
Figure 6.3 Displaying (a) TEM micrograph of the supernatant NCC shown inset with a red-dotted line of where the separation NCC and NFC can be seen, and (b) Stress-strain curves of compressed aerogels prepared via LSM and HSM
Figure 6.4 SEM analysis displays to sets of comparative micrographs with a-c displaying different compositions of aerogels prepared via HSM: (a) NC-PVA 50-50, (b) NC-PVA 60-40, (c) NC-PVA 70-30, and d-e displaying the before and after ambient moisture uptake of aerogels
Figure 6.5 Comparison of differing aerogel compositions as well as the weathering effect through (a stress-strain graph and (b) density and thermal conductivity bar chart of the aerogels
Figure 7.1 Comparative visual analysis of MCU-PVA and MCT-PVA SEM cross-sectional images 120
Figure 7.2 XRD spectrums of PVA aerogel composites
Figure 7.3 Shows (a) stress-strain graphs of the different PVA aerogel composites and (b) comparing their densities
Figure 8.1 FTIR spectra displaying (a) the overall peaks of NC-PVA, NC-PVA-GLY, NC-PVA-VTMS and NC-PVA-APTES, and (b) breakdown of NC-PVA-GLY spectra using NC-PVA and GLY peaks 130
Figure 8.2 Likely chemical reaction mechanisms of (a) NC-PVA (b) NC-PVA-GLY (c) NC-PVA-VTMS and (d) NC-PVA-APTES
Figure 8.3 Comparative visual analysis of NC-PVA with the addition of crosslinks via SEM cross sectional images of (a) NC-PVA(s), (b) NC-PVA(L), (c) NC-PVA-GLY(s), (d) NC-PVA-GLY(L), (e) NC-PVA-VTMS and (f) NC-PVA-APTES. The scale on the inset SEM images is at 2 μm
Figure 8.4 Shows (a) stress-strain graphs of the aerogel composites and (b) comparing their mean densities
Figure 8.5 XRD spectra comparing the peaks of coupled aerogels
Figure 9.1 Analysis of GO flakes via (a) Raman spectra and inset peak intensities analysed via OriginPro (b) FTIR spectra and functional groups142
Figure 9.2 SEM micrographs displaying (a) GO (b) GO-NC (c) GO-PVA (d) GO-NC-PVA with inser- enlargement of microstructural patterns at a scale of 100 μm
Figure 9.3 Stress-strain graphs comparing aerogels prepared through LSM (a) without PVA and (b) with PVA; along with (c) a density bar chart of the aerogel composites
Figure 9.4 SEM micrographs displaying (a) NC-GLY (b) NC-GO-GLY (c) PVA-GLY (d) NC-GO-PVA (e) NC GO-PVA-GLY (f) NC-rGO-PVA-GLY with inset enlargement of microstructural patterns at a scale of 20 μm
Figure 9.5 Stress-strain graphs of aerogels prepared through HSM (a) investigating the inclusion of PVA in aerogels and (b) comparing GO and rGO amalgamated aerogels, and (c) density bar chart of the aerogel composites

List of Tables and Equations

Table 2.1 Mechanical properties of notable cellulose particles [42]	14
Table 2.2 Property enhancements of several nanocellulose-based polymer nanocomposite	s [90] 23
Table 2.3 Property enhancements of several graphene-based polymer composites	
Table 2.4 Catalytic reactions using GO as a catalyst	
Table 3.1 Quantitative measurements of the peak sizes in Figure 3.5d	57
Table 5.1 Comparative quantitative measurements of suspensions	89
Table 5.2 Transmittance of NFC films at varying concentrations	
Table 5.3 Displays initial contact angle measurement, tensile strength, density an conductivity for the varying composition films	d thermal
Table 6.1 Mean compressive property of LSM and HSM NC-PVA aerogels	113
Table 6.2 Mean compressive property of varied and weathered aerogel compositions	116
Table 7.1 D-value of the PVA aerogel composites	123
Table 7.2 Compressive property of the PVA aerogel composites	125
Table 8.1 Average bond enthalpies [378]	132
Table 8.2 Mean compressive property of the aerogel composites	137
Table 9.1 Composition of suspensions mixed from 5% stock solution of the reagents	
Table 9.2 Mean compressive property of GO aerogels	
Table 9.3 Mean compressive property of GO and GLY aerogels	152

71

List of Abbreviations

MFC	Microfibrillated cellulose
MCC	Microcrystalline cellulose
BC	Bacterial cellulose
NC	Nanocellulose (NFC and NCC)
NFC, NCF	Nanofibrillated cellulose
NCC	Nanocrystalline cellulose
MCU	Untreated micro-cellulose
MCT	Treated micro-cellulose
PVA	Poly(vinyl) alcohol
GO	Graphene oxide
rGO	Reduced graphene oxide
LDPE	Low-density polyethylene
PLA	Polylactic acid
VTMS	Vinyltrimethoxysilane
APTES	(3-aminopropyl)triethoxysilane
GLY	Glyoxal
(s)	100×100×10 mm aerogel samples
(L)	100×100×15 mm aerogel samples
NaOCI, NaClO	Sodium hypochlorite
NaOH	Sodium hydroxide
HOCI	Hypochlorous acid
OCI	Hypochlorite ion
ОН	Hydroxide
MD	Machine direction
CD	Cross direction
SCT	Short-span compression test
ORP	Oxidation-reduction potential
GPTMS, GPTS	(3-glycidoxypropyl)trimethoxysilane
PMMA	Poly(methyl methacrylate)
PANi	Polyaniline
PU	Polyurethane
DMF	N,N-dimethylformamide
PS	Polystyrene

OPV	Organic photovoltaic
ITO	Indium tin oxide
PCE	Power conversion efficiency
QD	Quantum dot
CdS	Cadmium sulfide
РЗНТ	Poly(3-hexylthiophene)
PCBM	Phenyl-C61-butyric acid methyl ester
PEDOT	Poly(3,4-ethylene dioxythiophene)
PSS	Poly(styrene sulfonate)
Pt	Platinum
ТМВ	3,3,5,5-tetramethylbenzidine
TiO ₂	Titanium dioxide
wt%	Weight by weight percent
LSM	Low-shear mixing
HSM	High-shear mixing
LMZ	Lamellar morphological zone
IMZ	Interstitial morphological zone
DMZ	Dendritic morphological zone
SSZ	Steady-state zone
TZ	Transition zone
CA	Contact angle
FWHM	Full width at half maximum
TGA	Thermogravimetry analysis
TEM	Transmission electron microscopy
SEM	Scanning electron microscopy
EDX	Energy-dispersive X-ray
FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffraction
AFM	Atomic force microscopy
NTA	Nanoparticle tracking analysis
d-value	Basal spacing (d)
EA	Modulus of elasticity in axial direction
Eτ	Modulus of elasticity in transverse direction
Ιβ	Beta cellulose

Chapter 1 Introduction

1.1 Introduction

Climate change and the persisting global environmental degradation have placed significant pressure on the world population to resolve the unstainable nature of contemporary human societies. Materials science serves as the critical underpinning that will ultimately determine the success and pace of this development towards sustainability. The offer of sustainable, environmentally friendly materials facilitates the replacement of their unsustainable counterparts and opens up the potential for novel applications. Cellulose is one such material as the most abundant biological polysaccharide in the world. It is an inexpensive and sustainable natural polymer that presents an attractive material choice for researchers attempting to create environmentally friendly products. Functionalised nanoand micro-scale cellulose offer immense potential for scientists in creating advanced nanomaterials, reinforcements or to simply enhance the structure of macroscopic cellulose [1,2]. Existing methods of producing nanoscale fibrillated cellulose require high acid concentrations and energy consumption to produce relatively low yields of less than 30%. These methods, such as mechanical defibrillation, can damage the microfibril structure by reducing the degree of crystallinity and molar mass, and its performance requires high energy consumption (700-1400 MJ/kg) depending on the number of passes through a mechanical homogeniser [3–5]. Expensive pre-treatments, mainly TEMPO-NaBr-NaClO [6,7], are used to overcome such limitations presented by mechanical defibrillation despite removing non-cellulose composition and demanding treatment of liquid waste. The nano component of cellulose offers access to innovative tailoring in its material chemistry. The macroscopic structure of cellulose can thus be considerably enhanced by functionalising the nanoscopic unit, nanocellulose (NC), enabling existing cellulose products to be improved. Nanocellulose has extraordinary potential in various industry sectors, especially in paper and packaging. Depending on where it is added in a typical papermaking process, nanocellulose can enhance both the wet and dry strength of paper. Moreover, as a nanofibre, nanocellulose will mesh the pulp together in the stock preparation. Thus, improved material utilisation may be achieved from nanocellulose acting both as a strength agent and retention aid. Nanocellulose may be used to create a porous, ultralight material called an aerogel. Aerogels a class of nanomaterials possessing very desirable properties including high porosity, low density and low thermal conductivity [8]. They are typically produced using a supercritical extraction technique to replace the liquid component of a gel with a gas [9] and hold promise for applications in many industries including absorbents, gas sensors, energy storage and supercapacitors [10]. Their application has, thus far, been limited however due to the high costs of the raw materials required [11] and the high energy consumption needed for the supercritical production process. Inorganic aerogels have been the primary focus of research into aerogels in the past with these being very brittle and thus limited in their applicability [12–14]. This has encouraged research into the development of different composite aerogels that offer superior properties that overcome current limitations [15–18]. The use of cellulose within aerogels as part of a composite has been widely studied [19–25] with results revealing that such aerogels that incorporate cellulose fibrils possess higher elasticity and surface area [24]. This is a result of the high aspect ratio of cellulose fibres and the strong hydrogen bonds present which create networks that enhance stress transfer [24]. Cellulose may be functionalised with other compounds to impart desired material characteristics into a composite aerogel. The hydroxyl groups in the glucosyl units of cellulose (β -1,4-D-anhydroglucopyranose) at positions 2, 3 and 6 presents many possibilities for functionalisation to create useful derivative materials. The hydroxyl group at position 6 is considered the most reactive group with C-2 OH possessing a lower reactivity and C-3 OH being the weakest due to nearby oxygen atoms forming hydrogen bonds [26]. These hydroxyl groups can be functionalised through different reactions including polycondensation, acetalisation and esterification among others. A chemical substance may be used with at least two reactive groups to form covalent bonds between cellulose polymer chains by reacting with the hydroxyl groups. It may also bind weakly linked cellulose layers. Numerous substances have been found to act as crosslinking agents for cellulose such as glyoxal, dichloroethane, formaldehyde, vinyltrimethoxysilane (VTMS) and (3-Aminopropyl) triethoxysilane (APTES) [27]. Cellulose-based aerogels coated with methyltrimethoxysilane have exhibited high porosity, high oil

absorption capacity, super-hydrophobicity and very high flexibility [28]. Moreover, glyoxal is an environmentally friendly crosslinking agent that can improve the wet mechanical properties of cellulose [27]. Furthermore, VTMS may crosslink with cellulose to create compounds with increased permeability, lower crystallinity and higher flexibility [29]. APTES, on the other hand, is a toxic aminosilane that's commonly used to functionalise surfaces with alkoxysilane molecules in a process known as silanisation. APTES has previously been functionalised with nanocrystalline cellulose (NCC) where the thermal stability of the APTES modified NCC was increased with the decomposition of modified NCC occurring at a temperature of about 10 °C higher. APTES has also been found to increase the hydrophobicity of cellulose fibrils with a 90% reduction in the surface polarity of NFC observed [30].

1.2 Aims of research

The project aims to develop the enhanced nanocellulose, discern its potential as functional additives and explore its capacity for surface functionalisation. It also aims to develop functionalised nanocellulose aerogels and determine optimal production techniques. It intends to characterise these aerogels and ascertain their assorted properties for various industrial applications.

1.3 Specific objectives

To meet the aims of the research project, specific objectives have been set and are detailed as follows:

- Investigate and optimise the processing parameters for producing nanocellulose and graphene oxide as well as for preparing aerogels.
- Characterise the individual constituents of nanocellulose and graphene oxide for enhanced optimisation as well as develop an understanding for growing graphene on cellulose – observing the physical and chemical bonding structures.
- Inspect novel techniques in enabling the produced nanocellulose to be grafted with alien nanoparticles.
- Differentiate the different aspect ratios of nanocellulose fibres produced and determine their role in influencing the mechanical/physical property of aerogels.

- Explore the influence of tailoring the constituents using suitable crosslinkers and mechanism in influencing the mechanical and physical properties of the formulated nanocellulose aerogels.
- Synthesise the functionalised nanocellulose-graphene aerogel with the use of crosslinkers and optimise the formulation of the hybrid systems.

1.4 Outline of thesis

The presented thesis consists of ten chapters as illustrated in Figure 1.1. A brief overview of the chapters is outlined as follows:

Chapter one: Introduction

This chapter outlines an overview of the current interests revolving nanocellulose and aerogel materials with a scope of the research aims and objectives.

Chapter two: Literature review

This chapter presents a comprehensive review of nanocellulose and graphene aerogels, identifying the bottlenecks and potential capabilities of such materials. The review comprises full properties of both nanocellulose and graphene allotropes as well as the influence of tailoring these constituents with other nanomaterials and polymers on the aerogel functionality.

Chapter three: Methodology

This chapter describes the experimental works conducted for the preparation of nanocellulose and graphene oxide production as well as to prepare aerogel composites. It also details the characterisation techniques carried out for the prepared materials. This chapter also includes the methodologies for a pilot trial in strengthening recycled paper packaging using the produced nanocellulose as an additive.

Chapter four: Morphological and chemical transformation of nanocellulose to enable successive alien nanoparticle in-situ grafting

This chapter thoroughly investigates the use of TEMPO-free oxidation via hypochlorite bleaching to formulate a unique NFC capable of accommodating in-situ grafting of alien nanoparticles.

Characterisation of the developed NFC was used to determine the chemical and morphological effects of the TEMPO-free oxidation process.

Chapter five: Functionalised nanocellulose as functional additives and films

This chapter outlines the commercial applicability of the developed NC via adoption into pulp paper packaging and films. The addition of NC as an additive in recycled fibre was investigated for the mechanical and physical properties of brown paper. An alternative TEMPO-free oxidation in the form of peroxide bleaching was used to produce an NC additive which was also analysed and compared. Additionally, NC films were developed and tested to determine an optimal composition with lowdensity polyethylene.

Chapter six: Optimisation of cellulose-PVA aerogel content

This chapter studies the applicability of NC as an aerogel composite across different aspects, including the determination of the optimal production process, such as shear rates and constituent ratios for mechanical property performance and thermal conductivity. The effect of freeze-casting on the morphology and mechanical property of PVA aerogels was explored. The extent of moisture uptake and its effect on the aerogel performance was determined.

Chapter seven: Empowered cellulose aerogel composites via Tempo-free oxidation

This chapter details the effect of TEMPO-free oxidation treatment on the physical and mechanical properties of the cellulose-based aerogels. The resulting NC-PVA composites were analysed and a description of the structure and chemistry in relation to packing arrangement was provided.

Chapter eight: Functionalising cellulose aerogel composites with water-soluble dialdehyde and organosilanes

This chapter involves crosslinking NC-PVA aerogels with water-soluble coupling agents to amplify the mechanical properties. The functionalised composites were characterised with FTIR to identify the chemical profile and a description of the reaction mechanisms was presented. SEM imaging and mechanical testing were used to identify the morphology and performance characteristics of the composites with different thickness profiles.

Chapter nine: Functionalising cellulose aerogel composites with graphene oxide

This chapter discusses the functionalisation of cellulose-based aerogels with graphene oxide in relation to the mechanical properties. The composite was developed with the addition of components including NC, GO, PVA and GLY and the effect on the mechanical properties of the aerogels were compared with the addition of each component.

Chapter ten: Conclusion and future work

This chapter summarises the overall thesis findings, reflecting the significance to the research community as well as discussing prospects and recommendations.



Figure 1.1 Thesis layout

1.5 Novelty of research programme

1.5.1 Research significance

The research presents a comprehensive study into the development of nanocellulose via a novel TEMPO-free oxidation procedure in the form of NaClO including an analysis of the characteristic structural and physical properties exhibited. The treatment was found to cause the cellulose crystal structure to partially convert to an alternative arrangement. The treated NC was then functionalised with alien nanoparticles to test its capacity for surface functionalisation, namely with copper nanoparticles. For the tested case, it enables the development of conductive cellulose. The treated NC was investigated for its ability to serve as an immediate packaging additive where it was found to elevate the paper grade due to significant strength and retention enhancement. NC-PVA aerogels were then developed and investigated for optimal production techniques to achieve maximum property enhancements and test the effect of moisture absorption. Moreover, the aerogel functionalisation of PVA with different aspect ratios of nanocellulose was investigated including that of amalgamated nanocellulose aspect ratios to ascertain effects of each aspect ratio. It was determined that incorporating both aspect ratios into the aerogel imparts desirable properties from each form of cellulose aerogel including polydispersion and high mechanical toughness. Finally, the optimised NC-PVA aerogel was coupled with different crosslinking agents including Glyoxal and Graphene Oxide revealing significant compressive modulus, strength and toughness improvement. The study establishes multiple approaches towards enhancing the properties of nanocellulose and nanocellulose based aerogels and promotes the industrial applicability of such materials.

1.5.2 Contributions to the research community

1.5.2.1 Peer-reviewed journals (Appendix)

 Hassan Ahmad, Mizi Fan, Interfacial properties and structural performance of resin-coated natural fibre rebars within cementitious matrices, Cement and Concrete Composites (March 2018). <u>https://doi.org/10.1016/j.cemconcomp.2017.12.002</u>

- Hassan Ahmad, Mizi Fan, David Hui, Graphene oxide incorporated functional materials: A review, Composites Part B Engineering (July 2018). https://doi.org/10.1016/j.compositesb.2018.02.006
- 3. Hassan Ahmad, Aimée Hutton, Nanocellulose strength additives for recycled fibre, Paper Technology International, The Journal of the Bioforest Products Sector (November 2018).
- 4. Ao Li, Dezhong Xu, Lu Luo, Yalan Zhou, Wen Yan, Xin Leng, Dasong Dai, Yonghui Zhou, Hassan Ahmad, Jiuping Rao and Mizi Fan, *Overview of nanocellulose as additives in paper processing and paper products, Nanotechnology Reviews, (May 2021).*

https://doi.org/10.1515/ntrev-2021-0023

1.5.2.2 International conferences

- 1. Hassan Ahmad, Mizi Fan, Graphene oxide enhanced nanocellulose aerogel for highly insulated building materials, 25th International Conference on Composites/Nano Engineering (July 2017).
- 2. Hassan Ahmad, Mizi Fan, Nanocellulose for enhanced packaging papers, PITA PAPERmatters Conference (September 2018).
- 3. Hassan Ahmad, Functionalised nanocellulose & its enhanced products, CEPI Blue Sky Young Researchers & Innovation Award (November 2019).

1.5.2.3 Book chapter

1. Hassan Ahmad, Chapter 11 - Nanocellulose based composites, Plant Fibre: its chemistry, structure and advanced products (2020).

Chapter 2 Literature review

2.1 Introduction

This chapter provides a comprehensive review of nanocellulose and graphene, identifying the limitations and potential capabilities of such materials. The review details the characteristics and properties of both nanocellulose and graphene allotropes as well as the influence of tailoring these constituents with other nanomaterials and polymers on the material functionality as aerogel composites. Cellulose, an organic polysaccharide with a linear chain of repeating β -D-glucopyranose units, was first extracted and identified by Anselme Payen in 1838 from plants. It is a substance found naturally in plants and wood, working as a significant structural component of the primary cell wall. It is the most abundant organic polymer present in earth representing 40-50 wt% of the content of wood (around half is in nanocrystalline form with the other half being amorphous) as well as a large portion of other plants including 90 wt% of cotton fibres. The annual production of cellulose is estimated to be around 7.5 x 10¹⁰ tonnes. The increasing demand for renewable and sustainable products has put the spotlight on cellulose which also has the advantage of being non-toxic and biodegradable. Due to the hierarchical structure and semicrystalline nature of the material, nanoparticles can be isolated using mechanically or chemically induced processes. These nanoparticles, termed nanocellulose has attracted a lot of interest as functional nanomaterials and as reinforcing materials. The intensive research into the capabilities of nanocellulose has revealed many desirable properties including a reactive surface that can be used for surface modification, hydrophilicity, high modulus and specific strength. Nanocellulose was first isolated by Turbak et al in the early 1980s [31,32]. One of the main challenges in utilising nanocellulose is its strong tendency for self-association due to the presence of many surface hydroxyl groups causing aggregation during the preparation of a nanocomposite limiting its capability for mechanical reinforcement.

2.2 Nanocellulose: Types and properties

2.2.1 Nanocellulose via the top-down approach

The type of cellulose extracted varies depending on the material source and the approach to isolation.

A top-down approach encompasses the disintegration of lignocellulosic biomass (plant materials), the most abundantly obtainable raw material, and dates back to 1946 where Wuhrmann et al. is said to have used sonication methods to break down and separate natural cellulose fibres into finer fibrils while maintaining the fibrous texture [33]. Contemporary top-down methods toward producing nanocellulose may include the use of grinders to grind wood pulp using high shear fibrillation [34–38]. Nanocellulose produced through such an approach is termed nanofibrillated cellulose (NFC) where it is broken down from the parent microfibrillated cellulose (MFC). However, there are some misconceptions in the literature of distinguishing MFC from NFC fibres and has therefore somewhat broadened the aspect ratio range, thus overlapping each other. The high aspect ratio of NFC is considered to be at 500-2000 nm in length with a width of 4-20 nm, whereas the aspect ratio of MFC is about 500-10000's nm in length and width of 50-400nm. Microcrystalline cellulose (MCC) can be broken down from MFC fibres where its aspect ratio ranges at 10-50 μ m in length with a width of 10-50 µm, therefore you can expect the length MFC to reach a length of up to 50 µm. Cellulose nanocrystals with lengths of 50-500 nm length of 3-5 nm widths can also be produced by further mechanical or chemical procedures (see Figure 2.1). Typically, NCC is achieved through acid hydrolysis of cellulosic fibres. NCC has higher crystallinity relative to NFC with hydroxyl accessibility on its surface, giving rise to further functionalisation through surface modification.



Figure 2.1 Visual comparison via SEM/TEM images of (a) MCC, (b) MFC, (c) NFC, (d) NCC, and e) BC [39–42]

2.2.2 Nanocellulose via the bottom-up approach

The bottom-up approach towards producing nanocellulose involves biosynthesis through celluloseproducing bacteria such as the *Komagataeibacter* species. The nanocellulose produced in this way is called bacterial cellulose (BC) and features pure cellulose fibrils without any lignin or pectin content and possesses lateral dimensions between 25 and 85 nm with lengths up to several micrometres (see Figure 2.1). While the dimensions of BC and NFC are similar, differences in the fibrils mainly comprise the purity and crystallinity of the material. Whereas BC is pure cellulose, NFC is often a composite composed of cellulose and hemicellulose and is based on plant cell wall microfibrils. The two types of cellulose also possess different proportions of I_a and I_b crystal structures where BC consists of a high proportion of I_a (one chain triclinic unit cell crystal structure) while NFC is mainly composed of I_b (monoclinic unit cell). The two crystal structures coexist and form the intrinsic structure of natural cellulose. Bacterial cellulose may be produced by several species of bacteria including and principally that of *Komagataeibacter xylinus* (*formerly known as Acetobacter xylinum and Gluconacetobacter xylinus*) which is a highly pervasive species that is found in fermentation processes involving sugars and plant carbohydrates. *Komagataeibacter xylinus* has the ability to use several sugars to synthesise cellulose, of which glucose is commonly used in labs where a four-enzymatic step process has been characterised in the conversion. One of the key issues in the commercial production of BC is that a significant portion of the glucose supplied to *Komagataeibacter xylinus* is converted into gluconic acid, an undesired by-product, while around 50% of glucose is converted into cellulose. *Komagataeibacter xylinus* can produce nanocellulose with diameters between 10-30 nm. The bacterium can be guided to produce a network of fibrils of nearly any architecture.

2.2.3 Nanocellulose properties

In view of the different approaches to producing nanocellulose, there are also numerous processing techniques that could be adapted to utilise the desired nanocellulose for different purposes (see Figure 2.2). These processing techniques could also complement each other to feature different structural properties, increase functionality, or even to further reduce the energy consumption of manufacturing nanocellulose. For example, enzymatic treatment could be used before mechanical processing, such as high-pressure homogenisation, to reduce energy consumption by up to 15 folds [43]. One can, therefore, expect that the properties of nanocellulose are also variant between these approaches.



Figure 2.2 Various processing routes to achieving nanocellulose particles [44]

2.2.4 Mechanical and thermal properties

The mechanical properties of nanocellulose have been determined using AFM and spectroscopic techniques. However, the properties measured may be influenced by several factors that must be considered before comparing the properties of different samples including crystallinity, defects, the measurement techniques used, crystal structure and anisotropy. A summary of the mechanical properties of some cellulose types and the measurement instrument used is provided in Table 2.1. The difficulty associated with testing such small samples can be seen to have impacted the results with a high probability of errors.

Table 2.1 Mechanical	properties of notable cellulose i	particles [[42]	
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Material	E₄ (GPa)	E⊤ (GPa)	Instrument used	Ref
MCC	25 ± 4		Raman	[45]
NCC – plant	57, 105		Raman	[46]
NCC – wood		18-50	AFM indentation	[47]
t-NCC	143		Raman	[48]
t-NCC – acid	151 ± 29		AFM 3-pt bend	[49]
t-NCC – TEMPO	145 ± 31	9 ± 3	AFM 3-pt bend; & indentation	[49,50]
BC	78 ± 17; 114		AFM 3-pt bend; & Raman	[51,52]

Where: E_A = modulus of elasticity in axial direction, E_T = modulus of elasticity in transverse direction The elastic properties of nanocellulose have been the focus of a lot of research on the mechanical properties of nanocellulose where differences in the properties are observed for NCC due to its anisotropic nature causing different properties to be measured at different directions [53]. The elastic properties of cellulose I crystals have been examined both through theoretical estimations and experimentally where the latter has commonly involved measurements using X-ray diffraction (XRD) techniques coupled with in situ tensile tests [54]. These tests involve loading bulk specimens of parallel microfibrils axially and measuring the strain produced using XRD before calculating the elastic modulus in the axial direction (E_A). This allows the measurement of the crystalline properties because XRD only measures the displacement in the crystalline regions, although, the method assumes a seamless load transfer and orientation of cellulose crystals within fibrils along the loading axis. These assumptions are unlikely to be true and can thus lead to a lower modulus result than is actually the case. A different method used to measure axial elasticity that overcomes the concerns surrounding XRD involves the use of inelastic X-ray scattering to measure sound velocity as a function of phonon dispersion within the crystalline portions. This results in much larger elasticity results than that of XRD with around $E_A =$ 220 ± 50 GPa compared to E_A = 120-138 GPa with the XRD. It also allows the measurement of elastic modulus in the transverse direction (E_T) which has been found to be $E_T = 15 \pm 1$ GPa. NCC, which is the crystalline particles that have been isolated from the microfibrils, may possess different properties due to the influence of the extraction process on the particles [55]. NCC derived from plant material is very small in size and individual NCC particles cannot currently be tested for the elastic modulus. However, among the natural sources of cellulose, there exist a single known marine animal species that could produce cellulose in the outer tissues. This cellulose is structured in the form of microfibrils similar to plant cellulose with almost pure monoclinic structured beta-cellulose (I β) where the particles have longer lengths, cross-sections, uniform morphology and higher crystallinity. This allows tunicate NCC, unlike plant-based NCC, to be tested mechanically for the elastic modulus of the individual crystals which has been found to be $E_A = 151 \pm 29$ GP for particles extracted using acid

hydrolysis and $E_A = 145 \pm 31$ GPa for that extracted using a method called TEMPO-mediated oxidation. Atomic force microscopy (AFM) was used to perform a three-point bending test to determine these values. These measurements are subject to errors associated with the difficulty in calculating the cross-sections of the samples which are used to determine the modulus. Raman spectroscopy and in situ tensile tests have also been used to determine the axial elastic modulus of tunicate NCC which was found to be E_A = 143 GPa. The transverse elastic modulus of individual wood NCC and tunicate NCC was determined using high-resolution AFM indentation and modelling which was found to be E_T = 18–50 GPa and E_T = 9 ± 3 GPa, respectively. Yet, these results are subject to large uncertainties due to modelling assumptions and AFM sensitivity limits [42]. The elastic modulus for BC was determined using the same methods as that used for tunicate NCC which is possible because of the similar properties including large length, high crystallinity and large cross-section. An axial elastic modulus of $E_A = 78 \pm 17$ GPa was found when using the AFM three-point bending test and $E_A = 114$ GPa using Raman spectroscopy with the divergence likely being a result of the use of assumptions and difficulties in measuring the properties due to the small nature of the particles [42]. The coefficient of thermal expansion of NCC in the axial direction has been estimated at ~0.1 ppm/K which is similar to other anisotropic fibres with a high modulus like carbon fibre. The thermal chemical degradation of nanocellulose occurs usually between 200 and 300 °C depending on the type of cellulose, such as ~260 °C, for freeze-dried samples of NCCs. This degradation temperature also depends on other factors including surface modification and heating rate [42].

2.2.5 Liquid crystallinity and optical properties

NCC displays liquid crystalline behaviour because of the asymmetric rod structure. NCC may exhibit nematic behaviour due to the stiff rod-like structure when the rods align. The interaction between individual crystals is strong although they easily disperse in solution and exhibit lyotropic phase behaviour as a result. The lyotropic phase is a phase transition from an isotropic liquid into a liquid crystal that occurs by altering the concentration. The crystals possess a helical twist that results in a chiral nematic structure with a cholesteric phase across multiple planes with each plane rotated at a

phase angle along a perpendicular axis. This causes optical band gaps and creates a fingerprint texture in NCC suspensions. In addition, when nanocellulose is exposed to a magnetic field, its long axis becomes perpendicular to the magnetic field direction and the distance between the rods in a nematic plane is longer than that between nematic planes across the cholesteric axis [56]. This characteristic was explored further where nanocellulose based composites were found to possess much stronger mechanical properties in the direction perpendicular to an applied magnetic field relative to its parallel counterpart. The aspect ratio of nanocellulose is a major factor in the liquid crystallinity exhibited as higher aspect ratios cause increased anisotropy, resulting in increased liquid crystallinity at lower concentrations. Although, at copious lengths, the stiffness of the particles may be overcome causing the rod-like structures to behave more like strings thereby eliminating any ordering of the suspension [53]. Ionic strength is also a major factor where an increase in ionic strength would lead to less ordering, a higher critical lyotropic concentration, a reduction in separation and thus the agglomeration of the particles. The inclusion of an electrolyte into the suspension would reduce the repulsion between the particles and decrease the effective diameter. Furthermore, nanocellulose optical properties differ from that of other cellulose materials because of a few features including the nanoscale size, the anisotropic morphology and the ability to display lyotropic liquid crystalline behaviour depending on the structure and conditions. NCCs in suspension may develop a chiral nematic phase at a certain concentration where the suspension may be evaporated to attain a semitranslucent film that retains the crystal structure formed in the suspension [57]. New applications can be adopted using NCC films as they display particular optical properties including iridescence which is defined by the refractive index as well as the chiral nematic pitch. The NCC films can be red-shifted using ultrasound treatment where the chiral nematic pitch is increased in the suspension with increasing energy. The iridescence colours may be decided from the spectrum ranging from blue-violet to red by tuning the sonication treatment and electrolyte addition with the effects being permanent [58]. NCCs are also birefringent with a refractive index of 1.618 in the axial direction and 1.544 in the transverse [57].

2.3 Fabrication of nanocellulose

Nanocellulose may be isolated through mainly two different methods including mechanical or chemical fabrication. These methods result in different forms of nanocellulose produced depending on the pre-treatment and cellulose source used. The methods include high-intensity ultrasonication, acid hydrolysis, and high-pressure homogenisation. This is further illustrated in Figure 2.3.



Figure 2.3 Method routes to isolate nanocellulose fibrils and crystals

The sources used for the production of nanocellulose fall into three main types including plant cellulose, animal cellulose and bacterial cellulose. Plant cellulose is the most popular raw material for producing nanocellulose source and is usually derived from herbaceous plants, bast fibres, agricultural waste and wood. Animal cellulose is almost exclusively derived from tunicates including ascidians whose tunic possesses a polysaccharide named tunicin that is similar to cellulose. Bacterial cellulose is produced by acetic bacteria through oxidative fermentation with the gram-negative Acetobacter xylinum being the most studied and efficient BC producer [59]. BC is identical chemically to β -1,4-glucan cellulose produced by plants but differs in that the secreted protofibrils aggregate together to form cellulose nanofibril ribbons. BC exhibits many excellent properties including high water holding capacity, high degree of polymerisation, high mechanical strength with an elastic modulus of 78 GPa and high crystallinity of up 84 to 89% [44]. BC is a promising material for a wide variety of applications with demonstrated use in food packaging, high strength paper, multiple electronics-based applications and biomedical applications including bone scaffolding and tissue engineering [60].

However, the production of BC at an industrial level to meet potential demand for commercial applications is limited by the high costs and low yield produced.

2.3.1 Mechanical fabrication

Mechanical fabrication methods to produce nanocellulose include ultrasonication, grinding, highpressure homogenisation, cryo crushing among others with homogenisation being a popular choice [61]. During high-pressure homogenisation, cellulose passes through a small nozzle into a vessel at high pressure where the shear rate of the steam used reduces the size of cellulose to a nano-sized scale. This approach has proven effective due to its simplicity and efficiency while also being desirable because of the lack of solvents used. Mechanical treatments can cause the nanocellulose to be longer and entangled with other fibres which may lead to strong fibre networks and gels, albeit, it also tends to reduce the degree of crystallinity and molar mass causing damage to the microfibril structure. Moreover, when increasing the number of passes through the homogeniser, energy consumption is increased. Thus, pretreatments are often used to overcome these problems and reduce energy consumption with enzyme assisted and the chemo-mechanical pretreatments being the main approaches [62]. One such pretreatment is named alkaline-acid pre-treatment which is used to remove undesired hemicellulose and lignin. It involves different stages including removing lignin using an acidified sodium chlorite solution multiple times until the pulp becomes white before treating the pulp with 3 wt% potassium hydroxide and then 6 wt% potassium hydroxide separately for a set period of time. The latter stage is for the purpose of removing hemicellulose, pectin and residual starch. The samples are then washed with distilled water and filtered. Ionic liquid is another pretreatment approach that dissolves cellulose into a liquid to prepare it for a stage of nanocellulose production called electrospinning [63].

2.3.2 Production of cellulose nanocomposites

The performance and properties of composites rely on the constituents, i.e. the matrix and reinforcement, used and how their strengths or interfacial mechanisms interact. The composite property is also affected by the processing technique used to create the composite structure. The

dilemma with the preparation of NC as a reinforcement is the desire to avoid agglomeration whilst maximising the reinforcing ability of NC composites via the formation of a network structure. Primitive processing procedures need to be adopted to achieve closer proximities of a homogeneous NC dispersion; thereby enhancing composite performance significantly as well as achieving more reproducible results. This also reduces the effective NC particle sizes and thereby widens the interfacial area between the NC and matrix. These procedures could be adopted through mechanical processing techniques or through chemical means, e.g. enhanced biocompatibility and dispersion could be adopted using organic matrices, by functionalising the surface of NC. However, as this tampers the reinforcing ability of NC, modification may be unfavourable and thus a water-soluble polymer matrix may be considered, due to the intrinsic hydrophilic nature of NC, to maximise the reinforcement mechanical property. A number of processing techniques have been adopted over the years in the making of various types of NC composites. Processing techniques such as solution casting, melt-compounding, partial dissolution and electrospinning have been used to create polymer matrix composites reinforced with NC [64-75]. Here, some of these techniques will be discussed. The 'solution casting' processing method is usually used in the making of composite films or aerogels and is dependent on the mixing process. Generally, this technique involves dispersing a known quantity of NC in a specified solvent, e.g. water. NC loadings normally range between 0-10 wt% in solution, though, this can be varied to specific applications. Both the NC and polymer solutions are then mixed together under vacuum or ultra-sonication to minimise the presence of air bubbles. The suspension is ordinarily stirred at room temperature, though it can be increased to treat the polymer used and occasionally to enhance the NC/polymer interfacial bonding. The compositions of both constituents are subject to property prerequisites and thus the wt% ratio of NC/polymer composites can be as high a difference of 0/100 and vice versa [76,77]. These mixtures then undergo different processing techniques to produce the desired composite. For example, if thin films are the desired composite to be produced, the generic process that the mixture undergoes is as follows: the mixture is initially poured into a suitable mould which is then either evaporated, lyophilised and compression-moulded; or is first lyophilised, then extruded and finally compression-moulded. Suitable moulds that may be selected include ones made from glass, Teflon or PP so that minimal damage is dealt to the film when detaching it from the mould. To strengthen the NC and polymer interactions, cross-linkers are commonly also added as reinforcement agents [78–83]. Otherwise, if aerogels or solid foams were the desired composite to be produced, the mixture could undergo various procedures. One of these procedures could be, to rapid freeze the suspension once it's poured into the desired mould. Lyophilisation is used to freeze-dry the frozen mould, extracting out the water in ice form, to achieve the final light-weight aerogel composite. Rapid freezing could include the use of liquid nitrogen for increased control over the direction of freezing and thus establish a more uniform layered aerogel composite. Other typical processing techniques can be seen in

Figure 2.4.



Figure 2.4 Processing routes to achieving aerogels and foams from nanocellulose [78]

Another way of incorporating NC within composites is through the melt-compounding method, whereby, the reinforcement, in this case, NC, is thermal-mechanically mixed/compounded into thermoplastic polymers followed by extruding the melt suspension. For some applications, further processing may be implemented whereby compression moulding is used directly after extrusion [65,68,69,74]. In view of this processing technique, the reinforcing ability of NC would be affected by the high temperatures and shear pressures that may be required. Therefore, these parameters may well need to be adjusted/controlled to suit the NC reinforcement, which is otherwise prone to

degradation. This processing method also requires some investigation into the dispersion quality of NC in the thermoplastic used. As an example, the use of NC within polylactic acid (PLA) has been examined [84,85].

2.3.3 Modified cellulose and polymer aerogels

Cellulose possesses favourable properties when used as a precursor for the preparation of aerogels. They are rich in hydroxyl groups that can form intramolecular and intermolecular hydrogen bonds to create a stable 3D network structure, dismissing the need for crosslinking agents and simplifying the preparation process. The method of extraction, cellulose source and treatment process determine the type of crystallinity, out of the 6 different types, expressed by the cellulose [86]. Cellulose aerogels suffer from low mechanical strength and modulus, however, chemically modifying cellulose to enhance the mechanical and structural properties of the aerogel is relatively simple. Modification of cellulose aerogels can be achieved via 3 main approaches: inserting components into the cellulose solution/suspension, using a sol-gel method to apply components onto the cellulose gel surface and using one of several techniques to modify the surface of cellulose aerogels. For example, the lipophilicity and hydrophobicity of cellulose aerogels can be enhanced through surface modification via methods such as chemical vapour deposition, cold plasma treatment and atomic layer deposition [87].

2.4 Applications of nanocellulose and its polymer nanocomposites

Nanocellulose is a class of materials that represents the quest for developing green technology through nanotechnology. It's desirable material properties along with its minimal environmental impact is ideal in the pursuit of replacing environmentally damaging materials with those that cause less harm. It has received much attention as a cost-effective and green nanoscale filler alternative to materials including glass fibre, silica and carbon black in the reinforcement of polymer composites. Nanocellulose was initially used to reinforce such polymers as polypropylene and polyethylene before their reinforcing potential became apparent [88]. They have been reported to enhance the properties of a range of different polymer matrices including thermoplastic and thermoset polymers. These

polymers include poly(butylene adipate), poly(vinyl chloride), polylactic acid, chitosan, starch among others [89]. The properties of the nanocomposite may depend on several factors such as the aspect ratio, nanocellulose dispersion homogeneity, the processing method used, interfacial bonding, type of matrix and percolation threshold. Presently, NCC and NFC has attracted the attention of researchers as a reinforcement because of favourable mechanical characteristics, optical properties, surface chemistry and crystallinity. The addition of these as a reinforcement has proven to enhance the reinforcing capacity and mechanical properties of various composites for different industrial applications. Some notable examples of nanocellulose derivatives incorporation in polymer matrices (i.e. thermoplastics/thermosets/bio-matrices) as well as the property enhancements of the developed composites are given in Table 2.2.

NC/polymer composite	Property enhancement	Ref
NCCs/WBPU	Incorporation of NCCs improved the thermomechanical stability and hydrophilicity of developed nanocomposites through the solvent casting technique. It also increases moduli and stress at yield by 3 wt.% NCCs loading	[91]
NFCs/Biobased epoxy composites (LCM process)	Fabricated nanocomposites showed improved mechanical and tribological properties with respect to pure epoxy composites	[92]
NC-sugarcane bagasse/ semi-IPN of poly(vinyl alcohol)/polyacrylamide	Remarkable improvement in tensile strength, % elongation at break, modulus and toughness of composite films by adding 5 wt.% of nanocellulose	[93]
NC-oat husk/WPI	WPI-based nanocomposites containing 5% oat-NC has the best tensile strength, Young's modulus, solubility along with the lowest elongation at break and moisture content. But increasing the content (7.5 wt.%) of oat-NC leads to a decrease in the mechanical properties due to growing filler agglomeration	[94]
3-Aminopropyl triethoxysilane silanized NFCs and dodecanoyl chloride esterified NCCs- blue agave bagasse/PLA	Treated NFCs and NCCs addition at 0.5 wt% shows better mechanical properties by more than 20% of PLA composites	[95]
TEMPO-oxidised NFCs/ PVA and PPy	Oxidised NFCs incorporation improved the antibacterial activity of composites films, found in food	[96]

 Table 2.2 Property enhancements of several nanocellulose-based polymer nanocomposites [90]
NC-wood pulp/graphene/ PVA	Developed hybrid nanocomposite (PVA/NFC/ rGO) films show improved mechanical as well as conductivity properties with effective humidity sensors	[97]
NC-raw jute fibres/NR	Improved and better morphology, XRD and tensile strength indicate a strong interaction between filler and NR. The rate of biodegradation by vermicomposting is comparatively higher in non-crosslinked composites than in their crosslinked counterparts	[98]
NC-sugarcane bagasse/ PVA (linear and crosslinked state)	TGA indicates higher thermal stability of nanocomposites NC/crosslinked PVA with respect to NC/linear PVA. Tensile strength increases at 5wt.% and 7.5wt.% NC addition of crosslinked PVA and linear PVA respectively	[99]
NCCs/PLA	TGA shows that decomposition temperature increases by NCCs incorporation at (5 wt.%) of PLA/NCCs nanocomposites compared to pure PLA composites	[100]
NC-jute fibres/NR latex	Considerable improvements in Young's modulus and tensile strength of the nanocomposite were observed by adding NC in the NR latex as a matrix	[101]
NFCs/PCL/epoxy	Both healing efficiency by 26% and mechanical properties (tensile strength, elongation at break, and impact strength were improved by about 27%, 38%, and 38%, respectively) improved by the homogenous dispersion and bridging effect of added 0.2 wt% of NFCs to the polymer matrix. The glass transition temperature (Tg) of epoxy also increased by 12.8°C	[102]
NFCs-dry cellulose waste of softwood (<i>Pinus</i> sp.) and hardwood (<i>Eucalyptus</i> sp.)/UPR	Dynamic mechanical properties and thermal stability improved by the incorporation of NFCs particles	[103]
NFCs-bleached kraft eucalyptus fibres/ biobased epoxy	Low fracture toughness at interfaces observed for the developed NFCs/bio-based resin composites. Porosity also increased with increasing nanofiber content	[104]
NCC-wood/waterborne epoxy	Wood-NCC/waterborne epoxy nanocomposites show improved storage modulus, loss modulus, tensile strength, Young's modulus and Tg with increasing NCC content	[105]
NCCs-RS, WS, and BS/ CMC	Tensile strength increased by 45.7%, 25.2%, and 42.6%, and the water vapour permeability decreased by 26.3%, 19.1%, and 20.4% by adding 5 wt.% of NCCs obtained from RS, WS, and BS, respectively	[106]
NFCs-wood/UPR	Tg increases substantially with NFC content. Modulus and strength of UPR increase about three times at 45 vol% NFCs whereas ductility and apparent fracture toughness are doubled	[107]
m-CNWs-castor oil- based polyol/BPU	Incorporation of stiffer and rigid m-CNWs increases the tensile strength and modulus of BPU composites, compared with the BPU composites. DMA results showed increased in storage	[108]

modulus and loss tangent peak shifted toward higher temperatures by incorporation of m-CNWs

Where: *WBPU*= waterborne polyurethanes; *NFCs*= cellulose nanofibers; *LCM*= liquid composite moulding; *semi-PIN*= semi-interpenetrating polymer network; *WPI*= whey protein isolate; *PLA*= polylactic acid; *PVA*= polyvinyl alcohol; *PPy*= polypyrrole; *NR*= natural rubber; *NCC*= nanocrystalline cellulose; *NC*= nanocellulose; *MCC*= microcrystalline cellulose; *PCL*= poly(ε-caprolactone); *NFC*= nanofibrillated cellulose; *UPR*= unsaturated polyester resin; *RS*= rice straw; *WS*= wheat straw; *BS*= barley straw; *CMC*= carboxymethyl cellulose; *BPU*= bio-based polyurethane; *m-CNWs*= modified cellulose nanowhiskers.

The commercialisation of nanocellulose is yet to reach a considerable size in scale with the applications normally consisting of high-volume products such as automotive components and construction materials or low-value products and novel applications (see Figure 2.5). The latter applications may involve photonics where a chiral mesoporous material can be formed by compositing NCCs with a material of interest [109,110]. These materials have the potential to be applied as optical filters, chiral plasmonics, soft actuators, antireflective coatings and flexible electronics [111–116]. The liquid crystalline behaviour of NCCs may also be used to create iridescent and optically transparent films and NFC may be used as films for optoelectronics and as coatings [117–119]. Nanocellulose may also be used as films or foams where NCC films have been suggested for a wide variety of applications from electronics to packaging. NCC foams and aerogels could potentially be used as insulation in construction, as supercapacitors, in water filtration and other interesting applications, however, such foams have been not yet been investigated as thoroughly as NCC films [120]. Moreover, nanocellulose has been the subject of intense research into its use in medical applications due to the excellent biocompatibility and inherent low toxicity [121–124]. BC is generally considered as non-toxic, although, NCC and NFC may exhibit toxicity depending on the particle size, purity and surface chemistry [121]. Nanocellulose composites have been used to create tissue-engineered scaffolds and wound dressings using BC due to its suitability for cell adhesion and minimal rejection during cellular contact [125,126].



Figure 2.5 Potential application areas of different types of nanocelluloses based on their specific structure-properties relationships [127]

Nanocellulose is regarded as a renewable alternative to expensive, non-renewable reinforcement fillers and has been used to reinforce polymers, paper and other materials to improve the properties and biodegradability of composites. Nanocellulose may be interwoven to create mechanically strong bulk materials including papers and films [128,129]. The global market for nanocellulose has been projected to reach \$808.30 million by 2022 due to its potential as an alternative material to synthetic polymers and chemicals that require energy-intensive processes while petroleum costs are projected to increase.

2.4.1 Incorporation and performance of nanocellulose in construction

There are a wide variety of cementitious materials for different industries such as roads, buildings and waste management with a large amount of cement production annual at around 4 billion metric tons. The desired qualities in cement in these different industries are usually to achieve lower costs, higher durability, increasing sustainability, higher strength and faster setting times [130]. Additives are usually the primary means of achieving these qualities including fibre reinforcements, chemical admixtures and supplementary cementitious materials where the use of natural fibres has seen increasing attention in the push towards sustainability and renewable materials [131,132]. Examples of this may include the use of fibres in non-structural building material such as cladding and fibre cement boards and functionalised fibres in shrinkage cracking control and internal curing [133,134]. The use of natural fibres as an alternative to metals for reinforcement is disadvantaged by the reduced mechanical abilities in reinforcement, although, they prove favourable in other respects including the

lower costs and sustainability. Nanocellulose possesses properties that are more favourable compared to cellulose that is of other size scales for use in cementitious products such as the higher surface area to volume ratio and higher stiffness compared to microscale cellulose [42]. Using nanocellulose as additives in cement has been found to modify the setting times, mechanical properties and rheology of cement where low volumes of nanocellulose additives were found to increase the strength and stiffness of the composite due to changes in the hydration reactions [135,136]. This offers the possibility of improving the mechanical performance of cement by perfecting the hydration kinetics. However, thus far, no commercial cementitious product containing nanocellulose has been successfully developed and introduced to the market. Considering the patent literature regarding nanocellulose applications in cement, most of the literature revolves around the use of nanocellulose as an additive in concrete and cementitious composites. The incorporation of nanocellulose in fibrecement boards has been a focus among patents where nanocellulose is added for the purpose of internal curing and using NFC within the composite where an even dispersal of the NC is accomplished [137]. Such composites were found to possess a higher toughness and elastic modulus, lower shrinking during cement setting and reduced water adsorption [137–139]. Nanocellulose may also be used as an additive to improve concrete and cement properties which have also been a focus of many patents. The addition of nanocellulose may improve the strength, provide stability to self-compacting concrete and modify the viscosity and water retention of different cementitious products [140–143]. It has been found that the use of NCC additives to cement pastes may improve the flexural strength while NFC has been found to be able to raise the solidification delay time while sustaining good liquidity which reduces the porosity of the paste by enabling the release of entrapped gas [140,141]. This led to the enhancement of the mechanical properties of the slurry. Moreover, nanocellulose may be used as a substitute for cellulose ethers in cementitious materials [142]. Nonetheless, nanocellulose must overcome several challenges to significantly penetrate the cementitious material industry. Currently, the long-term durability of cementitious materials incorporating cellulose products has not been studied and requires further understanding as cellulose fibres are known to degrade in high alkali

conditions. Furthermore, the production of nanocellulose products needs to be increased significantly to become a viable additive and satisfy the potential demand in the cement industry due to the enormous scale of the industry. At present, there is a global annual production output of 4 billion metric tons of cement while the upper estimates of nanocellulose potential for use in cement are thought to be around 4.1 million metric tons [144,145]. For perspective, the global production of NCC is presently 650 tons per year and 1700 tons per year for NFC [146]. There also needs to be standards developed to quantify the material enhancements that would result as a consequence of using nanocellulose as an additive in cementitious composites along with supporting metrology, which is difficult to achieve considering the nanoscale size of the cellulose. These developments will accelerate the adoption of nanocellulose in the cement industry. The addition of nanocellulose in cementitious products is intended to attain a preferred particle packing and achieve desired properties due to the high specific surface area of the nanocellulose which can promote chemical reactions and act as nuclei within cement to increase the degree of hydration [147]. NFCs show potential as a reinforcement in cementitious products because of the high aspect ratios, tensile strength and moduli of elasticity. However, dispersion procedures need to be established for nanocellulose and other nanomaterials to be incorporated as there is a tendency for nanoparticles to agglomerate which can cause stress concentrations when loading is applied. Cement is the primary binder in concrete and its production is responsible for 2 to 3% of energy consumption and 5% of CO2 emissions globally [148]. Nanocellulose may improve the sustainability of cementitious materials as an additive where the resulting composite shows improved mechanical properties and durability. Nanocellulose may potentially be produced by the paper industry where a high volume of product can be produced at a low cost using renewable sources. NFC from softwood pulp added to general use limestone cement at 0.05%, 0.1%, 0.2%, and 0.4% loadings of cement weight was found to increase the setting time and degree of hydration in all loadings. These results were attributed to internal curing of NFC causing an increase in the degree of hydration and an increase in setting time because of alkaline hydrolysis of cellulose producing organic acids and other products [149]. The 0.1% NFC loading demonstrated an

optimum increase in flexural strength with microscopic data showing lower fibre agglomeration than higher loadings. NFC produced by high pressure homogenisation from eucalyptus pulp was incorporated within Portland cement and studied at 0.01%, 0.05%, 0.1%, 0.2%, 0.3%, and 0.5% loadings of cement weight [150]. The resulting composite at 0.3% loading showed a desirable strength increase of 43% in comparison with a control sample lacking NFC. An investigation into the autogenous and drying shrinkage of cement paste for high-performance fibre-reinforced cementitious composites found that NFC does not have the internal curing capacity compared to other larger cellulose fibres because of its nano-sized nature [151]. Although, it was theorised that the porous and hydrophilic nature of NFC may encourage self-healing behaviour within the cementitious composites. NFC produced in laboratory conditions with high numbers of hydroxyl groups (1.85 mmol/g) and a highwater retention capacity (3700%) were incorporated within Type I cement paste of 0.50 w/c at 0.15 wt% loading of NFC [140]. The resulting compressive strength increased by 20% and flexural strength by 15% with an increase in the degree of hydration and delay in the hydration reaction. The enhancement of the composite properties was attributed to the small size of the NFC facilitating crack bridging and the hydroxyl groups that increase the interaction between NFC and cement. NCCs were added to Type V cement paste with 0.04%, 0.1%, 0.2%, 0.5%, 1.0%, and 1.5% volume loadings and the resulting composites showed increased DOH with increased loadings [136]. The composite also displayed a 20% to 30% increase in flexural strength compared to cement paste lacking NCC with the 0.2% volume loading showing optimum results. The strength was also found to decrease with increasing loading which was likely because of increased agglomeration at increased loading. The dispersion of NCC within a cement composite is an important factor in trying to achieve ideal property enhancements. The critical concentration of NCC in a simulated cement pore solution to achieve the lowest possible yield stress was determined to be 0.18% of volume loading and the use of ultrasonication to improve dispersion and reduce agglomeration was found to increase the critical concentration to 1.38 vol% [152]. The ultrasonication treatment increased the flexural strength of the composite by up to 50% and Energy-dispersive X-ray spectroscopy attributed these results to

increased concentration of NCC at interfacial regions between cement paste and particles with increased NCC dispersion in the paste. In addition, nanoindentation tests found higher elastic moduli in cement paste regions with higher NCC concentrations.

2.4.2 Other notable applications of nanocellulose incorporation

2.4.2.1 Insulation

Nanocellulose may also be incorporated into aerogel structures for many different potential applications including as insulation in the construction industry. Aerogels are materials with very low densities (0.01–0.4 g/cm³), high surface areas (30–600 m²/g), high porosities and low thermal transport [90,153]. The abundance of surface hydroxyl groups found in nanocellulose and nanostructure parameters/dimensions serves as an ideal building block for functionalising and constructing novel hybrid nanomaterials. Aerogel composites composed of GO and TEMPO oxidised NFC has shown to have superior compressive strength than that of individual GO (more than 15-fold) and NFC (more than 5-fold) aerogels. With the addition of polyvinyl alcohol (PVA) and crosslinks, crosslinked PVA/GO/NFC aerogels have been reported to have more than quadruple the strength of GO/NFC aerogels. Nanocellulose degradation at elevated temperatures and reduction of mechanical properties at such temperatures limits its applicability. Nanocellulose usually degrades thermally at temperatures between 200 and 300 ±1 °C but can be chemically modified to alter the onset of thermal degradation.

2.4.2.2 Automotive

Nanomaterials including nanocellulose based materials are being adopted for use in the automotive industry to improve performance and meet regulatory requirements [154]. Thermoplastic matrices used in the industry are being modified with nanocellulose materials where plastic composites reinforced by nanocellulose are being applied as dashboards, bumper beams and underbody shields in automotives. The use of these composites reinforced by nanocellulose in automotive has increased considerably over the last few years due to the low costs and weight, corrosion resistance and design flexibility with the most common use of these composites being in the exterior body panels [155,156].

2.4.2.3 Medical

Nanocellulose shows potential for use as reinforcement in biocomposites due to the performance enhancement that is offered [157]. NFCs incorporated in biodegradable polymers have been found to be really versatile and applied to a variety of medical applications including tissue engineering scaffolds, articular cartilage repair, artificial skin, blood bags, urethral catheters, adhesion barriers among many others (see Figure 2.6) [158]. A report found that reinforcing polyvinyl alcohol with BC forms biocompatible nanocomposites similar to that of cardiovascular tissues [159]. Another study found that polyurethane with 5 wt% of nanocellulose increases the strength and stiffness of the composite while nanocellulose polyurethane vascular grafts have also reportedly been developed [160,161]. Bionanomaterials such as those incorporating nanocellulose have been applied in the development of applications across multiple medical sectors including veterinary, dental and pharmaceutical industries [162–164]. They may be applied in drug delivery, wound dressings, medical implants and tissue engineering [165–169].



Figure 2.6 3D bio-printed cartilage structures using Nanocellulose (left) and other applications where nanocellulose can be incorporated (right) [44,170]

2.4.2.4 Packaging

Nanocellulose has also been used in composites for packaging of different food types including beverages, frozen and fresh food [171]. This is, in addition, to use as pharmaceutical packaging [172,173]. Ideal packaging materials are those that offer durability, recyclability and non-contaminants. Nanocellulose has been found to improve the gas barrier properties and heat stability when incorporated in polymer composites which may be used in packaging [42,174–178].

2.5 Graphene Oxide incorporated functional materials

This section provides a comprehensive review of the latest advances in the preparation, properties and applications of graphene oxide (GO) and GO-based materials. The review shows that GO has been used to create a range of different composite structures and catalyse numerous reactions: GO could be incorporated as a composite filler through different fabrication techniques including melt blending for thermoplastics to enhance desired properties, such as fusing GO with polyethylene terephthalate to increase the electrical conductance from 1×10⁻¹⁴ to 2.11 S/m with 3.0 vol% GO content; GO may act as a metal-free catalyst and could catalyse reactions, such as the hydration of alkynes, oxidation of alkenes and alcohols with mild conditions to achieve excellent yields of desired products with simple catalyst recovery. Challenges in the development of GO applications are also presented, including the need for a better understanding of the GO structure, and for high catalyst loading in oxidative reactions and limitations of GO in supporting electrocatalysts due to a high density of defects. The review provides a comprehensive and most useful database for further innovations and understanding of GO-based materials for potential applications.

2.5.1 Graphene and Graphene Oxide

The discovery of graphene marks the beginning of a new era in material sciences research and may be the hallmark of a potentially new material age. The introduction of a new frontier in materials science by creating the first known 2D material allows scientists to probe a whole new set of theoretical predictions and create applications we have yet to conceive. Moreover, the material has been proven to exhibit especially good characteristics pertaining to condensed matter physics. Graphene is a oneatom-thick sheet of carbon atoms arranged in a honeycomb lattice. It acts as the building block for all other graphitic materials through the increased layering or through shaping into spherical and tubular forms. It was found that graphene contains exceptional quantum electrodynamic properties including 'relativistic' electrons travelling close to the speed of light, that are termed massless Dirac fermions [179]. The presence of these electrons was confirmed by scientists after the material's discovery, thereby attracting much of the scientific community's attention. It was thought that graphene could not realistically exist because it was believed that 2D materials were thermodynamically unstable [180–182]. This was due to the proven phenomenon of decreasing melting temperatures with decreasing material thickness and increasing instability where individual or groups of atoms separate from each other. It was thought that 2D materials only existed as part of a larger 3D structure [179]. These predictions were invalidated after the material's discovery by Andre Geim and Konstantin Novoselov in 2004 using scotch tape to separate graphite layers and obtain graphene crystals [183]. These crystals are of high quality and could be obtained on top of non-crystalline substrates, in liquid suspension and as membrane suspensions. It is believed that they do not decompose due to thermodynamic instability as predicted because of the strong interatomic bonds between the carbon atoms thereby preventing crystal dislocations and defects. Thin layer graphite research dates back to 1960 when the high conductivity of the intercalated graphite materials was discovered. At the time, the closest anybody got to the discovery of graphene was Fernandez-Moran, an electron microscopist, who endeavoured to create a thin graphite crystal. Graphite sheets of 5 nm thinness, about 15 graphene layers, were extracted through his micromechanical exfoliation method [184]. He did not realise how close he was to achieve a single layer graphene sheet. During the next 30 years, graphitic material research grew slowly until the early 1990s where the discovery of nanotubes and fullerenes led to the renewed interest in exploring various experimental studies of carbon materials. Before long, an exponential increase in research papers related to carbon nanostructures started and in 2004, the ingenuity of the simple 'scotch tape' method marked the ground-breaking discovery of the 2dimensional monolayer graphite sheet, now called graphene. The method involved using adhesive tape to repeatedly split a graphite crystal (about 6 times) and thereafter isolating graphene by transferring the residue to an oxidised silicon wafer. Other techniques of producing graphene were discovered soon after within a few months. Epitaxial growth of graphene layers on electrically insulating surfaces (a substrate) by sublimation [185,186] and chemical vapour deposition were another two approaches of producing graphene [187,188] that were later discovered. 2D graphene has been designated by scientists to mean graphene sheets that reach up to 10 layers after which it

should be termed 3D graphite. This classification appeared partially due to the fact that the electronic structure rapidly evolved with increasing layers as the number of layers approached 10 and the electronic spectrum becomes increasingly complicated.

2.5.2 Graphene-organic composites

Considering the graphene-organic polymer interface within the 3D lattice, graphene and GO-organic composites are effectively categorised into 3 types of arrangement, which are classified as graphene-filled organic composites, layered graphene-organic films, and organic-functionalised graphene nanosheets. The focus of this section examines the modification/development of GO-based materials via their reactive functional groups. The presence of oxygen functionalities in GO allows it to disperse more easily in water, organic solvents and different matrices which is advantageous for combining GO with ceramic or polymer matrices to improve the material properties. For instance, GO can be functionalised with amines for use in biodevices, drug delivery and optoelectronics applications [189].

2.5.2.1 Graphene and GO-filled composites

In recent years, graphene has been considered as a more promising filler for enhancing the desired properties, rather than the conventional carbon nanotubes, which have been regarded as the most effective filler materials, but with relatively high cost. Thus, the interaction via the dispersity and bonding of graphene-organic matrix needs to be unveiled, in order to achieve optimal properties of graphene-filled composites. Enhancements for the characteristic property of graphene induced composites rely on their specific fabrication method, in which good dispersity can be found between the compatible reagents. Some of the most common preparation methods for the production of graphene-organic composites include solution-phase mixing [190–195], melt blending [196–198], and in situ polymerisation [199–210]. Due to the hydrogen attracted oxygen functional groups of graphene oxide, a simple approach would be to dissolve GO in polar protic/aprotic solvents with known concentrations of water-soluble organic compounds, such as polyvinyl alcohol. This preparation method is known as solution-phase mixing. Sonication or high-speed shearing has been presented in conjunction with solution-phase mixing to optimise the dispersity as well as enabling GO/rGO to have

better solubility with non-polar solvents, such as poly(methyl methacrylate) (PMMA) [192], polyaniline (PANi) [195], polycaprolactone [193] and polyurethane (PU) [194,211]. Other than ultrasonication in polar water; ethylene glycol, N,N-dimethylformamide (DMF), N-methyl-2pyrrolidone, and tetrahydrofuran solvents have also been examined to exhibit good dispersion behaviour and long-term stability with full exfoliation of single-layered GO sheets realised after solutions were immersed in ultrasonication baths for 1 h [212] (Figure 2.7a and b). The thickness of the single GO sheets produced is between 1 and 1.4 nm. This is represented by the line profile taken along the green line for the two overlapping GO sheets within the magnified panel of the atomic force microscopy (AFM) images in Figure 2.7b. GO sheets are thicker than graphene sheets (which have a thickness of 0.345 nm) due to the oxygen functional groups and the sp³ bonds [213–217]. Rather than mechanical stirring, sonication is reported to also diminish the large GO flakes/sheets from several microns to several hundred nanometre sizes (Figure 2.7c). This includes the breakdown of graphitic fragments due to oxidation [212,218,219]. Although this breakdown is reviewed as a disadvantage in certain applications; it would be greatly beneficial and compatible when in need of bonding with other nanoparticles/materials, which are of nanometre sizes [220]. In addition, the larger variation of GO sized flakes created through sonication could be filtered to narrow/shorten the polydispersity index within the desired size limits to be used as a filler constituent [213,214,216].



Figure 2.7 GO dispersed in water and 13 organic solvents (a), AFM image of GO sheets deposited onto a mica substrate (b) and UV-vis absorption spectra (c). Reprinted with permission from [212] (Copyright (2008) American Chemical Society)

Nonetheless, the reduction in the surface area of graphene nanosheets due to agglomeration is inevitable, therefore graphene-fillers would need to be pre-functionalised to provide sufficient solubility with the other numerous solvents [221]. For example, the hydrophilic nature of GO can be reduced by treatment with isocyanates, whereby GO surface and edge bonded hydroxyl and carboxyl groups respectively substitute into amide and carbamate groups, to promote the solubility of GO in aprotic solvents, such as DMF or dimethyl sulfoxide, as well as diminish agglomeration due to the presence of amides and carbamate ester functional groups and hence show improved homogenous dispersion [222]. Furthermore, the solution-phase mixing of isocyanate-treated GO with styrenic organic compounds, such as polystyrene (PS), in DMF has been shown to also stimulate electrical conductivity of GO-organic composites [213]. Similarly, GO can become amphipathic and dispersible in both DMF and water through coupling diisocyanate modified GO with an amphiphilic oligoester (short analogue of polyester) [223]. Alternatively, GO can be fused together with thermoplastics through melt compounding of the organic matrix via high-temperature shear mixing. Owing to its large

specific area and high aspect ratio, GO-filled thermoplastic composites signify enhanced electrical conductance with increasing GO filler content as well as achieving percolation thresholds at very low filler loadings. Incorporation of 0.47 vol% reduced graphene oxide (rGO) filler to strongly electrically resistive polyethylene terephthalate resulted in a sharp increase in conductivity, reaching a terminal value of 2.11 S/m at filler content of 3.0 vol% [197]. Similar results were shown in solution mixed graphene-PS composites with only 0.1 vol%, reaching conductivity of ~1 S/m at 2.5 vol% [213]. However, solvent blending yields better dispersion of GO fillers as well as resulted in an increase in mechanical properties, such as the tensile modulus of composites more than that of composites prepared through melt compounding [224]. The high shear mixing in melt compounding has also shown to fissure the filler material [198]. 3 wt% of GO filled PVA composites prepared via solution mixing and vacuum filtration resulted in young's modulus of 4.8 GPa with a tensile strength of about 110 MPa. This improvement may be lower than what would be expected from monolayer graphene as a filler material, with young's modulus of 1.0TPa and breaking strength of 42N/m [225], which may be due to the compatibility and type of bonding with the matrix material. Optimal strength may not be achieved under a physically interacted composite due to the inefficient load transfer, as shown to be the case under external forces in GO-PVA composites. Hence, the need for chemical bonding/interactions at the filler-matrix interface should be realised. As a comparison, Young's modulus and hardness of GO-PU composites are shown to be superior by about 900% and 327%, respectively [194]. This increase is primarily due to the presence of the isocyanate functional group in the PU matrix which formulates covalent bonding with the oxygen groups of GO. This chemical bonding interlinks the strong features of graphene as a filler material, allowing more efficient load transfers, whilst diminishing dislocation lines formed via the physical interaction within the composite lattice microstructure. Other than solution mixing, graphene filler can be incorporated in organic polymer matrices, such as epoxy, PANi, PS and silicone, through in situ polymerisation. By simply adding a known/suitable curing agent after high shear mixing graphene with the polymer matrix, polymerisation can be initiated. This method has been used in efficiently enhancing the thermal

conductivity of graphene-epoxy composites by 30 folds, reaching values of k = 6.44W/mK at 25 vol% filler loading, as opposed to conventional fillers, e.g. SiO₂, that require 70 ±20 vol% loading to apprehend a similarity [199]. In comparison to the other fabrication methods, similar results were achieved in enhancing the electrical conductivity of rGO modified poly(vinyl chloride/vinyl acetate) copolymer composites at low percolation thresholds of 0.15 vol% filler loading [202]. In addition to the above property enhancements of organic polymer composites, functionalised graphene has been used to increase the thermal stability of thermoplastics and elastomers due to the strong filler-matrix interaction caused by the branched morphology of graphene. Thermoplastics including graphene modified PMMA or poly(acrylonitrile) composites, whereby their glass transition/degradation temperature was increased by 30° C/ 40° C with a filler loading of 0.05 and 1 wt%, respectively [190]. Graphene modified elastomers showing similar enhancements in degradation temperature with examples like silicone composites increasing by 55° C at a filler loading of 0.25 wt% [210]. Some further notable examples of GO incorporation in polymer matrices (i.e. thermoplastics/thermosets/bio-matrices) as well as the property enhancements of the developed composites are given in Table 2.3.

GO/polymer composite	Property Enhancement	Ref
Pluronic F127 (PF127)-	Functionalising rGO with PF127 surfactants show improved	[226–
rGO/Polyethylene glycol	dispersion in the PGA matrix due to significant interfacial	228]
plasticise gum arabic	interaction between the filler and polymer matrix as indicated	
(PGA)	by FESEM, WAXS and FTIR. Addition of 7.5 wt% PF127-rGO	
	strengthens the stress at break and Young's modulus of the	
	nanocomposite by 124% and 185%, respectively.	
GO/Poly(ethylene glycol)	Using GO in PEGDA for 3D printing polymer composites	[229–
diacrylate (PEGDA)	features tailoring of mechanical and electrical properties with	
	increasing GO content by low-cost UV-light induced Digital	
	Light Processing. The developed composite structure can be	
	thermally treated to enhance electrical conductivity due to	
	the reduction of GO.	
rGO/piperazine-based	Hybridising rGO with flame retardant compounds and	[233–
DOPO-phosphonamidate	incorporating in epoxy resin result in enhanced thermal	240]
(PD-rGO)/Epoxy	stability of the developed nanocomposite at elevated	
	temperatures whilst also improving the storage modulus and	
	tensile strength, due to graphene's exceptional stiffness.	
GO/Chitosan-Poly(vinyl	Incorporating GO in biopolymer matrices show highly	[241–

	Table 2.3 Property	/ enhancements of severa	I graphene-based	polymer composites
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alcohol) (CHT-PVA)	interconnected homogenous porosity of the overall biocomposite, reducing the density due to the increased porosity as indicated by SEM. CHT-PVA/GO also features potential bone regeneration due to its ability to grow hydroxyapatite (HA) crystals depending on the GO quantity.	245]
Ethylenediamine modified GO (EDA- mGO)/Polyurethane (PU) + triethylenetetramine modified GO (TET- mGO)/PU	Intercalating GO with EDA and TET features enhanced dispersibility in polar organic solvents due to the reduced oxygen groups of GO. Using varying amounts of both modified nanofillers alongside PU as a composite coating on nylon films exhibit strong adhesion. The coated films may be used as hydrogen gas barriers due to the significant reduction of hydrogen gas transmission rate by 93% with 22 wt% TET-mGO/PU as compared with unmodified nylon film.	[246– 249]
Fe ₂ O ₃ -reduced graphene oxide (FG)/Polypyrrole (PFG)	Oxidative polymerisation of pyrrole on FG composite surface exhibit high specific capacitance of 140 Fg ⁻¹ with exceptional capacitance retention of 93% after 5000 cycles at 1 Ag ⁻¹ . This enhancement may be associated with the synergistic interaction between the polypyrrole and FG composite.	[250– 253]
GO/Polyimide (PI)	Using RGO as a catalyst in PI has shown to improve the graphitisation properties of PI films at 2300 °C as well as enhancing the electrical properties with increasing RGO filler content. The resistivity of graphitised films with 3 wt% RGO sheets reached values of $4.8 \times 10^{-2} \Omega m$.	[254– 259]
GO–short glass fibre (SGF)/Polyethersulphone (PES)	Coating GO on SGF surfaces as reinforcement for PES matrices show improved tensile and flexural properties. This is due to the enhanced interfacial adhesion between the SGF and PES that GO coating has adopted as well as the fact that GO has a higher modulus than the PES matrix.	[260– 264]
GO–Poly(p- phenylenediamine) (PDA)/Epoxy	Modified GO with PDA as a nanofiller for epoxy exhibit enhanced strength, fracture strain and toughness at relatively low GO-PDA content (up to 0.2 wt%) when testing the cryogenic fracture behaviour at -120 °C due to the improved filler/matrix interfacial strength.	[265– 267]
GO/Poly(vinylidene fluoride) (PVDF)	Partially reduced GO/PVDF composites exhibit high dielectric constant and low dielectric loss with only 1 wt% GO content which proves exceptional dielectric properties. This enhancement may be attributed to the interfacial polarisation of GO, the formation of polar PVDF crystallites and the formation of local GO network structures.	[268– 272]

Where: FESEM= field emission scanning electron microscopy; *WAXS*= wide angle X-ray scattering; *FTIR*= Fourier transform infrared spectroscopy; *SEM*= scanning electron microscopy.

2.5.2.2 Layered graphene-based films

Some graphene derivatives can also be layered in composite structures as opposed to graphene fillers being dispersed at random. These layered graphene structures can be used to obtain favourable characteristics suitable for different applications including as electrodes in supercapacitors and photovoltaic devices as well as dielectrics and other structural and functional applications. A study incorporated graphene films, produced by a spin-coating method using graphene solutions, into bulk heterojunction polymer organic photovoltaic (OPV) cells as a transparent electrode (anode) to replace indium tin oxide (ITO) as an inexpensive alternative. The resulting photovoltaic device displayed power conversion efficiency (PCE) of 0.13%, with suggested possibilities for improvement, compared to that of ITO with 3.59% PCE under the same conditions [273]. A similar study with graphene films produced by chemical vapour deposition and functionalised non-covalently with Pyrenebutanoic acid succinimidyl ester improved the PCE to 1.71%, which represents a considerable step towards replacing ITO [274]. rGO layers have also been used as an acceptor in quantum dot (QD) based solar cells by initially coating ITO glass with a thin layer of graphene through electrophoretic deposition from aqueous solution. Subsequently, a layer of Cadmium Sulfide (CdS) QDs is then directly synthesised on the pre-deposited graphene layer by sequential chemical bath deposition. These two steps of graphene layer deposition followed by a layer of CdS QDs are repeated continuously to produce the photovoltaic device. The resulting device performed better than all reported carbon/QD solar cells with an incident photon-to-charge-carrier conversion efficiency of 16% and photoresponse of 1.08 mA cm⁻² under light illumination of 100 mW cm⁻² [275]. Moreover, rGO films have been used as the hole transport and electron blocking layer in OPVs by incorporating them between the photoactive poly(3hexylthiophene) (P3HT), phenyl-C61-butyric acid methyl ester (PCBM) layer and ITO. Uniform 2 nm thin films of rGO were deposited on top of ITO coated glass by spin coating to achieve OPV efficiencies of 3.5% PCE, which is comparable to devices fabricated with 30 nm of poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) as the hole transport layer that has efficiency values of around 3.6%. rGO films could, therefore, be a simple solution-processable alternative to

PEDOT:PSS as the effective hole transport and electron blocking layer in OPV and light-emitting diode devices [276]. All measurements were simulated under A.M. 1.5 illumination at 100 mW/cm². This phenomenon depicts chemically derived rGO thin films as promising alternatives with single sheet rGO (1-1.4 nm) being particularly promising as opposed to a bilayer of rGO (2 nm), represented in Figure 2.8. As illustrated, one would expect greater OPV efficiency and further optical transparency of single sheet rGO in comparison to pristine single layers of graphene, which show up to 2.3% white light absorbance (97.7% light transmittance) as seen in Figure 2.9 [277].



Figure 2.8 Photovoltaic device structure (a) and corresponding energy level diagram between the top (AI) and bottom (ITO) electrode (b). Current-voltage characteristics of photovoltaic devices with no hole transport layer (ITO only), with 30 nm PEDOT:PSS layer, and 2 nm thick GO film (c). Current-voltage characteristics of ITO/GO/P3HT:PCBM/AI devices with different GO thickness (d). Reprinted with permission from [276] (Copyright (2010) American Chemical Society)



Figure 2.9 A 50 μm aperture partially covered by graphene and its bilayer. The line scan profile shows the intensity of the transmitted white light along the yellow line. Inset: Transmittance of white light as a function of graphene layers (squares). Reprinted with permission from [277] (Copyright (2008) American Association for the Advancement of Science)

A layered GO-polymer composite supercapacitor has been created by placing polymers in between GO layers. The GO layers were made using a modified Hummers method and different polymers were used with different morphologies before a GO-polypyrrole composite was found to have the best performance. The polypyrrole polymer showed better results when used in a fibre form with a high specific capacitance of over 500 F g⁻¹ and good electrochemical stability after retaining 70% of the original capacitance at 1000 cycles [278]. Graphene nanosheets prepared through a liquid exfoliation technique have also been dispersed in thermoplastic polyurethane to create strong dielectric films with a high dielectric constant of 3.53×10^7 and a high dielectric tangent loss of 2515 for 0.1909 V_r [279]. A composite nanomembrane showed enhanced directional elastic modulus when using GO to encapsulate polyelectrolyte multilayers through layer-by-layer assembly via the Langmuir–Blodgett technique. The Langmuir–Blodgett technique was used to deposit GO sheets onto films of polyelectrolyte poly(allylamine hydrochloride) and poly(sodium 4-styrene sulfonate) multi-layers, which led to an increase in elastic modulus from 1.5 to 20 GPa compared to pure layer-by-layer membranes [280].

2.5.2.3 Functionalised nanosheets

Graphene products can also be functionalised with specific polymers to create hybrid nanosheets through primary or secondary bonding. The reactions during covalent functionalisation are mainly located between the functional groups of the polymer and the oxygenated groups on the rGO or GO surfaces. GO has been modified by esterification with PVA via the carboxylic groups in GO and the hydroxyl groups in PVA. The degree of esterification is mainly governed by the tacticity of PVA, while the resulting product showed a large decrease in the degree of crystallinity of the polymer and improved thermal stability due to the covalent bonds between the GO and PVA [281]. Amino functionalised GO (GO-NH₂) has been further functionalised with polyimide via in situ polymerisation and thermal imidization to create strong interfacial covalent bonds between $GO-NH_2$ and the polyimide matrix [282]. Carboxylic groups at the surface boundaries of GO sheets have also been conjugated to polyethylene glycol (PEG) via carbodiimide catalysed amide formation for the delivery of SN-38 as a hydrophobic anti-cancer drug. It has demonstrated the ability of GO-PEG to deliver aromatic water-insoluble drugs [283]. Another process of functionalising graphene products including GO involves grafting polymers using non-oxygenated functional groups on the GO. Graphene nanosheets, using GO synthesised by the modified Hummers method, have been functionalised with polystyrene chains through a grafting reaction involving a diazonium compound and an initiator (Methyl 2-bromopropionate) during atomic transfer radical polymerisation. The resulting product exhibited an increase in the glass transition temperature of up to 18°C and an increase in thermal conductivity that depends on the weight percentage of the graphene nanosheets added in the composite [284]. A different study managed to covalently graft a fluorene-thiophenebenzothiadiazole polymer onto rGO via diazonium coupling with phenyl bromide, followed by Suzuki coupling [285]. A polyethylene grafted GO hybrid material has also been fabricated using gammaaminopropyltriethoxysilane to coat GO sheets before maleic anhydride grafted polyethylene was grafted onto the coated GO sheets [286]. Furthermore, CH₂OH-terminated regioregular poly(3hexylthiophene) has been chemically grafted onto the carboxylic groups of GO via an esterification

reaction [287]. Graphene derivatives can be functionalised covalently in a variety of processes with different polymers and compounds, as shown in the previous examples, due to the diverse surface chemistry of graphene-based products. However, it can also be functionalised by non-covalent bonding including through dispersive forces, electrostatic interactions and π - π interactions, which are often easier and can create useful composite materials for the improved and new applications. GO has been used as means for targeted drug delivery of the drug named docetaxel (DTX) by covalent bonding before being functionalised with transferrin (Tf)-poly (allylamine hydrochloride) (PAH) through electrostatic interactions. The functionalisation of GO was based on the electrostatic interactions between negatively charged GO-DTX particles and positively charged PAH chains [288]. In addition, Graphene sheets have been functionalised non-covalently with PANi for the treatment of toxic hexavalent chromium [289]. rGO has also been functionalised non-covalently with l-tryptophan through π - π interaction with enhanced interaction and increased maximum water dispersibility by cleaning the oxidative debris of GO with the ammonia wash process [290].

2.5.3 Graphene derivatives as a catalyst support

The recent discovery of graphene holds promising results for the future of metal-free catalysis. Scientists have been searching for alternatives to precious metal catalysts with increasing desperation as supplies of these metals dwindle while their use remains widespread as common catalysts. The prospect of their replacement with low cost and abundant carbon materials is a major step towards achieving a sustainable future [291,292]. However, carbon materials, in general, are currently used mainly as heterogeneous catalyst supports, especially to support noble metal catalysts for fuel cell electrocatalysis and organic synthesis. Graphene is attractive for use as a catalyst support as it has proved compatible with many catalytically active species and demonstrated improved characteristics. The growing interest in its use stems partly from the chemical stability and high surface area that enables high catalyst loading and its use in basic and acidic environments without degrading. The chemical activity of supported catalysts depends in large part on the interaction between the catalyst and the support. However, the interaction between graphene and the supported metal catalyst is

usually weak due to the chemically inert nature of graphene, and thus defects and functional groups are instilled to improve this interaction. For example, it was found that tensile-straining graphene by 10%, improved the adsorption energies of various metal clusters (including isotopes of gold, platinum (Pt), silver, palladium and aluminium) by more than 100%. This was explained by the weakening of the π bonding between the carbon atoms caused by straining the graphene as schematically illustrated in Figure 2.10, where the arrows show the direction of stretching. This weakened bonding may strengthen the interaction between the carbon 2pz orbitals and the molecular orbitals of the adsorbed clusters, thus enhancing the chemical reactivity of graphene. The catalytic activity was probed by the chemical reaction of the CO oxidation of these clusters, where the application of strain led to a reduction in the reaction barrier of the catalysed CO oxidation from around 3.0 eV to less than 0.2 eV [293,294].



Figure 2.10 Schematic view of various metal clusters adsorbed on a stretched graphene sheet. Inset: The strain is applied uniformly in graphene along both zigzag and armchair directions. Reprinted with permission from [293] (Copyright (2010) American Chemical Society)

Point defects including vacancy defects have been found to also improve metal catalyst adsorption to graphene supports. Single metal atoms of common metal catalysts were observed to have an affinity toward single vacancy defects on graphene sheets with the trapping ability being significantly higher on the defective graphene than the pristine graphene [295]. Point defects were found to help bind Pt

clusters more strongly in graphene by several electron-volts compared to pristine graphene with unreconstructed defects being the strongest binding traps and reconstructed defects displaying strong trapping ability. A Bader analysis was also performed which revealed a positive correlation between the strength of the binding to the defect and the amount of charge transferred from Pt clusters to the graphene substrate. The Pt-carbon bonds at the defects also resulted in a significant downshift of the d-band centre in the Pt clusters [296,297]. GO is generally seen as a more advantageous catalyst support than pristine graphene due to the functional groups and defects inherent within its structure enabling active catalysts to easily bond through surface functionalisation [298]. These features help serve as anchoring and nucleation sites for the active species of the catalyst or its precursors. GO is usually more cost-effective and commercially available than its pristine counterpart with distinctive qualities including an amphiphilic nature with better dispersibility in aqueous and organic solvents making the supported catalyst more accessible to different reactants. GO also has higher binding energy to metal molecules leading to higher stability with a lower reaction barrier [220,299]. On the other hand, these structural defects and functional groups within GO hinder the excellent electronic properties inherent in pristine graphene as they present obstacles to the movement of electrons within the material. Thus, using GO to support electrocatalysts may be significantly more disadvantageous than its pristine counterpart, as a key principle for choosing a support for electrocatalysts involves high electric conduction with low electrical resistance resulting from a low density of defects. Studies supporting this conclusion include one where palladium electrocatalysts supported on low defect graphene were found to have doubled the electrochemically active surface area compared to that of palladium supported by rGO. The low defect graphene supporting palladium catalyst was supposedly achieved by a "soft chemistry method" involving the dispersion and exfoliation of bulk graphite on N-methyl-2-pyrrolidone before applying an ultrasonic treatment and oxidising the carbon sheets with NO₃⁻ and H⁺. The concentration of the oxidising agents used was low and not as strong as other oxidising agents traditionally used (including sulphuric and nitric acid) which is why the author of this study terms this a "soft chemistry method" [300]. Graphene and its

derivatives have also been used to support semiconductor photocatalysts and the presence of defects also exhibited a significant influence on the performance of the supported catalyst. Semiconductors such as zinc oxide can be used as photocatalysts because of the electronic structure involving a full valence band, where photons with the bandgap energy can excite the electrons from the valence band to the conduction band resulting in a 'hole' in the valence band. These photo-generated holes and electrons underlie many photocatalytic applications including the degradation of pollutants, solar energy conversion, hydrogen production and disinfection [301]. The graphene support is thought to act as an acceptor to the photo-generated electrons leaving the supported semiconductor, which improves the separation between the electrons and the holes preventing recombination and improving the photocatalytic efficiency. With the good electron conductivity, large specific surface area and high adsorption of graphene, it would seem to be an ideal catalyst support of photocatalytic applications. This photocatalytic efficiency is, therefore, dependent upon the electron conduction of the graphene support which is significantly influenced by surface defects as mentioned earlier. The defects on graphene are in turn dependent on the preparation method. A study compared two main solution-based methods for producing graphene for supporting titanium dioxide, including oxidationreduction and solvent exfoliation, which result in different defect densities. It was found that the titanium dioxide (TiO₂) supported by the solvent-exfoliated graphene with 0.27 wt% TiO₂ had higher photo-reductive activity than unsupported TiO₂ by 4.5 times under ultraviolet light and 7.2 times under visible light. This is in comparison to the rGO supported TiO_2 with no improvement under ultraviolet light and 2.3 times improvement under visible light compared to unsupported TiO₂. The high electron mobility of graphene and solvent-exfoliated graphene, in particular, greatly facilitates the diffusion of photogenerated electrons to the reactive sites [302].

2.5.4 GO as a catalyst

Carbon materials can also function as catalysts in their own right. There has been a large growth recently in the use of graphene derivatives as primary catalysts because of several unique properties that influence the catalytic reactions including the two-dimensional structure, high porosity, excellent

electronic properties, high thermal and mechanical stability, defects and heteroatom functionalities. The scope of reactivity can, therefore, be expanded by exploiting surface modifications and edge defects in graphene derivatives. Such defects and functional groups can provide performance benefits such as increased dispersibility in solvents. Most studies relating to carbocatalysis have focused on using GO and rGO which is also amphiphilic where the resulting chemical nature is influenced by the base or acid treatment applied to it. GO can be used as a carbocatalyst to replace precious metals in certain catalytic reactions including those specified in Table 2.4. The intrinsic catalytic activity of graphene-based carbocatalysts is thought to stem from the several features including functional groups, defects and doping (especially by oxygen and nitrogen containing groups which can be done through different methods). Moreover, steps into the potential replacement of commercial metal catalysts with novel graphene-based catalysts have shown promising results, notably electrocatalysis, fuel cells and organic synthesis [303–305].

Group	Reaction	GO mass mg	Temp °C	Time h	Conversion %	Yield %	No. of reuse	Ref
Alkyl	$\begin{array}{c} & \xrightarrow{GO} & \overleftarrow{f_n} \\ R & \xrightarrow{GO} & R \end{array}$	25 (2.5 wt%)	22	4	100	-	5 ~ 9.2% reduction	[306]
Epoxide	GO CH ₃ OH	5	r.t.p	1	99	96	3 ~ no reduction	[307]
Amine & Ketone	$ (\bigcup_{h \neq t}^{h \neq t} + \bigcup_{0 \neq H}^{0} + \bigcup_{0 \neq t}^{0} \bigcup_{h \neq t}^{0} \bigcup_{$	15	70	0.5	-	95	5 ~ 10% reduction	[308]

 Table 2.4 Catalytic reactions using GO as a catalyst

Where: r.t.p= room temperature and pressure (~20°C)

GO and rGO have been the focus of research into the potential of carbocatalysts as pristine graphene does not exhibit any catalytic activity in and of its own. GO contains many hydroxyl and epoxy functional groups on its basal plane, while its complete structure has been difficult to determine due to its non-stoichiometric amorphous nature, unlike graphene. Despite the widespread use of GO, its poorly understood structure has led to six different structural models being proposed (see Figure 2.11) including the Lerf–Klinowski model which is the most popular and accepted model after using NMR spectroscopy to identify two basal plane regions composed of pristine aromatic regions separated by aliphatic 6-membered rings containing hydroxyls, epoxyls (1,2-ethers), and C=C double bonds [220,309–311]. The model was later refined with the addition of small quantities of carboxylic groups at the edge sites before the Dékány model further proposed the existence of tertiary alcohols, quinone groups, phenols ketones and 1,3- ethers [312,313]. Later, it was shown that lactols were present at the peripheral edges of GO, while the latest model proposed by Tour suggests GO to be a system that experiences structural changes after interacting with water [314,315]. However, Tour agrees with the earlier models about the presence of the different functional groups including various oxygen functionalities, such as the epoxyls, carboxyls, carbonyls and hydroxyl groups [316]. Schematic models of graphite oxidation methods based either on chlorate or permanganate oxidation routes can be seen in Figure 2.12.



Figure 2.11 Proposed structural models of GO, including the most recent Lerf–Klinowski and Dékány model. Reprinted with permission from [311] (Copyright (2014) Royal Society of Chemistry)



Figure 2.12 GO model, demonstrating various oxygen functional group types distributed across aromatic regions (a) and graphite oxidation methods based either on chlorate or permanganate oxidation routes (b). Reprinted with permission from [316] (Copyright (2015) Royal Society of Chemistry)

The reduction of GO can remove many of the hydroxyl and epoxy groups, however, topological defects are usually observed as a result at the basal plane, while stable carbonyl and ether groups may remain at the surface edges [317]. It is these topological defects and functional groups that underlie the catalytic activity of GO and rGO. The role of different GO active sites during some catalytic reactions is still debated by scientists. It was found that GO could catalyse reactions including the hydration of alkynes, the oxidation of alkenes and alcohols with relatively mild conditions and produce excellent yields of the desired product with simple catalyst recovery [318]. A computational study was later performed to understand the reaction mechanism behind the oxidation and hydration reactions while using the oxidation of benzyl alcohol to benzaldehyde as a model. Density functional theory calculations later revealed that the reaction occurred using the transfer of hydrogen atoms from the organic molecules to the epoxide groups on the GO basal plane which was followed by the production of diols and dehydration resulting in a partially reduced GO, which could be restored and recycled as a catalyst using molecular oxygen. Graphite was found to have much higher reaction barriers because of the lack of functional groups present in GO [319]. GO could also be used as a carbocatalyst for the polymerisation of different olefins monomers including n-butyl vinyl ether, N-vinyl carbazole, styrene, and sodium 4-styrene sulfonate with average molecular weight (M_n) of 5000-8100 Da observed under varied GO loading for the first olefin and low Mn polymers obtained for the others including 400 Da for styrene and 1900 for N-vinyl carbazole. Table 2.4 shows the polymerisation reaction of N-butyl

vinyl ether under optimised conditions of 2.5 wt% GO loading with M_n of 5700 Da and a polydispersity index of 9.45. The catalytic activity of GO is found to have endured after five polymerisation cycles with these olefins without the need to regenerate the catalyst [306]. Carboxyl-modified GO (GO-COOH) was found to be able to catalyse 3,3,5,5-tetramethylbenzidine (TMB) in the presence of H_2O_2 to produce a blue colour reaction similar to the biocatalyst peroxidase with an even higher catalytic activity to TMB than the natural enzyme. This ability has been used to create a colorimetric method for the detection of glucose as a medical diagnostic. The reaction mechanism involves the transfer of electrons from graphene to the H₂O₂ and the adsorption of TMB to the graphene surface to donate lone-pair electrons from the amino groups to the graphene. GO–COOH works as a good alternative to peroxidase due to the ease of preparation, stability, cost-effectiveness, GO–COOH and high affinity to organic substrates [320]. There are studies that suggest that the introduction of sulphate groups into GO, that has been prepared by the Hummers oxidation of graphite, helps facilitate the GO catalysis of certain reactions including the ring-opening of epoxides (Table 2.4) with methanol at room temperature and other primary alcohols. This sulfation establishes enough acidity into the GO to make it an active acid catalyst, which is helped by its high solubility in water and alcohol and the abundance of active sites found in GO [307]. It has also been found to promote the acetalisation of aldehydes in methanol with these sulphate groups introduced spontaneously during Hummer's oxidation, being the sites responsible for the catalysis [321]. rGO has also been shown to have some intrinsic catalytic activity as a metal-free catalyst. It was found to be able to catalyse the hydrogenation of nitrobenzene at room temperature with high catalytic activity and stability. The ability to catalyse this reaction by rGO was attributed to the zigzag edges of the rGO containing unsaturated carbon atoms, which may act as catalytic active centres to activate reactant molecules by interacting with the two terminal oxygen atoms of nitrobenzene according to Density Functional Theory calculations [322]. Theoretical calculations suggest that smaller crystals of GO and rGO would improve the catalytic activity of oxygen-involving reactions due to the association with an increasing number of zigzag edges and oxygen-containing groups within these edges, where the activity seems to originate [323]. The

carboxylic acid groups and unpaired electrons at the edge defects of rGO was found to play a key role in carbocatalysing the oxidative coupling of various amines to imines. A base and acid treatment were found to greatly enhance this catalysis by activating the catalytic sites through increasing the density of edges with localised spins and recovering carboxylic groups. This treatment was found to improve yields to 98% at 5 wt% catalyst loading, under solvent-free, open-air conditions [324].

2.5.5 Conclusions

The continued research into graphene and its derivatives including GO has resulted in the development of a variety of graphene-based composites using multiple fabrication techniques. Graphene derivatives, particularly GO, have also been found to be effective catalyst supports and carbocatalysts with the preparation conditions identified. Graphene-based organic composites are mainly arranged in three different ways including, layering graphene components within composites - to improve the performance of different applications such as electrodes and dielectrics when used as films; using graphene as a filler material – to aid in electrical and thermal conduction, load transfer and the functional groups that improve the surface interaction due to their large surface area; and functionalising graphene derivatives to specific polymers to create hybrid nanostructures – such as conjugating the oxygenated groups of GO/rGO surfaces to create GO-polyethylene glycol for drug delivery or non-covalently bonding with polyaniline for treating toxic hexavalent chromium. GO also shows promise as metal-free catalysts and catalyst supports due to the presence of topological defects and functional groups: The functionalities of the former includes the hydration of alkynes, the oxidation of alkenes and alcohols, the polymerisation of olefin monomers, the hydrogenation of nitrobenzene; whereas the latter may support electrocatalysts for excellent electronic properties or support semiconductor photocatalysts to achieve high adsorption, large specific surface area and good electron conductivity for applications such as the degradation of pollutants and solar energy conversion.

Chapter 3 Methodology

3.1 Introduction

This chapter provides the specifications of the raw materials used throughout the study, including cellulose, polymers, crosslinkers/coupling agents, and water-repellents. The methodologies of producing cellulose-based aerogel composites through an environmental lyophilisation process are comprehensively explained and illustrated. Characterisation and standardised testing procedures are thoroughly reported.

3.2 Materials

3.2.1 Cellulose

For analytical and consistency purposes, untreated microcrystalline cotton cellulose (MCU) (Figure 3.1) powder from cotton linters was purchased from Sigma Aldrich (CAS Number 9004-34-6). The cellulose powder was processed and untreated with a mean particle size of 20 µm.



Figure 3.1 Chemical monomer structure of cellulose

3.2.2 Polyvinyl Alcohol and Polyethylene Oxide

99+% hydrolysed Polyvinyl alcohol (PVA) (Figure 3.2) with a molecular weight of 146,000- 186,000 Daltons (Da) and a density of $1.19-1.31 \text{ g/cm}^3$ with a melting point of 200 °C was obtained from Sigma Aldrich (CAS Number 9002-89-5). Polyethylene oxide powder with an average M_V of 100,000 was also obtained from Sigma Aldrich (CAS Number 25322-68-3) and used to create films similar to low-density polyethylene found in the inner lining of disposable coffee cups.



Figure 3.2 Chemical monomer structure of polyvinyl alcohol

3.2.3 Chemicals

Sodium hypochlorite (NaClO), 12.5% and sodium hydroxide (NaOH), analytical grade 98% were obtained from Sigma Aldrich and Fisher Scientific, respectively. Sulphuric acid (98%), hydrogen peroxide (30%) and potassium permanganate were all purchased from Sigma Aldrich.

3.2.4 Graphite (inorganic filler)

Powdered graphite with particle sizes <325 mesh (equivalent to 44 μ m) was purchased from easycomposites.

3.2.5 Crosslinkers

Coupling agents: Glyoxal (GLY) solution 40 wt% in H₂O (CAS Number 107-22-2), Vinyltrimethoxysilane (VTMS) 98% (CAS Number 2768-02-7), and (3-Aminopropyl)triethoxysilane (APTES) \geq 98% (CAS Number 919-30-2) were bought from Sigma Aldrich (Figure 3.3).



Figure 3.3 Chemical structure of (a) glyoxal, (b) vinyltrimethoxysilane, (c) (3-Aminopropyl) triethoxysilane

3.2.6 Deionised water

Purified deionised water, 0 μ S was used throughout this study via a Biopure 600-unit (Veolia Water Technologies).

3.3 Methods

The methodologies presented are procedures revolving aerogels. Aerogel production involves three predominant steps, as follows:

- 1. Preparation of suspensions,
- 2. Freeze-casting through liquid nitrogen (supercooling),
- 3. Lyophilisation (freeze-drying).

Specific details of alterations to the experimental method are noted where applicable in the chapters.

3.3.1 Preparation of stock suspensions

Material suspensions for the preparation of aerogels are prepared separately before combining desired amounts of each material for freeze-casting. The preparation of these suspensions is described below and depicted in Figure 3.7.

3.3.1.1 Nanocellulose production

Microcrystalline cellulose was suspended in de-ionised water. The suspension was swelled and later oxidised using NaOH (4 wt.%) and NaClO (20 wt.%), respectively. The oxidation reaction was highshear mixed using a Polytron system PT 2500 E (Kinematica ag) while an IKA HB 10 heating bath kept the mixture at 45 °C for 30 min. The homogenised slurry was then washed to pH 7 through cycles of centrifugation, using de-ionised water, followed by dialysis cycles for 48 hours to remove any salts and achieve an electrical conductance of <100 μ S. Approximate yield of 40% nanocellulose crystals (NCC) is produced through this process with the remainder yielding nanocellulose fibrils (NFC). The difference in density makes it easy to differentiate between NCC and NFC after centrifuging, as shown in Figure 3.4. The supernatant NCC was decanted after centrifugation to separate the NCC from NFC. Low-shear mixing for the oxidation reaction was also investigated using an overhead mixer at 900 rpm combined with an ultrasonic heating bath for continuous sonication under 65 °C for 5 hours. For the purpose of brevity, the untreated microcrystalline cellulose is termed MCU and once treated, the final slurry includes micro-fibrillated cellulose, NFC and NCC. The NCC appears as a separate layer at the top after centrifuging (supernatant) and the remainder is termed MCT because in addition to the NFC, there is a small amount of micro-fibrillated cellulose (yielding typically between 2-5%) present at the bottom of the NFC layer (precipitate). This is apparent in the micrographs in Figure 3.5 and Figure 4.1. The majority of NFC is in the form of a network of branches with the micro-fibrillated cellulose at the core as well as a small proportion of trapped NCC in the network.



Figure 3.4 Process of NC purification (a) Sigma 6k15 500 ml centrifuge flask displaying the salty water before decanting (b) Dialysis tube immersed in a 5L water tank and a conductivity meter (c) Centrifuge flask displaying supernatant NCC and NFC precipitate after purification (d) Yields of NCC:NFC ratio produced at different swelling agent dosages during oxidation reaction and (e) Analytical balance used to measure the concentration of purified NC produced

A schematic of the tempo-free reaction mechanism is depicted in Figure 3.5a and the resulting SEM images of the two Nanocellulose derivative profiles, NFC and NCC, is shown in Figure 3.5b and 3.5c, respectively. The width of the nanocellulose fibrils range between 5-20 nm as apparent in Figure 3.5bi and bii. Figure 3.5d shows the size distribution by intensity of nanocellulose using a 'dynamic light scattering particle size and zeta potential analyser' with a sample size of 2 microlitres (precision of \pm 1%). This was conducted periodically for quality checks with the peak averages presented in Table 3.1 and an overall Z-average of 346.5 d.nm.



Figure 3.5 (a) schematic of the tempo-free NC fabrication process; (b) TEM micrographs of the NFC network with the graphs in bi and bii corresponding to the width of the fibrils; (c) TEM micrograph of NCC; (d) size distribution of NC analysed by intensity

Table 3.1 Quantitative	measurements of the	e peak sizes in	Figure 3.5d
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	Size (d.nm)	% Intensity	St Dev (d.nm)
Peak 1	361.6	94.9	164.5
Peak 2	5082	5.1	561.3
Peak 3	~90	n/a	n/a

3.3.1.2 Graphene oxide production

Graphene oxide was prepared according to the modified Hummer's method from graphite. In a nutshell, 10 g of graphite powder (easycomposites) was stirred with 5 g of sodium nitrate and 230 ml of sulphuric acid (98%) (Sigma Aldrich), H₂SO₄ for 30 min. The mixture was transferred into an ice bath and 30 g of potassium permanganate (Sigma Aldrich), KMnO₄ was added to the mixture. This was stirred for 30 min raising the temperature to 35 °C. Once 460 ml of water was added to the mixture, the temperature was raised to 98 °C for 15 min adding an additional 800 ml of water along with 100 ml of hydrogen peroxide (30%) (Sigma Aldrich), H₂O₂. The final mixture was washed with 200 ml of hydrochloric acid (37%), HCl and centrifuged/dialysis till pH 7 was achieved (Figure 3.6). A sample of the GO was heat-treated overnight at 30 °C to evaporate the water to turn the suspended GO into a thin cake. This was for use to characterise the GO purity using analytical techniques.



Figure 3.6 Schematic illustration of GO production via modified Hummer's method

3.3.1.3 Polyvinyl Alcohol solution

To achieve a 5% stock solution, desired amounts of polyvinyl alcohol was dissolved in deionised water in a round-bottom flask and stirred at low shear speeds for 3 h in a heating bath at 90 °C. An overhead mixer was used for stirring at 300 rpm and was halted when the solution was clear with no remaining PVA solutes (Figure 3.7). When quenched, the solution was left to cool to room temperature before use.



Figure 3.7 Stock suspension of PVA

3.3.2 Preparing mixed suspensions and freeze-casting

Specific mixture compositions are detailed in each chapter. As an example, the preparation of NC-PVA suspension is detailed as follows: After preparing 5 wt% stock solutions, NC and PVA were mixed and diluted to a final composition of 2.5:2.5 weight by weight percent (wt.%) using Equation 1 [325]. Two mixing techniques were investigated at ambient temperatures:

- Low-shear mixing (LSM) via magnetic stirrers at 700-900 rpm for 24 hours, allowing constituents to fully blend together.
- High-shear mixing (HSM) at 7,000-10,000 rpm for 10 min to maximise the cellulose dispersion due to the deagglomeration caused by the electrostatic forces within the vortex and homogenise the final suspension

The mixing technique used is highlighted in the respective chapter.

$$c_1 m_1 = c_2 m_2$$
 Equation 1

Where, c is the concentration (wt.%) and m is the mass (g)

The final mixed suspension was later slowly poured (to avoid air bubbles) into aluminium foil moulds. Any surface air bubbles seen was removed using a pipette. For consistency, the poured suspensions were weighed to equal weightings. Two aerogel thickness panels were investigated using mould
dimensions of 100×100×10 mm and 100×100×15 mm and is specified where used in the respective chapters. The moulds were then placed on an aluminium tray of 3 mm thickness that holds a maximum of 6 sample moulds. The tray is designed to rest in a polystyrene box that is filled with liquid nitrogen enough to only allow vertical freezing (bottom to top) to occur from the underside of the aluminium tray. Once frozen, the sample moulds are placed in a freezer until a full batch of 21 moulds are frozen and ready to be lyophilised (N.B. the freeze-dryer can fit 22 samples) (Figure 3.8).



Figure 3.8 Procedure of producing aerogels (a) mixed NC-PVA suspensions poured in aluminium moulds and being weighed using tray (b) freeze-casting through liquid nitrogen with inset a thermal image of suspensions being frozen (c) lyophiliser freeze-drying the frozen sample (d) GO-NC (top) and NC-PVA (bottom) aerogels after freeze-drying

3.3.3 Lyophilisation (freeze-drying)

A Martin Christ Alpha 1-2 LD freeze-dryer was used to sublime the ice for all aerogel preparations. The lyophiliser chamber has a max ice condenser of 2kg/24hr at -55 °C. The temperature is set to -55 °C an hour before inserting the frozen aerogel samples for main drying. When the lyophiliser was ready and all the frozen samples were loaded, the vacuum pump was turned on to begin the main drying for 120 hours. This drying process is to allow the intrinsic gel structure to stay intact while the residual solid ice is sublimed and vacuumed out, to attain an aerogel composite (Figure 3.8 and Figure 3.9). Once the drying is complete, the aerogels are decanted, placed in resealable plastic and stored in a desiccator until ready for characterising and testing.



3.3.4 Alien nanoparticle incorporation into nanocellulose

An aliquot of 8ml 4% untreated cellulose (MCU) and oxidised cellulose (MCT) were added to 2ml CuNO₃ 0.25 mol in separate flasks. Six solutions were produced in total (3 of MCU and MCT) before

being heated to 60°C on a hotplate. An MCU and MCT solution each were removed from the hotplate after 5, 10 and 30 minutes. An Eppendorf of each solution was frozen using liquid nitrogen and lyophilised using a PowerDry LL3000 Freeze Dryer for EDX, FTIR and RAMAN analysis (Figure 3.10). The copper-incorporated samples are termed MCU-Cu and MCT-Cu in Chapter 4.



Figure 3.10 Copper incorporated solutions and freeze dryer used to lyophilise the Eppendorf's of each sample for characterisation

3.3.5 Nanocellulose additive for recycled paper production and nanocellulose as a film

Old corrugated containers (OCC) or Kraft liner shaving (KLS) pulp was received from a 100% recycled paper processing papermill at a 4% consistency, this was then diluted to a 1% consistency for ease of use and accuracy in the laboratory setting. The Axform Dynamic Sheet Former (DSF) replicates a papermachine process in that pulp is sprayed on to a wire producing a 900x250mm sheet of paper, with the ability to alter the efflux ratio via changes to the drum speed, the pressure of the pulp pump and diameter of the nozzle used (Figure 3.11a). The sheet is then couched and pressed using the Axform Press and Dryer and dried at 120°C on an oil-filled drum dryer (Figure 3.11b and c). Three 100 gsm sheets were produced for each type of nanocellulose tested (NCC via Hypochlorite treatment, NCC via Peroxide treatment, NCC & NCF via peroxide) as well as for each concentration of nanocellulose type ranging from 0.5-2.5% (Figure 3.11d). LDPE films were produced using powder according to the method outlined by [326]. The powder was mixed with de-ionised water for 3 h and a further 3 days with the NC suspension. The composite film was produced after drying for 24 h at 70 °C before being hot-pressed into a film.



Figure 3.11 Displays the production of recycled paper through (a) the Axform Dynamic Sheet Former, (b) Axform Press, (c) Axform Dryer and (d) the final 100 gsm paper sheets with varied nanocellulose dosages

3.4 Characterisation and testing

3.4.1 Physical properties

3.4.1.1 Apparent density

An analytical balance precise to ±0.005 mg and a digital Vernier calliper precise ±0.005 mm was used to measure the dry mass and volume of aerogel samples, respectively. Using Equation 2 (dry mass over volume), the density was calculated in accordance with ASTM D1622-98/D1622M-14 [327]. Average densities of six samples per composition were calculated.

$$\rho = \frac{m}{v}$$
 Equation 2

Where, p is density (g/cm³), m is mass (g) and v is volume (cm³)

3.4.1.2 Particle size analysis

Particle size distributions of cellulose fibres were retrieved through a light-scattering based system using a NanoSight LM10. Cellulose suspensions were diluted to 2 wt% and homogenised using the shear mixer at 10,000 rpm. A 0.45 µm filter was used to limit/control the range of fibre inlets for samples with larger fibre aspect ratios. A 1 ml aliquot of the filtered suspension was extracted and inlet into the Nanoparticle Tracking Analysis (NTA) whereby 5 cycles of 90 s was recorded, and particle paths tracked under Brownian motion analysed using the NTA 3.2 software. The aliquots were slowly

injected into the chamber at an angle, to avoid the formation of air bubbles that affect the detection of particles due to secondary light scattering. The temperature of the inlet suspension was constant at 22° C (Figure 3.12).



Figure 3.12 NanoSight LM10 Microscope and schematic illustration of NanoSight operation

3.4.1.3 Thermal conductivity

A FOX 200 instrument was used to measure the thermal conductivity of 100x100x10 mm samples based on a hot-cold plate setup according to standards (ASTM C518, ISO 8301 and EN 12667) [328–330]. The active area of the integrated heat flux transducer is 75x75 mm. The mean temperate was set to 10 °C (0 °C for the upper plate and 20 °C for the lower plate). The auto-thickness feature was used to measure the full aerogel thickness as well as keep the inserted aerogels air-tight when the system is in operation. Average thermal conductivity readings of three samples for each composition were taken across the thickness (Figure 3.13).



Figure 3.13 TA Fox 200 instrument and schematic illustration of thermal conductivity operation

3.4.1.4 Surface charge and sizing analysis

An Emtec Fibre Potential Analyser (FPA) was used for the measurement of the Zeta Potential of fibre suspension according to the Helmholtz-Smoluchowski equation by simultaneously measuring conductivity, pressure and the streaming current potential. An Emtec Charge Analysing System (CAS) was also used to measure the Streaming Potential of the water taken from the pulp (Figure 3.14a). Hach Sension+ was used to analyse the pH, conductivity and redox of the pulp and nanocellulose.



Figure 3.14 Displays (a) Emtec fibre potential analyser on the left and Emtec charge analysing system on the right, (b) L&W burst strength tester and (c) L&W Bendsten porosity tester

3.4.1.5 Burst and porosity index

Four 10x10cm squares were cut from each 100 gsm sheet with respect to the dosage of nanocellulose (0.5-2.5%). Each square was weighed for indexing the results and three burst tests were carried out on each square. A hydraulic paper L&W Burst Strength Tester was used for the measurement of pressure at which the sheet bursts and measured as kilopascal (kPa), indexed to kPa per basis weight in grams (g) (Figure 3.14b). An L&W Bendsten Tester was used to assess the porosity properties of the paper measured via the air permeability through the paper, measured via airflow millilitres per minute (ml/min) (Figure 3.14c). The same square samples used for burst testing were used and three porosity tests were carried out on each square. The porosity index was calculated and averaged.

3.4.1.6 Thermogravimetric analysis (TGA)

A TGA was used to define the thermal stability of nanocellulose and low-density polyethylene composite films by determining the temperature at which they decompose. The test was conducted at 5°C/min increments with a gas flow rate of 50ml/min. The temperature range was set at 25-600 °C.

3.4.2 Mechanical properties

3.4.2.1 Compressive strength

Aerogel composite samples were cut to 20x20x10 mm via a diamond band saw for compression testing (Figure 3.15). The test was conducted using an INSTRON 5900 series in a controlled environment of 23 °C and relative humidity of 45%. The applied load rate was set to 1 mm/min until a 50% strain was realised. The load was applied perpendicular to the axial grain orientation of the aerogel samples. Mean compressive modulus and yield strength of samples were taken. Due to foam-like behaviour, compressive moduli were determined from the most linear stiffness region before yielding using Equation 3. Specific modulus and specific strength were calculated by dividing the mechanical property (i.e. modulus and compressive stress at yield point) over the composite density to compare between compositions.

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$$
 Equation 3

Where, E is modulus (MPa), σ is stress (MPa) and ϵ is strain (mm/mm)



Figure 3.15 Aerogels cut to cuboid specimens using a diamond band saw and compression testing using Instron 5900 series

3.4.2.2 Tensile and compressive strength index

A Lloyd LRX Tester was used to measure the tensile strength of the paper sheets (Figure 3.16a). Six 15 mm wide by 150 mm long specimens were punched from each paper sheet in the machine direction and another six specimens were punched out in the cross-direction of each paper sheet using a

Messmer TMI 22-22 Sample Punch (Figure 3.16b). The specimens were weighed before tensile tested. The tensile index was calculated by dividing the tensile strength over the weight of the specimen. Averages of each paper sheet were taken and thereafter averages of the three repetitive paper sheet samples were taken for each set of nanocellulose dosage. An L&W compressive strength tester STFI was used to measure the compressive strength index (Figure 3.16c). After tensile testing, the same specimens for machine- and cross-direction were used to measure the compression strength and calculate the compression index using the specimen weight.



Figure 3.16 Displays (a) Lloyd LRX tensile strength tester, (b) Messmer TMI sample puncher and (c) L&W compressive strength tester

3.4.3 Analytical techniques

3.4.3.1 Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

A Perkin Elmer Spectrum One was used to analyse and characterise the functional groups of the cellulose derivatives and their composite material composition spectra (Figure 3.17). 30 scans were recorded per sample at a wavenumber range of 4000–600 cm⁻¹ with a resolution of 4 cm⁻¹. Prior to testing, FTIR samples were stored in a desiccator and known quantities used to cover the ATR crystal. OriginPro was used to analyse the peaks and convolute a curve fit via the Gauss distribution.



Figure 3.17 Perkin Elmer machine and schematic illustration of the ATR-FTIR mechanism

3.4.3.2 X-ray powder diffraction (XRD)

X-ray diffraction patterns of tested samples were obtained using the Bragg-Brentano Bruker D8 Advance equipped with Copper tube and LynxEye position sensitive detector (Figure 3.18). Samples were scanned between 20 of 5° to 60° with increments of 0.01° at a scan speed of 1.2 sec/step using the Cu K α radiation (λ = 1.540596 Å). The XRD patterns were interpreted using software's, Bruker Evaluation Diffrac, Topas and GSAS 2. The Crystallinity Index (CrI) and d-spacing were calculated using Equation 4 and Equation 5 (Bragg's law) [331].

$$CrI = \frac{(I_{002} - I_{am})}{I_{002}} \times 100$$
 Equation 4

$$n\lambda = 2dsin\theta$$
 Equation 5

Where, n is number of wavelengths (=1), λ is X-ray wavelength (Å), d is interatomic spacing (Å), and θ

is diffraction angle (°)



Figure 3.18 X-ray diffractometer Bruker machine and schematic illustration of Bragg's law reflection

3.4.3.3 Raman spectroscopy

Raman spectra of tested samples were obtained using a Renishaw InVia Micro Raman system fitted with a 514 nm laser (Figure 3.19). Raman maps were scanned across 100 - 3200 cm⁻¹ every 10 min. WiRE and OriginPro software's were used to analyse peaks and convoluted using Gaus distribution. D/G ratio was calculated using Equation 6.

Equation 6

Where, I_{D} is intensity at Raman shift D and I_{G} is intensity at Raman shift G

 $\frac{I_D}{I_G}$



Figure 3.19 Renishaw inVia Raman microscope and schematic illustration of Raman scattering

3.4.4 Microstructure characterisation

3.4.4.1 Scanning electron microscope (SEM) and Energy-dispersive X-ray (EDX)

The developed microstructures were characterised through scanning electron microscopy using a

Zeiss Supra 35VP FEG-SEM (Figure 3.20a). Cross-sections of the aerogel samples were cut to 1 by 1 cm

cubes via single-edge razor blades. The electron high tension was set at 5 kV and imaging was carried out using the SE2 detector. Due to the non-conductive nature, samples were sputter-coated with a thin layer of gold prior to imaging using a Polaron-SC7640 Sputter Coater for 2 min. Several areas were analysed for each examined sample under the microscope to determine the dominant motif and structure. EDX analysis was used to acquire images and data to highlight inorganic nanoparticles and evaluating any impurities.



Figure 3.20 Displays (a) Polaron-SC7640 Sputter Coater, (b) Agar Turbo Carbon Coater, (c) Zeiss Supra 35VP SEM with an EDX attachment and (d) JEOL JEM-2100F TEM

3.4.4.2 Transmission electron microscopy (TEM)

The structure of nanofibers, flakes and colloidal suspensions were examined using a JEOL JEM-2100F microscope operated at 200 kV (Figure 3.20b). Cellulosic suspensions were negatively stained using 1% uranyl acetate before they were drop-cast on to carbon holey film support copper 200 mesh grids. The holey carbon grids had been glow-discharged beforehand for 20 s using an Agar Turbo Carbon Coater set at 10mA. Excess sample and stain were wicked away with blotting paper. Prior to entry into the microscope, samples were plasma cleaned for 30 s using a Gatan Solarus. Fast Fourier transform (FFT) images were also obtained to measure distances between atomic planes. TEM lattice structures were analysed via the GMS 3 Gatan software.

3.4.5 Wettability

3.4.5.1 Moisture absorption

A controlled environmental chamber was used to measure moisture uptake of tested aerogels over a long duration of 31 days and to evaluate the impact on the aerogel microstructure and mechanical property as a result. The samples were subjected to a fixed temperature of 23 C and 60% relative humidity. Analytical balance precise to ± 0.005 mg was used to measure the mass of samples and the moisture absorption calculated using Equation 7 [332].

% mass increase =
$$\frac{m_w - m_d}{m_d} \times 100$$
 Equation 7

Where, m_w is wet mass (g) and m_d is dry mass (g)

3.4.5.2 Contact angle

The contact angle was measured using a 10 Ångstrom FTA 1000 drop shape analyser (Figure 3.21a). The static contact angle was determined from the shadow of a 3.5 μ l sessile drop of distilled water. The test was conducted in ambient conditions of 19 ± 2°C to minimise the error of contact angle associated with water evaporation. Average contact angles across both planar sides of the paper sheet surfaces were calculated and classified according to Figure 3.21b.



Figure 3.21 Displays (a) drop shape contact angle analyser and (b) contact angle classification

Chapter 4 Morphological and chemical transformation of nanocellulose to enable successive alien nanoparticle in-situ grafting

4.1 Introduction

The push towards a more sustainable society has attracted researchers to explore cellulose to create environmentally friendly products. However, macro scale cellulose offers few applications that can be developed due to its limited set of properties. This is why nano- and micro-scale cellulose are being explored that offer alternative properties and show promise in creating advanced nanomaterials, as a reinforcement product or to simply enhance the structure of macroscopic cellulose [1,2]. Such cellulose materials may be functionalised in a targeted manner to achieve desired properties for a specific application thus enabling this sustainable material to be utilised in a larger selection of applications. However, current production methods for nanoscale fibrillated cellulose present limitations including the need for high acid concentrations, high energy consumption (700-1400 MJ kg⁻¹) and low yields of less than 30% due to excessive degradation from the high acid concentrations [3–5]. Pre-treatments in the form of TEMPO-NaBr-NaClO are often used to overcome these problems associated with mechanical defibrillation despite being costly (approximately £20/g), removing noncellulose composition and demanding treatment of liquid waste [6,7,333]. A novel TEMPO-free treatment has been developed recently without these shortcomings, albeit, its effectiveness is yet to be determined. Here we show a transformation of micro-cellulose (MCU) to MCT, via a TEMPO-free oxidation, where expanded thin microcrystals are formed with a branched nano-fibrillated cellulose network. This NC bonds with other cellulose particles to create a 3D gel, forming a film when dried. Moreover, the treatment is revealed to partially convert cellulose I β to cellulose II, possible due to mercerisation. Consequently, the NFC within the MCT is capable of functionalising with alien nanoparticles, such as Cu, enabling the development of conductive cellulose. These findings offer us the freedom to further develop MCT in light of its ability to form composite aerogels and films.

72

4.2 Experimental work

Stock solutions of nanocellulose and PVA, as well as the preparation of NC-PVA aerogels, are described in section 3.3.1. The approximate yield of 40% NCC produced through the process described in section 3.3.1.1 was consequently separated through centrifugation for this study. The remaining 60% nanocellulose fibrils termed treated micro-cellulose (MCT) in this chapter, was used for this investigation and consequent aerogel preparation. For this study, untreated microcrystalline cotton cellulose was not able to form an aerogel because of its intrinsic incapability of forming a nano-scale 3D network. Nanoparticles were incorporated as described in section 3.3.4. Characterisation and testing are carried out according to section 3.4.

4.3 Results and discussion

4.3.1 Morphology of oxidised cellulose sol-gels

TEM micrographs were taken of the individual MCU and MCT fibres to observe their appearance and morphology (Figure 4.1a and b). It is clear that the MCU fibres are bulkier with a lower aspect ratio than MCT fibres. This means that the oxidation treatment may have split the individual fibrils, which were bonded together to make a single MCU fibre, though the fibrils are not fully detached from the original fibre. This splitting of the fibrils increases the surface area which in turn increases the number of unbounded – OH functional groups (Figure 4.3). The treatment seems to have also cut the longitudinal fibrils into shorter lengths as observed in Figure 4.1b. Thus, these fibrils form a branched network, adopting a larger area that is more susceptible to collide with other singlets due to their volume capacity. This is similar to the Sol-gel process, where the monomers are the MCU particles which are converted into a colloidal solution (sol) via oxidation (MCT) and these oxidised MCTs cluster together to form an integrated 3D network (gel). The MCT suspension forms a sheet layer when drying a droplet onto a glass slide, forming a film (Figure 4.1c). This is caused by the coalition of MCT clusters overlapping and depositing together due to the evaporation of the water solvent. Conversely, the MCU particles form the same powder that was originally mixed in with the water solvent, showing no

changes from the original morphology (Figure 4.1d). A branched network of MCT fibres is visualised in Figure 4.1b. These branched MCT networks are less dense than MCU fibres due to the branched network occupying a larger volume. This relates to the dispersion of the celluloses when suspended in water. After homogenising the suspensions at high shear speeds of 10,000 rpm for 5min, settlement starts occurring for MCU suspensions after a minute's observation. This phenomenon was not observed for MCT suspensions even after an hour's observation, whereas most of the MCU fibres were fully settled due to Stokes law. Homogenised MCT suspensions also seem less turbid than MCU suspensions.



Figure 4.1 Comparative visual analysis of MCU and MCT via TEM micrographs of (a) MCU particles and (b) MCT particles; SEM images of (c) an MCT sheet layer and (d) MCU particles; NTA particle

distribution graph of (e) MCT particles and (f) MCU particles; SEM cross-sectional images of (g) an MCT aerogel showing the distinct morphological profiles

4.3.2 Analytical and morphological study of treated cellulose gels

The treatment of cellulose resulted in a shift of the overall particle distribution (Figure 4.1e and f). The distributions of MCT particles have a narrow size range with a mean and standard error of 200.3 ± 9.0 nm measured across concentrations of $4.78 \times 10^8 \pm 2.78 \times 10^7$ particles/ml (Figure 4.1e). MCU particles, on the other hand, have a very broad size range with a mean of 294.4 ± 37.4 nm measured at concentrations of $3.30 \times 10^8 \pm 4.85 \times 10^7$ particles/ml (Figure 4.1f). Even though, the concentration is supposed to be a control variable the concentration for each particle type cannot be completely controlled and thus there is some discrepancy between the concentrations. This particle analysis offers a quantitative measurement while the TEM micrograph provides qualitative results which show a size spread of the treated cellulose fibrils. It is worth to note that several 450 nm filters were used for MCU to achieve the desired test volume due to the large particle sizes blocking the filter, which may have forced some of these larger particles through the filter as shown by the MCU distribution. Contrarily, only one filter was sufficient for MCT filtration. A higher concentration was filtered out from MCT than MCU, however, the concentration was less than the 2 wt% suspension (NTA requires a low particle concentration to measure effectively), which may be due to the branch-like shapes of MCT that increase the overall particle sizes and thus may get trapped in the filter. The trapped MCT particles may also reduce the pore size of the 450 nm filter. Due to the network structure, MCT particles are likely to merge together to form a larger-sized particle. This increases the retention of MCT particles through the filter as well as reducing the pore size of the filter in the areas where these particles were retained. This reduces the accuracy of the results. Also, the NTA instrument will treat the merged MCT particles that were inlet as one particle when tracking which reduces the accuracy of the particle size distribution. Another factor that may have reduced the result accuracy is the fact that the particles may not have been filtered correctly due to the high aspect ratios of MCU in comparison to the MCT where the latter is more spherical in nature due to its branched 3D network structure

whilst the former is more cylindrical. For example, in Figure 4.1f, the reason why sizes larger than 450 nm is recorded is that some larger particles were oriented across a smaller sized plane when being filtered before the larger sized plane was recorded by the NTA. Thus, Figure 4.1f may include the lengths and widths of different particles without differentiating between the two. On the other hand, for Figure 4.1e, the sizes recorded may not vary much across different planes due to the more spherical MCT. Thus, the accuracy of the results are limited by the NTA technique. When lyophilised, the freeze-casted MCU suspension was not able to form an aerogel structure. Instead, only MCU powder was formed with the same characteristics as the original powder, similar in effect to Figure 4.1d. On the other hand, lyophilised MCT formed a light aerogel with no powder formation. Figure 4.1g depicts the result of freeze-casting MCT to create the aerogel. The Figure can be seen to contain two distinct morphological profiles including a steady-state zone (SSZ) in the top region and a transition zone (TZ) comprising the majority of the image. The crystal morphology transition into the SSZ occurs due to an increased thermal buffer resulting from the growing ice front leading to the solidification velocity to decrease over time. This allows for more time for the ice crystals to grow perpendicular to the freezing direction causing the lamellae to possess a higher thickness as seen inset of Figure 4.1g [334]. The thermal gradient and particle redistribution determine the pore sizes and crystal morphology, where particle redistribution is defined by factors including the solidification front velocity, the angle between temperature gradient and crystal growth as well as the particle size. However, the most influential factor is the temperature gradient as a function of distance and time which governs the morphological structure of the lyophilised aerogel [335,336]. The TZ in Figure 4.1g can be seen to possess a homogenous and porous house-of-card layered structure. This is due to a higher solidification velocity during freeze-casting whereby the ice crystals are aligned parallel to the vertical thermal gradient along the ice front [337–339].

4.3.3 Influence of oxidation on the crystal structure of nanocellulose

Results of MCU powder diffraction pattern can be identified with cellulose type Iβ crystalline structure with a calculated crystallinity of 68 %. However, MCT powder X-Ray diffraction pattern shows some

77

changes. The crystallinity decreases to 54%. Cellulose-Iß peaks are fully recognisable, however, the ratio between (0 0 2) and the peaks (-1 0 1) and (1 0 1) decreases from 4:1 in the MCU to 2:1 in MCT indicating a change in molecular orientation of the cellulose, which normally crystallises in the (0 0 2) direction. Furthermore, full width at half maximum (FWHM) of 1.723 was observed on the (0 0 2) peak of MCU and FWHM of 1.502 was observed for the same peak for MCT. The width indicates crystallites sizes ranging ~50/60Å for both. Further differences are visible between the MCU and the MCT XRD patterns (Figure 4.2), in particular in the region of 12-13 degrees, where a pronounced tale of the (-1 0 1) peak is visible. An initial identification of this feature and the peak at 20.5 has been made with cellulose II, indicating respectively the (-1 1 0, 30% intensity) and (1 1 0, 100% intensity) of cellulose II, the other main peak of cellulose II being the (0 2 0, 80% intensity) which is at $2\theta = 23.6$ hence overlaps with the strongest line of cellulose I β (0 0 2). To confirm the interpretation, the calculation of a theoretical pattern of cellulose I β and cellulose II mixed was obtained using the MCU measured pattern and published measured pattern of cellulose II (PDF 2 ICDD database, entry 00-063-1436). The calculation showed the possible presence of ~10% of cellulose II. A further simulation was carried out using TOPAS and the structural data for cellulose IB (PDF 2 ICDD database, entry 00-056-1718) and cellulose II (PDF 2 ICDD database, entry 00-063-1436 and 00-056-1). The simulation resulted in R=3.63, confirming the co-existence of cellulose I β and II. Consequently, the treatment induces partial transformation of cellulose IB into cellulose II, possibly due to partial mercerisation in the presence of NaOH during reaction, and changes in molecular orientation in MCT compared to MCU and oxidation.



Figure 4.2 XRD spectra comparing MCU with MCT. The theoretical pattern of 90% cellulose Iβ + 10% cellulose II was also constructed using the cellulose II pattern from the ICDD database to signify its similarity to the MCT curve

The confirmation of the presence of cellulose II indicated that some of the chemical structures of cellulose strands (inter and intra bonding) are changed. In particular, the overall indication obtained by XRD and FTIR analysis shows that part of the inter-molecular bondings O(6)H-O(3) present in cellulose I β and new intra-molecular O(6)H-O(2) are formed. This structural change generates wider unit cells: 662.6 Å³ in cellulose I β [340] and 754.1 Å³ in cellulose II [341–343]. This increase in inter-and intra-molecular bonding fosters the decrease of density of the structure and increases the potential of the MCT to include alien materials in its structure, i.e. composite formation, functionalisation, quantum dots grafting. Furthermore, changes in crystal orientation of cellulose I β can be observed through the diffraction pattern, indicating a change from the preferential (0 0 2) crystallisation direction to a (0 0 2) and (-1 0 1) directions fostering a less fibrous crystal structure. This is confirmed by the data acquired using FTIR analysis (Figure 4.3). When observing the IR spectra for MCT, it can be seen that there is an increase in the O-H absorption peak, ranging between 3330-3230 cm⁻¹, in respect to the MCU spectra. MCT has both cellulose I β and cellulose II present. This means that the intermolecular O-H bond is different. Cellulose I β has O(6)H-O(3') intermolecular bonds, whilst cellulose II has O(6)H-O(2') intermolecular bonds, both cellulose II has O(6)H-O(3') intermolecular bonds,

Iβ and cellulose II have the same amount of O(5)H-O(3') intramolecular bonds present in their unit cells. Therefore, the O-H peak range should not be reduced in absorption because of the same total amount of O-H bonds present in the unit cell of both cellulose types, unless there is an increase amount of O-H functional groups present in the cellulose. This would be the case in MCT with a higher overall absorption change, which may reflect the oxidation process breaking down the cellulose chains with increased O-H functional groups. An alteration in the peak shape should also be observed due to the transformation of the intermolecular O-H bonds, from an O(6)H-O(3') in cellulose Iβ to an O(6)H-O(2') in cellulose II, which causes a shift in the absorption peak. However, the MCT O-H peak does not seem to show a major alteration in peak shape in respect to MCU, which may be due to the low quantity transformation of cellulose II (~10%) from cellulose Iβ (~90%). A similar divergence is observed for the 2850 cm⁻¹ peak, corresponding to the C-H bond, in MCT. The MCU spectra contains a 1642 cm⁻¹ absorption peak, corresponding to the C=C bond, suggesting the likely presence of lignin content.



Figure 4.3 FTIR spectra displaying (a) the overall peaks of MCU, MCT, MCU-Cu and MCT-Cu, (b) convoluted curves of MCU to highlight the peaks in the OH and double bond regions against the structure of cellulose Iβ, (c) convoluted curves of MCT to mark the shifts in the peaks against MCU

and compare against the structure of cellulose II, and (d) convoluted peaks of the MCT and MCT-Cu with proposed structure of cellulose II + Cu particles

The MCT spectrum, on the other hand, displays a large absorption peak corresponding to $R-C=O(O)^{-1}$ at 1606 cm⁻¹. Initial observation of this difference in the MCT spectra may be interpreted as a shift in peak from 1642 cm⁻¹ to 1606 cm⁻¹, suggesting that the C=C bond in lignin has been broken down. Although this may be possible to some extent, it is not the full explanation. Observing the overall change in spectra, the increase in absorption for O-H and C-H as well as the formation of a new peak in 1606 cm⁻¹ strongly correlates to the oxidation treatment in chemically breaking up the 1-4 glycosidic bonds to form an increase in reducing ends of carboxylic functional groups. In addition, cellulose Iβ in its natural state has R-C=O(H) functional groups present in its reducing end (Figure 4.3b). However, MCT has C-OH instead of C-H functional groups in this case (Figure 4.3c). This change in functional groups may be the fundamental reason for promoting the alteration in the intermolecular hydrogen bonding from an O(6)H-O(3') in cellulose I β to an O(6)H-O(2') in cellulose II and hence the transformation in the cellulose type (Figure 4.3). Observing the IR spectra for the addition of copper (Cu) nanoparticles (Figure 4.3d) shows alterations in the MCT absorption peaks inferring that chemical bonding has occurred. Conversely, no change was observed for the MCU peaks after the addition of C, inferring that the oxidation/cellulose transformation has favoured bonding with Cu. The MCT-Cu spectrum displays a divergence in both the 3300 cm⁻¹ and the 1055 cm⁻¹ absorption peaks, which refer to the –O-H and –C-O-H bonds, respectively.

4.3.4 Effect of copper nanoparticle incorporation on nanocellulose

The MCU and MCT processed in combination with copper nitrate were investigated to ascertain: if nanoparticles were formed using the procedures, what was their composition (ionic or metallic) and size, and what was their position in relation to the cellulose. The MCU showed the nanoparticles formed during the process, however, only a few of the particles were present on the surface of the MCU (Figure 4.4a) with a size ~30nm, while most of them were free in solution, hence they deposited on the sample holder substrate (Figure 4.4b), in aggregate about 30 nm in size while the single

82

particles showed an average size of 10nm. Conversely, the MCT showed dispersion of particles on the surface of the cellulose (Figure 4.4c). All the particles showed an average size of 10nm and can be observed as individual particles and small aggregates of ~30 to ~50 nm.



Figure 4.4 EDX images showing (a) nanoparticle on the surface of MCU (Inlens detector), (b) nanoparticles (bright spots) on the sample holder substrate (Inlens detector) and (c) copper nanoparticles (bright spots), individual and in aggregates, diffused on the surface of MCT

Raman investigation was conducted using a wavelength of 514nm to investigate if copper was in metallic form and if any changes occurred on the surface of the cellulose, in particular of MCT. It can be seen that the region below 1600 cm⁻¹ (especially below 700 cm⁻¹) is most sensitive to the conformation of the cellulose backbone, whereas the region above 2700 cm⁻¹ is more sensitive to hydrogen bonding [344]. In the use of 514 nm laser, the most highlighted area is the region below 1600 cm⁻¹. The processing with copper nitrate seems to show a loss of crystallinity of MCT, the peaks at 1095 and 1124 cm⁻¹ showing a broadening effect. These bands correspond to the COC stretching symmetric, as identified by Attalla and Wiley [345] and Schenzel and Fischer [346]. Furthermore, two new peaks are visible in the MCT treated with copper nitrate at 380 and 461 cm⁻¹, corresponding to δ (CCC), δ (CCO), ring deformation (Schenzel and Fischer [346]). Additionally, peaks at 2106 and 2168 cm⁻¹ are visible in the MCT powder, while they cannot be further detected in the MCT treated with copper nitrate. These peaks are identified as indicating (C \cong C) functional group [347]. Conversely, the MCU shows an increase in crystallinity after treatment with copper nitrate, and shows the presence of the peaks at 380 and 461 cm⁻¹, corresponding to δ (CCC), δ (CCO), ring deformation (Schenzel and Fischer [346]), and the ones at 2106 and 2168 cm⁻¹ indicating the (C \cong C) functional group [347]. CuO and Cu2O Raman peaks should be visible at 300, 350, 555 and 605 [348], or 520 and 630 [349] or 400 cm⁻¹ for Cu(OH) [350]. However, these peaks are neither detected on MCT or MCU. Metallic copper Raman shift is observable in the region 1300-1360 and 800 cm⁻¹ [351]. As these regions overlap with cellulose, the peaks are not fully identifiable (Figure 4.5).



Figure 4.5 Raman spectra analysis of Cu nanoparticles on MCU against MCT

4.4 Conclusion

In conclusion, we reported the increased aspect ratios and surface area with the formation of a branched network as a result of oxidation treatment on cellulose fibres. MCT had the capacity to form xerogel films as well as a homogenous house-of-card structured aerogel when lyophilised. Cellulose I β was partially transformed to cellulose II (~10%) in MCT with changes in molecular orientation. Quantitative measurements indicated the formation of new intramolecular O(6)H-O(2') bonds and intermolecular hydrogen bonding of O(6)H-O(3') in MCT. We attributed these results to the apparent reduction in density and manifested the potential of MCT to incorporate alien materials in its structure, i.e. composite formation, functionalisation, quantum dots grafting. Moreover, the treatment was found to break up 1-4 glycosidic bonds to form an increase in reducing ends of carboxylic functional groups in MCT.

Chapter 5 Functionalised nanocellulose as functional additives and films

5.1 Introduction

This chapter reveals a chlorine-free bleaching alternative for nanocellulose production and identifies the commercial potential of functionalised nanocellulose for several markets, including chemical industries that supply additives for bulk paper packaging producers. Nanocellulose films and coatings are also explored for disposable cup producers using an alternative lining to address the need for sustainable lining within products. The addition of the NC as an additive in recycled fibre was found to enhance the burst index pressure of brown paper by 91 % using only 2 wt.% as well as reduce the porosity index by 53 %. An alternative TEMPO-free oxidation in the form of peroxide bleaching was utilised due to commercial production needs to produce an NC additive. This alternative NC was found to enhance the properties further such as increasing the burst index of plain brown paper by 270 %. Developed NC films show low-density polyethylene (LDPE) lining currently used can be significantly reduced to an 80-20 % composition of NC-LDPE.

5.2 Experimental work

Nanocellulose additives for the recycled paper were prepared as described in section 3.3.5. Stock solutions of NFC, NCC and mixture of both nanocellulose types (NFC&NCC) were formulated (section 3.3.1.1). The recycled paper sheets and the NFC-LDPE composition films were characterised and tested according to section 3.4.

5.3 Results and discussion

5.3.1 Nanocellulose as coatings and as additives for paper stock preparation

Over the last two decades there has been a significant increase in the recovery and recycling of old corrugated containers (OCC), often referred to as Kraft liner shavings (KLS). From 1997 to 2017, an increase in the rate of recovery was recorded from 67.7% to 88.8% [352]. With increasing numbers of cycles a fibre is recycled, there is a reduction in the mechanical properties of paper and board due to a reduction in fibre bonding. Arguably, one of the main causes for the reduction in fibre bonding is the use of fillers commonly used for optical brightening. These negatively charged filler particles reduce

bonding between anionic cellulose fibres due to increasing ionic repulsion and consequent increase in bond length [353]. Therefore, it is critical to introduce dry strength agents; cationic polyacrylamides and cationic starch are often used to increase the bonds between fibres and attract anionic trash, increasing the strength of recycled paper.

Trials conducted at Axchem UK using their facilities involved the addition of NC in the wet end (stock preparation) show very promising results (Figure 5.1). It can be seen that both NC types give rise to an approximately 50% increase in burst strength with only a 0.5% addition and positive correlation with increasing NC increments thereafter (Figure 5.1). Similarly, the porosity index also shows a negative correlation with NC increments, inferring that more fines of the recycled pulp stock are likely to be retained (Figure 5.1b). Moreover, the NFC results show that around double (91%) the burst strength is reached with only a 2% addition of NFC. At the same time, the addition of 2% of NFC also halves the porosity index of paper sheets which as explained above, showing NC to be an excellent retention aid. NFC was found to exhibit a larger burst index than NCC when reinforcing paper sheets (100 gsm blank sheets). The results at an initial glance may seem to indicate that NFC is a better option relative to NCC, however, when the burst index is divided by the porosity index, NCC gives a higher burst strength for every reduction in porosity. This means that if more NCC were to be retained, it may be more effective and significant. This trial, therefore, presents positive results and offers the possibility for further advancement. This could either be to further treat the chemistry of NC to suit the intended application of enhancing the paper strength and retention ability or to combine both NFC and NCC together to complement each other for an all-in-one commercial additive.

86



Figure 5.1 Comparative results of NFC (green) and NCC (blue) against blank paper sheet as control, displaying (a) burst index and (b) porosity index

Blank paper sheets were also sprayed with three layers of NC coat to further examine its effectiveness. Trials conducted with NC addition as a spray coat show an alternative route to its addition in the wet stock (Figure 5.2). The paper sheets were characterised through SEM which show a smoother surface when an NC coat is applied in comparison to uncoated paper. It can also be seen that there are fewer pores when an NC coat is applied. This means that as well as adding NC in the wet section, NC can also be applied in the dry section of the papermaking machine alongside starch coating or as a replacement to starch due to its abundance and renewability.



Figure 5.2 Brown paper sheets coated with NC and SEM micrograph displaying stained NC to differentiate between NC coat and uncoated region

Overall, the data presented indicate that the addition of NC in the wet mix enhanced the dry strength of paper and thus may reduce breaks in papermaking machines. The data also indicates that the patented technology is able to increase retention and enhance the strength, consequently increasing the number of times the recycled fibres can be used without the addition of virgin fibre. One may envisage that with developments in technology, cellulose fibrils in the quantum scale may be isolated for further innovations.

5.3.2 Unveiling a totally chlorine-free nanocellulose additive alternative

As these results provided a motive to commercialise NC as an additive product, certain issues needed to be addressed and resolved for industrial manufacturing feasibility. This included the use of other chlorine-based bleach methods, such as sodium chlorite (NaClO₂), to produce NC since chlorinated chemicals are a health and environmental concern due to their corrosive and toxic nature at high exposures [354]. Therefore, hydrogen peroxide (H_2O_2) , an alternative oxidant, was trialled as a totally chlorine-free bleach replacement for a greener process since its decomposition is only oxygen and water. For a comparative study, all conditions were kept the same, including keeping the peroxide in excess yet at a tolerable level to not exceed a hazardous concentration of 30 wt.%. This was important to understand whether this change in the oxidant impacts the ability of the produced NC to provide dry strength. Suspensions of NC prepared from hypochlorite bleach and peroxide were tested using pH metres, charge and fibre potential analysers since these factors are critical for optimal paper production. These results are displayed in Table 5.1 and Figure 5.4. Firstly, pH measurements display the suspensions to be neutral except for NC prepared from peroxide displaying low alkalinity of 8.83. This may suggest the need for extra centrifugation cycles, however, considering the preparation of NC with both peroxide and hypochlorite being in excess, it also suggests peroxide to have a higher oxidation power. This would be true for the use of hydrogen peroxide in the presence of sodium hydroxide due to its conversion to sodium peroxide which has a higher oxidation potential than sodium hypochlorite. This means in optimal conditions of preparing NC, lower concentrations of peroxide than hypochlorite bleach may be required for oxidation to realise NC. In other words, for the same number of centrifugation cycles to realise a neutral pH state, a lower amount of peroxide results in the same pH of NC prepared from the hypochlorite bleach. However, this suggestion can be argued to not be fully accurate as the study has not considered optimising the pH of the reaction. While it is

88

true that the oxidation reaction is pH-dependent for achieving the highest oxidation-reduction potential (ORP), the purpose of this study was to reveal a suitable alternative to the use of sodium hypochlorite bleach that is also environmentally friendly and commercially feasible. The conclusion of this comparison may provide further research opportunities for optimisation of working conditions to develop this reaction and NC production further. A pH meter was used to measure the values in Table 5.1 for each sample, including the conductivity and ORP values.

	рН	Conductivity	ORP
		(µS/cm)	(mV)
Pulp	6.45	2050	-147.7
NCC (Hypochlorite)	7.34	149.9	283.0
NCC (Peroxide)	8.83	107.9	181.0
NCC & NFC (Peroxide)	7.57	17.04	269.0

Table 5.1 Comparative quantitative measurements of suspensions

In comparison to pulp, suspensions of NC prepared by hypochlorite and peroxide bleaching methods show positive ORP values (see Table 5.1), which indicate their oxidising ability and thereby potentially aiding the pulp from alkaline degradation (peeling). Again, these ORP values would be higher if the optimal working pH (as well as temperature and pressure) was considered for these bleaching chemicals. Since, the ORP value is directly proportional to the oxidising potential, increasing the ORP value increases the oxidation potential of the chemical used. For example, when comparing gaseous chlorine to sodium hypochlorite as oxidising agents, the oxidising effect is the same. That is, both produce hypochlorous acid, the oxidising agent present for disinfection in water and wastewater application. When chlorine gas is dissolved in water, the reaction forms hypochlorous acid and hydrochloric acid:

Cl₂ (chlorine gas) + H₂O = HOCl (hypochlorous acid) + HCl (hydrochloric)

When a hypochlorite is added to water, the reaction forms hypochlorite ion and hydroxide:

NaOCl (sodium hypochlorite) + $H_2O = OCl^-$ (hypochlorite ion) + OH (hydroxide)

Hypochlorous acid and hypochlorite ion are both disinfection agents. These forms can exist together, but their concentration depends on the pH of the solution. As can be reflected in Figure 5.3, HOCI \rightleftharpoons $OCI^- + H^+$ at 25° C and pH of 7.5, half of the chlorine present in a solution of OCI^- and half is HOCI. At higher pH values, the quantity of OCI^- increases at the expense of HOCI and at lower pH values, the shift is toward the conversion of OCI^- to HOCI. At a pH of about 5, nearly all the chlorine is present as HOCI, and at pH 8.5, nearly all the chlorine is present as OCI^- .



Figure 5.3 Relationship between hypochlorous acid (HOCl) and hypochlorite ion (OCl⁻) at various pH values (which is inversely proportional to the ORP)

The activity of hypochlorous acid as a disinfectant/oxidiser (i.e. higher ORP value) is greatly superior to that of the hypochlorite, being almost 80-100 times more effective [355]. Chlorine gas lowers the pH of the solution, thus more HOCI is present and is more effective. At pH 7, 76% of the chlorine is in solution as HOCI. Whereas, hypochlorite raises pH, losing its oxidation effectiveness. This may contribute to deposits on equipment and residues in hard water. Hypochlorites also produce NaCI (salt) which may have an adverse effect on the quality of the water or solution. Furthermore, hypochlorites are more sensitive to the organic matter in the water and thus lose their oxidation effectiveness faster. In order to reduce the pH, peroxy acids such as acetic acid need to be used which aids in secondary oxidation. On the other hand, the efficacy of hydrogen peroxide bleaching is directly proportional to increasing its pH. The significant increase in bleaching outcomes occurs at pH 6, with maximum effectiveness achieved at pH 9 [356]. Here, sodium hydroxide can be used to aid this increase and may help initiate the production of peroxy acids in the presence of hydrogen peroxide. Peroxy acids have an even greater oxidation potential than hydrogen peroxide and are capable of selectively oxidising lignin as well as brighten the NC pulp produced [354]. Since sodium hydroxide increases the resultant pH of oxidised NC suspensions, acetic acid can be used to neutralise the

suspension and minimise the use of centrifugation. Diminishing the need for centrifugation also reduces energy and loss of NC product through centrifuging cycles. Table 5.1 also shows the difference between the ORP of the pulp as a negative value and NC as a positive value. This is to be expected since the pulp is chemically unmodified cellulose, which is naturally anionic. When treated, cellulose is being oxidised which is the process of losing electrons or gaining hydrogen ions and making the overall/resultant oxidised cellulose cationic. In other words, the glycosidic bond C-O-C of anionic cellulose gets broken down in oxidation to C-O-H bonds by introducing two respective hydrogen ions. However, the positive value also includes excess residual of the bleaching chemicals which greatly contribute to the ORP value. Therefore, the positive ORP values may be ambiguous as to which is the major contributing factor even after several centrifugation cycles were made for purity of NC.



Figure 5.4 Comparative results of zeta potential and particle charge detection against anionic blank paper sheet as control

The zeta potential (mV) was measured to identify the surface charge strength of the stock suspensions. In the papermaking process, the zeta potential is measured to determine the optimal dosage of chemical additives that adsorb on the anion pulp fibre to stabilise the pulp suspension. The negatively charged pulp fibre (anionic) is normally in suspension with anionic trash (charged contaminants like pectic acid). The anionic trash affects the dosage quantity because the cationic chemical aids get caught by the anionic trash and are therefore not adsorbed. This means initial dosages of cationic additives may not or only marginally change the zeta potential of the fibre due to the anionic trash content present in the suspension. Therefore, an increased dosage of cationic additives is required to neutralise the anionic trash and beyond which zeta potential starts to change to a larger voltage. Increasing zeta potential shows retainment of the cationic additives on the anionic pulp fibre. Figure 5.4 displays the pulp fibre suspension labelled as 'blank' with a zeta potential of -8.43 mV in a concentration of 163.33 µeq/l charged particles. The zeta potential is increased when adding retention aid to -8.07 mV and further still with NCC & NFC addition at -7.77 mV. These results in conjunction suggest that the NCCs are being successfully retained on the fibres are not in the water phase of the pulp. NCC Hypochlorite produces the most negative zeta potential recorded at -10.03 mV while the NCC Peroxide produces the lowest negative zeta potential at -7.50 mV. Interestingly, the addition of NCC Hypochlorite to pulp fibre is displaying a more negative zeta potential than Blank pulp fibre without any additives, even though NCC Hypochlorite is identified to be cationic due to oxidation and is displayed in Table 5.1 with a positive ORP voltage. The zeta potential is affected by pH whereby the zeta potential becomes more negative when the pH is more alkaline. However, the NCC Hypochlorite is neutral at a pH of 7.34 meaning there is about a half of hypochlorous acid and hypochlorite ions present. Beside the conductivity conceivably affecting zeta potential, a possibility for the more negative voltage might be that the hypochlorous acid is reacting with the anionic trash present in the pulp suspension. Nevertheless, the zeta potential of NCC Peroxide is displayed to be the least negative of all the additives at -7.50 mV even though its pH is 8.83. This means that the zeta potential of the NCC Peroxide dosage should be even more positive and therefore the true voltage is not known due to its alkalinity.



Figure 5.5 Comparative mechanical and physical property results of NC additives against retention aid additive, displaying (a) tensile strength index, (b) compressive strength index, (c) burst strength index and (d) air permeability index

Mechanical test results show overall enhancement in mechanical strength when comparing tensile and compressive strength indices of NC additives against the standard retention aid additive used commercially (Figure 5.5). The mean tensile strength index when using the retention aid additive gives values of 0.294 N/gsm and 0.598 N/gsm for paper tested at the cross direction (CD) and machine direction (MD), respectively (Figure 5.5a). In comparison, the NCC hypochlorite additive is shown to have the highest improvement in tensile strength over the other additives tested. This is found at 4.4 % increase in CD and 6.2% increase in MD tensile strength. The NCC Peroxide gives similar results of 4.1 % and 5.5 % increase for CD and MD, respectively. On the other hand, the NCC & NFC additive shows the lowest increase in tensile strength at 2.7 % and 0.8 % for CD and MD, respectively. Results for the short-span compression test (SCT) show a similar overall trend to the tensile index expect for the NCC Peroxide displaying a higher average strength than NCC Hypochlorite (Figure 5.5b). NCC Peroxide addition gives a 7.02 % CD increase and 5.29 % MD increase to the retention aid, which has a compressive strength index of 11.4 N/gsm and 20.8 N/gsm at CD and MD, respectively. Results also show that the resistance to rupturing is also increased using NCC over the Retention Aid when comparing the burst strength index (Figure 5.5c). The burst strength for the retention aid is found at 0.907 kPa/gsm while the NCC Hypochlorite, NCC Peroxide and NCC & NFC additives are found to have a higher index at 8.4, 21.2 and 24.9 % increase, respectively. The use of the longer NFC fibrils alongside the NCC seems to have supported the increase burst strength as would be expected, however, it is found to increase the air permeability by 13.1 % in comparison to the Retention Aid, which has an air permeability index of 14.41 ml/min.gsm (Figure 5.5d). This means that the NFC fibrils in the NCC & NFC additive may not be aiding the reduction of the air permeability since the NCC Hypochlorite and NCC Peroxide additives show a reduction of 12.0 and 12.8 %, respectively. Figure 5.5, reveals the overall benefit of NCC additions to enhancing the mechanical property of paper, with NCC Peroxide additives exhibiting to be the most promising.

To conclude, no significant difference can be observed between NCC Hypochlorite and NCC Peroxide bleaching for tensile strength. A significant difference can be observed between NCC Hypochlorite and NCC Peroxide for SCT, however, this difference is mainly in the cross-direction samples, arguably no significant difference can be observed between the machine direction samples. NCC Peroxide provides higher burst strength than NCC Hypochlorite. No significant difference can be observed between NCC Hypochlorite and NCC Peroxide for air permeability. For both tensile strength and SCT, NCC & NFC can be observed to provide the least amount of increase in strength and the highest amount of air permeability through the sheet. However, NCC & NFC provides the highest overall burst strength. In conclusion, the use of Peroxide as a replacement of Hypochlorite does not impact the ability of the nanocellulose crystals to provide dry strength. It also means that the need for retention aid, which includes polyacrylamide and bentonite, can be reduced for a sustainable and less harmful NCC additive.

5.3.3 Investigating nanocellulose films as a potential alternative to polyethene lining of disposable cups 5.3.3.1 Realising optimum drying method and condition for NFC-based films

To produce NFC films, drying conditions of each NFC concentration was inspected through desiccating and air-drying at temperature- and humidity-controlled environment. It was established that the NFC films in the desiccator dried at a faster rate (faster water evaporation rate) than identical samples dried in a humidity-controlled environment set at the average room humidity, most likely due to the removal of moisture from the air surrounding the pots in the desiccator, compared with a constant (but mild) humidity in the humidity-controlled environment. Figure 5.6 displays the different concentrations of NFC films after air-drying to be compared with other drying methods. An NFC film with a concentration of 1.5 wt.% was also trialled, however, the suspension was relatively too viscous and produced an opaque film. The differences in thickness and strength of the NFC films were only apparent to the touch with clear visual transparency. As would be expected the opacity of the films increased with increasing concentrations due to increased fibril crosslinking which occludes light from transmitting through. Moreover, agglomerations of fibrils were visually found on the NFC films with concentrations above 0.8 wt.% NFC content. This may indicate to be unsuitable for oven-drying at concentrations of 0.8 wt.% and above since it may lead to excess agglomeration, affecting the uniformity of the film. Also, films with concentrations below 0.3 wt.% were torn too easily. Concentrations between 0.4-0.6 wt.% seemed to be suitable intervals, whereby no impurities were identified on the films and possessed reasonable tensile resistance.

95


Figure 5.6 Displays (a) NFC films at increasing NFC wt% concentration and (b) 0.4 wt% NFC film treated at varying drying conditions

A transmittance test was conducted for this interval, using a light transmittance meter, for drying through desiccating and oven drying. As seen in Table 5.2, oven drying is observed to be the most transparent due to the higher transmittance and as would be expected the lowest concentration of the interval (0.4 wt.%) exhibited the highest transmittance at 85.7%.

NFC concentration (wt.%)	Light transmittance (%)				
	Dried via a desiccator	Oven-dried at 70 °C			
0.4	72.1	85.7			
0.5	71.4	85.4			
0.6	71.1	85.1			

 Table 5.2 Transmittance of NFC films at varying concentrations

NFC concentrations of 0.4 wt.% and 0.5 wt.% were also air-dried in ambient conditions as well as ovendrying at 10 °C increment from 30 °C to 140 °C. The dried samples are illustrated in Figure 5.6 and show overall promising results as the films appear to decolourise to a brown shade due to oxidation beyond 110 °C. The samples dried at 100 °C only slightly hints a crispy feel after 24 hours but do not show signs of decolourisation. The oxidised samples increase in brittleness with increasing oven temperatures. Brittleness and decolourisation are undesired and unsuitable for application as a lining for disposable coffee cups, even if it is argued that the samples were exposed at high temperatures for a long duration of 24 hours. Also, some impurities were found in samples dried at temperatures below 50 °C. The optimal drying temperature is inspected to be within 70-90 °C to evaporate any moisture whilst also not causing any decolourisation and impurities to appear. Samples oven-dried at 70 °C were realised as optimum drying in accordance with mechanical strength after determining the highest tensile stiffness and strength out of the tested 70, 80 and 90 °C dried samples. Low-density polyethylene was introduced to NFC suspensions once optimum drying conditions were determined as 70 °C oven-drying for 24 hours for a weight concentration of 0.4 wt.%. LDPE was incorporated with NFC at various concentrations to inspect the opacity of the samples. Figure 5.7 displays the contrasting sample compositions and reveals increasing opacity with increasing LDPE addition. Moreover, compared to an NFC film, an LDPE film is observed to be fully opaque.



Figure 5.7 Compares the transparency of NFC-LDPE compositions to the pure LDPE film

5.3.3.2 Surface morphology and thermal stability of NFC-based films

NFC was also modified with (3-glycidoxypropyl)trimethoxysilane (GPTMS) to review the hydrophobicity of NFC-GPTMS films and any effect GPTMS incurs when modifying NFC as films. The surface structure of the NFC, NFC-LDPE, NFC-LDPE-GPTMS and NFC-GPTMS films were reviewed through SEM. Figure 5.8 shows overall smooth surfaces with minor impurities in the form of agglomerate clumped NFC fibrils after drying. These agglomerates are caused by irreversible hydrogen bonds formed between the nanofibrils and can potentially be resolved through the utilisation of a solvent exchange process with acetone to prevent the fibrils from sticking together. Freeze-drying the NFC can also prevent fibrils forming irreversible hydrogen bonds and thus create wrinkle-free NFC films as shown by Qing et al. [357]. The oven-dried pure NFC films appeared considerably smoother than the air-dried samples and those dried in a desiccator. The 0.4% NFC film oven-dried at 70 °C is presented in Figure 5.8a. Whilst this is not a perfectly smooth sample, the porous film was found to

be the most optically viable drying mechanism, time and cellulose concentration for the purpose of coating coffee cups. LDPE and GPTMS incorporated NFC films are displayed in Figure 5.8b and c, respectively. The incorporation of the LDPE matrix seems to allow for a greater level of isotropy across the surface of the composite, which allows for uniformity in strength tested at different directions. The NFC-GPTMS seem to be less porous than the pure NFC film in Figure 5.8a with no visible impurities.



Figure 5.8 SEM surface micrographs of (a) a 0.4 wt% NFC film treated at 70 °C, (b) NFC-LDPE 90-10% film and (c) NFC-GPTMS film

Thermogravimetry analysis (TGA) was conducted to quantitively analyse the thermal stability of the different film compositions as well as the value of integrating LDPE in NFC. Figure 5.9a and b display TGA results of the pure LDPE and pure NFC films, respectively. The LDPE sample is seen to withstand high temperatures, reaching 372 °C without loss of any mass. This means that there are no volatile components within its composition such as moisture or monomers (ethylene). The thermal resistance of 372 °C is one of the reasons why LDPE is desirable in its use for coffee cups since the liquid within the cup is not expected to resist temperatures beyond 150 °C. The ideal water temperatures for

brewing coffee is normally between 90-96 °C which LDPE is capable to resist. Time of heat resistance is another factor to add here and since the TGA machine test rate runs at 5 °C increment per minute, the LDPE sample withstood temperatures beyond 100 °C for about an hour (54 minutes, 24 seconds) without decomposing. This is significantly longer than required. Using newton's law of cooling, hot coffee initially at 90 °C cools to 80 °C in the first five minutes and 50 °C in 20 minutes while in room temperature of 20 °C. The LDPE sample fully decomposed at 499.6 °C leaving ash weight content of 1.8 %. This infers that the decomposition of the LDPE occurs over a temperature range of 127.6 °C and a time interval of ~25 min (between 372 °C and 499.6 °C). The NFC, on the other hand, displays loss of volatile components which is likely to be moisture or trapped water content within NFC. Most of this moisture is lost at 100 °C and fully lost at 140.39 °C with a weight loss of 7.55 %. This is a concern when considering coffee cups due to the sorption capability of NFC and thus needs to be modified potentially by surface treatment with a hydrophobic agent. The NFC sample starts to decompose beyond 240 °C, displaying decomposition of 67.25 % at 354.8 °C and full decomposition at 443.6 °C. This infers an overall higher decomposition reaction temperature of 203.6 °C (443.6 – 240 °C). The appearance of different degradation rates could be due to the presence of hemicellulose or the decomposition of functional groups (e.g. -OH groups), structural depolymerisation and chains breaking along the polysaccharide (e.g. glycosidic linkages) which decomposes relatively early [358,359]. The NFC-GPTMS sample in Figure 5.9c displayed almost identical characteristics to the pure NFC film with only reducing the volatile components, such as the moisture content, present in the NFC to below 5 %. The LDPE incorporated NFC samples show interesting results. The NFC-LDPE 90-10 % composition sample in Figure 5.9d shows a shift in the loss of volatile components beginning at 150 °C instead of at 28.64 °C for pure NFC. This is phenomenal considering only a 10 % LDPE incorporation and shows a better result than incorporating GPTMS. The thermal stability of the NFC has also increased with the decomposition initiating at 352 °C. The initial temperature for volatile component loss is significant in the NFC-LDPE 80-20 % composition shown in Figure 5.9e with a 6.1 % weight loss at 354.2 °C before the sample begins to decompose. The NFC-LDPE 70-30 % composition in Figure 5.9f is almost indistinguishable

compared to the pure LDPE sample with a weight loss of 6.89 % at 379.4 °C before decomposition. Extrapolating from these results suggest that incorporation of 20-30 % LDPE might be enough to satisfy its application for coffee cups with increasing LDPE incorporation fully shielding NFC's sorption ability. The higher LDPE incorporated samples in Figure 5.9g and h are shown to enhance the thermal stability by increasing the decomposition temperature beyond the pure LDPE sample exhibiting decomposition at 386 and 397 °C, respectively. The NFC-LDPE 60-40 and 50-50 % samples also fully decompose at higher temperatures. The 50-50 % sample is fully decomposed at 493.9 °C with weight loss of 95.1 % before combustion of carbon is initiated and inert ash content found at about 600 °C. The decomposition reaction temperature is calculated at 96.9 °C (493.9 – 397 °C). An NFC-LDPE 90-10% with GPTMS composition was also tested and is shown in Figure 5.9i. The sample is seen as the best alternative in comparison to the pure NFC and the NFC-LDPE 90-10 % composition since it starts degrading after 210 °C. This suggests a possible benefit in adding GTPMS in NFC compositions with increased LDPE content.



Figure 5.9 DSC-TGA graphs of (a) pure LDPE, (b) pure NFC, (c) NFC-GPTMS 98-2%, (d) NFC-LDPE 90-10%, (e) NFC-LDPE 80-20%, (f) NFC-LDPE 70-30%, (g) NFC-LDPE 60-40%, (h) NFC-LDPE 50-50% and (i) NFC-LDPE 90-10% modified with GPTMS

5.3.3.3 Wettability, mechanical performance and thermal conductivity of NFC-based films

Wettability of the films is an important measure when considering its use as a barrier in coffee cups.

A satisfactory boundary needs to be established for it to be suitable and is normally kept at contact

angles above 90°. Table 5.3 displays the contact angle (CA) measurements of the film compositions.

Pure NFC film is expected to be hydrophilic with a CA of 49°, however, pure LDPE films were on the boundary of hydrophilicity-hydrophobicity with a CA of 89°. This signifies potential use in NFC content since the difference in wettability is not far apart and can be adjusted through modification of the NFC. Incorporating LDPE at set increments is seen to be proportional to the CA leading towards similar CA as pure LDPE. The highest difference change in CA was seen at NFC-LDPE 70-30% with an angle of 78°. Further increase in LDPE only slightly increased the CA beyond the 70-30% composition reaching CA of 86° at NFC-LDPE 50-50%. Addition of GPTMS seems to boost the CA of NFC towards hydrophobicity with a CA reaching 84° which is only a few degrees from pure LDPE at 89°. A sample of NFC-LDPE 90-10% modified with GPTMS was also tested and was found to achieve a CA of 85° which is an increase towards hydrophobicity. This suggests the possible addition of GPTMS to the NFC-LDPE 70-30% composition for its barrier application to be feasible.

Table 5.3 Displays initial contact angle measurement, tensile strength, density and thermal conductivity for the varying composition films

Film	LDPE	NFC	NFC-GPTMS	NFC-LDPE				
Composition (%)	100	100	98-2	90-10	80-20	70-30	60-40	50-50
Contact angle (° ±1°)	89	49	84	57	64	78	81	86
Young's Modulus (GPa)	0.20	2.23	2.56	2.12	1.50	1.45	1.10	0.65
Yield strength (MPa)	10	56	54	34	28	22	11	12
Elongation at break (%)	1095	7	7	8	10	11	15	80
Density (g/cm ³)	0.92	0.017	0.048	0.11	0.20	0.29	0.39	0.47
Thermal conductivity	0.22	0.49	0.47	0.42	0.40	0.27	0.24	0.21
(W/mK)	0.33	0.48	0.47	0.42	0.40	0.37	0.34	0.31

Moisture absorption test was conducted to compare the sorption behaviour of the film composition (Figure 5.10). A general increase of moisture is seen for all sample composition and is more significant in pure NFC and least significant in pure LDPE with a moisture absorption at 48 hours of 15.1% and 7.8%, respectively. NFC-GPTMS, NFC-LDPE 60-40% and NFC-LDPE 50-50% compositions exhibit close moisture absorptions to pure LDPE at 8.3, 8.3 and 8.0%, respectively which is within a 6% difference. The moisture absorption of NFC-LDPE 70-30% is also within range of the pure LDPE film at 8.7% after 48 hours. Interestingly, the moisture absorption trend of pure NFC, LDPE and NFC-LDPE samples all

increase linearly with time except for the NFC-GPTMS which indicated stabilisation between 4 and 48 hours.



Figure 5.10 Moisture absorption comparison between the varied compositions after a 48-hour test Mechanical properties were studied through tensile testing. The test revealed a ductile nature for pure LDPE film at modulus and elongation at break of 0.20 GPa and 1095%, respectively (Table 5.3). Whilst the pure NFC film displayed toughness at modulus and elongation at break of 2.23 GPa and 7%, respectively. The NFC-GPTMS indicated a slight increase in stiffness with a modulus of 2.56 GPa. Addition of LDPE content reduces the stiffness of NFC-LDPE films displaying modulus of 0.65 GPa. This infers a 3-fold increase in stiffness compared to pure LDPE with some ductility characteristic demonstrating elongation at break of 80%, which is an 11-fold increase compared to pure NFC. The NFC-LDPE 70-30% displayed reasonable tensile performance in terms of young's modulus and yield strength where this ratio achieved a 7-fold higher young's modulus compared to the pure LDPE film. Although increasing the NFC constituent increases the stiffness, the ductility is hindered, therefore a compromise between the two aspects must be made. The elongation at break is an important property for the production of paper cups as a high value is required for the mouth roll forming process, a standard process during production. The elongation at break value increases dramatically with increasing LDPE beyond 40% composition ratio. This suggests that if no modifications were to be

103

made in NFC to improve its ductility, then a small addition, between 5-30%, of NFC in a NFC-LDPE composite may be a feasible material for use in coffee cups as the elongation is projected to be high enough. This is while the addition of NFC improves the other properties mentioned in Table 5.3 for the purpose of coffee cup use.

A thermal conductivity test was undertaken, to ensure the pure NFC films and composites were suitably insulating to emulate LDPE. Whilst the primary function of the barrier film within coffee cups is not to insulate (one of the primary functions of the outer cardboard layer is to insulate), it is important to establish whether replacing LDPE film with NFC will cause considerable heat leaks, which could lead to health and safety risks (the cup becomes too hot to handle), or a decrease in function of the cup (the cup as a whole cannot keep hot liquids warm for a suitable period of time). Table 5.3 displays the thermal conductivity results. The pure NFC shows an expected higher conductivity than pure LDPE at 0.48 and 0.33 W/mK, respectively. Interestingly, NFC-LDPE 50-50% demonstrated a lower conductivity than pure LDPE at 0.31 W/mK as well as lowering the density by half at 0.47 g/cm³. This indicates a good synergy between NFC and LDPE to produce an enhanced thermally insulating film whilst also reducing the weight of the cup.

All in all, nanocellulose composited with increasing concentrations of low-density polyethylene in the form of films, displays improved hydrophobicity and thermal stability compared to pure NFC films. The optimal concentration and drying temperature to fabricate pure nanofibrillated cellulose films was found to be 0.4% at 70°C for 24 hours. TGA analysis of LDPE-NFC composites showed that the initial degradation temperature was 32.2% greater for an NFC-LDPE 80-20% composition than for a pure NFC film. This figure rose to 36.7% for an NFC-LDPE 70-30% composition. Both concentrations mitigated the 'immediate degradation' effect that occurred at lower nanocellulose concentrations. NFC-LDPE composites could replace 100% LDPE at a concentration of NFC-LDPE 80-20%. However, when the nanocellulose was modified with GPTMS, the concentration of required LDPE halved to NFC-LDPE 90-10% with GPTMS modification. Moreover, it was found that an NFC-LDPE 70-30% nanocomposite had a contact angle of 78°, whilst NFC alone had a contact angle of 49°. NC-GPTMS

104

films allowed for a contact angle of 84°, only 5° less than pure LDPE. When NFC-GPTMS was composited with LDPE (at NFC-LDPE 90-10%), the contact angle rose slightly to 85°. The minimum concentration of LDPE in NFC composites to function suitably in coffee cups was found to be 30%. Pure NFC films possess a 6-fold higher yield strength and 11-fold higher young's modulus than pure LDPE where the introduction of LDPE into an NFC composite serves to decrease these mechanical properties. NFC modified with GPTMS performed similarly to unmodified NFC, highlighting the suitability of GPTMS-modified NFC as a replacement for LDPE films. Therefore, it is possible to decrease polyethylene usage in coffee cups by 90% when LDPE is composited with nanofibrillated cellulose modified with (3-glycidoxypropyl)trimethoxysilane.

5.4 Conclusion

The addition of NC in the wet mix enhanced the dry and wet strength of paper made from recycled papers. This reduced breaks in papermaking machines and means papermaking may potentially be accelerated leading to a reduction in energy consumption. The data also indicated an increase in retention and strength, consequently increasing the number of times the recycled fibres can be used without the addition of virgin fibre. Secondly, the use of Peroxide as a replacement to Bleach did not impact the ability of nanocellulose crystals to provide dry strength. It means that the need for a retention aid, including polyacrylamide and bentonite, can be reduced for a sustainable and less harmful NCC additive. Peroxide bleaching offered several advantages over the use of hypochlorite including a higher burst strength index for paper sheets. Finally, the optimal concentration and drying temperature to fabricate pure nanofibrillated cellulose films was found to be 0.4% at 70°C for 24 hours. TGA analysis of NFC-LDPE composites showed that the initial degradation temperature was 32.2% greater for an NFC-LDPE 80-20% composition than for a pure NFC film and could replace 100% LDPE at that concentration. However, when the nanocellulose was modified with GPTMS, results show that the concentration of required LDPE can be halved to a composition of NFC-LDPE 90-10%. Moreover, it was found that an NFC-LDPE 70-30% nanocomposite had a contact angle of 78°, whilst NFC alone had a contact angle of 49°. NC-GPTMS films allowed for a contact angle of 84°, only 5° less than pure LDPE. When NFC-GPTMS was composited with LDPE (at NFC-LDPE 90-10%), the contact angle rose slightly to 85°. The minimum concentration of LDPE in NFC composites to function suitably in coffee cups was found to be 30%. NFC possesses a higher yield strength (6-fold) and stiffness (11fold) than LDPE where the introduction of LDPE into an NFC composite serves to decrease these mechanical properties. NFC modified with GPTMS performed similarly to unmodified NFC, highlighting the suitability of GPTMS-modified NFC as a replacement for LDPE films. Therefore, it is possible to decrease polyethylene usage in coffee cups by 90% when LDPE is composited with nanofibrillated cellulose modified with (3-glycidoxypropyl)trimethoxysilane.

106

Chapter 6 Optimisation of cellulose-PVA aerogel content

6.1 Introduction

Nanocellulose forms hydrogels in water [360–362] which is exploited in the production of NC aerogels by removing the liquid through supercritical- or freeze-drying while preserving the solid aerogel network structure. However, cellulose aerogels suffer from low mechanical strength and modulus, so studies have focused on the production of composite cellulose-based aerogels to improve performance and impart desired properties. This includes composite constituents such as PVA which is a soluble, non-toxic, thermoplastic polymer that has a relatively low cost and possesses good mechanical properties [363]. This chapter details the effect of different production techniques on the properties of NC-PVA aerogels to determine an optimal approach that maximises the aerogel performance. The effect of content ratios of each constituent and the rate of shear mixing during aerogel production on the properties of the resulting NC-PVA aerogel was investigated. Moreover, the effect of the rate of freezing during freeze-casting on the aerogel was evaluated as well as the effect of moisture uptake on the aerogel mechanical properties. Optimal conditions were determined through high shear mixing of 60-40% NC-PVA aerogel composition and led to a three-fold increase in specific modulus to 37 kNm/kg and thermal conductivity of 32 mW/mK.

6.2 Experimental work

NC and PVA stock solutions were prepared according to section 3.3.1. Pure PVA aerogel suspensions and compositions of NC-PVA 50-50, 60-40 and 70-30% were formulated at HSM as well as LSM (section 3.3.2). Characterisation and testing were carried out according to section 3.4.

6.3 Results and discussion

6.3.1 Investigation of PVA aerogel morphology and mechanical property

The effect of freeze-casting on the morphology of polyvinyl alcohol suspensions was evaluated. Firstly, the freezing temperature of alcohol is lower than that of water which enables thermally induced phase separation to take place on freeze-casting. The water crystallises and solidifies before PVA and directs the PVA particles according to the water freezing front. In addition, the PVA loaded is of a heavier molecular weight (mol Mw: 146 – 186,000 \approx 166 kDa), which greatly reduces the mobility of the polymer molecules with minute PVA addition in the solution. In other words, at 5% concentration, the PVA suspension is viscous. This viscosity impedes ice growth and inhibits ice nucleation [364]. This helps reduce the explosive crystal growth that normally occurs at nucleation which causes particle entrapment due to the engulfment of suspended particles by the oncoming ice front and thus producing a non-ordered structure. As seen by the lamellar morphological zone (LMZ) in Figure 6.1, the morphology appears ordered and anisotropic, evidencing nullified aggressive solidification velocities. With a slower rate of freezing the suspension particles have more time to redistribute and develop a spatially homogeneous lamellar crystal structure as represented in LMZ, portraying vertical lamellar ice growth along the direction of the ice front. This growth is seen to reach approximately 28% in height of the overall aerogel cross-section found in Figure 6.1 until the morphology alters abruptly into the interstitial morphological zone (IMZ) with a clear boundary. The IMZ is seen to have lamellae with lateral bridges spanning out from either side making the lamellae seem thicker. This occurrence is related to the freezing rate reducing as the temperature difference between the suspension and that of the supercooling liquid (liquid nitrogen) is decreasing. The second competing ice crystal growth direction follows the lateral plane according to the thermal gradient. This featherlike pattern morphology occupies about 36% before altering in the pattern again and displaying dendritic growth. This area that is responsible for about 30% is termed dendritic morphological zone (DMZ) and is represented in Figure 6.1 by the thick lamellae curving laterally. This growth transition is peculiar as it reveals the freezing rate to favour the second crystal growth population adopted in IMZ. Predominantly, the ice crystals have grown vertically along the thermal gradient until equilibrium (i.e. the suspension temperature is equal to the freezing temperature) is reached. When close to equilibrium the ice crystals reduce in solidification velocity parallel to the gradient and instead speeds up in lateral growth perpendicular to the gradient [365]. A thermal buffer is reached beyond the DMZ.



Figure 6.1 SEM micrograph of PVA aerogel and inset enlargements of the three distinct morphologies: Dendritic morphological zone (DMZ), interstitial morphological zone (IMZ), and lamellar morphological zone (LMZ)

PVA aerogels were loaded under compression to examine the mechanical property. The stress-strain graph depicted in Figure 6.2 follows an interesting profile. The curve follows three stiffness regions (shown as dashed lines) before yielding and thereafter displaying densification. These regions seem closely related to the distinct microstructures of LMZ, IMZ, and DMZ discussed in observation of the PVA aerogel morphology shown in Figure 6.1. These are highlighted in Figure 6.2 revealing the progress of failure of each morphology region starting from DMZ showing the lowest density profile to LMZ displaying the highest density profile. The density seems to be the highest for LMZ based on the high compactness of the lamellae that's observed in Figure 6.1 with scarcely any voids in between. In addition, it is thought that the colloid suspension may be prone to settle due to gravity which will lead to a denser region forming after freeze-casting. On the other hand, the IMZ region display voids located between the lamellae bridges, which probably reduces the overall density of the morphology zone. This is also the case for DMZ, albeit more profound and thus having a lower density region. The

density of the PVA aerogel studied in Figure 6.2 is found to be 0.060 g/cm³. The load during the compression test is shared across the entire profile of the aerogel sample. However, in Figure 6.2 there are characteristic regions that may relate to different structures within the sample including the aforementioned LMZ, IMZ, and DMZ. The shape of the first dashed line in Figure 6.2 is thought to relate partly to the stiffness of the DMZ with a modulus of 1.22 MPa which follows densification of the microstructure after yielding at approximately 0.04 MPa and 4% compressive strain and is shown by the solid yellow line. This is followed by a second dashed line where the IMZ is thought to play a major role in the stiffness with the line having a lower stiffness modulus of 1.09 MPa and compressive strength of 0.11 MPa before yielding at 13% compressive strain. The reason for this reduction lies with the microstructure in IMZ having more horizontal bridges that are easier to compress axially. After yielding, the IMZ microstructure collapses and becomes easier to compress. This is shown by the solid blue line. The final dashed line is thought to be associated with the stiffness of LMZ. The high stiffness modulus of 1.55 MPa and compressive strength of 0.31 MPa is matched with the compactness and a high number of lamellae in LMZ that are parallel to the load direction. It is worth to note that the densification of the DMZ beyond its yield point aids the increase in stiffness modulus of the IMZ. Thus, the true stiffness of IMZ is ambiguous and difficult to determine. The same case applies to the stiffness of LMZ (the final green dashed line) in that the increase in stiffness modulus is partially due to densification of both DMZ and IMZ after their respective yielding. Overall, the PVA aerogel may be compared to elastomer material composites due to the large compressive strain experienced by the aerogel before yielding at approximately 31%. The modulus of all the PVA aerogels was taken across the final stiffness and calculated to a mean specific modulus of 25.0 kNm/kg. The mean density of the aerogels was found to be 0.064 g/cm³ and the mean specific strength was calculated to 5.41 kNm/kg with mean yield compressive strain of 38%. The thermal conductivity of the PVA aerogels was measured at 38.7 mW/mK. This is not commercially appealing when considering standard thermal insulation and the energy input to produce the PVA aerogels. More importantly, although PVA aerogels display notable stiffness moduli the compressive behaviour suggests low elasticity before

110

microstructure starts to collapse. For this reason, aerogels need to be further modified and functionalised with additional properties to attract the commercial benefit of producing insulative aerogel composites. This is studied in the proceeding thesis sections with the use of nanocellulose.



Figure 6.2 Compressive stress-strain plot of PVA aerogel and corresponding SEM cross-section of PVA microstructure to scrutinise the morphological zones' effect on the mechanical property

6.3.2 Effect of high shear mixing on NC-PVA suspensions and aerogel mechanical property

Oxidation treatment of cellulose into nanocellulose and thereafter the coalescence of NC and PVA suspensions were prepared through shear mixing. This was trialled at a range of increasing shear speeds to observe the final utilisation of NC yields as well as the homogenisation of NC for increased bonding contact with PVA. Two such speeds have been analysed here; Low shear mixing (LSM) speeds at 700 rpm (revolutions per minute) and high shear mixing (HSM) speeds at 7000 rpm. The use of HSM during treatment of cellulose included a greater visual reaction demonstrated by the high increase in the effervescence of the reaction suspension causing a thick layer of froth. This froth thickened very quickly trapping gases from escaping and thus had to be mixed thoroughly to stop the trapped gases from causing secondary reactions. When quenched and cleansed through centrifugation, two distinct

layers could be found. When conducting the preparation of NC using HSM revealed a greater supernatant when centrifuging. This supernatant is shown inset of Figure 6.3a and represents the attainment of nanocellulose crystals. The NCC is defined by a lower density as suggested by the centrifugation which also shows a denser precipitate revealing the attainment of nanocellulose fibrils. In addition, more NCC supernatant was found with successive centrifugation after extracting the primitive NCC supernatant. This suggests quantities of NCC trapped within the precipitate of NFC. This is in contrast with LSM which only exhibited a very fine layer of supernatant that was scarcely visible after centrifuging. TEM micrographs shown in Figure 6.3a reveals the NCCs with approximate average lengths of 250 nm.



Figure 6.3 Displaying (a) TEM micrograph of the supernatant NCC shown inset with a red-dotted line of where the separation NCC and NFC can be seen, and (b) Stress-strain curves of compressed aerogels prepared via LSM and HSM

The prepared NC was mixed with PVA via LSM and HSM to produce aerogels for comparative mechanical property analyses. Compressive stress-strain results display low density and tougher aerogels when produced through HSM (Figure 6.3b). In comparison to LSM aerogels, NC-PVA aerogels prepared via HSM show approximately triple the specific modulus at 26.8 kNm/kg and double the specific strength at 2.14 kNm/kg (Table 6.1). Notably, the yield strain of HSM aerogels has slightly decreased due to the increased stiffness. This means the preparation of NC, as well as aerogels through HSM, is more ideal for increased surface contact due to increased homogenisation of suspensions. An investigation into NCC and NFC properties as well as focusing on whether NCC supports NFC aerogels when combined has been studied in Chapter 7.

	Density	Specific Modulus	Specific Strength	Yield Strain
	(g/cm³)	(E/ρ) (±0.01 kNm/kg)	(σ/ρ) (±0.01 kNm/kg)	(%)
NC-PVA 50-50 (HSM)	0.041	26.75	2.14	15.77
NC-PVA 50-50 (LSM)	0.050	9.55	1.25	20.17

Table 6.1 Mean compressive property of LSM and HSM NC-PVA aerogels

6.3.3 Effect of NC content on NC-PVA aerogel morphology

The composition of NC-PVA aerogels has been studied to understand how increasing NC content interacts with PVA. Figure 6.4 displays the morphology of three NC-PVA aerogel compositions; 50-50, 60-40, and 70-30%. For NC-PVA 50-50, the microstructure shows a layered systematic pattern resembling dendritic growth. In comparison, the 60-40 aerogel in Figure 6.4b reveals a more compact microstructure with a similar pattern to Figure 6.4a. NC-PVA 70-30, on the other hand, portrays a more distinct microstructure with a feather-like pattern. The NC-PVA 50-50 aerogel composition was left in ambient conditions to study the change in morphology with respect to the moisture uptake. Figure 6.4d shows the profile of NC-PVA aerogel after freeze-drying with inset a magnification of the pattern lamellar structure. In contrast, Figure 6.4e shows the microstructure is more compact due to shrinkage in Figure 6.4e. The long-term moisture absorption seems to have considerably damaged the microstructure, deforming and shrinking the lamellae. Thus, lowering the structural integrity.



Figure 6.4 SEM analysis displays to sets of comparative micrographs with a-c displaying different compositions of aerogels prepared via HSM: (a) NC-PVA 50-50, (b) NC-PVA 60-40, (c) NC-PVA 70-30, and d-e displaying the before and after ambient moisture uptake of aerogels : (d) NC-PVA 50-50 at day 1, (e) NC-PVA 50-50 at day 31. Note, the aberration of microstructure in d (and e) is caused by the blade cutter used to reveal the cross-section profile

6.3.4 Effect of NC content on NC-PVA aerogel mechanical property and thermal conductivity

A range of aerogel compositions was compressively tested to examine the trend of the mechanical property with increasing NC content. Figure 6.5 shows three compositions ranging from 50-70% NC addition using the same NC-PVA aerogels observed through SEM (Figure 6.4). When loaded the aerogels follow general compressive stress-strain curves, yielding between 5-20% compressive strain and initiating exponential stiffness after about 30% strain. The NC-PVA 50-50 curve followed a slightly more distinct profile than the rest of the aerogels that had more NC content. The elastic region followed alterations in increasing stiffness before yielding. This phenomenon is closely correlated to

the PVA aerogels with no NC content as depicted in Figure 6.2, revealing an interesting hypothesis. The supposition of increasing PVA content initiates altered patterns towards dendritic growth as seen in Figure 6.1. This means that PVA impedes the growth of ice crystals towards crystallisation and requires increasing freezing temperatures to realise crystallisation shown by the subsequent morphed patterns [364,366]. Note that alcohols generally have lower freezing temperatures than water inferring PVA to have a higher resistance to solidification. Hence, the alteration in the aerogel microstructure due to freezing solidification affecting the effectiveness of resisting and distributing compressive stress.



Figure 6.5 Comparison of differing aerogel compositions as well as the weathering effect through (a) stress-strain graph and (b) density and thermal conductivity bar chart of the aerogels

The NC-PVA 60-40 aerogel is found to considerably increase in strength with greater stiffness and overall toughness than the 50-50 aerogel composition with specific modulus and strength calculated at 36.9 and 3.1 kNm/kg, respectively (Table 6.2). The mean yield strain marginally increased at 16.1%. The 70-30 aerogel, on the other hand, displayed a drastic decrease in mechanical property in comparison to both 50-50 and 60-40 aerogels. This may reflect the aerogel microstructures where the 60-40 aerogel displayed a more compact structure with minimum gaps between the lamellae as well as showing a pattern that seems to converge in-between the 50-50 and 70-30 aerogel. The densities are found to negatively correlate with NC content, whereby increasing the NC content from 50-50 NC-PVA loadings proportionally reduces the overall density of the aerogel at 0.041, 0.036 and 0.030 g/cm³,

respectively. In respect to the thermal conductivity of the aerogels, NC-PVA 60-40 aerogels displayed slightly lower conductivities at 32.3 mW/mK. Whereas both 50-50 and 70-30 aerogels had similar conductivities approximated to 32.9 mW/mK. Note that it may be expected for thermal conductivities to reduce with increasing NC content, however, this may not be the case between the tested composition since other factors, such as the microstructure of the aerogel, contribute in affecting the thermal conductivity. Overall, these data results show aerogels with a 60-40% NC-PVA composition to be optimal with respect to the mechanical property. The aerogels were also compression tested after a month of exposure to ambient conditions. Stress-strain curves show a significant drop in the mechanical property for all three compositions with reduced elasticity. Specific modulus and strength revealing about a five-fold decrease when compared to the same aerogels tested directly after lyophilisation (Table 6.2). The weathered aerogels were also denser as a consequence of moisture absorption. Both 50-50 and 60-40 aerogels reached approximately double their initial densities at 0.080 g/cm³. Conversely, the 70-30 aerogel reached approximately 1.5-fold at 0.047 g/cm³, which interestingly is not as high considering the increased NC content. Thermal conductivities were also increased with values reaching 36.0, 35.0 and 34.1 mW/mK for increasing NC additions from 50-70%, respectively. This concludes the need for aerogel modification to increase hydrophobicity to diminish this limitation without hindering mechanical property. This has been critiqued in Chapter 8.

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	Specific Modulus	Specific Strength	Yield Strain
NC-PVA	(E/ρ) (±0.01 kNm/kg)	(σ/ρ) (±0.01 kNm/kg)	(%)
50-50	26.75	2.14	15.77
60-40	36.89	3.07	16.10
70-30	14.94	0.86	7.80
	D	ay 31	
50-50	4.83	0.75	19.20
60-40	5.44	0.31	7.58
70-30	3.17	0.49	13.10

Table 6.2 Mean compressive property of varied and weathered aerogel compositions

6.4 Conclusion

PVA and NC-PVA aerogels have been extensively analysed, exploring the effect of freeze-casting on the morphology and mechanical property of PVA aerogels; achieving optimised shear mixing rates for enhanced colloid suspensions and NCC yields as well as optimised compositions for NC loadings for superior mechanical property performance and low thermal conductivities; determining the extent of moisture uptake and its effect on the aerogel performance. PVA aerogels produced via freeze-casting resulted in three differing microstructures (LMZ, IMZ and DMZ) to be embedded. This led to a differing compressive stress-strain behaviour for each microstructure due to their varied densities. High shear mixing of 7000 rpm was found to significantly increase the NCC yields at roughly 30-40% as opposed to lower shear mixing which yielded a low NCC amount of <2%. HSM was found to also promote the NC-PVA aerogel mechanical properties by two-fold at specific modulus and strength of 26.8 and 2.14 kNm/kg, respectively. When testing the optimal NC-PVA composition for maximising aerogel performance, the 60-40% NC-PVA aerogel displayed a 1.5-fold increase in specific modulus at 37 kNm/kg when compared to PVA aerogels with no NC loadings. Furthermore, the 60-40 aerogel composition displayed thermal conductivity values averaging at 32 mW/mK. Finally, the limitation concerning moisture absorption was evaluated over 31 days under ambient conditions. The test findings revealed a considerable increase in density due to moisture uptake and consequently a significant reduction in mechanical performance by about seven-fold in specific modulus. This helped highlight the importance of modifying the aerogel further in order to null the limitation effect of hydrophilicity on the aerogels mechanical performance and is thus further investigated in Chapter 8.

Chapter 7 Cellulose aerogel composites via Tempo-free oxidation

7.1 Introduction

This chapter describes the development of cellulose-based aerogel composites enhanced via a new refinement process. The behaviour and microstructure of treated cellulose aerogel composites are examined including, how the constituents interact and contribute to the overall aerogel composite mechanism. The various forms of cellulose such as MCT, NCC and NC is also compared. Treated cellulose/Polyvinyl alcohol (PVA) aerogel composites show reinforced microstructural systems that enhance the mechanical property of the aerogels. The specific modulus of treated cellulose aerogels, reaching specific moduli of 21 kNm/kg. The specific strength of treated cellulose aerogels was also increased by four-folds at 1.7 kNm/kg. These results provide insight into the understanding of the morphology and structure of treated cellulose-based aerogel composites.

7.2 Experimental work

Untreated microcrystalline cellulose termed MCU was converted into four different products including (1) MCT – (thin microcrystalline cellulose with branched nano-fibrillated cellulose (NFC)) obtained by partial conversion of the MCU; (2) NFC – nanocellulose fibrils that are detached from MCTs and may be linked to other NFCs with branched nanocrystalline cellulose (NCC); (3) NCC – nanocellulose crystals that are detached from NFCs and may be linked to other NCCs; (4) NC – nanocellulose that includes NFCs and NCCs before separation methods through decanting the supernatant of the centrifuged nanocellulose. These were produced in accordance with section 3.3.1.1. Cellulose types were incorporated with PVA to compare the following aerogel compositions at 50-50%: MCU-PVA, MCT-PVA, NCC-PVA and NC-PVA (sections 3.3.1.3, 3.3.2 and 3.3.3). Pure MCU, MCT and PVA were prepared to compare against. Characterisation and testing were carried out according to section 3.4.

7.3 Results and discussion

7.3.1 Comparison of MCU and MCT suspensions in PVA dispersions

Figure 7.1 shows TEM micrographs of MCT-PVA and MCU-PVA suspensions. It is clear that there is a significant difference between the two suspensions. MCT-PVA (Figure 7.1c) shows a homogenous suspension with a large, almost complete web-like network between the fibres. This is highlighted in the inset image of Figure 7.1c. The larger MCT fibres are small in number, however, are not separated from the network of the finer fibrils. Rather they are within the network structure due to their open surface of branched fibres, which are of similar aspect ratio to the surrounding finer fibrils, and therefore able to form a web-like network structure. In comparison, the suspension of MCU-PVA (Figure 7.1d) struggles to form a network structure, displaying large voids and bulkier fibres. Also, there seem to be a number of large grey sheets, depicting PVA, where more voids would otherwise be formed. This infers that there may also be MCU fibres without much bonding formed with PVA due to dispersion and/or characteristic of MCU fibres. Hence, this could be the reason for PVA preferentially bonding with itself to form the displayed grey sheets even though both suspensions were shear mixed at 10,000 rpm. These PVA sheets are not displayed in MCT-PVA. This may very well be due to the more homogenous network dispersion of MCT as well as the higher aspect ratio of the fibres granting more active –OH surfaces to bond with PVA. This also infers that the PVA is binding along the increased surface of the highly dispersed MCT fibres. Thus, the network of fibres is more strongly linked as displayed by the darker patches at the joints of the fibre network (inset image of Figure 7.1c). The darker shade of the MCU fibres explains a thicker dimension with very low aspect ratio compared to the MCT fibres whereby the shade of grey is marginally darker to the fine fibrils. The MCU fibres also seem to have a much sharper and more distinct surface edge, contrast to the branched MCT fibre surface. The overall reduction in fibre dimension sizes, as well as the branched network structure of MCT particles, may aid in the packing arrangement with PVA as the smaller MCT particles may occupy the cavities between the larger particles during freeze-casting, entrapping longer chains of particles – i.e. forming more continuous and branched solid layers once lyophilised. This may relate to a more a homogenous aerogel density and hence increased mechanical strength due to enhanced efficiency in load transfer. This distinction in the dispersity of both suspensions sets a significant discrepancy in freeze-casting and thus in the final aerogel morphology.



Figure 7.1 Comparative visual analysis of MCU-PVA and MCT-PVA SEM cross-sectional images of (a) MCT-PVA aerogel with corresponding morphological profiles (ai)-(aiii) and (b) MCU-PVA aerogel with corresponding profiles (bi)-(biii); TEM micrographs of (c) MCT-PVA suspension and (d) MCU-PVA suspension

7.3.2 Morphology of MCU-PVA and MCT-PVA aerogel composites

The microstructure of the lyophilised cellulose aerogels is an important consideration in distinguishing the mechanical and physical properties of the aerogel composites. The architectural structure of the aerogels determines its effectiveness to dissipate stress when loaded. It is apparent from Figure 7.1a and b that both MCU- and MCT-PVA aerogel composites form a layered architectural lamellar structure though are considerably different. The full cross-section of MCT-PVA aerogel in Figure 7.1a shows an ordered lamellar structure with a growing tree-like profile. It can be seen that when comparing the lower (Figure 7.1aii) and upper (Figure 7.1ai) sections of Figure 7.1a the vertical lamellae layers are increasingly separating in the lateral direction, displaying dendritic growth. This is due to the perpendicular growth of the layers. The thickness of the upper section can be linked to the freeze-casting stage, whereby the solidification velocity of the growing ice crystals in the vertical direction decreases which results in increased lateral growth. On the other hand, MCU-PVA aerogel displays a more incoherent structure, containing ordered and disordered regions. The upper (Figure 7.1bi) and lower (Figure 7.1bii) sections of Figure 7.1b portray a similar effect to the MCT-PVA in that the lamellar layers grow thicker in the upper region. However, the lamellar layers in Figure 7.1bi increase in thickness with wider cavities as opposed to the occurrence of dendritic growth in Figure 7.1ai. Nevertheless, the thickness of the MCU-PVA layers is still a fraction of the MCT-PVA layers. As shown in Figure 7.1aiii, the MCT-PVA grow notable larger in thickness filling more of the voids in between in contrast to Figure 7.1biii where the layers grow up to half the thickness of MCT-PVA with slightly wider cavities. The larger voids are also displayed in the lower (Figure 7.1bii) section of MCU-PVA in comparison to MCT-PVA where the lower (Figure 7.1aii) section shows an increased number of lamellar layers with a large number of bridges in-between the layers that occupy the majority of the voids. As discussed earlier, this may be due to the packing arrangement of PVA with the branched MCT network in suspension. This is desirable in reducing thermal conductivity, whereby the increased vertical layers increase lateral heat flow cycles of conduction and convection. The bridges act as struts providing a more tortuous heat flow path/system as well as give way to an increased number of air pockets whilst reducing the pocket size. In addition to increasing porosity, the struts also increase the sturdiness of the composite. Under stress, these bridges may aid in the energy distribution more efficiently and thus increase the aerogel stiffness. The overall microstructural observation of the two aerogels is linked back to the distribution of their suspensions before freeze-casting. The incoherent structure of MCU-PVA aerogel (Figure 7.1b) is similar to its irregular and cluttered suspension (Figure 7.1d). Similarly, the layered and dendritic patterns of MCT-PVA aerogel (Figure 7.1a) are parallel to the homogenous network structure of its suspension (Figure 7.1c). Furthermore, a notable amount of fibres is perceived in the MCU composite. This may be due to the bulkiness of the MCU fibres in suspension, whereby the PVA binds around the low surface area of –OH active sites of MCU fibres. This means for a 50-50% ratio of MCU-PVA formulation excess PVA allows for more intra-PVA bonding. This may also mean that the PVA in the MCU aerogel composites contributes more towards the

strength of the composite as the MCU fibres do not form a network and that the needle-like patterns may represent PVA layers.

7.3.3 Influence of cellulose treatment on the basal spacing of MCT-PVA aerogel

The MCU-PVA and MCT-PVA composites and individual raw materials (MCU, MCT, PVA) were analysed using XRD to ascertain whether the composite manufacturing process incurs structural (d-spacing) or crystallinity changes (Figure 7.2). It can be observed that the cellulose peaks both MCU and MCT shift once PVA is inserted in the structure. The shifts in the graph indicate the changes in d-spacing caused by the presence of PVA in the structure (Table 7.1). In particular, it can be observed that d-spacing decreases both in MCU and MCT, however, the phenomenon is more pronounced in the MCT (around 3 times larger). The phenomenon is orientation-dependent, strongest along the (0, 0, 2) plane in both materials. Moreover, the MCU samples do not show changes in crystallinity (~80%) before and after the manufacturing of the composites as the cellulose and PVA crystallise separately. The full width at half maximum (FWHM) for the cellulose [0, 0, 2] plane calculated for each composite and raw material was found to be 1.58±0.03, indicating a crystalline size of ~60Å. However, small changes can be observed for the MCT. The crystallinity remains 50% both for MCT and for the MCT-PVA composite, however, the cellulose crystallite size seems to decrease from ~70, with a FWHM of 1.26 for the [0, 0, 2] of the MCT to ~60Å with a FWHM of 1.6. Consequently, the results seem to indicate that the crystalline structure of the MCT allows for larger compressive stresses to its lattice which induces a relatively wider shift of d-spacing relative to the untreated cellulose. PVA has a semi-crystalline nature with a monoclinic unit, whereby is has both crystalline and amorphous domain in the matrix [367,368]. Observing the PVA spectrum against the other composite spectra, it can be seen that the (0, 0, 1) plane of the PVA is not visible in MCU-PVA, which means that the peak in MCT-PVA may not be attributed with the PVA (0, 0, 1) peak, rather more directly to the cellulose II of the MCT peak. The reduction of the (0, 0, 1) peak may be attributed to the random dispersion of cellulose, inferring that possible distortion of the structure has occurred in the (0, 0, 1) direction/plane and hence this would

be due to the bonding of PVA with cellulose. A similar reduction is shown for the (0, 4, 1) peak of PVA in MCU- and MCT-PVA, while the (1, 1, 0) peak can only be seen in MCT-PVA.



Figure 7.2 XRD spectrums of PVA aerogel composites

		MCU-I	PVA	MCT-PVA		Overall change	
[LUZI]	Specimen	d-value	Δd	d-value	Δd	d-value	Δ d MCT/
נחגנן		(Å)	(Å)	(Å)	(Å)	change	Δ d MCU
[0 0 2]	composite	3.93	0.02	3.95	0.01	0.03	0.4
[0,0,2]	cellulose	3.95	-0.05	3.96	-0.01	0.01	
[-3,1,1],	composite	2.59	0.01	2.64	0.05	0.05	1.0
[-2,2,2]	cellulose	2.60	-0.01	2.69	-0.05	0.01	-1.9
[101]	composite	5.81	0.07	5.88	0 10	0.07	25
[-1,0,1]	cellulose	5.88	-0.07	6.07	-0.19	0.18	2.5
[1 0 1]	composite	5.34	0.05	5.41	-0.03	0.07	0.4
[1,0,1]	cellulose	5.39	-0.05	5.44		0.05	-0.4

Table 7.1 D-value of the PVA aerogel composites

7.3.4 Compressive property of cellulose-PVA aerogels

The compressive stiffness of aerogel composites is typically dependent on the effectiveness of the microstructure in its ability to efficiently transfer the applied stress and is also dependent on the solid content which increases the density resulting in a stiffer composite. It can be seen that the composite graphs follow a generic compressive profile where the composites yield between 10-20% strain and

plastic deformation occurs until the aerogels start to deform exponentially beyond ~30% strain (Figure 7.3). MCT-PVA possesses significantly higher strength and stiffness compared to MCU-PVA with the data (Table 7.2). This is despite MCU-PVA possessing a higher density than MCT-PVA (Figure 7.3). There is a 3.6-fold higher specific modulus and a 2.9-fold higher specific strength in MCT relative to the MCU composite (Table 7.2). The increased stiffness and strength of MCT-PVA may be a result of the superior microstructure and bonding interface between MCT and PVA. Evidence for this may be found from the TEM micrographs (Figure 7.1) where the oxidised MCT fibres appear to possess higher aspect ratios and are more branched as per MCU bulk fibre. Firstly, the increased aspect ratio due to the splitting of cellulose fibrils via oxidation adopts additional surfaces of –OH active sites for PVA bonding to occur. This yields an increased number of PVA reinforced cellulose layers and thus stiffens the overall macro sheet layer, which stacks together to form the aerogel composite. Secondly, the chain of connected branched fibres adopts more effective load distribution which increases the stiffness and strength. The increased stiffness from these phenomena may also contribute to the increased mean yield stress of the MCT aerogel.



Figure 7.3 Shows (a) stress-strain graphs of the different PVA aerogel composites and (b) comparing their densities

NC-PVA was also investigated to understand how a composite MCT and NCC behave. It can be seen from Figure 7.3 that the mechanical properties of NC-PVA outperform that of NCC-PVA and MCT-PVA individually. NCC-PVA possessed the lowest density between the four composites and seems to have lowered the density of the overall NC-PVA composite. Combining NCC and MCT seems to have improved the underlying microstructure of the composite possibly through crosslinks between the two agents and PVA. This has resulted in significantly higher stiffness and strength whilst reducing the density of the overall NC-PVA composite (Table 7.2).

Specific Modulus		Specific Strength	Viold Strain	
	(E/ρ) (±0.01 kNm/kg)	(σ/ρ) (±0.01 kNm/kg)		
MCU-PVA	4.45	0.42	14.88	
MCT-PVA	15.79	1.24	12.90	
NCC-PVA	9.13	1.29	18.31	
NC-PVA	20.55	1.71	17.13	

Table 7.2 Co	mpressive	property of	the PVA	aerogel	composites
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7.4 Conclusion

The behaviour and structure of their suspensions and the developed aerogels have been thoroughly investigated to determine their physical and mechanical properties. MCT-PVA suspensions showed expansive robust network structures due to the homogenous network dispersion of MCT as well as the higher aspect ratio of the fibres in comparison to MCU granting more active –OH surfaces to bond with PVA and adding to the packing arrangement with PVA. This has affected the architecture of the developed MCT-PVA aerogel showing ordered lamellar structures with dendritic growth that displayed superior strength and stiffness to the MCU-PVA aerogel composite. XRD and SEM explained the effective load distribution under compressive stress due to the formation of bridges in the microstructure, alteration of crystallinity in basal spacing and high aspect ratio.

Chapter 8 Functionalising cellulose aerogel composites with water-soluble dialdehyde and organosilanes

8.1 Introduction

Herein, cellulose-based aerogels have been functionalised using water-soluble coupling agents to amplify the storage modulus. The investigation focuses on the reaction mechanisms between each reagent, critiquing the effect of crosslinking on the morphology and mechanical properties of coupled aerogels. Furthermore, solidification of thicker aerogel profiles is evaluated and compared. Numerous substances have been found to act as crosslinking agents for cellulose such as glyoxal, dichloroethane, formaldehyde, vinyltrimethoxysilane (VTMS) and (3-Aminopropyl) triethoxysilane (APTES) [27]. Three of these crosslinking agents were tested when applied to create a nanocellulose-PVA-crosslink aerogel. Glyoxal is a non-toxic chemical that is endogenously produced during cellular metabolism and is metabolised by the glyoxylates' enzymatic group. High concentrations of glyoxal favour the acetylation of cellulose. This leads to a lower water sorption and fibre strength where curing conditions (especially with higher temperatures) contributed to acetylation as glyoxal concentrates in the fibres. It is claimed, however, that the reaction mechanism between glyoxal and cellulose is more complicated than simply the development of acetal [26]. Glyoxal is biodegradable and can be acquired from renewable sources as a by-product of biological processes as well as the oxidation of lipids. Thus, it may be considered an environmentally friendly crosslinking agent for cellulose. Glyoxal has mainly been used in the textile industry to improve the wet mechanical properties of cotton fabrics. The mechanical properties of cellulose are diminished when exposed to water as the inter- and intramolecular hydrogen bonding of cellulose is disrupted, therefore glyoxalisation reduces the effect of the disruption by crosslinking the cellulose polymer chains [27]. VTMS is commonly used to modify polymers through grafting reactions where the grafted polymer undergoes crosslinking after fabrication and exposure to moisture. A study investigated the functionalisation of cellulose acetate with VTMS via the hydroxyl groups of the cellulose. The resulting compound was found to possess

increased permeability, lower crystallinity and higher flexibility than unmodified cellulose acetate. It would, therefore, be interesting to see the effect of VTMS when functionalised with the nanocellulose-PVA to create the compound aerogel [29]. APTES is an aminosilane that's commonly used to functionalise surfaces with alkoxysilane molecules in a process known as silanisation. It may also be used for other purposes including the synthesis of Octa(3-aminopropyl)silsesquioxane and to covalently bond thermoplastics to poly(dimethylsiloxane) [369,370]. APTES is a toxic compound with APTES fumes capable of damaging the upper respiratory tract [371]. APTES has previously been functionalised with cellulose nanocrystals and found no significant effect on the surface morphology characteristics of the nanocrystals while the thermal stability of the APTES modified NCC was increased with the decomposition of modified NCC occurring at a temperature of about 10 °C higher. APTES has also been found to increase the hydrophobicity of cellulose fibrils where a 90% reduction in the surface polarity of NFC has been observed when the maximum amount of the silane was added [30].

8.2 Experimental work

5 wt% stock solutions of NC, PVA, GLY, VTMS and APTES were prepared (Chapter 3). The combined mixtures were diluted along with each respective coupling agent to compose final suspensions of NC-PVA-GLY, NC-PVA-VTMS and NC-PVA-APTES at 2-2-2 wt% for each composition as well as NC-PVA at 2.5-2.5 wt%. The suspension was later poured on 100×100×10 mm (s) and 100×100×15 mm (L) aluminium foil moulds and frozen in a liquid nitrogen bath (section 3.3.2). The frozen samples were freeze-dried according to section 3.3.3 to attain the aerogel composites. Characterisation and testing were carried out according to section 3.4.

8.3 Results and discussion

8.3.1 Functional groups of crosslinked NC aerogels

The FTIR spectrum of the NC-PVA and the crosslinked aerogels of GLY, VTMS and APTES are presented in Figure 8.1a. For clearer observation and comparison of peaks, a second NC-PVA spectrum (with higher absorption due to a larger mass of sample tested) was used in Figure 8.1b. The spectra containing crosslink additions show only slight alteration in peak absorptions when compared to the NC-PVA spectrum. The IR peaks were analysed with reference to a number of IR charts, including George Socrates' "Infrared and Raman Characteristic Group frequencies" [372–375]. The weak band at 3292 cm⁻¹ is linked to the O-H stretch from the intra- and inter-molecular hydrogen bonds present between the hydroxyl-rich cellulose and PVA polymers. Similarly, GLY spectra in Figure 8.1b shows a strong broad band at 3400-3250 cm⁻¹ corresponding to the O-H hydrogen bonding. The GLY spectra also display two sharp peaks at 1645 cm⁻¹ and 1078 cm⁻¹ corresponding to the aldehyde C=O and the C-OH stretch, respectively. These peaks are not visible in the NC-PVA-GLY spectra evidencing successful crosslinking reaction of the GLY with the NC-PVA. This is expected since the C=O group of the glyoxal fully breaks down to C-OH when saturated (in water). The C-OH then undergoes condensation whereby the glyoxal covalently bonds to the cellulose and PVA chains via a C-O-C bond (see Figure 8.2). This essentially bridges the polymer chains together with a more stable and higher bond enthalpy than hydrogen bonds. The C-O-C bond has several frequencies in the range of 1250-1050 cm⁻¹ which may not be clearly visible when observing the NC-PVA-GLY spectra due to the overlap of peaks. This is the same case with the 1078 cm⁻¹ peak corresponding to the C-OH band. However, the full width at half maximum of the peaks between 1215-880 cm⁻¹ is considerably larger in NC-PVA-GLY than GLY and NC-PVA when compared/referenced against the O-H broad peaks (between 3700-2980 cm⁻¹) – this data obtained is within the consideration of the background spectra not being present. This infers a greater absorbance of C-O-C bonds present. Furthermore, the significant reduction of the broad O-H peak in NC-PVA-GLY compared to GLY evidences the reduction of C-OH bonds due to reduced absorbance of O-H hydrogen bonds, indicating that condensation has occurred. It is worth to note that the 1645 cm⁻¹ peak may be argued to lie outside the range of 1740-1690 corresponding to the C=O aldehyde stretch and inside the range of 1680-1620 cm⁻¹ C=C Alkenyl stretch as well as in the range of 1670-1645 cm⁻¹ C=O ketoaldehydes as enols. However, the C=C is identified by a strong and sharp peak whereas the peak displayed at 1645 cm⁻¹ is broad and weak (u-shaped), therefore the 1645 cm⁻¹ peak may be more implicated with the C=O stretch bond. Also, glyoxal is the

smallest dialdehyde denoted by RC(H)=O or RC(H₂)-OH functional groups when saturated in water so is unable to adopt a ketone group in its chemical structure to comprise as a ketoaldehyde. Furthermore, unless saturated, the C=O is more stable (higher bond enthalpy) than the C=C bond. VTMS and APTES are both organosilanes with Si functional groups. This means they both share some similar peaks when bonded with cellulose, i.e. C-O-Si and Si-O-Si bonds. Since siloxanes are present (Si-O-Si), the Si-alkoxy (C-O-Si) is apt to be masked by the stronger Si-O-Si absorption. However, since the C-O-Si and Si-O-Si bands lie in the range of 1110-1000 and 1130-1000 cm⁻¹, respectively, they are difficult to determine (hidden) due to the overlap from the C-OH and C-O-C abundance found in NC-PVA. This overlap may also be due to the broader absorptions of Si-O-Si bonds when siloxane chains become longer or branched. This would be expected for both crosslinks when surface treating cellulose and PVA polymer chains (Figure 8.2). VTMS is identified in the spectra by its alkenyl functional group, in other words, the Si-CH=CH₂ band. This is found in the NC-PVA-VTMS spectrum at 1602 and 1410 cm⁻¹ with sharp peaks.



Figure 8.1 FTIR spectra displaying (a) the overall peaks of NC-PVA, NC-PVA-GLY, NC-PVA-VTMS and NC-PVA-APTES, and (b) breakdown of NC-PVA-GLY spectra using NC-PVA and GLY peaks

Also, since there are no other alkenyl and aryl groups present in the NC-PVA-VTMS composition, C-H bands at 3060 (3062) and 3020 (3023) cm⁻¹ found in the spectrum help identify Si-CH=CH₂ group [375]. Overall, the hydrated glyoxal enables bridging between cellulose and PVA chains, forming stronger chemical bonding between NC-PVA chains. This interaction differs considerably when considering the

organosilanes as crosslinkers. APTES and VTMS seem to only surface-treat NC-PVA chains and not able to bridge them together (Figure 8.2). This may not be an ideal option for reinforcing the lamellae. While silylation of cellulose may treat the composite, e.g. towards hydrophobicity, the organosilanes may alter the microstructure and thus affect the mechanical property of the overall composite [376,377].

8.3.2 Reaction mechanisms of NC-PVA coupling

With bond enthalpies in mind, the chemical reactions displayed give an insight into the mechanism of the resulting composite suspensions. When examining the reaction between cellulose and PVA, two different interfacial bonding may occur with the one in Figure 8.2a being the most likely, irrespective of other affecting factors, such as the differences in electronegativities or orientations. When calculating the bond enthalpy of the NC-PVA reaction, Figure 8.2a is found to have minimum total energy required to break the C-OH bond of cellulose and C-H bond of PVA at +771 kJ/mol (Table 8.1). The second possible reaction requires +821 kJ/mol to break the C-OH bond of cellulose and CO-H bond of PVA. This difference is due to the higher bond enthalpy required to break the O-H bond at +463 kJ/mol as opposed to the lower enthalpy of breaking the C-H bond at +413 kJ/mol. It is worth noting that another such reaction mechanism that may occur includes the C-H of cellulose bonding to C-OH of PVA, resulting in the same bond enthalpy of +771 kJ/mol required to form a C-C bond between the organic polymers. This scenario is less likely to occur due to the electronegativity of oxygen being greater than carbon, therefore causing a larger polar effect between the O-H. In addition, the cellulose ring adds to the electronegativity of its hydroxyl groups, causing the overall chain to have a larger partial (delta) positive surface than the PVA hydroxyl surface. Hence, the attraction between the C-OH of the cellulose and the partially negative surface, C-H, of the PVA over the partially positive hydroxyl surface of PVA. Figure 8.2b to d shows the reaction mechanisms that are a result of crosslinking NC-PVA chains when adding the respective dialdehyde and organosilanes.


Figure 8.2 Likely chemical reaction mechanisms of (a) NC-PVA (b) NC-PVA-GLY (c) NC-PVA-VTMS and (d) NC-PVA-APTES

able 8.1 Average bond enthalpies [378]							
Bond	C-H	C-C	C-N	C-0	Si-C	Si-O	O-H
Average Bond Energy (kJ	/mol) 413	348	293	358	301	368	463

Та

These compounds when hydrated react and form hydroxyl groups via nucleophilic addition/substitution. The hydrated molecules are then attached to the NC-PVA chains. In the case of Figure 8.2b, the hydrated glyoxal forms a C-O-C bond with the NC-PVA polymer chain and releasing water molecules in the process. When glyoxal is fully hydrated, i.e. having four hydroxyl groups, the molecule can form four C-O-C bonds (two C-O-C bonds with NC-PVA on each carbon side of glyoxal), allowing NC-PVA polymer chains to bridge together. Moreover, glyoxal may also align the NC-PVA chains due to its ability to form two C-O-C bonds on each NC-PVA surface. This is modelled in Figure 8.2b with other crosslinking possibilities shown in reduced transparency. Conversely, silanol (hydrated VTMS) forms single Si-O-C bonds with NC-PVA and becomes polymerised through Si-O-Si bonds with other silanol molecules as demonstrated in Figure 8.2c. Furthermore, the alkenyl group present in silanol limits it from bridging NC-PVA chains together. Although less likely due to the disparity in molecular length, the second and third hydroxyl group present in silanol is also able to form Si-O-C bonds with NC-PVA. This may compact the NC-PVA chains, yet also disorder their orientation. Similarly, the reaction mechanism is also true for APTES (Figure 8.2d). Hydrated APTES only differs from silanol due to the amine group present instead of the alkenyl group, otherwise, APTES behaves the same as silanol.

8.3.3 Morphology of aerogel composites

SEM micrographs of the aerogel composites were taken across the cross-section for observation of the microstructures (Figure 8.3). Observing the microstructure of Figure 8.3a, the architecture starts to develop dendritic growth at the top of the cross-section aerogel profile. This may be related to the freezing-casting conditions whereby the freezing front slows down as it ascends vertically upwards, possibly due to an existing thermal gradient profile with a higher temperature at the top surface. This may have activated the NC-PVA lamellar to grow dendritically near the top surface of the aerogel cross-sectional profile. The dendritic growth section seems to be at about 20° lateral to the vertical lamellar ice growth. In contrast, Figure 8.3b shows a more developed stage of the dendritic growth with lateral growth at an angle of about 60° to the vertical lamellar growth. This may be due to the larger/taller profile of aerogel cross-section which means there is more area for dendritic growth to develop. The larger profile of NC-PVA (Figure 8.3b) may be weaker due to the dendritic growth causing increased lateral horizontal crystal growth hindering the structural resistance when its load is applied and as a result, the microstructure architecture is more susceptible to deformation – less stiff. Dendritic growth patterns are not found when observing aerogel composites with the addition of glyoxal (Figure 8.3c and d). Instead, struts perpendicular to the vertical lamellar is seen. These struts seem more profound in Figure 8.3d, bridging the layers together with an overall homogenous pattern structure. Glyoxal seems to strengthen the interfacial bonding crosslinking the lamellar layers and thus promoting enhanced/improved load distribution. Therefore, even if lateral horizontal growth was to occur, glyoxal seems to add vertical struts, bridging the layers together forming a 3D network structure. This again is similar to composites containing VTMS and APTES (Figure 8.3e and f) showing no dendritic growth with an overall pattern like NC-PVA-GLY. However, there are significantly fewer horizontal struts to bridge the lamellae together - only a small area of cross-links can be seen in the inset image of Figure 8.3f. This can be reflected to the molecular bonding as discussed in Figure 8.2 whereby the glyoxal bridges the NC-PVA chains, empowering the overall structure through the new perk of load transfer. This is contrary to the organosilanes which only attach to the NC-PVA chains as a surface treatment.



Figure 8.3 Comparative visual analysis of NC-PVA with the addition of crosslinks via SEM crosssectional images of (a) NC-PVA(s), (b) NC-PVA(L), (c) NC-PVA-GLY(s), (d) NC-PVA-GLY(L), (e) NC-PVA-VTMS and (f) NC-PVA-APTES. The scale on the inset SEM images is at 2 μm

8.3.4 Compressive property of cellulose-PVA aerogels

When loaded, the NC-PVA aerogel samples follow a generic compressive profile, yielding at 10-20% strain before deforming plastically (Figure 8.4a). The profile is similar in effect with NC-PVA-VTMS and NC-PVA-APTES aerogel composites, displaying ductility with large straining at low stress. Interestingly, the NC-PVA-GLY composites follow a different profile, displaying toughness with a sudden peak in

stress reaching an elastic yield of ~0.4MPa at 4% strain. The composite elasticity is followed by secondary resistance before necking towards a similar profile to the other aerogels – whereby the composites plastically deform exponentially beyond ~30% strain. The morphological study of the aerogel composites offers a deeper understanding when observing the compressive behaviour. NC-PVA(s) and NC-PVA(L) is observed to be directly related to their microstructure. Although both aerogels yield at similar stresses, NC-PVA(s) shows a larger specific modulus. As displayed in Figure 8.3b, NC-PVA(L) has more developed branched dendritic growth which hinders axial stress resistance and thus favouring plastic deformation. Whereas the NC-PVA(s) is more compact (Figure 8.3a). This also explains the lower density of NC-PVA(L) in Figure 8.4b. The similarity in the stress-strain profiles may be due to the developed branching of NC-PVA(L) which may provide stress distribution and thus secondary resistance. In contrast, the NC-PVA-GLY(L) aerogel performs better than its thinner counterpart (NC-PVA-GLY(s)) with an 8-fold increase in specific modulus reaching 132.6 kNm/kg (Table 8.2). Again, this can be reflected to the molecular structure as well as the microstructure of the aerogel where the NC-PVA-GLY(L) portray stacks of homogenous vertical lamellae compacted together by horizontal struts, reinforcing the structure and distributing stress. The aerogels with the addition of VTMS and APTES does not seem to enhance the overall mechanical property as well as the aerogel with GLY addition. In comparison to NC-PVA(L), VTMS doubles the specific modulus (2.5-fold) with a slight increase in strength, while APTES does not seem to add much value in stiffness with only a marginal increase in strength. The NC-PVA-GLY(L) on the other hand, shows a significant increase in stiffness (9-fold) and strength (3-fold). The GLY addition is also denser than the other aerogel composition. This may be linked to the crystallisation effect during solidification of the NC-PVA-GLY suspension via supercooling by which the coupled NC-PVA lamellae become highly ordered. This is reliant on the sol-gel (or hydrogel) which in the case of GLY coupling shows strong linkage between NC-PVA (Figure 8.2) that coalesces into a larger gel network (high degree of crosslinking) and results in faster cooling towards glassy state beyond glass transition due to conduction. This helps explain the larger storage modulus of NC-PVA-GLY aerogels as portrayed by its high stiffness (Figure 8.4).

136



Figure 8.4 Shows (a) stress-strain graphs of the aerogel composites and (b) comparing their mean densities

	Specific Modulus	Specific Strength	Viold Strain	
	(E/ρ) (±0.01 kNm/kg)	(σ/ρ) (±0.01 kNm/kg)	rielu Strain	
NC-PVA (s)	25.7	1.71	17.13	
NC-PVA-GLY (s)	16.2	1.77	21.17	
NC-PVA (L)	14.5	1.76	14.83	
NC-PVA-GLY (L)	132.6	4.95	5.55	
NC-PVA-VTMS (L)	36.2	2.51	9.67	
NC-PVA-APTES (L)	14.9	2.01	16.50	

Table 8.2 Mean compressive property of the aerogel composites

8.3.5 Influence of crosslinkers on the basal spacing of NC-PVA aerogels

The crystal structure of the coupled NC-PVA aerogels was examined to study any developments in the material properties. The XRD spectra of these aerogels are presented in Figure 8.5. A comparison of the different composites indicates that no shift is visible both on the PVA and cellulose components, pointing at the fact that there are no d-spacing changes in the different treatments. However, a detailed comparison between the NC-PVA-VTMS and NC-PVA aerogel indicates that the extraction process (to produce NC-PVA) enhances the presence of cellulose (I β) in the mixture, as shown by the increase in the ratio between the peak at 20 22.5° (cellulose) and the peak at 20 20° (PVA). On the other hand, NC-PVA-APTES shows an opposite behaviour with a decrease in the ratio mentioned above seeming to indicate a relative increase of PVA in the mixture. However, in NC-PVA-APTES we also observe the appearance of the peak at $2\vartheta 10^\circ$, which might indicate the enhancement of the PVA molecular chain along the (0, 0, 1 direction), triggered by the addition of APTES in the mixture. The FWHM of the peaks also increases in this composite pointing towards a loss of crystallinity and a finer crystal size of both cellulose and PVA. The crystallinity is calculated at 8% compared to the NC-PVA which is calculated at 22%. The addition of Glyoxal in the mixture seems to have a lesser impact on the cellulose/PVA structure. The pattern profile does not show changes from the original composite A, aside from a minor loss of intensity on the (-1,0,1) peak at 2ϑ 14°, which might indicate a limited change in molecular orientation of the cellulose Iβ. The addition of VTMS, on the other hand, shows a behaviour mirroring the one investigated in the addition of APTES, with a more pronounced peak in the region of 2ϑ 10°, which seem to indicate the co-existence of cellulose II and cellulose I β .

138



Figure 8.5 XRD spectra comparing the peaks of coupled aerogels

8.4 Conclusion

NC-PVA aerogel composites were functionalised with different coupling agents including glyoxal, VTMS and APTES. The functionalised composites were characterised with FTIR to identify the chemical profile and, with the aid of bond entropy data, a description of the reaction mechanisms was presented. SEM imaging and mechanical testing were used to identify the morphology and performance characteristics of the composites with different thickness profiles. It was observed that the glyoxal functionalised composites possessed a densely packed, ordered structure displaying a 9-fold stiffness and 3-fold strength enhancement relative to unfunctionalised NC-PVA. On the other hand, VTMS and APTES were found to only surface treat the NC-PVA chains with fewer cross-links bridging the lamellae together. As a result, the VTMS and APTES composites exhibited lower stiffness, strength and density than their glyoxal counterpart. In comparison to NC-PVA(L), VTMS doubles the specific modulus (2.5-fold) with a slight increase in strength, while APTES only marginally increases the strength. These features were subsequently rationalised in the context of the chemical composition identified for the composites.

Chapter 9 Robustness of graphene oxide amalgamated cellulosic aerogel composites

9.1 Introduction

Cellulosic aerogels have been developed as an alternative to inorganic aerogels due to their sustainable, environmentally friendly and flexible nature. Yet, their performance is hindered by their weak mechanical properties. Herein, a cellulosic aerogel has been functionalised with graphene oxide (GO), reduced GO (rGO), polyvinyl alcohol (PVA) and glyoxal (GLY) to enhance the performance characteristics, investigating the effect of each reagent. The effect of the magnitude of shear mixing during production was also studied where the resulting mechanical and morphological properties of the aerogels was discussed. The mechanical properties were found to vary depending on the type of functionalisation where NC-rGO-PVA-GLY aerogel had a specific modulus, specific strength and yield strain of 23.53 kNm/kg, 2.88 kNm/kg and 21.33% respectively, NC-GO-PVA aerogel with 28.3 kNm/kg, 1.93 kNm/kg and 10.97%, and NC aerogel with 7.37 kNm/kg, 1.13 kNm/kg and 19%. High shear mixing (\approx 7000 rotations per minute [RPM]) was found to enhance the mechanical properties of the aerogels compared to low shear mixing (LSM) (700 RPM). This is exemplified by the NC-GO-PVA aerogel with specific modulus magnified by seven-fold and specific strength by six-fold relative to the aerogel produced by LSM.

9.2 Experimental work

GO stock solution was prepared according to section 3.3.1.2. Aerogel suspensions were prepared according to the compositions set in Table 9.1 via LSM and HSM methods. Characterisation and testing were carried out according to section 3.4.

Sample	LSM (%)	HSM (%)
NC	5	
GO	5	
NC-GO	2.5-2.5	
NC-PVA	2.5-2.5	2.5-2.5
GO-PVA	2.5-2.5	
NC-GO-PVA	2-2-2	
NC-GLY		2.5-2.5
PVA-GLY		2.5-2.5
NC-PVA-GLY		2.5-2.5
NC-GO-GLY		2-2-2
NC-GO-PVA-GLY		2-0.1-2-2
NC-rGO-PVA-GLY		2-0.1-2-2

Table 9.1 Composition of suspensions mixed from 5% stock solution of the reagents

9.3 Results and discussion

9.3.1 Purity of GO

The prepared GO cake was characterised through analytical techniques and microstructure characterisations to analyse its chemistry and purity. These attributes/measurements are shown in Figure 9.1. Figure 9.1a displays the Raman spectra between 1100 – 1800 cm⁻¹ where the D and G peaks lie. This was measured to scrutinise the overall Raman profile against the generic graphitic Raman spectra as well as to calculate the ratio of the D/G bands to measure the defects present in the GO structure. The G band at ~1600 cm⁻¹ measures the in-plane vibrations of sp² hybridised carbon bonds evidencing the presence of planar C=C stretch vibrations, while the D band at ~1350 cm⁻¹ measures the out-of-plane vibrations of sp³ hybridised bonds attributing structural defects and thus evidences the presence of functional groups (these functional groups are inspected in the FTIR section). Both bands are present in the Raman spectrum as would be expected of GO analysis as opposed to pristine graphene which shows D/G ratio of approximately zero due to negligible defects from sp³ bonds present [379–381]. The diagram inset of Figure 9.1a serves as a visual of the G and D band explanation with the sp² planar bonds displayed as outer blue arrows from the hydrocarbon ring and sp³ out-of-plane bonds shown as vertical red arrows. OriginPro was used to plot a curve fitting that neglects the background and analyses the peaks to accurately define the position of the D and G peaks. This is

shown inset of Figure 9.1a along with peak coordinates. The D peak is observed at 1352 cm⁻¹ with an intensity of 8132, while the G peak is observed at 1603 cm⁻¹ with intensity 9008. This calculates to a D/G ratio of 0.90 (using Equation 6). This is higher than graphite which evidences the disruption of sp² bonds due to oxidative functional groups and thus concludes the success of graphite oxidation. The distribution of sp² bonds infers that the sp² bonds are broken due to oxidation which in turn means there are more sp³ bonds. It is worth to note that the original coordinates of the D and G peaks are also displayed to scrutinise the data lost from background removal through curve fitting. The D/G ratio for the original coordinates is calculated to be 0.93 which means the D/G ratio of 0.90 from curve fitting is a close approximation and thus acceptable.



Figure 9.1 Analysis of GO flakes via (a) Raman spectra and inset peak intensities analysed via OriginPro, (b) FTIR spectra and functional groups colour-coded to respective wavelength peaks [372–374], (c) SEM micrograph showing edge and inset top surface of GO sheet (scale bar is 2 μm), and (d) TEM displaying enlarged micrograph of inset GO flake (scale bar is 200 nm) as well as a 2D FFT and an area line profile of the greyscale intensity as a function of distance with bright contrast as zero measured along the dashed area αβ

FTIR analysis was performed to inspect the chemistry of the GO prepared and the functional groups present. The GO spectrum is shown in Figure 9.1b along with the functional groups which are colourcoded to the respective wavelength peaks. Generally, there are numerous medium to strong sharp peaks seen even though it may be more difficult to detect peaks when conducting FTIR on dark materials due to its tendency to absorb most of the IR. It can be seen that the GO sample has some unsaturated hydrocarbons as represented by the 1628 cm⁻¹ peak belonging to a conjugated alkene that is cis-disubstituted (C=C stretch bond) and the 984 cm⁻¹ peak which lies in the region of both monosubstituted and trans-disubstituted C=C bond. The 1628 cm⁻¹ peak suggests the presence of polyaromatic hydrocarbons as would be expected with reference to the carbon to oxygen (C/O) ratio of 0.90 and the heat treatment of the GO analytical cake sample. The 775 and 795 cm⁻¹ peaks also evidence the presence of alkenes that are trisubstituted since they belong to the 1,2,3-trisubstituted aromatic C-H bending bonds. Note that the trisubstituted C=C bond peak is more stable and is thus likely to be overlapped by the C-H peaks that have stronger intensities. The 865 cm⁻¹ is associated with an isolated aromatic C-H as well as 1,3-disubstituted C-H bond which reinforces the presence of trisubstituted C=C and disubstituted C=C bonds (1628 and 984 cm⁻¹), respectively. The aromatic molecules also contain hydroxyls as shown by the 1340 cm⁻¹ peak conforming to O-H bending alcohols including phenols. This is supported by the C-O stretch bond at 1085 and 1176 cm⁻¹ associated with primary and tertiary alcohols, respectively. However, these two C-O stretch peaks are ambiguous as they are also associated to aliphatic ether groups at 1085 cm⁻¹ and ester groups at 1176 cm⁻¹; both of which are present in an anhydride group. As seen in the IR spectrum, anhydrides are also present in the GO sample. This is represented by the C=O stretch bond at 1817 cm⁻¹ as well as the CO-O-CO stretching bond at 1031 cm⁻¹. Subsequently, the 1031 cm⁻¹ peak may also confirm the presence of formate or α , β -unsaturated ester groups (R-OCOH) as well as aldehyde groups due to the presence of the 1728 cm⁻¹ peak associated with a C=O stretch bond. The 1728 cm⁻¹ peak may also be overlapping the C=O stretching bond peak associated to the presence of carboxyl groups. This is supported by the 1397 cm⁻¹ peak denoting O-H bending bonds of the carboxyl groups. A considerably large and broad

OH peak ranging from about 3700 – 2500 cm⁻¹ can be seen which overlaps most of the C-H peaks at 2951 and 2890 cm⁻¹. This is closely correlated with the O-H stretching band of carboxyl groups which is usually centred at about 3000 cm⁻¹ with a strong and broad intensity. The stronger intensity peaks at 3362 and 3238 cm⁻¹ denote the presence of intermolecular O-H stretching bonds while the overlapped sharp 3600 cm⁻¹ peak denotes free O-H bonds. SEM micrographs of the GO cake were taken on the edge and surface as shown in Figure 9.1c. The micrograph shows numerous GO sheets stacked together which is expected since the drying of the GO suspension settled the GO flakes/sheets together. The sheets seem to be textured displaying wrinkles and folds. The surface micrograph inset of Figure 9.1c also displays some folds of the graphene sheet. EDAX was performed on the GO sheet surface to analyse the weight % of elements present and hence its purity. The GO sheet was found to contain approximately 52% carbon and 42% oxygen with the remaining 6% containing remnants from the oxidation reaction of graphite. These remnants include sodium, sulphur and potassium as well as the gold due to the coating applied in preparation for SEM analysis. The figures were analysed with an error margin of +/- 3%. The EDAX result indicates that the GO sample contains an approximate C/O ratio of about 80%. This may be linked to the D/G ratio of 0.90 calculated from Raman analysis, evidencing the oxidative disruption to the sp² hybridised carbon bonds. GO flakes were also isolated under a TEM. The examined flake shown in Figure 9.1d contained a monolayer and a few-layer of GO folded together. When magnified, the sheet seemed to be distorted comprising a varied lattice structure with areas showing hexagonal arrangements separated by 1.4 Å representing the presence of graphene and rGO. Two-dimensional fast Fourier transform (FFT) taken from area $\alpha\beta$ displays sets of distinct spots with lattice distances analysed at 0.9 and 0.7 Å suggesting AB Bernal stacked fewlayer graphene atomic arrangement [382].

9.3.2 Interaction of GO with NC as aerogel composites via low shear mixing

Prepared aerogel compositions were analysed through SEM to compare the microstructure and how this may affect the overall aerogel composite. When comparing the GO and GO-NC aerogels, the GO microstructure (Figure 9.2a) shows stacks of thin GO flakes that are ordered and connected by aggregated GO particles whilst GO-NC (Figure 9.2b) shows two distinct microstructure patterns. The microstructure of GO-NC shows a cluster of thin layers homogeneously stacked together with random aggregated particles in between the layers and another cluster of compact thick layers. These thick layers seem more profound and uniform in GO-PVA (Figure 9.2c). The thick layers are noticeably more compacted together with minute gaps in between the layers due to the numerous bridges linking the layers together. When observing GO-NC-PVA aerogel (Figure 9.2d), the microstructure also shows two pattern clusters with most of the microstructure displaying a feather-like pattern. This seems to be overlaid with a similar pattern to the GO-PVA aerogel (Figure 9.2c), albeit with thinner sheets. These divergent pattern structures could relate to the loaded materials governing the formed microstructures, whereby the feather-like pattern belongs to NC and the latter thick layer pattern belonging to GO. Furthermore, the PVA addition in GO-NC-PVA could have aided the growth of the feather-like patterns as it is more distinct than the pattern observed in the GO-NC aerogel micrograph (Figure 9.2b). The same could be said about the compaction of the thick sheets due to the bridging effect seen in Figure 9.2c and d as opposed to Figure 9.2b where this is not seen. So, in effect, the PVA is binding the layers together in each type of pattern structure.



Figure 9.2 SEM micrographs displaying (a) GO (b) GO-NC (c) GO-PVA (d) GO-NC-PVA with inset enlargement of microstructural patterns at a scale of 100 μm

The aerogel composites were loaded axially under compression. At first glance, Figure 9.3a demonstrates that with increasing compressive strain both GO and NC have relatively similar compressive stress. Whereas, when amalgamated the result is an increase in compressive stress by about two-folds. In contrast, Figure 9.3b shows that NC-GO-PVA is roughly a third the compressive stress of GO-PVA and NC-PVA aerogels. However, this is without considering the density of the loaded aerogel composites. Figure 9.3c displays the densities of the aerogels, showing GO to have a low density of 0.025 g/cm³ in comparison to NC with a density of 0.036 g/cm³. As would be expected the densities increase with the addition of PVA displaying a density of 0.064 g/cm³ for NC-GO-PVA which is about double the density of NC-GO aerogel at 0.030 g/cm³. This infers the mechanical properties to be more significant as displayed in Table 9.2. Generally, it is seen that the aerogels with the addition of PVA have higher compressive yield strain than the aerogels without PVA, apart from GO-PVA. As shown in Table 9.2, the GO-PVA aerogel is marginally stiffer than the GO aerogel at specific modulus of 12.0 kNm/kg albeit with lower specific strength and yield strain at 1.23 kNm/kg and 11.8%, respectively. Similarly, NC-PVA aerogels are stiffer than NC aerogels, however with lower specific

modulus than GO-PVA aerogels at 9.55 kNm/kg. GO-PVA and NC-PVA aerogels appear to have similar specific strengths though yielded at different strains. This may relate to the physical property of NC with its ability to form more advanced 3D network structures in comparison to GO and hence may explain the overall increase in yield strains. In respect to the combined NC-GO-PVA aerogel, Table 9.2 demonstrates a large reduction in stiffness and strength in comparison to NC-GO aerogels at specific modulus and specific strength of 3.94 and 0.32 kNm/kg, respectively. This phenomenon is an unexpected result and may relate to the divergent microstructures, as displayed in Figure 9.2d, that may have altered the stress field around dislocation and thus favouring failure.



Figure 9.3 Stress-strain graphs comparing aerogels prepared through LSM (a) without PVA and (b) with PVA; along with (c) a density bar chart of the aerogel composites

	Specific Modulus	Specific Strength	Yield Strain
	(E/ρ) (±0.01 kNm/kg)	(σ/ρ) (±0.01 kNm/kg)	(%)
GO	11.03	1.49	14.50
NC	7.37	1.13	19.00
GO-NC	14.69	2.78	24.90
GO-PVA	11.96	1.23	11.83
NC-PVA	9.55	1.25	20.17
GO-NC-PVA	3.94	0.32	36.08

Table 9.2 Mean compressive property of GO aerogels

9.3.3 Strengthening NC-GO composites with glyoxal via high-shear mixing

Addition of glyoxal seems to modify the microstructure of the aerogels. As shown in Figure 9.4a the GLY seems to layer the NC into smooth sheets. These layers become porous when coming together whilst progressing vertically along the freezing front. This phenomenon is also illustrated in NC-GO-GLY (Figure 9.4b), though, with more layers converging together as well as forming horizontal links between the layers. PVA-GLY aerogels were also reviewed to see the effect glyoxal has on PVA. The micrograph in Figure 9.4c displays the cross-section of this aerogel and reveals bundles of randomised layer stacks. The layers also exhibit long bridges which could be associated with the glyoxal addition. Here, NC-GO-PVA aerogels were analysed again but with a minute amount of GO addition in the aerogel composition and prepared through HSM. The micrograph in Figure 9.4d shows a similar representation of feather-like layers dominating the microstructure in comparison to Figure 9.2d. These feather-like layers seem to be growing out of numerous thick lamellae which is different from the micrograph shown in Figure 9.2d. Addition of glyoxal to the NC-GO-PVA composition seems to distort the microstructure with layers hardly visible and defined. The microstructure in Figure 9.4e appears to show more of a network of lamellae randomly webbed together. It is worth to note that the holes shown in the micrograph correspond to the air bubbles that were present during freezing of the suspension. This is due to the HSM of the suspension which tends to foam up due to the glyoxal addition. It could be argued that the presence of air bubbles may act as nucleation sites triggering a distortion in solidification around the air bubble which could elucidate the pattern of the microstructure shown in Figure 9.4e.

148



Figure 9.4 SEM micrographs displaying (a) NC-GLY (b) NC-GO-GLY (c) PVA-GLY (d) NC-GO-PVA (e) NC-GO-PVA-GLY (f) NC-rGO-PVA-GLY with inset enlargement of microstructural patterns at a scale of 20 μm

In the case of Figure 9.4f, the microstructure reveals an ordered anisotropic layered structure with lamellae linked by long bridges. These bridges stretching at about 60-80 μ m in length may be reflected to the PVA-GLY aerogel shown in Figure 9.4c reinforcing the argument of glyoxal adopting these bridges. Note, that a form of bridging is also seen in Figure 9.4b when adding GO to the NC-GLY aerogel

which could infer that GO is adopting crosslinking between layers. However, this may only be an aid to bridging lamellae in the case of Figure 9.4f as only a minute amount of rGO is present in the composition of NC-rGO-PVA-GLY aerogels.



Figure 9.5 Stress-strain graphs of aerogels prepared through HSM (a) investigating the inclusion of PVA in aerogels and (b) comparing GO and rGO amalgamated aerogels, and (c) density bar chart of the aerogel composites

There is a considerable difference between the inclusion of PVA and the lack thereof. This is displayed in Figure 9.5a and b, whereby the PVA-GLY is seen to have a significantly greater increase in compressive strength than both NC-GLY and NC-GO-GLY aerogels. Moreover, the aerogels lacking PVA portray brittle behaviour and following no increase in compressive resistance when loaded beyond their yield point. This is in contrast to the addition of PVA in the composition of aerogels which show foam-like behaviour whereby the compressive resistance increases exponentially beyond the yield point. Yet PVA adds weight, forming PVA-GLY aerogels that are roughly double the density of NC-GLY (0.055 g/cm³) and NC-GO-GLY (0.057 g/cm³) at 0.097 g/cm³. Hence, the mean specific strength of the PVA-GLY aerogels is calculated to be 2.5 kNm/kg, yielding at 31% as seen in Table 9.3. This is approximately triple the stress and strain of NC-GLY and NC-GO-GLY aerogels, however, NC-GLY is calculated to be stiffer at mean specific modulus of 35 kNm/kg which is approximately three-fold the PVA-GLY. This infers that GLY adopts stiffness and most effective when added to NC compositions, likely due to the effective chemical crosslinking. On the other hand, PVA adopts strength as all as prolonging the yield strain. This is demonstrated when considering NC-PVA with respect to NC-GLY whereby the aerogel is found to yield at a greater compressive stress of 1.7 kNm/kg and strain of 17%. Observing Figure 9.5a, NC-PVA follows a gradual increase in stress with respect to compressive strain before the aerogel stiffens and thereafter yielding. This contrasts with NC-GLY, where the curve follows a constant increase. Furthermore, when PVA and GLY are amalgamated with NC, the stressstrain curve follows a stiffer gradual increase reaching superior strength compared to NC-PVA. Nevertheless, the specific modulus of NC-PVA-GLY aerogels is calculated to be lower than NC-PVA aerogels at 16 kNm/kg as seen in Table 9.3. This is because of the significant increase in density, due to more effective crystallisation as a result of GLY crosslinking between NC and PVA lamellae. As elaborated more thoroughly in Chapter 8, GLY-based aerogels grow stronger with thicker aerogel profiles. Therefore, this signifies the need for both PVA and GLY additions as a prerequisite of amplified aerogel stability as well as prolonging the yield point. A similarity is seen for NC-GO-PVA and NC-GO-PVA-GLY in Table 9.3, whereby GLY addition enhances the specific strength while reducing the specific modulus and forming denser aerogels. In comparison to NC-PVA-GLY, the minute addition of GO is found to further improve the mechanical property, displaying increased toughness without compromising the aerogel density. Replacing lab-based GO with industrial-grade rGO improves the mechanical properties further still than both NC-PVA-GLY and NC-PVA-GO-GLY aerogels, demonstrating more superior toughness. This again is without compromising the aerogel density, as represented in Figure 9.5 and Table 9.3, inferring graphene oxide to be a suitable strengthening agent. The toe region of the stress-strain curves is unusual since they normally relate to the uncrimping effect of fibres. However, this is unlikely in this case since the aerogels are being compressed axially along

151

the lamellae rather than flexure tested. It could relate to the variant segments within the aerogel profile (see section 6.3.1 and Figure 6.2).

	Specific Modulus	Specific Strength	Yield Strain
	(Ε/ρ) (kNm/kg)	(σ/ρ) (kNm/kg)	(%)
NC-GLY	34.8	0.82	10.67
PVA-GLY	12.46	2.54	31.15
NC-PVA	25.7	1.71	17.13
NC-PVA-GLY	16.2	1.77	21.17
NC-GO-GLY	14.9	0.73	9.33
NC-GO-PVA	28.3	1.93	10.97
NC-GO-PVA-GLY	18.9	2.58	27.87
NC-rGO-PVA-GLY	23.53	2.88	21.33

Table 9.3 Mean compressive property of GO and GLY aerogels

9.4 Conclusion

Graphene oxide was produced from graphite via the modified Hummer's method and the resulting purity and yield of graphene oxide were determined via non-destructive tests including Raman spectroscopy, FTIR, SEM and TEM. The D/G ratio was resolved to 0.90 denoting the extent of sp³ outof-plane bonds in the prepared GO. The FTIR results found that the GO sample was rich in variant oxygenated functional groups including anhydrides, carboxyls, aldehydes, phenolics among other functional groups. There are strong peaks in the results associated with the presence of aromaticity which correlates with the G-band (sp² planar C=C bonds) in the Raman spectroscopy. GO flakes were isolated and visualised to verify the lattice structure via TEM micrographs. The GO was functionalised with nanocellulose using low shear mixing (700 revolutions per minute [RPM]) to create NC-GO composite aerogels that were investigated for their morphological and mechanical properties. The composite aerogels were found to have a compressive strength significantly higher (2.8 kNm/kg) than individual NC (1.1 kNm/kg) and GO (1.5 kNm/kg) aerogels. However, when introducing PVA into the NC-GO composite aerogel, the compressive strength was greatly reduced (0.3 kNm/kg) in contrast NC-PVA (1.3 kNm/kg) and GO-PVA (1.2 kNm/kg) aerogel strength being enhanced considerably. This was attributed to the extensive agglomeration of GO when mixed in suspension with PVA for the NC-GO-PVA aerogel composite, with agglomeration being more significant in the former case than for GO-

PVA aerogels. The degree of shearing when mixing the suspensions was investigated to determine the effect on the resulting aerogels. High shear mixing (≈7000 RPM) enhanced the NC-GO-PVA aerogel specific modulus by seven-fold (28.3 kNm/kg) and the specific strength by six-fold (1.9 kNm/kg) relative to the aerogel produced with LSM. The addition of glyoxal into the NC-GO-PVA composition toughens the aerogel, increasing the specific strength by 34% (2.6 kNm/kg) and the density by two-fold (84 kg/m³). Finally, industrial-grade reduced graphene oxide was compared to lab-based GO where similar properties were observed. The prepared GO was found to have 10% lower specific strength and 20% lower specific modulus than the rGO.

Chapter 10 Final appraisals

10.1 Summary of the research

This thesis presents an analysis of NC based materials including a description of NC transformation to enable in-situ grafting of alien nanoparticles as well as a new commercially feasible approach to NC production. The effectiveness of NC and NC based composites as alternatives to petroleum-based additives and films is also detailed. Moreover, the properties of functionalised NC aerogels including the chemistry and morphology is expounded. The positive results attained from these studies suggest that such NC based materials are promising constituents for functionalisation across a range of other applications.

10.2 Major conclusions

The major contributions of this thesis to the scientific community is summarised in the following six conclusive statements:

- (1) Oxidation treatment on cellulose fibres was found to result in the formation of a branched network where an increase in aspect ratios and surface area is observed. MCT had the capacity to form xerogel films as well as a homogenous house-of-card structured aerogel when lyophilised. Cellulose Iβ was partially transformed to cellulose II (~10%) in MCT with changes in molecular orientation. Quantitative measurements indicated the formation of new intramolecular O(6)H-O(2') bonds and intermolecular hydrogen bonding of O(6)H-O(3') in MCT. These results were attributed for the apparent reduction in density and the potential of MCT to incorporate alien materials in its structure, i.e. composite formation, functionalisation, quantum dots grafting. Moreover, the treatment was found to break up 1-4 glycosidic bonds to form an increase in reducing ends of carboxylic functional groups in MCT.
- (2) The addition of NC in the wet mix enhanced the dry and wet strength of paper. This reduces breaks in papermaking machines and means papermaking may potentially be accelerated leading to a reduction in energy consumption. The data also indicates an increase in retention and strength, consequently increasing the number of times the recycled fibres can be used

without the addition of virgin fibre. Secondly, the use of Peroxide as a replacement to Bleach did not impact the ability of nanocellulose crystals to provide dry strength. It means that the need for a retention aid, including polyacrylamide and bentonite, can be reduced for a sustainable and less harmful NCC additive. Peroxide bleaching offered several advantages over the use of hypochlorite including a higher burst strength index for paper sheets. Finally, the optimal concentration and drying temperature to fabricate pure nanofibrillated cellulose films was found to be 0.4% at 70°C for 24 hours. TGA analysis of NFC-LDPE composites showed that the initial degradation temperature was 32.2% greater for an NFC-LDPE 80-20% composition than for a pure NFC film and could replace 100% LDPE at that concentration. However, when the nanocellulose was modified with GPTMS, the concentration of required LDPE halved to NFC-LDPE 90-10% with GPTMS modification. Moreover, it was found that an NFC-LDPE 70-30% nanocomposite had a contact angle of 78°, whilst NFC alone had a contact angle of 49°. NC-GPTMS films allowed for a contact angle of 84°, only 5° less than pure LDPE. When NFC-GPTMS was composited with LDPE (at NFC-LDPE 90-10%), the contact angle rose slightly to 85°. The minimum concentration of LDPE in NFC composites to function suitably in coffee cups was found to be 30%. NFC possesses a higher yield strength (6-fold) and stiffness (11-fold) than LDPE where the introduction of LDPE into an NFC composite serves to decrease these mechanical properties. NFC modified with GPTMS performed similarly to unmodified NFC, highlighting the suitability of GPTMS-modified NFC as a replacement for LDPE films. Therefore, it is possible to decrease polyethylene usage in coffee cups by 90% when LDPE is composited with nanofibrillated cellulose modified with (3-glycidoxypropyl)trimethoxysilane.

(3) PVA and NC-PVA aerogels were investigated, exploring the effect of freeze-casting on the morphology and mechanical properties of PVA aerogels; achieving optimised shear mixing rates for enhanced colloid suspensions and NCC yields as well as optimised compositions for NC loadings for superior mechanical property performance and low thermal conductivities; determining the extent of moisture uptake and its effect on the aerogel performance. PVA aerogels produced via freeze-casting resulted in three differing microstructures (LMZ, IMZ and DMZ) to be embedded. This led to a differing compressive stress-strain behaviour for each microstructure due to their varied densities. High shear mixing of 7000 rpm was found to significantly increase the NCC yields at roughly 30-40% as opposed to lower shear mixing which yielded a low NCC amount of <2%. HSM was found to also promote the NC-PVA aerogel mechanical properties by two-fold at specific modulus and strength of 26.8 and 2.14 kNm/kg, respectively. When testing the optimal NC-PVA composition for maximising aerogel performance, the 60-40% NC-PVA aerogel displayed a 1.5-fold increase in specific modulus at 37 kNm/kg when compared to PVA aerogels with no NC loadings. Furthermore, the 60-40 aerogel composition displayed thermal conductivity values averaging at 32 mW/mK. Finally, evaluating the moisture absorption over 31 days revealed a considerable increase in density due to moisture uptake and consequently a significant reduction in mechanical performance by about seven-fold in specific modulus.

- (4) The behaviour and structure of MCT-PVA suspensions and aerogels were thoroughly investigated to determine their physical and mechanical properties. MCT-PVA suspensions showed robust network structures due to the homogenous network dispersion of MCT as well as the higher aspect ratio of the fibres in comparison to MCU, granting more active –OH surfaces to bond with PVA and adding to the packing arrangement with PVA. This affected the architecture of the developed MCT-PVA aerogel where it was found to possess ordered lamellar structures with dendritic growth while displaying superior strength and stiffness compared to the MCU-PVA aerogel. XRD and SEM were used to rationalise the effective load distribution under compressive stress in the MCT-PVA aerogel where it was attributed to the formation of bridges in the microstructure which caused alterations in the basal spacing crystallinity and increased the aspect ratio.
- (5) NC-PVA aerogel composites were functionalised with different chemical agents including glyoxal, VTMS and APTES. The functionalised composites were characterised with FTIR to

156

identify the chemical profile and a description of the reaction mechanism was presented. SEM imaging and mechanical testing were used to identify the morphology and performance characteristics of the composites. It was observed that the glyoxal functionalised composite possessed a densely packed, ordered structure displaying a 9-fold stiffness and 3-fold strength enhancement relative to unfunctionalised NC-PVA. These features were subsequently rationalised in the context of the chemical composition identified for the composites.

(6) Lab-based GO was successfully prepared. It was functionalised with nanocellulose to create NC-GO composite aerogels which were found to have a compressive strength significantly higher (2.8 kNm/kg) than individual NC (1.1 kNm/kg) and GO (1.5 kNm/kg) aerogels. However, when introducing PVA into the NC-GO composite aerogel, the compressive strength was greatly reduced (0.3 kNm/kg) in contrast NC-PVA (1.3 kNm/kg) and GO-PVA (1.2 kNm/kg) aerogel strength being enhanced considerably. This was attributed to the extensive agglomeration of GO when mixed in suspension with PVA for the NC-GO-PVA aerogel. The degree of shearing when mixing the suspensions was investigated to determine the effect on the resulting aerogels. High shear mixing (≈7000 RPM) enhanced the NC-GO-PVA aerogel specific modulus by seven-fold (28.3 kNm/kg) and the specific strength by six-fold (1.9 kNm/kg) relative to the aerogel produced with low shear mixing (700 RPM). The addition of glyoxal into the NC-GO-PVA composition was found to considerably toughen the aerogel, increase the specific strength by 34% (2.6 kNm/kg) and the density by two-fold (84 kg/m³).

10.3 Future work

This thesis presents a considerable amount of knowledge contributing to our understanding of the materials investigated. Further research is required to fully exploit the potential applications of the developed materials reviewed in this study, including the following proposals:

 The potential electrical properties of the developed TEMPO-free nanocellulose may present interesting results as a sustainable conductive material. To explore the full potential of this nanocellulose in regard to its electrical properties it may be functionalised with various metal nanoparticles and investigate its potential utilisation in electronic applications such as computer chips.

- 2) The experiments described in chapter 5 may be further expanded upon by utilising functionalised nanocellulose grafted with hydrophobic nanoparticles before compositing with LDPE or alternative polymers to limit the use GPTMS, which is considered hazardous to human health. In addition, the experiments may be repeated with alternative treatments to GPTMS that are considered safe, such as beeswax and carnauba wax which can be used in coating the inner lining of coffee cups.
- 3) The experiments carried out in chapter 8 and 9 helped partly to prove the ability of nanocellulose-based aerogels to be utilised as insulation products in the construction industry. They proved the mechanical robustness and thermal insulating ability of the aerogels. To establish the aerogels as suitable insulating materials, the flammability and hydrophobicity of the materials need to be further studied. The aerogels may be enhanced via in-situ grafting of the base nanocellulose with particles possessing the desired properties to impart these properties on the aerogel and ensure its applicability. The aerogels may also be useful as an electrically conductive material possibly for energy storage applications and this may similarly be accomplished via in-situ grafting of the nanocellulose as a composite with graphene allotropes in the form of aerogel for energy storage applications.
- 4) A life cycle analysis could be performed to find out the effects on the environment and the energy consumption required in the production of nanocellulose and nanocellulose-based products at a large-scale. This will establish the environmental benefits of using such products on a commercial scale.

References

- S. Ling, D.L. Kaplan, M.J. Buehler, Nanofibrils in nature and materials engineering, Nat. Rev. Mater. 3 (2018) 18016.
- [2] I. Siró, D. Plackett, Microfibrillated cellulose and new nanocomposite materials: a review, Cellulose. 17 (2010) 459–494.
- [3] D. Bondeson, A. Mathew, K. Oksman, Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis, Cellulose. 13 (2006) 171–180.
- [4] F. Jiang, S. Han, Y.-L. Hsieh, Controlled defibrillation of rice straw cellulose and self-assembly of cellulose nanofibrils into highly crystalline fibrous materials, RSC Adv. 3 (2013) 12366.
- [5] P. Stenstad, M. Andresen, B.S. Tanem, P. Stenius, Chemical surface modifications of microfibrillated cellulose, Cellulose. 15 (2008) 35–45.
- [6] Q. Xu, W. Li, Z. Cheng, G. Yang, M. Qin, TEMPO/NaBr/NaClO-Mediated Surface Oxidation of Nanocrystalline Cellulose and Its Microparticulate Retention System with Cationic Polyacrylamide, BioResources. 9 (2013) 994–1006. doi:10.15376/biores.9.1.994-1006.
- [7] M.C. Vieira, T. Heinze, R. Antonio-Cruz, A.M. Mendoza-Martinez, Cellulose derivatives from cellulosic material isolated from Agave lechuguilla and fourcroydes, Cellulose. 9 (2002) 203– 212.
- [8] M.A. Aegerter, N. Leventis, M.M. Koebel, Aerogels Handbook, 2012.
- J. Fricke, T.M. Tillotson, Aerogels: production, characterization, and applications, Thin Solid Films. 297 (1997) 212–223.
- [10] C. Zhang, T. Zhai, L.-S. Turng, Aerogel microspheres based on cellulose nanofibrils as potential cell culture scaffolds, Cellulose. 24 (2017) 2791–2799.
- [11] E. Cuce, P.M. Cuce, C.J. Wood, S.B. Riffat, Toward aerogel based thermal superinsulation in buildings: A comprehensive review, Renew. Sustain. Energy Rev. 34 (2014) 273–299.
- [12] A. Corma, From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis, Chem. Rev. 97 (1997) 2373–2419.
- [13] M.E. Davis, Ordered porous materials for emerging applications, Nature. 417 (2002) 813–821.
- [14] M.M. Dubinin, The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Nonuniform Surfaces, Chem. Rev. 60 (1960) 235–241.
- [15] M. Ann, B. Meador, E.J. Malow, R. Silva, S. Wright, D. Quade, S.L. Vivod, H. Guo, J. Guo, M.

Cakmak, Mechanically Strong, Flexible Polyimide Aerogels Cross-Linked with Aromatic Triamine, ACS Appl. Mater. Interfaces. 4 (2012) 536–544.

- H. Guo, M. Ann, B. Meador, L. Mccorkle, D.J. Quade, J. Guo, B. Hamilton, M. Cakmak, G. Sprowl, Polyimide Aerogels Cross-Linked through Amine Functionalized Polyoligomeric Silsesquioxane, ACS Appl. Mater. Interfaces. 3 (2011) 546–552.
- [17] D.P. Mohite, S. Mahadik-Khanolkar, H. Luo, H. Lu, C. Sotiriou-Leventis, N. Leventis, Polydicyclopentadiene aerogels grafted with PMMA: I. Molecular and interparticle crosslinking, Soft Matter. 9 (2013) 1516–1530.
- [18] C. Tan, B.M. Fung, J.K. Newman, C. Vu, Organic Aerogels with Very High Impact Strength, Adv. Mater. 13 (2001) 644–646.
- [19] C. Aulin, J. Netrval, L. Wågberg, T. Lindström, Aerogels from nanofibrillated cellulose with tunable oleophobicity, Soft Matter. 6 (2010) 3298–3305.
- [20] W. Chen, H. Yu, Q. Li, Y. Liu, J. Li, Ultralight and highly flexible aerogels with long cellulose I nanofibers, Soft Matter. 7 (2011) 10360–10368.
- [21] W. Zhang, Y. Zhang, C. Lu, Y. Deng, Aerogels from crosslinked cellulose nano/micro-fibrils and their fast shape recovery property in water, J. Mater. Chem. 22 (2012) 11642–11650.
- [22] D.O. Carlsson, G. Nyström, Q. Zhou, L.A. Berglund, L. Nyholm, M. Strømme, Electroactive nanofibrillated cellulose aerogel composites with tunable structural and electrochemical properties, J. Mater. Chem. 22 (2012) 19014–19024.
- [23] H. Sehaqui, Q. Zhou, L.A. Berglund, High-porosity aerogels of high specific surface area prepared from nanofibrillated cellulose (NFC), Compos. Sci. Technol. 71 (2011) 1593–1599.
- [24] M. Pääkkö, J. Vapaavuori, R. Silvennoinen, H. Kosonen, M. Ankerfors, T. Lindström, L.A. Berglund, O. Ikkala, Long and entangled native cellulose I nanofibers allow flexible aerogels and hierarchically porous templates for functionalities, Soft Matter. 4 (2008) 2492–2499.
- [25] S. Liu, Q. Yan, D. Tao, T. Yu, X. Liu, Highly flexible magnetic composite aerogels prepared by using cellulose nanofibril networks as templates, Carbohydr. Polym. 89 (2012) 551–557.
- [26] J. Rojas, E. Azevedo, Functionalization and crosslinking of microcrystalline cellulose in aqueous media: A safe and economic approach, Int. J. Pharm. Sci. Rev. Res. 8 (2011).
- [27] F. Quero, M. Nogi, K.-Y. Lee, G. Vanden Poel, A. Bismarck, A. Mantalaris, H. Yano, S.J. Eichhorn, Cross-Linked Bacterial Cellulose Networks Using Glyoxalization, ACS Appl. Mater. Interfaces. 3 (2011) 490–499.

- [28] J. Feng, S.T. Nguyen, Z. Fan, H.M. Duong, Advanced fabrication and oil absorption properties of super-hydrophobic recycled cellulose aerogels, Chem. Eng. J. 270 (2015) 168–175.
- [29] C.S.K. Achoundong, N. Bhuwania, S.K. Burgess, O. Karvan, J.R. Johnson, W.J. Koros, Silane Modification of Cellulose Acetate Dense Films as Materials for Acid Gas Removal, Macromolecules. 46 (2013) 5584–5594.
- [30] E. Robles, L. Csóka, J. Labidi, E. Robles, L. Csóka, J. Labidi, Effect of Reaction Conditions on the Surface Modification of Cellulose Nanofibrils with Aminopropyl Triethoxysilane, Coatings. 8 (2018) 139.
- [31] A.F. Turbak, F.W. Snyder, K.R. Sandberg, Microfibrillated cellulose, a new cellulose product: Properties, uses and commercial potential, J. Appl. Polym. Sci. 37 (1983) 815–827.
- [32] A.F. Turbak, F.W. Snyder, K.R. Sandberg, Suspensions containing microfibrillated cellulose. US Pat. 4452721., 1984.
- [33] K. Wuhrmann, A. Heuberger, K. Mühlethaler, Elektronenmikroskopische Untersuchungen an Zellulosefasern nach Behandlung mit Ultraschall, Experientia. 2 (1946) 105–107. doi:10.1007/BF02172568.
- [34] A.F. Turbak, F.W. Snyder, K.R. Sandberg, Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential, J. Appl. Polym. Sci. Appl. Polym. Symp.; (United States). 37 (1983) 459–94.
- [35] F.W. Herrick, R.L. Casebier, J.K. Hamilton, K.R. Sandberg, Microfibrillated cellulose: morphology and accessibility, J. Appl. Polym. Sci. Appl. Polym. Symp.; (United States). 37 (1983) 797–813.
- [36] S. Iwamoto, A.N. Nakagaito, H. Yano, M. Nogi, Optically transparent composites reinforced with plant fiber-based nanofibers, Appl. Phys. A. 81 (2005) 1109–1112. doi:10.1007/s00339-005-3316-z.
- [37] D. Dai, M. Fan, P. Collins, Fabrication of nanocelluloses from hemp fibers and their application for the reinforcement of hemp fibers, Ind. Crops Prod. 44 (2013) 192–199. doi:10.1016/j.indcrop.2012.11.010.
- [38] D. Dai, M. Fan, Green modification of natural fibres with nanocellulose, RSC Adv. 3 (2013)4659–4665. doi:10.1039/c3ra22196b.
- [39] A. Dufresne, J.-Y. Cavaille, M.R. Vignon, Mechanical behavior of sheets prepared from sugar beet cellulose microfibrils, J. Appl. Polym. Sci. 64 (1997) 1185–1194. doi:10.1002/(SICI)1097-4628(19970509)64:6<1185::AID-APP19>3.0.CO;2-V.

- [40] T. Saito, S. Kimura, Y. Nishiyama, A. Isogai, Cellulose Nanofibers Prepared by TEMPO-Mediated
 Oxidation of Native Cellulose, Biomacromolecules. 8 (2007) 2485–2491.
 doi:10.1021/BM0703970.
- [41] Shinsuke Ifuku, Masaya Nogi, Kentaro Abe, Keishin Handa, Fumiaki Nakatsubo, H. Yano, Surface Modification of Bacterial Cellulose Nanofibers for Property Enhancement of Optically Transparent Composites: Dependence on Acetyl-Group DS, Biomacromolecules. 8 (2007) 1973–1978. doi:10.1021/BM070113B.
- [42] R.J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood, Cellulose nanomaterials review: structure, properties and nanocomposites, Chem. Soc. Rev. 40 (2011) 3941. doi:10.1039/c0cs00108b.
- [43] B. Pereira, V. Arantes, Nanocelluloses From Sugarcane Biomass, Adv. Sugarcane Biorefinery Technol. Commer. Policy Issues Paradig. Shift Bioethanol By-Products. (2018) 179–196. doi:10.1016/B978-0-12-804534-3.00009-4.
- [44] J. Rojas, M. Bedoya, Y. Ciro, Current Trends in the Production of Cellulose Nanoparticles and Nanocomposites for Biomedical Applications, in: Cellul. - Fundam. Asp. Curr. Trends, 2015: pp. 194–228. doi:10.5772/61334.
- [45] S.J. Eichhorn, R.J. Young, The Young's modulus of a microcrystalline cellulose, Cellulose. 8 (2001) 197–207. doi:10.1023/A:1013181804540.
- [46] R. Rusli, S.J. Eichhorn, Determination of the stiffness of cellulose nanowhiskers and the fibermatrix interface in a nanocomposite using Raman spectroscopy, Appl. Phys. Lett. 93 (2008) 033111. doi:10.1063/1.2963491.
- [47] R.R. Lahiji, X. Xu, R. Reifenberger, A. Raman, A. Rudie, R.J. Moon, Atomic Force Microscopy Characterization of Cellulose Nanocrystals, Langmuir. 26 (2010) 4480–4488. doi:10.1021/la903111j.
- [48] A. Šturcová, G.R. Davies, S.J. Eichhorn, Elastic Modulus and Stress-Transfer Properties of Tunicate Cellulose Whiskers, Biomacromolecules. 6 (2005) 1055–1061. doi:10.1021/BM049291K.
- [49] S. Iwamoto, W. Kai, A. Isogai, T. Iwata, Elastic Modulus of Single Cellulose Microfibrils from Tunicate Measured by Atomic Force Microscopy, Biomacromolecules. 10 (2009) 2571–2576. doi:10.1021/bm900520n.
- [50] M.T. Postek, A. Vladár, J. Dagata, N. Farkas, B. Ming, R. Wagner, A. Raman, R.J. Moon, R. Sabo,
 T.H. Wegner, J. Beecher, Development of the metrology and imaging of cellulose nanocrystals,

Meas. Sci. Technol. 22 (2011) 024005. doi:10.1088/0957-0233/22/2/024005.

- [51] Y.-C. Hsieh, H. Yano, M. Nogi, S.J. Eichhorn, An estimation of the Young's modulus of bacterial cellulose filaments, Cellulose. 15 (2008) 507–513. doi:10.1007/s10570-008-9206-8.
- [52] G. Guhados, W. Wan, H. Jeffrey L., Measurement of the Elastic Modulus of Single Bacterial Cellulose Fibers Using Atomic Force Microscopy, Langmuir. 21 (2005) 6642–6646. doi:10.1021/LA0504311.
- [53] K. De France, Z. Zeng, T. Wu, G. Nyström, Functional Materials from Nanocellulose: Utilizing Structure–Property Relationships in Bottom-Up Fabrication, Adv. Mater. 33 (2021) 2000657. doi:10.1002/ADMA.202000657.
- [54] F.L. Dri, L.G. Hector, R.J. Moon, P.D. Zavattieri, Anisotropy of the elastic properties of crystalline cellulose Iβ from first principles density functional theory with Van der Waals interactions, Cellulose. 20 (2013) 2703–2718. doi:10.1007/S10570-013-0071-8.
- [55] I. Diddens, B. Murphy, M. Krisch, M. Müller, Anisotropic Elastic Properties of Cellulose Measured Using Inelastic X-ray Scattering, Macromolecules. 41 (2008) 9755–9759. doi:10.1021/MA801796U.
- [56] T. Abitbol, E.D. Cranston, Chiral Nematic Self-Assembly of Cellulose Nanocrystals in Suspensions and Solid Films, (2014) 37–56. doi:10.1142/9789814566469_0035.
- [57] R.J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood, Cellulose nanomaterials review: structure, properties and nanocomposites, Chem. Soc. Rev. 40 (2011) 3941. doi:10.1039/c0cs00108b.
- [58] G. DG, Recent Advances in Chiral Nematic Structure and Iridescent Color of Cellulose Nanocrystal Films, Nanomater. (Basel, Switzerland). 6 (2016). doi:10.3390/NANO6110213.
- [59] K. Aswini, N.O. Gopal, S. Uthandi, Optimized culture conditions for bacterial cellulose production by Acetobacter senegalensis MA1, BMC Biotechnol. 2020 201. 20 (2020) 1–16. doi:10.1186/S12896-020-00639-6.
- [60] F.G. Torres, J.J. Arroyo, O.P. Troncoso, Bacterial cellulose nanocomposites: An all-nano type of material, Mater. Sci. Eng. C. 98 (2019) 1277–1293. doi:10.1016/J.MSEC.2019.01.064.
- [61] A. Kadimi, K. Benhamou, Y. Habibi, Z. Ounaies, H. Kaddami, Nanocellulose Alignment and Electrical Properties Improvement, Multifunct. Polym. Nanocomposites Based Cellul. Reinf. (2016) 343–376. doi:10.1016/B978-0-323-44248-0.00011-0.
- [62] A. Mtibe, T.H. Mokhothu, M.J. John, T.C. Mokhena, M.J. Mochane, Fabrication and

characterization of various engineered nanomaterials, Handb. Nanomater. Ind. Appl. (2018) 151–171. doi:10.1016/B978-0-12-813351-4.00009-2.

- [63] J. Thunberg, Chemical Modification of Electrospun Cellulose Nanofibers, (2015). https://research.chalmers.se/en/publication/225223 (accessed July 27, 2021).
- [64] My Ahmed Said Azizi Samir, Fannie Alloin, Alain Dufresne, Review of Recent Research into Cellulosic Whiskers, Their Properties and Their Application in Nanocomposite Field, Biomacromolecules. 6 (2005) 612–626. doi:10.1021/BM0493685.
- [65] M.A. Hubbe, O.J. Rojas, L.A. Lucia, M. Sain, CELLULOSIC NANOCOMPOSITES: A REVIEW, BioResources. 3 (2008) 929–980.
- [66] M.S. Peresin, Y. Habibi, J.O. Zoppe, J.J. Pawlak, O.J. Rojas, Nanofiber Composites of Polyvinyl Alcohol and Cellulose Nanocrystals: Manufacture and Characterization, Biomacromolecules. 11 (2010) 674–681. doi:10.1021/bm901254n.
- [67] R.T. Olsson, R. Kraemer, A. López-Rubio, S. Torres-Giner, M.J. Ocio, J.M. Lagarón, Extraction of Microfibrils from Bacterial Cellulose Networks for Electrospinning of Anisotropic Biohybrid Fiber Yarns, Macromolecules. 43 (2010) 4201–4209. doi:10.1021/ma100217q.
- [68] Y. Habibi, L.A. Lucia, O.J. Rojas, Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications, Chem. Rev. 110 (2010) 3479–3500. doi:10.1021/cr900339w.
- [69] S.J. Eichhorn, A. Dufresne, M. Aranguren, N.E. Marcovich, J.R. Capadona, S.J. Rowan, C. Weder, W. Thielemans, M. Roman, S. Renneckar, W. Gindl, S. Veigel, J. Keckes, H. Yano, K. Abe, M. Nogi, A.N. Nakagaito, A. Mangalam, J. Simonsen, A.S. Benight, A. Bismarck, L.A. Berglund, T. Peijs, Review: current international research into cellulose nanofibres and nanocomposites, J. Mater. Sci. 45 (2010) 1–33. doi:10.1007/s10853-009-3874-0.
- [70] O.J. Rojas, G.A. Montero, Y. Habibi, Electrospun nanocomposites from polystyrene loaded with cellulose nanowhiskers, J. Appl. Polym. Sci. 113 (2009) 927–935. doi:10.1002/app.30011.
- [71] J.O. Zoppe, M.S. Peresin, Y. Habibi, R.A. Venditti, O.J. Rojas, Reinforcing Poly(ε-caprolactone) Nanofibers with Cellulose Nanocrystals, ACS Appl. Mater. Interfaces. 1 (2009) 1996–2004. doi:10.1021/am9003705.
- [72] W.-I. Park, M. Kang, H.-S. Kim, H.-J. Jin, Electrospinning of Poly(ethylene oxide) with Bacterial Cellulose Whiskers, Macromol. Symp. 249–250 (2007) 289–294. doi:10.1002/masy.200750347.
- [73] W.L.E. Magalhães, X. Cao, L.A. Lucia, Cellulose Nanocrystals/Cellulose Core-in-Shell

Nanocomposite Assemblies, Langmuir. 25 (2009) 13250–13257. doi:10.1021/la901928j.

- S. Kamel, Nanotechnology and its applications in lignocellulosic composites, a mini review, Express Polym. Lett. 1 (2007) 546–575. doi:10.3144/expresspolymlett.2007.78.
- [75] P. Lu, Y.-L. Hsieh, Cellulose nanocrystal-filled poly(acrylic acid) nanocomposite fibrous membranes, Nanotechnology. 20 (2009) 415604. doi:10.1088/0957-4484/20/41/415604.
- [76] Anna J. Svagan, A. My A. S. Azizi Samir, L.A. Berglund, Biomimetic Polysaccharide Nanocomposites of High Cellulose Content and High Toughness, Biomacromolecules. 8 (2007) 2556–2563. doi:10.1021/BM0703160.
- S. Anna J., H. Mikael S., B. Lars, Reduced water vapour sorption in cellulose nanocomposites with starch matrix, Compos. Sci. Technol. 69 (2009) 500–506. doi:10.1016/J.COMPSCITECH.2008.11.016.
- [78] D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, A. Dorris, Nanocelluloses:
 A new family of nature-based materials, Angew. Chemie Int. Ed. 50 (2011) 5438–5466.
 doi:10.1002/anie.201001273.
- [79] M.A.S.A. Samir, F. Alloin, J.-Y. Sanchez, N. El Kissi, A. Dufresne, Preparation of Cellulose Whiskers Reinforced Nanocomposites from an Organic Medium Suspension, Macromolecules. 37 (2004) 1386–1393. doi:10.1021/MA030532A.
- [80] P. Shweta A., S. John, L. John, Poly(vinyl alcohol)/cellulose nanocrystal barrier membranes, J.
 Memb. Sci. 320 (2008) 248–258. doi:10.1016/J.MEMSCI.2008.04.009.
- [81] N.E. Marcovich, M.L. Auad, N.E. Bellesi, S.R. Nutt, M.I. Aranguren, Cellulose micro/nanocrystals reinforced polyurethane, J. Mater. Res. 21 (2006) 870–881. doi:10.1557/jmr.2006.0105.
- [82] G. Lee, M. Aji, O. Kristiina, G. Paul, R. Arthur J., A novel nanocomposite film prepared from crosslinked cellulosic whiskers, Carbohydr. Polym. 75 (2009) 85–89. doi:10.1016/J.CARBPOL.2008.06.017.
- [83] My Ahmed Saïd Azizi Samir, Fannie Alloin, Jean-Yves Sanchez, Alain Dufresne, Cross-Linked Nanocomposite Polymer Electrolytes Reinforced with Cellulose Whiskers, Macromolecules. 37 (2004) 4839–4844. doi:10.1021/MA049504Y.
- [84] O. K., M. A.P., B. D., K. I., Manufacturing process of cellulose whiskers/polylactic acid nanocomposites, Compos. Sci. Technol. 66 (2006) 2776–2784. doi:10.1016/J.COMPSCITECH.2006.03.002.
- [85] D. Bondeson, K. Oksman, Dispersion and characteristics of surfactant modified cellulose

whiskers nanocomposites, Compos. Interfaces. 14 (2007) 617–630. doi:10.1163/156855407782106519.

- [86] A. Zaman, F. Huang, M. Jiang, W. Wei, Z. Zhou, Preparation, Properties, and Applications of Natural Cellulosic Aerogels: A Review, Energy Built Environ. (2019).
- [87] L.-Y. Long, Y.-X. Weng, Y.-Z. Wang, Cellulose Aerogels: Synthesis, Applications, and Prospects, Polym. 2018, Vol. 10, Page 623. 10 (2018) 623. doi:10.3390/POLYM10060623.
- [88] K.Y. Lee, Y. Aitomäki, L.A. Berglund, K. Oksman, A. Bismarck, On the use of nanocellulose as reinforcement in polymer matrix composites, Compos. Sci. Technol. 105 (2014) 15–27. doi:10.1016/J.COMPSCITECH.2014.08.032.
- [89] M. Jawaid, S. Boufi, A.K.H.P. S, Cellulose-Reinforced Nanofibre Composites, (2017) 563.
- [90] M. Jawaid, S. Boufi, A. Khalil, Cellulose-reinforced nanofibre composites : production, properties and applications, 2017.
- [91] S.-E. Arantzazu, U. Lorena, G.-A. Clara, A. Aitor, C. Maria Angeles, E. Arantxa, Cellulose nanocrystals reinforced environmentally-friendly waterborne polyurethane nanocomposites, Carbohydr. Polym. 151 (2016) 1203–1209. doi:10.1016/J.CARBPOL.2016.06.069.
- [92] B. Barari, E. Omrani, A. Dorri Moghadam, P.L. Menezes, K.M. Pillai, P.K. Rohatgi, Mechanical, physical and tribological characterization of nano-cellulose fibers reinforced bio-epoxy composites: An attempt to fabricate and scale the 'Green' composite, Carbohydr. Polym. 147 (2016) 282–293. doi:10.1016/j.carbpol.2016.03.097.
- [93] M. Arup, C. Debabrata, Characterization of nanocellulose reinforced semi-interpenetrating polymer network of poly(vinyl alcohol) & polyacrylamide composite films, Carbohydr. Polym. 134 (2015) 240–250. doi:10.1016/J.CARBPOL.2015.07.093.
- [94] Q. Zeinab, K. Mahdi, Properties of whey protein isolate nanocomposite films reinforced with nanocellulose isolated from oat husk, Int. J. Biol. Macromol. 91 (2016) 1134–1140. doi:10.1016/J.IJBIOMAC.2016.06.077.
- [95] R. Eduardo, U. Iñaki, L. Jalel, S. Luis, Surface-modified nano-cellulose as reinforcement in poly(lactic acid) to conform new composites, Ind. Crops Prod. 71 (2015) 44–53. doi:10.1016/J.INDCROP.2015.03.075.
- [96] B. Benoit, B. Julien, S. Seema, D. Claude, L. Eric, Mechanical and antibacterial properties of a nanocellulose-polypyrrole multilayer composite, Mater. Sci. Eng. C. 69 (2016) 977–984. doi:10.1016/J.MSEC.2016.08.005.

- [97] X. Shuman, Y. Wenjin, Y. Xuelin, Z. Qin, F. Qiang, Nanocellulose-assisted dispersion of graphene to fabricate poly(vinyl alcohol)/graphene nanocomposite for humidity sensing, Compos. Sci. Technol. 131 (2016) 67–76. doi:10.1016/J.COMPSCITECH.2016.05.014.
- [98] A. Eldho, E. P.A., D. B., J. P., P. L.A., N. S.S., T. S., X-ray diffraction and biodegradation analysis of green composites of natural rubber/nanocellulose, Polym. Degrad. Stab. 97 (2012) 2378– 2387. doi:10.1016/J.POLYMDEGRADSTAB.2012.07.028.
- [99] M. Arup, C. Debabrata, Studies on the mechanical, thermal, morphological and barrier properties of nanocomposites based on poly(vinyl alcohol) and nanocellulose from sugarcane bagasse, J. Ind. Eng. Chem. 20 (2014) 462–473. doi:10.1016/J.JIEC.2013.05.003.
- [100] K. R.Z., I. H., C. W.S., Thermal and Morphological Properties of Poly (Lactic Acid)/Nanocellulose Nanocomposites, Procedia Chem. 19 (2016) 788–794. doi:10.1016/J.PROCHE.2016.03.086.
- [101] T. Martin George, A. Eldho, J. P., M. Hanna J., P. Laly A., T. Sabu, Nanocelluloses from jute fibers and their nanocomposites with natural rubber: Preparation and characterization, Int. J. Biol. Macromol. 81 (2015) 768–777. doi:10.1016/J.IJBIOMAC.2015.08.053.
- [102] Y. Zhang, L. Li, C. Guo, D. Mu, B. Feng, X. Zuo, Y. Li, Effects of probiotic type, dose and treatment duration on irritable bowel syndrome diagnosed by Rome III criteria: a meta-analysis, BMC Gastroenterol. 16 (2016) 62. doi:10.1186/s12876-016-0470-z.
- [103] L. Alessandra, S. Lisete Cristine, Z. Ademir José, Dynamic-mechanical and thermomechanical properties of cellulose nanofiber/polyester resin composites, Carbohydr. Polym. 136 (2016) 955–963. doi:10.1016/J.CARBPOL.2015.10.008.
- [104] M. R., E.-H. R.F., P. K.M., S. R., Mechanical characterization of cellulose nanofiber and bio-based epoxy composite, Mater. Des. 36 (2012) 570–576. doi:10.1016/J.MATDES.2011.11.042.
- [105] X. Shanhong, G. Natalie, S. Gregory, S. Meisha L., M. J. Carson, Mechanical and thermal properties of waterborne epoxy composites containing cellulose nanocrystals, Polymer (Guildf). 54 (2013) 6589–6598. doi:10.1016/J.POLYMER.2013.10.011.
- [106] O. Ahmed A., R. Jong-Whan, Isolation of cellulose nanocrystals from grain straws and their use for the preparation of carboxymethyl cellulose-based nanocomposite films, Carbohydr. Polym. 150 (2016) 187–200. doi:10.1016/J.CARBPOL.2016.05.020.
- [107] A. Farhan, S. Mikael, B. Lars, Nanostructured biocomposites based on unsaturated polyester resin and a cellulose nanofiber network, Compos. Sci. Technol. 117 (2015) 298–306. doi:10.1016/J.COMPSCITECH.2015.07.004.
- [108] P. Sang Ho, O. Kyung Wha, K. Seong Hun, Reinforcement effect of cellulose nanowhisker on bio-based polyurethane, Compos. Sci. Technol. 86 (2013) 82–88. doi:10.1016/J.COMPSCITECH.2013.07.006.
- [109] W.Y. Hamad, Photonic and Semiconductor Materials Based on Cellulose Nanocrystals, (2015) 287–328. doi:10.1007/12_2015_323.
- J.A. Kelly, M. Giese, K.E. Shopsowitz, W.Y. Hamad, M.J. MacLachlan, The Development of Chiral Nematic Mesoporous Materials, Acc. Chem. Res. 47 (2014) 1088–1096. doi:10.1021/ar400243m.
- [111] M. Schlesinger, M. Giese, L.K. Blusch, W.Y. Hamad, M.J. MacLachlan, Chiral nematic cellulose– gold nanoparticle composites from mesoporous photonic cellulose, Chem. Commun. 51 (2015) 530–533. doi:10.1039/C4CC07596J.
- [112] H. Qi, K.E. Shopsowitz, W.Y. Hamad, M.J. MacLachlan, Chiral Nematic Assemblies of Silver Nanoparticles in Mesoporous Silica Thin Films, J. Am. Chem. Soc. 133 (2011) 3728–3731. doi:10.1021/ja110369d.
- [113] A. Querejeta-Fernández, G. Chauve, M. Methot, J. Bouchard, E. Kumacheva, Chiral Plasmonic Films Formed by Gold Nanorods and Cellulose Nanocrystals, J. Am. Chem. Soc. 136 (2014) 4788–4793. doi:10.1021/ja501642p.
- [114] G. Chu, X. Wang, H. Yin, Y. Shi, H. Jiang, T. Chen, J. Gao, D. Qu, Y. Xu, D. Ding, Free-Standing Optically Switchable Chiral Plasmonic Photonic Crystal Based on Self-Assembled Cellulose Nanorods and Gold Nanoparticles, ACS Appl. Mater. Interfaces. 7 (2015) 21797–21806.
- [115] A. Querejeta-Fernández, B. Kopera, K.S. Prado, A. Klinkova, M. Methot, G. Chauve, J. Bouchard,
 A.S. Helmy, E. Kumacheva, Circular Dichroism of Chiral Nematic Films of Cellulose Nanocrystals
 Loaded with Plasmonic Nanoparticles, ACS Nano. 9 (2015) 10377–10385.
 doi:10.1021/acsnano.5b04552.
- [116] A. Lukach, H. Thérien-Aubin, A. Querejeta-Fernández, N. Pitch, G. Chauve, M. Méthot, J. Bouchard, E. Kumacheva, Coassembly of Gold Nanoparticles and Cellulose Nanocrystals in Composite Films, Langmuir. 31 (2015) 5033–5041. doi:10.1021/acs.langmuir.5b00728.
- [117] X. Mu, D.G. Gray, Droplets of cellulose nanocrystal suspensions on drying give iridescent 3-D "coffee-stain" rings, Cellulose. 22 (2015) 1103–1107. doi:10.1007/s10570-015-0569-3.
- [118] X. Mu, D.G. Gray, Formation of Chiral Nematic Films from Cellulose Nanocrystal Suspensions Is a Two-Stage Process, Langmuir. 30 (2014) 9256–9260. doi:10.1021/la501741r.

- [119] A.G. Dumanli, H.M. van der Kooij, G. Kamita, E. Reisner, J.J. Baumberg, U. Steiner, S. Vignolini, Digital Color in Cellulose Nanocrystal Films, ACS Appl. Mater. Interfaces. 6 (2014) 12302– 12306. doi:10.1021/am501995e.
- [120] X. Yang, K. Shi, I. Zhitomirsky, E.D. Cranston, Cellulose Nanocrystal Aerogels as Universal 3D Lightweight Substrates for Supercapacitor Materials, Adv. Mater. 27 (2015) 6104–6109. doi:10.1002/adma.201502284.
- [121] M. Roman, Toxicity of Cellulose Nanocrystals: A Review, Ind. Biotechnol. 11 (2015) 25–33. doi:10.1089/ind.2014.0024.
- [122] H. Martínez Ávila, S. Schwarz, E.-M. Feldmann, A. Mantas, A. von Bomhard, P. Gatenholm, N. Rotter, Biocompatibility evaluation of densified bacterial nanocellulose hydrogel as an implant material for auricular cartilage regeneration, Appl. Microbiol. Biotechnol. 98 (2014) 7423– 7435. doi:10.1007/s00253-014-5819-z.
- [123] B. Jia, Y. Li, B. Yang, D. Xiao, S. Zhang, A.V. Rajulu, T. Kondo, L. Zhang, J. Zhou, Effect of microcrystal cellulose and cellulose whisker on biocompatibility of cellulose-based electrospun scaffolds, Cellulose. 20 (2013) 1911–1923. doi:10.1007/s10570-013-9952-0.
- [124] G. Helenius, H. Bäckdahl, A. Bodin, U. Nannmark, P. Gatenholm, B. Risberg, In vivo biocompatibility of bacterial cellulose, J. Biomed. Mater. Res. Part A. 76A (2006) 431–438. doi:10.1002/jbm.a.30570.
- [125] R.M.A. Domingues, M.E. Gomes, R.L. Reis, The Potential of Cellulose Nanocrystals in Tissue Engineering Strategies, Biomacromolecules. 15 (2014) 2327–2346. doi:10.1021/bm500524s.
- [126] Y. Li, S. Wang, R. Huang, Z. Huang, B. Hu, W. Zheng, G. Yang, X. Jiang, Evaluation of the Effect of the Structure of Bacterial Cellulose on Full Thickness Skin Wound Repair on a Microfluidic Chip, Biomacromolecules. 16 (2015) 780–789. doi:10.1021/bm501680s.
- [127] A. Harlin, M. Vikman, Developments in advanced biocomposites, 2010.
- [128] J. Cai, S. Liu, J. Feng, S. Kimura, M. Wada, S. Kuga, L. Zhang, Cellulose-Silica Nanocomposite Aerogels by In Situ Formation of Silica in Cellulose Gel, Angew. Chemie. 124 (2012) 2118–2121. doi:10.1002/ange.201105730.
- [129] H. Sehaqui, A. Liu, Q. Zhou, L.A. Berglund, Fast Preparation Procedure for Large, Flat Cellulose and Cellulose/Inorganic Nanopaper Structures, Biomacromolecules. 11 (2010) 2195–2198. doi:10.1021/bm100490s.
- [130] K.E. Kurtis, Innovations in cement-based materials: Addressing sustainability in structural and

infrastructure applications, MRS Bull. 40 (2015) 1102–1109. doi:10.1557/mrs.2015.279.

- [131] P.-T. Fernando, J. Said, Cementitious building materials reinforced with vegetable fibres: A review, Constr. Build. Mater. 25 (2011) 575–581. doi:10.1016/J.CONBUILDMAT.2010.07.024.
- [132] F. Ridi, E. Fratini, P. Baglioni, Cement: A two thousand year old nano-colloid, J. Colloid Interface Sci. 357 (2011) 255–264. doi:10.1016/J.JCIS.2011.02.026.
- [133] B. L.R., O. C., S. S.P., Fiber-matrix interaction in microfiber-reinforced mortar, Adv. Cem. Based Mater. 2 (1995) 53–61. doi:10.1016/1065-7355(95)90025-X.
- [134] A. Mezencevova, V. Garas, H. Nanko, K.E. Kurtis, Influence of Thermomechanical Pulp Fiber Compositions on Internal Curing of Cementitious Materials, J. Mater. Civ. Eng. 24 (2012) 970– 975. doi:10.1061/(ASCE)MT.1943-5533.0000446.
- [135] M. Ardanuy, J. Claramunt, R. Arévalo, F. Parés, E. Aracri, T. Vidal, Nanofibrillated cellulose (NFC) as a potential reinforcement for high performance cement mortar composites, BioResources. 7 (2012) 3883–3894.
- [136] C. Yizheng, Z. Pablo, Y. Jeff, M. Robert, W. Jason, The influence of cellulose nanocrystal additions on the performance of cement paste, Cem. Concr. Compos. 56 (2015) 73–83. doi:10.1016/J.CEMCONCOMP.2014.11.008.
- [137] T. Sherry L., O. David J., W. John A., S. Bing, Method of making a fiber cement board with improved properties and the product, US 8293003 B1, 2012.
- [138] W. S. Ananda, S. Harshadkumar M., Fiber for fiber cement and resulting product, US 8791178 B2, 2013.
- [139] W. S. Ananda, O. David J., Internally curing cement based materials, US 9056792 B2, 2012.
- [140] H. Dai, L. Jiao, Y. Zhu, C. Pi, Nanometer cellulose fiber reinforced cement-based material, CN 105174768 A, 2015.
- [141] Y. Jeffrey Paul, Z. Pablo Daniel, M. Robert John, W. William Jason, C. Yizheng, Cellulose nanocrystal additives and improved cementious systems, US 20160075601 A1, 2014.
- [142] L. Shaul, S. Oded, G. Tord, C.-G. Lea, Nano crystalline cellulose in construction applications, WO 2015177795 A1, 2015.
- [143] L. Antti, T. Jan-Erik, L. Markku, K. Hannele, K. Kirsi, N. Antti, Material to be used as a concrete additive, US 9174873 B2, 2010.
- [144] J. Cowie, E.M.T. Bilek, T.H. Wegner, J.A. Shatkin, Market projections of cellulose nanomaterial-

enabled products - part 2: Volume estimates, 13 (2014) 57–69.

- [145] J. Miller, NANOCELLULOSE: Technology, Applications and Markets, RISI, 2014.
- [146] J. Miller, NANOCELLULOSE STATE OF THE INDUSTRY, 2015.
- [147] S. Florence, S. Konstantin, Nanotechnology in concrete A review, Constr. Build. Mater. 24 (2010) 2060–2071. doi:10.1016/J.CONBUILDMAT.2010.03.014.
- [148] D. J.S., L. J., H. D., S. D., G. E.M., Sustainable development and climate change initiatives, Cem. Concr. Res. 38 (2008) 115–127. doi:10.1016/J.CEMCONRES.2007.09.008.
- [149] O. Obinna, P. Daman K., S. Mohini, Properties of nanofibre reinforced cement composites, Constr. Build. Mater. 63 (2014) 119–124. doi:10.1016/J.CONBUILDMAT.2014.04.072.
- [150] R. Mejdoub, H. Hammi, J.J. Suñol, M. Khitouni, A. M'nif, S. Boufi, Nanofibrillated cellulose as nanoreinforcement in Portland cement: Thermal, mechanical and microstructural properties, J. Compos. Mater. 51 (2017) 2491–2503. doi:10.1177/0021998316672090.
- [151] L. Ferrara, S.R. Ferreira, M. della Torre, V. Krelani, F.A. de Silva, R.D.T. Filho, Effect of Cellulose Nanopulp on Autogenous and Drying Shrinkage of Cement Based Composites, in: Nanotechnol. Constr., Springer International Publishing, Cham, 2015: pp. 325–330. doi:10.1007/978-3-319-17088-6 42.
- [152] Y. Cao, P. Zavattieri, J. Youngblood, R. Moon, J. Weiss, The relationship between cellulose nanocrystal dispersion and strength, Constr. Build. Mater. 119 (2016) 71–79. doi:10.1016/j.conbuildmat.2016.03.077.
- [153] L. Heath, W. Thielemans, Cellulose nanowhisker aerogels, Green Chem. 12 (2010) 1448. doi:10.1039/c0gc00035c.
- [154] A. Kiziltas, B. Nazari, D.J. Gardner, D.W. Bousfield, Polyamide 6-Cellulose Composites: Effect of Cellulose Composition on Melt Rheology and Crystallization Behavior, Polym. Eng. Sci. 54 (2014) 739–746. doi:10.1002/pen.23603.
- [155] B. S.D., V. U.K., Performance of long fiber reinforced thermoplastics subjected to transverse intermediate velocity blunt object impact, Compos. Struct. 67 (2005) 263–277. doi:10.1016/J.COMPSTRUCT.2004.07.023.
- [156] N. Ayrilmis, S. Jarusombuti, V. Fueangvivat, P. Bauchongkol, R.H. White, Coir fiber reinforced polypropylene composite panel for automotive interior applications, Fibers Polym. 12 (2011) 919–926. doi:10.1007/s12221-011-0919-1.
- [157] A. Chakraborty, M. Sain, M. Kortschot, Cellulose Microfibers as Reinforcing Agents for

Structural Materials, in: 2006: pp. 169–186. doi:10.1021/bk-2006-0938.ch012.

- [158] J. Maya Jacob, T. Sabu, Biofibres and biocomposites, Carbohydr. Polym. 71 (2008) 343–364. doi:10.1016/J.CARBPOL.2007.05.040.
- [159] L.E. Millon, W.K. Wan, The polyvinyl alcohol-bacterial cellulose system as a new nanocomposite for biomedical applications, J. Biomed. Mater. Res. Part B Appl. Biomater. 79B (2006) 245–253. doi:10.1002/jbm.b.30535.
- [160] C. Bibin Mathew, L. Alcides Lopes, de S. Sivoney Ferreira, T. Sabu, P. Laly A., K. M., Isolation of nanocellulose from pineapple leaf fibres by steam explosion, Carbohydr. Polym. 81 (2010) 720– 725. doi:10.1016/J.CARBPOL.2010.03.046.
- [161] L.M.M. Costa, G.M. de Olyveira, B.M. Cherian, A.L. Leão, S.F. de Souza, M. Ferreira, Bionanocomposites from electrospun PVA/pineapple nanofibers/Stryphnodendron adstringens bark extract for medical applications, Ind. Crops Prod. 41 (2013) 198–202. doi:10.1016/j.indcrop.2012.04.025.
- [162] M. Nuruddin, A. Chowdhury, S.A. Haque, M. Rahman, S.F. Farhad, M.S. Jahan, A. Quaiyyum, Extraction and characterization of cellulose microfibrils from agricultural wastes in an integrated biorefinery initiative, 45 (2011) 347–354.
- [163] B. M. Douglas, K. Catherine E., S. Jason C., W. Yuanfei, K. Howard, L. Yakov, S. Molly S., An injectable drug delivery platform for sustained combination therapy, J. Control. Release. 138 (2009) 205–213. doi:10.1016/J.JCONREL.2009.05.009.
- [164] M.N. Nadagouda, R.S. Varma, Green synthesis of silver and palladium nanoparticles at room temperature using coffee and tea extract, Green Chem. 10 (2008) 859. doi:10.1039/b804703k.
- [165] S. B.L, O. T.C, P. A, Polymeric biomaterials for tissue and organ regeneration, Mater. Sci. Eng. R Reports. 34 (2001) 147–230. doi:10.1016/S0927-796X(01)00035-3.
- [166] J.S. Capes, H.Y. Ando, R.E. Cameron, Fabrication of polymeric scaffolds with a controlled distribution of pores, J. Mater. Sci. Mater. Med. 16 (2005) 1069–1075. doi:10.1007/s10856-005-4708-5.
- [167] K. Dieter, S. Dieter, U. Ulrike, M. Silvia, Bacterial synthesized cellulose artificial blood vessels for microsurgery, Prog. Polym. Sci. 26 (2001) 1561–1603. doi:10.1016/S0079-6700(01)00021 1.
- [168] Y. Ikada, Challenges in tissue engineering., J. R. Soc. Interface. 3 (2006) 589–601. doi:10.1098/rsif.2006.0124.

- [169] K. Rajendran, R. Selvaraj Mohana, P. Arunachalam, K. Venkatesan Gopiesh, C. Subhendu, Agricultural waste Annona squamosa peel extract: Biosynthesis of silver nanoparticles, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 90 (2012) 173–176. doi:10.1016/J.SAA.2012.01.029.
- [170] Subrata; Mondal, Preparation, properties and applications of nanocellulosic materials, Carbohydr. Polym. 163 (2017) 301–316. doi:10.1016/J.CARBPOL.2016.12.050.
- [171] Y. Ahmed M., E.-S. Magda Ali, A.R. Mona H., Preparation of conductive paper composites based on natural cellulosic fibers for packaging applications, Carbohydr. Polym. 89 (2012) 1027–1032. doi:10.1016/J.CARBPOL.2012.03.044.
- [172] N. Abdorreza Mohammadi, A. Abd Karim, M. Shahrom, R. Marju, Antimicrobial, rheological, and physicochemical properties of sago starch films filled with nanorod-rich zinc oxide, J. Food Eng. 113 (2012) 511–519. doi:10.1016/J.JFOODENG.2012.07.017.
- [173] N. Zadbuke, S. Shahi, B. Gulecha, A. Padalkar, M. Thube, Recent trends and future of pharmaceutical packaging technology., J. Pharm. Bioallied Sci. 5 (2013) 98–110. doi:10.4103/0975-7406.111820.
- [174] A.K. H.P.S., D. Y., I. Md. Nazrul, M. Asniza, S. K., D. Rudi, J. M., Production and modification of nanofibrillated cellulose using various mechanical processes: A review, Carbohydr. Polym. 99 (2014) 649–665. doi:10.1016/J.CARBPOL.2013.08.069.
- [175] S. Kalia, S. Boufi, A. Celli, S. Kango, Nanofibrillated cellulose: surface modification and potential applications, Colloid Polym. Sci. 292 (n.d.) 5–31. doi:10.1007/s00396-013-3112-9.
- [176] H.C. LEWIS, O. WICHMANN, E. DUIZER, Transmission routes and risk factors for autochthonous hepatitis E virus infection in Europe: a systematic review, Epidemiol. Infect. 138 (2010) 145. doi:10.1017/S0950268809990847.
- [177] M.G. Freire, A.R.R. Teles, R.A.S. Ferreira, L.D. Carlos, J.A. Lopes-da-Silva, J.A.P. Coutinho, Electrospun nanosized cellulose fibers using ionic liquids at room temperature, Green Chem. 13 (2011) 3173. doi:10.1039/c1gc15930e.
- [178] X. Zhang, M. Tu, M.G. Paice, Routes to Potential Bioproducts from Lignocellulosic Biomass Lignin and Hemicelluloses, BioEnergy Res. 4 (2011) 246–257. doi:10.1007/s12155-011-9147-1.
- [179] A.K. Geim, K.S. Novoselov, The rise of graphene, Nat. Mater. 6 (2007) 183–191.
- [180] L.D. Landau, Zur eorie der phasenumwandlungen II, Phys. Z. Sowjetunion. 11 (1937) 26–35.
- [181] R.E. Peierls, Quelques proprietes typiques des corpses solides, Ann. I. H. Poincare. 5 (1935)

177–222.

- [182] O.A. Shenderova, V.V. Zhirnov, D.W. Brenner, Carbon Nanostructures, Crit. Rev. Solid State Mater. Sci. 27 (2002) 227–356.
- [183] Scientific Background on the Nobel Prize in Physics 2010, GRAPHENE, STOCKHOLM, 2010.
- [184] H. Fernandez-Moran, Single crystals of graphite and of mica as specimen support for electron microscopy, J. Appl. Phys. 31 (1960) 1844.
- [185] A. Van Bommel, J. Crombeen, A. Van Tooren, LEED and Auger electron observations of the SiC (0001) surface, Surf. Sci. 48 (1975) 463–472.
- [186] C. Berger, Z. Song, T. Li, X. Li, Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphene-based nanoelectronics, J. Phys. Chem. B. 108 (2004) 19912–19916.
- [187] T. Land, T. Michely, R. Behm, J.C. Hemminger, G. Comsa, STM investigation of single layer graphite structures produced on Pt (111) by hydrocarbon decomposition, Surf. Sci. 264 (1992) 261–270.
- [188] P. Sutter, J. Flege, E. Sutter, Epitaxial graphene on ruthenium, Nat. Mater. 7 (2008) 406–411.
- [189] M. Ioniţă, G.M. Vlăsceanu, A.A. Watzlawek, S.I. Voicu, J.S. Burns, H. Iovu, Graphene and functionalized graphene: Extraordinary prospects for nanobiocomposite materials, Compos. Part B Eng. 121 (2017) 34–57.
- [190] T. Ramanathan, A.A. Abdala, S. Stankovich, D.A. Dikin, M. Herrera-Alonso, R.D. Piner, D.H. Adamson, H.C. Schniepp, X. Chen, R.S. Ruoff, S.T. Nguyen, I.A. Aksay, R.K. Prud'Homme, L.C. Brinson, Functionalized graphene sheets for polymer nanocomposites., Nat. Nanotechnol. 3 (2008) 327–331.
- [191] Y. Xu, W. Hong, H. Bai, C. Li, G. Shi, Strong and ductile poly(vinyl alcohol)/graphene oxide composite films with a layered structure, Carbon N. Y. 47 (2009) 3538–3543.
- [192] T. Ramanathan, S. Stankovich, D.A. Dikin, H. Liu, H. Shen, S.T. Nguyen, L.C. Brinson, Graphitic nanofillers in PMMA nanocomposites—An investigation of particle size and dispersion and their influence on nanocomposite properties, J. Polym. Sci. Part B Polym. Phys. 45 (2007) 2097– 2112.
- [193] D. Cai, M. Song, A simple route to enhance the interface between graphite oxide nanoplatelets and a semi-crystalline polymer for stress transfer, Nanotechnology. 20 (2009) 315708.
- [194] D. Cai, K. Yusoh, M. Song, The mechanical properties and morphology of a graphite oxide nanoplatelet/polyurethane composite., Nanotechnology. 20 (2009) 085712.

- [195] Q. Wu, Y. Xu, Z. Yao, A. Liu, G. Shi, Supercapacitors Based on Flexible Graphene/Polyaniline Nanofiber Composite Films, ACS Nano. 4 (2010) 1963–1970.
- [196] I.-H. Kim, Y.G. Jeong, Polylactide/exfoliated graphite nanocomposites with enhanced thermal stability, mechanical modulus, and electrical conductivity, J. Polym. Sci. Part B Polym. Phys. 48 (2010) 850–858.
- [197] H.-B. Zhang, W.-G. Zheng, Q. Yan, Y. Yang, J.-W. Wang, Z.-H. Lu, G.-Y. Ji, Z.-Z. Yu, Electrically conductive polyethylene terephthalate/graphene nanocomposites prepared by melt compounding, Polymer (Guildf). 51 (2010) 1191–1196.
- [198] A. Dasari, Z.-Z. Yu, Y.-W. Mai, Electrically conductive and super-tough polyamide-based nanocomposites, Polymer (Guildf). 50 (2009) 4112–4121.
- [199] A. Yu, P. Ramesh, M.E. Itkis, E. Bekyarova, R.C. Haddon, Graphite Nanoplatelet-Epoxy Composite Thermal Interface Materials, J. Phys. Chem. C. 111 (2007) 7565–7569.
- [200] X. Xiao, T. Xie, Y.-T. Cheng, Self-healable graphene polymer composites, J. Mater. Chem. 20 (2010) 3508–3514.
- [201] H. Hu, X. Wang, J. Wang, L. Wan, F. Liu, H. Zheng, R. Chen, C. Xu, Preparation and properties of graphene nanosheets-polystyrene nanocomposites via in situ emulsion polymerization, Chem. Phys. Lett. 484 (2010) 247–253.
- [202] T. Wei, G. Luo, Z. Fan, C. Zheng, J. Yan, C. Yao, W. Li, C. Zhang, Preparation of graphene nanosheet/polymer composites using in situ reduction–extractive dispersion, Carbon N. Y. 47 (2009) 2296–2299.
- [203] M.A. Rafiee, J. Rafiee, I. Srivastava, Z. Wang, H. Song, Z.-Z. Yu, N. Koratkar, Fracture and Fatigue in Graphene Nanocomposites, Small. 6 (2010) 179–183.
- [204] X. Zhou, T. Wu, B. Hu, G. Yang, B. Han, Synthesis of graphene/polyaniline composite nanosheets mediated by polymerized ionic liquid, Chem. Commun. 46 (2010) 3663–3665.
- [205] K. Zhang, L.L. Zhang, X.S. Zhao, J. Wu, Graphene/Polyaniline Nanofiber Composites as Supercapacitor Electrodes, Chem. Mater. 22 (2010) 1392–1401.
- [206] J. Yan, T. Wei, B. Shao, Z. Fan, W. Qian, M. Zhang, F. Wei, Preparation of a graphene nanosheet/polyaniline composite with high specific capacitance, Carbon N. Y. 48 (2010) 487– 493.
- [207] H. Wang, Q. Hao, X. Yang, L. Lu, X. Wang, Effect of Graphene Oxide on the Properties of Its Composite with Polyaniline, ACS Appl. Mater. Interfaces. 2 (2010) 821–828.

- [208] H. Wang, Q. Hao, X. Yang, L. Lu, X. Wang, Graphene oxide doped polyaniline for supercapacitors, 2009.
- [209] D.-W. Wang, F. Li, J. Zhao, W. Ren, Z.-G. Chen, J. Tan, Z.-S. Wu, I. Gentle, G.Q. Lu, H.-M. Cheng, Fabrication of Graphene/Polyaniline Composite Paper via In Situ Anodic Electropolymerization for High-Performance Flexible Electrode, ACS Nano. 3 (2009) 1745–1752.
- [210] R. Verdejo, F. Barroso-Bujans, M.A. Rodriguez-Perez, J. Antonio de Saja, M.A. Lopez-Manchado, Functionalized graphene sheet filled silicone foam nanocomposites, J. Mater. Chem. 18 (2008) 2221.
- [211] J. Liang, Y. Xu, Y. Huang, L. Zhang, Y. Wang, Y. Ma, F. Li, T. Guo, Y. Chen, Infrared-Triggered Actuators from Graphene-Based Nanocomposites, J. Phys. Chem. C. 113 (2009) 9921–9927.
- [212] J.I. Paredes, S. Villar-Rodil, A. Martínez-Alonso, J.M.D. Tascón, Graphene Oxide Dispersions in Organic Solvents, Langmuir. 24 (2008) 10560–10564.
- [213] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner,
 S.T. Nguyen, R.S. Ruoff, Graphene-based composite materials, Nature. 442 (2006) 282–286.
- [214] C. Gómez-Navarro, R.T. Weitz, A.M. Bittner, M. Scolari, A. Mews, M. Burghard, K. Kern, Electronic Transport Properties of Individual Chemically Reduced Graphene Oxide Sheets, Nano Lett. 7 (2007) 3499–3503.
- [215] Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, Flexible Graphene Films via the Filtration of Water-Soluble Noncovalent Functionalized Graphene Sheets, J. Am. Chem. Soc. 130 (2008) 5856–5857.
- [216] H.A. Becerril, J. Mao, Z. Liu, R.M. Stoltenberg, Z. Bao, Y. Chen, Evaluation of Solution-Processed Reduced Graphene Oxide Films as Transparent Conductors, ACS Nano. 2 (2008) 463–470.
- [217] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen,
 R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, Carbon N. Y. 45 (2007) 1558–1565.
- [218] Z. Li, W. Zhang, Y. Luo, J. Yang, J.G. Hou, How Graphene Is Cut upon Oxidation?, J. Am. Chem. Soc. 131 (2009) 6320–6321.
- [219] L. Zhang, J. Liang, Y. Huang, Y. Ma, Y. Wang, Y. Chen, Size-controlled synthesis of graphene oxide sheets on a large scale using chemical exfoliation, Carbon N. Y. 47 (2009) 3365–3368.
- [220] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, The chemistry of graphene oxide, Chem. Soc. Rev. 39 (2010) 228–240.
- [221] S. Stankovich, R.D. Piner, X. Chen, N. Wu, S.T. Nguyen, R.S. Ruoff, Stable aqueous dispersions

of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate), J. Mater. Chem. 16 (2006) 155–158.

- [222] S. Stankovich, R.D. Piner, S.T. Nguyen, R.S. Ruoff, Synthesis and exfoliation of isocyanatetreated graphene oxide nanoplatelets, Carbon N. Y. 44 (2006) 3342–3347.
- [223] C. Xu, X. Wu, J. Zhu, X. Wang, Synthesis of amphiphilic graphite oxide, Carbon N. Y. 46 (2008) 386–389.
- [224] H. Kim, S. Kobayashi, M.A. AbdurRahim, M.J. Zhang, A. Khusainova, M.A. Hillmyer, A.A. Abdala,
 C.W. Macosko, Graphene/polyethylene nanocomposites: Effect of polyethylene functionalization and blending methods, Polymer (Guildf). 52 (2011) 1837–1846.
- [225] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene, Science (80-.). 321 (2008) 385–388.
- [226] R.K. Layek, M.E. Uddin, N.H. Kim, A.K. Tak Lau, J.H. Lee, Noncovalent functionalization of reduced graphene oxide with pluronic F127 and its nanocomposites with gum arabic, Compos. Part B Eng. 128 (2017) 155–163.
- [227] Y. Li, J. Liu, H. Dong, G. Liu, H. Hu, Engineering of a Pluronic F127 functionalized magnetite/graphene nanohybrid for chemophototherapy, Nanotechnology. 25 (2014).
- [228] S. Zu, B. Han, Aqueous Dispersion of Graphene Sheets Stabilized by Pluronic Copolymers : Formation of Supramolecular Hydrogel, J. Phys. Chem. C. 113 (2009) 13651–13657.
- [229] A. Chiappone, I. Roppolo, E. Naretto, E. Fantino, F. Calignano, M. Sangermano, F. Pirri, Study of graphene oxide-based 3D printable composites: Effect of the in situ reduction, Compos. Part B Eng. 124 (2017) 9–15. http://dx.doi.org/10.1016/j.compositesb.2017.05.049.
- [230] H. Korhonen, L.H. Sinh, N.D. Luong, P. Lehtinen, T. Verho, J. Partanen, J. Sepp??!?, Fabrication of graphene-based 3D structures by stereolithography, Phys. Status Solidi Appl. Mater. Sci. 213 (2016) 982–985.
- [231] X. Wang, M. Jiang, Z. Zhou, J. Gou, D. Hui, 3D printing of polymer matrix composites: A review and prospective, Compos. Part B Eng. 110 (2017) 442–458. http://dx.doi.org/10.1016/j.compositesb.2016.11.034.
- [232] D. Lin, S. Jin, F. Zhang, C. Wang, Y. Wang, C. Zhou, G.J. Cheng, 3D stereolithography printing of graphene oxide reinforced complex architectures, Nanotechnology. 26 (2015).
- [233] W. Guo, B. Yu, Y. Yuan, L. Song, Y. Hu, In situ preparation of reduced graphene oxide/DOPObased phosphonamidate hybrids towards high-performance epoxy nanocomposites, Compos.

Part B Eng. 123 (2017) 154–164. http://dx.doi.org/10.1016/j.compositesb.2017.05.024.

- [234] Q. Yao, J. Wang, A.G. Mack, Process For The Preparation Of Dopo-Derived Compounds And Compositions Thereof, 2013.
- [235] S.-H. Liao, P.-L. Liu, M.-C. Hsiao, C.-C. Teng, C.-A. Wang, M.-D. Ger, C.-L. Chiang, One-Step Reduction and Functionalization of Graphene Oxide with Phosphorus-Based Compound to Produce Flame-Retardant Epoxy Nanocomposite, Ind. Eng. Chem. Res. 51 (2012) 4573–4581.
- [236] C.H. Lin, S.X. Cai, C.H. Lin, Flame-retardant epoxy resins with high glass-transition temperatures. II. Using a novel hexafunctional curing agent: 9,10-dihydro-9-oxa-10phosphaphenanthrene 10-yl-tris(4-aminophenyl) methane, J. Polym. Sci. Part A Polym. Chem. 43 (2005) 5971–5986.
- [237] S.C. Shiu, J.L. Tsai, Characterizing thermal and mechanical properties of graphene/epoxy nanocomposites, Compos. Part B Eng. 56 (2014) 691–697. http://dx.doi.org/10.1016/j.compositesb.2013.09.007.
- [238] Z. Wang, P. Wei, Y. Qian, J. Liu, The synthesis of a novel graphene-based inorganic-organic hybrid flame retardant and its application in epoxy resin, Compos. Part B Eng. 60 (2014) 341– 349. http://dx.doi.org/10.1016/j.compositesb.2013.12.033.
- [239] B. Perret, B. Schartel, K. Stöß, M. Ciesielski, J. Diederichs, M. Döring, J. Krämer, V. Altstädt, Novel DOPO-based flame retardants in high-performance carbon fibre epoxy composites for aviation, Eur. Polym. J. 47 (2011) 1081–1089. http://dx.doi.org/10.1016/j.eurpolymj.2011.02.008.
- [240] X. Wang, L. Song, W. Xing, H. Lu, Y. Hu, A effective flame retardant for epoxy resins based on poly(DOPO substituted dihydroxyl phenyl pentaerythritol diphosphonate), Mater. Chem. Phys. 125 (2011) 536–541. http://dx.doi.org/10.1016/j.matchemphys.2010.10.020.
- [241] A.M. Pandele, M. Ionita, L. Crica, E. Vasile, H. Iovu, Novel Chitosan-poly(vinyl alcohol)/graphene oxide biocomposites 3D porous scaffolds, Compos. Part B Eng. 126 (2017) 81–87. http://dx.doi.org/10.1016/j.compositesb.2017.06.010.
- [242] M.Y. Kim, J. Lee, Chitosan fibrous 3D networks prepared by freeze drying, Carbohydr. Polym.
 84 (2011) 1329–1336. http://dx.doi.org/10.1016/j.carbpol.2011.01.029.
- [243] A.M. Pandele, M. Ionita, L. Crica, S. Dinescu, M. Costache, H. Iovu, Synthesis, characterization, and in vitro studies of graphene oxide/chitosan-polyvinyl alcohol films, Carbohydr. Polym. 102 (2014) 813–820. http://dx.doi.org/10.1016/j.carbpol.2013.10.085.

- [244] A.R. Unnithan, C.H. Park, C.S. Kim, Nanoengineered bioactive 3D composite scaffold: A unique combination of graphene oxide and nanotopography for tissue engineering applications, Compos. Part B Eng. 90 (2016) 503–511. http://dx.doi.org/10.1016/j.compositesb.2016.01.012.
- [245] Z. Yenier, Y. Seki, I. Sen, K. Sever, O. Mermer, M. Sarikanat, Manufacturing and mechanical, thermal and electrical characterization of graphene loaded chitosan composites, Compos. Part B Eng. 98 (2016) 281–287.
- [246] P. Bandyopadhyay, T.T. Nguyen, X. Li, N.H. Kim, J.H. Lee, Enhanced hydrogen gas barrier performance of diaminoalkane functionalized stitched graphene oxide/polyurethane composites, Compos. Part B Eng. 117 (2017) 101–110. http://dx.doi.org/10.1016/j.compositesb.2017.02.035.
- [247] Margarita Herrera-Alonso, Ahmed A. Abdala, Michael J. McAllister, A. Ilhan A. Aksay, R.K. Prud'homme, Intercalation and Stitching of Graphite Oxide with Diaminoalkanes, Langmuir. 23 (2007) 10644–10649.
- [248] H. Kim, Y. Miura, C.W. Macosko, Graphene/Polyurethane Nanocomposites for Improved Gas Barrier and Electrical Conductivity, Chem. Mater. 22 (2010) 3441–3450.
- [249] P. Bandyopadhyay, W.B. Park, R.K. Layek, M.E. Uddin, N.H. Kim, H.G. Kim, J.H. Lee, Hexylamine functionalized reduced graphene oxide/polyurethane nanocomposite-coated nylon for enhanced hydrogen gas barrier film, J. Memb. Sci. 500 (2016) 106–114. http://dx.doi.org/10.1016/j.memsci.2015.11.029.
- [250] A. Moyseowicz, A. Śliwak, E. Miniach, G. Gryglewicz, Polypyrrole/iron oxide/reduced graphene oxide ternary composite as a binderless electrode material with high cyclic stability for supercapacitors, Compos. Part B Eng. 109 (2017) 23–29.
- [251] W.K. Chee, H.N. Lim, I. Harrison, K.F. Chong, Z. Zainal, C.H. Ng, N.M. Huang, Performance of Flexible and Binderless Polypyrrole/Graphene Oxide/Zinc Oxide Supercapacitor Electrode in a Symmetrical Two-Electrode Configuration, Electrochim. Acta. 157 (2015) 88–94.
- [252] H. Wang, X. Yuan, Y. Wu, X. Chen, L. Leng, H. Wang, H. Li, G. Zeng, Facile synthesis of polypyrrole decorated reduced graphene oxide-Fe3O4magnetic composites and its application for the Cr(VI) removal, Chem. Eng. J. 262 (2015) 597–606. http://dx.doi.org/10.1016/j.cej.2014.10.020.
- [253] P. Li, Y. Yang, E. Shi, Q. Shen, Y. Shang, S. Wu, J. Wei, K. Wang, H. Zhu, Q. Yuan, A. Cao, D. Wu, Core-Double-Shell, Carbon Nanotube@Polypyrrole@MnO2 Sponge as Freestanding,

Compressible Supercapacitor Electrode, ACS Appl. Mater. Interfaces. 6 (2014) 5228–5234.

- [254] Y. Niu, Q. Fang, X. Zhang, J. Zhao, Y. Li, Structural evolution, induced effects and graphitization mechanism of reduced graphene oxide sheets/polyimide composites, Compos. Part B Eng. (2017).
- [255] M. Yoonessi, Y. Shi, D.A. Scheiman, M. Lebron-Colon, D.M. Tigelaar, R.A. Weiss, M.A. Meador, Graphene Polyimide Nanocomposites; Thermal, Mechanical, and High-Temperature Shape Memory Effects, ACS Nano. 6 (2012) 7644–7655.
- [256] J.-Y. Wang, S.-Y. Yang, Y.-L. Huang, H.-W. Tien, W.-K. Chin, C.-C.M. Ma, Preparation and properties of graphene oxide/polyimide composite films with low dielectric constant and ultrahigh strength via in situ polymerization, J. Mater. Chem. 21 (2011) 13569.
- [257] J. Lim, H. Yeo, S.G. Kim, O.K. Park, J. Yu, J.Y. Hwang, M. Goh, B.C. Ku, H.S. Lee, N.H. You, Pyridinefunctionalized graphene/polyimide nanocomposites; mechanical, gas barrier, and catalytic effects, Compos. Part B Eng. 114 (2017) 280–288. http://dx.doi.org/10.1016/j.compositesb.2016.12.057.
- [258] Y. Niu, X. Zhang, Q. Fang, Y. Li, Fabrication, optical and electrical properties of solvethermal reduced graphene oxide/polyimide composites by in situ polymerization, Synth. Met. 224 (2017) 86–91.
- [259] O.K. Park, S.G. Kim, N.H. You, B.C. Ku, D. Hui, J.H. Lee, Synthesis and properties of iodo functionalized graphene oxide/polyimide nanocomposites, Compos. Part B Eng. 56 (2014) 365– 371.
- [260] S. Sen Du, F. Li, H.M. Xiao, Y.Q. Li, N. Hu, S.Y. Fu, Tensile and flexural properties of graphene oxide coated-short glass fiber reinforced polyethersulfone composites, Compos. Part B Eng. 99 (2016) 407–415.
- [261] M. Aurilia, L. Sorrentino, L. Sanguigno, S. Iannace, Nanofilled polyethersulfone as matrix for continuous glass fibers composites: Mechanical properties and solvent resistance, Adv. Polym. Technol. 29 (2010) 146–160.
- [262] F. Li, Y. Liu, C.-B. Qu, H.-M. Xiao, Y. Hua, G.-X. Sui, S.-Y. Fu, Enhanced mechanical properties of short carbon fiber reinforced polyethersulfone composites by graphene oxide coating, Polymer (Guildf). 59 (2015) 155–165.
- [263] J. Chen, D. Zhao, X. Jin, C. Wang, D. Wang, H. Ge, Modifying glass fibers with graphene oxide: Towards high-performance polymer composites, Compos. Sci. Technol. 97 (2014) 41–45. http://dx.doi.org/10.1016/j.compscitech.2014.03.023.

- [264] X.J. Shen, L.X. Meng, Z.Y. Yan, C.J. Sun, Y.H. Ji, H.M. Xiao, S.Y. Fu, Improved cryogenic interlaminar shear strength of glass fabric/epoxy composites by graphene oxide, Compos. Part B Eng. 73 (2015) 126–131. http://dx.doi.org/10.1016/j.compositesb.2014.12.023.
- [265] A. Hussein, S. Sarkar, K. Lee, B. Kim, Cryogenic fracture behavior of epoxy reinforced by a novel graphene oxide/poly(p -phenylenediamine) hybrid, Compos. Part B Eng. 129 (2017) 133–142.
- [266] A. Hussein, S. Sarkar, D. Oh, K. Lee, B. Kim, Epoxy/p-phenylenediamine functionalized graphene oxide composites and evaluation of their fracture toughness and tensile properties, J. Appl. Polym. Sci. 133 (2016).
- [267] X.-J. Shen, Y. Liu, H.-M. Xiao, Q.-P. Feng, Z.-Z. Yu, S.-Y. Fu, The reinforcing effect of graphene nanosheets on the cryogenic mechanical properties of epoxy resins, Compos. Sci. Technol. 72 (2012) 1581–1587.
- [268] X. ling Xu, C. jin Yang, J. hui Yang, T. Huang, N. Zhang, Y. Wang, Z. wan Zhou, Excellent dielectric properties of poly(vinylidene fluoride) composites based on partially reduced graphene oxide, Compos. Part B Eng. 109 (2017) 91–100.
- [269] P. Fan, L. Wang, J. Yang, F. Chen, M. Zhong, Graphene/poly(vinylidene fluoride) composites with high dielectric constant and low percolation threshold, Nanotechnology. 23 (2012) 365702.
- [270] L. Chu, Q. Xue, J. Sun, F. Xia, W. Xing, D. Xia, M. Dong, Porous graphene sandwich/poly(vinylidene fluoride) composites with high dielectric properties, Compos. Sci. Technol. 86 (2013) 70–75.
- [271] Y. Wu, X. Lin, X. Shen, X. Sun, X. Liu, Z. Wang, J.K. Kim, Exceptional dielectric properties of chlorine-doped graphene oxide/poly (vinylidene fluoride) nanocomposites, Carbon N. Y. 89 (2015) 102–112.
- [272] J. Sun, Q. Xue, Q. Guo, Y. Tao, W. Xing, Excellent dielectric properties of Polyvinylidene fluoride composites based on sandwich structured MnO2/graphene nanosheets/MnO2, Compos. Part A Appl. Sci. Manuf. 67 (2014) 252–258.
- [273] Y. Xu, G. Long, L. Huang, Y. Huang, X. Wan, Y. Ma, Y. Chen, Polymer photovoltaic devices with transparent graphene electrodes produced by spin-casting, Carbon N. Y. 48 (2010) 3308–3311.
- [274] Y. Wang, X. Chen, Y. Zhong, F. Zhu, K.P. Loh, Large area, continuous, few-layered graphene as anodes in organic photovoltaic devices, Appl. Phys. Lett. 95 (2009) 063302.
- [275] C.X. Guo, H. Bin Yang, Z.M. Sheng, Z.S. Lu, Q.L. Song, C.M. Li, Layered Graphene/Quantum Dots

for Photovoltaic Devices, Angew. Chemie Int. Ed. 49 (2010) 3014-3017.

- [276] S.-S. Li, K.-H. Tu, C.-C. Lin, C.-W. Chen, M. Chhowalla, Solution-Processable Graphene Oxide as an Efficient Hole Transport Layer in Polymer Solar Cells, ACS Nano. 4 (2010) 3169–3174.
- [277] R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, N.M.R. Peres, A.K. Geim, Fine Structure Constant Defines Visual Transparency of Graphene, Science (80-.). 320 (2008) 1308.
- [278] L.L. Zhang, S. Zhao, X.N. Tian, X.S. Zhao, Layered Graphene Oxide Nanostructures with Sandwiched Conducting Polymers as Supercapacitor Electrodes, Langmuir. 26 (2010) 17624– 17628.
- [279] R. Jan, A. Habib, I.H. Gul, Stiff, strong, yet tough free-standing dielectric films of graphene nanosheets-polyurethane nanocomposites with very high dielectric constant and loss, Electron. Mater. Lett. 12 (2016) 91–99.
- [280] D.D. Kulkarni, I. Choi, S.S. Singamaneni, V. V. Tsukruk, Graphene Oxide–Polyelectrolyte Nanomembranes, ACS Nano. 4 (2010) 4667–4676.
- [281] H.J. Salavagione, M.A. Gómez, G. Martínez, Polymeric Modification of Graphene through Esterification of Graphite Oxide and Poly(vinyl alcohol), Macromolecules. 42 (2009) 6331– 6334.
- [282] C. Wang, Y. Lan, W. Yu, X. Li, Y. Qian, H. Liu, Preparation of amino-functionalized graphene oxide/polyimide composite films with improved mechanical, thermal and hydrophobic properties, Appl. Surf. Sci. 362 (2016) 11–19.
- [283] Z. Liu, J.T. Robinson, X. Sun, H. Dai, PEGylated Nanographene Oxide for Delivery of Water-Insoluble Cancer Drugs, J. Am. Chem. Soc. 130 (2008) 10876–10877.
- [284] M. Fang, K. Wang, H. Lu, Y. Yang, S. Nutt, Single-layer graphene nanosheets with controlled grafting of polymer chains, J. Mater. Chem. 20 (2010) 1982.
- [285] A. Midya, V. Mamidala, J.-X. Yang, P.K.L. Ang, Z.-K. Chen, W. Ji, K.P. Loh, Synthesis and Superior Optical-Limiting Properties of Fluorene-Thiophene-Benzothiadazole Polymer-Functionalized Graphene Sheets, Small. 6 (2010) 2292–2300.
- [286] Y. Lin, J. Jin, M. Song, Preparation and characterisation of covalent polymer functionalized graphene oxide, J. Mater. Chem. 21 (2011) 3455–3461.
- [287] D. Yu, Y. Yang, M. Durstock, J.-B. Baek, L. Dai, Soluble P3HT-Grafted Graphene for Efficient Bilayer–Heterojunction Photovoltaic Devices, ACS Nano. 4 (2010) 5633–5640.

- [288] F. Nasrollahi, J. Varshosaz, A.A. Khodadadi, S. Lim, A. Jahanian-Najafabadi, Targeted Delivery of Docetaxel by Use of Transferrin/Poly(allylamine hydrochloride)-functionalized Graphene Oxide Nanocarrier, ACS Appl. Mater. Interfaces. 8 (2016) 13282–13293.
- [289] D.K.L. Harijan, V. Chandra, Polyaniline functionalized graphene sheets for treatment of toxic hexavalent chromium, J. Environ. Chem. Eng. 4 (2016) 3006–3012.
- [290] M. Zhi, W. Huang, Q. Shi, K. Ran, Improving water dispersibility of non-covalent functionalized reduced graphene oxide with I-tryptophan via cleaning oxidative debris, J. Mater. Sci. Mater. Electron. 27 (2016) 7361–7368.
- [291] H. Hu, J.H. Xin, H. Hu, X. Wang, Y. Kong, Metal-free graphene-based catalyst—Insight into the catalytic activity: A short review, Appl. Catal. A Gen. 492 (2015) 1–9.
- [292] Y. Tian, Y. Ye, X. Wang, S. Peng, Z. Wei, X. Zhang, W. Liu, Three-dimensional N-doped, plasmaetched graphene: Highly active metal-free catalyst for hydrogen evolution reaction, Appl. Catal. A Gen. 529 (2017) 127–133.
- [293] M. Zhou, A. Zhang, Z. Dai, Y.P. Feng, C. Zhang, Strain-Enhanced Stabilization and Catalytic Activity of Metal Nanoclusters on Graphene, J. Phys. Chem. C. 114 (2010) 16541–16546.
- [294] H. Cao, P. Srivastava, K. Choi, S. Kim, K.-R. Lee, Early stage oxynitridation process of Si(001) surface by NO gas: Reactive molecular dynamics simulation study, J. Appl. Phys. 119 (2016) 125305.
- [295] Y. Tang, Z. Yang, X. Dai, Trapping of metal atoms in the defects on graphene, J. Chem. Phys. 135 (2011) 224704.
- [296] I. Fampiou, A. Ramasubramaniam, Binding of Pt Nanoclusters to Point Defects in Graphene: Adsorption, Morphology, and Electronic Structure, J. Phys. Chem. C. 116 (2012) 6543–6555.
- [297] D.-H. Lim, J. Wilcox, DFT-Based Study on Oxygen Adsorption on Defective Graphene- Supported Pt Nanoparticles, J. Phys. Chem. C. 115 (2011) 22742–22747.
- [298] V. Georgakilas, M. Otyepka, A.B. Bourlinos, V. Chandra, N. Kim, K.C. Kemp, P. Hobza, R. Zboril,
 K.S. Kim, Functionalization of graphene: covalent and non-covalent approaches, derivatives and applications., Chem. Rev. 112 (2012) 6156–214.
- [299] M.N. Groves, C. Malardier-Jugroot, M. Jugroot, Improving Platinum Catalyst Durability with a Doped Graphene Support, J. Phys. Chem. C. 116 (2012) 10548–10556.
- [300] H. Huang, X. Wang, Pd nanoparticles supported on low-defect graphene sheets: for use as highperformance electrocatalysts for formic acid and methanol oxidation, J. Mater. Chem. 22

(2012) 22533-22541.

- [301] Q. Xiang, J. Yu, M. Jaroniec, Graphene-based semiconductor photocatalysts, Chem. Soc. Rev. 41 (2012) 666–796.
- [302] Y.T. Liang, B.K. Vijayan, K.A. Gray, M.C. Hersam, Minimizing Graphene Defects Enhances Titania Nanocomposite-Based Photocatalytic Reduction of CO 2 for Improved Solar Fuel Production, Nano Lett. 11 (2011) 2865–2870.
- [303] Y. Li, J. Yang, N. Zhao, J. Huang, Y. Zhou, K. Xu, N. Zhao, Facile fabrication of N-doped threedimensional reduced graphene oxide as a superior electrocatalyst for oxygen reduction reaction, Appl. Catal. A Gen. 534 (2017) 30–39.
- [304] J.L. Tan, A.M. De Jesus, S.L. Chua, J. Sanetuntikul, S. Shanmugam, B.J. V. Tongol, H. Kim, Preparation and characterization of palladium-nickel on graphene oxide support as anode catalyst for alkaline direct ethanol fuel cell, Appl. Catal. A Gen. 531 (2017) 29–35.
- [305] W.-H. Zhang, P.-P. He, S. Wu, J. Xu, Y. Li, G. Zhang, X.-Y. Wei, Graphene oxide grafted hydroxylfunctionalized ionic liquid: A highly efficient catalyst for cycloaddition of CO2 with epoxides, Appl. Catal. A Gen. 509 (2016) 111–117.
- [306] D.R. Dreyer, C.W. Bielawski, Graphite Oxide as an Olefin Polymerization Carbocatalyst: Applications in Electrochemical Double Layer Capacitors, Adv. Funct. Mater. 22 (2012) 3247– 3253.
- [307] A. Dhakshinamoorthy, M. Alvaro, P. Concepción, V. Fornés, H. Garcia, Graphene oxide as an acid catalyst for the room temperature ring opening of epoxides, Chem. Commun. 48 (2012) 5443–5445.
- [308] N. Kausar, P. Mukherjee, A.R. Das, Practical carbocatalysis by graphene oxide nanosheets in aqueous medium towards the synthesis of diversified dibenzo[1,4]diazepine scaffolds, RSC Adv. 6 (2016) 88904–88910.
- [309] H. He, J. Klinowski, M. Forster, A. Lerf, A new structural model for graphite oxide, Chem. Phys. Lett. 287 (1998) 53–56.
- [310] H. He, T. Riedl, A. Lerf, J. Klinowski, Solid-State NMR Studies of the Structure of Graphite Oxide, J. Phys. Chem. 100 (1996) 19954–19958.
- [311] D.R. Dreyer, A.D. Todd, C.W. Bielawski, Harnessing the chemistry of graphene oxide., Chem. Soc. Rev. 43 (2014) 5288–5301.
- [312] A. Lerf, H. He, Forster, Michael, J. Klinowski, Structure of Graphite Oxide Revisited, J. Phys.

Chem. B. 102 (1998) 4477–4482.

- [313] T. Szabó, O. Berkesi, P. Forgó, K. Josepovits, Y. Sanakis, D. Petridis, I. Dékány, Evolution of Surface Functional Groups in a Series of Progressively Oxidized Graphite Oxides, Chem. Mater. 18 (2006) 2740–2749.
- [314] W. Gao, L.B. Alemany, L. Ci, P.M. Ajayan, New insights into the structure and reduction of graphite oxide, Nat. Chem. 1 (2009) 403–408.
- [315] A.M. Dimiev, L.B. Alemany, J.M. Tour, Graphene Oxide. Origin of Acidity, Its Instability in Water, and a New Dynamic Structural Model, ACS Nano. 7 (2013) 576–588.
- [316] A. Yong Sheng Eng, C. Kiang Chua, M. Pumera, Refinements to the structure of graphite oxide: absolute quantification of functional groups via selective labelling, Nanoscale. 7 (2015) 20256– 20266.
- [317] C. Gómez-Navarro, J.C. Meyer, R.S. Sundaram, A. Chuvilin, S. Kurasch, M. Burghard, K. Kern, U. Kaiser, Atomic Structure of Reduced Graphene Oxide, Nano Lett. 10 (2010) 1144–1148.
- [318] D.R. Dreyer, H.-P. Jia, C.W. Bielawski, Graphene Oxide: A Convenient Carbocatalyst for Facilitating Oxidation and Hydration Reactions, Angew. Chemie. 122 (2010) 6965–6968.
- [319] D.W. Boukhvalov, D.R. Dreyer, C.W. Bielawski, Y.-W. Son, A Computational Investigation of the Catalytic Properties of Graphene Oxide: Exploring Mechanisms by using DFT Methods, ChemCatChem. 4 (2012) 1844–1849.
- [320] Y. Song, K. Qu, C. Zhao, J. Ren, X. Qu, Graphene Oxide: Intrinsic Peroxidase Catalytic Activity and Its Application to Glucose Detection, Adv. Mater. 22 (2010) 2206–2210.
- [321] A. Dhakshinamoorthy, M. Alvaro, M. Puche, V. Fornes, H. Garcia, Graphene Oxide as Catalyst for the Acetalization of Aldehydes at Room Temperature, ChemCatChem. 4 (2012) 2026–2030.
- [322] Y. Gao, D. Ma, C. Wang, J. Guan, X. Bao, Reduced graphene oxide as a catalyst for hydrogenation of nitrobenzene at room temperature, Chem. Commun. 47 (2011) 2432–2434.
- [323] D. Deng, L. Yu, X. Pan, S. Wang, X. Chen, P. Hu, L. Sun, X. Bao, Size effect of graphene on electrocatalytic activation of oxygen, Chem. Commun. 47 (2011) 10016–10018.
- [324] C. Su, M. Acik, K. Takai, J. Lu, S. Hao, Y. Zheng, P. Wu, Q. Bao, T. Enoki, Y.J. Chabal, K. Ping Loh, Probing the catalytic activity of porous graphene oxide and the origin of this behaviour, Nat. Commun. 3 (2012) 1298.
- [325] N.J. Tro, Introductory Chemistry Essentials, 2015.

- [326] J. Sapkota, J.C. Natterodt, A. Shirole, E.J. Foster, C. Weder, Fabrication and Properties of Polyethylene/Cellulose Nanocrystal Composites, Macromol. Mater. Eng. 302 (2017) 1600300. doi:10.1002/MAME.201600300.
- [327] ASTM Committee D-20 on Plastics. Section D20. 70.01. Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement, 1991.
- [328] ASTM C518-17, Standard Test Method for Steady-State Thermal Transmission Properties, Astm. (2017).
- [329] ISO, ISO 8301:1991 Thermal insulation Determination of steady-state thermal resistance and related properties — Heat flow meter apparatus, (2008).
- [330] British Standards Institution, BS EN 12667:2001 Thermal performance of building materials and products. Determination of thermal resistance by means of guarded hot plate and heat flow meter methods. Products of high and medium thermal resistance, British Standards Institution, 2001.
- [331] L. Segal, J.J. Creely, A.E. Martin, C.M. Conrad, An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer, Text. Res. J. 29 (1959) 786– 794.
- [332] ASTM D5229/D5229M-92. Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials, (2014).
- [333] MERCK, Tempo Sigma-Aldrich, (2021). https://www.sigmaaldrich.com/GB/en/search/tempo?focus=products&page=1&perPage=30 &sort=relevance&term=tempo&type=product.
- [334] R.S. Macomber, Thermal buffers: An illustrative analogy, J. Chem. Educ. 56 (1979) 710.
- [335] W.L. Li, K. Lu, J.Y. Walz, Freeze casting of porous materials: review of critical factors in microstructure evolution, Int. Mater. Rev. 57 (2012) 37–60.
- [336] S. Deville, E. Maire, A. Lasalle, A. Bogner, C. Gauthier, J. Leloup, C. Guizard, In Situ X-Ray Radiography and Tomography Observations of the Solidification of Aqueous Alumina Particles Suspensions. Part II: Steady State, J. Am. Ceram. Soc. 92 (2009) 2497–2503.
- [337] S.S.L. Peppin, M. Grae Worster, J.S. Wettlaufer, Morphological instability in freezing colloidal suspensions, Proc. R. Soc. A Math. Phys. Eng. Sci. 463 (2007) 723–733. doi:10.1098/rspa.2006.1790.
- [338] S. Deville, E. Maire, A. Lasalle, A. Bogner, C. Gauthier, J. Leloup, C. Guizard, In Situ X-Ray

Radiography and Tomography Observations of the Solidification of Aqueous Alumina Particle Suspensions-Part I: Initial Instants, J. Am. Ceram. Soc. 92 (2009) 2489–2496.

- [339] T. Waschkies, R. Oberacker, M.J. Hoffmann, Investigation of structure formation during freezecasting from very slow to very fast solidification velocities, Acta Mater. 59 (2011) 5135–5145.
- [340] Y. Nishiyama, P. Langan, H. Chanzy, Crystal Structure and Hydrogen-Bonding System in Cellulose Iβ from Synchrotron X-ray and Neutron Fiber Diffraction, J. Am. Chem. Soc. 124 (2002) 9074–9082.
- [341] P. Langan, N. Sukumar, Y. Nishiyama, H. Chanzy, Synchrotron X-ray structures of cellulose Iβ and regenerated cellulose II at ambient temperature and 100 K, Cellulose. 12 (2005) 551–562.
- [342] P. Langan, Y. Nishiyama, H. Chanzy, X-ray Structure of Mercerized Cellulose II at 1 Å Resolution, Biomacromolecules. 2 (2001) 410–416.
- [343] M. Wada, Y. Nishiyama, H. Chanzy, T. Forsyth, P. Langan, The structure of celluloses, Adv. X-Ray Anal. 51 (2008) 138–144.
- [344] M. Szymańska-Chargot, J. Cybulska, A. Zdunek, Sensing the structural differences in cellulose from apple and bacterial cell wall materials by Raman and FT-IR spectroscopy., Sensors (Basel).
 11 (2011) 5543–60.
- [345] J.H. Wiley, R.H. Atalla, Raman Spectra of Celluloses, in: Appleton, WI, USA, 1987: pp. 151–168. doi:10.1021/bk-1987-0340.ch008.
- [346] K. Schenzel, S. Fischer, NIR FT Raman Spectroscopy–a Rapid Analytical Tool for Detecting the Transformation of Cellulose Polymorphs, Cellulose. 8 (2001) 49–57.
- [347] Horiba Jobin Yvon, Raman data and analysis Raman Spectroscopy for Analysis and Monitoring, 2019.
- [348] F.A. Akgul, G. Akgul, N. Yildirim, H.E. Unalan, R. Turan, Influence of thermal annealing on microstructural, morphological, optical properties and surface electronic structure of copper oxide thin films, Mater. Chem. Phys. 147 (2014) 987–995.
- [349] Y. Suffren, F.-G. Rollet, C. Reber, Raman spectroscopy of transition metal complexes: molecular vibrational frequencies, phase transitions, isomers, and electronic structure, Comments Inorg. Chem. 32 (2011) 246–276. doi:10.1080/02603594.2012.659776.
- [350] D.C. Pereira, D.L.A. de Faria, V.R.L. Constantino, Cu II hydroxy salts: characterization of layered compounds by vibrational spectroscopy, J. Braz. Chem. Soc. 17 (2006) 1651–1657.
- [351] Z. Jie, W. Xinyu, Z. Pengyue, Q. Jiamin, Z. Yong, Surface-enhanced Raman scattering activities

of graphene-wrapped Cu particles by chemical vapor deposition assisted with thermal annealing, Opt. Express. 24 (2016) 24551.

- [352] Paper recycles, Recovery use of Old Corrugated Containers (OCC), (n.d.). https://www.paperrecycles.org/statistics/recovery-use-of-old-corrugated-containers-(occ).
- [353] AIChE, New Trends to Improve the Quality of Recycled Papers, 15 AIChE Annu. Meet. (2015). https://aiche.confex.com/aiche/2015/webprogram/Paper421613.html.
- P. Bajpai, Hydrogen Peroxide Bleaching, in: Environ. Benign Approaches Pulp Bleach., 2nd ed., Elsevier, 2012: pp. 97–134. doi:10.1016/B978-0-444-59421-1.00005-3.
- [355] P. Telford, Basic Chemistry of Chlorination, 2018. http://www.hydroinstruments.com/files/Basic Chemistry of Chlorination.pdf.
- [356] C.R.G. Torres, E. Crastechini, F.A. Feitosa, C.R. Pucci, A.B. Borges, Influence of pH on the effectiveness of hydrogen peroxide whitening, Oper. Dent. 39 (2014) 261–268. doi:10.2341/13-214-L.
- [357] Y. Qing, Y. Wu, Z. Cai, R. Sabo, Effect of freeze dry on the properties of cellulose nanofibrils/phenol formaldehyde nanocomposites, in: Proc. 2012 Int. Conf. Biobase Mater. Sci. Eng. BMSE 2012, 2012: pp. 217–221. doi:10.1109/BMSE.2012.6466215.
- [358] A. Khenblouche, D. Bechki, M. Gouamid, K. Charradi, L. Segni, M. Hadjadj, S. Boughali, Extraction and characterization of cellulose microfibers from Retama raetam stems, Polimeros. 29 (2019) 1–8.
- [359] J. Aburto, M. Moran, A. Galano, E. Torres-García, Non-isothermal pyrolysis of pectin: A thermochemical and kinetic approach, J. Anal. Appl. Pyrolysis. 112 (2015) 94–104.
- [360] M. Pääkko, M. Ankerfors, H. Kosonen, A. Nykänen, S. Ahola, M. Österberg, J. Ruokolainen, J. Laine, P.T. Larsson, O. Ikkala, T. Lindström, Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels, Biomacromolecules. 8 (2007) 1934–1941.
- [361] M. Henriksson, G. Henriksson, L.A. Berglund, T. Lindström, An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers, Eur. Polym. J. 43 (2007) 3434–3441.
- [362] T. Saito, M. Hirota, N. Tamura, S. Kimura, H. Fukuzumi, L. Heux, A. Isogai, Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions, Biomacromolecules. 10 (2009) 1992–1996.

- [363] S. Matsumura, H. Kurita, H. Shimokobe, Anaerobic biodegradability of polyvinyl alcohol, Biotechnol. Lett. 15 (1993) 749–754.
- [364] B. Wowk, POLYVINYL ALCOHOL COMPOUNDS FOR INHIBITION OF ICE GROWTH, US 6,391,224 B1, 2002.
- [365] G. Shao, D.A.H. Hanaor, X. Shen, A. Gurlo, Freeze Casting: From Low-Dimensional Building Blocks to Aligned Porous Structures—A Review of Novel Materials, Methods, and Applications, Adv. Mater. 32 (2020) 1907176. doi:10.1002/ADMA.201907176.
- [366] K.G. Libbrecht, The physics of snow crystals, Reports Prog. Phys. 68 (2005) 855–895. doi:10.1088/0034-4885/68/4/R03.
- [367] B.G. COLVIN, Crystal structure of polyvinyl alcohol, Nature. 248 (1974) 756–759.
- [368] C.W. BUNN, Crystal Structure of Polyvinyl Alcohol, Nature. 161 (1948) 929–930.
- [369] M. Janeta, Ł. John, J. Ejfler, S. Szafert, High-Yield Synthesis of Amido-Functionalized Polyoctahedral Oligomeric Silsesquioxanes by Using Acyl Chlorides, Chem. - A Eur. J. 20 (2014) 15966–15974.
- [370] V. Sunkara, D.-K. Park, H. Hwang, R. Chantiwas, S.A. Soper, Y.-K. Cho, Simple room temperature bonding of thermoplastics and poly(dimethylsiloxane), Lab Chip. 11 (2011) 962–965.
- [371] SIGMA-ALDRICH, Safety Data Sheet of (3-Aminopropyl)trimethoxysilane according to Regulation (EC) No. 1907/2006, 2018.
- [372] G. Socrates, Infrared and Raman Characteristic Group Frequencies, John Wiley & Sons, London, 2004.
- [373] M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der organischen Chemie, eighth ed., Georg-Thieme, 2014.
- [374] IR Spectrum Table & Chart, Merck. (2019). https://www.sigmaaldrich.com/technicaldocuments/articles/biology/ir-spectrum-table.html.
- [375] P.J. Launer, B. Arkles, INFRARED ANALYSIS OF ORGANOSILICON COMPOUNDS: SPECTRA-STRUCTURE CORRELATIONS, in: Silicon Compd. Silanes Silicones, 2013: pp. 175–178.
- [376] Z. Zhang, G. Sèbe, D. Rentsch, T. Zimmermann, P. Tingaut, Ultralightweight and flexible silylated nanocellulose sponges for the selective removal of oil from water, Chem. Mater. (2014).
- [377] P. Phanthong, G. Guan, S. Karnjanakom, X. Hao, Z. Wang, K. Kusakabe, A. Abudula, Amphiphobic nanocellulose-modified paper: Fabrication and evaluation, RSC Adv. (2016).

- [378] Bond Dissociation Energies, Prop. ATOMS, RADICALS, Bond. (2013). https://labs.chem.ucsb.edu/zakarian/armen/11---bonddissociationenergy.pdf (accessed July 27, 2021).
- [379] P.N. Diagboya, B.I. Olu-Owolabi, K.O. Adebowale, Synthesis of covalently bonded graphene oxide-iron magnetic nanoparticles and the kinetics of mercury removal, RSC Adv. (2015).
- [380] P.N. Diagboya, B.I. Olu-Owolabi, D. Zhou, B.H. Han, Graphene oxide-tripolyphosphate hybrid used as a potent sorbent for cationic dyes, Carbon N. Y. (2014).
- [381] J. Bin Wu, M.L. Lin, X. Cong, H.N. Liu, P.H. Tan, Raman spectroscopy of graphene-based materials and its applications in related devices, Chem. Soc. Rev. (2018).
- [382] J.H. Warner, M.H. Rümmeli, L. Ge, T. Gemming, B. Montanari, N.M. Harrison, B. Büchner, G.A.D. Briggs, Structural transformations in graphene studied with high spatial and temporal resolution, Nat. Nanotechnol. 4 (2009) 500–504.

Appendix

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Interfacial properties and structural performance of resin-coated natural fibre rebars within cementitious matrices



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ABSTRACT

This paper investigates the interface and behaviour of continuous natural fibre rebar reinforced cementitious composites. Various resins were used to coar sisal fibres which were then used as reinforcement within the composites. Non-destructive tests (SEM, OM, FTIR) were employed to evaluate the interfacial bonding and interaction between the sisal, resin and cementitious matrix. The results showed that the uncoated fibre could not develop a compact interface due to the moisture absorption/desorption of the fibre, which caused low mechanical properties of the composite. The coating was able to improve the strength of the rebars and reduce the OH⁺ concentration, which improved the interfacial bonding and integrity. The flexural stress-strain relation of the composite exhibited three regions with two clear dips, reflecting the progressive stress transfer and failure of the composite constituents and their interactions. The comparable mechanical properties to those of steel rebar reinforcement demonstrate the potential of the resin-coated sial fibre rebar for structural applications.

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1. Introduction

Various forms of fibres have been developed to overcome the limitations of concrete as a quasi-brittle material that is weak in tension. Fibres typically act to restrict crack growth within concrete. Natural fibres are traditionally classified into four categories according to their origin: stem/bast, leaf, fruit/surface and wood/ cellulose [1]. Leaf fibres provide the fundamental rigidity and strength of leaves and are extracted by means of scraping and drying crushed leaves. In comparison to stem/bast fibres, the leaf fibres are commonly tougher, rougher in texture and stronger on average. For example, the strength and stiffness of sisal fibre range from 550 to 750 MPa and 17–38 GPa compared to those of jute fibre from 300 to 800 MPa and 10–30 GPa respectively [2–8].

Sisal fibres, being the most common type of leaf fibres, are produced from various varieties of the agave plant, which is indigenous to the arid regions of Africa and South America, mainly Brazil – the biggest commercial producer of Agave sisalana amounting to an estimate of 150,000 tonnes [9]. Known to have one of the strongest natural fibres, the agave plant is characterised by its leaves, which grow to a length of over one metre, and yield a long creamy white and very strong fibre. Sisal is a fast-growing plant that remains reproductive for 10-12 years and produces 180 to 240 leaves in a lifetime. In addition, having a total annual production of approximately 300,000 tonnes with a low-cost production, sisal fibre is increasingly being used in the building industry, particularly for plaster reinforcement. As sisal has been used for many years for reinforcing gypsum products, there is an emerging potential for sisal fibres being used to reinforce other composites for low-cost housing applications, namely reinforcing concrete matrices [10-13].

The characteristics and performance of the fibre-reinforced composites depend on the properties of the individual components within the composites including the fibre, the individual matrices and the interfaces between them. One must, therefore, investigate the nature of each of these components to gain a comprehensive understanding of the properties of the final composite. When considering vegetable fibre reinforced composites, the major research challenge has been trying to achieve a strong interface, especially a dense interfacial transition zone, within the composites. However, the surface chemistry of natural fibres and the negative effects of moisture diffusion between the fibre and the inorganic-bonded-matrix (e.g. mortar) on the interfacial bonding complicate this. In realising and optimising the requirements for

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Graphene oxide incorporated functional materials: A review

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ABSTRACT

Keywordz: Graphene oxide functional materials Nano-estuctures Polymer-matrix composites (PMCs) Chemical properties Physical and mechanical properties This article provides a comprehensive review of the latest advances in the preparation, properties and applications of graphene oxide (GO) and GO-based materials. The review shows that GO has been used to create a range of different composite structures and catalyse numerous reactions: GO could be incorporated as a composite filler through different fabrication techniques including melt blending for thermoplastics to enhance desired properties, such as fusing GO with polyethylene terephthalate to increase the electrical conductance from 1×10^{-14} to 2.115/m with 3.0 vol% GO content; GO may act as a metal-free catalyst and could catalyse reactions, such as the hydration of alkynes, oxidation of alkenes and alcohols with mild conditions to achieve excellent yields of desired products with simple catalyst recovery. Challenges in the development of GO applications are also presented, including the need for a better understanding of the GO structure, and for high catalyst loading in oxidative reactions and limitations of GO in supporting electrocatalysts due to a high density of defects. The review provides a comprehensive and most useful database for further innovations and understanding of GO-based materials for potential applications.

1. Introduction

The discovery of graphene marks the beginning of a new era in material sciences research and may be the hallmark of a potentially new material age. The introduction of a new frontier in materials science by creating the first known 2D material allows scientists to probe a whole new set of theoretical predictions and create applications we have yet to conceive. Moreover, the material has been proven to exhibit especially good characteristics pertaining to condensed matter physics.

Graphene is a one-atom-thick sheet of carbon atoms arranged in a honeycomb lattice. It acts as the building block for all other graphitic materials through the increased layering or through shaping into spherical and tubular forms. It was found that graphene contains exceptional quantum electrodynamic properties including 'relativistic' electrons travelling close to the speed of light, that are termed massless Dirac fermions [1]. The presence of these electrons was confirmed by scientific community's attention. It was thought that graphene could not realistically exist because it was believed that 2D materials were thermodynamically unstable [2–4]. This was due to the proven phenomenon of decreasing melting temperatures with decreasing material thickness and increasing instability where individual or groups of atoms separate from each other. It was thought that 2D materials only existed as part of a larger 3D structure [1]. These predictions were invalidated after the material's discovery by Andre Geim and Konstantin Novoselov in 2004 using scotch tape to separate graphite layers and obtain graphene crystals [5]. These crystals are of high quality and could be obtained on top of non-crystalline substrates, in liquid suspension and as membrane suspensions. It is believed that they do not decompose due to thermodynamic instability as predicted because of the strong interatomic bonds between the carbon atoms thereby preventing crystal dislocations and defects.

Thin layer graphite research dates back to 1960 when the high conductivity of the intercalated graphite materials was discovered. At the time, the closest anybody got to the discovery of graphene was Fernandez-Moran, an electron microscopist, who endeavoured to create a thin graphite crystal. Graphite sheets of 5nm thinness, about 15 graphene layers, were extracted through his micromechanical exfoliation method [6]. He did not realise how close he was to achieving a single layer graphene sheet. During the next 30 years, graphitic material research grew slowly until the early 1990s where the discovery of nanotubes and fullerenes led to the renewed interest in exploring various experimental studies of carbon materials. Before long, an exponential increase in research papers related to carbon nanostructures started and in 2004, the ingenuity of the simple 'scotch tape' method marked the ground-breaking discovery of the 2-dimensional monolayer

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Patented Nanocellulose Strength Additives for Recycled Fibre

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What is Nanocellulose?

Cellulose is an abundant material that is found in plants. It is an inexpensive and sustainable natural polymer that presents an attractive material choice for researchers attempting to create environmentally friendly products. Nanocellulose is the microscopic building block that makes up the larger cellulose fibres after bundling together many fibrils. Nanocellulose is currently the focus of intense research as a sustainable nanomaterial that possesses many desirable material properties.

Cellulose is one of three components (namely cellulose, hemicellulose and lignin) that define the strength of plant matter. What is interesting about utilising the nano-component of cellulose is the access to innovative tailoring in its material chemistry. The macroscopic structure of cellulose can thus be considerably enhanced by functionalising the nanoscopic unit, nanocellulose, enabling existing cellulose products to be improved.

Similar to graphene, an allotrope of graphite found in your pencil lead, nanocellulose has extraordinary potential in various industry sectors, especially in paper and packaging. Depending on where it is added in a typical papermaking process, nanocellulose may enhance both the wet and dry strength of paper. Moreover, as a nanofibre, nanocellulose will help mesh the pulp together during formation. Thus, improved material utilisation may be achieved from nanocellulose acting both as a strength agent and retention aid.

The term nanocellulose encompasses three nano-forms/types of cellulose: Nano-fibrillated cellulose (NFC), Nano-crystalline cellulose (NCC), and Bacterial cellulose (BC). These forms can be attained through two approaches: the top-down route for NFC & NCC and bottom-up route for BC. At Brunel University London, intensive research has been conducted under Professor Mizzi Fan to explore both routes and has led to a unique patented process to achieve this wonder nanomaterial via the top-down approach. As seen in Figure 1, there are different yields depending on the processing parameters. The patent technologies are applicable to the full variety of cellulosic materials (wood and non-wood plant fibres) to produce functional nanocelloluses. These yields correspond to the nanocrystal form (termed Brunel's NCC (BNCC)) of the cellulose with the remainder corresponding to the fibrillated form (termed Brunel's NFC (BNFC)) of the nanocellulose.

Brunel

London

University

Essentially NCC particles are cut-offs of NFC. This is similar to microcellulose, where microcrystalline cellulose (MCC) has a similar relationship with microfibrillated cellulose (MFC).

One of Brunel's nanocellulose technologies has successfully enhanced recycled fibre for paper production and thus a number of commercial pilot trials have been conducted. For the paper and packaging industry, it has been found that the ideal addition would be the fibrillated form of cellulose since it causes a higher retention of fines and is more likely to link with the paper structure rather than permeating through it compared to NCC.

Importance of Dry Strength Agents

Over the last two decades there has been a significant increase in the recovery and recycling of old corrugated containers (OCC), often referred to as kraft liner shavings (KLS). From 1997 to 2017, an increase from 67.7% to 88.8% rate of recovery was recorded [1]. With the increasing number of cycles a fibre is reused, there is a reduction in the mechanical properties of paper and board due to a reduction in both intrinsic fibre strength and inter-fibre bonding. This is where dry strength agents come into play; cationic polyacrylamides and cationic starch are often used to increase the bonds between fibres and in addition to attract anionic trash, so increasing the strength of recycled paper.



Figure 1. Brunel's patented production process for nanocellulose (BNC)