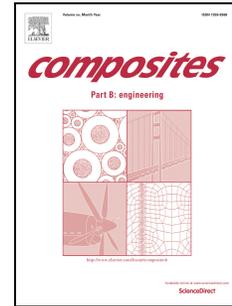


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Development of facture free clay-based aerogel: Formulation and architectural mechanisms

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mechanisms

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Abstract

Clay aerogel could potentially be ideal insulation materials for many industrial sectors because of its natural resource, green and low cost production. However, there is a dilemma between thermal conductivity and integrity, which are also highly related to density and microstructure. These could be manipulated through formulation compositions and processing parameters. This paper employs cellulose nanowhisker (CNW) as the reinforcement to develop novel 3-component systems of aerogel by exploring optimum formulation and architectural microstructure systems. The results shows that fracture free clay aerogel can be developed with solid content less than 4 wt%, enabling optimum thermal insulation performance of 0.034 W/mK; optimum micro-network and hence much more enhanced bonding systems can be built with strategical interactions within and between clay platelets, PVA and CNW; and an architecture of 'CNW-clay (mechanically)+CNW-PVA (chemically)+CNW-clay' 3-component clay aerogels could be established, achieving excellent mechanical property (e.g. compressive strength and shape recovery).

Key words: A. Hybrid; B. Mechanical properties; B. Fracture; B. Thermal properties.

1 Introduction

Featured with low density (high porosity) and excellent network systems at nano and micro scales, aerogel has drawn tremendous attentions in many industrial sectors, such

as building construction [1, 2], water purification [3, 4] and catalyst [5, 6]. Clay, a layered silicate, has owned its reputation in the reinforcement of nanocomposites [7]. Moreover, with house-card-like structure [8], abundant resource, easy-to-process [9] and resistance to fire [10], clay is considered an ideal candidate to fabricate aerogel, especially for thermal insulation use of the clay-based materials.

There are two main approaches to fabricate aerogel. One is supercritical drying [11], which is restricted to non-aqueous solvent and mainly used in inorganic aerogel preparation. The other is freeze drying, which is widely used in pharmaceutical [12] and food industry [13, 14]. This process is potentially applicable for massive production of aerogel. In super cold condition, pure ice crystal has a preferred growth direction parallel to the temperature gradient, and the solids existing in water are expelled from the ice growth front and trapped within channels between the ice crystals, which together then forms the laminae. If the freezing rate is fast enough, the impurities are entrapped within ice front and form bridges between layers. The lower temperature, the more bridges and smaller pore size can be obtained. Therefore, manipulating the freezing rate is able to control the microstructure. After the sublimation of the ice crystal, the resulting aligned layers form the porous materials-aerogel [15]. It is well known that the mechanical property of aerogel highly depends on the interaction between clays and the strength of bridges between layers [16]. Liquid nitrogen has been considered an excellent freezing media to precisely tailor the microstructure, but the temperature is far below the glass transition of ice crystals (around $-123\text{ }^{\circ}\text{C}$) [17], making the aerogel easy to crack in the process of freezing, which is intolerable to scale-up production. Alternatively, much work has been attempted to use freezing bath with higher temperature, producing continuous path, which will make higher thermal conductivity [18, 19]. Moreover, thermal shock [20] occurred in the transition from one

to another stage of the process is another factor contributing to fractures during production.

Therefore, polymers, e.g. casein [21], pectin [22], chitosan [22] and cellulose materials [23-25], have been attempted to improve the mechanical property of clay aerogel through bonding neighbouring clays together, which makes the solid in the ice front stable and form bridges between laminar, and such providing the aerogel elasticity through the flexible polymer chain. Among these polymers, poly (vinyl alcohol) (PVA) is widely used for the strong hydrogen bonding between hydroxyl groups and the clay surface [26].

However, the entanglement and poor mechanical strength of polymer chain require sufficient loading of polymer to withstand the stress generated by the transition of water to ice. Raising the polymer content inevitably leads to the increase of density and decrease of pore size, which are both unfavourable to thermal insulation. While it is hard to make balance between thermal insulation and mechanical strength through this approach, some researchers try to strengthen the aerogel by primary cross-linking in wet state before freezing and then conduct secondary curing after freezing-dry [27]. This may incur complicated procedure and unwanted chemical reaction. From the perspective of safety requirement for building materials, to fabricate aerogel in environment-friendly way is more preferred. Inspired by applying carbon nanotube to reinforce the graphene giving an ultralight aerogel [28], the incorporation of nanoscale fibre with promising mechanical properties is a necessity. In lieu of its low density, high mechanical property [29, 30], environment-friendly and abundant resources, cellulose nanowhisker (CNW) has been tried as reinforcing filler in many scientific applications [31, 32]. Although CNW, PVA and clay have been applied to produce freeze-dried aerogel [23], the mechanism of reinforcement has not been well understood. To well establish the roles of components in the reinforcement of aerogel, in this study, CNW

by freeze-drying processing technology. The manufacture process was evaluated by recording the fracture development during preparation. Thermal property, porosity and mechanical property were assessed and the mechanisms and roles of aerogel constituents were determined. The effectiveness of this 3-component system was evaluated.

2 Materials and methods

2.1 Materials

Commercial polyvinyl alcohol (Mw 31,000-50,000, 98-99% hydrolyzed, Sigma), Cellulose microcrystal (Medium size, Sigma), sulphuric acid (98 wt%, Fisher Scientific) and Poly(acrylic acid) (Mw ~100,000, 35 wt% in H₂O, Sigma) were used as received. Clay (Sodium bentonite from Tubofuro, Portugal) was filtered by sieving it through 60µm mesh before use in order to remove the oversize particles and impurities.

2.2 Preparation of CNW

Cellulose nanowhisker (CNW) was acid-hydrolysed. Typically, 5 g of cellulose microcrystal was dispersed in 45 mL of distilled water and then 50 mL Of concentrated sulfuric acid was added drop by drop with the flask placed in water-ice mixture bath. Afterwards, the suspension was heated up to 50°C for 1h. 4 L of distilled water was added to slow down the process. Finally, the suspension was centrifuged until pH reaches 5.

SEM examination was carried out to ensure the quality of the developed CNW: A drop of the processed CNW suspension was placed on silica wafer and dried in ambient atmosphere. The dried samples were then subjected to SEM characterization.

2.3 Fabrication of aerogel

Clay was fully exfoliated in Warrant Blender for 8min at the concentration of 5 wt% before use. A certain amount of PVA solution was slowly added into the clay

suspension with gentle stirring. After 24 h, CNW suspension was introduced and the stirring lasted for another 2h to produce a homogenous suspension. The final solution was transferred to aluminium mould with foil wrapped up on the surface and then immersed into liquid nitrogen bath. After completely frozen, the samples were placed in vacuum chamber (Alpha 1-2 LD) to perform a thorough freeze drying.

For a comparison, pure clay aerogel, CNW clay aerogel and PVA clay aerogel are fabricated and evaluated in parallel.

2.4 Characterization

Definition of crack: Three samples were made for each formulation. If one of them cracks during preparation, aerogel with this formulation is defined as “crack”.

The microstructure of the developed aerogel was determined by scanning electron microscopy (SEM), using a Leo® 1430VP scanning electron microscope. Prior to imaging, the samples were sputter-coated with gold.

Thermal conductivity of aerogel was measured on the Fox 200 with the minimum required dimension of 75x75x10mm. The upper plate was set to be 0 °C and bottom plate 20 °C. Each test was repeated for 3 times, giving a average value.

X-ray diffraction (XRD) patterns of the prepared products were recorded using an X'Pert PRO X-ray diffractometer with CuK α radiation ($\lambda=0.15406$ nm).

The compressive strength measurement was performed on INSTRON 5900 at the speed of 2 mm/min by using aerogel of 20 x 20 x 10 mm. The shape recovery of aerogel was recorded starting from 10% or 40% compressive strain 24h after the removing of the stress. Seven samples were tested for each formulation.

The specific surface area was estimated by Micromeritics ASAP 2000 gas adsorption apparatus, where density and pore size determinations were based on the isotherms of adsorption and desorption of nitrogen at 77 K, following the international standard-ISO 9277.

3.1 Fracture development

As expected, cracks occur in all pure clay aerogels with different levels of clay loading (from 1 wt% to 5 wt%) during freezing process. Typically, the fracture starts from the edges and propagates through the whole frozen ice in several seconds (Figure 1). After freeze drying, the obtained aerogel breaks into small pieces. It is so fragile that the aerogel turns into powder under gentle squeezing. The low strength of pure clay aerogel may be due mainly to the poor interaction between clay platelets (Figure 4a). Although the pure clay can be exfoliated into layering structure, there is little connection between the layers.

The incorporation of CNW into pure clay may not be able to improve the networking structure of the developed aerogel, although CNW may work as a simple mechanical reinforcement within individual clay platelets. There is no improvement in crack prevention and handling property of the developed products (Figure 2). More detailed mechanisms will be discussed in next sections.

The introduction of PVA results in an improved aerogel; The strength of aerogel increases with increasing concentration of PVA, aerogel showing better handling property. However, the fracture cannot be prohibited until the amount of PVA exceeds 3 wt% (Figure 3a and 3b).

A combination of CNW with PVA and clay results in a significant improvement in shape integrity and handling property of three component-systems. As showed in Table 1, at a low concentration level of PVA e.g. 1 wt%, even small amount of CNW is able to prevent cracks substantially. However, when the PVA concentration is lower than 1 wt%, the developed aerogel tends to crack during freezing. With the increase of PVA concentration, the strength of the developed aerogel increases further. To CNW, the

concentration should be controlled below 1 wt% to prevent fracture. More details of the

roles in which CNW plays will be discussed in next sections.

3.2 Morphology

Despite the clay platelets, negatively charged in plane and positively charged on the edge, tend to form a house-card structure in solution state, they are unlikely to keep this structure under the push of ice front in considering skeleton wall of 1nm in thickness. The interaction, mainly Van Der Waal force, between face to face is too weak to compete with electrostatic repulsion. Accordingly, little bonding is built between clay platelets and the solid in ice front is easy to rearrange. The final product tends to be discontinuous layers full of holes, a sign of poor interaction, and few bridges are built between layers (Figure 4a).

The CNW-clay aerogel gives the similar structure as the pure clay aerogel, as showed in Figure 4b. The platelets are still full of holes and there is little bridging between laminar, suggesting poor interaction between CNW and clay platelets. However, a scrutiny of Figures 4a and 4b indicates that each single platelet layer seems to be more compact for CNW clay aerogel than pure aerogel, this may be due to the mechanical reinforcement of CNW to clay. This can also be seen from Figure 4c that CNW with length up to micrometres are randomly attached onto the surface of clay (white arrow in Figure 4d). However, the size scale of CNW may not be sufficient to mechanically bridge inter-layers of the platelets without chemical reaction. Therefore, the efficacy of CNW on the reinforcement of aerogel is very limited.

An introduction of PVA into clay suspension results in a formulation of 3D networking platelets within aerogel (Figure 4e, 4f and 4g). A comparison of pure clay aerogel and PVA-clay aerogel clearly indicates the generation of bridging channels between layers. As the concentration of PVA increases, the number of the bridging channels increases and hence the integrity improves. Furthermore, along with the increase of bridging

channels with the PVA concentration, the laminar also becomes thicker, which may reduce the chance of cracking.

To take advantages of both CNW and PVA, 3-component system has been developed; CNW, PVA and clay were all formulated together. It is apparent that the integrity of the produced aerogel was greatly enhanced. As depicted in Figure 5a, 5b and 5d, while raising the content of PVA, more bridges are built and the aerogel becomes much stronger. When the content of CNW keeps 0.5 wt%, there is seldom bridges built between laminar in aerogel with 0.7 wt% PVA. However, the aerogel with 1 wt% PVA shows the increased number of bridgings. With the increased loading of PVA, the bridges seem to become thicker. By contrast, with the increased loading of CNW, the number of bridgings is declined and the aerogel shows decreased tolerance to crack, the reasons for this change are detailed in next section (Figure 5b and 5c). As illustrated in Figure 5d, 5e, 5f and Figure 4f, when the content of PVA stays at 2 wt%, comparing with the one without CNW, the aerogels with CNW less than 1 wt% show improved integrity and increased bridges. However, when CNW is more than 1 wt%, the laminar gradually loses its integrity and has decreased interactions. This is well in agreement with the performance of aerogel during freeze.

3.3 Architectural mechanisms of 3-component clay aerogel

The development of nano network system and hence integrity of 3-component clay aerogel are due mainly to the synergistic effect between CNW, PVA and clay, which can be simplified in Figure 6. Both negatively charged surfaces of clay and CNW do not allow them to bond with each other. A special medium with double functionalities should be introduced and PVA was considered most suitable materials to play this role. Due to the abundant hydroxyl groups on the surface, PVA acts as a glue/bridging medium between clay and CNW. With this strategical concept, PVA is firstly absorbed onto the surface of clay and partly screen the charge of the clay. This means a decrease

of surface charge, which provides a suitable condition for CNW to be absorbed on the outer surface of clay platelets through hydrogen bonding provided by the PVA and clay. A bridging connection between neighbouring clays thus is generated. Furthermore, the large in longitude make CNW easier to bridge between clay platelets than an entangled polymer chain, and compared with polymer, the excellent mechanical property of CNW can provide the aerogel better resistance to crack development. Combined with the flexible polymer chain, the frozen 3-component suspension can withstand the dimensional expansion caused by freezing and gain better elasticity. However, increasing the concentration of CNW will inevitably result in an increase in the surface charge of nanocomposite, creating unbalanced condition of negative and positive charges within the suspension. Therefore, the aerogels with 1.5 wt% or more CNW will break automatically during preparation. In summary, the concentration of CNW greatly affects the bonding between clay platelets and determines whether the electrostatic repulsion or hydrogen bonding will dominate the interaction. It is worth to note that due to the combined functionalities of 3-component system, less solid content within the suspension can be achieved, making the resulted aerogel less thermally conductible.

In this 3-component system, the PVA should be ensured sufficient to occupy clay platelets, otherwise, the electrostatic repulsion from clay cannot be fully screened; thereby, less CNW can be absorbed onto clay, that is, less CNW bridges can be established between clay platelets. This is why, when the PVA decreased down to 0.7 wt%, even the CNW content remains the same, 0.5 wt%, little bridges can be recognized in SEM image compared to those aerogels with higher load of PVA (Figure 5a) although each layer keeps its integrity and parallel to each other in uniform distance. To confirm this hypothesis, XRD was employed to examine the d-spacing change of clay platelets before and after the incorporation of polymer and CNW. The value of 2θ in XRD spectrum enables the evaluation of the d-spacing of the intercalated structures,

into clay platelets. As showed in Figure 7, the X-ray profile of the pure clay aerogel has a characteristic diffraction peak at $2\theta = 6.8^\circ$ (d-spacing=1.3 nm), which does not emerge in PVA clay aerogels. For the composition of 1 wt% PVA in 2.5 wt% clay, this peak shifts to lower value, but slightly higher than $2\theta \approx 3.8^\circ$. It must be noted that due to the overlapping of neighbouring peak, the angle cannot be precisely determined. For the composition of 1 wt% CNW in 2.5 wt% clay, there is seldom change of XRD spectrum, indicating CNW fail to penetrate clay platelets alone. After the incorporation of 0.5 wt% of CNW into 2.5 wt% clay and 1 wt% PVA suspension, the corresponding peak shifts to $2\theta = 3.8^\circ$ (d-spacing=2.3 nm), which is the same as that of aerogel with 2.5 wt% clay and 1 wt% PVA. This does indicate the failed penetration of CNW because of the large in width and small in number of CNW used.

The hypothesis was further confirmed through replacing CNW by poly(acrylic acid) [33], which has negatively charged surface and is three fold larger in molecular weight than that of PVA, as the third component to PVA-clay aerogel. In a wide range of PAA content from 0.1 wt% to 1 wt%, all of the aerogels made cracked during freezing or transferring processes, indicating that much stiffer and longer CNW than PAA plays a key role in building more and stronger bridges between layers(Figure 5g).

3.4 Compressive strength of 3-component system aerogels

As aforementioned, the incorporation of polymer into clay aerogel greatly prevent the crack during freezing process, consequently the mechanical strength of aerogels greatly increases. As showed in Figure 8, the increased content of PVA in 3-component system clay aerogel leads to the improvement of the compressive strength both at 10% and 40% compressive strain. The aerogel with 1 wt% PVA exhibits 6.5 kPa at 10% of compressive strain and 19.1 kPa at 40% of compressive strain; the aerogel with 2 wt% PVA achieves a compressive strength of 16.5 kPa and 41 kPa at 10% and 40%

compressive strain respectively; the aerogel with 3 wt% PVA had a compressive strength of 26 kPa and 56 kPa at 10% and 40% compressive strain respectively.

An incorporation of CNW resulted in a significant increase of compressive strength. The compressive strength at 10% and 40% compressive strain are remarkable enhanced. Especially, to the aerogel with 0.5 wt% CNW, 2 wt% PVA and 2.5 wt% clay, the compressive strength reached to 34 kPa, which is 160% increase at 10% compressive strain compared to that of aerogel without CNW. However, further increase of PVA gradually slows down the tendency of reinforcement and the increase in compressive strength seems to level off, indicating the efficient effect of CNW, especially at low concentration of PVA. However, continuing to increase CNW from 0.5 wt% to 1 wt% did not bring about the same effect as that from 0 to 0.5 wt%. The compressive strength of aerogel with 2 wt% PVA at 10% strain increased by 59% compared to aerogel with 1 wt% PVA, lower than that of aerogel with 0.5 wt% CNW. In principle, compressive strength at 40% strain presents the similar tendency, which supports the fact that the higher load of CNW leads to the increase of repulsion between the 3-component systems.

3.5 Shape recovery

The flexibility of PVA chain may also help shape recovery of the 3-component system aerogel (Figure 9). It is apparent that an increase in the PVA content consistently improve the shape recovery of PVA-clay aerogel, from 65% to 86% when PVA increases from 1 wt% to 3 wt%. Due to the increased number of bridge built by CNW, this efficacy was enhanced, especially when PVA increase from 0 to 1 wt% for 0.5 wt% loading CNW, the recovery increased from 67.8% to 92.5% at the content of 1 wt% PVA, but the recovery ability levelles off with the continuing increase of PVA content. However, increasing CNW from 0.5 wt% to 1 wt% results in the shape recovery property declining slightly from 94% down to 90% when PVA stays at 2 wt%,

interaction between hybrids.

3.6 Thermal conductivity

The thermal conductivity is a key parameter to be assessed for the developed aerogel. In lieu of the application in practice, the shape integrity should be maintain, therefore, those cracked aerogels during preparation were not being used for further characterization.

Theoretically, thermal conductivity is closely related to the solid content. As a result, the density of aerogel in some extent affects the thermal conductivity of aerogel. As illustrated in Table 2, aerogel with 3 wt% PVA obtains density of 0.078 g/cm^3 and thermal conductivity of 0.044 W/mK which is overwhelmingly higher than those of fracture free aerogel with CNW. This demonstrates that the incorporation of CNW results in increased tolerance to the expansion of water crystallization. The impurity of the clay material limits the improvement of thermal insulation of resulted aerogel. To diminish this effect, pure clay (Cloisite Na^+ , Rockwood) was used to prepare aerogel, and due to the high efficiency of exfoliation, integrated aerogel can be fabricated while the clay content is decreased to 1 wt% by adding small amount of CNW and PVA. The decrease in solid content gives rise to the final aerogel a thermal conductivity 0.034 W/mK , showing that it is achievable to lower the solid content by incorporation of CNW to produce fracture free aerogel with better thermal insulation.

4 Conclusions

3-component systems, fracture free aerogels, have been successfully developed. Main conclusions can be summarised as follows:

- 1) Cellulose nanowhisker (CNW) played key roles for formulating/bridging clay aerogel structures to prevent cracks and achieve good mechanical property (strength and shape recovery);

- 2) The increase of PVA loading gave rise to an improvement of compressive strength and shape recovery, while CNW did adversely, indicating that unbalanced level of charges of 3 constituents might weaken the interaction between the hybrids;
- 3) Optimum micro/network and hence much more enhanced bonding systems were built within and between laminar after strategical propotional designs of compositions and polarity characteristics of constituents, developing fracture free clay-based aerogel;
- 4) Architectural structure of the CNW reinforced clay platlets mechanically (CNW-C) and PVA chemically CNW-P) together with the chemical bonding between CNW-C and CNW-P was established for the novel 3-component clay aerogels;
- 5) The reduction in solid content, enhancement in mechanical property and improvement in thermal insulation have been achieved. This development could provide a novel route for the scale-up production of strong fracture free clay-based aerogel through freeze drying process.

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Figure 1 Typical fracture development of aerogel with 1 wt% (a), 2.5 wt% (b) and 5 wt% (c) clay during freezing

Figure 2 Morphology of aerogel with 2.5 wt% clay and 1 wt% CNW.

Figure 3 Fracture development of aerogel with 2 wt% (a) and 3 wt% (b) PVA.

Figure 4 SEM image of pure clay aerogel (a), aerogel made of Clay and CNW with different magnification (b) and (c), (Inserted (d): SEM image of CNW) and aerogel made of 2.5 wt% Clay plus amounts of 1 wt% (e), 2 wt% (f) and 3 wt% (g) PVA.

Figure 5 SEM images of aerogel with 0.5 wt% CNW and 0.7 wt% PVA (a), 0.5 wt% CNW and 1 wt% PVA (b), 1 wt% CNW and 1 wt% PVA (c), 0.5 wt% CNW and 2 wt% PVA (d), 1 wt% CNW and 2 wt% PVA (e), 1.5 wt% CNW and 2 wt% PVA (f), 1 wt% PAA and 2 wt% PVA (g).

Figure 6 An example of interaction between PVA, CNW and clay platelets.

Figure 7 XRD spectrum of corresponding materials.

Figure 8 Compressive strength of aerogel with different content of CNW 0 wt% (A), 0.5 wt% (B) and 1 wt% (C) at 10 wt% (a) and 40 wt% (b) compressive strength.

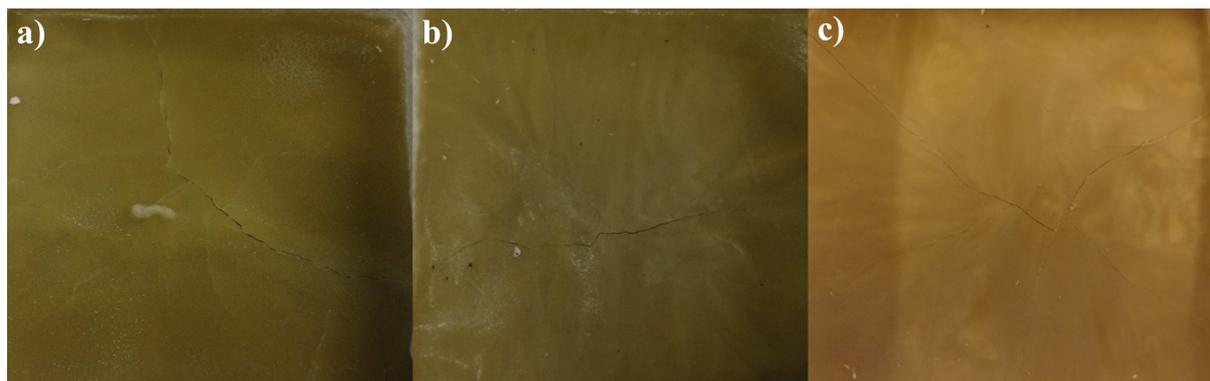
Figure 9 Shape recovery of aerogel with CNW 0 wt% (A), 0.5 wt% (B) and 1 wt% (C) starting from 10 % compressive strain.

Table 1 Visual strength of aerogel during processing

Table 2 Porosity and thermal conductivity of aerogel.

Sample	Clay (%)	PVA (%)	CNW (%)	Fracture
P1	2.5	-	-	√
P2	2.5	1	-	√
P3	2.5	2	-	√
P4	2.5	3	-	None
P5	2.5	0.7	0.5	√
P6	2.5	1	0.5	None
P7	2.5	1	1	None
P8	2.5	2	0.5	None
P9	2.5	2	1	None
P10	2.5	2	1.5	√
P11	2.5	2	2	√

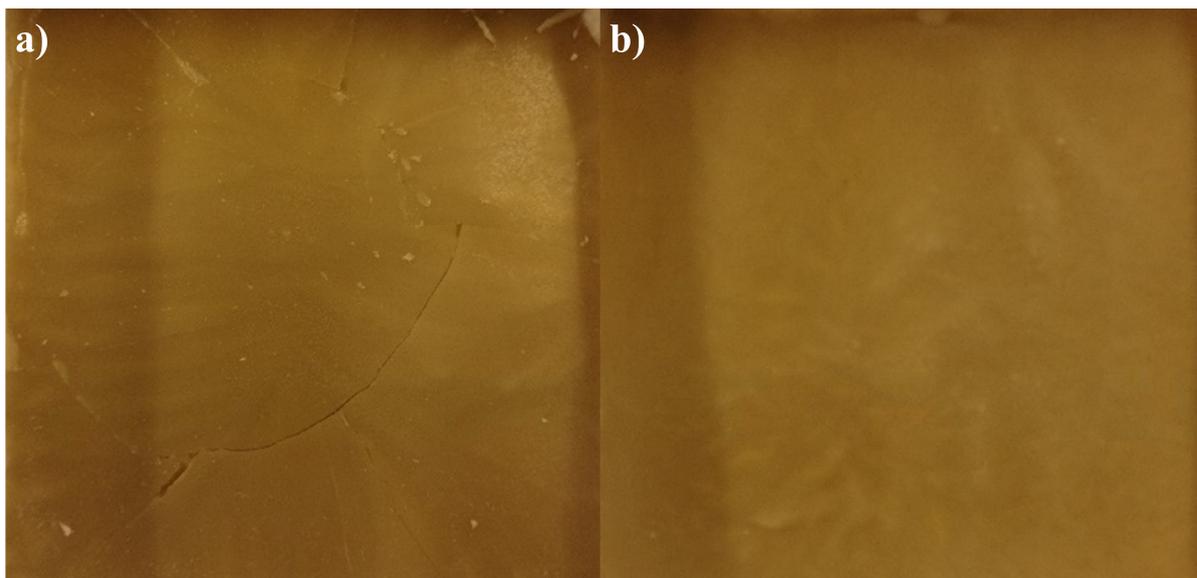
	Porosity (%)	Density (g/cm³)	Thermal conductivity (W/mK)
P2	80.9	0.050	-
P3	86.3	0.063	-
P4	79.5	0.081	0.044
P6	82.3	0.055	0.041
P7	81.6	0.062	0.042
P8	84.9	0.077	0.043
P9	83.6	0.108	0.044



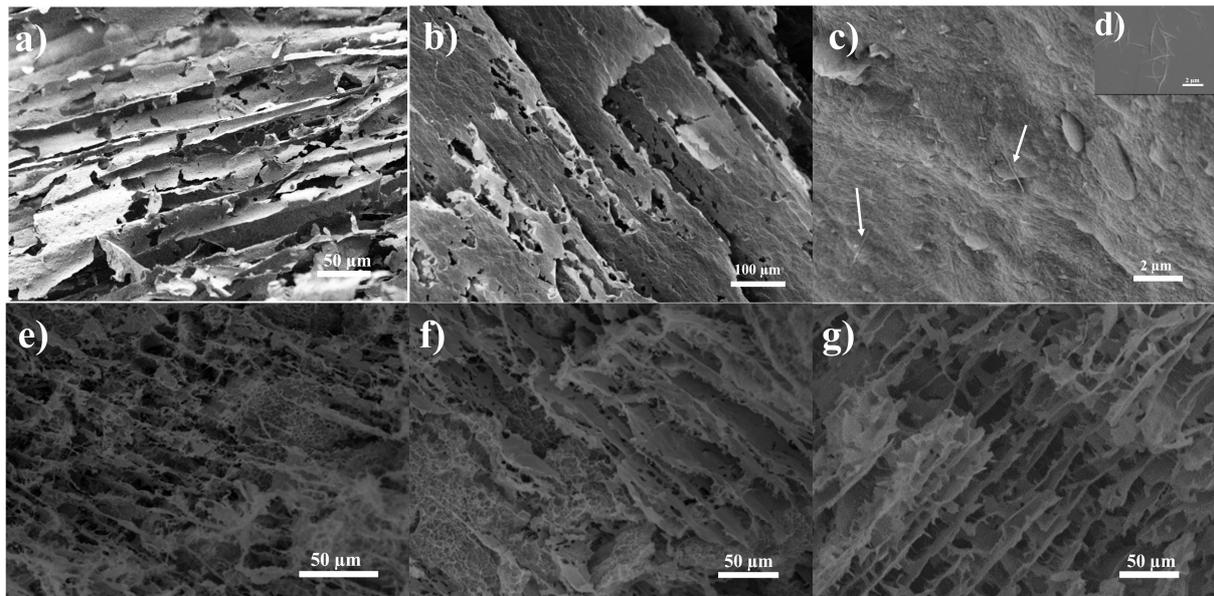
ACCEPTED MANUSCRIPT



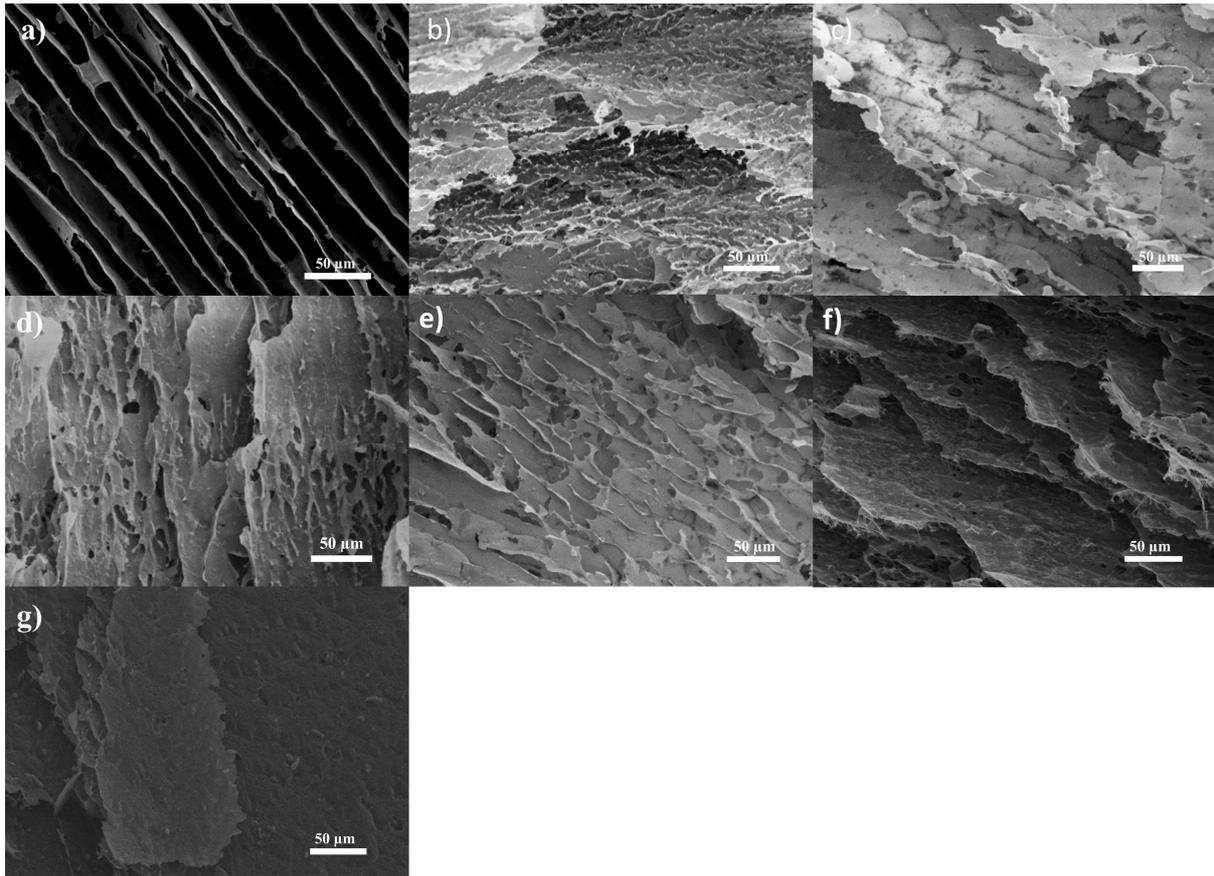
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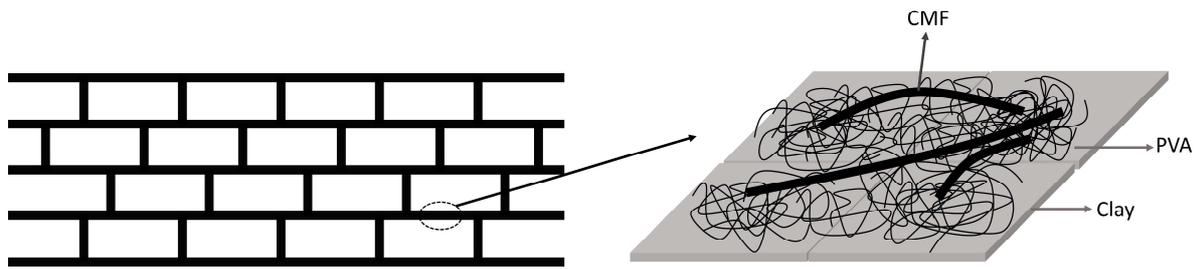
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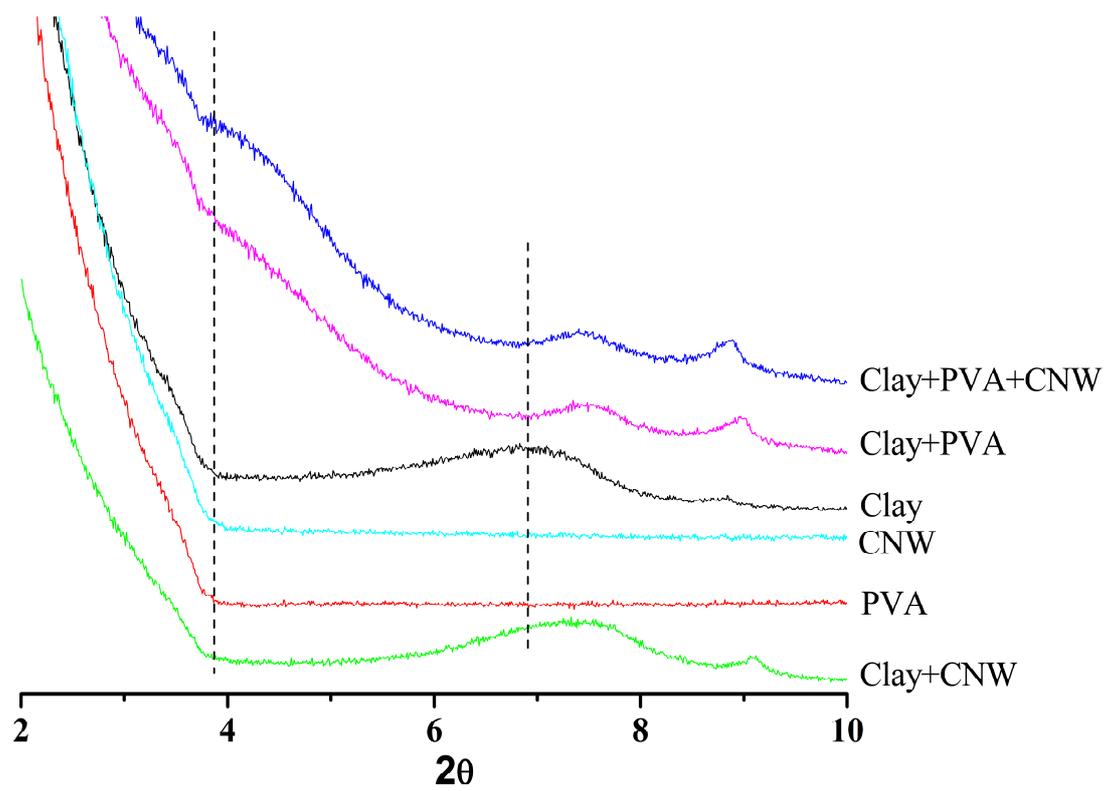
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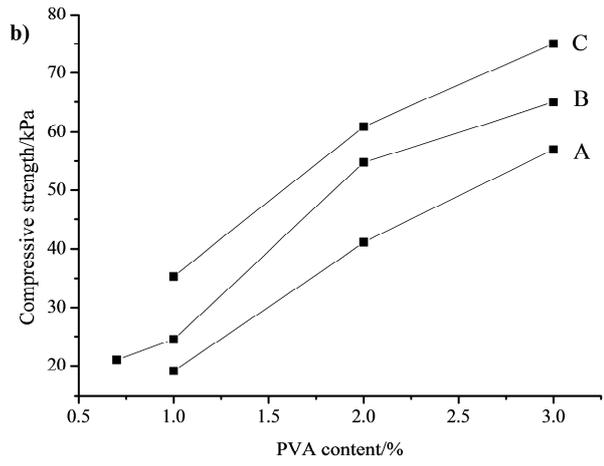
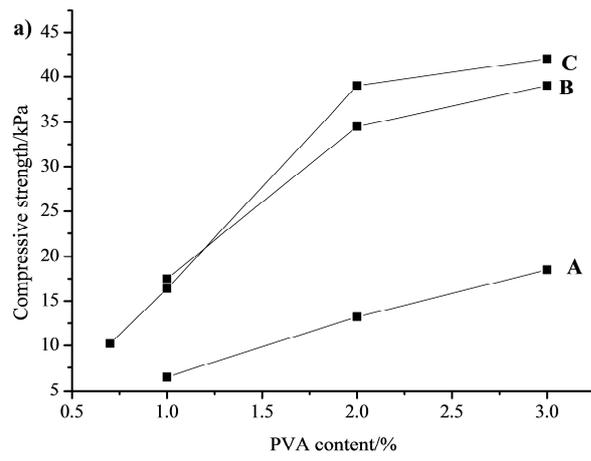


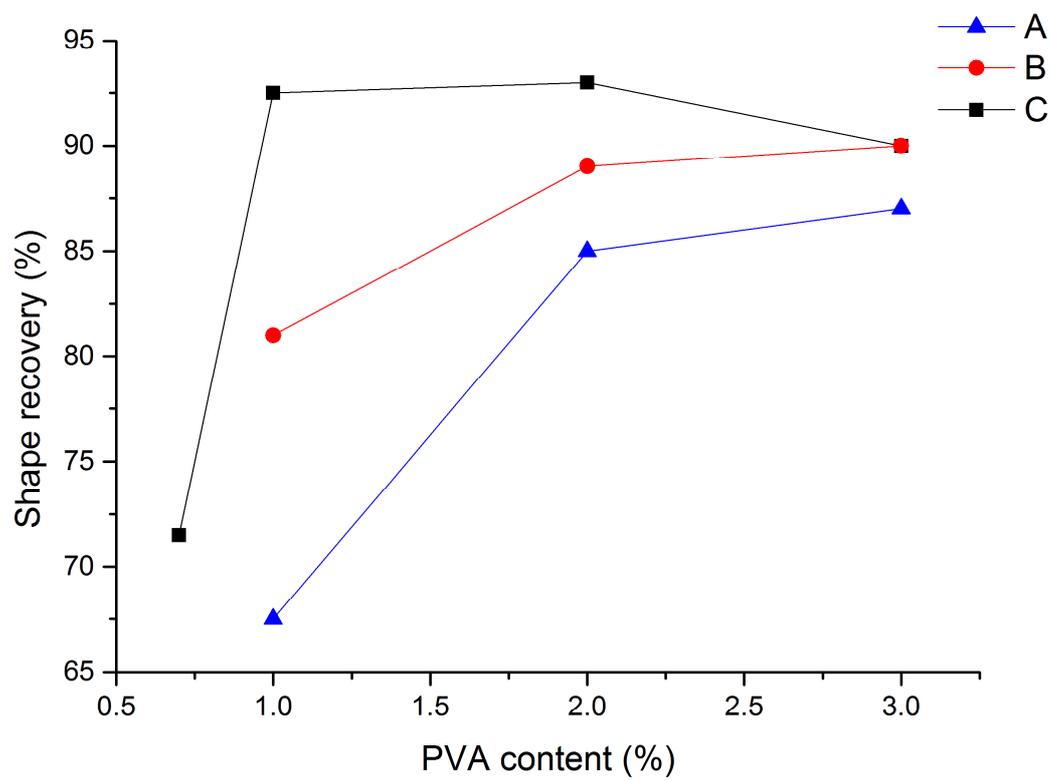
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ACCEPTED MANUSCRIPT







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