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Poly(vinyl alcohol)-Agar Double Network Hydrogels: Linking Formulation to Mechanical and Rheological Properties

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ABSTRACT

Hydrogels are used widely in healthcare disciplines due to factors such as their high water content and safety profile. However, the materials are typically soft and may not be suitable for applications under stress, such as implantation into load-bearing sites. It has been shown that tough hydrogels may be formed by combining brittle chemically-cross-linked polymers with a physically-entangled system to give "double-network" hydrogels. However, the process for chemically cross-linking polymers typically requires reactive species, which are unsafe to use outside of specialised facilities. Furthermore, once the chemical network is formed, the material cannot be remolded. In this study, double-network hydrogels have been formed from two physical networks, namely agar and PVA hydrogels. Agar forms a helical polymer network supported by non-covalent interactions, whereas PVA can form a so-called "cryogel" by freeze-thaw cycling to induce crystallites, which cross-link the network. It has been shown that this approach to producing double-network hydrogels gives tough materials without harsh cross-linking agents. Relationships between PVA molecular weight and gel mechanical properties are probed by approaches including needle-injection, tensile testing, and shear rheometric methods. Formulation factors such as concentration, freeze time, and storage time are also explored.

1 | Introduction

Hydrogels are widely used across multiple sectors, including healthcare, cosmetics, food, and biotechnology. Hydrogels are typically three-dimensionally cross-linked polymers that are swollen with water but retain a solid-like macroscopic form. The broad utility of these materials arises from benefits including high water content, tailorable mechanical properties, and often optical transparency. However, a crucial limitation of traditional hydrogel materials is that they are typically weak and brittle with low fracture energies and low elastic moduli, which limits their use for applications requiring high resistance to stress, such as soft robotics, implantation at load-bearing sites, and in wearable bioelectronics [1, 2].

Classically, hydrogels are formed from a single network of polymer chains cross-linked either by covalent interactions (chemical cross-links) or by polymer entanglements supported by non-covalent interactions (physical cross-links) [3]. It has been demonstrated that the formation of "double network hydrogels" can be achieved by having two separate cross-linking mechanisms occurring in the same hydrogel [4]. The original example of these double network hydrogels utilised an interpenetrating polymer network of poly(2-acrylamido-2-methylpropanesulfonic

acid) and poly(acrylamide), leading to a hydrogel with 90 % water content but fracture stresses of up to 21 MPa under compression [4]. This model of a first "hard and brittle" network of chemically cross-linked polyelectrolyte (e.g., poly(2-acrylamido-2-methylpropanesulfonic acid)) and a second "soft and ductile" chemically cross-linked network (e.g., poly(acrylamide)) became the most common approach to generating tough double network hydrogels [1, 5]. The strength of these materials is typically attributed to "sacrificial bonds" in the first network that break under deformation and dissipate energy, sustain stress, and store elastic energy, all whilst allowing retention of the second network [6].

Chemically cross-linked materials have several disadvantages, including the difficulty of synthesis requiring specialist equipment and irreversible bond breakage after fracture, which may be alleviated by the use of physical cross-links in double network hydrogels [6]. Physically cross-linked hydrogels may be produced by several mechanisms, including temperature-dependent conformational changes [7], crystallisation [8], and ionotropic gelation [9]. This gives rise to the possibility of multiple, distinct, cross-linking mechanisms in a single hydrogel to allow physical double network hydrogels.

Agar, a temperature-sensitive gel-former derived from algae, has previously been used as a component of double-network hydrogels [6]. Agar is a mixture of gel-forming agarose (a linear polymer of alternating (1→3)-linked β-D-galactopyranose and (1→4)-linked 3,6 anhydro-α-L-galactopyranose) and agaropectin [10]. In aqueous solution, agarose chains are believed to take a random and stiff coil conformation at high temperatures. On cooling, these chains order into double helices, which form physical junctions in a three-dimensional network leading to the formation of a rigid gel [10, 11]. It is proposed that this agar network could exist complementarily to a second physical network induced by an alternative cross-linking mechanism [6], such as crystallisation of poly(vinyl alcohol) (PVA). PVA forms so-called "cryogel" by processing aqueous solutions of the polymer through freeze-thaw cycles [12, 13]. When an aqueous solution of PVA is cooled, water will eventually freeze, concurrently expelling PVA into phase-separated regions where the polymer becomes concentrated. The proximity of the polymer chains induces crystallite formation, which cross-links PVA into a hydrogel structure [8]. Double network hydrogels formed from PVA/agar mixtures are poorly explored in the literature. The mixture of agar with borax cross-linked PVA results in soft viscoelastic materials ($G' < 10$ kPa), which self-heal readily [14]. To our knowledge, the first PVA/agar hydrogel with crystallisation-induced PVA cross-linking was reported by Sabzi et al. [15]. They report the effect of PVA/agar ratio on the tensile properties of the hydrogels and study the self-healing of the gels. Later, Sun et al. investigated the effect of agar concentration with a secondary PVA (75 kg mol^{-1}) cryogel network, then soaked the system with ammonium persulfate to create conductive hydrogels [16]. Han et al. investigated PVA/agar hydrogels containing ethylene glycol with additional borax cross-linking to give materials of up to 600 kPa tensile strength and strains at break of up to 962% [17]. PVA/agar/poly(ethylene oxide) mixed hydrogels have also been reported using high-energy electron Beam Irradiation to induce chemical cross-linking of PVA [18]. Despite the efforts in this area, there is a lack of understanding of how polymer structure links to properties in these double network systems.

In this study, we systematically investigated a physically crosslinked double network (DN) hydrogel system based on poly(vinyl alcohol) (PVA) and agar—two biocompatible and widely available polymers. Unlike conventional chemically crosslinked DN systems, our approach avoids toxic crosslinkers by leveraging agar's thermo-responsive gelation and PVA's crystallite formation through freeze–thaw cycling. Mechanical testing is combined with rheological analysis to evaluate performance across a range of stress conditions, while physicochemical characterisation is performed using infrared (IR) spectroscopy and differential scanning calorimetry (DSC). We explored how formulation parameters—such as polymer concentration, molecular weight, and number of freeze–thaw cycles—influence the mechanical and rheological behaviour, demonstrating how network structure governs material properties. The resulting PVA–agar hydrogels offer a sustainable and tunable platform with potential applications in biomedical engineering, soft robotics, and food biotechnology.

2 | Materials and Methods

2.1 | Materials

Polyvinyl alcohol (PVA molecular weight of 61,000 g/mol, 145,000 g/mol and 195, 000 g/mol with a degree of hydrolysis > 99%), and PVA samples of molecular weights 145,000 g/mol and 31,000 g/mol with a degree of hydrolysis of 89% were obtained from Sigma-Aldrich (St. Louis, Missouri, United States). Agar powder (with a melting point of 85 ± 5°C) was purchased from Sigma-Aldrich (St. Louis, Missouri, United States). Deionised water was used throughout the experiments.

2.2 | Hydrogel Preparation

Agar solutions were formulated by dissolving 2%–8% w/v agar in DI water with magnetic stirring at 200 rpm for 30 min at 120°C temperature. After the agar powder was homogenised in suspension, the heating was removed. The agar solution was then left at room temperature for 1 h to allow the agar gel to form.

For a typical preparation of PVA cryogel and PVA/agar double network hydrogel, a homogeneous solution of PVA was first obtained by dissolving 12% w/v amount of PVA in 100 mL deionised water at reflux (hot plate set to 120°C) under vigorous stirring for circa 2 h; the beaker was sealed with parafilm to prevent water loss. To produce PVA/agar double network hydrogels, 6% w/v of the agar powder was then added to the stirring solution of PVA. The solution was left in static placement at room temperature for 2 h to gradually cool the solution to room temperature. The gel was then placed through a single freezing/thawing (F-T) cycle (cooled to −10°C at 1°C/min followed by thawing at room temperature), with the aim of promoting crystallite formation in PVA. The sealed samples were stored in the refrigerator (circa 5–10°C) until experimental work was conducted. PVA/Agar gels were prepared with different proportions of agar and PVA at a constant 18% w/v total polymer content. The influence of PVA molecular

TABLE 1 | The parameters of PVA/agar gel formation.[a]

Factor/Sample name	PVA	Agar
89 mol %	12% w/v	6% w/v
99 mol %	12% w/v	6% w/v
61 kg mol^{-1}	12% w/v	6% w/v
145 kg mol^{-1}	12% w/v	6% w/v
195 kg mol^{-1}	12% w/v	6% w/v
−20°C	12% w/v	6% w/v
−80°C	12% w/v	6% w/v
0.25Day_Freeze	12% w/v	6% w/v
1Day_Freeze	12% w/v	6% w/v
2Day_Freeze	12% w/v	6% w/v
5Day_Freeze	12% w/v	6% w/v
2Day_Storage	12% w/v	6% w/v
5Day_Storage	12% w/v	6% w/v
13Day_Storage	12% w/v	6% w/v
PVA	18% w/v	0
Agar	0	4% w/v
PVA/Agar	9% w/v	9% w/v
2PVA/Agar	12% w/v	6% w/v

[a]The weight-to-volume (w/v) ratio is expressed as the ratio of the weight of material added to a fixed volume of water.

weight, hydrolysis degree, freeze time, and storage time on gel formation has also been investigated. The investigated parameters of PVA/Agar gel are summarised in Table 1.

2.3 | Needle Injection Test

The needle force injection test was implemented on a TA.XTPlus Texture Analyser (Stable Micro Systems, Surrey, UK) combined with a P/2N needle probe. The stainless-steel needle probe has a total length of 4 cm and 2 mm with a taper of 9° to 10°. In the needle injection tests, the injection speed was 2 mm/s, and the injection test was stopped when the injection distance reached 30 mm (Figure 1). The data on needle injection distance and force were plotted. Three replicates were tested for each sample. All data are expressed as mean ± standard deviation. Data were compared using a paired, two-tailed Student's *t*-test. In all cases, $p < 0.05$ was the minimum value considered acceptable for rejection of the null hypothesis.

2.4 | Tensile Testing

PVA/agar cryogel prepared in Petri dishes for rheological analysis was also used for tensile testing. The hydrogels were cut into rectangular sections using a 75 x 26 mm glass slide as a guide, then accurately measured using a pair of callipers. Tensile analysis was conducted using a TA.XT Plus Texture Analyser (Stable Microsystems, UK), using the tensile grips accessory. Samples were loaded into the tensile grips with an approximate height of 30 mm, which was accurately measured for each sample with a pair of callipers. Extension of the sample was conducted at 1 mm/s until the yield of the sample.

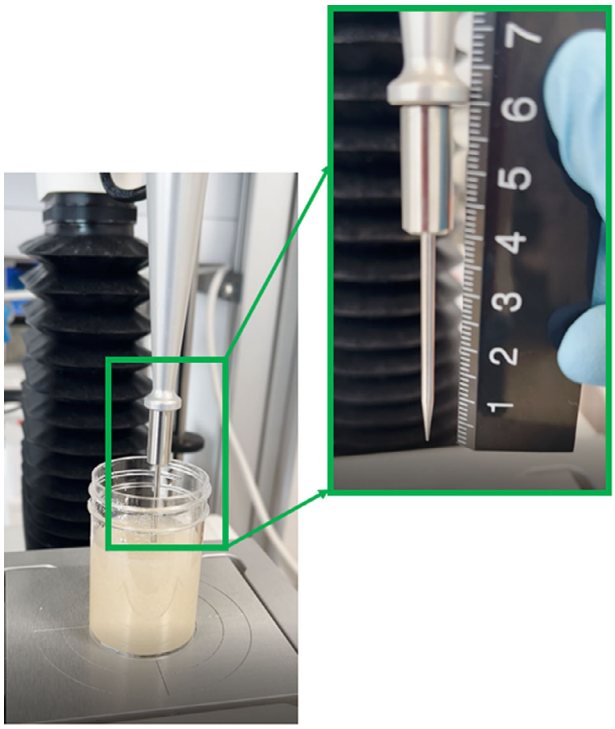

FIGURE 1 | Setup and dimensions of the needle injection test.

2.5 | Shear Rheological Analysis

Samples were prepared by casting hydrogels into 180 mm diameter Petri dishes before cutting into 40 mm diameter cylinders of height circa 1.2 mm. Small-amplitude shear rheological analysis was then conducted on an AR 1500ex oscillatory shear rheometer (TA instruments, USA) equipped with a Peltier temperature control unit and a 40 mm parallel plate geometry with a specified gap distance of 1200 μm. Amplitude sweeps were conducted at a fixed frequency of 6.283 rad/s between 0.1 and 1000 % oscillatory strain at a temperature of 20°C. Oscillatory frequency sweeps were conducted at 0.1 % oscillatory strain across an angular frequency of 0.5 to 100 rad/s at 20 or 90°C. Temperature ramps were conducted at a fixed strain (0.1 %) and angular frequency (6.283 rad/s) between 20 and 90°C at a ramp rate of 2°C/min. All samples were left to rest for 3 min at the starting temperature prior to analysis.

2.6 | Material Characterisation

An ATR Fourier transform infrared (FTIR) spectrophotometer (Perkin Elmer 2000, PerkinElmer, Inc., Waltham, Massachusetts, USA) was used to examine the raw materials and the gels. The spectra were collected over a wavenumber range of 500–4000 cm^{-1} with a resolution of 2 cm^{-1} at room temperature. All measurements were performed in triplicate.

The thermal properties of raw polymers and gels were characterised using a Q1000 differential scanning calorimeter (DSC) (TA

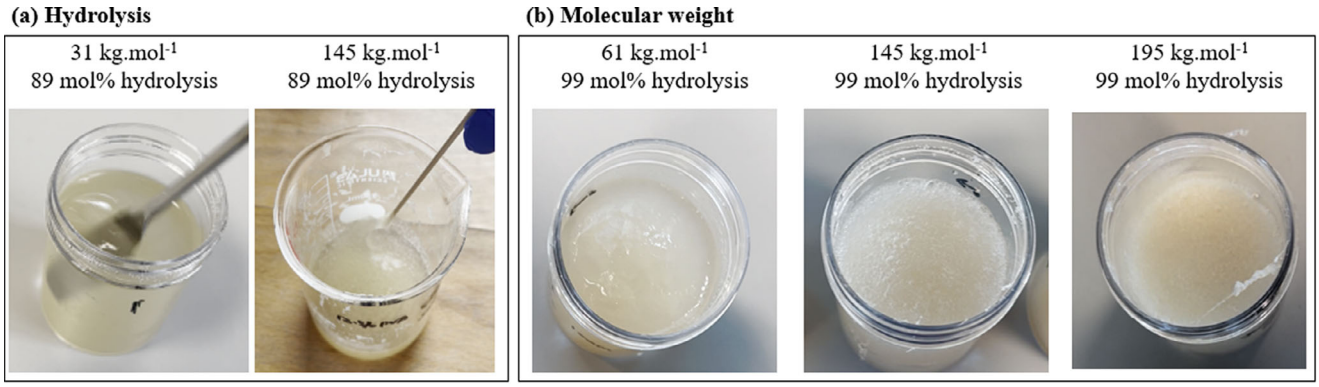

FIGURE 2 | PVA/Agar hydrogels formulated with various PVA degrees of hydrolysis (a) and molecular weight (b).

Instruments, Delaware, United States). TA Universal Analysis software was used for the data analysis on the duplicated samples, and the mean value was used to represent the results. DSC was performed to acquire the peak melting temperatures of the raw polymer, PVA/Agar gels. The sample (3–5 mg) was accurately weighed in an Aluminium crimped T-zero DSC pan, and sealed using a hermetic lid with a pinhole. All samples were tested from 0° to 350 °C at a rate of 5 °C/min. Nitrogen purge gas with a flow rate of 50 mL/min was used throughout the experiments. Empty pans were used as a reference.

3 | Results and Discussion

The influence of PVA degree of hydrolysis and molecular weight on PVA/Agar gel formations was initially evaluated visually. As shown in Figure 2, the PVA/Agar gel formulated with either low or high Mw of PVA and a hydrolysis degree of 89 mol% did not achieve gelation. However, the PVA with a hydrolysis degree of 99 mol% can form a gel at all molecular weights assayed. PVA is initially prepared as poly(vinyl acetate), which is then treated to hydrolyse the acetate ester to the final PVA product. PVA with degrees of hydrolysis of 89 % may therefore be analogous to a random copolymer of vinyl alcohol and vinyl acetate. The ability of only the 99 % hydrolysis PVA to undergo gelation is likely to be the result of greater crystallisation of the PVA at higher degrees of hydrolysis due to factors such as reduced steric constraints from acetyl groups. Additionally, the potential to interact with other polar polymers would be expected to vary as a function of the degree of hydrolysis [19]. Thus, no further evaluation of PVA with a degree of hydrolysis less than 99% was conducted.

The needle injection response of PVA/Agar gel with various molecular weights was assessed, as shown in Figure 3a. These experiments measure the compression force required to penetrate the needle probe into the gel. The results indicate that PVA with a molecular weight of 145 kg mol^{-1} requires the highest axial force for needle penetration (4.10 ± 0.15 N), compared to 61 kg mol^{-1} and 195 kg mol^{-1}, which require 0.16 ± 0.02 N and 2.41 ± 0.04 N, respectively. For the preparation of PVA hydrogels, the PVA molecular weight has a clear influence on the strength of the materials, as shown in Figure 3b. The needle puncture test was then conducted on agar, PVA, and mixtures of the two at different ratios. The needle injection force of 18% w/v PVA and agar is lower than that of the 18% w/v PVA/agar gel, giving initial evidence of synergism. However, there is no observable difference in needle injection properties when the PVA/Agar ratio is 1:1 or 2:1.

Figure 3c shows the influence of freeze time on the needle injection property of PVA/Agar gel. The results show that with the freeze time (within the −10°C freezer) increasing from 0.25 day to 2 days, the required needle injection force was significantly higher. However, when the freeze time increases from 2 days to 5 days, there is no statistically significant difference ($p > 0.05$, $n = 3$) in the needle injection force. The storage time within the refrigerator (5°C) also influenced the needle injection property. As shown in Figure 3d, when the storage time is 2 days, the highest needle axial force is circa 0.5 N, however, the needle injection force increased circa three-fold after storage at 5 ± 2°C for 2 days. When stored in the refrigerator for a further 5 days, there is no difference in comparison with 2 days of storage. This effect is attributed to the crystallisation of PVA over time. It is known that while phase separation during freezing drives crystallisation and phase-separated dense regions, the process of crystallisation may occur from a single-phase solution over time periods of days to weeks to form relatively weak gels [8]. This temporal crystallisation is therefore the likely mechanism for hardening during storage, as observed for PVA cryogel [20, 21].

Shear rheological analysis of agar, PVA, and PVA-agar double-network hydrogels was conducted. Amplitude strain and frequency sweeps were collected for the gels assayed here. Amplitude strain sweeps allow evaluation of the system response to strain loads. Amplitude sweeps for the system assayed are shown in Figure 4a. The absolute value of strain at which the system transitions from $G' > G''$ to $G'' > G'$ is considered to be "yield strain" (γ_y) for the gels studied, the point at which liquid-like behaviour dominates ($\tan \delta > 1$) and the sample behaves as a viscoelastic liquid [22]. The plateau region that precedes the yield point is the so-called linear viscoelastic region (LVR) and marks the region where the rest structure of the gel is preserved during the strain cycle. The agar gel is characterised by a high value of G' in the LVR plateau (G'_P), ca 49 kPa, but a low γ_y, at 5 % strain. Thus, the material may be considered to be a brittle gel. PVA cryogel (12% w/v, Figure 4a) has a distinctly different rheology characterised by relatively low values of G'_P but a high γ_y. Thus, although the PVA cryogels are relatively easy to deform, the gels may be stretched to a larger deformation before any irreversible yield. PVA/agar double-network hydrogels have the benefits of both systems, giving greater strength (G'_P) than the PVA gels

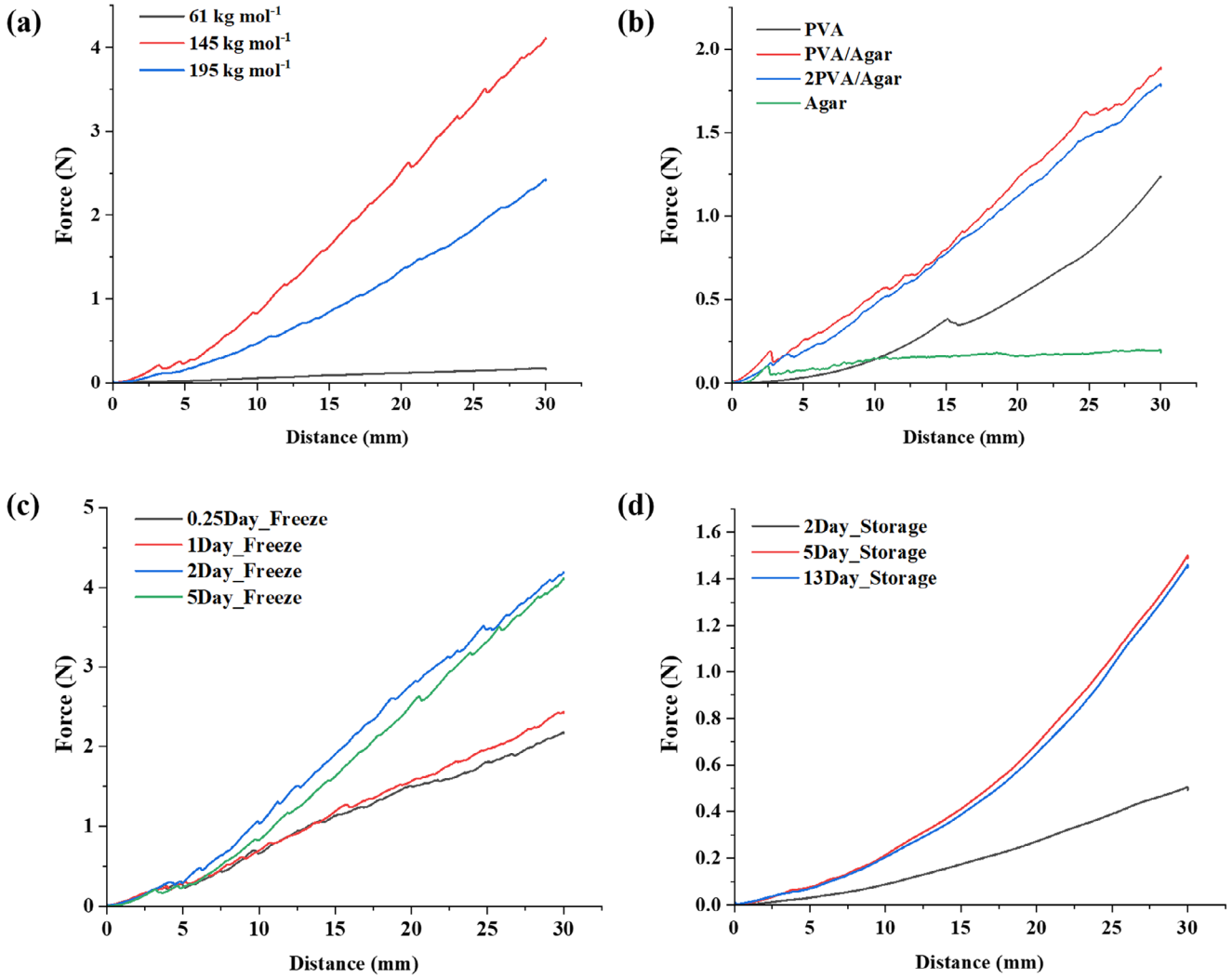

FIGURE 3 | Needle injection property with different (a) molecular weight; (b) agar/PVA ratio; (c) freeze time (-10°C, within freezer); (d) storage time (5°C, within refrigerator).

whilst resisting a higher degree of deformation than the agar gel, having greater values of γ_y.

Molecular weight effects are clear in amplitude sweeps of both PVA cryogel and PVA/agar double network hydrogels (Figure 4a). In the PVA gels, G'_P had values of ca 0.2, 0.9, and 1 kPa at 61, 145, and 195 kg mol^{-1} M_n, respectively. This increase in elasticity is ascribed to the increased likelihood of polymer chains bridging crystallites in the PVA as molecular weight increases. Additionally, in the non-crystalline phases, the increased molecular weight enhances the likelihood of polymer entanglement occurring. The relationship between G′ and G″ on strain shows another distinct effect. The system switches from the classical yield behaviour in the 61 and 145 kg mol^{-1} PVA, to a strain hardening-type effect in the 195 kg mol^{-1} cryogel. Based on the G'(γ) analysis in Figure 4a, the observed upturn in G' for the 195 kg/mol PVA gel is indicative of strain hardening behaviour. This finding aligns with results reported in other relevant studies [23, 24] on PVA hydrogels, where an increase in storage modulus (G') with increasing strain amplitude (γ) is associated with strain hardening. Strain hardening has previously been reported in PVA/borax hydrogels, in which the mechanisms of the effect were probed [23]. The phase angle of the 195 kg mol^{-1} PVA/agar double network hydrogel decreases monotonically with strain (e.g, $\delta = 10.78$ and 11.91 at 0.1 and 100 % oscillatory strain, respectively), which indicates that the strain hardening effect is likely contributed to by non-Gaussian stretching of the polymer chains [23]. The PVA/agar double network hydrogels show a similar trend to the PVA cryogel, with molecular weight causing toughening of the system, giving rise to G'_P of 5.7, 11.7, and 14.1 kPa, for 61, 145, and 195 kg mol^{-1} PVA, respectively. γ_y was 26 and 86 % for the 61 and 195 kg mol^{-1} PVA/agar systems, approximately 5 and 17-fold greater than agar alone. The intermediate M_n, 145 kg mol^{-1} showed no γ_y with tan $\delta < 1$ at all strains measured.

Frequency sweeps (Figure 4b) were recorded for all materials. This technique probes the effect of angular frequency on G′ and G″ at a fixed small amplitude within the LVR (0.1 %). The rheograms obtained give characteristic profiles dependent upon the nature of the system. Gels are often defined as having tan $\delta < 1$ at all frequencies. Gels can be further split into chemical, permanent, and physical, transient gels. Chemical gels are characterised by permanent, or long-lived, network junctions. That results in frequency sweeps where G' and G″ are frequency

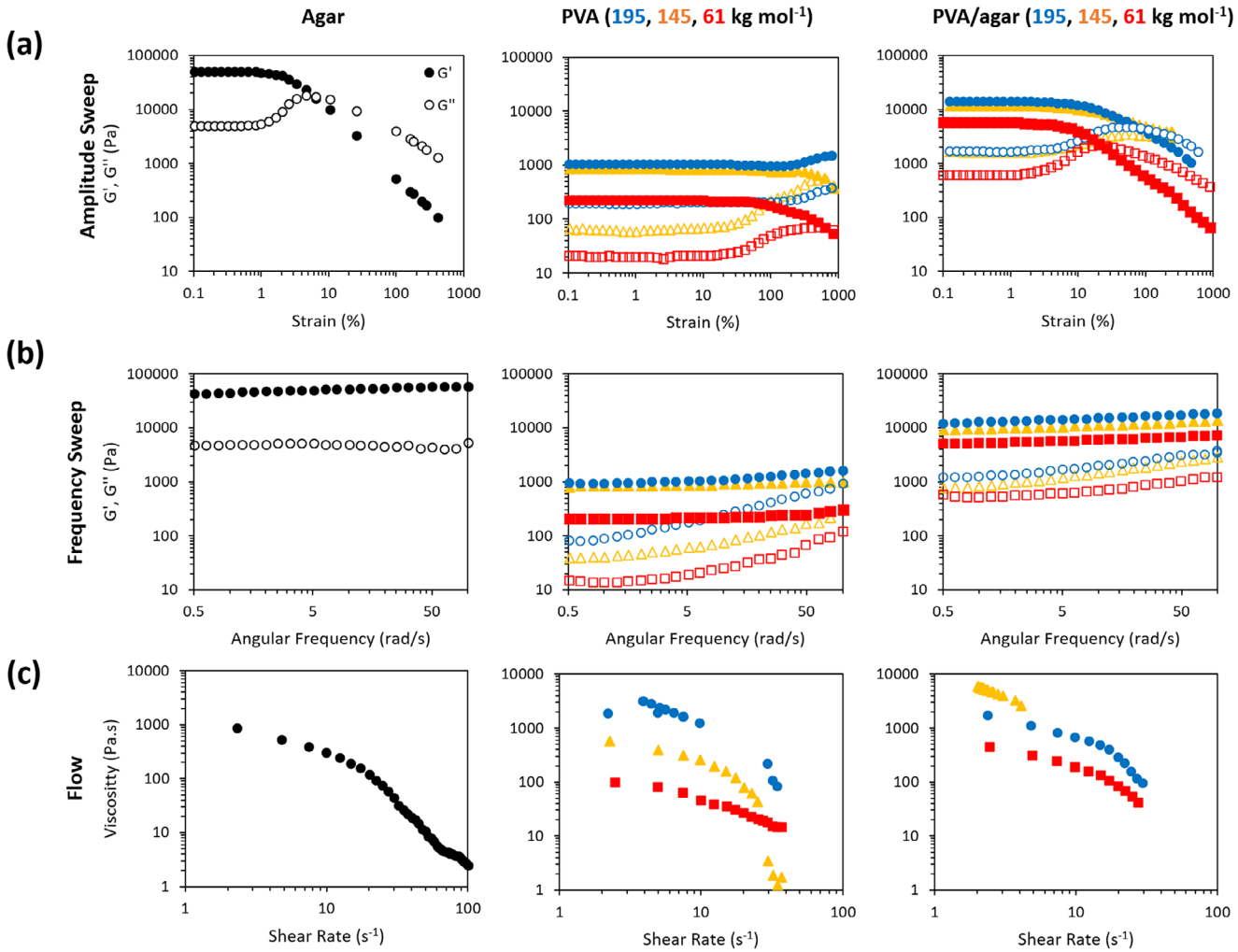

FIGURE 4 | Rheological evaluation of agar, PVA, and PVA/agar double network (DN) hydrogels, including (a) amplitude sweeps, (b) frequency sweeps, and (c) flow rheology. Storage modulus G′ is shown in closed symbols, and loss modulus G″ is shown in open symbols. For PVA and PVA/agar: 195, 145, and 61 kg mol^{-1} M_n PVA is shown in blue circles, yellow triangles, and red squares, respectively.

independent. This criterion arises from "permanent" covalent networks which do not have characteristic frequencies at which elastically-active chains are disrupted [25, 26]. Physical gels are formed by transient junction networks that are capable of relaxing within the time window of the measurement, resulting in G', G″ showing frequency dependence. The agar, PVA, and PVA/agar systems were all shown to have low frequency dependence, showing them to behave as permanent gels within the frequency range probed.

Flow rheology was then conducted on the materials (Figure 4c). In these experiments, the shear applied to the sample is not oscillatory, and thus the structure at rest is not preserved. The experiment is considered to mimic high shear applications, such as flow. In these experiments, the apparent viscosity can be determined as a function of shear rate. The agar material shows typical shear-thinning behaviour along with the PVA cryogel, which shows pseudoplastic rheology with the rank order viscosity 61<145<195 kg mol^{-1}. The PVA/agar double network hydrogels exhibit a nonmonotonic effect of molecular weight, giving the rank order viscosity: 61> 195> 145 kg mol^{-1}. The 145 kg mol^{-1} PVA/agar hydrogel gave particularly great resistance to deformation, reaching the maximal torque of the instrument.

Thermal effects on the PVA/agar systems were also evaluated by small-amplitude oscillatory temperature ramps (Figure 5). Agar (6% w/v) shows a softening with temperature but remains a weak gel (tan $\delta < 1$) even at 90°C, confirmed in frequency sweeps. PVA cryogel shows a distinct profile, with a two-stage melt, one at ca 25°C and another at ca 75°C. The first melt is putatively assigned to transient physical interactions in the system via non-crystalline domains, which leads to a reduction in G′ and G″ but without loss of the gel network formed from crystallites. The second melt at 75°C aligns with the melt of these crystalline domains. As such, at 90°C, frequency sweeps confirm a liquid-like behaviour. The PVA/agar double network hydrogels exhibit a reduction in G′ and G″ in line with the melting of the PVA crystallites (ca 75°C), but retain a gel state, also apparent in the frequency sweeps. A cooling curve was also determined for the PVA/agar system, which shows an incomplete recovery of gel strength due to the irreversibility of the PVA melt, which requires freezing to induce cross-linking via crystallisation.

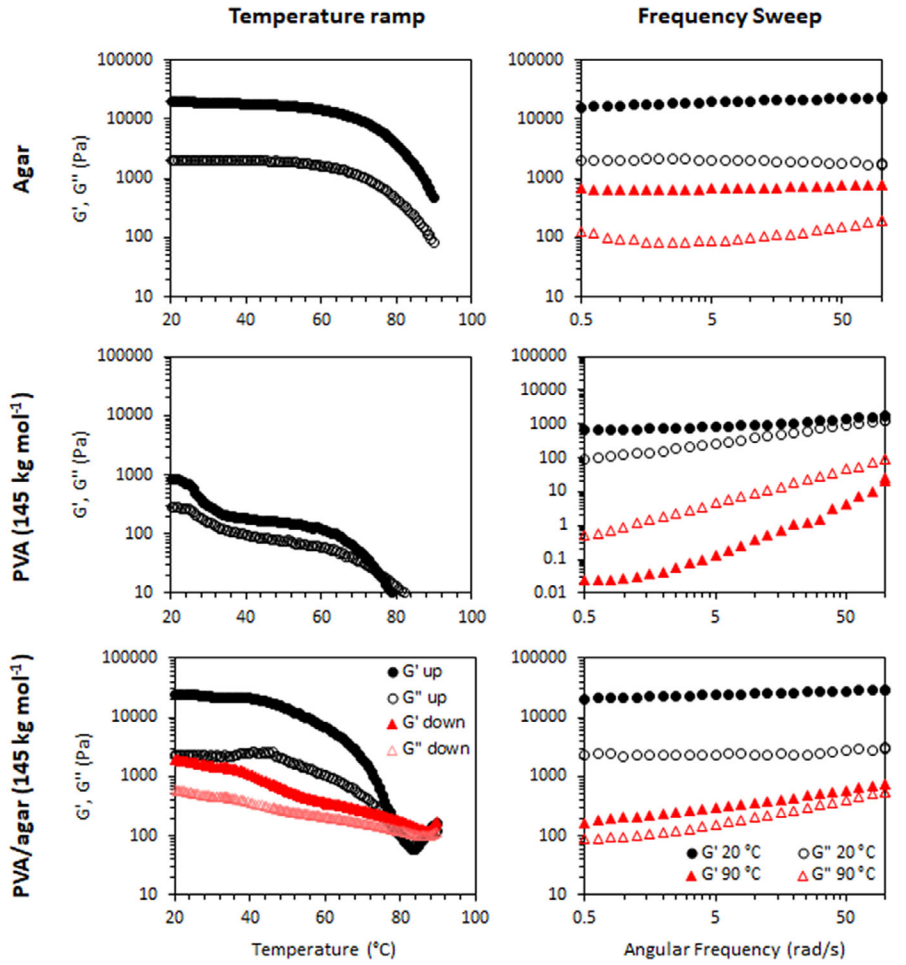

FIGURE 5 | Rheological study of thermal effects in agar, PVA, and PVA/agar double network hydrogels, using 145 kg/mol^{-1} PVA. Temperature ramps were conducted at 6.283 rad/s and 0.1 % strain heating between 20°C and 90°C (left), showing the cooling "down" curve in red for the PVA/agar hydrogel. Frequency sweeps were conducted (right) at both 20°C and 90°C, shown in black and red, respectively. G' is shown in filled symbols, G″ is shown in open symbols.

Tensile testing was then conducted on the PVA/agar double network hydrogels (Figures 6a,b). The 61 kg mol^{-1} materials were dramatically weaker than the other two, yielding at 2 kN m^{-2} and a strain of 0.4. The 195 and 145 kg mol^{-1} double network hydrogels exhibited dramatic increases in strength, reaching yield stresses of 120 and 134 kPa, with yield strains of 2.3 and 2.5, respectively. To benchmark this data, the yield stress of 120 kPa approaches human cartilage [27, 28]. Furthermore, the 145 and 195 kg mol^{-1} PVA/agar double network hydrogel exhibited evidence of strain hardening, as observed in the PVA cryogel (195 kg mol^{-1}) during oscillatory amplitude sweeps. Elastic moduli calculated from linear fits of the 0.1–0.2 tensile strain region (Figure 6 c,d) gave the rank order 61<195<145 kg mol^{-1}, with values of 6, 19, and 33 kPa, respectively. The 145 kg/mol sample outperforms the 195 kg/mol PVA in tensile tests, although rheological analysis shows that the latter has a slightly higher storage modulus due to its greater entanglement density (as shown in Figures 4a,b). The greater entanglement in the 195 kg/mol sample restricts chain mobility, limiting strain-induced alignment and crystallization. In contrast, the 145 kg/mol PVA strikes a better balance—providing sufficient entanglement for load-bearing while maintaining enough mobility for effective molecular orientation and crystallization—resulting in superior tensile strength and ductility. This observation aligns with findings from other studies and underscores

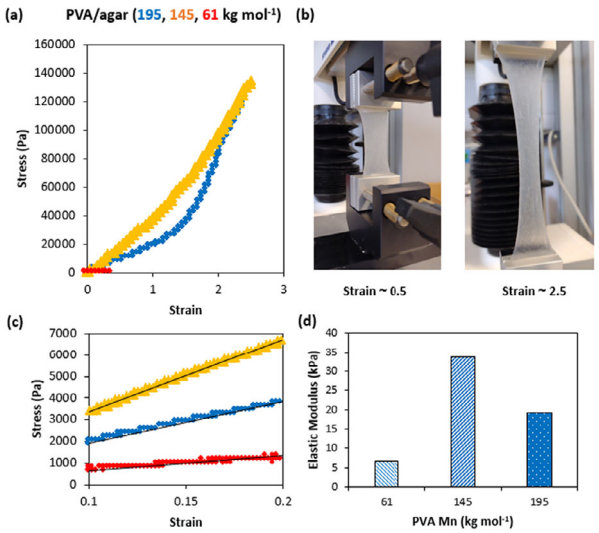

FIGURE 6 | Tensile testing of PVA/agar with 61 (red), 145 (yellow), and 195 (blue) kg mol^{-1} PVA (a). Photographs showing 145 kg mol^{-1} PVA/agar double network hydrogel material at low and high levels of tensile strain (b), Note that the stress-strain curves are cut at the point of yield. The 0.1–0.2 strain region is expanded to demonstrate linearity (c), the gradient of this fit is the elastic modulus (d).

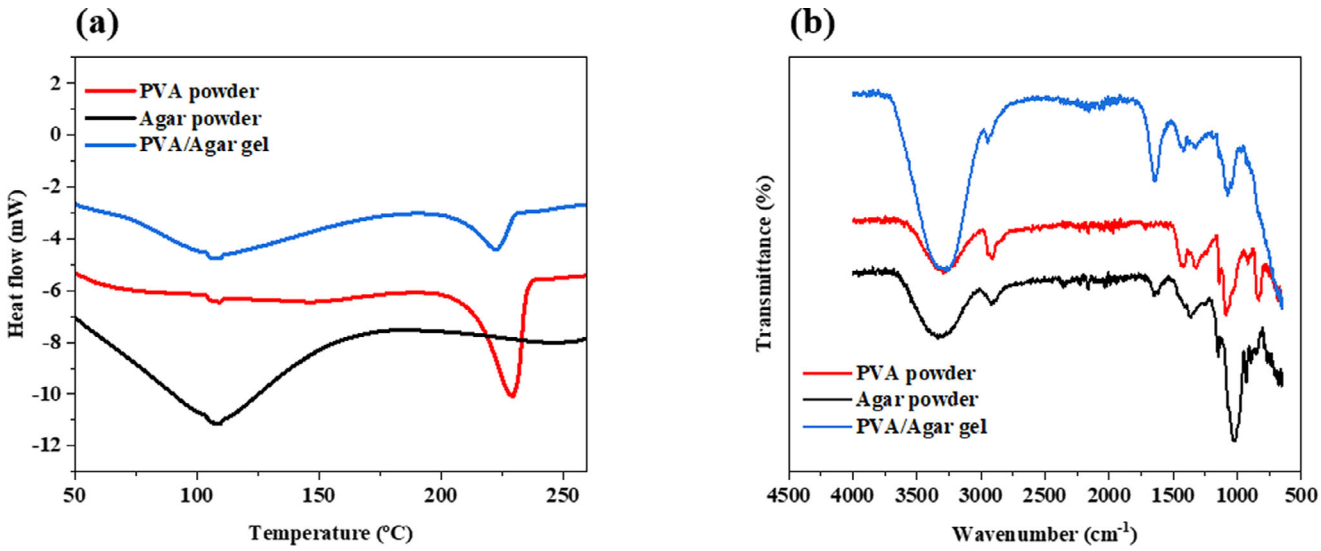

FIGURE 7 | DSC traces (a) and FTIR (b) of the raw polymers and PVA/Agar gel samples.

the distinct molecular mechanisms governing shear and tensile responses [29, 30]. It is worth mentioning, for benchmarking the elastic modulus of the PVA/agar gel, that human muscle has an elastic modulus of approximately 5–170 kPa, while an 8% chemically cross-linked acrylamide SDS-PAGE gel has a modulus of around 9 kPa [28]. The system behaves differently under extension than under low shear oscillatory rheology, in which the materials gave the rank order of G′ 61< 145< 195 kg mol^{-1}.

The thermal DSC traces of the raw polymers and 145 kg mol^{-1} PVA/Agar gel are shown in Figure 7a. The observed melting peak of raw PVA and Agar was 221.64 ± 5.85 °C and 109.40 ± 1.20 °C, respectively. The PVA/Agar gel has shown two distinct clear peaks at 227.13 ± 2.37 °C and 108.15 ± 2.15°C. There is no statistically significant difference in their results in comparison to the pure powder format. The closely matching melting peaks of PVA and Agar with the corresponding peaks in the blended gel confirm that the two polymers showed physical crosslinking in the matrix. FTIR analysis of the system is shown in Figure 7b. The main peaks of PVA were observed at 3400 cm^{-1} assigned to the O—H stretching vibration of the hydroxyl group, 2900 cm^{-1} CH_2 asymmetric stretching vibration, 1600 cm^{-1} C═O carbonyl stretching, 1400 cm^{-1} CH_2 asymmetric stretching vibration, 1300 cm^{-1} C—H deformation vibration, 1081 cm^{-1} C—O stretching of acetyl groups and 900 cm^{-1} C—C stretching vibration [25]. The main peaks observed for the Agar were similar to the PVA, with the difference of the peak at 1647 $cm^{-1,}$ which is also observed in the PVA & Agar. The FTIR spectra of the raw polymer and PVA/Agar gel have no detectable differences in peak position, giving no indication of interaction between PVA and agar. Overall, this indicates that the likely dominant effects causing elasticity in the gel system are physical interactions within the two constituent macromolecules, rather than synergic effects between the two.

4 | Conclusions

Tough double-network hydrogels may be formed from two physical systems, agar and PVA. This process requires agar network formation from a heat-cool cycle, followed by PVA crystallisation using freeze-thaw cycling. The resultant materials combine the mechanical properties of both elements to give a hydrogel with high stretchability and toughness, without the need for chemical cross-linking. Differential scanning calorimetry and FTIR spectroscopy indicated that both networks were formed without substantial emerging structures formed from agar-PVA interactions. Molecular weight was shown to impact the strength of the materials, determined by needle-injection, tensile testing, and shear rheometry, with higher molecular weight PVAs forming tougher gels. In high-strain experiments, a 145 kg mol^{-1} PVA/agar material gave the strongest response, which may be used for the development of tough hydrogel systems in future research. The materials are attractive for applications that require high water content hydrogels with robust mechanical characteristics.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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