

Effect of processing conditions on gel formation in ternary cellulose acetate systems

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Abstract A series of ternary systems composed of cellulose acetate (CA), N,N-dimethylacetamide (DMA), and water were prepared by varying the mixing temperature and order of component addition with increasing water content. The viscoelastic properties of the resulting ternary systems were measured using steady state and dynamic rheology. The CA/DMA/H₂O mixture formed physical gels at 17.5 and 19 wt% water concentrations after heating to 50 and 70/90 °C, respectively. Gel formation was characterized by the loss of a Newtonian plateau in the steady state as well as the transition of the elastic (G') modulus becoming greater than the viscous (G'') modulus in the dynamic state. The order of component addition dramatically affected phase behaviour. Adding CA to the DMA/water solution resulted in lower moduli gels and the formation of a two-phase phase separated system at high nonsolvent contents in those prepared at low temperatures. The kinetics of phase separation was improved by subjecting the gels to a thermal treatment of 90 °C. In this case, the gels previously heated at 50 and 70 °C showed a one-phase phase separated gel with higher viscous and elastic moduli.

Keywords Cellulose acetate · Network gels · Phase separation

Introduction

Materials made from renewable resources have gained popularity in recent years due to the rapid depletion and increasing energy demand for fossil fuels. Cellulose, the most abundant yet perhaps most underutilized biopolymer, can be chemically or mechanically modified to complement or replace certain materials currently dominated by the synthetic polymer market. One example is cellulose acetate (CA), which dissolves in many common organic solvents (e.g. acetone, chloroform, and THF) and as a result are utilized in various applications including films, filters, coatings, and membranes.

Solvent-induced phase separation is of current interest as a means towards asymmetric membrane formation for separation and purification purposes (Shibata 2004); acetate membranes have been used, for example, in the desalination industry for the purification of drinking water. Cellulose acetate is the ideal polymeric template as it is biocompatible and contains both hydrophilic (OH groups) and hydrophobic (acetyl groups) components. This gives it a good balance between flux and rejection. The most common method for the production of acetate membranes is by

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phase-inversion where the polymer solution undergoes gelation by phase separation followed by subsequent coagulation by either solvent evaporation or contact with a non-solvent. In the latter case a ternary system forms in the coagulation bath.

Viscoelastic and microstructural properties of these ternary systems are dependent on the conditions in which these gels are prepared. Specifically, the structure and concentration of the solvent can influence the pore size of the gel formed (Reuvers et al. 1986; Kadla and Korehei 2010, 2011). For example, non-solvents with hydrophilic and hydrophobic components are able to manipulate the rheological properties of the resulting gels (Kadla and Korehei 2010, 2011). CA solution studies have also show that phase separation can be enhanced by temperature changes (Suzuki et al. 1981) where intermolecular associations lead to physical cross-linking and the formation of three dimensional networks. Both intermolecular hydrogen bonding and hydrophobic acetyl interactions between the polymer and the solvent affect its behaviour in solution, which in turn can ultimately influence gel formation. Recently we found that gel properties are dramatically affected by the method of preparation, i.e. component order of addition; the addition of CA to a DMA/water solution lead to a two-layer system with a clear polymer solution over a polymer gel, whereas a homogenous gel was obtained when water was added to a CA/DMA solution. Moreover, the prior could be made homogeneous upon heating to 100 °C (Appaw et al. 2010). Therefore, it is hypothesized that the cellulose acetate ternary system will exhibit different rheological and microstructural properties when prepared under different conditions and subjected to different thermal treatment. Higher temperature facilitates polymer dissolution and increases the ability of CA to interact with the solvent and non-solvent components as the system cools and gels. In this paper we report the effect of mixing temperature and the order of component addition on the formation of the CA ternary system using steady state viscosity and dynamic rheology.

Experimental materials and methods

Materials

Cellulose acetate (39.7 wt% acetyl content, average M_n ca. 50,000) was purchased from Sigma–Aldrich

and used as received. Reagent grade N,N-dimethylacetamide (DMA) was purchased from Fisher Scientific and used as received.

Ternary system preparation

Two gel preparation methods were investigated; the addition of water (non-solvent) to a CA/DMA solution (Dissolution method 1) and the addition of CA to a DMA/water solution (Dissolution method 2).

Dissolution method 1

A bulk solution (150 mL) of cellulose acetate (14.3 wt% in DMA) was first prepared in a 250 mL Erlenmeyer flask. The mixture was heated to 100 °C in an oven for about 20 min and mechanically mixed to produce a homogeneous solution. The mixed solvent systems were then prepared by adding the appropriate mass and proportion of water/DMA to the CA/DMA solution in 20 mL glass scintillation vials. The final CA concentration was 10 wt% and the total weight of each ternary system was 15 g. Five water (non-solvent) concentrations were prepared: 12.5, 15, 17.5, 20, and 22.5 wt%. In each case the non-solvent was added at room temperature and the samples were mechanically mixed and conditioned for 24 h. The samples were then heated at three temperatures; 50, 70, and 90 °C for 10 min in an oven and mixed again to ensure complete miscibility. Once cooled, they were purged with nitrogen and left at room temperature for exactly 1 week prior to analysis.

Dissolution method 2

Using 20 mL glass scintillation vials, samples were prepared with 1.875, 2.25, 2.625, 3, and 3.75 g of water and made up to 13.5 g with DMA. The samples were equilibrated to room temperature and 1.5 g of CA was added to each vial to make the final mass 15 g. Again, three sets of five concentrations of non-solvent, 12.5, 15, 17.5, 20, and 22.5 wt% were prepared. The vials were mixed and conditioned for 24 h at room temperature and then heated to 50, 70, and 90 °C for 10 min in an oven and mixed mechanically to ensure complete miscibility. The samples were purged with nitrogen and stored at room temperature for exactly 1 week prior to analysis.

Rheology

Rheological experiments were conducted with an AR 2000 Rheometer (TA Instruments, New Castle, DE) at 25 °C using either a cone (60 mm diameter, 2° angle) and plate or parallel plate (25 mm diameter) geometry. For solutions, the cone geometry was lowered to the adjusted zero gap and excess solution around the geometry was removed. For gels, the glass vial in which they were made was carefully broken and removed to maintain the gel intact and care was taken not to disrupt the gel structure. A sharp blade was then used to slowly cut the gel evenly to a thickness of 1–2 mm and then mounted on the rheometer. In the case of biphasic gel systems, rheological measurements were performed on the lower gel-like layer, where the upper liquid layer was removed by pipette before cutting and loading the gel into the rheometer. A variable geometry gap of 1,000–2,000 μm with an applied force of less than 0.2 N was applied for the gel samples with the parallel plate geometry. Steady shear measurements were performed by subjecting a sample to steady shear at a rate of 0.01–500 s^{-1} . The viscosity (η) was then measured as a function of steady shear rate. Prior to frequency sweep experiments, dynamic stress sweep experiments (0.01–1,000 Pa) were performed to determine the linear viscoelastic (LVR) region while maintaining a constant frequency of 1 Hz. Stress sweep experiments were also used to determine the critical stress or onset of nonlinearity of the gels. This is the point where the samples no longer exhibit a linear stress–strain relationship, but rather deviate from linear viscoelastic behaviour and start to deform or rupture. The elastic (G') and viscous (G'') moduli were determined by frequency sweep experiments over the range of 0.1–100 rad/s at a constant oscillation stress of 0.1 or 1 Pa depending on the LVR.

Data analysis

All rheological analyses were performed within an error of less than 10%. The error was determined by running replicates per sample (minimum 4 replicates per sample). The multiple samples were averaged and the difference between the highest and lowest values was less than 10%. This was a consistent case for all of the samples studied. Therefore, rheological analyses were run in triplicates and the results were within the

10% error range. The raw data presented is from one of the replicate runs.

Results and discussion

Dissolution method 1: effect of varying mixing temperature on ternary system formation

Aggregation-induced phase separation via non-solvent addition has been utilized as a method to create uniform pore structures for membrane formation (Smolders et al. 1992; Reuvers et al. 1986; Appaw et al. 2010; Kadla and Korehei 2010, 2011). CA/DMA/water ternary systems were prepared with different water concentrations and mixing temperatures: 50, 70 and 90 °C. The ternary systems exhibited Newtonian behaviour at low shear stress followed by shear thinning as shear stress increased (Fig. 1), consistent with previously reported results (Appaw et al. 2007; Kadla and Korehei 2010).

At low non-solvent concentration (12.5 and 15 wt%), similar viscosity curves are observed for the different mixing temperatures. However, at higher water content (17.5 wt%) a difference in viscosity profiles is apparent between the mixing temperatures. The samples prepared at 50 °C shows a disappearance of the zero-shear viscosity plateau while those prepared at 70 and 90 °C still show polymer solution-like behaviour and lack structure development.

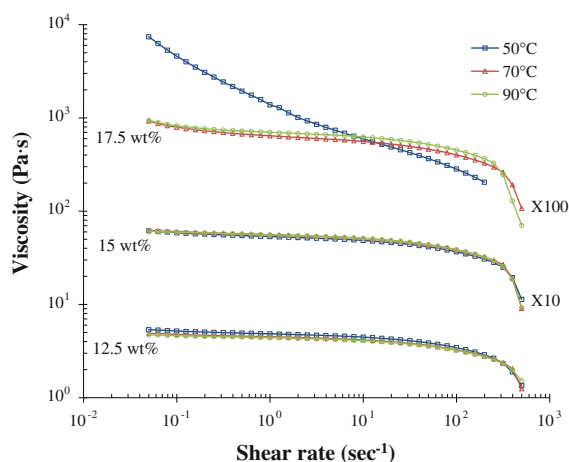


Fig. 1 Effect of mixing temperature on steady shear viscosity for ternary systems with 10 wt% CA and 12.5–17.5 wt% water. Samples were prepared using dissolution method 1- addition of water to a CA/DMA solution

The disappearance of the Newtonian plateau at the lower mixing temperature marks the start of the non-Newtonian or power-law region suggesting the development of microstructure along with the intensification of intermolecular interactions within the sample. The observed shear thinning is likely caused by disentanglement of the polymer coils in solution and/or increased orientation of the polymer coils in the direction of flow (Clasen and Kulicke 2001). At this point, the system starts to become cloudy most likely due to aggregate formation.

Increasing viscosity with non-solvent content is an indication of increasing molecular entanglement in the polymer solution (Hoernschemeyer 1974). These entanglements, or polymer–polymer interactions, act as temporary cross-links or junction zones, decreasing the relative motion of molecules and their ability to flow (Winter 1999; Ross-Murphy 2005). Figure 2 illustrates the progressive increase in shear viscosity with increasing non-solvent content for the different temperatures, 50, 70, and 90 °C. Data was obtained by extrapolating the viscosity curves to zero shear. Preparing the gels at lower temperature (50 °C) produced ternary systems with the highest viscosity values at the liquid to solid transition; between 17.5 and 19 wt% non-solvent. Once a solid gel formed at ~20 wt% water, the viscosity values were within 20% of each other regardless of the different preparation temperatures used.

At low water contents (10–12.5 wt%) the polymer is solubilised to a greater extent than the systems with greater than 17.5 wt% water, as indicated by the lower solution viscosity and onset of phase separation (Fig. 2). In concentrated solutions, viscosity increases with increasing water concentration more rapidly in poor solvent systems than in good solvent systems. As solvent power or range of solvency decreases as the number of chain entanglements increases, the solvent–non-solvent system is unable to solubilize the polymer in poorer solvent systems (Hoernschemeyer 1974). Thus, samples mixed at 50 °C likely contain more chain entanglements or polymer–polymer association complexes than those mixed at 70 and 90 °C.

Figure 3 shows the elastic (G') and viscous (G'') moduli as a function of frequency at three different water contents for 10 wt% CA solutions prepared at 90 °C. According to the Winter and Chambon (1986) criterion for gel formation both the viscous and elastic moduli should have the same slope. From Fig. 3 it can

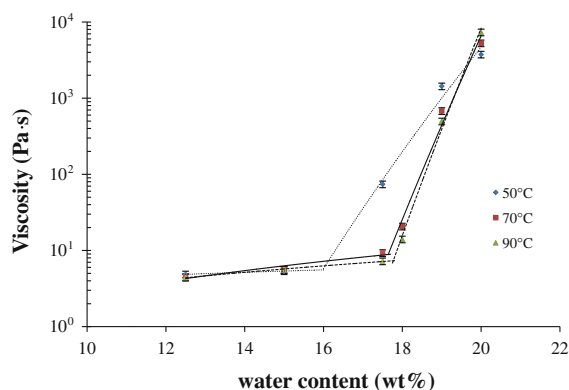


Fig. 2 Effect of mixing temperature on the viscosity enhancement of 10 wt% CA ternary systems with 12.5–20 wt% water (values extrapolated to zero-shear viscosity). Data represent the average of 3 replicates

be seen that at 15 wt% non-solvent, both moduli are increasing and are relatively frequency dependent. By 20 wt% non-solvent, both moduli appear to be frequency independent with G' higher than G'' at small angular frequencies and a cross-over is observed at an angular frequency of 3.40 rad/s. Increasing water content leads to greater entanglement in the system leading to slower relaxation times for the polymer chains. The entanglement points now act more like a fixed network. Consequently, the ability of the polymer network to store the imposed energy increases, and therefore starts to behave more like an elastic solid. As the ternary system reaches 25 wt% water, solid gel formation takes place and both G' and G'' are frequency independent with slopes $\cong 0$ and $G' > G''$, characteristic of a 3-dimensional elastic gel.

Physical gels consist of extensive macromolecular clusters held together by interactions such as hydrogen bonding and hydrophobic interactions. In basic solvents like DMA, the carbonyl group interacts with the hydroxyl groups of the CA. With the addition of water, a hydrogen bond donor and acceptor, new interactions form between the non-solvent and DMA as well as non-solvent and CA, dramatically affecting the systems viscoelastic properties (Appaw et al. 2010). The stress sweep experiment can be used as an indicator of structure stability, where higher elastic modulus is associated with a well-dispersed and stable system (Kavanagh and Ross-Murphy 1998). Figure 4 shows that the stress amplitude of the elastic modulus of the CA ternary system increases with water content. At low oscillation stress levels the materials are relatively

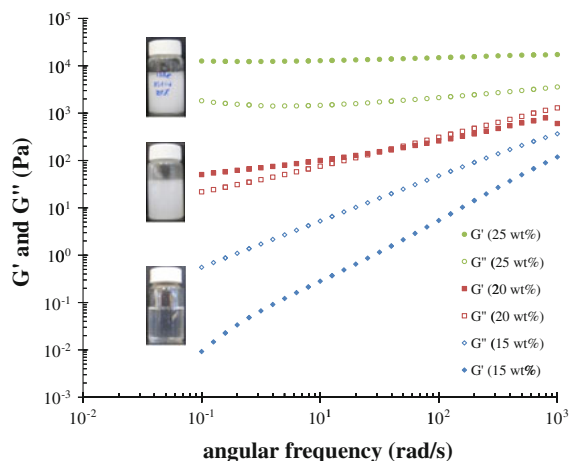


Fig. 3 Elastic (G') and viscous (G'') moduli for 10 wt% CA solution at 15, 20, and 25 wt% water mixed at 90 °C. With increasing water content a transition can be visually observed from a clear solution, to a cloudy system, and ultimately to a gel

independent of the applied stress, indicating that they are within the linear viscoelastic region (LVR). At non-solvent concentration below the gel point (15 wt%), G' remains almost the same for all three temperatures. However, above the gel point at 20 wt% non-solvent, the elastic modulus increases with increasing mixing temperature. In addition at high stress levels, shear thinning occurs as the aggregates start breaking up. It can also be seen that the critical stress increases with increasing oscillation stress, i.e. the onset of nonlinearity shifts to higher stress with increasing temperature making these gels strong-linked (Shih et al. 1990).

The effect of water content on G' and G'' in the CA ternary system prepared at 50 °C is shown in Fig. 5. As the water content increases, the samples slowly start showing gel-like features: $G' > G''$ and becoming weakly frequency dependent with G' having a slope of 0.10 and G'' a slope of 0.38, a pattern similar to that shown in Fig. 3 for 90 °C. It is of significance to note that at 20 wt% water content the samples prepared at 50 °C are already gels ($G' > G''$) and that both viscoelastic moduli within the same frequency range possess higher values than those in the system prepared at 90 °C, which undergo a G'/G'' crossover at this water content. Therefore, the ternary systems mixed by dissolution method 1 undergo a gel transition at lower non-solvent content and exhibit stronger viscoelastic properties when prepared at lower temperature.

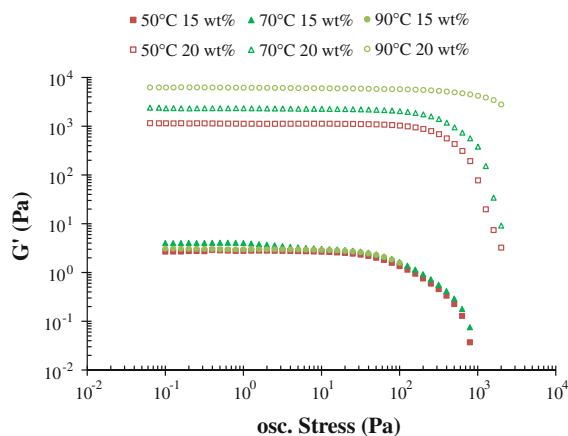


Fig. 4 Stress sweep experiment for samples with 10 wt% CA and 15–20 wt% non-solvent at different mixing temperatures. Experiments were performed at a fixed frequency of 1 Hz

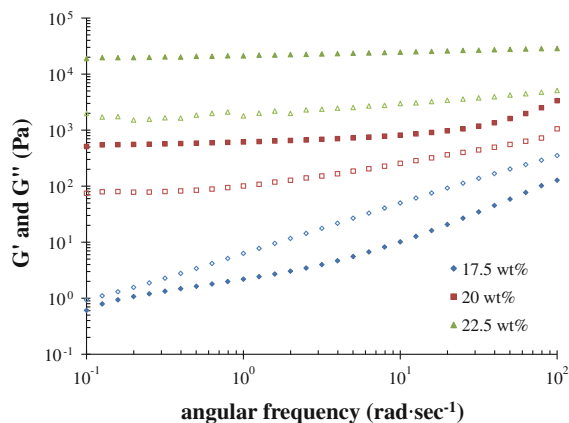


Fig. 5 Frequency dependence of the elastic and viscous moduli for 10 wt% CA/DMA/H₂O mixtures, mixed at 50 °C. G' is represented by solid filled shapes while G'' is unfilled

At the liquid to solid transition phase, the structure of the gel network can be considered as a collection of flocs, which, according to scaling theory, are fractal objects closely packed throughout the sample. The nature of these flocs can be classified as weak-linked or strong-linked depending on the values of the elastic moduli G' . Using scaling theory, Shih et al. (1990) described strong-linked gels as an aggregated network where particle interactions between the flocs (inter-flocs) are stronger than those within the flocs (intra-flocs), while weak-linked gels have intraflocs stronger than interflocs. In the case of strong-linked gels, failure under deformation would occur through breaking the intrafloc linkages, and would be observed as a

decrease in the linear viscoelastic region as sample concentration increases under strain (Eissa and Khan 2005). Figure 6 shows the effect of increasing non-solvent on the elastic modulus as a function of percentage strain.

The gels mixed at the three different temperatures were all classified as strong-linked gels, but the rate of change in nonlinearity differed between temperatures. The system prepared at 50 °C showed the largest change in nonlinearity, while those formed at 70 and 90 °C were essentially the same. With increasing non-solvent content, the gels formed at 50 °C will be more sensitive to strain. Despite the higher values of G' , gels heated at 50 °C exhibited lower strain tolerance and ruptured at lower strain levels compared to those heated at higher temperatures. These results imply that heating at 50 °C creates networks with relatively weaker interfloc links.

For strong-linked gels, $G' \sim \phi^n$, where ϕ is the volume fraction and the power exponent $n = (d + x)/(d - D)$, where x is the backbone fractal dimension of the flocs, d is the Euclidean dimension, and D is the gel fractal dimension. For colloidal gels, the backbone fractal dimension ranges from 1 to 1.3 (Wu and Morbidelli 2001). For our calculations the value of x was arbitrarily set to the midpoint 1.15 as the range of x only differs by 0.3 and would change the values of D by $\sim 2\%$ (Eissa and Khan 2005). For strong-linked gels the breaking of bonds occurs within a floc; therefore the limit of linearity ($\gamma_0 \sim \phi^{-(1+x)/(d-D)}$) is the point at which the weakest bonds forming the network break and the linear elastic behaviour

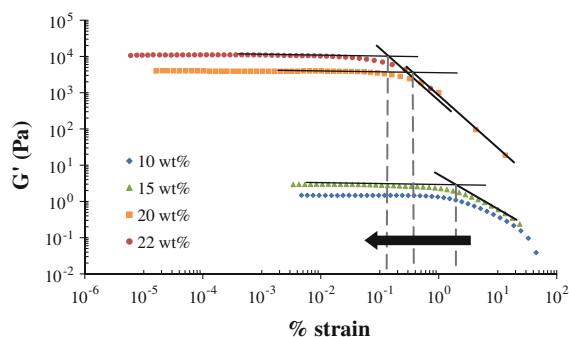


Fig. 6 Elastic modulus versus % strain for a 10 wt% CA ternary system mixed at 50 °C. The limit of linearity (percentage strain at the intersection between the tangent of the drop in G' and the linear viscoelastic region) shifts to lower strain as non-solvent concentration increases from 10 to 22 wt%

vanishes. By equating experimental and theoretical power law exponents and substituting $d = 3$ (particles propagate in three dimensions), the fractal dimensions D for the systems mixed at 50, 70, and 90 °C were found to be ~ 2.91 . Similar fractal dimension values ($D \sim 3$) have been reported for fat crystals (Narine and Marangoni 1999; Marangoni 2002). The similar values of D for the various gels suggest similar structures, with the high fractal dimension values being associated with more homogeneous spatial distributions of network mass.

Fractal dimensions approaching 3 are indicative of slow aggregation (Amal et al. 1990), or reaction-limited aggregation (RLA) where cluster formation is partially reversible and particles rearrange in order to form multiple contacts with neighbouring particles (Shih et al. 1990). Thus, the fractal dimension close to 3 for the CA/DMA/H₂O system suggests a RLA mechanism and the formation of a compact aggregate three-dimensional network.

Since the ternary system studied forms physical gels, the network structure can be disrupted by the application of thermal energy. By applying a temperature sweep, one can visually observe the transition from gel at 25 °C to solution as the temperature increases. This transition can also be observed through changes of the elastic modulus. Figure 7 shows the elastic and viscous modulus of 20 wt% non-solvent gels with 10 wt% CA prepared at various temperatures undergoing a temperature sweep at 1 °C/min from 25 to 80 °C. A transition from a completely opaque to a clear colorless solution could be visually observed.

In this oscillation experiment, both elastic and viscous moduli decrease with increasing temperature as the mobility of the polymer increases with thermal energy. The elastic modulus decreases faster than the viscous modulus. The dependence of G' and G'' on temperature provides a good indication of the transition from solution to gel and vice versa. We can classify three regions in the ramp experiment. The first region is characterized by a relatively low dependence on temperature for both G' and G'' . This region is smaller for the gel mixed at 50 °C than at 70 and 90 °C. Beyond this region at above approximately 40 °C, G' and G'' start to decrease rapidly as more cross-links break until reaching a crossover point at about 42, 55, and 52 °C for samples mixed at 50, 70, and 90 °C respectively. G'' is now greater than G' and the samples are now solutions.

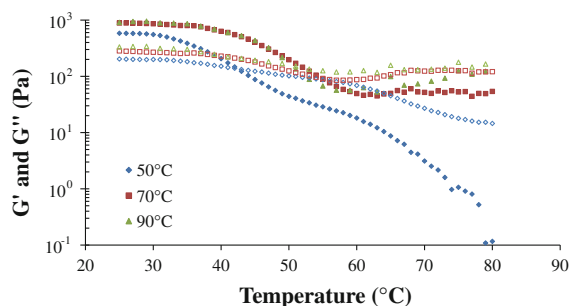


Fig. 7 Temperature sweep experiments conducted at 1 °C/min for 10 wt% CA and 20 wt% non-solvent mixed at 50, 70, and 90 °C. G' is represented by solid filled shapes while G'' is unfilled

The gels formed at 50 °C undergo the gel-solution crossover at lower temperature than those formed at 70 and 90 °C. This is due to the interactions between the components being much weaker as less thermal energy is required to transition from an elastic solid to a solution; this system is not as homogeneous as those mixed at higher temperature. The rate of decrease in both G' and G'' is also much faster for the gel mixed at 50 °C, exhibiting a stepwise decrease in both moduli with increasing temperature indicating lower stability of the gel. Those gels mixed at 70 and 90 °C were able to maintain relatively temperature independent moduli both before and after the G' and G'' crossover point.

This relationship between mixing temperature and thermal response correlates well with the other observations where strong-linked gels prepared at 70 and 90 °C were less sensitive to changes in deformations (strain) with increasing water content than gels prepared at 50 °C. Thus, the ternary system prepared at 50 °C has weaker interfloc links despite possessing higher G' at low frequency ranges of 1 rad/s. This behaviour is typical of a physical weakly cross-linked gel, in which there are a minute number of cross-link connections and a system of finite distribution of macromolecular clusters (Winter and Mours 1997).

Dissolution method 2: effect of varying mixing temperature on ternary system formation

Adding the polymer last to the ternary system and then heating the mixture produced a system similar to that formed with dissolution method 1 at high temperature (90 °C) but differed when mixed at lower temperature

(50 and 70 °C). Figure 8 shows the change in viscosity as non-solvent content increases when the polymer is added to a solution of DMA and water (dissolution method 2). The viscosity values in this case, however, are less than those obtained with dissolution method 1 (see Fig. 1), signifying weaker polymer–polymer interactions in the ternary system.

At low non-solvent content Newtonian behaviour was observed at low shear rates followed by shear thinning at high shear rates. The shear thinning effect is pronounced at low shear rates for samples with higher water content. The non-Newtonian behaviour and disappearance of the Newtonian plateau implies the development of microstructure in the sample resulting from enhanced intermolecular interactions as non-solvent content increases, this is more evident in the samples heated at 50 and 70 °C.

The demixing behaviour in the ternary cellulose acetate solution occurs via liquid–liquid phase separation (spinodal decomposition) or the formation of aggregates (nucleation and growth) (Reuvers and Smolders 1987). During the gel formation process, the system is in a metastable state on cooling where it can either (1) separate into two liquid phases through nucleation and growth of one of the phases, or (2) demix due to polymer molecules aggregating and precipitate out of solution. Ternary systems phase separate via different mechanisms depending on the temperature and conformational changes in the polymer (Butler and Heppenstall-Butler 2003). In the case of dissolution method 2, the ternary system forms two

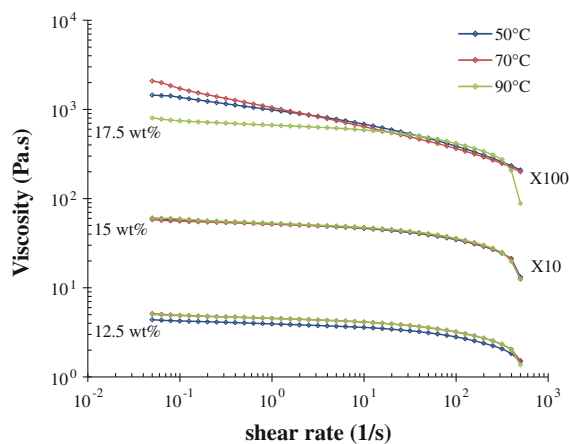


Fig. 8 Temperature effect on steady shear viscosity for a 10 wt% CA ternary systems at 12.5–17.5 wt% water, dissolution method 2- addition of polymer to a water/DMA solution

phases due to the slow rate of diffusion of the polymer into the DMA/H₂O mixture at high non-solvent content, where the kinetics of phase separation is likely faster than the kinetics of gelation. At higher temperatures, however, the polymer undergoes different conformational changes and is able to overcome the diffusion energy barrier to form new interactions in which the polymer is completely dissolved in solution. For dissolution method 1, the polymer was already in solution before the addition of non-solvent, which led to faster gelation resulting in a homogeneous phase, which was an elastic solid at high water content. Reuvers and Smolders (1987) have also pointed out that there is a difference between the temperature in which aggregates are formed or dissolved. The former is when gelation occurs and the latter is when the structure becomes a fluid.

A plot of G' and G'' as a function of frequency for samples prepared at 50 °C is shown in Fig. 9. A G' – G'' crossover is observed for the sample with 20 wt% non-solvent at an angular frequency of 18.2 rad/s. According to the Winter and Chambon (1986) criterion for gel formation, the system transitions from solution to gel at approximately 22.5 wt% water as both the log G' and log G'' have the same slope of 0.16.

Comparing the results obtained from dissolution method 1 to dissolution method 2, adding polymer last leads to lower G' and lower G'' for gels at the same non-solvent concentration (see Fig. 5). The samples are relatively frequency independent at 22.5 wt% non-solvent and exhibit elastic moduli an order of magnitude smaller than those produced using dissolution method 1.

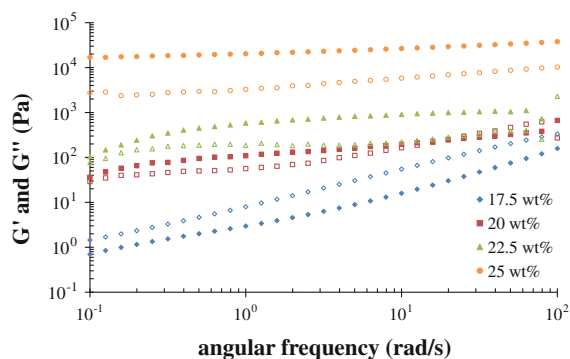


Fig. 9 Elastic (G' , filled shapes) and viscous (G'' , unfilled shapes) moduli of 10 wt% CA gels prepared at 50 °C as a function of frequency

Stress sweeps also indicate weaker gels compared to those obtained from dissolution method 1 (Fig. 10). At 15 wt% non-solvent content, the system is still in the solution phase and is relatively independent of the applied stress at low oscillation stress levels. The same shear thinning behaviour can be observed at higher stress. Close to the gel point at 20 wt% water, the sample prepared at 50 °C exhibited a stepwise decrease in G' with increasing applied stress. At this stage of network formation, the applied stress is sufficiently high enough to disrupt the cross-links, but cannot rupture the system. As a result, G' temporarily drops in the viscoelastic region until reaching the critical stress at around 400 Pa. With dissolution method 1, the system heated at 50 °C did not show any stepwise decrease in G' . Instead, it exhibited a long linear viscoelastic region followed by a sharp drop (system rupture) at high applied stress due to the formation of a strong network structure with infinite macromolecular clusters. For both mixing temperatures of 70 and 90 °C, the observed critical stress for samples prepared with dissolution method 1 was markedly higher than those prepared by dissolution method 2. This was also true for the elastic moduli of these samples.

Samples heated at 90 °C allow for more molecular movement within the ternary system, and the components rearrange in the most thermodynamically stable conformation as the gels cool. Samples heated at 50 °C, cooled, and reheated to 90 °C end up exhibiting almost the same viscosity as that heated initially to 90 °C. Listed in Table 1 are the viscosity values

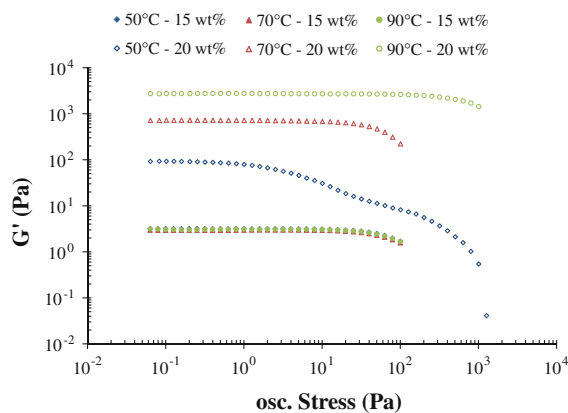


Fig. 10 Temperature effect on stress sweep for 10 wt% CA ternary systems prepared with dissolution method 2—addition of polymer to a water/DMA solution

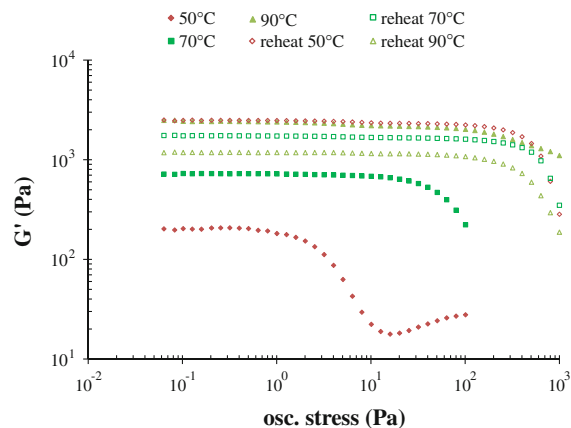
Table 1 Zero shear viscosity values for samples with 20 wt% non-solvent prepared by dissolution method 1, dissolution method 2 and dissolution method 2 reheated to 90 °C

Mixing temperature	Gel preparation method		
	Dissolution method 1 (Pa.s)	Dissolution method 2 (Pa.s)	Reheating to 90 °C (Pa.s)
50 °C	429.2 ± 10.9	66.43 ± 21.2	350.8 ± 10.4
70 °C	495.7 ± 32.4	95.11 ± 28.3	309.9 ± 16.8
90 °C	692.1 ± 14.1	419.4 ± 28.1	298.0 ± 9.1

extrapolated to zero shear for samples containing 20 wt% water prepared by the two different methods. These samples were then reheated to 90 °C to determine the thermoreversibility of the gels.

A characteristic of physical gels is that the non-covalent cross-links can reversibly form or break (Ross-Murphy 1995). In this case, thermal treatment led to the formation of new polymer–solvent–non-solvent interactions that led to a decrease in the elastic modulus. When the ternary systems are at the liquid to solid transition point, the viscosity decreases with increasing shear rate without a Newtonian plateau. Instead, the samples exhibit a shear thinning profile characteristic of aggregate formation. By reheating the ternary systems to 90 °C, the samples originally heated to 50 and 70 °C increased in viscosity whereas reheating a gel originally prepared at 90 °C decreased in viscosity. Interestingly none of the reheated samples had zero shear viscosity values as high as those originally prepared at 90 °C.

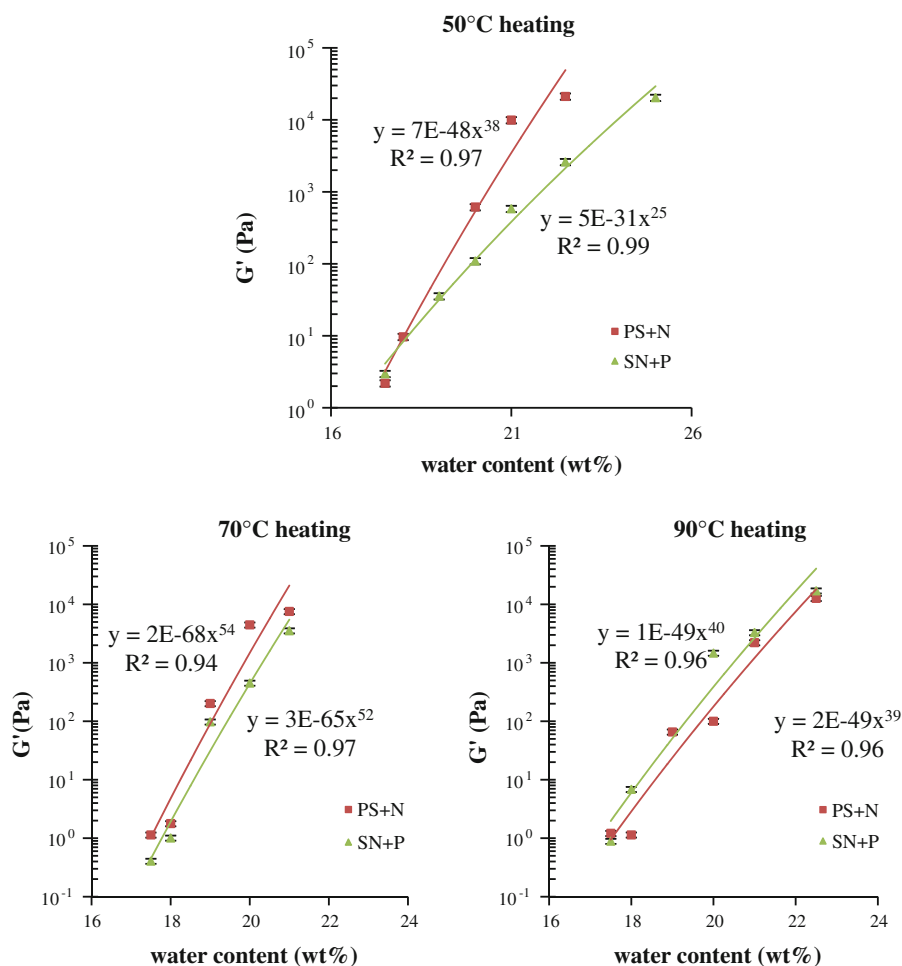
Plotted in Fig. 11 is the response of the elastic moduli to stress for samples heated at different temperatures and reheated at 90 °C. Samples heated at 50 °C show a stepwise decrease in G' at low oscillation stress, indicating weak network formation. After heating the sample to 90 °C, however, the modulus increases, exhibits a longer linear viscoelastic region and has a higher critical stress. Samples heated at 70 °C and further reheated to 90 °C also show an increase in elastic modulus and higher critical stress, leading to a more stable gel. The two-phase systems formed at 50 and 70 °C resulted in a homogeneous phase gel similar to that from dissolution method 1. Therefore, the results obtained from dissolution method 1 can be obtained with dissolution method 2 only by heating the gels to higher temperature.

**Fig. 11** Stress sweep experiment for 10 wt% CA gels prepared at 50, 70 and 90 °C as well as the corresponding gels reheated to 90 °C at 20 wt% non-solvent

The gels prepared using this CA/DMA/water ternary system have been shown to fractal in nature, therefore a power law behaviour should exist between G' and non-solvent volume fraction (Appaw et al. 2007, 2010). Figure 12 illustrates that the power law exponents vary between the different preparation temperatures and the different methods of addition (i.e. dissolution method 1 and 2). In dissolution method 1, the power-law exponent varied depending on the preparation temperature; about 38 for gels prepared at 50 °C, 54 for gels prepared at 70 °C, and 39 for the gels prepared at 90 °C. Similarly, the gels prepared by dissolution method 2 showed a similar trend wherein the power law exponents increased from 25 to 52 when mixed at 50 and 70 °C respectively, and decreased to 40 when mixed at 90 °C.

Previous studies with cellulose derivatives showed that phase separation in ternary systems with certain non-solvent concentrations is dependent on the dielectric constant of the non-solvent added (Khalil 1973). Water possesses a relatively high dielectric constant (ϵ) of 80.4 at 20 °C and decreases with increasing temperature. For pure DMA, ϵ is about 38.9 at 25 °C (Wohlfarth 2008). Therefore, adding water to DMA increases the dielectric constant of the binary mixture. Increasing the water content from 12.5 to 22.5 wt%, increases the dielectric constant from 40.2 to 42.2. High dielectric constants produce flocculates, while lower dielectric constants produce gels. At low non-solvent content heated at low temperature, the binary mixture is expected to be more polar; with the addition of polymer, hydrophilic interactions are expected to

Fig. 12 G' values (obtained at 1 rad/s) for 10 wt% CA ternary systems heated at (top) 50 °C, (bottom left) 70 °C, and (bottom right) 90 °C



dominate. With increasing temperature and non-solvent content, lower dielectric constants lead to a more non-polar mixture and hydrophobic interactions are expected to dominate. Water, a hydrogen bonding donor, builds strong interactions with the solvent and polymer. However, as non-solvent content increases, the solvent quality decreases as the polymer is less soluble in the binary system and leads to phase separation at about 20 wt% water. Thermal treatment increases interactions between solvent and polymer leading to a more homogeneous mixture. As evidenced by stress sweep experiments, during the liquid to solid transition at 20 wt% water, interactions between ternary system components are stronger for gels heated at higher temperature (higher G') and possess a higher critical stress than those heated at lower temperature.

Conclusions

A series of cellulose acetate/DMA/water ternary systems were prepared by varying the mixing temperature and order of component addition. At low non-solvent content, the ternary systems remained a solution and possessed approximately the same viscosity values regardless of order of component addition. Steady state rheology measurements indicated the presence of aggregates in solution at 50 °C but not at 70 and 90 °C. Dynamic frequency sweep measurements showed higher viscous (G'') and elastic (G') modulus when the samples were prepared at lower temperature, consistent with the fact that cellulose acetate possesses a lower critical solution temperature. Unlike the ternary systems that were formed by adding water to the CA/DMA solution, the

addition of CA to a DMA/water solution led to the formation of a two-phase phase separated system at high nonsolvent contents for samples prepared at low temperatures. However, reheating the two-phase phase separated gel system at 90 °C resulting in one-phase phase separated gels with higher viscous and elastic moduli. These results suggest that the gels prepared by adding CA to the DMA/water solutions lacked thermal reversibility and are in a metastable state.

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