

Phase separation and heat-induced gelation characteristics of cellulose acetate in a mixed solvent system

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Abstract The addition of cellulose acetate (CA) to a mixed solvent of *N,N* dimethylacetamide (DMA) and water is examined at different CA concentrations and water contents. Unlike the addition of water to a CA/DMA solution, the addition of CA to a DMA/water solution leads to a transition from a homogeneous solution at low water content to a two-phase system at higher water contents. The two-phase system has an upper liquid layer with an almost clear “solution-like” appearance and a lower gel-like layer. Treating the two-phase system at 100 °C for 30 min results in the formation of a uniform gel structure, similar to that produced by directly adding water to a CA/DMA solution. Although the phase behavior of these systems is similar, their viscoelastic properties are not. The moduli of the heat treated gels do not significantly vary from that of the bottom gel-like portion of the original two-phase samples. This may indicate that thermal treatment at 100 °C is not

able to disrupt the pre-established CA intra- and intermolecular interactions and form the stronger CA-DMA interactions.

Keywords Cellulose acetate gels · Gelation · Viscoelastic behaviour · Elastic modulus · Viscous modulus · Phase separation

Introduction

Cellulose acetates (CA) are extensively used in filtration, membrane and encapsulation applications (Boчек and Kalyuzhnaya 2002; Gomez-Bujedo et al. 2004; Kesting et al. 1965; Pilon et al. 1971). In such systems sophisticated network structures are required. This is typically achieved through aggregation-induced phase separation (Khalil 1973; Pilon et al. 1971), which can be induced by solvent evaporation, changes in temperature, or the addition of a nonsolvent (Vogrin et al. 2002). In nonsolvent-induced phase separation, the concentration of polymer, solvent, and nonsolvent are critical (Kunst and Sourirajan 1970; Matsuyama et al. 2000). Depending on the system phase separation can lead to physical gel formation (Vaessen et al. 2002), which occurs as a result of nonsolvent-induced polymer aggregation and the formation of large macromolecular associates and clusters (Reuvers et al. 1986; Hao and Wang 2001).

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Recently, we reported the viscoelastic behaviour of cellulose acetate in a mixed solvent system (Appaw et al. 2007). The addition of a nonsolvent (water) to a CA/*N,N*-dimethylacetamide (DMA) solution led to phase-separated gel formation. The elastic modulus of the gels correlated well with the Hansen hydrogen-bonding solubility parameter index of the solvent system, suggesting hydrogen-bonding interactions as the major route initiating the sol–gel process. Increasing polymer and/or water concentration led to a denser gel network and increased elastic modulus and critical stress to yield.

Cellulose acetate molecules are never completely molecularly dispersed in solution (Kawanishi et al. 1998), rather existing as complex molecular associates, the extent of which depends on the strength and amount of the intra- and intermolecular interactions (e.g., hydrogen bonding). DMA, which readily dissolves CA of DS ranging from 0.49 to 2.92 (Kawanishi et al. 1998), shows evidence of aggregates or associates of CA molecules even in dilute solution, the result of long-range hydrogen bond interactions between DMA and CA (Kawanishi et al. 2000).

In this study, we further examine the effect of specific interactions within the CA/DMA/water ternary system on the resulting phase behavior and viscoelastic properties. We investigate the sequence of component addition, specifically, the addition of CA to various DMA/water solutions. Unlike the previous system (Appaw et al. 2007) in which water was added to CA/DMA solutions, the addition of CA to DMA with various water contents resulted in a two-phase system with distinctly different viscoelastic properties.

Experimental

Materials

Cellulose acetate (CA) with a molecular weight of 50,000 g/mol and acetyl content of 39.7wt%, HPLC grade *N,N* dimethylacetamide (DMA) and deionized water were used in this study. Both CA and DMA were purchased from Sigma–Aldrich and used as received.

Sample preparation

The mixed solvent system was prepared by adding CA to mixed fractions of DMA and water. The initial

dissolution step involved preparation of different ratios but constant weight of DMA/water solutions followed by addition of a constant weight of CA. The final CA concentration was 10wt% and all solutions were prepared on weight basis. After addition of CA, the mixture was stirred and kept at room temperature for 1 day. Subsequently, the system was purged with nitrogen to ensure an inert atmosphere and heated for 10 min at 70 °C to produce clear/homogeneous samples. In this paper, the dissolution process is termed “*dissolution method 2*”, as compared to that previously reported (Appaw et al. 2007) in which water was added to CA/DMA solutions (*dissolution method 1*). In both systems the heated samples (at 70 °C) are clear homogeneous solutions.

Rheological measurements

A TA Advanced Rheometer (AR 2000) was used to measure the rheological properties of the samples at ambient temperature (25 °C). The viscosity of the samples was obtained from the steady state experiments (Morrison 2001; Maestro et al. 2002) using a cone and plate geometry configuration for samples below the gelation point. Dynamic stress sweep experiments were performed to determine the linear viscoelastic (LVE) regime, after which a small oscillatory shear was applied to the gel samples and the corresponding elastic (G') and viscous (G'') moduli measured as a function of frequency. Frequency ranges from 0.01 rad/s to 100 rad/s were conducted on the gel samples. The shape and magnitude of the elastic and viscous moduli as a function of frequency provides a signature of the state (e.g., solution, gel) of a system (Chauvelon et al. 2003; Lazaridou et al. 2003; Pai and Khan 2002). Parallel plate geometry was used to measure dynamic viscoelastic properties of extremely viscous mixtures and gels. Experiments were repeated a minimum of 3 times to ensure reproducibility and consistency, with an associated error of 10%.

Results and discussion

Increasing water content from 0 to 14.4wt% led to an increase in the viscosity of the CA/DMA/water system. Figure 1 shows the steady state viscosity of samples as a function of shear rate for varying composition of water at a constant CA concentration

of 10wt%. At low water content the viscosity exhibits a large Newtonian plateau followed by a power-law regime. With increasing water content there is an increase in viscosity along with a gradual disappearance in the zero-shear viscosity plateau, indicative of microstructure development.

Figure 2 illustrates the effects of water content on the CA/DMA system; addition of water leads to phase separation and the formation of a self-supporting gel-like network. Interestingly, the sequence of addition of system components appears to have a dramatic effect on the phase behavior of the ternary system. When the nonsolvent (water) is added to the dissolved polymer solution (CA/DMA) (*dissolution method 1*) a phase separated gelation occurs (Appaw et al. 2007). However, when CA is dissolved in the DMA/water solution (*dissolution method 2*) a transition from a low water content homogenous solution to a high water content two-phase system is observed. The two-phase system has an upper liquid layer with an almost clear “solution-like” appearance, while the lower layer forms a viscous white precipitate; similar to that formed when water is added to the CA/DMA solution (Fig. 2b). This process was slow and equilibrium between the two phases was established after about 4 days.

The upper liquid layer exhibits an almost Newtonian viscosity pattern (Fig. 3i). This is illustrated for two different water content. Based on the viscosity obtained, this region is most likely a water-rich solution with some CA and DMA present. By contrast, the viscosity pattern for the viscous lower

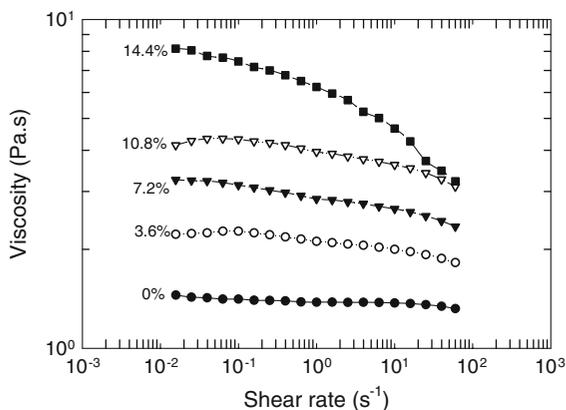


Fig. 1 Effect of water content on the steady shear viscosity of cellulose acetate in DMA/water. CA concentration is 10wt%. Water content was varied from 0 to 14.4wt%

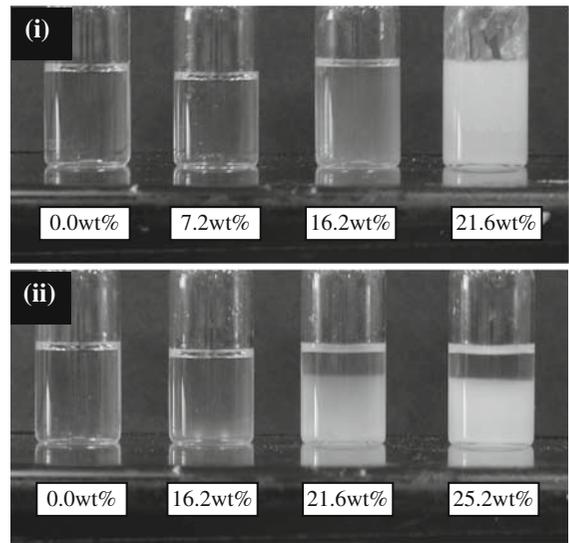


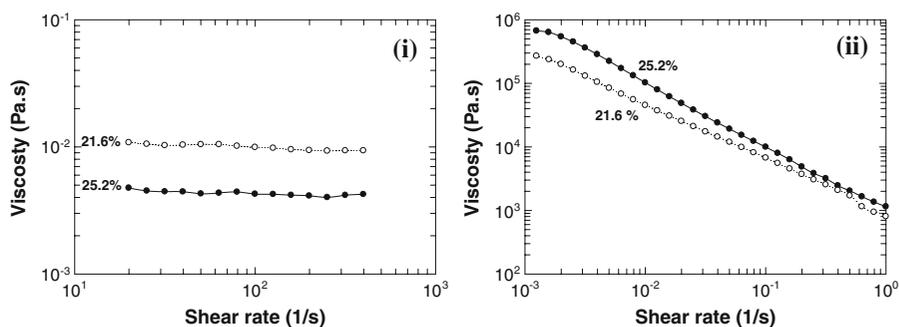
Fig. 2 Effect of water content on the phase behavior of cellulose acetate in DMA. (i) dissolution method 1—addition of water to CA/DMA solution and (ii) dissolution method 2—addition of CA to a DMA/water solution. CA concentration is 10wt%. Water content listed in figure

layer (Fig. 3ii) exhibits a shear thinning profile for all ranges of shear rate studied. Increasing water content from 21.6 to 25.2wt% resulted in a slight increase in the viscosity pattern for the viscous lower layer, while the upper liquid layer showed a substantial drop in viscosity. This is likely the result of further partitioning of CA into the viscous lower layer. The increased viscoelastic properties and shear thinning behavior at low shear rates in the lower layer indicates complex microstructure formation.

To quantify the sol–gel behavior of the CA ternary system the elastic (G') and viscous (G'') moduli are plotted as a function of frequency. Figure 4 illustrates the dynamic viscoelastic behavior of the viscous lower layer. The G' is larger than G'' over the entire frequency range studied, with both G' and G'' being relatively frequency independent, both features characteristic of a three-dimensional elastic gel (Pai et al. 2002; Raghavan et al. 2000; Lazaridou et al. 2003). Increasing the water content from 21.6 to 25.2wt% increases the magnitude of both G' and G'' , although almost identical frequency dependence was observed.

The two-phase behavior at high water contents may result from the competitive interaction for DMA by CA and water, with both having a strong affinity for DMA. Water is completely miscible with DMA,

Fig. 3 Viscosity pattern for the two-phase region at two different water contents of 21.6 and 25.2wt%. CA concentration is constant at 10wt%. (i) Upper liquid phase; and (ii) Lower viscous cloudy phase



and it is envisaged that water forms stronger bonds with DMA as compared to with CA. Moreover, these interactions are established prior to the addition of CA (*dissolution method 2*), therefore the concentration of water and CA will be very important. At low water content, both CA and water may interact favorably with DMA. But as the water content is increased, there is not sufficient DMA to interact with the CA, and some CA chains are displaced leading to aggregation and phase separation.

Figure 5 illustrates the effect of water content on G' and G'' for gels prepared using *dissolution methods 1* and 2. At the same water content it is clearly visible that both G' and G'' are affected by the sequence of water addition. Gels prepared by adding water to homogeneous CA/DMA solutions (*dissolution method 1*) exhibit higher moduli than those prepared by adding CA to DMA/water solutions (*dissolution method 2*); although both systems appear identical at 70 °C, only changing in appearance upon cooling. Increasing water content from 21.6 to

25.2wt% results in enhanced moduli in both systems, however the increase in viscoelastic properties of the gels formed by *dissolution method 1* are slightly higher. The observed phenomenon may be due to the complete dispersion of CA when dissolved within the DMA/water system in *dissolution method 1*, which upon cooling leads to gelation and the formation of gels with uniform CA dispersion and enhanced viscoelastic properties. While in *dissolution method 2*, a typical two-phase separation into a dilute and concentrated phase is observed with gelation in the concentrated phase occurring by the partial aggregation of CA segments or the possible formation of small crystallites as cross-links due to the poor solubility in the DMA/water solvent system.

The concentration of CA, DMA and water is different in both systems, the latter (*dissolution method 2*) likely having a higher concentration of CA within the gel. However, the viscoelastic properties are weaker, suggesting a difference in intermolecular interactions being present. It is proposed that under the conditions used in *dissolution method 2* to form the CA/DMA/water gels that a series of intermolecular interactions are formed between water and DMA prior to CA addition. Upon addition of CA and subsequent heating at 70 °C some of these interactions are disrupted and new interactions with CA are established. However, it seems that a substantial amount of DMA/water interactions still exist which lead to partial aggregation of CA segments which reduced the viscoelastic properties of the gel. Therefore, it is postulated that by increasing the thermal energy to the gels prepared using *dissolution method 2*, the pre-existing intermolecular interactions between DMA and water and within CA can be broken and new interactions between CA and DMA formed leading to gels with viscoelastic properties analogous to those prepared

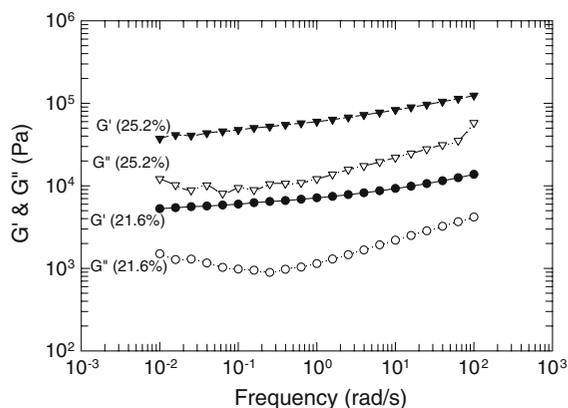
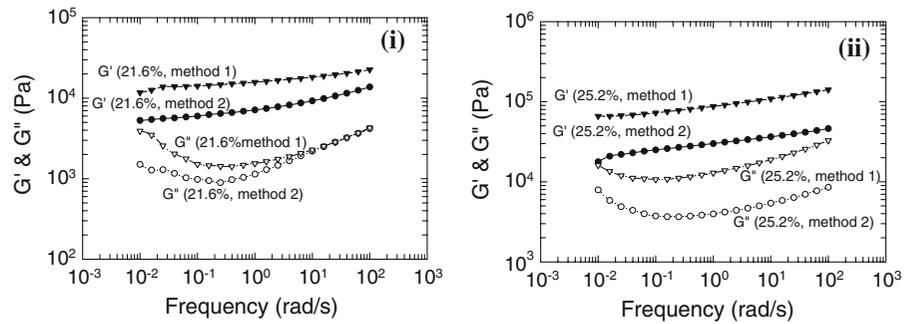


Fig. 4 Effect of water content (21.6 and 25.2wt%) on the viscous (G'') and elastic (G') moduli for CA/DMAc/water system. CA concentration is 10wt%

Fig. 5 Effect of water content (i) 21.6wt% and (ii) 25.2wt% water on the viscous (G'') and elastic (G') moduli for CA/DMAc/water gels prepared using *dissolution method 1* and 2. CA concentration is 10wt%



using *dissolution method 1*. To test this hypothesis the two-phase system formed at high water contents were subjected to temperature treatments spanning from 60 to 100 °C for 30 min. This procedure was performed to investigate if temperature could induce the system to exhibit a heat-induced gelation process and form a single-phase gel system. Heating the two-phase gels at 100 °C for 30 min resulted in the formation of a complete gelled texture with little or no solvent around the gel matrix (Fig. 6).

The dynamic viscoelastic properties of the two-phase gels heated to 100 °C are shown in Fig. 7. The heat-induced gels prepared from *dissolution method 2*

containing 21.6wt% water exhibit almost identical, within experimental error, G' and G'' behavior as compared to those prepared using *dissolution method 1* (Fig. 7i). However, a different pattern was observed at the higher water content of 25.2wt% (Fig. 7ii). For the heat-induced gels, G' and G'' were significantly lower in comparison to the dynamic properties of the gels prepared from *dissolution method 1*. Further, there does not seem to be any enhancement in the elastic properties by heating the gels, G' is essentially the same before (Fig. 5) and after heat treatment (Fig. 7). These results seem to indicate that the interactions established within and between CA molecules cannot be disrupted upon heating to higher temperatures, despite the observation of a clear/homogeneous solution.

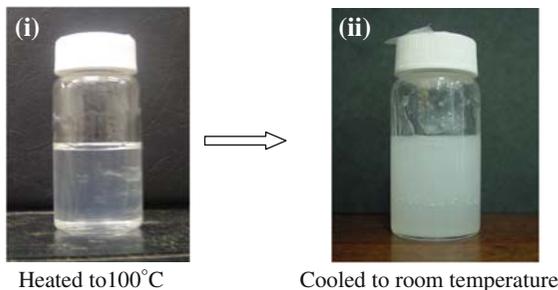
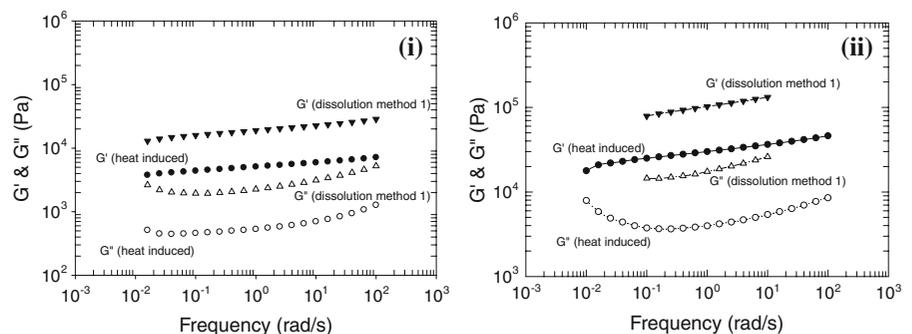


Fig. 6 Effect of heat treatment on the phase behavior of the CA in DMA/water gel. Sample was (i) heat treatment at 100 °C for 30 min and (ii) subsequently cooled to room temperature. CA concentration is 10wt% and water content is 21.6wt%

Fig. 7 Viscous (G'') and elastic (G') moduli of heat-induced gels prepared from *dissolution method 2* and *dissolution method 1* gels at (i) 21.6wt% and (ii) 25.2wt% water. CA concentration is 10wt%



Conclusions

The effect of sample preparation on CA in mixed solvents of DMA and water were investigated using steady-state and dynamic rheology. Depending on the sequence of component addition dramatically different solution and gel behavior were observed. The addition of CA to a DMA/water solution (*dissolution method 2*) underwent a transition from a

homogeneous solution at low water content to a two-phase system at higher water contents; the two-phase system having an upper liquid layer with an almost clear “solution-like” appearance and a lower layer being a viscous gel. Treating the two-phase system at 100 °C for 30 min resulted in the formation of a uniform gel structure, similar to that produced by directly adding water to a CA/DMA solution (*dissolution method 1*). Although the phase behavior of these systems was similar, their viscoelastic properties were not. The moduli of the heat induced gels produced from *dissolution method 2* did not significantly vary from that of the bottom gel-like portion of the original two-phase samples. Interestingly, the moduli of these heat induced gels are substantially lower than those obtained from *dissolution method 1*. It is proposed that specific intermolecular interactions are formed between components which are dependent on the order of addition. Depending on the nonsolvent concentration some of these can be disrupted upon heating, but at the higher nonsolvent concentrations investigated in this study there appears to be a limit as to the extent microstructure can be manipulated and viscoelastic behavior recovered.

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