Gelation Behaviors of Cellulose/PE-co-AA Alkaline Solutions

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ABSTRACT

The miscibility of alkaline solutions of cellulose and poly(ethylene-co-acrylic acid) (PE-co-AA) were characterized by optical microscopy and different rheological methods. It was found that not only the mixing time and intensity were important but also controlling the gelation behavior had major effect on the properties of these solution mixtures.

INTRODUCTION

Cellulose and cellulose based materials are one of the key bio-based substances when looking at alternative materials for petroleum based polymers and new ways to prepare for instance packaging plastics. One way to prepare functional cellulose based polymeric materials is to blend cellulose with synthetic polymers. Regenerated cellulose grades can be blended with synthetic polymers in solutions by using non-aqueous solvent systems such as N-methyl-2-pyrrolidinone/LiCl[1], N,N-dimethylacetamide/LiCl[2,3] or DMSO/paraformaldehyde[4,5]. However, to reduce the pollution from organic solvents, aqueous solvent systems are becoming more favoured.

One convenient way to prepare cellulose/synthetic polymer blend is to use thermoplastic ethylene acrylic acid copolymer as the synthetic part. These both polymers are soluble in alkaline water phase and they precipitate simultaneously by acidic treatment. Exactly this type of solution mixed blends hasn't been studied much, but thermoplastic blends of starch and poly(ethylene-co acrylic acid) were of interest for agricultural purposes a number of years starting at the end of the seventies by Otey et al.[6] In addition Fanta et al.[7] and many other research groups[8,9] studied starch-poly(ethylene-co-acrylic acid) blends and other starch containing plastics in early 90s.

In this study, the miscibility and gelation behaviour of the cellulose/poly(ethylene-co-acrylic acid) solution was followed by rheological means. Rheological properties of dissolved cellulose solutions has been studied much over the last decade[10,11,12,13]. Furthermore, gelation behaviour of cellulose solutions dissolved in NaOH/water, NaOH/urea, NaOH/thiurea has been reported as function of time, temperature, molecular weight and concentration.[11,14,15,16]

MATERIALS AND METHODS

Alkaline cellulose water solution (3 wt-% cellulose, 6 wt-% NaOH, 1.3 wt-% ZnO) was received from the Tampere University of Technology. The preparation of this solution is described in the patent application of Vehviläinen et al.[17] Alkaline polyethylene-co-acrylic acid water solution (20 wt-% PE-co-AA, pH ~10) was obtained from BIM Finland Oy.

Mixing of the solutions was done in 100 ml glass vessel under vigorous magnetic stirring. Dosages of PE-co-AA solution were added with a syringe and needle by feeding it slowly to the vortex of cellulose

solution (cellulose batch ~30-35 ml). To prevent solutions from gelation, the solutions were prepared also so that after 24 hours of mixing, they were frozen and melted, and stirred for another 24h. The compositions of the solutions are presented in Table 1.

Characterization

In order to estimate the changes in solution structure during the mixing, the rheological characterization was done with Anton Paar Physica MCR 301 rotational rheometer. Parallel plates of 50mm diameter (PP50) with 0.4 mm gap and concentric cylinders (CC27) were used to perform oscillatory measurements. Frequency sweep measurements were carried out with strain of 0.2% in linear viscoelastic region. To clarify rheological results, changes in the solution structure were also estimated with Olympus BH-2 optical microscopy equipped with a digital camera. A drop of the solution was placed between microscope glass plates and the pictures were taken with 100 times magnification.

RESULTS

The basic idea of blending cellulose and PE-co-AA laid on the fact that both of the polymers were soluble in alkaline water phase, where they were expected to form a homogeneous blend, and both of the polymers would regenerate fast and simultaneously by acidic treatment, where the homogeneous morphology of the blend should be maintained (i.e. diminished phase separation during regeneration). In practice, however, the preparation of the cellulose/PE-co-AA blend via solution mixing was not so straightforward.

Optical microscopy pictures (Fig. 1A) showed that PE-co-AA solution started to form gel particles when it was added in cellulose solution. It became obvious that the PE-co-AA was soluble only in modestly alkaline solution (pH 10) whereas at higher pH's (cellulose solution pH 14) the solubility was diminished. Therefore, a long mixing time (24 h) was required to break down the PE-co-AA gel particles and improve the homogeneity in the solution.
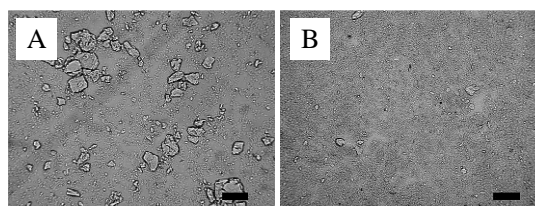

Figure 1. Optical microscopy pictures of 50/50 cellulose/PE-co-AA solutions after A) 15min and B) 24h of mixing. Scale bar 100μm

After 24h of mixing the morphology of the solutions were quite uniform as it is demonstrated in Fig. 1B. At this point characterization was continued with frequency sweep studies in order to quickly clarify elastic and viscous properties of the solutions. Fig. 2A presents frequency sweep study for 90/10 and 50/50 cellulose/PE-co-AA solutions after 24h of mixing. In addition, Fig. 2B presents the corresponding complex oscillation viscosity $|\eta^*|$ data representing a viscosity values of 90/10 and 50/50 solutions. Neat cellulose and PE-co-AA solutions are presented in Fig. 3.

Table 1. The polymer compositions of the solutions

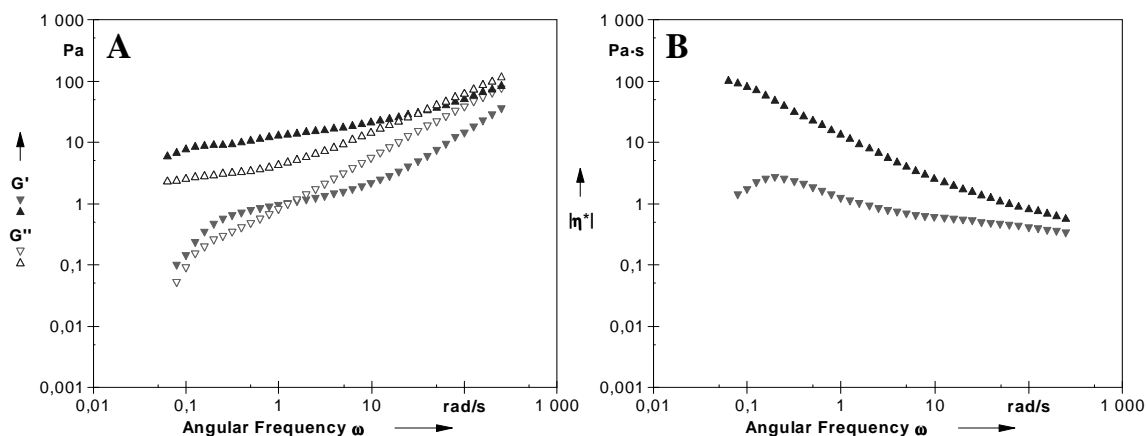| Solution ID	Cell./PE-co-AA solutions volume ratio	Polymer concent. (wt-%)	Cellulose (wt-%)	PE-co-AA (wt-%)	Mixing (h)	Freeze-Melted
90/10	100/1.67	3.3	90	10	24	-
50/50	100/15=6.7	5.2	50	50	24	-
50/50 f-m	100/15=6.7	5.2	50	50	48	yes
50/50 48h	100/15=6.7	5.2	50	50	48	-

Figure 2. Parallel plate (PP50) frequency sweep studies for 50/50 (▲) and 90/10 (▼) solutions after 24h of mixing. A) Storage modulus G' (filled symbols) and loss modulus G'' (open symbols), and B) corresponding Complex viscosity |η*| (Pa s) as a function of angular frequency ω (rad/s).

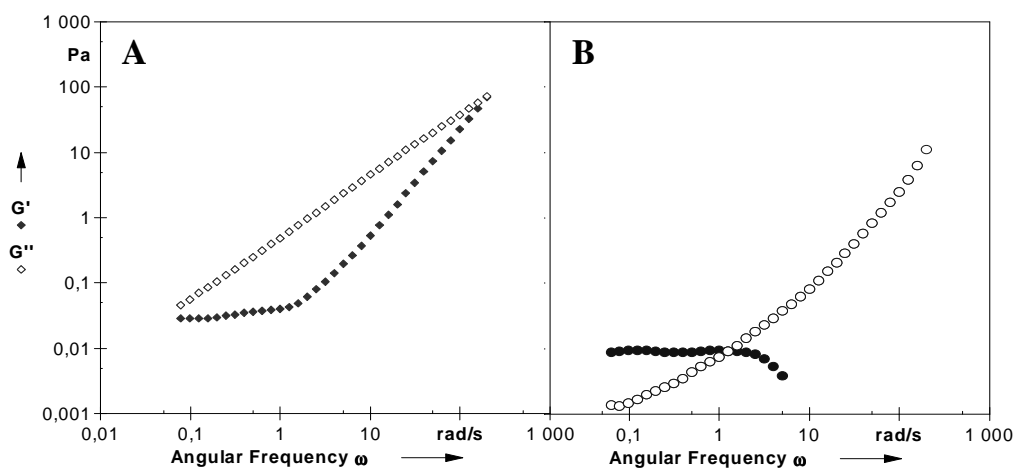Figure 3. Storage modulus G' (filled symbols) and loss modulus G'' (open symbols) as a function of angular frequency ω (rad/s) for the neat A) 3 wt-% cellulose and B) 20 wt-% PE-co-AA solutions.

From the frequency sweep studies, seen in Fig. 2 it can be stated that these solutions are viscoelastic liquids that have elastic solid type of behavior at low frequencies. In other words, solutions develop a weak elastic solid structure at rest which breaks up and starts to flow under shear.

Based on these figures it could also be assumed that the elevated storage modulus G' seen for 50/50 solution mixture at low frequencies is a sign of an elastic network structure formation between the polymers, but this assumption is not completely true. In parallel with the representative 50/50 solution, we 'succeeded' also to prepare highly viscous 50/50 solutions (Fig 4).

It became obvious that also the cellulose may form partly gelled structure. On average, the used neat cellulose solution is known to gel if stored at RT for prolonged times (> 24h). Also the drop wise addition of the PE-co-AA reduced locally (for a while) the pH in the cellulose solution which may have triggered the cellulose gel formation. Therefore it can be stated that growth of storage modulus at low frequencies is not complete due to interaction between polyethylene and cellulose but may originate also from the gelation of the cellulose.
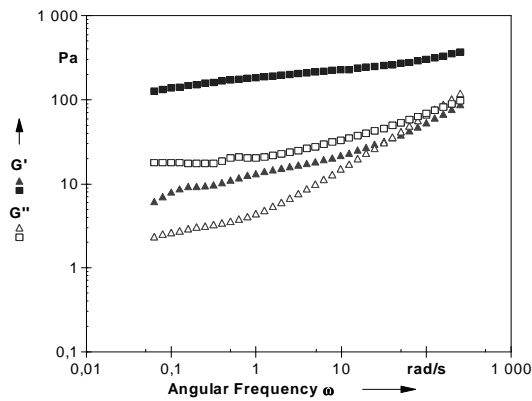

Figure 4. Storage modulus G' (filled symbols) and loss modulus G'' (open symbols) for 50/50 (▲), highly gelled 50/50 (■).

In addition to gelation behavior of these solutions, it was found also that the used geometry had to be taken account when evaluating the reliability of these results (Fig 5). In parallel plates, the outer edge is the most sensitive to external changes such as moisture variation. In our case this meant that the outer layer of solution soaked up moisture or dried, depending on moisturizing conditions on the chamber. Instead of parallel plates, the relative volume of the outer layer was minor in concentric cylinders and therefore this film formation tendency has no major effect on the frequency sweep results.
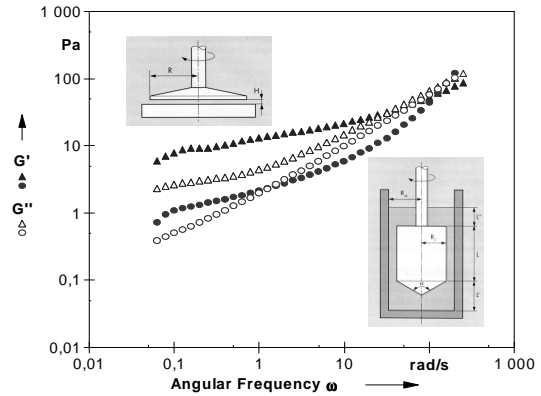

Figure 5. Frequency sweeps of 50/50 solutions measured with PP50 (▲) and CC27 (●). Storage modulus G' (filled symbols) and loss modulus G'' (open symbols).

Finally, any further gelation was reduced by freezing the cellulose/PE-co-AA solution after 24h mixing, which was then allowed to melt back at RT while mixing another 24h (freezing following slow melting with vigorous stirring). This procedure was based on method of dissolving cellulose described in the patent application by Vehviläinen et al.[17]. A notable change in storage modulus levels are seen if solution is mixed straight 48h without freeze-melting procedure in between (see Fig 6). Based on this result, it was quite obvious that at longer mixing procedures the freezing-melting step was required to avoid any influence of cellulose gel.
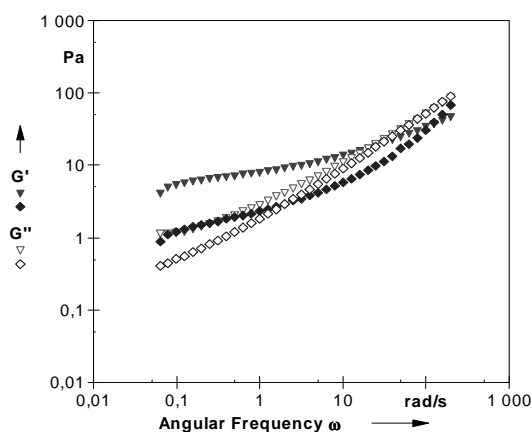
Figure 6. Storage modulus G' (filled symbols) and loss modulus G'' (open symbols) for 50/50 f-m (♦), 50/50 48h (▼) solutions measured with CC27.

CONCLUSIONS

Based on the rheological results it can be stated that a uniform quality solution and the best possible miscibility between cellulose and poly(ethylene-co-acrylic acid) solutions were attained with a method in which the solution was frozen and melted between the mixing. As a conclusion it can be also stated that the final texture of studied solution mixtures are depending on the solution stage and can be influenced by changing mixing time and conditions.

ACKNOWLEDGMENTS

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