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Storage modulus changes with temperature in poly(vinyl alcohol), PVA,/poly(acrylic acid), PAA, blends

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Summary

Poly(vinyl alcohol), PVA, and poly(acrylic acid), PAA, blends were prepared by solution casting. These polymers were found to be miscible in the whole composition range as determined by DSC even though some crystallinity remains in blends with PVA concentrations above 50wt%. Dynamic mechanical measurements of these blends and PAA as a function of temperature show an increase in storage modulus, E', when they reach a temperature of 140°C that is well beyond their softening point. The E' increase in PAA beyond 140°C is attributed to an intramolecular reaction of cyclic anhydride formation that stiffens the chain. Isothermal storage modulus test as a function of time and FTIR measurements at 160°C of PAA and three blends show that this increase in E' is due to cyclic anhydride formation.

Introduction

Water soluble polymers are important from an industrial viewpoint. They are used in several applications in the food processing industry, barnishes, paints, adhesives and as floculants in separation processes (1-3). This has lead to an increased interest in blends of these polymers which could show improved properties not found in the homopolymers. Two important water soluble polymers are poly(vinyl alcohol), PVA, and poly(acrylic acid), PAA, that are water soluble and in widespread use in several applications. Some studies show that these polymers form miscible blends at all compositions (4,5). These findings could be used to control the properties of the blends for different applications such as controlled release matrices, hydrogels with different ionic strengths, or membranes for liquid separation by pervaporation (3-5). A recent study also suggests that thermal treatment of PVA/PAA blends would promote crosslinking between these polymers, as has been found for other water soluble polymers (5).

In here we report the behavior of the storage modulus, E', as a function of temperature for several PVA/PAA blends as well as the changes observed in their dynamic mechanical behavior when they are cured isothermally. The changes in storage modulus of these blends are related to those observed by infrared spectroscopy when they are subjected to isothermal treatment.

Methods and materials

The poly(vinyl alcohol), PVA, and poly(acrylic acid), PAA used for blend preparation were obtained from Polysciences, Inc. PVA with a hydrolysis degree of 99.7 mol% and molecular weight of 78,000. Differential scanning calorimetric, DSC, measurements give a Tg for this polymer at 65°C and a Tm at 223°C. PAA has a molecular weight of 450,000 with a Tg at 105°C as measured by DSC. Blends of PVA/PAA were prepared with a concentration of 20, 40, 50, 60 and 80 wt% of PVA by solution blending these polymers in distilled ion-free water. In all cases solutions with polymer concentration of 5 % wt/vol were prepared in the following way. Initially, the required amount of PVA was dissolved in the solvent by heating the solution to 90°C until the solution was clear. Then, the solution was cooled to 30°C. To the cooled solution, the required amount of PAA was added and the solution stirred until it was clear. From these solutions, films were cast on a smooth non-stick surface. The films were dried slowly at 30°C for 72 hrs. Then, they were dried under vacuum for 24 hrs at 60°C and 24 hrs at 100°C.

Determination of the glass transition temperature, Tg, on the pure polymers and blends, was performed by differential scanning calorimetry in a DSC-7, Perkin Elmer Inc., between 40 and 175°C for the pure polymers and their blends at a scanning rate of 10°C/min, under nitrogen atmosphere. Tg values in homopolymers and blends are reported after the second heat. Wide angle x-ray diffraction (WAXD) measurements were performed in a Philips 1140 diffractometer with KαCu radiation, $\lambda = 1.54$ Å, on films prepared as described above between 4 and 60 degrees 2θ.

Dynamic mechanical properties of PVA/PAA blends and homopolymer films as a function of temperature and time were obtained in a DMA-7 (Perkin Elmer Inc.), in the extension mode. All tests were performed at a frequency of 10 Hz between 25 and 175°C at a scan rate of 2°C/min under nitrogen atmosphere. Isothermal DMA test were carried out at 160°C for up to 60 min, at the same frequency than those described above for blends containing different molar ratios of hydroxyl to carboxylic groups as follows; PVA/ PAA 0.5/1.5, called PVA 0.5, PVA/PAA 1/1, denoted as PVA 1, and PVA/PAA 1.5/0.5, called PVA 1.5.

Qualitative changes that occur during thermal treatment of blends and homopolymer films were followed using FTIR. These measurements were performed in a Nicolet Protege 460 between 500 and 4,000 cm^{-1} with 100 scans and a resolution of 2 on thin films of the blends and homopolymers treated at intervals of 10 minutes up to 40 minutes at 160°C.

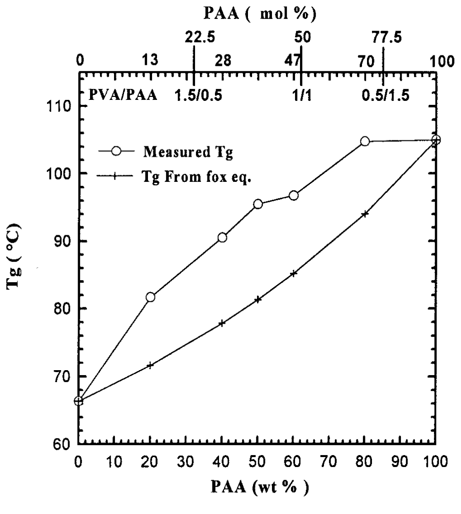

Figure 1. Glass transition temperatures for PVA/PAA blends.

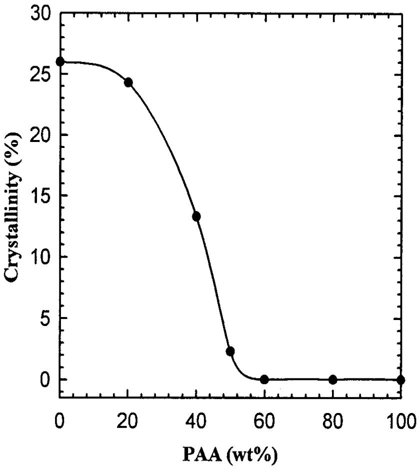

Figure 2. Crystallinity change as a function of PAA concentration on PVA/PAA blends.

Results and discussion

Thermal analysis by differential scanning calorimetry shows that all blends, without thermal treatment, have a single Tg for all compositions tested, see Figure 1. The occurrence of a single Tg in all blends is a strong indication of miscibility between PVA and PAA, a fact that has been reported in the literature before (4,5) for this system. Furthermore, as can be seen in Figure 1, there is a positive deviation from an ideal mixing rule indicating that the interaction between PVA and PAA is strong. The miscibility between PVA and PAA has been attributed to the capacity of these polymers to form intermolecular H-bonding (4,5). It must be pointed out also that, the displacement of the Tg towards intermediate temperatures between the two homopolymers is quite noticeable, even though there is some crystallinity remaining in the blends at concentrations of PVA above 50 wt%, as discussed below in the X-ray diffraction measurements. There is no apparent phase separation in the blends. Painter et al.(6) have discussed that this behavior is often found in blends of polymers where there is H-bonding interactions. They attribute this to a positive ΔHm of mixing due to a self-association of at least one of the pure polymers that form the blend that, in turn, gives rise to an increase in entropy of mixing. In this pair of polymers PVA presents such a behavior.

Wide angle X-ray diffraction, (WAXD), spectra of the blends without thermal treatment (not shown) indicate that the initial crystallinity of PVA decreases as the concentration of PAA increases in the blends, see Figure 2. The initial crystallinity of PVA, as determined from the partial area above the amorphous region in the x-ray diffraction spectra, is 26%. It decreases to less than 2% when the concentration of PVA is 50 wt% in the blend. Despite this fact, there is no apparent phase separation, as was observed in the calorimetric experiments that show a single Tg for all blend compositions. However a change in the trend of the Tg's is observed when the blend is rich in PAA. This is attributed to the interaction of PAA with PVA that disrupts the crystallinity of the latter. This result is similar to that found by Daniluc (4) by DSC measurements. It is also interesting to note that the same effect of diminishing crystallinity with increasing concentration of water in PVA was reported by Hodge et. al (7) for samples with different concentrations of water. Their proposed mechanism for the disruption of PVA crystallinity is that water locates mainly in the amorphous region of the polymer and diminish the crystallinity of PVA by attacking the crystallites at the amorphous-crystalline interface. In the specific case of PVA/PAA blends tested here, since they were prepared by solution casting, we could envision a slightly different mechanism. In these blends, the crystallites are formed

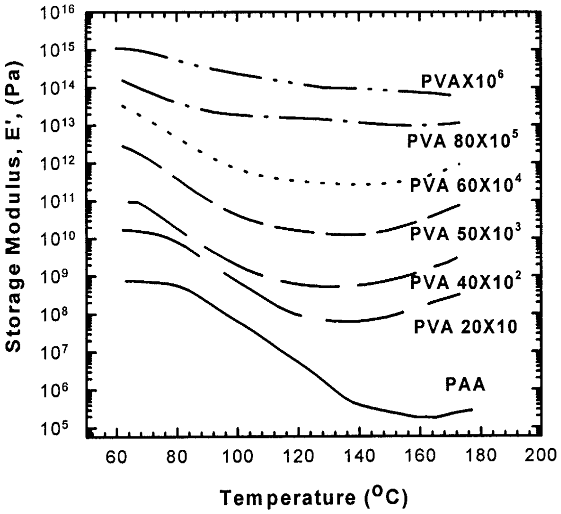

Figure 3. Storage modulus behavior as a function of temperature and concentration for PVA/PAA blends.

first in PVA during the drying process and a preferential interaction between PVA and PAA develops in the amorphous region. As the amount of PAA in the blend increases, the ability of PVA to crystallize gets impaired because there is a strong H-bonding interaction between these two polymers in the amorphous region that interferes with the ability of PVA to crystallize. As a result, the crystallinity disappears and blends with PAA concentration larger than 50 wt% are amorphous.

Dynamic mechanical properties

The storage modulus, E', of pure PVA, PAA and their blends between 30 and 175°C are shown in Figure 3. In order to facilitate their comparison, the curves have been shifted by the order of magnitude that appears at each of them respect to their original values. The storage modulus of PAA is the only one showing the actual values. The storage modulus, E', of PVA starts to decrease at 55°C with a smooth plateau up to 175°C. In contrast, the E' of the blends shows a decrease at a slightly larger temperature depending on the concentration of PAA in the blend. Finally, PAA shows a decrease on the E' at around 73°C. However, the behavior observed in the blends and PAA storage modulus when they reach a temperature of approximately 140°C is quite different from PVA. They show an increase in storage modulus, E', that depends on PAA concentration in the blend. It has been reported that PVA and PAA blends and pure PAA can undergo crosslinking, intermolecularly between the two polymers, and intramolecularly, in pure PAA, when subject to thermal treatment (5,8-9). Thus, the increase in E' observed for the blends and pure PAA at this temperature could be attributed to intermolecular and intramolecular crosslinking. Figure 4 shows a schematic of the possible reactions between PVA and PAA that could take place during thermal treatment.

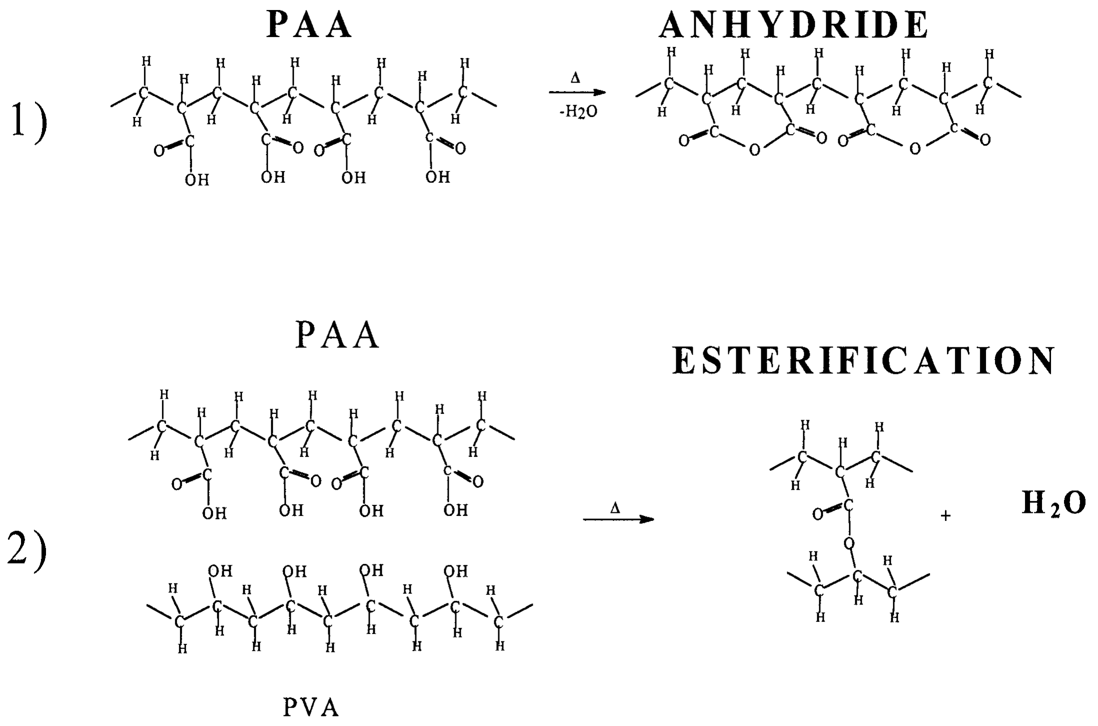

Figure 4. Possible reaction that would take place in PVA/PAA blends (1) Intramolecular and (2) Intermolecular.

In order to follow the observed increase in storage modulus, E', in thermally treated PVA/PAA blends and pure PAA in the 140-175°C range, dynamic-mechanical isothermal experiments were performed. The temperature used was 160°C for times up to 45 min. These measurements were done in blends with PVA/PAA molar ratio of 0.5/1.5, 1/1, 1.5/0.5 and their changes in E' followed as a function of time. In order to facilitate the identification, PVA's molar concentration is used to denote the blend (e.g. PVA 0.5 corresponds to PVA/PAA 0.5/1.5). It was found that the increase in modulus is very sharp initially and levels up at around 40 min. After this point, the increase in E' is small. The results of E' changes obtained with thermal treatment of these blends and the homopolymers under the same conditions are given in Figure 5. As can be seen the modulus increase in PVA is the smallest followed by that obtained in PAA. The increase in the storage modulus of PAA can be attributed to cyclic anhydride formation, see Figure 4 scheme 1. This was tested by infrared spectroscopy. In Figure 6, the IR spectra for pure PAA at different thermal treatment times is shown. It can be seen that the band at 1805 cm^{-1} grows as thermal treatment time increases. This band is due to the formation of

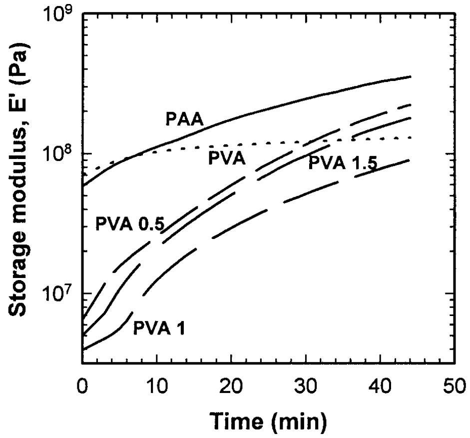

Figure 5. Isothermal increase of storage modulus with time at 160°C for PVA/PAA blends.

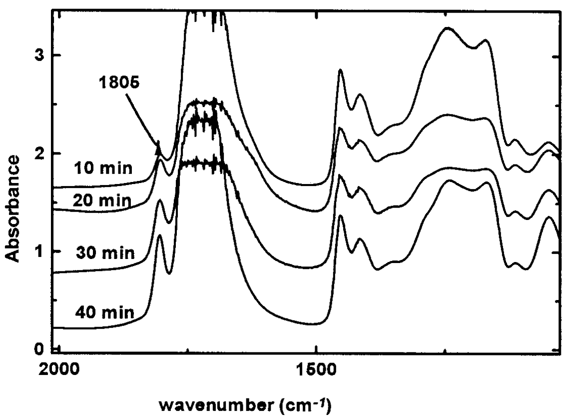

Figure 6. Changes in the 1805 cm^{-1} band on PAA with thermal treatment time at 160°C.

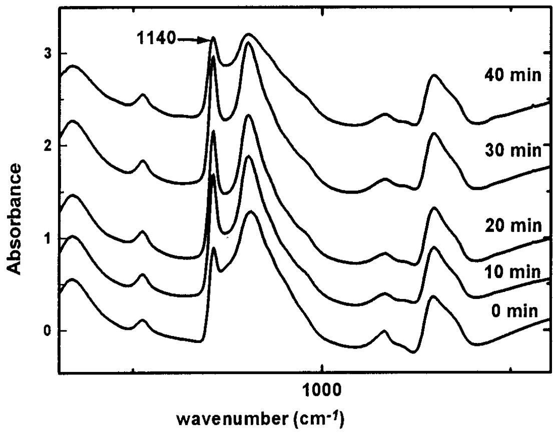

Figure 7. Change in the 1140 cm $^{-1}$ band on PVA with thermal treatment time at 160°C

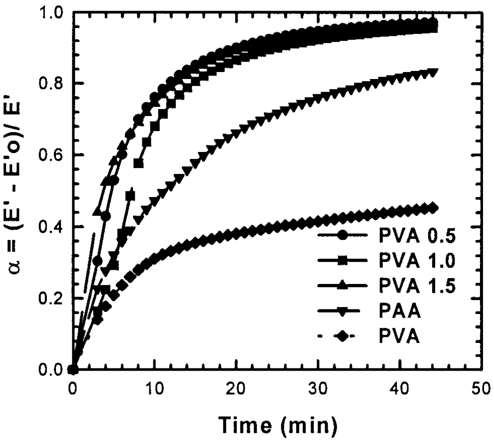

Figure 8. Normalized fractional increase of storage modulus with time at 160°C for PVA/PAA blends and homopolymers.

cyclic anhydrides (10); thus, the increase in storage modulus observed in PAA is attributed to rigidization of the polymer due to the formation of this cyclic structure. In the case of PVA, the increase in E', is related to an increase in crystallinity. This increase in crystallinity can be followed by FTIR since the band appearing at 1140 cm^{-1} has been related to it (11-12). In this case it is clear that this band increases with thermal treatment time up to 30 min and then decreases slightly, see Figure 7. An increase in crystallinity reflects in the storage modulus as an increase in rigidity of PVA. In the case of the blends two differences arise: first, they present a lower initial storage modulus at this temperature. Second, the E' increase spans one order of magnitude more than that of the pure polymers. This behavior must be related to the relative amounts of each polymer in the blend. Thus the initial E' of the blend PVA 1.5 is higher than the one with equal molar ratio, PVA 1, and higher than that for PVA 0.5. Given the difficulty to compare the storage modulus, E,' of the blends with that of the homopolymers, both were normalized using the following equation:

$$\alpha = \frac{E'(t) - E'o}{E'(t)}$$

where E'(t) is the storage modulus at time t, E'o is the initial storage modulus, and α is the fractional increase in storage modulus. This normalized results will give α-> when E'(t) becomes very large and α-->0 when E'(t) -->E'0. The results of the normalization are given in Figure 8. They indicate that E' grows rapidly in the case of the blends as compared to the homopolymers. In the case of the blend PVA 0.5, the FTIR spectra shows that the band at 1805 cm^{-1}, cyclic anhydride formation, grows with thermal treatment time although this is not as high as in the case of pure PAA. This band is not present in the other blends. Overall all blends after 40 minutes reach the same fractional modulus increase, (α). It is also seen that the blends with a larger concentration of PAA tend to reach a larger increase on E' with thermal treatment in shorter times. This is attributed mainly to the rigidization due to the cyclic anhydride formation. In the case of the PVA 1 and PVA 1.5 blend, the increase in E' is not as fast initially but they finally reach the same fractional increase (α). That all blends reach the same fractional increase in storage modulus, E', after 40 minutes seems to be related to three different aspects. Storage modulus increase in the blend rich on PAA is due to cyclic anhydride formation and intermolecular crosslinking. Thus it attains a larger fractional increase in E' in short times, α is 0.8 in about 10 minutes. The blend rich in PVA, PVA 1.5, increases its

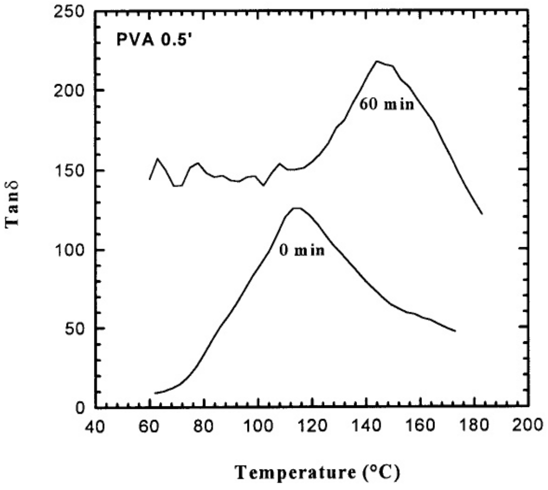

Figure 9. Effect of thermal treatment time on the α-transition of PVA 0.5 blend.

rigidity due to an increase in crystallinity and intermolecular crosslinking. From these results, it appears that the crystallization process takes longer times than the one for cyclic anhydride formation which in turn makes the maximum increase in E' to occur at slightly longer times. Finally, the intermolecular crosslinking reaction, which is the expected main reason of rigidization in the blend with equimolar concentration of hydroxyl and carboxylic groups, PVA 1, takes longer time to reach the same fractional increase in E' observed in the other blends. In the later blend, this is attributed to a higher intermolecular crosslinking since the formation of crystallinity or cyclic anhydrides was not detected by infrared spectroscopy. Strong evidence of intermolecular crosslinking as thermal treatment time increases is given by the fact that the water swelling capacity of the blends decreases strongly. As an example, the absorption of water by a PVA 0.5 blend decreases from around 200% by weight uptake for a non-treated sample to 29% after 25 minutes of thermal treatment at 160°C. A similar behavior was observed in blends PVA 1 and PVA 1.5 under the same conditions. Overall it was found that the increase in modulus in the blends is mainly due to changes undergone by PAA during thermal treatment either due to intramolecular or intermolecular crosslinking. This could be the reason that other authors have found that phase separation takes place (13-15) in this kind of blends when they are subjected to thermal treatment. PAA structural changes may induce phase separation by diminishing the hydrogen bonding interactions with PVA. Analysis of tan δ behavior of PVA 0.5 blend treated thermally at 160°C by 60 min, Figure 9, shows a displacement of the α-transition maximum towards higher temperatures. There is also evidence of a small α-transition at 70°C which is that expected for PVA. This indicates that PAA α-transition has increased due to cyclic anhydride formation. Also the small α-transition at the same temperature as that of PVA is an evidence of phase separation since each α-transition appears separately.

Conclusion

Blends of poly(vinyl alcohol), PVA, and poly(acrylic acid), PAA, were prepared at different concentration by solution casting. Their miscibility, assessed by DSC measurements, indicates that the blends as prepared are miscible in all compositions even though there is some crystallinity present in blends rich on PVA. This behavior was attributed to the ability of these polymers to form H-bonding as has been observed for other polymers with the same characteristics. Dynamic mechanical measurements performed show that all blends have a tendency to increase the storage modulus after they reach 140°C. This behavior was also observed in pure PAA.

Isothermal storage modulus measurements as a function of time, at 160°C, for blends with different molar ratios of hydroxyl and carboxylic groups showed that the increase in modulus observed was dependent on PAA concentration in the blend. However, all blends reach the same fractional increase in storage modulus after 40 minutes. The increase in storage modulus, E', is attributed to structural changes due to intramolecular crosslinking in PAA and intermolecular crosslinking between PVA and PAA. In blends rich on PAA, the formation of cyclic anhydrides brings about rigidization of this polymer and apparently phase separation of the blend.

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