

CONTRIBUTIONS OF POLYMER CHAIN ENTANGLEMENTS AND HYDROGEN BONDING TO ADHESIVE AND MECHANICAL PROPERTIES OF POLY(N-VINYL PYRROLIDONE) BLENDS WITH POLY(ETHYLENE GLYCOL)

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Introduction

Two different non-permanent and rapidly relaxing networks have been recently shown [1] to determine both the pressure-sensitive adhesion and mechanical properties of the blends of high molecular weight PVP with short-chain PEG. One of them is made of physical entanglements of longer PVP chains, while another one is formed through hydrogen bonding of PEG terminal hydroxyls to the complementary carbonyl groups in the PVP repeating units. Accurate deconvolution of the contributions of these networks into adhesive and viscoelastic properties is a difficult problem [2]. We expect that the contribution of longer PVP chain entanglements should be attenuated with the decrease in PVP chain length. At the same time, the density of the network of H-bonds formed between the terminal OH groups of PEG and the carbonyls in the repeating units of the PVP backbone is a function of PEG chain length [3]. The longer the PEG chain length, the sparser the H-bond network due to the decrease in both the concentration of OH groups and entropic factor controlling the thermodynamics of PVP-PEG interaction.

In this work the contribution of PVP chain entanglements to the adhesive and mechanical behavior of PVP-PEG blends has been investigated by comparing results obtained with two PVP with two different molecular weights. The effect of hydrogen bonding has been evaluated by mixing the PVP with dimethyl ether of PEG (PEGDME) and with a series of PEG's with variable molecular weight.

Experimental

PVP of higher and lower MW (HMW, $M_w = 1,000,000$ and LMW, $M_w = 30,000$ g/mol), PEG ($M_w = 200, 400, 600$ g/mol) and PEGDME ($M_w = 550$ g/mol) were obtained from the BASF and Aldrich, respectively. The films of 0.4 mm. in thickness were prepared by dissolving the polymers in a common solvent (ethyl alcohol) followed by casting and drying the solution at ambient temperature. Tensile properties were studied with an Instron 1122 tensile tester in the course of uniaxial drawing at a fixed rate of 20 mm/min. 180° Peel tests were performed with the same tensile tester using a polyethylene terephthalate (PET) film as a substrate at a peel rate of 20 mm/min.

Results and Discussion

1. Effects of PVP chain entanglements

The blends of HMW PVP with PEG-400 deform like rubbers, whereas the films made of LMW PVP blends with the same amount of plasticizer (PEG-400) exhibit a deformation mode closer to that of yield stress fluids (Fig. 1). The initial slopes of the stress-strain curves are very similar, indicating a negligible effect of PVP chain length on the elastic modulus within a region of linear elastic deformation. However at larger strains the effect of PVP chain entanglements on the shape of the stress-strain curves is dramatic.

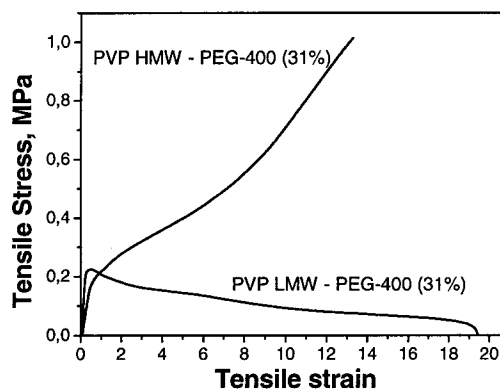


Figure 1. Effect of PVP chain length on the nominal stress-strain curves of PVP-PEG400 31% blends.

Under uniaxial stretching, the films of LMW PVP with PEG-400 deform in a non-uniform fashion along the stretching direction and become liquid-like as soon as the value of the yield point is achieved (Fig. 2). This behavior is in strong contrast to the blends of HMW PVP with the same plasticizer (Fig. 3). The yield stress decreases sharply with plasticizer concentration, whereas the values of critical strain corresponding to the transition from the glassy to the liquid-like state are only slightly affected by the PEG concentration (Fig. 2).

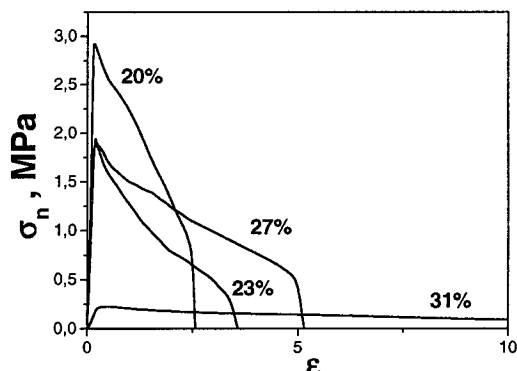


Figure 2. Effect of PEG content on the stress-strain curves of LMW PVP blends with PEG-400.

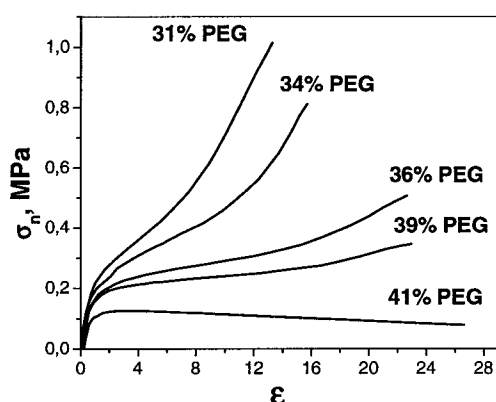


Figure 3. Stress-strain curves for the blends of PVP HMW PVP with PEG-400 [1].

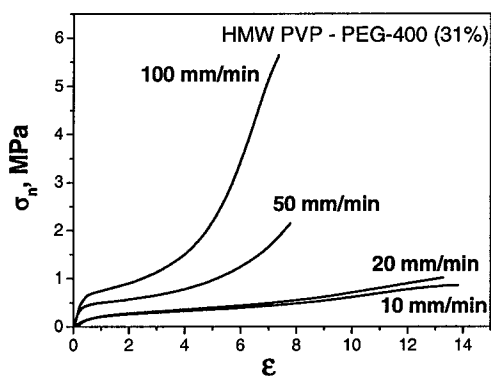


Figure 4. Effect of extension rate on tensile properties of HMW PVP blends with 31 wt % PEG-400.

A specific feature of the blends of HMW PVP with PEG is a sharp transition from elastic liquid to rubber deformation, which occurs within a narrow range of drawing rate (between 20 and 50 mm/min, Fig. 4). The decrease in PVP MW profoundly modifies the effect of drawing rate (Fig. 5). The yield stress appears to be affected strongly by

the drawing rate but no apparent change of mechanism in the large strain part of the curve is observed.

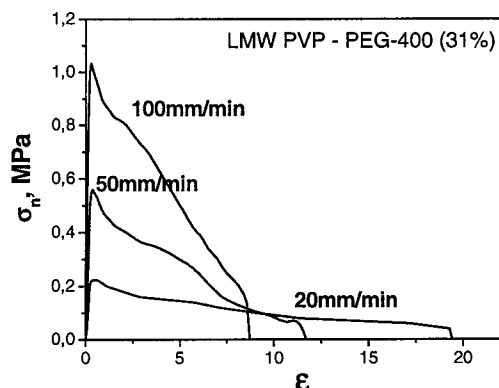


Figure 5. Effect of extension rate on tensile properties of LMW PVP blends with 31 wt % of PEG-400.

The peel force as a function of composition of the blends of LMW PVP with PEG-400 is surprisingly similar to that of HMW PVP (Fig. 6). With the decrease in PVP MW, the maximum of peel force shifts to the compositions containing less plasticizer. Depending on plasticizer concentration, either an adhesive or cohesive mode of debonding occurs, but not a miscellaneous mechanism of adhesive bond failure.

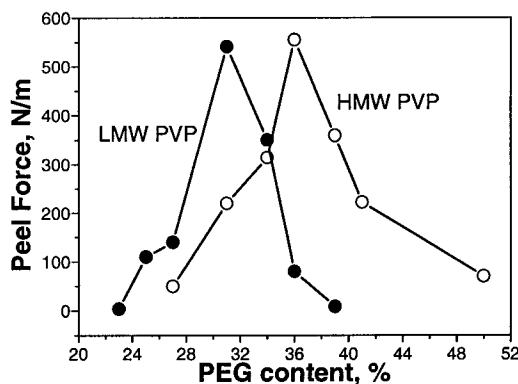


Figure 6. Effect of PVP MW on 180° peel adhesion of PVP—PEG-400 hydrogels.

At the point of maximum adhesion LMW PVP blends fails in a brittle manner with the cracking in the bulk while the high MW PVP-PEG-400 (36%) blend reveals fibrillar failure. LMWPVP-PEG-400 blends that contain more than 31% of PEG display a liquid-like debonding mechanism of failure due to the absence of entanglements.

2. Effects of PVP-PEG H-bonds

No adhesion has been found for HMW PVP blends with PEGDME, indicating that the contribution of PVP-PEG hydrogen bonds is of crucial importance for the adhesive behavior. The PVP-PEGDME blends are only partly miscible.

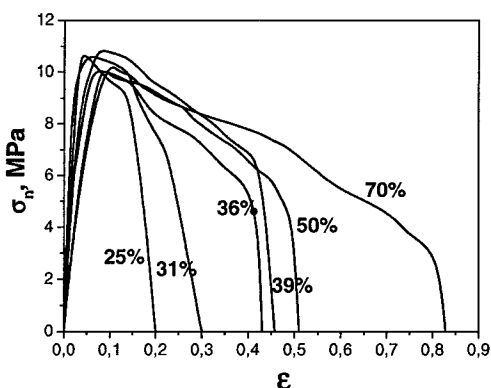


Figure 7. Effect of PEGDME content on the tensile properties of HMW PVP blends with PEGDME.

The deformation of the PVP-PEGDME films (Fig. 7) is typical of brittle plastics. Note the high value of yield stress, independent of concentration and the very low value of maximum extension denoting brittle fracture.

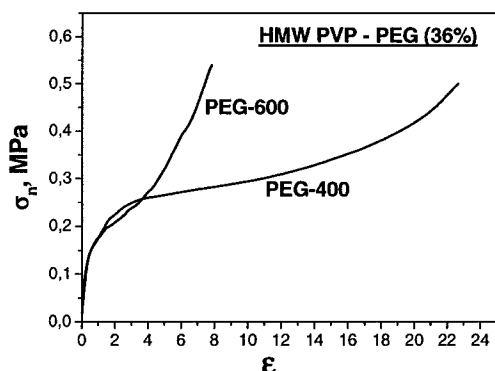


Figure 8. Effect of PEG molecular weight on the stress-strain behavior of HMW PVP blends.

The above described PVP-PEG hydrogels contain normally 8 – 9 % of water sorbed from the surrounding atmosphere or residual after gel preparation.

The longer the PEG chain, the lower the H-bond network density [3]. If we assume that the amount of energy required to deform and break an adhesive film in tension (the area under stress-strain curve in terms of true stress) is proportional to the amount of reformable H-bonded PEG-crosslinks, we can predict that the total work of deformation and fracture of PVP-PEG films should be higher for PVP blends with PEG-400 as compared with PEG-600 (Fig. 8). Although the nominal ultimate tensile stress is approximately the same for the fracture of PVP blends with PEG-400 and PEG-600, the true ultimate stress is higher for PEG-400 since in this case the fracture occurs at higher values of elongation. If the deformation is homogeneous the true tensile stress is a product of nominal stress by absolute elongation. Comparison of the values of ultimate tensile stress (which is a measure of cohesive strength) with a total work of viscoelastic deformation and breaking of a sample allows us to evaluate the total work of fracture.

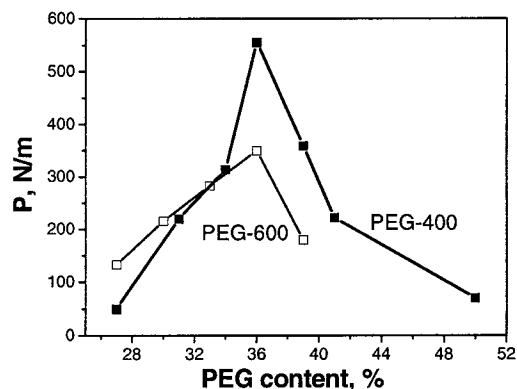


Figure 9. 180° Peel adhesion of HMW PVP blends with PEG of different molecular weights.

In contrast to the impact of PVP MW which profoundly modifies the mechanism of deformation of the blend, the dependence of the peel adhesion of the PVP blends on PEG content is very similar for PEG-400 and PEG-600. However the maximum in adhesion for the PVP blends with 36 % of PEG, is appreciably lower with PEG-600 than that with PEG-400 which provides a denser H-bond network.

Conclusions

We have shown that the entanglement structure of the PVP chains plays a major role in controlling the rubber elastic behavior and therefore the adhesive properties of the blends at large strains. On the other hand the H-bonded network structure controls both the small strain behavior, significantly stiffening the structure, and if entanglements are present, slows down disentanglement, effectively increasing the dissipative properties of the adhesive.

Acknowledgements

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References

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