Polymer Bulletin 40, 63–67 (1998)

Polymer Bulletin

Poly(*N*-1-alkylitaconamic acids)/poly(*N*-vinyl-2-pyrrolidone) blends

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Received: 30 July 1997/Revised version: 3 November 1997/Accepted: 20 November 1997

Summary

Blends containing poly(N-1-alkylitaconamic acids) (PNAIA) and poly(N-vinyl-2-pyrrolidone) (PVP) of two different weight average molecular weights, were studied by differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA), and infrared spectroscopy (FTIR). The phase behaviour of the blends is analyzed in terms of the side chain structure and the specific interactions involved, mainly due to the free carboxylic group and the amide groups in PNAIA and the carbonyl group of PVP. The strength of the interaction was analyzed in terms of the Gordon-Taylor parameters.

Introduction

Miscibility between polymers is thermodynamically unfavourable due to entropic reasons. When two high molecular weight polymers are blended the gain in combinatorial entropy upon mixing is negligible. Therefore the predominant term in the free Gibbs energy of mixing is the enthalpic one. A number of papers report the miscibility behaviour in blends composed of polymers with dissimilar chemical structures. These polymers provide specific interactions between chains, and therefore an exothermic heat of mixing (1). Miscibility of blends containing donor and acceptor polymers like those containing acid and/or basic units has been reported (2). It has been demonstrated that poly(N-vinyl-2-pyrrolidone) (PVP) interacts strongly with polymers of a wide variety of structures. Miscibility of PVP with poly(vinylidene fluoride) (3-6) poly(vinylalcohol) (7-11) poly(2,6-dimethyl-1,4-phenylene oxide) (12), poly(mono-n-alkylitaconates) (13) etc. has been reported previously. However, to our knowledge, no works dealing with blends containing PVP and poly(N-1-alkylitaconamic acid) (PNAIA) (See Scheme 1) have been reported. PNAIA are polymers which present two interacting groups, i.e. a free carboxylic group and one amide group bearing aliphatic chains with different lengths. The presence of these two groups in PNAIA should enhance inter and intramolecular interactions which can be important in the study of polymer blends. On the other hand, the presence of long aliphatic side chains is a factor to take into account due to the possibility of hydrophobic interactions which could also play an imporant role in the miscibility process.

The aim of the present work is the study of the miscibility of blends of PVP samples of two different molecular weights with PNAIA containing 1-butyl (PNBIA), 1-hexyl (PNHIA) and 1-octyl (PNOIA) groups in the side chains. The analysis of the effect of the specific interacctions on the miscibility will be analyzed using diferential scanning calorimetry (DSC) infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA).

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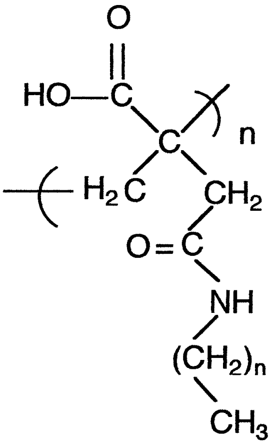

n= 3 : PNBIA
n =5 : PNHIA
n =7 : PNOIA

Scheme 1

Experimental

Monomers and Polymer Preparation

Commercial samples of poly(N-vinyl 2- pyrrolidone) (PVP) from Aldrich with weight average molecular weight ($\overline{M}_w$): 24.000 (PVP_{24}) and 10.000 (PVP_{10}) respectively were used. N-1-alkylitaconamic acids (NAIA) were synthesized by reaction of itaconic anhydride with the corresponding 1-alkylamine in chloroform following procedures previously reported (14) and improved by us. PNBIA, PNHIA and PNOIA were obtained by radical polimerization in bulk at 343-393 K (depending on the N-1-alkylitaconamic acid used) under nitrogen, using, α,α'-azobisisobutyronitrile (AIBN) (0.6% mol) as initiator. Purification of the polymers was achieved by reprecipitation with methanol in THF solution, before vacuum drying.

Thermogravimetric measurements

Dynamic thermogravimetric measurements were performed using a Mettler TA-3000 calorimetric system equipped with a TC-10A processor, and a TG-50 thermobalance with a Mettler MT5 microbalance. The samples were heated in Al_2O_3 pans. Measurements were carried out between 308 and 873 K at 20 °min^{-1}, under N_2.

Preparation of the blends

Blends of different compositions were prepared by solution casting using chloroform as solvent and then evaporated at room temperature and vacuum dried at 298 K for 72 h. The polymer concentration in the solution was about 2% (w/w).

DSC Measurements

The glass transition temperatures (Tg) of the pure polymers and blends were measured with a Mettler TA-3000 system equipped with a TC-10A processor with a DSC-20 cell. Polymer samples were dried under reduced pressure in a vacuum oven prior measurements. Dry nitrogen was used as purge gas and thermograms were measured in the range 308 to 453 K at a scan rate of 20 °min^{-1}.

FTIR Measurements

Infrared spectra of pure polymers and blends were recorded on a Vector 22 Bruker Fourier Transform Infrared spectrophotometer. The spectra were recorded with a resolution of 1 cm^{-1}. The samples were prepared directly in KBr pellets.

Results and discussion

The DSC thermograms of dried samples, containing initially different amounts of PVP of two different molecular weights ($\overline{M}_w$): 24.000 (PVP$_{24}$) and 10.000 (PVP$_{10}$)respectively and PNAIA exhibit distinct single glass transition temperatures (Tg) this is indicative of one-phase material.

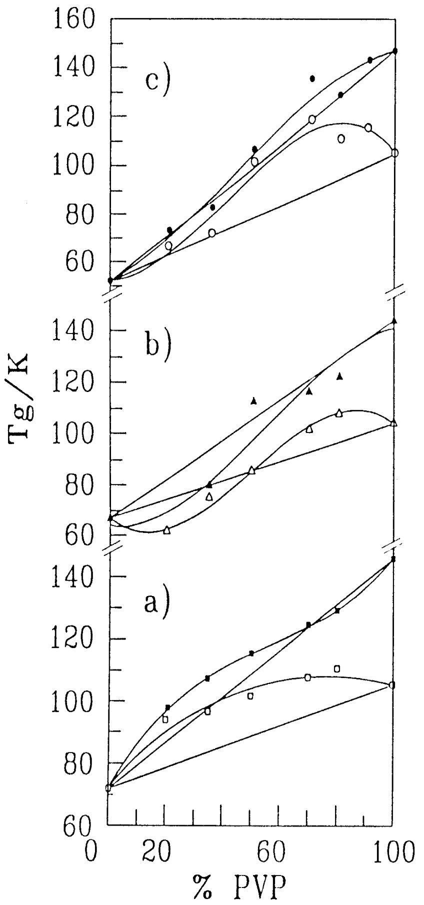

Figure 1. Variation of the glass transition temperature, Tg, for blends containing: a) PNBIA with PVP$_{10}$ (□) and PVP$_{24}$ (■); b) PNHIA with PVP$_{10}$ (Δ) and PVP$_{24}$ (Δ); c) PNOIA with PVP$_{10}$ (O) and PVP$_{24}$ (•).

Figure 1-a, 1-b and 1-c show the dependence of Tg on composition for blends of PNBIA, PNHIA and PNOIA with PVP$_{10}$ and PVP$_{24}$ respectively. These Tg values are intermediate between the Tg of PVP$_{10}$ and/or PVP$_{24}$ and the corresponding PNAIA. This behaviour would indicate miscibility over the whole range of composition irrespective of the molecular weight of PVP and the PNAIA. Nevertheless, it is interesting to note that a continuous variation of Tg is observed. There is a qualitative difference depending on the PNAIA. In fact, the degree of curvature of the plots are rather different. Blends containing PNBIA show curves over the weighed values of Tg between the pure components and also show an appreciable degree of curvature. In the case of blends with PNHIA two different curves can be observed for PVP$_{10}$ and PVP$_{24}$ respectively. In the former a sinusoidal shape is observed, and for PVP$_{24}$ the curve is always below the weighed value between the pure components. For blends containing PNOIA the behaviour is qualitatively similar to that of PNBIA. In order to analyze quantitatively way the calorimetric behaviour of these systems, the Gordon-Taylor (GT) equation (15) was used to estimate the strength of the interaction.Table 1 compiles the GT constant (K_{GT}) for the systems studied. This parameter can be considered a semiquantitative measure of the strength of the interaction between the groups of the polymeric components (16). According to the K_{GT} values summarized in Table 1, the interaction between PVP and PNAIA is sufficient to favour miscibility.

Table 1. Constant of the Gordon-Taylor (K_{GT}) equation for blends of PVP_{10} and PVP_{24} with PNBIA, PNHIA and PNOIA.

PVP	PNAIA	K_{GT}
PVP_{10}	PNBIA	0.44
	PNHIA	0.98
	PNOIA	0.53
PVP_{24}	PNBIA	0.62
	PNHIA	0.73
	PNOIA	0.95

Intra and inter molecular association of PNAIA cannot be disregarded because of the presence of the free carboxylic and amide groups. In fact, -C=O or -NH groups can interact via hydrogen bonding or by association to another polymeric chain. This phenomenon can be seen in the FTIR spectra Due to the existence of three different carbonyl groups i.e. the -NH-CO, the -CO-OH and the vinylpyrrolidone >N-C=O, the analysis of the I.R. spectra is very complex. However, it is possible to observe a variation ($\Delta\nu \cong$ 5-6 cm^{-1}) of the absorption band corresponding to the associated carbonyl (-NH-CO-) (1690-1700 cm^{-1}) when the pure polymers are blended with PVP relative to the pure components. On the other hand, it is possible to follow the variation of the stretching absorption of the >NH amide group at 3460 cm^{-1} which corresponds to an associated band for the three PNAIA studied. This associated absorption is shifted 25-30 cm^{-1} as function of the blend composition depending on the PNAIA considered. These results would confirm the calorimetric analysis in the sense that these blends are miscible over the whole range of compositions.

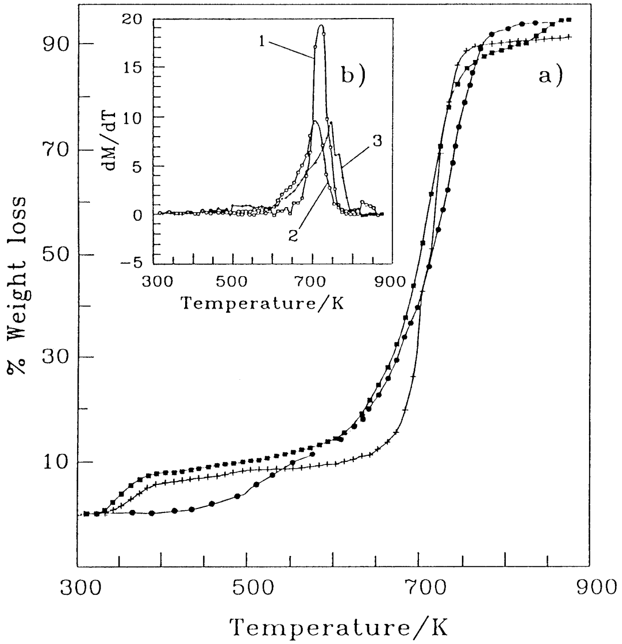

Figure 2. Thermogravimetric profiles for: a) PVP_{24} (+), PVP_{24}/PNHIA blend (50% w/w) (■) and PNHIA (•) and b) First derivative of the weight loss (dM/dT) for: PVP (curve 1), PVP_{24}/PNHIA blend (50% w/w) (curve 2) and PNHIA (curve 3).

Figure 2 shows thermogravimetric profiles for PVP_{24}, PNHIA and a blend of 50% composition as a representative example of the thermal behaviour of the blends. The blend decomposes at a lower temperature than that of the pure components, as can be observed in Figure 2-b. In this Figure the first derivative of weight loss (dM/dT) against the temperature is represented, to see better the position of the maxima. This result can be considered as another argument indicating miscibility.

In conclusion blends of PNAIA and PVP are miscible over the whole range of composition, and can be confirmed by calorimetric, infrared and thermogravimetric analysis.The miscibility between these systems is explained by hydrogen bonding formation. Autoassociation of PNAIA cannot be disregarded and may be another factor to take into account for the miscibility.

Acknowledgements: We express our thanks to **Fondo Nacional de Desarrollo Científico y Tecnológico (Fondecyt)**, project 8970011 for partial financial support. M.U. acknoledges to CONICYT for a Graduate Fellowship. D.R. and A.O. thank to **Catedra Presidencial en Ciencias'95** for financial help.

REFERENCES

1. Paul, D.R, J. W. Barlow and H. Heskkula (1988) Encyclopedia of Polymer Science and Engineering, 2nd Ed., Mark, Bikales, Overberger, Menges Eds., John Wiley & Sons. N. York.
2. Opazo A, Gargallo L, RadiC D, (1996) Polym. Bull., 36: 511
3. Galin M, (1996) Makromol. Chem., Rapid Commun. 5:119
4. Galin M, (1987) Makromol. Chem., 188: 1391
5. Alfonso G, Turturro A, Scandola M, Ceccorulli G, (1989) J. Polym. Sci., Polym. Phys. Edn, **27**: 1195
6. Ceccorulli G, Pizzoli M,Scandola M, Alfonso G, Turturro A, (1989) Polymer **27**, 1195
7. Ping Z, Nguyen Q, Neel J, (1989) Makromol. Chem. 190: 437
8. Ping Z, Nguyen Q, Neel J, (1990) Makromol. Chem. 191: 185
9. Thyagarajan G, Janarthanan V, (1989) Polymer 30: 1797
10. Nishio Y, Haratani T, Takahashi, T. J. (1990) Polym. Sci.,Polym. Phys. Edn., 28, 355
11. Zhang H, Yin J, (1990) J. Makromol. Chem. 191: 375
12. Opazo A, Gargallo L, RadiC D, (1991) Polym. Bull., 27: 205
13. Opazo A, Gargallo L, RadiC D, (1994) Makromol. Chem., Macromol. Symp. 84, 289
14. Oishi T, (1980) Polym. J. 12:719
15. Gordon M, Taylor J (1952) J. Appl. Chem. 2:493
16. Belorgey G, Prud'Homme R (1982) J. Polym. Sci., Polym. Phys. 20:91