Miscibility of poly(*N*-vinyl-2-pyrrolidone) with a copolyamide

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Blends of poly(*N*-vinyl-2-pyrrolidone) (PVP) with a copolyamide (CoPA) randomly composed of 1:1:1 (wt) nylon 6, nylon 66 and nylon 610 structural units were prepared by casting from a common solvent. They were found to be miscible and show a single, composition-dependent glass transition temperature (T_g). The addition of PVP to CoPA significantly lowers the crystallinity owing to an increasing T_g of the system. The observed miscibility is proposed to be the result of specific interactions between the proton acceptor groups of PVP and the amide groups of CoPA.

(Keywords: poly(*N*-vinyl-2-pyrrolidone); copolyamide; polymer blend; polymer miscibility; specific interaction)

INTRODUCTION

Polymer pairs which achieve miscibility via specific interactions such as dipole–dipole interactions and hydrogen bonding have received particular attention in recent years[1]. Specific interactions are usually considered to be the driving forces for miscibility and their important role in the miscibility of polymer blends has been clearly elucidated. Poly(*N*-vinyl-2-pyrrolidone) (PVP) is a water-soluble tertiary amide polymer and a strong Lewis base. The proton acceptor groups of PVP can interact through hydrogen bonding with proton donor polymers. It has been proved that PVP exhibits miscibility with poly(vinylidene fluoride)[2–5], poly(vinyl alcohol)[6–10], poly(*p*-vinyl phenol)[11], poly(vinyl butyral)[12], poly(hydroxyether of bisphenol A)[12], poly(hydroxyethyl methacrylate)[13], poly(hydroxypropyl methacrylate)[13] and styrene–allyl alcohol copolymers[13].

In previous work we found that PVP is miscible with poly(vinyl chloride)[14], poly(epichlorohydrin)[14], poly(vinyl formal)[15], poly(ether sulphone)[16], phenolphthalein poly(ether sulphone)[16], phenolphthalein poly(ether ether ketone)[16] and poly(hydroxyether of phenolphthalein)[17]. In this report, blends of PVP with a copolyamide (CoPA) are studied and the miscibility of PVP with CoPA is established.

EXPERIMENTAL

The PVP had a viscosity molecular weight $=57000$ determined in water at 25°C and was supplied by Shanghai Synthetic Resins Co., Shanghai, China. The CoPA was commercially obtained from the Harbin Nylon Factory, Harbin, China. It was a random copolymer composed of 1:1:1 (wt) nylon 6, nylon 66 and nylon 610 structural units and had an intrinsic viscosity $=0.49\ \mathrm{dl\,g^{-1}}$ when measured in *m*-cresol at 40°C. *N,N'*-dimethylformamide (DMF) was AR grade and was used as received.

All the PVP/CoPA blends were prepared by solution casting from DMF at 80°C. To remove the residual solvent, the blends were then dried in a vacuum oven at 80°C for 2 weeks.

The calorimetric measurements were made on a Perkin-Elmer DSC-2C differential scanning calorimeter. The instrument was calibrated with an indium standard. All samples were first heated to 180°C to melt any crystallinity followed by quenching to −50°C. A heating rate of $20^\circ\mathrm{C\,min^{-1}}$ was used in all cases. The glass transition temperature (T_g) and the crystallization temperature (T_c) were taken as the midpoint of the transition and the minimum of the exothermic peak, respectively, while the melting point temperature (T_m) was taken as the maximum of the endothermic transition.

RESULTS AND DISCUSSION

The PVP/CoPA blends with high PVP content were transparent at room temperature. All the blends were clear at temperatures above the melting point of CoPA and no phase separation occurred by heating up to ~280°C. The blends then became dark brown owing to depolymerization of PVP. It could be considered that the phase separation temperatures of PVP/CoPA blends are higher than the depolymerization temperature of PVP.

D.s.c. thermograms (second heat) shown in *Figure 1* revealed a single T_g which varied with overall blend composition as indicated in *Figure 2*. The appearance of a single T_g and overall T_g variation strongly suggests that the blend presents a homogeneous single amorphous phase, i.e. the two components are completely miscible at all compositions for temperatures above the melting temperature of the CoPA in the blends.

Several theoretical and empirical equations have been used to describe the T_g–composition dependence of miscible blends. One of these, the Gordon–Taylor equation[18], is written as:

$$T_g = (W_1 T_{g_1} + kW_2 T_{g_2})/(W_1 + kW_2) \qquad (1)$$

where T_g is the glass transition temperature of the blend,

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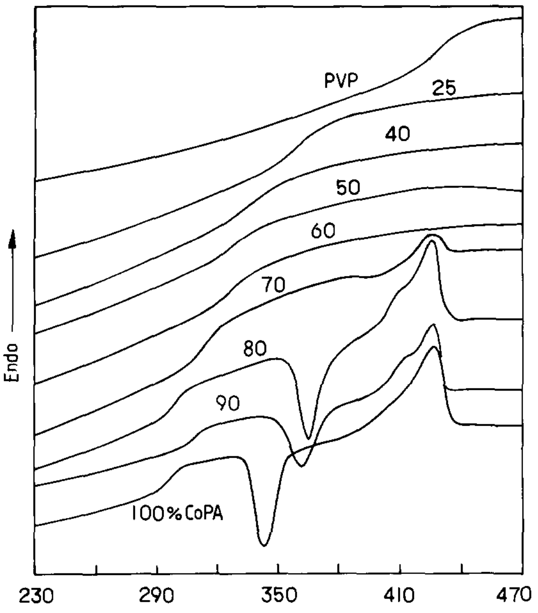

Figure 1 D.s.c. thermograms of PVP/CoPA blends

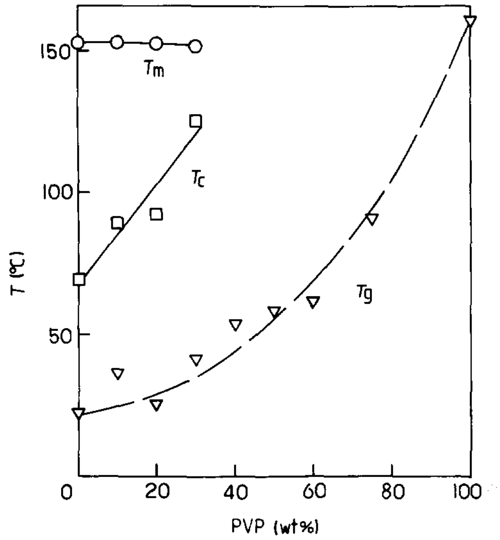

Figure 2 Transition behaviour of PVP/CoPA blends. The broken curve was calculated from the Gordon–Taylor equation with $k = 0.32$

T_{g_1} and T_{g_2} are the glass transition temperatures of components 1 and 2, respectively, W is the weight fraction and k is a constant. The broken curve in *Figure 2* is drawn using the Gordon–Taylor equation with a k value of 0.32, fitting the experimental data well. The marked positive deviation from the Gordon–Taylor equation at high CoPA content (90 wt% CoPA) is because of the crystallization of CoPA in the blend during quenching. A similar phenomenon has been observed for other compatible crystalline/amorphous blend systems[19–22].

Figure 2 shows also the T_c and T_m of the quenched samples as functions of blend composition. It can be seen that T_c increases with increase in PVP content, indicating that the crystallization of CoPA in the blend becomes progressively more difficult with increasing PVP content. The blend with 40 wt% or more PVP content did not show any crystallization exotherm. By measuring the areas under the melting peaks, it should be possible to evaluate the heat of fusion. The results obtained (*Table 1*) imply that the crystallinity of CoPA in the blend greatly decreases with increasing PVP content, which supports the idea that PVP is completely miscible with CoPA over the entire composition range in the melt. The decrease in the crystallinity of CoPA with PVP content is due to an increasing T_g of the system.

It has been shown by Fourier transform infra-red spectroscopy[6–8,11,17] that there are hydrogen bonding interactions involving the proton-acceptor groups of PVP and other proton-donor polymers. In the present case, it is likely that the formation of miscible PVP/CoPA blends also involves hydrogen bonding interactions between the amide N–H groups of CoPA and the proton-acceptor groups of PVP.

To summarize, PVP is miscible with CoPA. Homogeneous films were obtained for temperatures above the T_m of the CoPA in the blends. Phase separation of the PVP/CoPA blends could not be induced by heating up to 280°C. The existence of a single, composition-dependent T_g reveals that the blend presents a homogeneous single amorphous phase. Adding PVP to CoPA greatly lowers the crystallinity owing to an increasing T_g of the system. Miscibility of PVP with CoPA can be considered to be due to the hydrogen bonding interactions between the components.

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Table 1 Thermal properties of PVP/CoPA blends

PVP/CoPA	T_g (°C)	T_c (°C)	ΔH_c(blend) (J g^{-1})	ΔH_c(CoPA) (J g^{-1})	T_m (°C)	ΔH_f(blend) (J g^{-1})	ΔH_f(CoPA) (J g^{-1})
0/100	23	69	−23.5	−23.5	152	36.7	36.7
10/90	36	89	−22.8	−25.3	152	28.7	31.9
20/80	25	92	−16.9	−21.1	152	28.1	35.1
30/70	41	125	−1.1	−1.6	151	3.4	4.9
40/60	54						
50/50	58						
60/40	61						
75/25	90						
100/0	160						

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