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Miscibility of poly(methyl methacrylate-co-vinyl pyridine) and poly(butyl acrylate-co-acrylic acid) blends

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Summary

In order to enhance the miscibility of poly(methyl methacrylate) and poly(butyl acrylate), pyridyl and carboxylic acid groups were introduced on the component polymer chains by free radical copolymerization. Differential scanning calorimetry shows that the blend of component polymers containing less than 10 mole% of carboxylic acid and pyridyl groups is immiscible, but the blend of more than 10 mole% become partially to completely miscible as the functionality increases. The chemical interaction between carboxylic acid and pyridyl group in the blend was manifested by a blue shift of 9 cm^{-1} in the infrared stretching frequency of pyridyl group.

Introduction

Most polymer pair are thermodynamically immiscible since the entropy gain upon mixing is normally negligibly small while the enthalpy of mixing is usually positive unless a specific interaction is present (1,2).

Recently, many polymer pairs have been compatibilized by introducing a specific interaction between constituents of the individual polymer chains. Pearce et al (3) reported that copolymers of styrene and hydroxyl containing monomers were miscible with poly(ethylene oxide) via hydrogen bonding. Ionic and ion-dipole interactions have been employed to yield miscible blends of otherwise immiscible pairs (4-7).

In this study, it is attempted to enhance the miscibility of blends of poly(methyl methacrylate)(PMMA) and poly(butyl acrylate)(PBA) by introducing 4-vinyl pyridine and acrylic acid units into the component polymer chains.

Experimental

The PBA and poly(butyl acrylate-co-acrylic acid)(BA/AA) of different composition were polymerized in ethanol using AIBN as a free radical initiator (8). The acrylic acid content of the copolymers was determined by titration in ethanol with standardized ethanolic NaOH using phenolphthalein as an indicator.

The PMMA and poly(methyl methacrylate-co-4-vinyl pyridine)(MMA/VP) were synthesized by bulk polymerization in a sealed glass ample using AIBN as an initiator (9). To determine the vinyl pyridine content, the copolymer was titrated in a mixture of glacial acetic acid and acetonitrile (20/80 v/v) with a solution of $HClO_4$ and glacial acetic acid using crystal violet as an indicator. The copolymer composition and other properties are listed in Table 1. As shown in Table 1, the glass transition temperature of copolymers increases monotonically as the comonomer content increases, which indicates that the comonomer units are randomly distributed along the polymer chain. Intrinsic viscosities were measured at 25°C from ethanol solution.

The blends was prepared by dissolving the component polymers in chloroform/methanol mixture (90/10 v/v). The solution was cast on a glass plate at room temperature. The solvent was evaporated in a vacuum oven at 50°C for at least two days, and then the resulting films were preheated in a vacuum oven at 150 and 180° C for 30 min. The polymer compositions and blend ratios for the stoichiometric equivalence of interacting groups in the blend are listed in Table 2. The blend ratio is reported on a weight basis.

Thermal analysis was performed on a DuPont 910 differential scanning calorimeter (DSC) equipped with a mechanical cooling accessory. The scanning rate is 20 °C/min. The infrared spectra were obtained using a Bruker IFS-85 FTIR spectrometer. One hundred scans at a resolution of 2 cm^{-1} were signal averaged.

Results and Discussion

Figure 1 shows the DSC thermograms of the blends containing stoichiometric amounts of interacting groups with varying copolymer composition. In the blend of two homopolymers, two distinct Tg's corresponding to those for the parent polymers are observed, and the film of the blend is opaque. These facts indicate that the blends of PMMA and PBA are immiscible (10).

The transitions of blends B and C and the transparency of their films are similar to those of the immiscible blend A, but the transitions are shifted to higher and lower temperatures than those of their parent polymers,respectively. In the case of blends D and E, a single but less well defined Tg is observed, and their films are transparent. The glass transition of blend F ($\sim$20 mole% of interacting groups) is single and relatively sharp and its film is completely transparent. These results suggest that miscibility is enhanced with increasing the content of interacting groups.

Figure 2 shows the glass transition behaviors of blends of BA/AA-21.8 and MMA/VP-20.0 when the blends were annealed at 150°C for 30 min. For all blend ratios examined, a single glass transition is observed. The same result was observed for the blends annealed at 180 °C for 30 min, indicating the LCST of the blend is higher than 180°C. In other words this blend exists in a single phase up to 180° C. When the composition dependence of Tg is compared with the Fox equation, a satisfactory agreement between experimental and theoretical values could not be attained. Instead the positive deviation of Tg from the interpolated weight-average values is observed at 40-70 % loading levels of MMA/VP-21.8.

The LCST behavior of these miscible blends was examined by the cloud point measurement, but no cloudiness appeared up to the degradation temperature 200 °C. The LCST behavior in polymer blends is due to the

Table 1. Properties of Copolymers

Sample Code	Copolymer Composition (Mole% of AA or VP)	Intrinsic Viscosity (dL/g)	Tg (°C)
PBA	0.0	0.34	-48
BA/AA-4.9	4.9	0.24	-41
BA/AA-8.6	8.6	0.26	-38
BA/AA-10.5	10.5	0.19	-34
BA/AA-13.3	13.3	0.13	-31
BA/AA-21.8	21.8	0.10	-22
PMMA	0.0	0.58	117
MMA/VP-4.9	4.9	0.35	120
MMA/VP-8.5	8.5	0.74	122
MMA/VP-10.3	10.3	1.13	123
MMA/VP-13.3	13.3	1.55	124
MMA/VP-20.0	20.0	1.60	126

Table 2. Preparation of Polymer Blends

Blend	Polymer Component		Blend Ratio of BA/AA and MMA/VP(wt./wt.)
	I	II	
A	PBA	PMMA	1:1
B	BA/AA-4.9	MMA/VP-4.9	1.25:1
C	BA/AA-8.6	MMA/VP-8.5	1.21:1
D	BA/AA-10.5	MMA/VP-10.3	1.19:1
E	BA/AA-13.3	MMA/VP-13.5	1.22:1
F	BA/AA-21.8	MMA/VP-20.0	1.05:1

equation of state or free volume contribution to the second derivatives of the free energy of mixing with respect to composition (11). Hence the intermolecular contribution seems to be dominant at 200°C.

In the present system, there might exist several possible types of specific interactions such as self-association of carboxylic acid groups, hydrogen bonding between carbonyl and carboxylic acid groups, and the acid-base interaction between carboxylic acid and pyridyl groups. The self-association of carboxylic acid groups is undesirable for miscibility.The hydrogen bonding between carbonyl and carboxylic acid groups may not play an important role in enhancing miscibility because carbonyl groups are present in both blend components. Consequently the

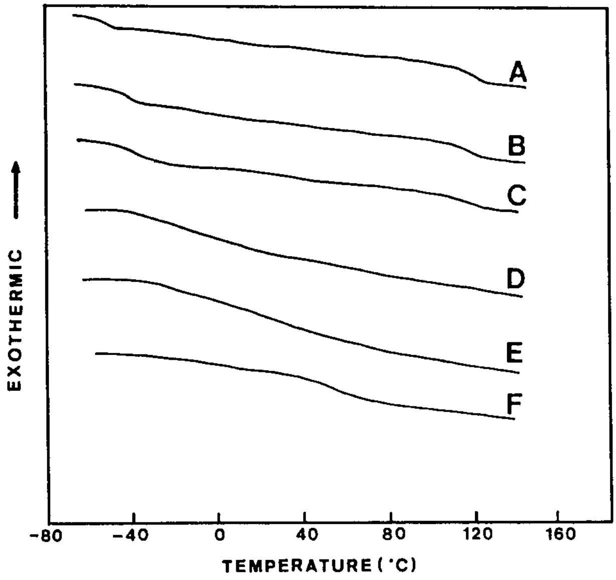

Figure 1. DSC thermograms of the blends containing stoichiometric amounts of acidic and basic groups.

driving force for miscibility may be an intermolecular acid-base interaction between carboxylic acid and pyridyl groups.

In order to investigate the nature of the acid-base interaction in the blend, FTIR study was performed. Figure 3 shows infrared spectra of the MMA/VP-20.0 copolymer and the blends containing stoichiometric amounts of interacting groups in the range 1520-1640 cm^{-1}. Two bands at 1598 and 1559 cm^{-1} in the spectrum of MMA/VP-20.0 are assigned to coupled C=N and C=C stretching vibrations in the pyridine ring (12). When the nitrogen atom of a pyridine compound is complexed to yield a pyridinium salt,the band at 1598 cm^{-1} of the pyridine ring shifts to higher frequency 1640 cm due to the localization of the electrons in the pyridine ring (13). In this blend system, a new band is observed at 1607 cm^{-1} which is higher than the absorption band at 1598 cm^{-1} for pyridine ring but relatively lower than that of pyridinium salt at 1640 cm^{-1}, and the intensity at 1604 cm^{-1} increases with the interacting group content. Therefore it is reasonable to say that the nature of the acid-base interaction in the blends is hydrogen bonding between carboxylic acid and pyridyl group rather than the ionic interaction.

Conclusions

The intermolecular acid-base interaction can be introduced in originally immiscible polymer blends to enhance miscibility. When the content of interacting group (in the present system, carboxylic acid and

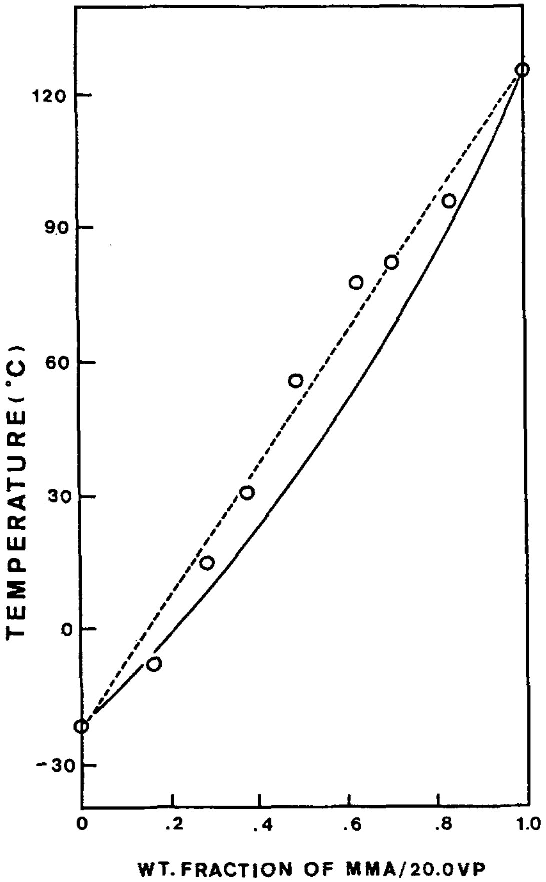

Figure 2. Glass transition behavior for blends of MMA/VP-20.0 and BA/AA-21.8. Solid and dashed lines represent the Fox equation and weight-average values.

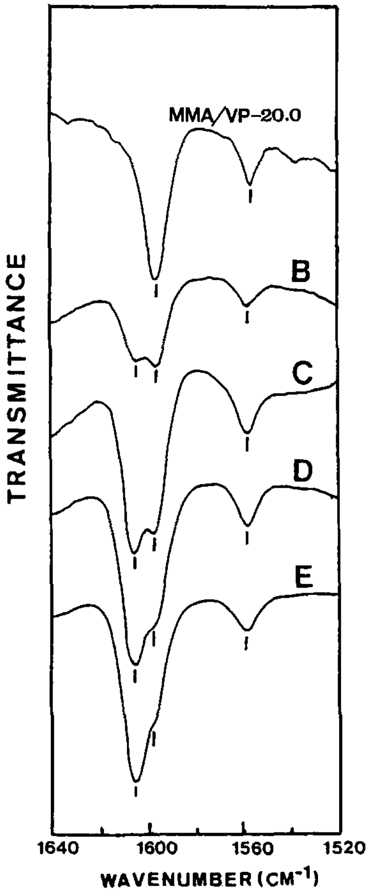

Figure 3. FTIR spectra for MMA/VP-20.0 copolymer and blends containing stoichiometric amounts of interacting groups.

pyridyl group) is lower than 8 mole%, the blend is immiscible. However, as the interacting group content increases further, the blend becomes partially to completely miscible. It is found that the minimum content for complete miscibility lies between 13 and 20 mole%, which may be dependent upon the strength of the specific interaction.

FTIR studies have shown that there is a significant band shift suggesting that intermolecular hydrogen bonding is formed between carboxylic acid and pyridyl groups. It is conclusive that this interaction is primarily responsible for the apparent miscibility observed in thermal analysis.

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