Blends and Interpenetrating Networks of Phenolic Resins and Polyamides

T. P. YANG, T. K. KWEI, and E. M. PEARCE, *Polymer Research Institute, Polytechnic University, Brooklyn, New York 11201*

Synopsis

Blends and interpenetrating networks of phenolic resins and polyamides were prepared. Control of miscibility was achieved by modifying nylon 6I through copolymerization and *N*-alkylation. The phenolic resin was also modified by partial conversion of the hydroxy groups to cinnamyloxy groups. The phase behaviors of these blends and semi-IPNs were investigated.

INTRODUCTION

In a previous paper,[1] the miscibility of phenolic resins, poly(hydroxymethylene phenylenes) with poly(*N,N*-dimethylacrylamide) was studied. The driving force for miscibility is hydrogen bonding between phenol and substituted amide groups. We have now extended our investigation to blends of the same phenolic resin with polyamides of the nylon type. In the latter polymers, interchain hydrogen bonding is strong and it is the purpose of this study to see whether an exchange of hydrogen bonds from hydroxy–hydroxy and amide–amide to hydroxy–amide groups can produce miscible pairs. Evidence for hydrogen bond exchange will be presented in another publication. In general, however, the presence of crystalline regions in many polyamides resulted in poor solubility and miscibility. Therefore, our study has made use of copolyamides or *N*-substituted polymers for the purpose of reducing self-association and crystallinity. At the same time, we have also reduced self-association in phenolic resins by partially converting the hydroxy groups to alkoxy groups. Blends and interpenetrating networks were prepared from these modified polymers and the phase behaviors examined.

EXPERIMENTAL

Materials

(a) Poly[(1-hydroxy-2,6-methylene)phenylene](PHMP) was synthesized from phenol and formaldehyde at 165°C in the presence of calcium hydroxide as catalyst. The reaction condition results in highly specific ortho-ortho methylene linkages without noticeable amounts of the side reactions[2] as confirmed by infrared spectra and by chemical shifts in proton and carbon-13 NMR spectroscopy. The number average molecular weight of PHMP was determined by vapor phase osmometry to be 1000–1100.

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(b) O-cinnamylation of PHMP: Four hundred grams of DMSO and 1.21 g of sodium hydride were charged to a three-neck flask and heated to 75–80°C for 4 h under nitrogen protection. Then 1 g of PHMP was introduced and kept for 4 h at that temperature. After cooling to room temperature, 9.24 g (10% mole excess) of cinnamyl chloride was added and stirred for 12 h. The polymer was precipitated from solution into water, redissolved in dioxane, filtered, reprecipitated, and dried in a vacuum oven at 60°C. From the result of elemental analysis, the degree of substitution of the hydroxy groups was calculated to be about 40%. This material is designated as sPHMP in the ensuing text. The T_g of sPHMP was 35°C.

(c) Polyamides: Nylon 66 was synthesized by melt polymerization, using the salt of adipic acid and hexamethylenediamine. The intrinsic viscosity in formic acid was determined to be 1.7 dL/g at 25°C. Nylon 6I was similarly synthesized from the salt of isophthalic acid and hexamethylenediamine. The 6I polymer which is amorphous has an intrinsic viscosity of 0.37 dL/g, determined in sulfuric acid at 30°C. The procedure for N-ethylation is as follows: DMSO (400 g) and sodium hydride (1.21 g) were reacted at 75–80°C for 4 h under nitrogen. Twelve grams of the 6I polymer were then introduced and kept at that temperature for 4 h. After cooling to room temperature, 3.4 g of ethyl bromide were introduced and stirred for 12 h at room temperature. The polymer was precipitated from solution in water, redissolved in dioxane, filtered, reprecipitated, and dried in a vacuum oven at 60°C.

From the result of the elemental analysis and the disappearance of the NMR peak of NH at 6.5 ppm, the N-ethylation reaction is judged to be essentially complete. The conclusion is supported by infrared spectroscopic data. The amide group of nylon 6I is characterized by absorption at 3320 cm^{-1} for the NH group. In the N-ethylated 6I polymer, the peak at 3320 cm^{-1} was hardly discernible. The N-ethylated 6I polymer is also amorphous.

(d) Copolyamides: Mixtures of 6I and 66 salts were placed in an autoclave and polymerization was allowed to take place at 250°C for 3 h. The copolymer containing 70% 6I has an intrinsic viscosity of 0.44 dL/g, determined in sulfuric acid at 30°C. It shows a small melting endotherm in the DSC scan with a melting point of 96°C. This was the only copolymer for which blending studies were conducted.

Preparation of Films

Blend films of 66/PHMP, 6I/PHMP, 6Ico66/PHMP, and 6Ico66/sPHMP were cast from m-cresol solutions and dried in a vacuum oven at 1 mm Hg pressure for 2 weeks at 100°C. The films were then immersed in methanol for 4 days to leach out residual m-cresol, if any, and redried. Films of N-ethylated 6I were prepared from a mixed solvent containing 90% 1,4-dioxane and 10% DMSO. Dioxane was found to be a good solvent for both N-ethylated 6I and sPHMP and was therefore used to prepare blend films for that system.

Differential Scanning Calorimetry

Measurement of glass transition temperatures was carried out with a differential scanning calorimeter, DuPont Model 9900. A heating rate of 10°C/min was used in all experiments. The glass transition temperature was deter-

mined as the onset (extrapolated) of the abrupt increase in the specific heat of the sample. The results of the second thermal scan were reported in this paper. The T_g values are reproductible to ± 2°C.

Cloud Point Measurement

The cloud temperature was determined by monitoring the intensity of light transmission by the polymer film with the use of a Nikon microscope equipped with a hot stage.

RESULTS AND DISCUSSION

Blend films of nylon 66 and PHMP cast from m-cresol or mixed in the molten state showed a single T_g for each film.[3] In these blends, extensive degradation set in before thermally induced phase separation could be detected. The interpretation of the physical properties of these blends, however, is complicated by the crystallinity of nylon 66. Therefore, we have chosen to study nylon 6I, which is amorphous. A 1 : 1 blend of 6I and PHMP exhibited a glass transition at 104°C. Upon heating, there was no evidence of phase separation even at 280°C, at which degradation of the polymers became extant. In our study of the effect of chemical structure on miscibility, we synthesized a series of copolymers of 66 and 6I. Copolymers containing 80% (by weight) or more 6I are amorphous, but the 70% copolymer is crystalline. The degree of crystallinity of this copolymer, estimated from DSC melting endotherm, is low and the melting point is 96°C. Its blends with PHMP were found to be amorphous. For this reason, this copolymer was selected for systematic measurements. In contrast with 6I/PHMP blends, the 6Ico66/PHMP blends underwent phase separation at about 250°C. The cloud point curve is represented by curve A in Figure 1. It should be mentioned that the T_g values of 6Ico66 and PHMP, 81 and 84°C, respectively, were too close to each other for DSC measurements to ascertain whether the blend had a single T_g. However, the observation of the lower critical solution temperature (LCST) phenomena implies that the two polymers are miscible at lower temperatures over the entire range of composition.

When the PHMP component of the 6Ico66 blends was crosslinked by HMTA at 170°C, the semi-IPNs had glass transition temperatures in the range between 114 and 141°C (Table I). Phase separation in these semi-IPNs occurred at temperatures lower than the corresponding values for the blends, as shown by curve B in Figure 1.

In a different set of experiments, the semi-IPNs were maintained at their respective cloud temperatures for 10 min, followed by quenching in liquid nitrogen. The glass transition temperatures of the quenched samples were then measured. Four of the five samples under investigation showed two T_g's, characteristic of a two-phase system (Table I). Only the film containing 20% PHMP showed a single T_g, apparently because the sample was able to revert to the single phased state either during quenching, or during heating in the DSC experiment.

The second approach to chemical modification consists of N-substitution of polyamides to reduce interchain hydrogen bonding of the amide groups. Among
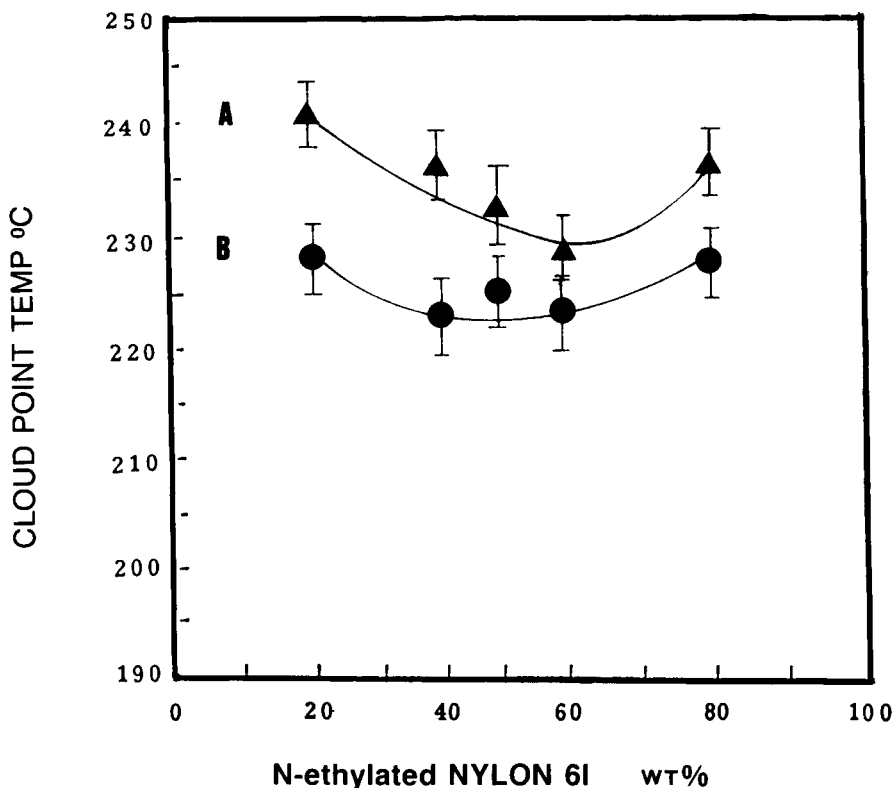
Fig. 1.   Cloud point curves for 6Ico66/PHMP blends (A) and semi-IPNs crosslinked at 170°C (B).

the substituted nylons, the N-methylated 6I polymer is soluble only in m-cresol. However, the N-ethylated 6I polymer dissolves in common organic solvents such as methanol, dioxane, and dichloroethane. Its solubility characteristics facilitate the film casting process. Therefore, the N-ethylated 6I was chosen for detailed studies.

TABLE I
Glass Transition Temperatures of Semi-Interpenetrating Network of 6Ico66/PHMP

Composition (wt % nylon)	T_g (°C)	
	As prepared IPN	After annealing at cloud point
100	107	107
80	114	114
60	117	100, 126
50	134	88, 132
40	131	91, 134
20	141	88, 130
0	140	140

A 1 : 1 blend of N-ethylated 6I with PHMP has a single T_g at 94°C. Its cloud point is too high to be observed. Since the phenol moiety interacted strongly with substituted amide group through hydrogen bonding, we sought to reduce the enthalpic interaction between the two components by partial conversion of the OH groups in PHMP to OR groups. Cinnamyloxy group was used because it was originally planned to use a photosensitizer as initiator for interpenetrating network formation. The photoinitiator method, however, was not pursued in this study. Instead, we opted to use azobisisobutyronitrile as the radical initiator. The reaction results in a completely insoluble material. Blends of N-ethylated 6I with substituted phenolic resin, sPHMP, showed a single T_g for each mixture, as listed in Table II. The experimentally determined glass transition temperatures are higher than the corresponding weight average values. Similarly high glass transition temperatures, have been observed in many other blends in which strong interpolymer interactions are operative.[1,4-6]

Semi-IPNs were prepared from N-ethylated 6I/sPHMP by two different methods. In the first set of experiments, the sPHMP component was crosslinked at 65°C by using AIBN as the initiator. The glass transition temperatures of the semi-IPNs are, as expected, somewhat higher than the values for the corresponding blends. The cloud points are too high to be observed experimentally.

When the same system was crosslinked at 170°C by the use of hexamethylenetetramine, HMTA, the T_g values were comparable to those crosslinked at 65°C (Table II). However, in contrast with the latter semi-IPNs, phase separation now occurred at temperatures below the cloud point curve for the blend (Fig. 2). The two sets of semi-IPN films have different chemical structures and the observed differences in their phase behaviors cannot be attributed to a single cause. Among the various factors influencing phase separation are the increase in the molecular weight of PHMP upon crosslinking, the extent of interpolymer hydrogen bonding at the temperature of reaction and the thermal reversibility of the hydrogen bonding association-dissociation phenomenon caused by network formation. These factors have been discussed previously[7,8] and will not be elaborated here. Nevertheless, it is of interest that the cloud temperature of an interpenetrating network can be manipulated by selecting different reactions carried out at different temperatures.

TABLE II
Glass Transition Temperatures of Blends and Semi-IPNs of N-Ethylated 6I/sPHMP

Composition (wt % nylon)	T_g (°C)		
	Blend	IPN crosslinked at 65°C	IPN crosslinked at 170°C
100	10		
80	28	34	37
60	22	37	38
50	24	34	38
40	32	37	41
20	32	39	44
0	35	42	45
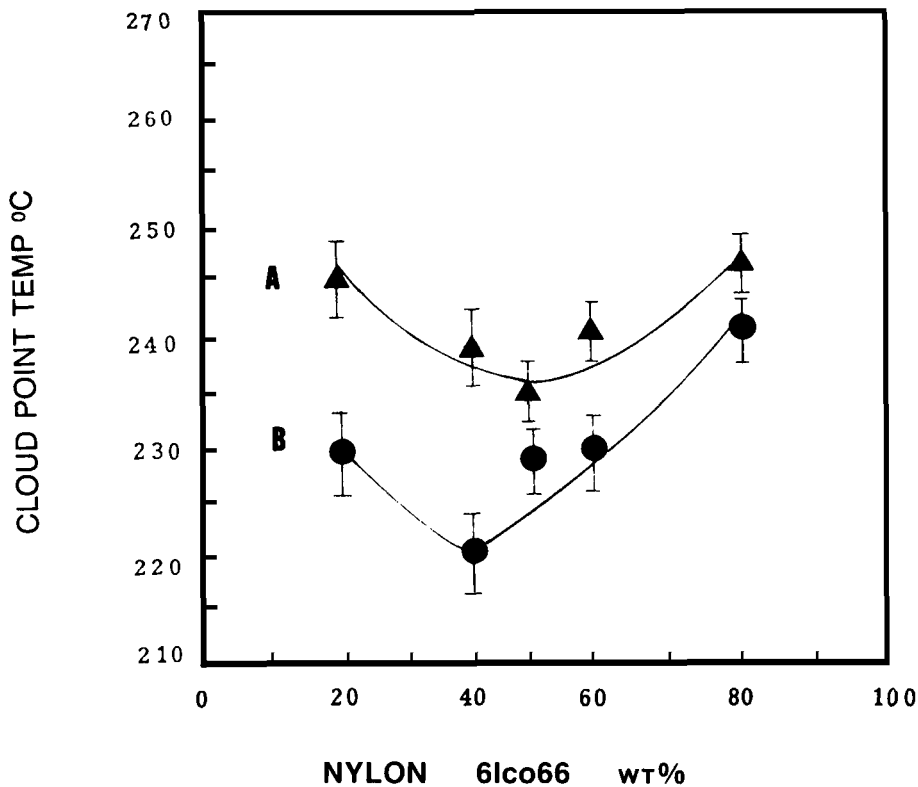
Fig. 2. Cloud point curves for N-ethylated 6I/sPHMP blends (A) and semi-IPNs crosslinked at 170°C (B).

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