Studies on the Compatibility of Poly(Styrene-co-Vinyl-Phenyl Hexafluorodimethyl Carbinol) with Nylon 6,12 and N,N'-Dimethyl-Substituted Nylon 6,12

The increasing interest in polymer blending is due mainly to the growing needs for new materials, having diverse combination of properties, and to the problem of plastic waste reuse.[1] However, only a few miscible polymer blends with industrial application have been reported so far.[2] The specific (proton donor–acceptor) interaction between polymers has proven to play an important role for achieving compatibility. Hydrogen bonding interactions have been credited to yield miscibility in systems, such as poly(methacrylic acid)/poly(ethylene oxide),[3] poly(methacrylic acid)/poly(vinyl pyrrolidone),[4] poly(butylene terephthalate)/poly (hydroxyether of bisphenol A),[5] poly(vinyl chloride/poly(methyl methacrylate),[6] poly(vinyl chloride)/poly(ε-caprolactone),[7] poly(vinyl chloride)/poly(butylene terephthalate),[8] nylon-6/poly(ethylene-co-acrylic acid),[9] poly(vinyl chloride)/poly(ethylene-co-N,N'-dimethyl acrylamide[10] and others.

Recently the synthesis of a new polymer, poly(styrene-co-vinyl phenyl hexafluorodimethyl carbinol) (PHFA), was reported.[11] PHFA was found to be compatible with bisphenol A polycarbonate, poly(butyl methacrylate), and poly(2,6-dimethyl-1,4-phenylene oxide).[11] Evidence for hydrogen-bonding interaction was detected by IR spectroscopy.

This paper is an attempt to investigate the possibility of obtaining miscible polyamide/PHFA blends, as well as the eventual use of PHFA as a compatibilizer (coupling agent) for polyamide/polystyrene blends.

In this study, the criterion of a single glass transition temperature for the mixture is used to determine miscibility. For best results, the polyamide used had to exhibit melting and glass transition at temperatures far away from the T_g of polystyrene (PS) and PHFA. Nylon 6,12 (T_g = 46°C and T_m = 206–215°C)[12] was chosen as an appropriate material. In order to determine the influence of the PA crystallinity on the polymer miscibility, we synthesized the noncrystalline N,N'-dimethyl-substituted nylon 6,12[13] and copolymers with different amounts of substitution.

EXPERIMENTAL

Preparation of Polymers

The polyamides were obtained by polycondensation of the nylon salts. Equimolar solutions of hexamethylenediamine or N,N'-dimethyl hexamethylenediamine and 1, 10-decanedicarboxylic acid at 10% concentration in absolute ethanol were combined, and the mixture was refluxed for 0.5 h. Crystals of the nylon salt were precipitated from the solution after storage for 24 h in a refrigerator. In the case of the N,N'-dimethyl-substituted amine, the nylon salt was separated after addition of ether to the alcoholic solution. The nylon salts were recrystallized from ethanol or ethanol-ether. The melting points of the 6,12 nylon salt and the N,N'-dimethyl substituted 6,12 nylon salt were 158°C and 106, respectively. The polycondensation and copolycondensation of the nylon salts were carried out via three stages: heating at 220°C for 3 h in a container, sealed under reduced pressure; heating at 270°C for 2 h in N_2 atmosphere; and heating at 270°C for 1 h at 1 mm Hg. The polymers produced were stored for 1 week in a desiccator prior to characterization:

$$PHFA, \ (-CH_2-CH)_x-(CH_2-CH-)_y$$
$$\qquad\qquad\quad |\qquad\qquad\quad |$$
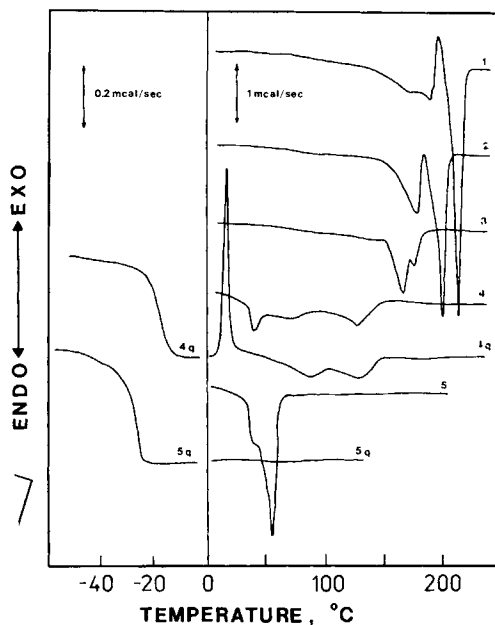$$\qquad\qquad\quad C_6H_5 \qquad\quad C_6H_4-C(CF_3)_2OH$$
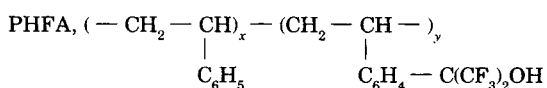
Fig. 1. DSC thermograms of N,N'-dimethyl-substituted nylon 6,12 polymers: (1) 0% subst.; (2) 25% subst.; (3) 50% subst.; (4) 75% subst.; (4q) 75% subst., after quenching; (5) 100% subst.; (5q) 100% subst., after quenching.

where $y = 30$ mol %, determined by elemental analysis of fluorine atom, was used.[14] PHFA showed a glass transition at 109°C.

PS used was Dow Chemical Co., Styron-685 D, MW $= 3 \times 10^5$ with $T_g = 101$°C. The viscosity measurements were made on 0.5% solution in m-cresol at 25°C.

Preparation of Blends

All polymer blends were prepared by the solution-casing method. m-Cresol was used as a common solvent for PHFA/PA and PHFA/PA/PS blends. Films were cast on a glass plate, and the solvent was removed by drying the films to constant weight at 50–70°C and 1 mm Hg (~72 h). The polymer mixtures were kept in a desiccator for a week before characterization. Blend composition is reported in this communication as weight ratios of the components.

Thermal Analysis

A differential scanning calorimeter (DSC, DuPont 990) was used to determine the glass-transition temperature (T_g), melting point (T_m), and temperature of "cold" crystallization (T_c) of the PA and blends. The thermograms were obtained at a programmed heating rate of 10°C/

TABLE I
N,N'-Dimethyl-Substituted Nylon 6,12 Polymers[12]

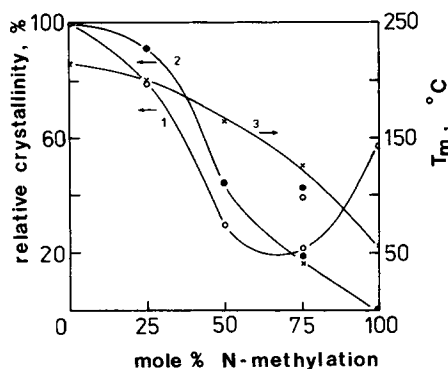| No.	% of N,N'-Dimethyl substitution of Nylon 6,12	Density	η_{sp}/c	T_g (°C)	T_m (°C) First run	After quenching
1	0	1.08	0.54	40	214	214
2	25	1.07	0.32	30	201	200
3	50	1.06	0.38	−16	168	165
4	75	1.04	0.38	−21	128	126
5	100	1.01	0.46	−30	56	—

Fig. 2. Crystallinity and T_m of N,N'-dimethyl-substituted nylon 6,12 polymers vs. degree of substitution (1) after annealing 7 days at 25°C and (2) after quenching.

min under nitrogen atmosphere. A second run after quenching from a temperature above T_m with dry ice–acetone mixture was made for the crystalline samples. T_g was determined as the intersection of the extrapolated low temperature baseline with the tangent to the heat capacity endotherm. The relative degree of crystallinity was calculated as a first approximation, by comparing the heat of fusion of the sample with that of nylon 6,12.

RESULTS AND DISCUSSION

The DSC thermograms of nylon 6,12 and the N-methylated polyamides show features associated with the glass transition of the amorphous phases and with the premelting, recrystallization and melting of the crystalline regions (Fig. 1). An in-depth understanding of the complex melting phenomena is beyond the scope of this study. Rather, the DSC data are used primarily for the purpose of identifying multiple phases. Therefore, in the context of the present investigation, only three characteristics of the thermograms are recorded, namely, the glass transition temperature (T_g), the final melting point (T_m), and the heat of fusion of the final melting endotherm from which the relative degree of crystallinity is calculated. The
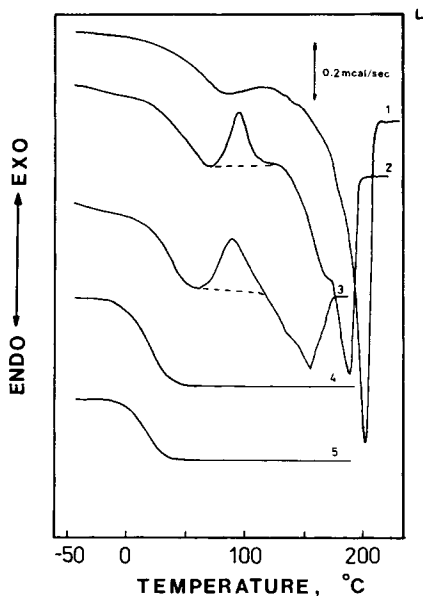

Fig. 3. DSC thermogram of PHFA/PA blends: (1) 0% subst.; (2) 25% subst.; (3) 50% subst.; (4) 75% subst.; (5) 100% subst. Exothermal peaks (2,3) appear after quenching.

TABLE II
PHFA/PA Blends

No.	Type of PA in blend	T_m (°C)	T_g (°C)	Reduction of crystallinity of PA phase (%)	
				First run	After quenching
1	6,12	203	43	0	10
2	25% N-subst.	187	25	4	15
3	50% N-subst.	156	20	15	41
4	75% N-subst.	—	2	—	—
5	100% N-subst.	—	0	—	—

T_g and T_m values of the five polyamides (PA) are listed in Table I together with their densities and reduced viscosities.

The substituted polymers are all semicrystalline. The melting temperatures and the relative degrees of crystallinity of the quenched samples decrease with increasing degree of N-methylation (Fig. 2). The 100% substituted polymer loses all its crystallinity and became amorphous ($T_g = -30$°C) upon quenching. But crystallinity is regained after standing at 25°C for 7 days.

For the 50%, 75%, and 100% N-substituted polyamides, the glass temperatures also decrease with increasing methylation.

Thus a series of polyamides with different physical properties are available for blending studies.

PHFA/PA Blends

Equal parts by weight of PHFA and polyamides were blended. Visual observation of the cast films showed that they varied from transparent and elastic (with 100% methylated PA) to opaque and brittle (with nylon 6,12). With the increase of the N-methylation content of the PA component the transparency and elasticity of the blend are improved.

This order of compatibility is confirmed by the DSC data shown in Figure 3 and Table II. When 100% N, N′-dimethyl substituted and 75% substituted nylon were blended with PHFA (samples nos. 5 and 4, respectively), completely amorphous mixtures were obtained. The PA component did not crystallize and broad glass transitions were observed with the transition temperatures intermediate between the T_g's of PHFA and PA (Table II, Fig. 3).

The blend containing 50% N-substituted PA displays a more complex structure. It contains an amorphous phase with a T_g of 20°C, which is intermediate between the T_g's of the component polymers, and a crystalline phase with a T_m 12°C lower than the original PA material. After quenching from the melt, the blend undergoes crystallization when heated to 90°C (Fig. 3), but the amorphous phase appears to be stable at room temperature. The thermogram of the PHFA/25% N-substituted PA blend exhibits similar features. In both cases, the depression of the melting point of the crystalline region may have arisen from the imperfection of PA crystals in the blend and from the interaction between PA and PHFA.

TABLE III
PS/PHFA/PA Blends

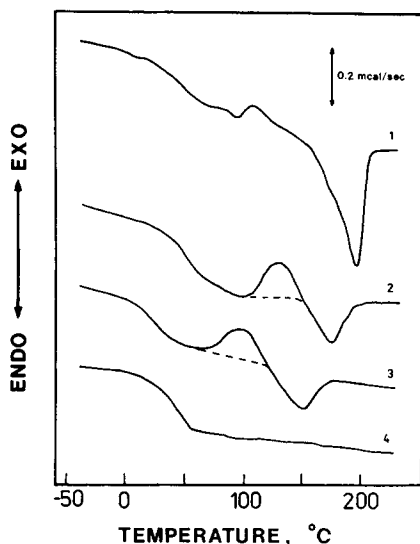| No.	Type of PA in blend	Weight composition of PS/ PHFA/PA blend	T_m (°C)	T_g (°C)	Reduction of crystallinity of PA phase	
					First run	After quenching
1	6,12	1:1:1	198	20	28	42
2	6,12	1:2:1	175	35	37	71
3	50% N-subst.	1:1:1	153	10	44	50
4	50% N-subst.	1:2:1	—	20	—	—

Fig. 4. DSC thermogram of PS/PHFA/PA blends: (1) 0% subst.; PS:PHFA:PA=1:1:1; (2) 0% subst., PS:PHFA:PA=1:2:1; (3) 50% subst., PS:PHFA:PA=1:1:1; (4) 50% subst., PS:PHFA:PA=1:2:1.

An amorphous phase (T_g = 43°C) is found even in the mixture with unmodified nylon 6,12. The melting temperature is lowered by 11°C, compared to the unblended polymer (Table II).

Thus in all cases a new single amorphous phase appears in the blend. The glass-transition temperature of each blend is intermediate between that of the component polymers. The glass transition intervals are very broad, 50–60°C, compared to about 25°C for PHFA and different PAs.

The results suggest that partially compatible to completely compatible PHFA/PA blends can be obtained.

PS/PHFA/PA Blends

The possible utilization of PHFA as a compatibilizer for PS/PA blends was studied in a series of ternary blends (Table III and Fig. 4). PS/PHFA/FA blend in weight ratio 1:1:1, where PA is nylon 6,12, displayed a glass-transition temperature of 20°C and a melting peak at 198°C. Doubling the quantity of PHFA leads to a reduced degree of crystallinity, a greater depression of T_m and to a more pronounced recrystallization of the quenched sample when heated to about 100°C. We note that the experimentally detected glass-transition temperature, 20°C, of the blend is lower than the T_g of each constituent. It is likely that another T_g, representing a second amorphous phase in the ternary blend, has been masked by the complex thermal response near 100°C.

On the other hand, reducing the crystallinity of the PA via 50% N,N'-dimethyl substitution enhances miscibility. The 1:1:1 blend still undergoes recrystallization at about 70°C, but the 1:2:1 blend is completely amorphous with T_g = 20°C.

It should be emphasized that no change of properties is induced by heating above T_m of blend and quenching (restoration of H-bonds), which implies that these or similar blends could be prepared by the conventional methods of polymer processing.

The results obtained suggest a possible way for the preparation of compatible or partially compatible polystyrene/polyamide mixtures through the use of PHFA as a "compatibilizer."

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