Blends of Polyamide 6 with Bisphenol-A Polycarbonate. I. Thermal Properties and Compatibility Aspects

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Synopsis

Blends of polyamide 6 (PA6) and polycarbonate (PC) have been investigated, over a full range of composition, to check interactions between them. SEM observations show that the mixtures are characterized by domains of clearly segregated homophases and voids between the two polymers. DSC and DMTA data indicate the presence of two T_g's, corresponding to two separate phases, with the T_g of the PC phase decreasing on increasing the PA6 amount. Moreover, the crystallization kinetics of PA6 is slightly slowed down by the PC. Chemical reactions between the two polymers are supposed to give rise to low molar mass compounds, as shown by GPC; these species plasticize the PC and partially dissolve into the molten polyamide, causing decrease of PC T_g and reduction of overall crystallization rate of PA6. Apparent influence of PC on melting temperature and enthalpy of PA6 is also discussed.

INTRODUCTION

The possibility of either improving the properties of traditional polymers or designing totally new materials by blending is involving people in industry and academy. The full potentialities of polymer mixtures have not yet been completely explored; nevertheless, several blends are marketed and others are under investigations.

Fundamental researches are concerned with the theoretical and experimental problems inherent to miscibility in high molecular mass compounds. The phenomenological aspects of hundreds of different systems are deeply investigated and well outlined in several reviews,[1-4] but, up to date, a full understanding of the subject has not been achieved: A comprehensive thermodynamic theory is far from being completed and the *a priori* forecasting of miscible pair is difficult even on a semiempirical basis.

In comparison with this huge amount of papers and patents, few works are available on blends containing polyamides, despite the industrial relevance of this class of polymers, especially polyamide 6 (PA6) and polyamide 6,6.

Since the pioneering work by Inoue,[5] only a few years ago PA6 based multicomponent systems have received attention from the scientists. Several authors have reported interactions between polyamide 6 and poly(methyl methacrylate),[6] ionomers,[7] polyetheresteramide,[8] polyetheresters,[9] and acrylonitrile–butadiene–styrene copolymer.[10]

To our knowledge no indication exists about polymers completely miscible in the amorphous phase with polyamide 6. On the other hand, many papers have been published on immiscible blends[11–14] mainly concerning PA6 toughening, which is the major problem for many applications, especially at low temperature.

Moisture take-up is another important point to be solved: The absorption of humidity involves the decrease of the glass transition temperature T_g, thus affecting dimensional stability and lowering performance of manufacts. Expensive conditioning treatments, often performed during the polymer processing, might be taken over by blending, since mixtures with copolymers, containing hydrophobic blocks and polar moieties, seem to be strongly effective in reducing water absorption.

In this work we shall present results on the polyamide 6–bisphenol-A polycarbonate (PC) system. The latter was selected taking into account its very good physicomechanical properties; if miscible, PC might increase PA6 T_g and decrease water take-up, whereas PA6 would enhance the solvent resistance of PC.

The first part of this paper will be devoted to the compatibility aspects, with special attention to T_g, melting, and crystallization behavior. It is well known that crystallinity and crystallization kinetics can be greatly influenced by a second component as shown, e.g., for poly(ϵ-caprolactone)/poly(vinyl chloride),[15] poly(vinylidene fluoride)/poly(methyl metacrylate),[16,17] poly(ethylene oxide)/poly(methyl metacrylate),[18] and poly(vinylidene fluoride)/poly(vinyl pyrrolidone)[19] mixtures. The whole subject was reviewed by Paul and Barlow.[20]

EXPERIMENTAL

Materials. The polymers used as starting materials were commercial grade products supplied by Enichem Tecnoresine, Spa: Polyamide 6 was a hydrolytic poly(ϵ-caprolactam), labeled Nivionplast E333F, with a number average molecular weight $\overline{M}_n = 22.5 \times 10^3$; bisphenol-A polycarbonate, labeled Synvet 201, had $\overline{M}_n = 20 \times 10^3$. Both materials, free of additives, were used without further purification.

Blends Preparation. Blends of PA6 and PC, in composition ranging from 95/5 to 5/95 wt/wt, were prepared by melt blending in a single screw extruder. The die temperature was 250°C. Dog-bone-shaped specimens and bars for stress–strain and impact strength measurements, respectively, were injection molded. All samples were stored in desiccator under P_2O_5 for 2 months before examination.

Thermal Properties. The melting (T_m), crystallization (T_c), and glass transition (T_g) temperatures were measured with a Perkin-Elmer DSC 2 differential scanning calorimeter, equipped with a 3600 Data Station. Specimens, about 5 mg by weight, were cut from injection-molded pieces and underwent the following thermal cycle: heating at 20°C/min from 10 to 260°C (I melting), annealing for 5 min at 260°C, cooling at 10°C/min, reheating at 20°C/min (II melting). Isothermal crystallizations were performed after annealing at 260°C, cooling down the specimen rapidly at 320°C/min to the selected T_c temperature. T_m and T_c were determined as

peak temperatures; T_g was recorded in the first run as the temperature corresponding to the midpoint of the specific heat change.

Density. Blend density was measured using a gradient column filled with n-heptane and carbontetrachloride in such proportion as to obtain a density range from 1.120 to 1.190 g/cm^3 at $T = 20°C$. In order to avoid possible PC crystallization induced by CCl_4, all measurements were done as soon as the sample reached apparent equilibrium level.

Morphological Observations. Cryogenically fractured surfaces were covered with gold by a sputtering coating unit (Agar Aids Model PS3) and observed in a scanning electron microscope (Cambridge Stereoscan Model 250 MK 2).

Dynamic Mechanical Analysis. Dynamic mechanical spectra were recorded on a computer-assisted Polymer Laboratories DMTA, applying the single cantilever method at a frequency of 3 Hz. Heating rate was 3°C/min. Samples in form of small bars, measuring approximately 15 × 5 × 3 mm, were used.

Gel Permeation Chromatography. For GPC analysis, the blends were dissolved in methylene chloride and the suspended PA6 fraction was filtered off; the solution, diluted to 0.1% w/v, was injected in a Waters high pressure liquid chromatography apparatus (pump 600A; injector U6K; UV detector 440; μ styragel column set 10^5–10^4–10^3–500Å; $\lambda = 254$ nm).

RESULTS AND DISCUSSION

Glass Transition Temperature. Table I shows the T_g values, measured by DSC and DMTA. The two sets of data are not directly comparable since techniques and heating rates are very different. The particularly low values of PA6 T_g by DMTA can be due to water absorption during measurements. Furthermore, owing to sensitivity, DSC cannot detect clearly T_g of the single component at concentrations lower than 10% by weight. Nevertheless, the general features correspond satisfactorily.

Two T_g's are always present at every composition, clearly indicating the existence of two amorphous phases. The T_g of PA6 phase can be considered constant and that of the PC phase diminishes slightly but continuously on

TABLE I

T_g Values of PA6/PC Blends from Calorimetric and Dynamic Mechanical Measurements

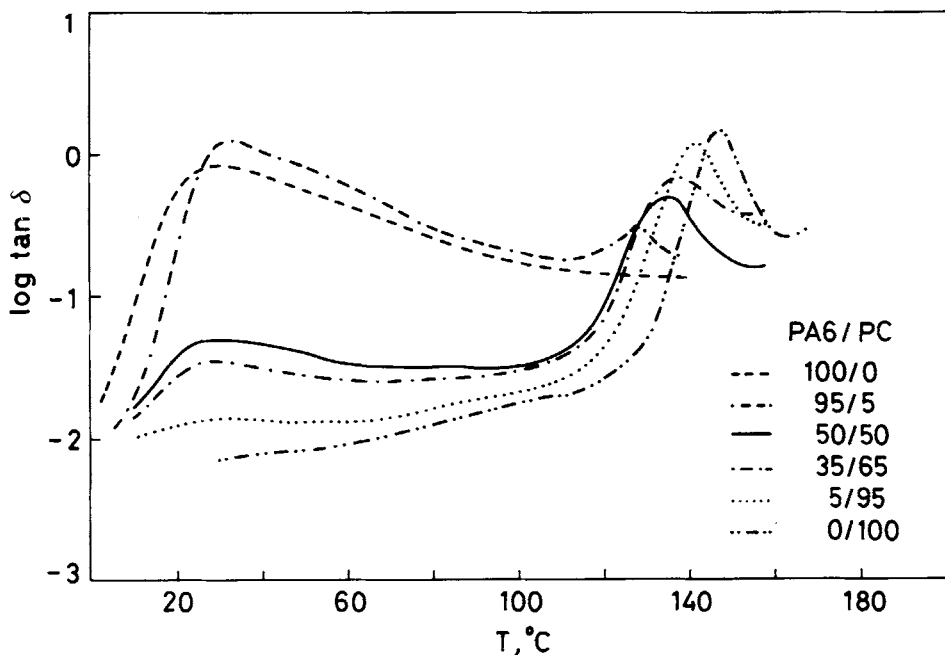| PA6/PC (w/w)	DSC		DMTA	
	$T_{g\ PA6}$ (°C)	$T_{g\ PC}$ (°C)	$T_{g\ PA6}$ (°C)	$T_{g\ PC}$ (°C)
100/0	50	—	31	—
95/5	45	—	33	126
90/10	46	—	30	123
60/40	50	140	31	132
50/50	50	139	29	134
20/80	50	144	33	139
10/90	50	146	—	—
5/95	—	145	31	140
0/100	—	150	—	147

Fig. 1.   Loss factor as a function of temperature and blend composition.

increasing PA6 content. The higher mobility of glassy PC is confirmed by the broadening of the transition region as shown in Figure 1.

This behavior might suggest that PA6 is partially soluble in PC. However, the constancy of PA6 T_g, over the whole composition range, together with the morphological and thermal analysis discussed later on, suggests that the compatibility should not be large enough to justify the observed T_g reduction. Other phenomena could account for that trend. Several authors[21-23] have shown that, during high temperature extrusion, PC reacts with other polycondensation polymers (e.g., polyesters), giving block and random copolymers. To check this point, molded pieces of PA6/PC blends were extracted in Soxhelet with chloroform for 48 h; both the dissolved fraction and the insoluble residue were analyzed via IR spectroscopy. The results indicate that the chloroform dissolved fraction corresponds to pure PC, while the insoluble part is pure PA6. On the other hand, Illing[24] and Chang and Han[25] have reported significant examples showing the presence of interfacial agent between PA6 and functionalized rubber particles in PA6/rubber blends, since grafting of rubber to PA6 would occur during melt extrusion.

Our morphological analysis, as shown later on, seems to indicate that graft copolymer is formed only when PC is about 5% by weight in the blend. However, we were not able to analytically determine it owing to its very small concentration and difficult separation.

Finally, the presence of degradative effects induced in PC by blend processing were investigated by gel permeation chromatography. The GPC chromatograms, shown in Figure 2, point out two main features. The whole curve moves toward higher elution volumes as a consequence of thermal degradation
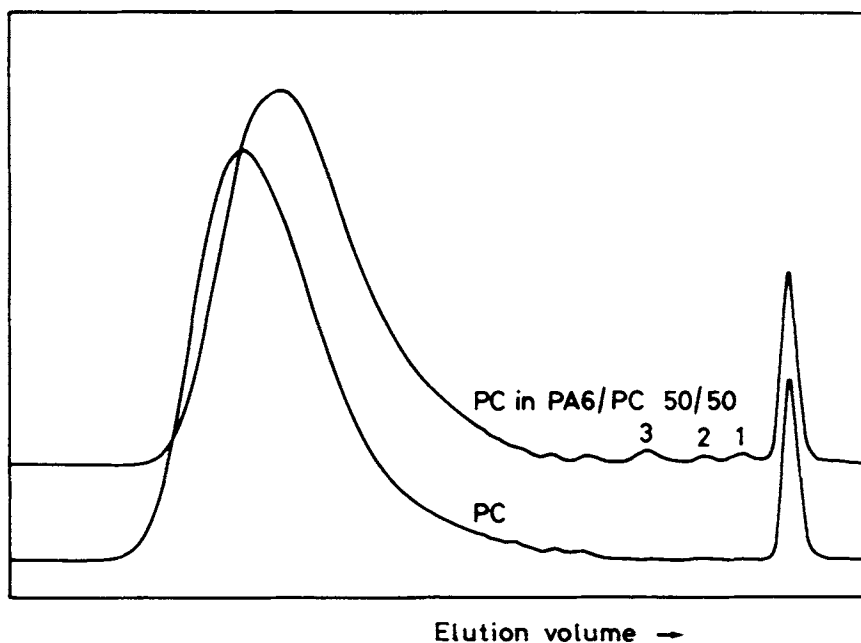
Fig. 2.   GPC chromatograms of PC extracted from the 50/50 blend.

and aminolysis due to the NH_2 terminal groups of the polyamide chains.[26] The degradation involves the highest molecular masses, causing an $\overline{M}_n$ reduction of about 15% in 50/50 blend. Beside that, the low molecular mass fraction undergoes substantial rearrangement on increasing PA6 content, leading to very low molar mass compounds (peaks 1 and 2 in Fig. 2). The peak 3 corresponds to ϵ-caprolactam; its amount does not depend on the blend composition, but mainly on PA6 dispersion and extraction efficiency.
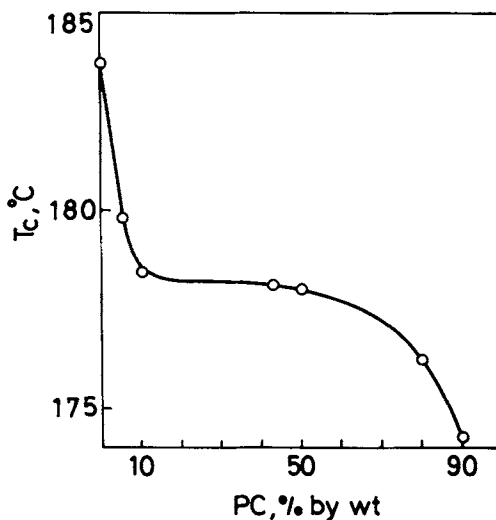

Fig. 3.   Dependence of nonisothermal crystallization temperature on blend composition.

TABLE II
Rate Constant K and Avrami Index n of PA6 from Isothermal
Crystallization Experiments

PA6/PC (w/w)	T_c (°C)	n	K (min^{-n})
	190	4.1	1.2×10^{-1}
100/0	193	4.6	2.0×10^{-2}
	196	4.7	5.5×10^{-4}
	185	3.0	4.3×10^{-1}
90/10	190	3.3	1.4×10^{-2}
	196	3.2	3.9×10^{-4}
	185	3.4	5.8×10^{-1}
65/35	190	3.5	5.2×10^{-3}
	196	3.9	2.0×10^{-5}

In conclusion, we believe that the PC T_g decrease is due both to the plasticizing effects of low molar mass species and to the overall degradation. These very low molar mass compounds might be soluble in PA6 and responsible for the PA6 T_g small decrease measured by DSC for 95/5 and 90/10 PA6/PC blends.

Crystallization Kinetics. The crystallization kinetics was studied both in isothermal and nonisothermal conditions. PA6 is able to crystallize whatever the blend composition. Nonisothermal crystallization temperatures show peculiar dependence on PC concentration as illustrated in Figure 3. The slowing down of the crystallization kinetics, for small addition to PC to PA6, might be due to the solubility of PC low mass species in the molten PA6: Degradative effects of PA6 NH_2 should increase on increasing PA6/PC ratio. The retarding effect is supported by isothermal crystallization; the data of Table II, computed according to the Avrami equation,[27] show that PC slightly depresses the rate constant K and the Avrami index n of PA6.

Several authors[28, 29] have shown that the crystallization rate is reduced when partial miscibility between the two polymers in the melt occurs. For incompatible blends (e.g., in the very case of PA6/rubber), others[30] suggest that the crystallization rate reduction is due to the increase of blend melt viscosity.

In our case the melt viscosity of PC is much higher than that of PA6 (at 260°C, shear rate 1000 s^{-1}, η_{app} = 8000 and 50 P, respectively), but it is difficult to accept the simple correlation between the global viscosity of the system and the diffusion processes during PA6 crystallization in the concentration range where PA6 forms a continuous matrix. Therefore, we feel that small quantities of low molar mass PC might dissolve in the PA6 melt, acting as diluent.

Melting Behavior. Table III collects temperature and enthalpy of melting, recorded both for as-received samples (T_m^I, ΔH_m^I) and specimens nonisothermally crystallized in the calorimeter (T_m^{II}, ΔH_m^{II}). The data refer only to the PA6 phase, since PC does not crystallize from the melt.

One must remember that the cooling during injection molding is much faster than the thermal scanning in the calorimeter. Nevertheless, due to

TABLE III
Melting Temperature and Enthalpy of PA6 Crystalline Phase in PA6/PC Blends;
Samples (I) As-Received and (II) Crystallized in the DSC

PA6/PC (w/w)	T_m^I (°C)	ΔH_m^I (cal/g PA6)	T_m^{II} (°C)	ΔH_m^{II} (cal/g PA6)
100/0	220.2	15.9	213.9	15.8
95/5	218.0	15.4	213.4	15.2
90/10	216.0	13.2	212.8	14.8
60/40	215.8	13.6	211.5	14.1
50/50	214.6	15.6	211.4	14.3
20/80	213.8	16.5	210.0	13.8
10/90	214.2	13.4	211.1	12.3

stress orientation effects, extruded and molded samples usually melt at higher temperatures than unoriented crystallized materials.

Both sets of data show negligible dependence of T_m on PC content. The small melting point depression can be attributed to morphological effects (lamella thickness, defects, spherulitic morphology) as reported by several authors.[31-34]

The heat of melting of samples nonisothermally crystallized in the calorimeter (ΔH_m^{II}) slightly decreases with PC content, in agreement with the kinetic data discussed before.

On the contrary, the dependence of the ΔH_m^I on composition is more complex and a minimum followed by a maximum is shown off. Measurements at different heating rate (20 and 80 K/min) give the same values of ΔH_m^I, this supporting that ΔH_m^I is related to the original crystalline structure, without any annealing effect due to the scanning.[35-37] We do not have a definite explanation, but the phenomena occurring during the extrusion might give some suggestions. The phase dispersion in the melt and consequently the blend morphology could affect the apparent heat of melting. Han[38] has shown that the deformation of dispersed droplets or domains is dependent on their size. Since PA6 has a much lower melt viscosity than PC, the PA6 phase is subjected to very different shear rate and stress in case it constitutes the matrix or the dispersed phase. Without entering into the details of the morphological analysis, which will be discussed in Part II, we underline that the PA6 phase goes from a continuous matrix [Fig. 4(a)] to dispersed spherical droplets [Fig. 4(c)] through a structure based on the segregation of elongated domains [Fig. 4(b)]. In the intermediate range, the depressing effects of PC on ΔH_m (see Table III) could be counterbalanced by the crystallization induced by the shear stress orientation. This shear stress orientation is lost when the sample is molten and crystallized in the calorimeter; the domains coalesce in larger ones as Figure 4(d) shows.

A further support to the ΔH_m^I trend for blends up to 20% PC is supplied by density measurements (Fig. 5), which show evidence that the experimental values are always lower than predicted by simple additivity (dashed line). Despite the fact that the amorphous PC density is higher than that of PA6, the values for 95/5 and 90/10 PA6/PC blends remain constant and equal to pure PA6. Assuming that the PC density does not change with composition,
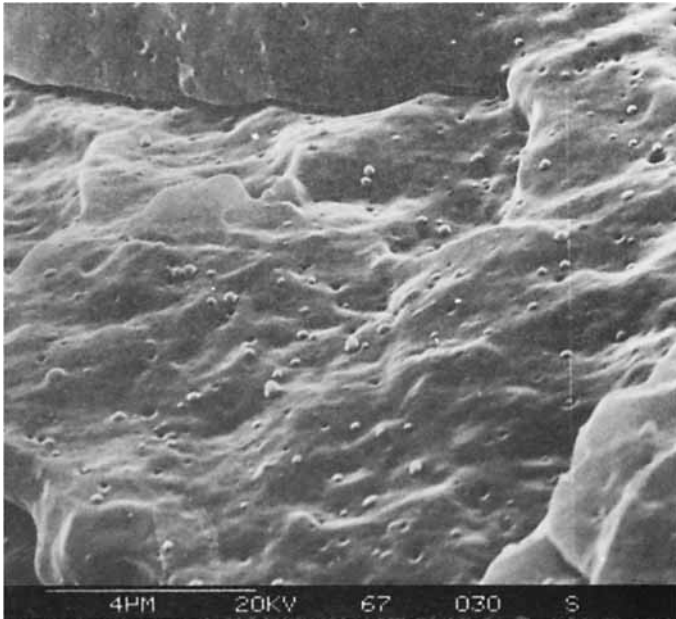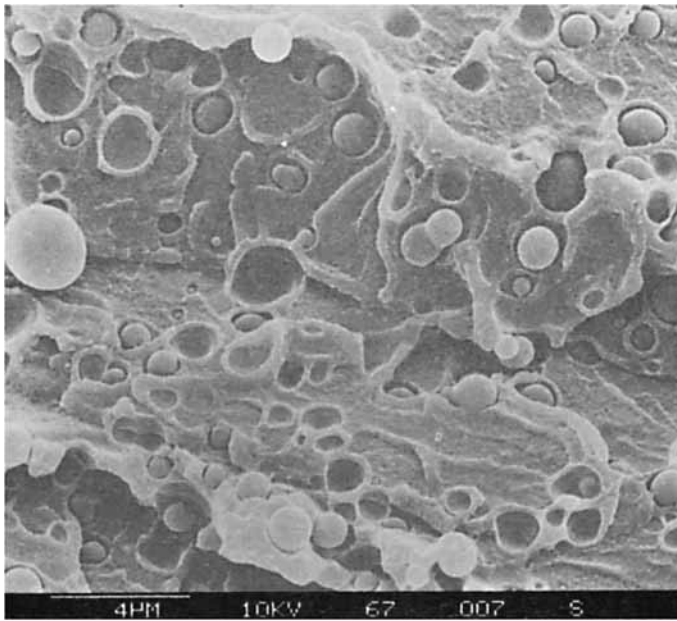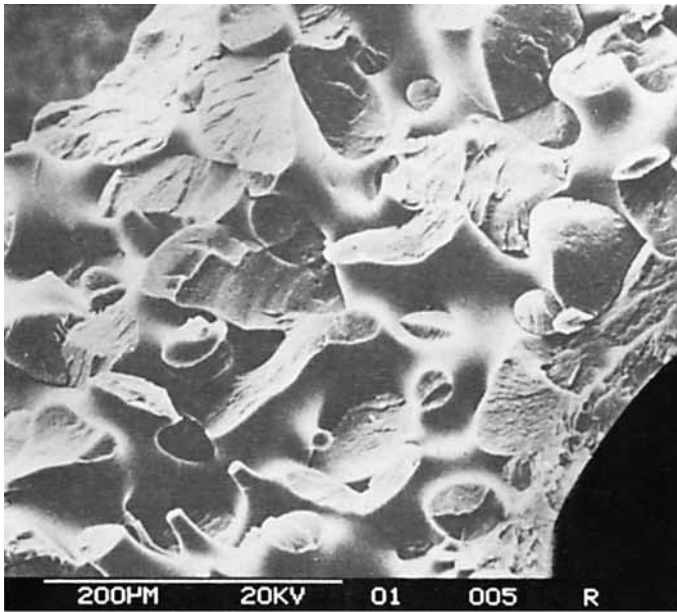
(a)
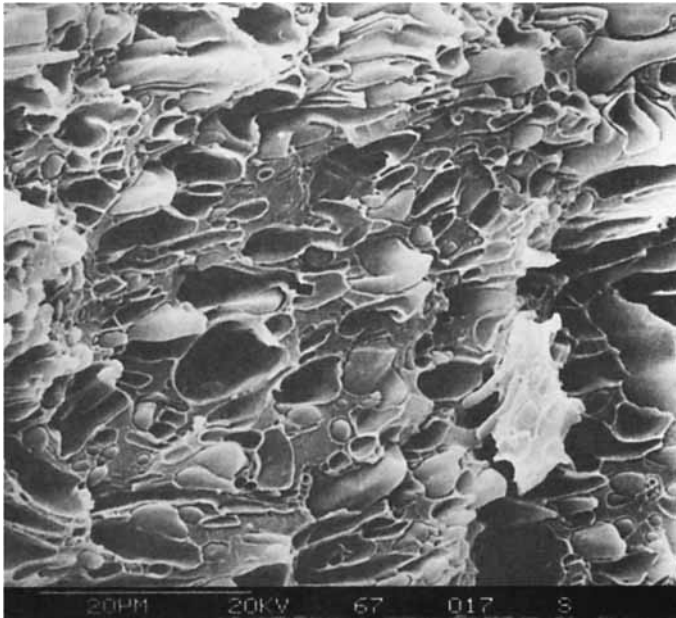
(b)

Fig. 4. SEM micrographs of fracture surface of PA6/PC blends: (a) 95/5; (b) 50/50; (c) 10/90; (d) 50/50 after thermal treatment.
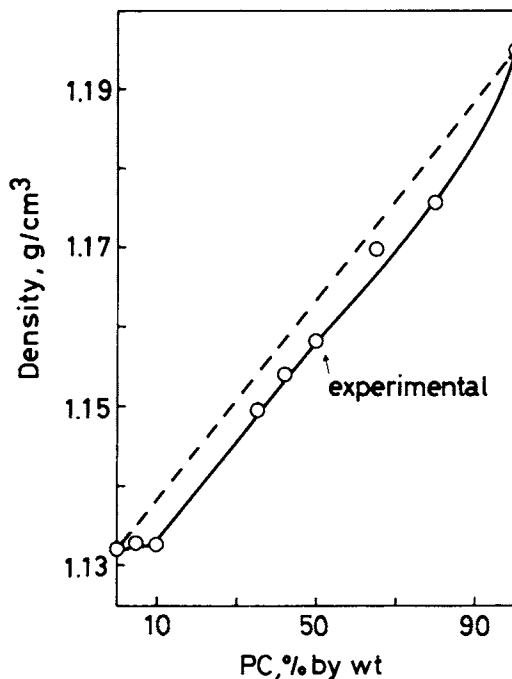
(c)

(d)

Fig. 4.   (*Continued from the previous page.*)

Fig. 5.   Blend densities as a function of compositions.

this result implies that the PA6 phase density decreases, in agreement with ΔH_m^I vs. composition behavior.

In the composition range from 20 to 95% PC [Figs. 4(b/c)], the blend structure is characterized by the presence of voids and holes among the domains; therefore, it is impossible to relate the density values to the ΔH_m^I trend.

CONCLUSIONS

The present results globally indicate that PA6 and PC are substantially immiscible. Blends show always two glass transition temperatures and their morphologies are characterized by two well-defined homophases of PC and PA6. Nevertheless, the decrease of PC T_g as well as slower crystallization kinetics of PA6 would suggest the presence of some interactions between the two polymers.

Degradative phenomena which take place during the extrusion at 250°C are responsible for the production of small molar mass species of PC, as shown by GPC, and probably of some copolymer between two components. Although our attempts of analytical determination of this copolymer were unsuccessful, we feel that, especially for blends containing very low PC percentage (5%), chemical reaction between two polymers is highly probable, due to the high concentration of NH_2 groups of polyamide. Indeed a good adhesion of PC particles to the PA6 matrix is only observed in the case of 95/5 PA6/PC blend. Moreover, preliminary results on the effect of long mixing time (30 min)

show that significant amounts of PA6/PC copolymer are formed in PA6-rich blend.

Finally, slower crystallization rate for PA6 blends have been reported by several authors. Partial miscibility in the molten state is often proposed as a possible explanation for this effect. In our case this cannot be excluded especially considering the formation of low molar mass compounds in consequence of PC degradation. These findings, which show immiscibility between polyamide 6 and polycarbonate, are also in agreement with the conclusion which could be drawn from the solubility parameter analysis. According to Krause's scheme,[37] the difference between the solubility parameter $\Delta\delta = \delta_{PC} - \delta_{PA6}$ is 6.5 MPa$^{1/2}$; the following Hansen's procedure,[39]

$$\Delta\delta = \left[\left(\delta^d_{PC} - \delta^d_{PA6} \right)^2 + \left(\delta^p_{PC} - \delta^p_{PA6} \right)^2 + \left(\delta^h_{PC} - \delta^h_{PA6} \right)^2 \right]^{1/2}$$

$$= 10.3 \text{ MPa}^{1/2}$$

where δ^d, δ^p, and δ^h are the dispersion, polar, and hydrogen bonding contributions, respectively, to the solubility parameter. The data for PA6 were obtained from our previous work[40]; those of PC were deduced from solubility maps based on values by Heiss.[41]

In both cases, $\Delta\delta$ is much higher than 1 MPa$^{1/2}$, suggested as an upper limit to obtain miscibility.

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