

Blends of Polyamide 6 with Bisphenol-A Polycarbonate. II. Morphology–Mechanical Properties Relationships

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Synopsis

The relationships between morphology and mechanical properties in polyamide 6/bisphenol-A polycarbonate blends have been investigated by means of Scanning Electron Microscopy and tensile tests. The immiscibility of the two polymers gives rise to biphasic blends in which the polycarbonate constitutes the matrix when its concentration is higher than 35 wt %. The morphology of the blends is controlled by the thermal and rheological characteristics, as well as by the mixing conditions. In general, the adhesion at the interface between the phases is absent. Moreover, polycarbonate-rich blends can be considered as polycarbonate matrix with holes. As a consequence, the blends are mechanically much weaker than the pure components both in terms of Young's modulus and strength at break. Blends very rich in polyamide, more than 90% by weight, behave differently, probably because of chemical, interchain interactions. This is reflected positively in the impact behavior, which was improved in this composition range.

INTRODUCTION

Heterogeneous blends containing polyamide 6 (PA6) have been studied by several authors with special concern for the need to improve impact resistance: although PA6 is per se a tough material, its toughness is greatly decreased in the dry state and at low temperatures as well as by notch sensitivity. Due to the obvious industrial relevance of this characteristic, many efforts have been devoted to the solution of the problem. A remarkable example for its comprehensiveness is a patent by Epstein,¹ in which hundreds of different compositions based on blends of PA6 and 66 with various rubbers are considered.

Very good results have also been obtained blending PA6 with ethylene-propylene rubber modified with maleic anhydride,² ethylene multifunctional rubbers,³ carboxy modified nitrile rubbers,⁴ ethylene acrylic acid copolymers,⁵ and ABS-type rubbers.⁶

Blends with nonrubbery polymers have also been explored to exploit polyamide qualities in a variety of fields such as the preparation of new membranes,⁷ multicomponent fibers,⁸ molecular composites systems,⁹ and others. To successfully tailor the blend properties, one can utilize three important factors: chemical reactions, physical interactions, and, in the processing steps, the rheology of the system.

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On any aspect, the processing conditions defined by temperature, time, and mixing techniques play an important role in controlling the morphology of the final blend, as widely discussed by Han.¹⁰ Single or twin screw extruders or other kinds of mixers exert very different shear stress on the polymer mixtures, leading to various degrees of mixing and ultimately to disparate final properties.

In the first part of this work¹¹ we showed that polyamide 6 and bisphenol-A polycarbonate (PC) are immiscible in any proportion. In these blends, prepared with an industrial single screw extruder, complete phase separation takes place, resulting in a heterogeneous, multiphase structure.

In this paper we report on the investigation of PA6/PC biphasic blends with the final aim of correlating the morphology with the mechanical properties, namely the tensile and impact characteristics.

EXPERIMENTAL

Blends of PA6 and PC were prepared by mixing carefully dried materials in a single screw extruder at 260°C as described in part 1 of this paper.¹¹ The concentration is expressed as percentage by weight unless otherwise specified. The surfaces of the cryogenically fractured samples were coated with gold in a SEM coating unit, mod. Agar Aid PS3, and the morphology was observed in a scanning electron microscope, mod. Cambridge Stereoscan 250 MK2. Stress-strain measurements of dog-bone-shaped specimens, prepared by injection moulding, were carried out on an Instron 1122 at room temperature; the cross head speed was 50 mm/min. The Izod impact strength on notched samples was measured using an Universal Pendulum, CEAST 6545. The reported values were averaged over 20 measurements for impact and 10 measurements for stress-strain. The Vicat softening temperature was measured with a Ceast HDT/Vicat 6510, according to ASTM D 1525. All samples were dried overnight at 110°C and stored in desiccator under P₂O₅ until use.

RESULTS AND DISCUSSION

Morphology

Heterogeneous polymer blends can be considered very similar to composite systems in which each component acts as the filler or the matrix, depending on the composition. This allows the prediction of the mechanical properties using theoretical models and equations originally developed for real composite systems or even nonpolymeric materials. To discriminate among the various treatments, it is necessary to have information about the morphological aspects: the nature of the matrix and the dispersed phase, the dimensions and distribution of the dispersed particles, the extent and nature of the interfacial adhesion, etc. To achieve this information, we thoroughly investigated the blend morphology by scanning electron microscopy.

Figures 1-7 show the morphology of the fracture surfaces of the blends at increasing PC content. The two polymers can be easily distinguished from the surface characteristics: the PA6 fracture surface is very smooth compared to globules of PC that break originating a rough surface. The general features,

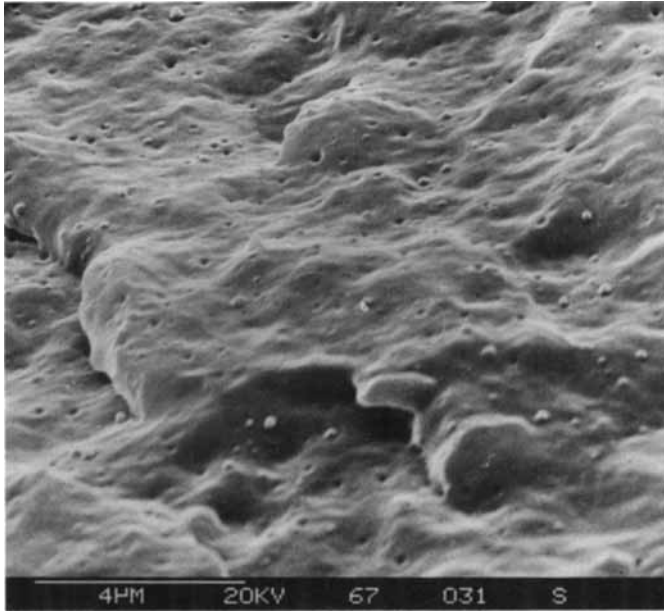


Fig. 1. SE micrograph of fracture surface of PA6/PC blend 95/5.

typical of an incompatible, biphasic system, are visible throughout the whole range of composition; within this pattern several interesting aspects are worth being stressed.

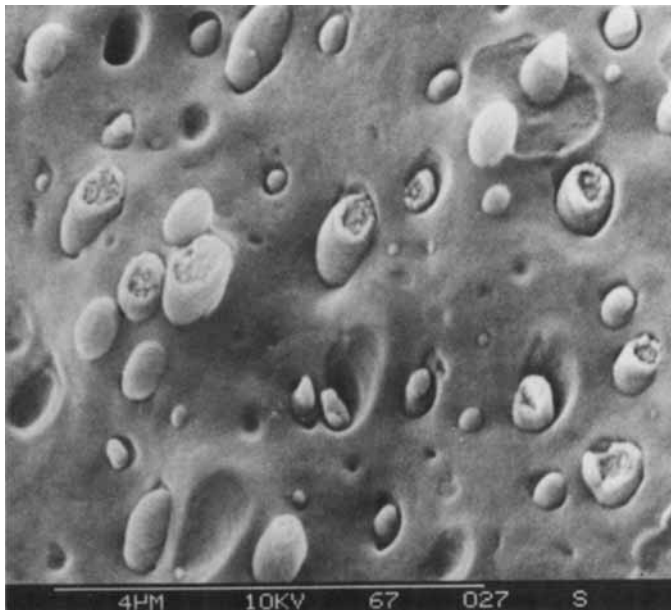


Fig. 2. SE micrograph of fracture surface of PA6/PC blend 90/10.

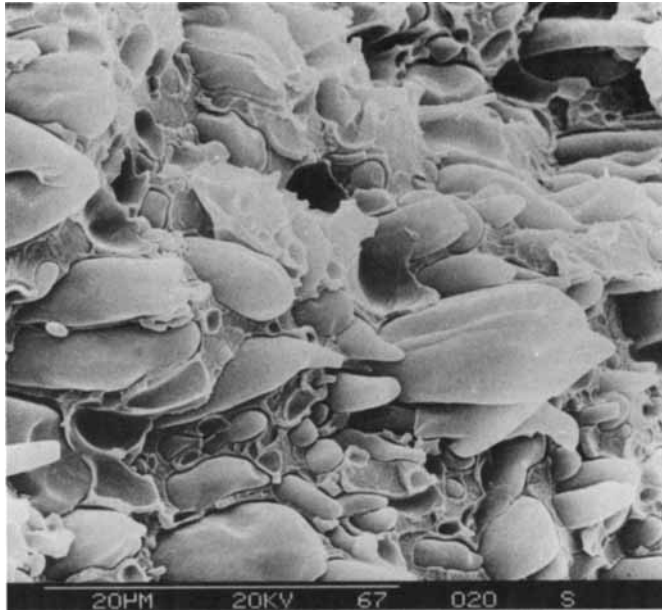


Fig. 3. SE micrograph of fracture surface of PA6/PC blend 50/50.

1. In PA6-rich blends, down to 65% PA6, the dispersed phase is constituted by PC: with as little as 10% PC its domains already change their shape from spherical to rod-like (Figs. 1-2). For all other compositions, PC clearly constitutes the continuous phase. At concentration equal 50%, the PA6 is dispersed

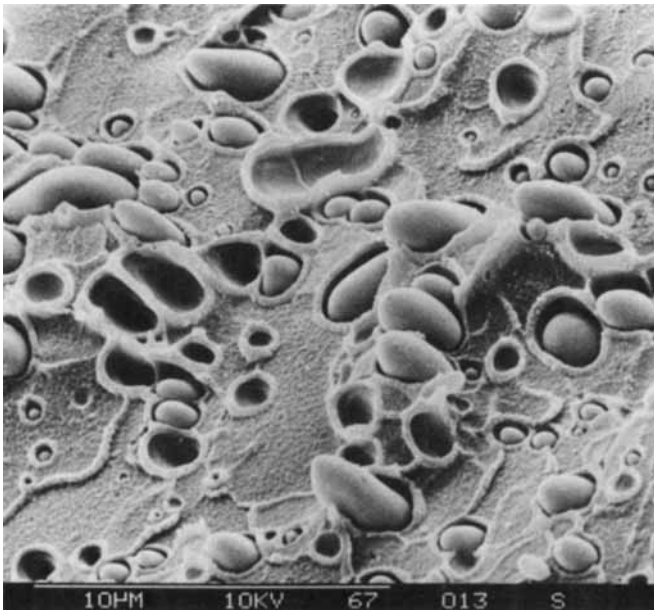


Fig. 4. SE micrograph of fracture surface of PA6/PC blend 20/80.

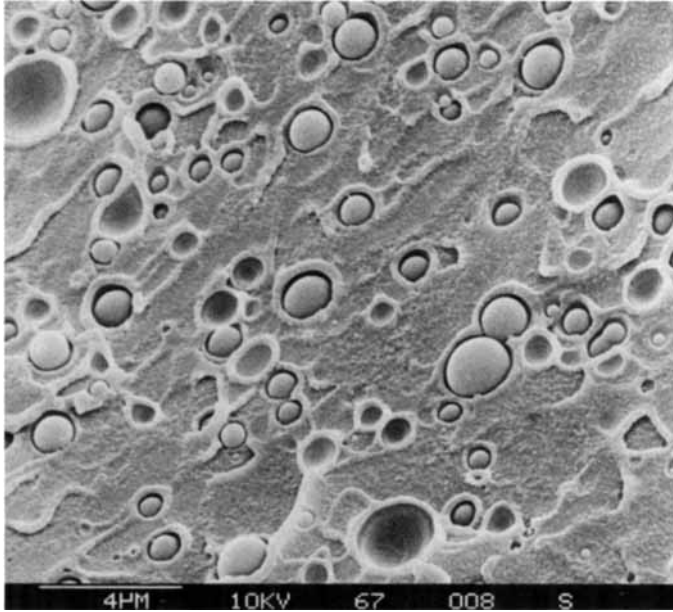


Fig. 5. SE micrograph of fracture surface of PA6/PC blend 10/90.

as very large domains (Fig. 3); at concentration equal 10% the PA6 particles are still spherical, and tend to become ellipsoidal around 20% concentration (Figs. 4–5).

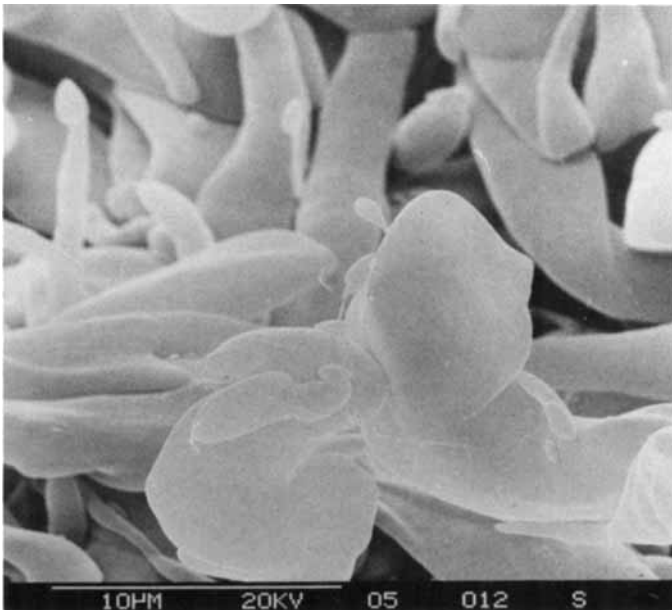


Fig. 6. SE micrograph of PA6/PC blend 50/50 after extraction of PC with methylene chloride.

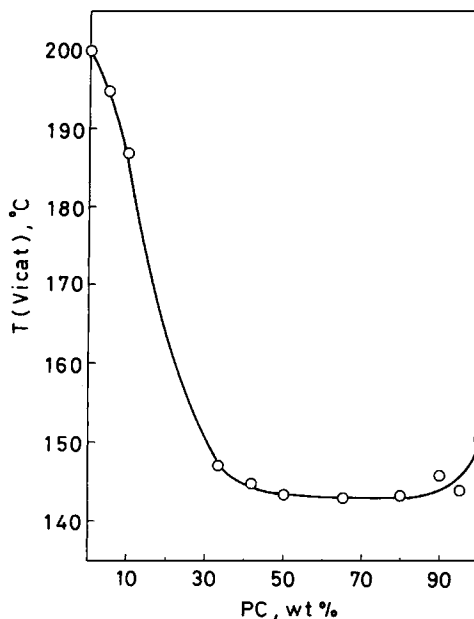


Fig. 7. Vicat softening temperature of PA6/PC blends as a function of PC weight fraction.

2. The phase inversion takes place at compositions around 30–40% PC. This was confirmed by selective dissolution of the PC with chloroform from the 65/35 blend. The insoluble PA6, freed from the PC matrix, is present as separated, elongated domains visible in Figure 6.

These morphological aspects can be interpreted in terms of different melt viscosity, as suggested by Han.¹⁰ During the extrusion process the less viscous molten PA6 is masticated much better than the highly viscous PC. As a consequence, the PC constitutes the continuous matrix even at concentrations lower than 50%; only at very low concentration can it be efficiently reduced to small particles.

3. Partial adhesion seems to be present in PA6-rich blends, such as 95/5 and 90/10 PA6/PC; when the PC constitutes the matrix, independently of composition, voids are visible at the phase boundary. The formation of voids can be explained considering the different volume contraction occurring during the thermal transitions of the two polymers. Namely, due to the fast cooling in the mould, the segregated PA6 crystallizes inside an almost glassy matrix; the full crystallization of the polyamide domains causes a volume decrease higher than the thermal shrinkage of the PC phase. On the other side, the same mechanism could contribute to induce a weak adhesion between the two homopolymers in PA6 rich blends, visible in Figures 1–2.

Actually, given the notorious tendency of carbonates to react with basic compounds, one should consider the possibility of chemical reactions between PC and PA6. As shown in part 1 of this work,¹¹ during the melt blending procedure adopted by us, chemical reactions are generally negligible, with the exception of PA6/PC 95/5, in which the very high concentration of $-\text{NH}_2$ groups enhances the probability of chemical reactions between the two ho-

mopolymers, likely with the formation of adhesion promoting copolymers. Indeed, we have shown¹²⁻¹³ that, changing the blending conditions, the chemical reactions become significant. Namely, the longer the mixing time, the lower the PA6 concentration needed to form PA6-PC copolymers.

Softening Temperature

The above morphological analysis shows that PC acts as the matrix in a wide range of concentrations. This result is also found measuring the softening temperature according to Vicat procedure. Figure 7 reports the softening temperature vs. PC percentage. The softening temperature decreases very sharply, passing from 0-30% PC, then remains constant through the whole composition range at about 145°C, a value very close to that of pure PC (150°C). This behavior would support the existence of a PC continuous matrix up to 60-70% PA6.

Mechanical Properties

Stress-strain curves of PA6/PC blends are shown in Figure 8. The blends containing 95 and 90% PC show relevant yielding typical of pure PC, but compared to the pure polymer a lowering of the elongation at break and the ultimate strength is obtained.

On the other side of the composition range, PA6-rich blends exhibit higher elongations at break, which may result in higher breakage resistance. In the intermediate range all blends have very poor mechanical properties, breaking with rather brittle behavior.

Elastic Modulus

Several theories have been suggested to describe the elastic modulus of multicomponent polymer systems; a thorough review can be found in ref. 14. Taking

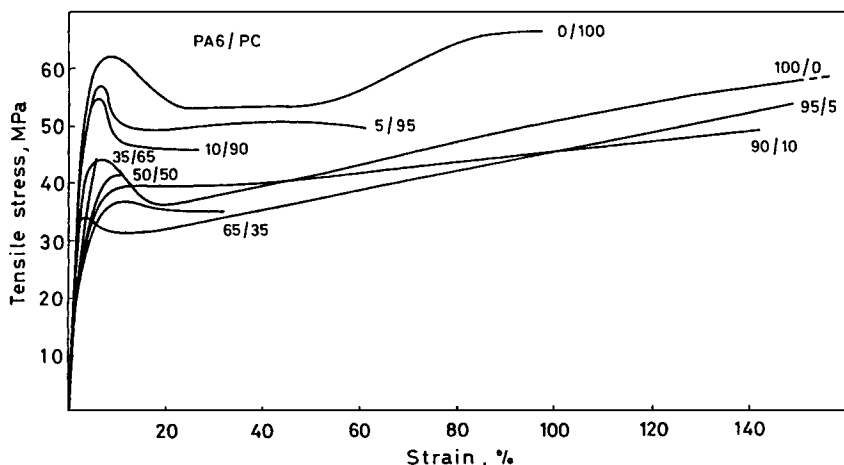


Fig. 8. Stress-strain curves of PA6/PC blends obtained at room temperature and a cross head speed of 5 cm/min.

into account the morphological observations, we will consider only the theories dealing with the case of poor or absent adhesion between the dispersed and the continuous phases. A classic, widely used model is the Kerner's model.¹⁵ Originally developed for systems having perfect adhesion at the phase boundary, it can be modified assuming that the modulus of the dispersed phase does not contribute to the blend modulus; in this case

$$E_b = \frac{E_m}{1 + \phi_d/\phi_m[15(1 - \nu_m)/(7 - 5\nu_m)]} \quad (1)$$

where the subscripts *b*, *d*, and *m* refer to blend, dispersed phase, and matrix, respectively; *E* is the Young's modulus; ϕ is the volume fraction and ν is the Poisson's ratio.

A refined treatment by Uemura and Takayanagi,¹⁶ specially adapted for polymeric systems containing holes or particulate fillers loosely adhering to the matrix, leads to a relation that is equivalent to eq. (1). Both equations were derived in terms of the shear modulus *G*, but the authors suggested that these can be converted to Young's modulus using the well-known relationship between *E* and *G*, provided that the matrix and the inclusions are incompressible, i.e., Poisson's ratio equal to 0.5.

Sato and Furukawa¹⁷ proposed an equation for the modulus of systems showing weak adhesion, in which ellipsoidal cavities are formed during the matrix deformation

$$E_b = E_m \{ [1 + 0.5\phi_d^{2/3}/(1 - \phi_d^{1/3})] [1 - (\phi_d\tau/3)(1 + \phi_d^{1/3} - \phi_d^{2/3}/1 - \phi_d^{1/3} + \phi_d^{2/3})] - [\phi_d^{2/3}\tau/3(1 - \phi_d^{1/3})] [(1 + \phi_d^{1/3} - \phi_d^{2/3})/(1 - \phi_d^{1/3} + \phi_d^{2/3})] \} \quad (2)$$

The parameter τ is assumed equal to 0 if perfect adhesion is present and equal to 1 when no adhesion at the phase boundary exists.

Starting from the elasticity theory with the assumption that both matrix and dispersed phase have the same Poisson's ratio, Paul¹⁸ suggested the following eq. (3) for foam-like systems:

$$E_b = E_m(1 - \phi_d^{2/3})/[1 - \phi_d^{2/3}(1 - \phi_d^{1/3})] \quad (3)$$

Figure 9 shows the experimental moduli plotted with the curves derived by the described theoretical equations. Left hand lines represent PA6 matrix with PC inclusions; right hand lines refer to PC matrix with PA6 inclusions. Here Poisson's ratios of 0.39 and 0.40 for PA6 and PC, respectively, were used¹⁹ and the volume fractions were calculated assuming constant density for the two components through the whole composition range. This assumption is justified by the small variation of crystallinity degree of PA6 in the blends, as reported in part 1 of this work,¹¹ and then negligible for the following calculations. Density values of 1.132 and 1.195 g/cm³ for PA6 and PC, respectively, were used. Moreover, in agreement with others²⁰⁻²² we think that, although different from the theoretical condition of 0.5, the actual Poisson's ratios can be applied to our case.

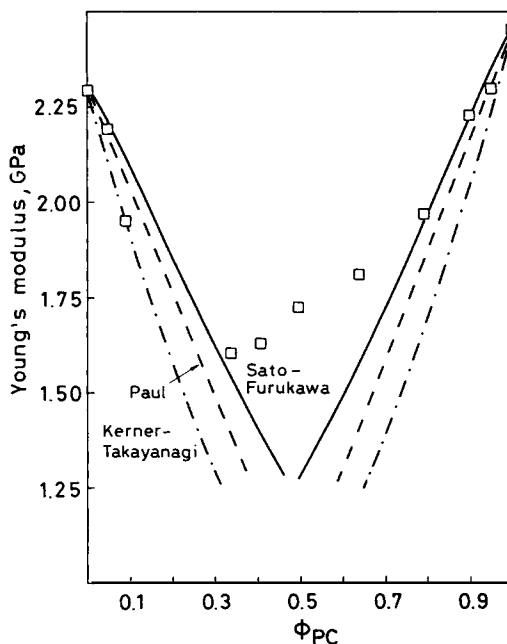


Fig. 9. Young's modulus of PA6/PC blends as a function of volume fraction of PC. Experimental data (\square) are compared with theoretical predictions (solid and broken lines) of eqs. (1), (2), and (3).

When the inclusions of PC are spherical as in PA6/PC 95/5 blends (Fig. 1), the experimental modulus fits the theoretical model of Sato and Furukawa for the case of no adhesion between the two components ($\tau = 1$). The experimental value of E of the 90/10 mixture is lower than the theoretical one. Since Figure 2 shows an apparent good adhesion between PC inclusions and PA6 matrix, one would expect a positive deviation instead of a negative one. At the moment we have no explanation for the behaviour of this mixture.

On the other side of composition range up to 20% PA6, the experimental E values fit the Sato-Furukawa equation in good agreement with the morphology characterized by more or less spherical domains, loosely dispersed in the matrix without visible adhesion. Above 20% PA6 rod-like inclusions appear and the blend structure is no more isotropic: since isotropy is a condition for the applicability of the above equations, the differences between the experimental data and the theoretical curves are not unexpected. In this range the higher experimental moduli are the result of the contribution of both phases through several mechanisms such as partial mechanical adhesion, normal stresses, and frictional phenomena.

It is interesting to compare our results with the findings of Kunori and Geil for the system PC/high-density polyethylene (HDPE).²¹ In both systems the morphology of PC rich blends is very similar as the PA6 or the HDPE spherical domains are dispersed with no adhesion inside the PC matrix. However, the moduli of PC/HDPE blends fit very well the Kerner equation up to about 20% PC. A deeper examination of the morphology puts only into evidence that the size of the dispersed particles is in general much smaller for PA6 compared to

HDPE. As an example, in the 90% PC mixture the average size of PA6 domains is about 1 micron for PA6 and about 7 for HDPE.

On the ground of the theories, the elastic modulus of composite materials should not depend on the size of the filler particles. However, there are several experimental data showing that the modulus increases as the particles size decreases.²³

Anyway, as reported by Manson and Sperling,¹⁴ the Kerner's model represents a lower boundary for biphasic systems and positive deviations have often been observed.

Tensile Strength

It is commonly accepted that the tensile strength of composite systems depends on the area fraction of the dispersed phase. More controversy arises when trying to replace the area fraction with the volume fraction, a much more accessible quantity. According to Piggot and Leidner²⁴ the area fraction in systems containing spherical inclusions is proportional to the first power of the volume fraction and the strength at break of an incompatible blend system can be described by the following equation

$$\sigma_b = \sigma_m(1 - \phi_d) \quad (4)$$

where σ_b and σ_m are the tensile strength of the blend and the matrix, respectively.

Nielsen²⁵ suggested instead a two-third power dependence, proposing the equation

$$\sigma_b = \sigma_m(1 - \phi_d^{2/3})S \quad (5)$$

S represents a stress concentration factor and is introduced to account for the effects due to morphological aspects or phase boundary characteristics. S is equal to 1 if no stress concentration is present.

Nicolais and Narkis²⁶ worked out a model specially suited for composites with lack of adhesion between the components, deriving the following equation

$$\sigma_b = \sigma_m(1 - 1.21\phi_d^{2/3}) \quad (6)$$

Figure 10 reports the experimental values of σ_b as a function of the blend composition with the curves derived from eqs. (4), (5), and (6).

For the PA6-rich blends (0–30% PC), eq. (4) fits best the experimental values, suggesting that the stress distribution in these mixtures is favoured by the higher degree of interaction present (see Figs. 1, 2). Indeed, Figure 2 shows that the rod-like PC inclusions are in good mechanical contact with PA6 phase so that they fracture solidly with the matrix. In the central composition range the morphology is complicated by the presence of highly elongated inclusions, co-continuous domains, and other features that make the application of the simple theoretical models very questionable. However, as for the modulus, the experimental values of strength at break are higher than the theoretical prediction. Very low values have been obtained for mixtures containing 5 and 10% polyamide. These values can be predicted by eq. (5), introducing a stress con-

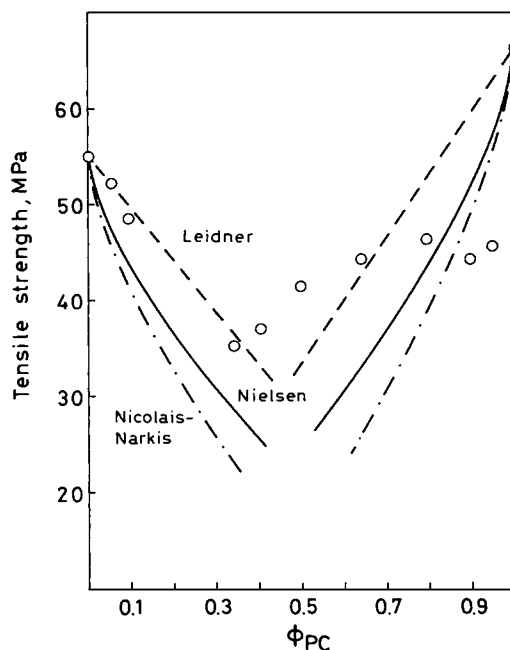


Fig. 10. Tensile strength at break of PA6/PC blends as a function of volume fraction of PC. Experimental data (O) are compared with theoretical predictions (solid and broken lines) of eqs. (4), (5), and (6).

centration factor of 0.85. This agreement can be explained considering the nonadhesion of PA6 spheres to the matrix and the possibility of discontinuous stress distribution at the phase boundary.

Impact Resistance

The impact behaviour reported in Figure 11 reveals very interesting features. The outstanding impact resistance of polycarbonate is dramatically reduced from 700 to 58 J/m by the addition of only 5 wt % of PA6. Increasing the content of polyamide, the impact strength is gradually reduced, reaching a minimum for 50/50 blend.

Surprisingly, the impact strength of PA6 is improved up to two times the initial value by the addition of 5 and 10% PC. The interactions observed at the morphological level seems to be strong enough to modify the impact behaviour. As we suggested previously, in this range of concentration chemical reactions are possible with the consequent formation of interface active products, capable of promoting the stress distribution and the impact energy transfer to the dispersed PC phase.

CONCLUSIONS

PA6 and PC are immiscible polymers. Their blends present typical biphasic structure, controlled by the rheological and thermal characteristics of the com-

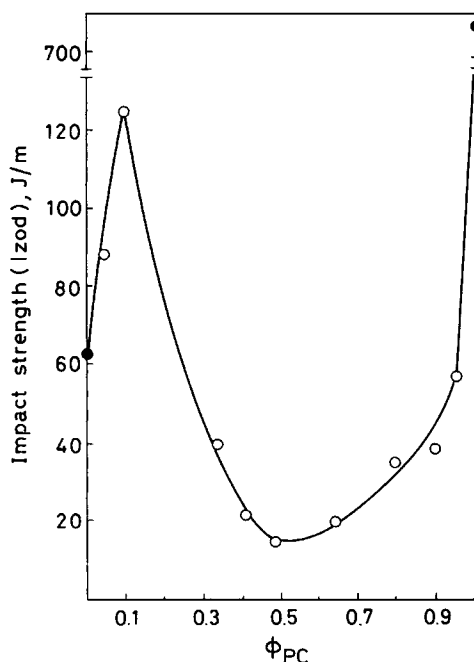


Fig. 11. Izod impact strength of PA6/PC blends as a function of PC weight fraction.

ponents. The interactions and then the adhesion between the two phases are generally absent, with the exception of polyamide-rich blends, which present some interactions, possibly favoured by PA6-PC copolymers chains, that are produced by chemical reactions between the two homopolymers during the melt mixing at 260°C.

The melt viscosity of PC is much higher than that of PA6, so the latter is much more easily masticated during the blending and is dispersed into the PC over a wide range of composition: only for content higher than 65% does the PA6 constitute the matrix of the blend.

As a result, the mechanical properties are very poor and the elastic modulus and the strength at break much inferior to those of the pure constituents. A comparison with the theoretical predictions, pertinent with the observed morphology, shows that at low concentration of one polymer in the other the experimental values of the modulus E fit the Sato-Furukawa equation while the strength at break is well described by the Leidner's model. In the intermediate range of composition the comparison with these models is prevented by the complicated morphology, with the experimental values always higher than the theoretical ones.

Especially remarkable is the increase of the impact strength of PA6 with 5–10% PC, while the loss of E is limited. In our opinion this aspect is worthy of further investigation to clarify whether this improvement is maintained at low temperature and at different test conditions. Moreover, it would be interesting to investigate whether modifying the blending, i.e., increasing the extent of interactions, allows one to obtain positive and significant effects on the final properties of the material.

References

1. B. N. Epstein, U.S. Patent 4,174,358.
2. G. Illing, in *Polymer Blends: Processing Morphology and Properties*, E. Martuscelli, R. Palumbo, and M. Kryszewsky, Eds., Plenum, New York, 1980, p. 167.
3. C. D. Han and H. Chuang, *J. Appl. Polym. Sci.*, **30**, 2431 (1985).
4. S. Cimmino, L. D'Orazio, R. Greco, G. Maglio, M. Malinconico, G. Mancarella, E. Martuscelli, R. Palumbo, and G. Ragosta, *Polym. Eng. Sci.*, **24**, 48 (1984).
5. D. Braun and W. Illing, *Die Angew. Makromol. Chem.*, **154**, 179 (1987).
6. K. Udipi, *J. Appl. Polym. Sci.*, **36**, 117 (1988).
7. R. Y. M. Huang, A. Moreira, R. Notarfonzo, and Y. F. Xu, *J. Appl. Polym. Sci.*, **35**, 1191 (1988).
8. S. M. Wickliffe, M. F. Malone, and R. J. Farris, *J. Appl. Polym. Sci.*, **34**, 931 (1987).
9. M. Takayanagi, T. Ogata, M. Morikawa, and T. Kai, *J. Macromol. Sci. Phys.*, **B17**, 591 (1980).
10. C. D. Han, *Multiphase Flow in Polymer Processing*, Academic Press, New York, 1981.
11. E. Gattiglia, A. Turturro, and E. Pedemonte, *J. Appl. Polym. Sci.*, **38**, 1807 (1989).
12. E. Gattiglia, A. Turturro, F. La Mantia, and A. Valenza, *Polym. Bull.*, **21**(1), 10 (1989).
13. E. Gattiglia, A. Turturro, F. La Mantia, and A. Valenza, in preparation.
14. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum Press, New York, 1976.
15. E. H. Kerner, *Proc. Phys. Soc.*, **69B**, 808 (1956).
16. S. Uemura and M. Takayanagi, *J. Appl. Polym. Sci.*, **10**, 113 (1966).
17. Y. Sato and J. Furukawa, *Rubber Chem. Technol.*, **35**, 857 (1962).
18. B. Paul, *Trans. Metall. Soc. AIME*, **218**, 36 (1960).
19. *Modern Plastics Encyclopedia*, McGraw Hill, New York, 1980, vol. 57, 10A, p. 576.
20. L. E. Nielsen, *J. Compos. Mater.*, **1**, 100 (1967).
21. T. Kunori and P. H. Geil, *J. Macromol. Sci. Phys.*, **B18**, 93 (1980).
22. L. Nicolais, *Polym. Eng. Sci.*, **15**, 137 (1975).
23. L. E. Nielsen, *Mechanical properties of polymers and composites*, Marcel Dekker, New York, vol. 2, 1974.
24. M. R. Piggot and J. Leidner, *J. Appl. Polym. Sci.*, **18**, 1619 (1974).
25. L. H. Nielsen, *J. Appl. Polym. Sci.*, **10**, 97 (1966).
26. L. Nicolais and M. Narkis, *Polym. Eng. Sci.*, **11**, 194 (1971).

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