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Synergistic mechanical behaviour in new polyamide 6/poly(amino-ether) blends

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New polyamide 6 (PA)/poly(amino-ether) (Blox) blends were obtained by direct injection moulding covering the full composition range. The blends comprised an almost pure PA phase and a Blox-rich phase in which significant amounts of PA were miscibilized. A very positive mechanical response was obtained, as synergisms were observed both in Young's modulus/yield stress and in elongation at break. The combined effects of the observed partial miscibility, and the very small dispersed phase size, are stated as the main factors responsible for the mechanical behaviour.

1. Introduction

Polymer blending has received much attention during the last decades because it is a low-cost technique to obtain new materials with specific properties that could not be satisfied by a single polymer. Moreover, additive or synergistic behaviours in properties can be obtained, provided the components are compatible. In miscible blends, this compatibility is assured, but the general rule in immiscible non-reacted blends is poor mechanical behaviour, particularly in large-strain properties. However, this poor mechanical behaviour can be ameliorated mainly by addition of a compatibilizer, or by partial miscibility between the blend components. Partial miscibility should improve the interaction level between the two phases; some interaction is critical for good mechanical properties, because a minimum adhesion level is usually needed to obtain synergistic or even additive mechanical behaviour [1–3].

Poly(ε-caprolactam) or polyamide 6 (PA) is a widely used semicrystalline thermoplastic that shows good mechanical properties, solvent resistance with the exception of water, and favourable price. These are also the main reasons for the large number of studies dealing with its blends. Although miscibility of PA with an ethylene-vinyl alcohol copolymer has been reported [4], most PA blends studied in recent years, containing rubbers [5, 6], polyolefins or copolymers [7, 8], other thermoplastics [3, 9–12] or liquid crystal polymers [13, 14], have been reported to be completely immiscible.

Poly(hydroxyether of ethanolamine and bisphenol A) (Blox) is a very recently commercialised material. It is an amorphous thermoplastic with excellent barrier properties to gases; and superior mechanical toughness and stiffness [15]. Due to its recent commercialization, no blend including Blox has been studied to our knowledge. This offers the possibility of developing new polymeric materials based on Blox. Moreover, the presence of three polar pendant hydroxyl groups in its structure makes it an attractive candidate to be blended. This is because these groups facilitate hydrogen-bonding interactions, opening the possibility of obtaining blends with different miscibility levels. In fact, this behaviour has been observed in a polymer chemically comparable to Blox, poly(hydroxy ether of bisphenol A) (phenoxy), with only one hydroxyl group in its structure, which is able to form a number of blends both fully [16–19] and partially miscible [20–23].

The hydroxyl groups of Blox impart a proton-donor nature, that is complementary with the proton-acceptor nature of PA. Therefore, the presence of interactions in PA/Blox blends, and the occurrence of some miscibility between them is expected. Moreover, the mechanical properties of amorphous and semicrystalline materials are usually complementary. As a consequence, the production of compatible PA/Blox blends with attractive mechanical properties should be possible.

In this work, PA/Blox blends were obtained by melt mixing across the full composition range. Blending was attempted by direct injection moulding that has been shown to be effective in some thermoplastic blends [1, 24]. The phase behaviour of the blends was studied both by DSC and DMTA, the morphology by SEM, and the mechanical properties by tensile testing.

2. Experimental

The polymers used in this work were PA (Durethan B30S from Bayer Hispania S. A., Barcelona, Spain) and an experimental poly(amino-ether) resin kindly supplied by Dow Chemical under the name Blox. The PA has a molecular weight Mv = 29,000, determined by viscosimetry at 25°C in aqueous formic acid (85%). Blox has a melt flow index (MFI) of 9.0 g/10 min, determined at 200°C and with a 2.16 kg load. Both polymers were dried before processing in order to avoid

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moisture-induced degradation reactions, the PA for 14 hours at 80°C *in vacuo* and Blox for 6 hours at 65°C in an air circulation oven.

Pellets of PA and Blox were mixed at the desired weight ratios and tumbled together before injection moulding. The polymers were directly melt mixed and injection moulded in a Battenfeld BA 230E reciprocating screw injection moulding machine. The barrel temperature was 230°C and the mould temperature 20°C. The choice of barrel temperature was determined by the melting temperature of PA and the possibility of degradation reactions of Blox at higher temperatures. The screw of the plasticisation unit was a standard screw with a diameter of 18 mm, L/D of 17.8, compression ratio of 4, and helix angle of 17.8°. No mixing devices were present. The injection speed and pressure were 6.1×10^{-6} m^3/s and 1500 bar, respectively. Tensile (ASTM D-638, type IV) specimens were obtained. The injection moulded specimens were stored in a dessicator.

The crystallization-melting and the phase behaviours of the blends were studied by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA), respectively. A Perkin-Elmer DSC-7 calorimeter was used at a heating rate of 20°C/min in a nitrogen atmosphere. Two heating scans were carried out between 15 and 260°C. Cooling between both scans was carried out at the maximum rate provided by the calorimeter. The thermal transitions, melting heats and corresponding crystalline contents were determined in the usual way. Dynamic mechanical tests were carried out in a Polymer Laboratories apparatus, at a frequency of 1 Hz in flexural mode and at a heating rate of 4°C/min from −50 to 150°C. Samples were cut from the central section of the injection moulded tensile specimens.

Density measurements were carried out on samples taken from the tensile specimens, by the displacement method using n-butyl alcohol as the immersion liquid. A Mirage SD-120L electronic densitometer was used. Three determinations were made per value. The temperature of the immersion liquid was determined with a precision of 0.1°C.

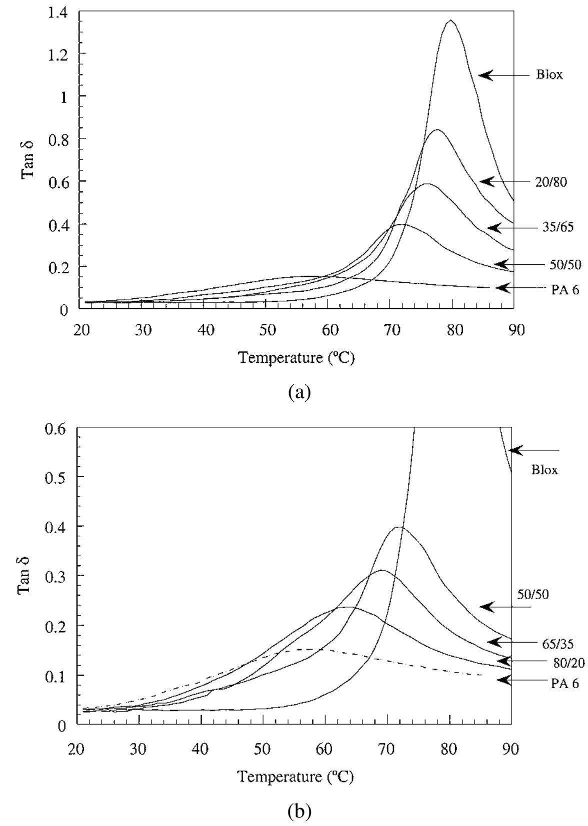
Tensile testing was carried out in an Instron 4301 tester at 23 ± 2°C and 50 ± 5% relative humidity in 2-mm-thick ASTM D-638, type IV specimens. A crosshead speed of 20 mm/min was used. The mechanical properties (Young's modulus (E) measured as the tangent modulus at zero strain, yield stress (σ_y), and break strain (ε_b)) were determined from the force-displacement curves. A minimum of eight specimens was tested for each reported value.

Scanning electron microscopy (SEM) (Hitachi S-2700) was carried out after gold coating on cryogenically fractured surfaces at an accelerating voltage of 15 kV.

3. Results and discussion

3.1. Phase behaviour

The phase behaviour of the PA/Blox blends was studied by DMTA, because the T_g of PA was difficult to observe by lower resolution techniques [25] such as DSC. In the DMTA scans, the intensity of the tan δ peak of Blox was ten-fold that of PA. This led to the characteristics of the PA-rich blends being very difficult to observe in the plots with all the blend compositions. Therefore, the tan δ-T plots of Blox-rich and PA-rich blends are shown respectively in Fig. 1a and b.



(a)

(b)

Figure 1 Tan δ-temperature plots for neat Blox, PA and Blox-rich (a) and PA-rich (b) blends.

Fig. 1a shows the tan δ plots of the Blox-rich blends, and those of the pure polymers as a reference, against temperature. As can be seen, the peak of Blox is sharp, easy to identify and centered at 80°C. That of PA, however, is very wide and centered at roughly 55°C. As can also be seen, the plots of all the Blox-rich blends show a clear sharp peak that must correspond to a Blox-rich phase and that slips towards lower temperatures as the PA content of the blend increases. Moreover, when the plots of the blends and that of pure Blox are compared in the 50–70°C range, the presence of a shoulder in the 35/65 and 50/50 blends can be seen. Moreover, the change of the tan δ peak temperature from that of Blox to the 50/50 blend for instance, is too small (approximately 9°C) compared with the difference in T_g of the two components of the blend (25°C). This indicates the presence of a second PA-rich phase.

In the case of the PA-rich blends of Fig. 1b, the large peak of the Blox-rich phase is also clearly seen, despite the low Blox content. The presence of a shoulder indicating the presence of a PA phase is only slight in the 50/50 and 65/35 compositions, but the fall of tan δ at the left of the tan δ peak of Blox is clearly sharper in the pure Blox than in the blends. The biphasic nature of the blends will be corroborated later by SEM observations.

The position of the peak of the Blox-rich phase is clear, and that of the PA-rich phase can be calculated by means of the temperature at which the difference in tan δ

TABLE I Temperatures of the maximum of the tan δ peak of Blox-rich phase of the blends and pure components

Blend	Temperature (°C)
Blox	80
20/80	77
35/65	76
50/50	71
65/35	69
80/20	64
PA	–

TABLE II PA content in the Blox-rich phase of the PA/Blox blends, estimated by the Fox equation

Blend	%PA in the Blox-rich phase
20/80	8
35/65	13
50/50	30
65/35	40
80/20	62

between the plot of pure Blox and the corresponding blend is the largest. The position of the low temperature peak of the PA-rich phase was almost that of pure PA, whatever the composition, indicating the presence of a practically pure PA amorphous phase. The values of the maxima of the peaks that correspond to the T_g of the Blox-rich phases are collected in Table I. As can be seen, in the case of the high temperature peak, the slip of the transition and the consequent partial miscibility of PA in Blox are evident.

The position of the peaks is determined by the composition of the corresponding amorphous phases. Thus, the amount of PA in the Blox-rich phase can be calculated by means of the Fox equation [26]

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \tag{1}$$

where T_g is the glass transition, ω the weight fraction and the subscripts 1 and 2 refer to the two components of the blends. The results are collected in Table II. As can be seen, the miscibility of PA in Blox is very high. This is because the composition of the Blox-rich phase is not very different from that of the whole blend, and because the 80/20 blend is composed of the aforementioned pure PA amorphous phase, and a second Blox-PA phase, which is also rich in PA, as it has a composition of 62/38.

The partial miscibility of these blends is probably due to the interactions that should exist due to the proton-donor nature of Blox and the proton-acceptor nature of PA. This partial miscibility also agrees with that previously observed between PA and phenoxy (Ph) which has a chemical structure comparable to that of Blox. When the T_g change of the Blox-rich phase of this study is compared with that of the Ph-rich phase of PA/Ph blends [23], the T_g variation with respect to that of the pure components, and as a consequence the miscibility level of PA, is higher in the case of the Blox-rich phase than in the Ph-rich phase. If we look for the structural reasons leading to this difference in miscibility, we realize that the hydroxyl group/carbon atom ratio of Blox (3/23) is much higher than that of Ph (1/18). This must give rise to stronger interactions between Blox and PA, and explains the higher miscibility of the PA/Blox blends of this study. The lack of complete miscibility can be attributed to an unsuitable interacting units/non-interacting units ratio in either of the two components of the blend. It is known [27, 28] that this ratio has a clear influence on the miscibility level of polymer blends. In the case of Ph, for example, it is miscible with PBT but not with PET [29], the interacting units/non-interacting units ratio being the main structural difference between PBT and PET.

No exothermic peak was observed in either the first or the second DSC scans, indicating that PA fully crystallized during cooling both in the mould and in the calorimeter. The measured melting enthalpy of the PA in the blends was proportional to the PA content. This indicates that the crystalline content of PA in the blends is the same as that in the pure state (30% taking 64 J/g as the melting heat of pure PA), and that neither the presence of the Blox-rich phase, nor the presence of miscibilized PA in the Blox-rich phase, influenced the crystallization ability of PA. The change of the melting temperature of PA was within the experimental error, whatever the Blox content. These DSC results indicate that neither the crystallization ability of PA nor the perfection of its crystalline phase changed from the pure PA to the blends.

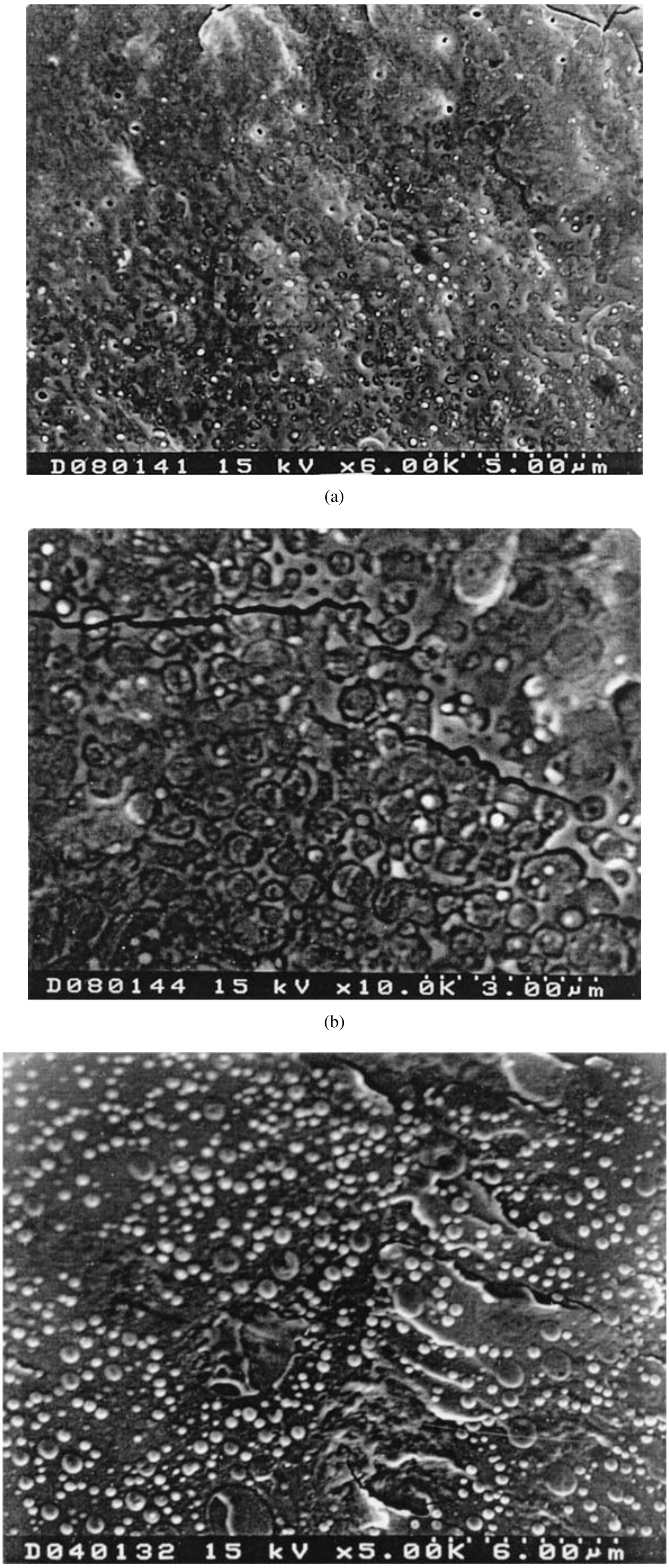
3.2. Morphology

The morphology of the cryogenically broken surfaces of the 80/20, 50/50 and 35/65 blends is shown respectively in Fig. 2a–c. The morphology of the 90/10 and 65/35 blends was similar to that of Fig. 2a, and that of the 20/80 and 10/90 blends similar to that of Fig. 2c.

With respect to the 80/20 blend of Fig. 2a, the morphology is not very clear, and the observed presence of a dispersed phase is smaller than that composition indicates. Therefore, to better define its morphology, this blend and the 50/50 blend were treated with tetrahydrofuran (THF) for 3.5 hours, and the resultant micrograph of the 80/20 blend is shown in Fig. 2d. As can be seen, the biphasic nature of the PA-rich blends is proved by SEM, as the holes where Blox was present are clearly seen.

With respect to the 50/50 blend, the surface was very irregular and difficult to observe by SEM; big holes appeared, but the integrity of the specimen was maintained indicating the PA nature of the matrix.

As can also be seen, the dispersed phase size, even in the 50/50 blend, is very small, with a mean value of 0.3 μm in the 80/20 blend and typically 0.5 μm or smaller in the 50/50 blend. This indicates that mixing was very effective, even with the direct injection moulding technique used that allows the elimination of the usual previous mixing stage. This possibility of homogeneous blending by direct injection moulding has been successfully used in our laboratory in a number of blends, even in the case of completely immiscible components [24, 30].

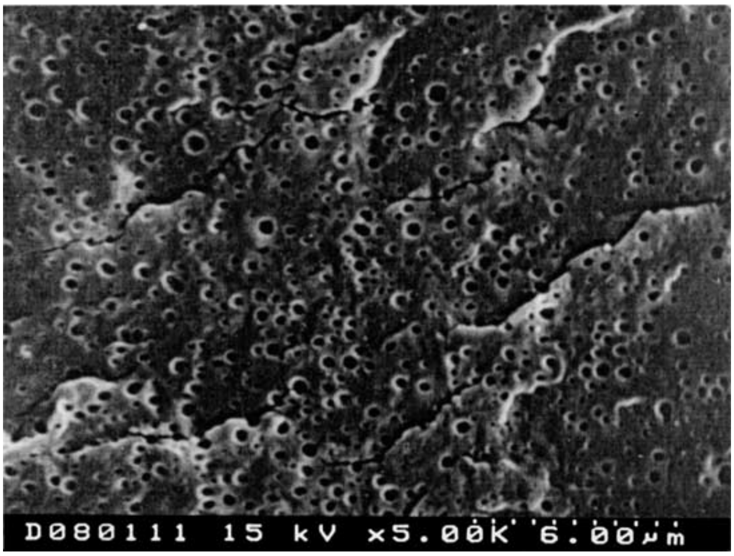


(a)

(b)

(c)

Figure 2 SEM photomicrographs of the PA/Blox blends at Blox contents of 20% (a), 50% (b) and 65% (c), and of the PA/Blox (80/20) blend after treatment with THF for 3.30 h (d). (*Continued.*)



(d)

Figure 2 (*Continued*).

With respect to the Blox-rich blends, the photograph of Fig. 2c shows dispersed spheres, that are suspected of being a microscopy artifact. This is because of both their very regular and clear shape as compared to that of the dispersed particles of the other compositions, and the absence of holes on the surface of the matrix. Some larger and less perfect spheres are also scattered in Fig. 2c. Thus, the presence of a dispersed phase is not clear by SEM; however, this is not the only experimental fact indicating the existence of two phases in Blox-rich compositions. The presence of a PA-rich phase in the Blox-rich blends was inferred from the DMTA scans of Fig. 1a. Therefore, after analysis of the DMTA and SEM results together, the presence of two amorphous phases is inferred whatever the blend composition.

3.3. Mechanical properties

The Young's moduli of the blends against composition are shown in Fig. 3. As can be seen, there is an overall slight positive deviation of the modulus of the blends with respect to the values predicted by the direct rule of mixtures that is depicted as a broken tie line. The positive deviation is noticeable mainly in the case of the Blox-rich blends. In addition to a mean deviation of roughly 5%, both the modulus of the 20/80 and within the confidence limit that of the 10/90 blends, are larger than those of either of the two components.

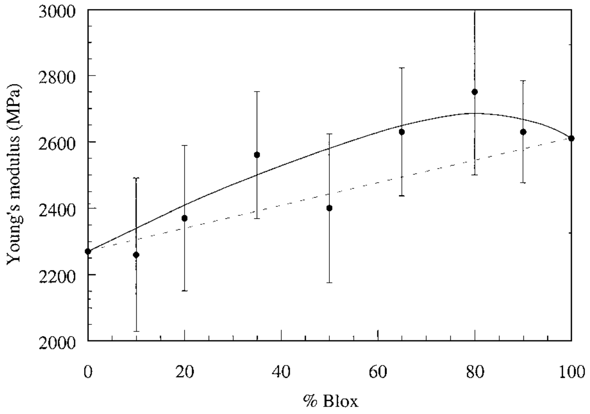


Figure 3 Young's modulus vs. composition of PA/Blox blends.

As can also be seen, there is an apparent discontinuity in the value of the 50/50 blend. Compositions close to that of phase inversion sometimes show discontinuities in the mechanical properties [31]. Therefore this discontinuity has not been taken into account in the curve drawn. Moreover, the value on the curve is within the standard deviation, no significant discontinuity on morphology related to similar compositions was seen, and such a discontinuity in the modulus of elasticity will not be seen in the yield stress value that usually shows a behaviour similar to that of the modulus of elasticity.

Miscibility and positive deviations in the Young's modulus are often related [32, 33] through the occurrence of blending-induced negative volume of mixing. Therefore, the density of the blends was measured. The crystallinity of PA did not significantly change upon blending. Therefore, the plots of the specific volume of both the blends and the amorphous phase of the blends against composition should show the same tendencies. As a consequence the change in the specific volume on blending will be discussed with reference to the whole blend rather than to the amorphous phase only. The specific volume of the blends is proportional to the composition. Therefore, there was no negative volume of mixing. This indicates that in these blends, there must be another parameter that influences the modulus. A different orientation of the components of the blend in the pure state and in the blends could lead to such modulus behaviour.

The yield stress of the blends is shown in Fig. 4 as a function of composition. The broken line corresponds to the values predicted by the direct rule of mixtures. As can be seen, the discontinuity of modulus of the 50/50 composition does not appear in the case of the yield stress. As can also be seen, the largest deviations from the rule of mixtures of the modulus take place in the Blox-rich blends, just where the deviation of the T_g of the Blox-rich phase (Table I), and as a consequence partial miscibility, is the largest. Moreover, an

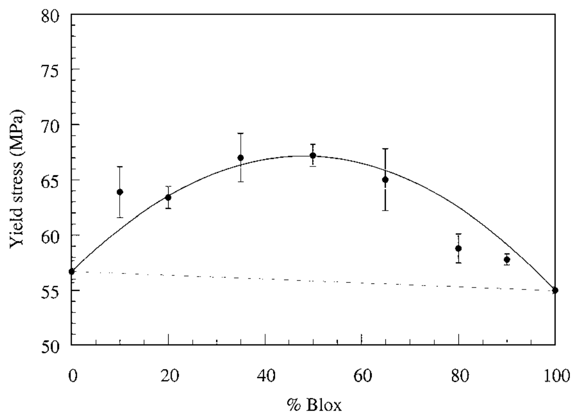


Figure 4 Yield stress vs. composition of PA/Blox blends. The continuous curve corresponds to the modified rule of mixtures.

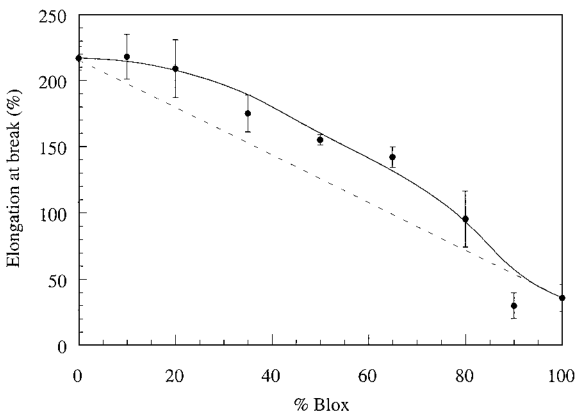


Figure 5 Ductility vs. composition of PA/Blox blends.

attractive synergistic behaviour appears whatever the composition. The synergism is absolute as the values of the blends are higher than those of either of the two pure components. Moreover, the deviation is quantitatively important as it has a mean value of 8 MPa (14% of that of the pure components) and a maximum deviation of 11 MPa (20%) in the case of the 50/50 blend.

This important synergism in yield stress of Fig. 4 can be quantified by means of the modified rule of mixtures proposed by Nielsen [34]

$$P = P_1\phi_1 + P_2\phi_2 + \beta_{12}\phi_1\phi_2 \qquad (2)$$

where P and ϕ are the studied property and the volume fraction respectively, the subscripts 1 and 2 refer to the two components of the blend and β_{12} is an empirical parameter that can be calculated as

$$\beta_{12} = 4P_{12} - 2P_1 - 2P_2 \qquad (3)$$

where P_{12} is a property of the 50/50 blend. The parameter β_{12} quantifies the deviation and has been tentatively related to the compatibility of the blend [33]. As can be seen, the continuous curve of Fig. 4 that corresponds to Equation 2 clearly fits the experimental values. The β_{12} parameter used was 45.4 MPa.

If we compare the Young's modulus and yield stress values of these blends with those of the parent PA/Ph blends [23], the increase with respect to the direct rule of mixtures of both properties is clearly higher in the blends of this work. Moreover, in PA/Ph blends the synergisms observed appeared only in the PA-rich compositions. This more positive response of the PA-Blox blends is probably related to their also larger partial miscibility level.

With respect to the break properties, the ductility measured as elongation at break is shown in Fig. 5. The notched impact strength of the blends was very low, a consequence of the large notch sensitivity of both PA and Blox. As can be seen in Fig. 5, the ductility of most of the blends was above that predicted by the direct rule of mixtures (broken line). This is unexpected, in part due to the biphasic nature of the blend, but mainly because of the previously observed presence of positive behaviours for both the modulus and the yield stress. This is because the presence of a synergism is not very unusual, but a synergism in stress-related properties such as the modulus or yield stress usually leads to low ductility values; and large ductility values are usually linked to low modulus and yield stress.

Considering the reasons for this ductility behaviour, the miscibility level is not the only parameter that influences ductility. Large ductility values have also been observed in almost fully immiscible blends such as those of poly(ether ether ketone) with both polysulfone and poly(ether sulfone) [1, 30]. In addition to miscibility and the consequent good adhesion between the components, additional parameters [1, 30, 35] such as the crystalline level of the components in the blends, the presence of highly oriented structures, different Poisson's moduli of the components, and the dispersed phase size, have also been studied as parameters that can influence ductility.

Of these possibilities, neither the crystalline content of PA, nor the specific volume, changed in the blends. Therefore they did not influence the observed ductility values. The presence of a highly deformed dispersed phase was proposed as a reason for the ductility of the PA/Ph blends [23]. However, the morphologies of the blends of this work are not highly oriented, probably because of the different viscosity ratio of the components of the blends.

A difference in the Poisson's modulus can lead to large ductility values, as a possible compressive stress on the dispersed phase would impede debonding. That of Blox was not available, but the values can be calculated [36] and are 0.40 and 0.39 for PA and Blox, respectively. Thus, Poisson's moduli of the two components are very similar, indicating that they did not influence ductility.

Finally, the dispersed phase size of these blends was very small, almost an order of magnitude smaller than that typically found in polymer blends. This could be the reason for the observed large ductility values of PA/Blox blends. Fully immiscible blends such as bisphenol A polycarbonate (PC)/poly (methyl methacrylate) and PC/AS poly(acrylonitrile-co-styrene) [37, 38] with dispersed particle size between 0.2 and 2 μm also had large ductility values. In this way, large and unexpected ductility values [39] are also observed in nanocomposites, with dispersed particles much more rigid and undeformable than Blox, and with particle sizes (10–100 nm) not very different from that observed in the PA/Blox blends of this study.

4. Conclusions

New partially-miscible PA/Blox blends were obtained by direct injection moulding without any previous mixing step. The blends are composed of an almost pure PA phase and a second Blox-rich phase, in which the PA is highly miscible. The presence of Blox did not affect either the crystallization ability or the crystalline characteristics of PA even when it was highly miscibilized in the Blox-rich phase.

The blends showed an unusual very fine structure with a dispersed phase size of the order of 0.1–0.5 μm at least in PA-rich blends. Unexpected synergisms in both stress related and large strain properties were seen at most compositions. The observed partial miscibility in the case of the yield stress, and the very small dispersed particle size observed in the case of ductility, are proposed as the main reasons for the mechanical behaviour.

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References

1. A. ARZAK, J. I. EGUIAZABAL and J. NAZABAL, *J. Appl. Polym. Sci.* **58** (1995) 653.
2. D. W. BARTLETT, J. W. BARLOW and D. R. PAUL, *ibid.* **27** (1982) 2351.
3. J. I. EGUIAZABAL and J. NAZABAL, *Plast. Rubb. Process. Appl.* **14** (1990) 211.
4. N. YAMAGUCHI, S. AKIYAMA and M. TOKOH, *Kobunshi Robunshu* **53** (1996) 842.
5. Y. KAYANO, H. KESKKULA and D. R. PAUL, *Polymer* **38** (1997) 1885.
6. A. J. OSHINSKI, H. KESKKULA and D. R. PAUL, *Ibid.* **37** (1996) 4891.
7. J. D. LEE and S. M. YANG, *Polym. Eng. Sci.* **35** (1995) 1821.
8. R. ARMAT and A. MOET, *Polymer* **34** (1993) 977.
9. S. HORIUCHI, N. MATCHARIVAKUL, K. YASE, T. KITANO, H. K. CHOI and V. M. LEE, *ibid.* **38** (1997) 59.
10. T. O. AHN, S. C. HONG, H. M. JEONG and J. H. KIM, *ibid.* **38** (1997) 207.
11. E. GATTIGLIA, A. TURTURRO, F. P. LA MANTIA and A. VALENZA, *J. Appl. Polym. Sci.* **46** (1992) 1887.
12. E. GATTIGLIA, A. TURTURRO, E. PEDEMONTE and G. DONDERO, *ibid.* **41** (1990) 1411.
13. F. P. LA MANTIA, M. PACI and P. L. MAGAGNINI, *Rheol. Acta* **36** (1997) 152.
14. Y. SEO, *J. Appl. Polym. Sci.* **64** (1997) 359.
15. Commercial information from Dow Chemical.
16. J. M. MARTINEZ, J. I. EGUIAZABAL and J. NAZABAL, *J. Macromol. Sci-Phys.* B **30** (1991) 345.
17. L. M. ROBESON and A. B. FURTEK, *J. Appl. Polym. Sci.* **23** (1979) 645.
18. G. DEFIEUW, G. GROENINCKX and H. REYNAERS, *Polymer* **30** (1989) 2164.
19. M. IRIARTE, E. ESPI, A. ETXEBARRIA, M. VALERO, M. J. FERNANDEZ and J. J. IRUIN, *Macromolecules* **24** (1991) 5546.
20. M. VANESTE and G. GROENINCKX, *Polymer* **35** (1994) 162.
21. R. ERRO, M. GAZTELUMENDI and J. NAZABAL, *J. Appl. Polym. Sci.* **74** (1999) 1539.
22. *Idem., ibid.* **77** (2000) 2978.
23. G. GUERRICA-ECHEVARRIA, J. I. EGUIAZABAL and J. NAZABAL, *ibid.* **72** (1999) 1113.
24. R. ERRO, M. GAZTELUMENDI and J. NAZABAL, *ibid.* **45** (1992) 339.
25. C. B. BUCKNALL in “Toughened Plastics” (Applied Science Publishers, London, 1977).
26. T. G. FOX, *Bull. Amer. Phys. Soc.* **1** (1956) 123.
27. M. J. FERNANDEZ, M. VALERO, A. MARTINEZ DE ILARDUYA, E. ESPI and J. J. IRUIN, *Polymer* **34** (1993) 38.
28. R. ERRO, M. GAZTELUMENDI and J. NAZABAL, *J. Polym. Sci., Polym. Phys. Ed.* **34** (1996) 1055.
29. J. I. EGUIAZABAL and J. J. IRUIN, *Mater. Chem. Phys.* **18** (1987) 147.
30. A. ARZAK, J. I. EGUIAZABAL and J. NAZABAL, *J. Appl. Polym. Sci.* **65** (1997) 1503.
31. S. BASTIDA, J. I. EGUIAZABAL and J. NAZABAL, *Polymer* **37** (1996) 2317.
32. J. R. FRIED, W. J. MACKNIGHT and F. E. KARASZ, *J. Appl. Polym. Sci.* **50** (1979) 6052.
33. L. W. KLEINER, F. E. KARASZ and W. J. MACKNIGHT, *Polym. Eng. Sci.* **19** (1979) 519.
34. L. E. NIELSEN, in “Predicting the Properties of Mixtures” (Marcel Dekker, New York, 1978).
35. A. ARZAK, J. I. EGUIAZABAL and J. NAZABAL, *Macromol. Chem. Phys.* **198** (1997) 1829.
36. D. W. VAN KREVELEN, in “Properties of Polymers” (Elsevier, Amsterdam, 1976).
37. L. A. UTRACKI, in “Two-Phase Polymer Systems” (Hanser Publishers, New York, 1991).
38. K. KOO, T. INOUE and K. MIYASAHA, *Polym. Eng. Sci.* **25** (1985) 741.
39. T. D. FORNES, P. J. YOON, H. KESKKULA and D. R. PAUL, *Polymer* **42** (2001) 9929.

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