

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Water Sorption in Polyamide 6/Poly(Amino-ether) Blends. II. Mechanical Behavior

G. Guerrica-Echevarría^a; J. I. Eguiazábal^a; J. Nazábal^a

^a Departamento de Ciencia y Tecnología de Polímeros and Instituto de Materiales Poliméricos "POLYMAT", Facultad de Química, UPV/EHU, San Sebastian, Spain

Online publication date: 05 December 2003

To cite this Article Guerrica-Echevarría, G. , Eguiazábal, J. I. and Nazábal, J.(2003) 'Water Sorption in Polyamide 6/Poly(Amino-ether) Blends. II. Mechanical Behavior', *Journal of Macromolecular Science, Part A*, 40: 7, 705 – 714

To link to this Article: DOI: 10.1081/MA-120021420

URL: <http://dx.doi.org/10.1081/MA-120021420>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



JOURNAL OF MACROMOLECULAR SCIENCE®

Part A—Pure and Applied Chemistry

Vol. A40, No. 7, pp. 705–714, 2003

Water Sorption in Polyamide 6/Poly(Amino-ether) Blends. II. Mechanical Behavior

G. Guerrica-Echevarría, J. I. Eguiazábal,* and J. Nazábal

Departamento de Ciencia y Tecnología de Polímeros and Instituto de Materiales Poliméricos “POLYMAT”, Facultad de Química, UPV/EHU, San Sebastian, Spain

ABSTRACT

Polyamide 6 (PA)/poly(amino-ether of bisphenol A) (Blox) blends were placed in water for different times in an attempt to both find out whether the positive effects of Blox on the mechanical properties of PA are maintained in wet conditions, and to study the effects of solvent sorption on the mechanical properties of polymer blends.

After one week's sorption, the positive effects of the presence of Blox on the mechanical properties of PA were much larger than the composition would indicate, as 20% Blox led to a 100% increase in the modulus of elasticity with respect to that of the wet PA. After sorption for six weeks, the positive effects had decreased, attributed to a decrease in the interactions between PA and Blox, which was a consequence of the high miscibilized water content. The sorption/desorption process appeared to be only partially reversible as significant water contents remained in the blends even after very long desorption times and cracking was observed in blends very rich in Blox.

Key Words: Polyamide 6; Poly(amino-ether); Water sorption; Mechanical properties.

*Correspondence: J. I. Eguiazábal, Departamento de Ciencia y Tecnología de Polímeros and Instituto de Materiales Poliméricos “POLYMAT”, Facultad de Química, UPV/EHU, P.O. Box 1072, 20080 San Sebastian, Spain; E-mail: popegori@sq.ehu.es.

INTRODUCTION

Polyamides are widely used polymers due to their favorable combination of mechanical properties, easy processing, and comparatively low price. However, unlike other polymers, and due to their strong proton-acceptor nature, polyamides are prone to absorb large amounts of water (up to 11%), both as liquid and also as atmospheric moisture. Careful processing is required to minimize large-scale plasticization in the solid state,^[1] that leads to important decreases in both the T_g and in mechanical properties such as stiffness and tensile strength. The water sorption mechanisms^[2-4] and resulting changes in some properties of pure polyamides^[5] have been known for some time.

As in the case of other deficiencies of polymers, such as low impact strength, blending may be used to overcome the undesired behavior of polyamides in wet conditions. Thus, the incorporation of a polymer less sensitive to water uptake than PA will probably be beneficial. This effect is due not only to the presence of a hydrophobic polymer, but also to the more complicated penetration paths for moisture.^[6] This should take place both when the second component is mixed at a molecular scale (miscible blends) and at a microscopic scale (immiscible blends).

Poly(amino-ether of bisphenol A) (Blox) is a recently commercialized polymer, which is characterized by its excellent barrier properties to gases and superior mechanical toughness and stiffness.^[7] Recently,^[8] PA/Blox blends appeared as partially miscible blends, which comprised an almost pure PA phase, and a second phase where Blox is the major component and PA is mixed in increasing amounts (up to 62% in the 80/20 blend for instance) as the PA content of the whole blend increases. These blends exhibited a desirable level of mechanical properties in the dry state,^[8] particularly in the case of the 80/20 blend, as their modulus of elasticity, yield stress, and ductility, were larger than those predicted by the rule of mixtures.

In the first part of this paper, both water sorption of the PA/Blox blends and the phase behavior of the wet blends were studied. After water sorption, the presence of two clearly differentiated wet and dry PA phases with a T_g difference of 60°C, and also that of both dry and fully wet Blox phases were seen. Water sorption was much slower in the blends than that corresponding to the Blox content. This positive characteristic was seen as a decrease in the diffusion coefficient of 38% compared to that of pure PA in a 20% Blox blend.

As in the case of the diffusion coefficient, due to water sorption in PA, the decrease in mechanical properties can be clearly less negative in the presence of Blox. This should increase the interest of PA/Blox blends, as they would possess attractive mechanical properties, not only in the dry state, but also in the often-present wet state.

Moreover, this would also provide information on the effects of liquid sorption on the mechanical behavior of polymer blends, which is a research subject that has seldom been studied. In recent years, to our knowledge, very few studies dealing with this topic have appeared, either in the case of polyamide-based blends^[9,10] or other blends.^[11,12]

In this study, the effects of different amounts of water uptake on the mechanical properties of PA/Blox blends of different compositions are studied by means of tensile testing after medium and long sorption times, and the results are compared with the properties of dry blends and those of pure PA. The reversibility of the sorption process is investigated and the mechanical properties are analyzed as a function of the water content in the case of the 80/20 blend, the one with the best mechanical properties.

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 $M_v = 29,000$, 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 with a 2.16 kg load. Both polymers were dried before processing in order to avoid moisture-induced degradation reactions, the PA for 14 h at 80°C *in vacuo*, and Blox for 6 h at 65°C in an air circulation oven.

To obtain the blends, pellets of PA and Blox were mixed at the desired weight ratios and tumbled together before injection molding. The polymers were directly melt mixed and injection-molded in a Battenfeld BA 230E reciprocating screw injection molding machine. The barrel temperature was 230°C and the mold temperature 20°C. The choice of the 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 plasticization 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 cm³/s and 1500 bar, respectively. Tensile ASTM D-638, type IV specimens with a thickness of 2 mm were obtained.

The sorption measurements were carried out at 23°C on injection molded tensile specimens. The samples were immersed in distilled water for periods up to 6 weeks. Subsequent desorption experiments were performed at room temperature for up to 12 days. The solvent content in the samples at the time *t* was calculated as:

$$\% \text{ solvent} = (\text{weight at time } t - \text{initial weight}) \times 100 / \text{initial weight}$$

Tensile testing after each sorption or desorption time was carried out on an Instron 4301 tester at $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ 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*), yield stress (σ_y), and break strain (ϵ_b)) were determined from the force–displacement curves. A minimum of eight specimens were tested for each reported value.

RESULTS AND DISCUSSION

Effects of the Composition of the Blends

The overall effect of the presence of water in PA/Blox blends is shown in Fig. 1, in which the tensile stress–strain curve of the 80/20 PA/Blox blend, as an example, after water sorption during one week (curve b) is compared with that of the pure PA also after one week sorption (curve c), and with that of the dry blend (curve a). As can be seen when curves b and a are compared, the water presence leads to a clear plasticizing effect and associated decreases in the modulus of elasticity and yield stress (stress of the rubber-plateau in the case of rubber-like behavior) and to a curve similar to that of rubber-like materials. Decreases in mechanical properties as the water content increased have also been observed in a PA/rubber blend,^[9] and in an amorphous PA/ethylene–vinyl alcohol

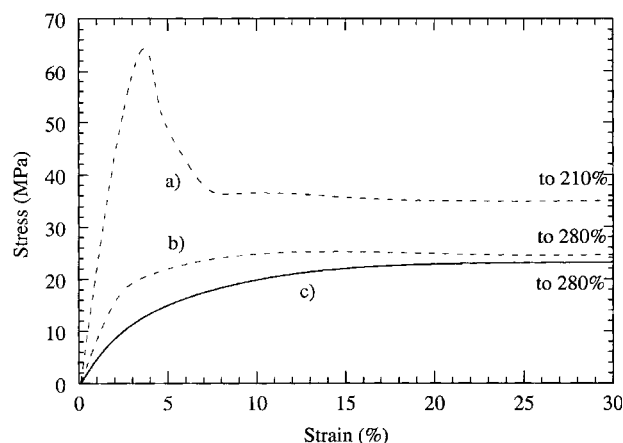


Figure 1. Stress–strain curves of 80/20 PA/Blox (a) before and (b) after 1 week's sorption time (discontinuous lines). Curve c corresponds to pure PA after 1 week's sorption.

copolymer (EVOH) blend.^[10] However, as can be seen, when the curves of the wet blend and wet PA (curves b and c, respectively) are compared, the presence of 20% Blox^[8] led to larger yield stress and modulus of elasticity. The ductility values, despite the presence of two phases, are close to that of pure PA, and are much higher than that of pure Blox (36%). The mechanical properties of the blends as a function of composition and at several water contents are discussed in the following paragraphs.

Figure 2 shows the modulus of elasticity of the blends, after sorption for a week (curve a) and six weeks (curve b). The curve of the blends before sorption (curve c) is also shown as a comparison. The position of these points in the sorption curve is seen in Fig. 3. As can be seen in Fig. 2, the clearly smaller modulus of elasticity of the wet blends compared with

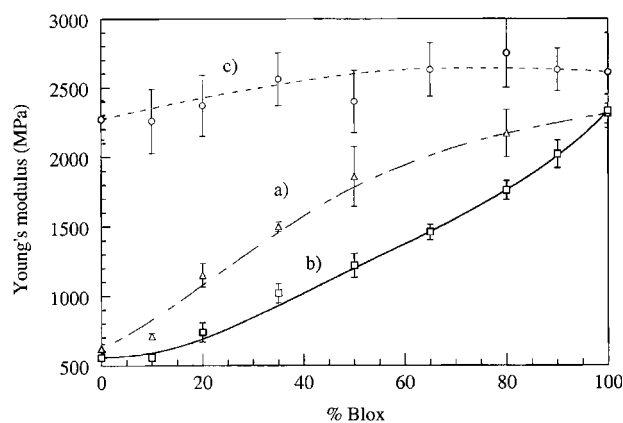


Figure 2. Young's modulus vs Blox content in PA/Blox blends after 1 week (Δ), long sorption times (\square) and before sorption (\circ).

Water Sorption in PA/Blox Blends. II

709

that of the dry blends indicates that plasticization, induced by water, is important in all the PA/Blox blends, despite the slight plasticization effect of water in Blox. The modulus of Blox after six weeks sorption is 88% of that of dry Blox, while in the case of the wet PA it is only 27% of the modulus of dry PA. This indicates that the plasticizing effect of water in PA is much larger than in Blox. This is because, after long sorption times, the water content of Blox is around half that of PA, but its plasticization, measured by the modulus decrease, is much lower than that of PA.

As can also be seen in Fig. 2, the plasticization effect is much smaller in the blends than in pure PA. This is because the very large differences between the modulus of the dry and the two wet PAs on the left of Fig. 2, become progressively smaller as the Blox content of the blends increases. Smaller differences in modulus between the dry and fully wet blends as the content of the less absorbing component increased have also been seen in amorphous PA/EVOH and crystalline nylon-containing ionomer/EVOH blends.^[10] No plot of the mechanical properties at intermediate sorption times was provided in Ref.^[10]. This stiffening effect of the presence of Blox in the wet PA is very positive, as it is much larger than that the Blox content could suggest. This is because the moduli of the wet blends with 20 and 35% Blox are, respectively, more than two and three-fold that of pure PA.

As can also be seen, the modulus of the blends after one week's sorption is higher than that predicted by the rule of mixtures, which would link by means of a tie line the values of the two pure components (it is not depicted for clarity). Although the plasticizing effect on the modulus does not have to be proportional to the water content, this modulus above that predicted by the law of mixtures is probably due to the higher water content of the components of the blends in the pure state compared with that in the blends after the same sorption conditions. This smaller water content in the blends is seen, as the curves of the blends after one week of Fig. 3 are at a position closer to that of Blox than that they should be according to their composition. However, after long times the distance between the curves is

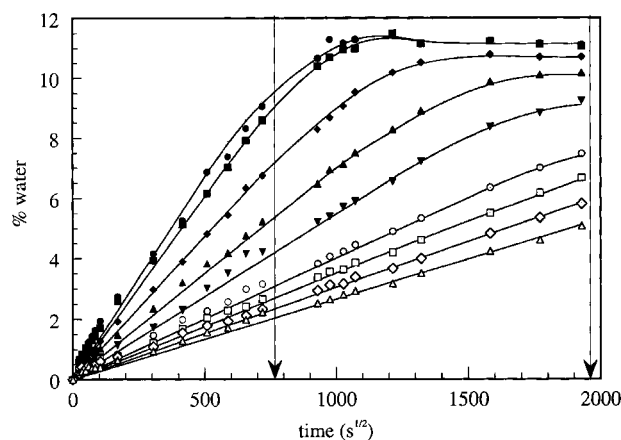


Figure 3. Water uptake of the PA/Blox blends against the square root of time: (●) pure PA, (■) 90/10, (◆) 80/20, (▲) 65/35, (▼) 50/50, (○) 35/65, (□) 20/80, (◇) 10/90 and (△) pure Blox. The arrows show the times at which mechanical properties were measured.

that expected from the composition change. The study of the change of mechanical properties as a function of the water content will be reported in the second part of this paper.

The yield stress of the blends at the same sorption conditions as in Fig. 2 is shown in Fig. 4. In the case of wet PA, and to a lesser extent in the wet blends very rich in PA, the maximum of the yield peak was not clearly seen, so the plotted values correspond to the stress of the rubber-like plateau, and are depicted as a broken line. The value of wet Blox after six weeks does not appear, as breaking took place (at 47.9 MPa) before yielding. As can be seen, the plasticizing effect on the yield stress is also very important and fairly similar to that of the Young's modulus, as might be expected because of the usually similar behavior of both modulus of elasticity and yield stress that has been often seen experimentally^[13] and that has even been predicted by theoretical models.^[14] When decreases of the yield stress with respect to the values of the dry blend were calculated, the yield stress decreases due to water sorption were slightly larger than those of the modulus of elasticity. This smaller positive effect of the presence of Blox on yield stress can be influenced by the fact that the modulus of elasticity is a bulk property, in which the whole section contributes to stress. Yielding, however, is a more localized process that can easily initiate in the more plasticized zone of heterogeneous materials, such as the wet PA/Blox blends.

Moreover, when yield stress is discussed (and to a lesser extent the modulus of elasticity as it is measured at much smaller strain) the effects of the significant presence of water on the interactions between PA and Blox should be taken into account. This is because, as an important amount of PA is miscibilized in the Blox-rich phase where water is also present, the interactions by hydrogen bonding between PA and Blox will be hindered by the proton-donor water molecules, and this will take place at a microscopic scale in the bulk specimen. This is in agreement with the progressively lower positive effect of the presence of Blox on the yield stress as the water content and the sorption time increase. A decrease in the polymer-polymer interactions and an increase in the polymer-solvent ones in swollen blends with respect to dry ones has also been proposed as responsible for the overall decrease in mechanical properties of swollen SBR/NR blends.^[11]

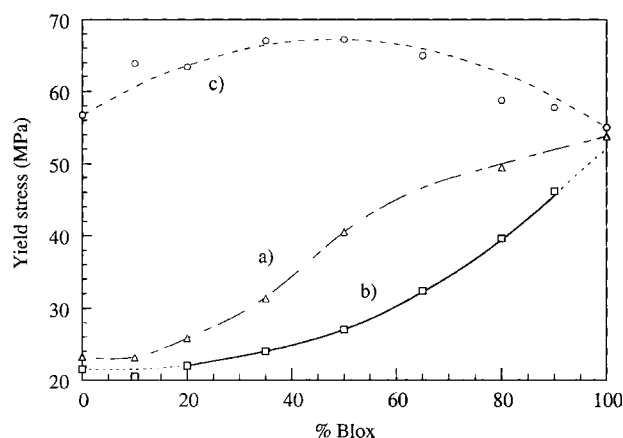


Figure 4. Yield stress vs Blox content in PA/Blox blends. Symbols as in Fig. 2.

Water Sorption in PA/Blox Blends. II

711

The ductility of the blends after one week (curve a) and six weeks (curve b) is shown in Fig. 5 against composition. The ductility of the blends in the dry state is also shown (curve c) as a reference. The comparison between the ductility values after different water sorption times is not easy to make, as the deformation mechanism at long strains suffers a clear change, from that typical of a partially crystalline polymer with multiple yielding and cold drawing processes, towards the rubber-like behavior of the wet materials, which was seen in Fig. 1. Despite this fact, the ductility of PA-rich blends in Fig. 5 is greater than the direct rule of mixtures (it is not drawn in Fig. 5 for clarity) would predict, and higher than in the case of the dry blend. Moreover, as in EVOH/PA blends,^[10] the positive effect of plasticization in ductility is found in almost all the compositions, opposite to the large ductility decrease of wet EVOH/nylon-containing ionomer blends^[10] in the presence of only 30% ionomer. The ductility of pure Blox and of the blends very rich in Blox is surprising as it decreased upon water sorption. This effect appears to be significant, as it takes place in most of the three water sorption levels and three blend compositions (0, 10 and 20% Blox). This decrease in ductility of the blends upon water sorption can be related to the appearance upon desorption of small cracks distributed across the specimen that were seen in part I of this study.^[1] Permanent damage in poly(butylene terephthalate) (PBT) materials and in short fibre reinforced PBT^[15] upon water immersion at temperatures around 50°C was explained as a consequence of the formation of microvoids due to hydrolysis. These microvoids will act as stress concentrators that can initiate matrix cracking.^[12] Although the effects observed in this study are very similar, such a reaction cannot take place in Blox. Neither were the cracks found in this study due to the presence of two phases, as they also appeared in the pure Blox at room temperature. It is difficult to relate them to the volume contraction during desorption, therefore the cracks are attributed to the volume increase of the specimen upon sorption that can be heterogeneous at microscopic level, leading to microcracking that must affect ductility.

With respect to desorption, at medium desorption times, the mechanical properties were the same to those during sorption at the same water content. At long desorption times,

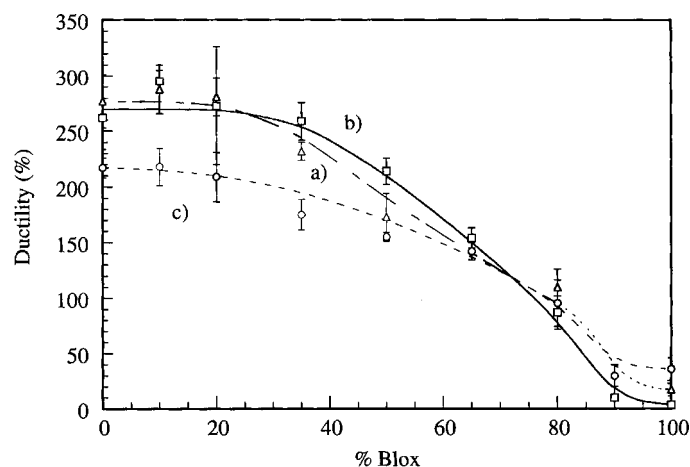


Figure 5. Ductility vs Blox content in PA/Blox blends. Symbols as in Fig. 2.

the initial values of the mechanical properties were not recovered as residual water remained. This indicates that water sorption is a partially reversible process both from a sorption and mechanical properties point of view.

Effects of the Water Content

Finally, taking into account the attractive balance of properties of the 80/20 blend, that was seen in Ref.^[8], the effects of different amounts of water on the mechanical properties of this blend composition were studied at six sorption times. The results for the modulus of elasticity and the yield stress are shown in Figs. 6 and 7, respectively. The values of pure PA are also plotted as a reference. The ductility of the 80/20 blend did not change much (from 210% in the dry blend to 280% in the wet blends) as the dry blend was able to cold draw, and as was expected due to plasticization.

As can be seen in Fig. 6, the decrease in modulus of elasticity is directly related to the increase in water content. This takes place up to 9% water content, which corresponds approximately to the point at which Fickian behavior finished. It has been seen by PALS^[16] that in PA both the free volume cavity size and the amount of free volume sites decrease during initial sorption, up to around 8% of the maximum water uptake. This should give rise to an increase in the modulus of elasticity that does not take place, either in the pure PA or in the blend of Fig. 6. This suggests that plasticization by water takes place at different volume scales, and that the free volume increase, that leads to plasticization and to modulus decreases, has a dimension which is not detected by PALS. As can also be seen, the higher modulus of elasticity of the dry blend compared to that of PA holds upon water sorption. The direct relation between yield stress and water content disappears at sorption times shorter than those

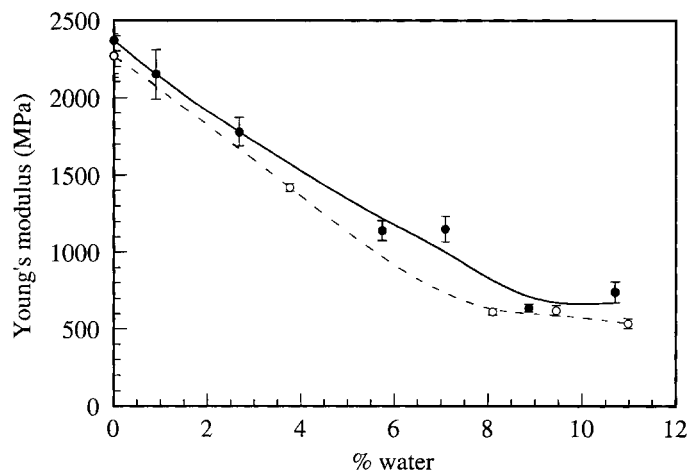


Figure 6. Young's modulus vs water content for the 80/20 PA/Blox blend (●) and pure PA (○).

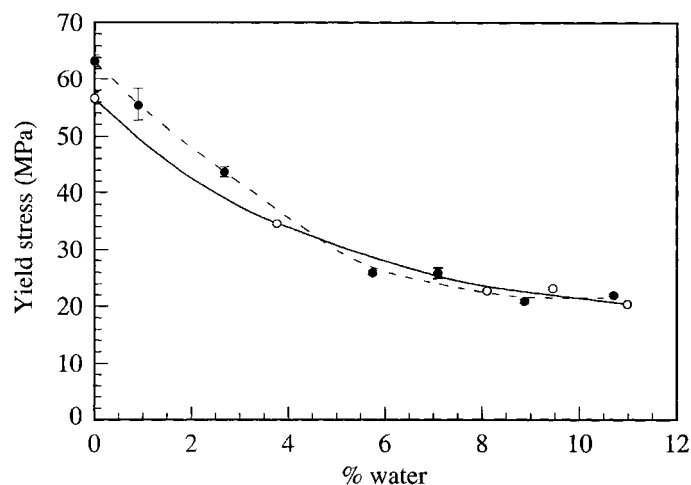


Figure 7. Yield stress vs water content for the 80/20 PA/Blox blend (●) and pure PA (○).

in the case of the modulus, probably because of the larger sensitivity of yield stress to heterogeneities in local composition.

CONCLUSIONS

The severe plasticization of PA by water is clearly diminished by means of the presence of only small levels of Blox, both after intermediate (one week) and long (six weeks) sorption times. This is in part due to the slower water uptake of the blends after intermediate sorption times, and leads to moduli of elasticity two and three-fold that of the wet PA in wet blends with 20 or 30% Blox. Thus, the loss of rigidity characteristic of PA upon water sorption is clearly reduced. After long sorption times, the positive effects of the Blox presence were less important, as the large miscibilized water content probably hinders the interactions between PA and Blox.

The sorption/desorption process in pure Blox and in blends very rich in Blox leads to generalised cracking in the specimens, which is probably the reason for the observed low ductility of these materials. This cracking effect, and the presence of some water in the blends even after very long desorption times, indicate that the sorption process in these blends is only partially reversible.

ACKNOWLEDGMENTS

The financial support of the University of the Basque Country (Project no. 9/UPV-13540/2001) is gratefully acknowledged. The authors also acknowledge Dr. Ha Q. Pham and Dr. Asjad Shafi, from Dow Chemical Company for supplying the Blox sample.

REFERENCES

1. Guerrica-Echevarría, G., Eguiazábal, J.I., Nazábal, J. J. *Macromol. Sci., Pure Appl. Chem.*, **2003**, *A40*, 557–569.
2. Deopura, B.L.; Sengupta, A.K.; Verma, A. Effect of moisture on physical properties of nylon. *Polym. Commun.* **1983**, *24*, 287–288.
3. Kohan, I.H., Ed. *Nylon Plastics*; John Wiley and Sons: New York, 1973.
4. Rowland, S.P., Ed. *Water in Polymers*; American Chemical Society: Washington, 1980.
5. Reimschuessel, H.K.J. Relationship on the effect of water on glass transition temperature and Young's modulus of nylon 6. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1229–1236.
6. Paul, D.R., Newman, S., Eds. *Polymer Blends*; Academic Press: London, 1978.
7. Technical information from Dow Chemical.
8. Guerrica-Echevarría, G., Eguiazábal, J.I., Nazábal, J. J. *Mater. Sci.*, **2002**, *37*, 4529–4535.
9. Kumar, C.R.; Francis, B.; Thomas, S. Transport of water through polyamide–nitrile rubber blends and its influence on mechanical properties. *Polym. Polym. Comp.* **2001**, *9* (4), 247–256.
10. Lagaron, J.M.; Jiménez, E.; Gavara, R.; Saura, J.J. Study of the influence of water sorption in pure components and binary blends of high barrier ethylene–vinyl alcohol copolymer and amorphous polyamide and nylon-containing ionomer. *Polymer* **2001**, *42*, 9531–9540.
11. George, S.C.; Ninan, K.N.; Groeninckx, G.; Thomas, S. Styrene–butadiene rubber/natural rubber blends: morphology, transport behavior, and dynamic mechanical and mechanical properties. *J. Appl. Polym. Sci.* **2000**, *78*, 1280–1303.
12. Mohd Ishak, Z.A.; Ishiaku, U.S.; Karger-Kocsis, J. Hygrothermal aging and fracture behavior of styrene–acrylonitrile/acrylate based core-shell rubber toughened poly(butylene terephthalate). *J. Appl. Polym. Sci.* **1999**, *74*, 2470–2481.
13. Brostow, W.; Corneliusen, R.D. *Failure of Plastics*; Hanser: Munich, 1986.
14. Struick, L.C.E. Some problems in the nonlinear viscoelasticity of amorphous glassy polymers. *J. Non-Cryst. Solids* **1991**, *131–133*, 395–407.
15. Mohd Ishak, Z.A.; Lim, N.C. Effect of moisture absorption on the tensile properties of short glass fiber reinforced poly(butylene terephthalate). *Polym. Eng. Sci.* **1994**, *34* (22), 1645–1655.
16. Robertson, J.E.; Ward, T.C.; Hill, A.J. Thermal, mechanical, physical and transport properties of blends of novel oligomer and thermoplastic polysulfone. *Polymer* **2000**, *41*, 6251–6262.

Received August 2002

Revision January 2003