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Properties of aliphatic block copolyamides and homopolyamide blends prepared by combined polymerization

Jaroslav Stehlíček*, Jana Kovářová, František Lednický and Rudolf Puffr
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

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Poly(6-hexanelactam)-*block*-poly(12-dodecanelactam) copolymers containing a minor part of poly(6-hexanelactam) (PA6) and poly(12-dodecanelactam) (PA12) were compared with PA6–PA12 blends as regards their crystallization behaviour, thermal properties, sorption of water vapour, morphology and mechanical properties. All blends were prepared by the combined polymerization procedures described earlier. The differences found are ascribed to the different composition of amorphous phases, specifically to the compatibilization effect of the diblock copolymer. Copyright © 1996 Elsevier Science Ltd.

(Keywords: block copolymers; aliphatic polyamides; physical properties)

INTRODUCTION

Different semicrystalline aliphatic polyamides are virtually immiscible and exhibit phase separation in both the amorphous and crystalline phases of their blends as proved by differential calorimetric and dynamic mechanical studies[1-4]. Incompatibility, however, may change to compatibility by transamidation reactions, which proceed relatively easily above the melting temperature of polyamide components in the presence of reactive end-groups and/or residues of polymerization catalysts[5]. Miscibility, manifested by the formation of a single amorphous phase, is probably attained earlier than the random copolyamide is formed.

This is why immiscibility was confirmed for similar polyamides, such as polyamide-6 (PA6) and polyamide-6,6, only with their blends prepared by coprecipitation from a common solvent[1] at low temperature. True miscibility of PA6 and polyamide-12 (PA12) was observed only at high pressure and temperature[3].

In the previous paper[6], we described the preparation of poly(6-hexanelactam)-*block*-poly(12-dodecanelactam) (PA6-*block*-PA12) copolymers containing also some PA6 homopolymer (≤ 4.0 wt%) and PA12 homopolymer (1.5–10.6 wt%). The total concentration of PA12 component (blocks and homopolymer) was 5.3–21.2 wt%. The copolymers were obtained by the anionic polymerization of 6-hexanelactam initiated with PA12 polymers bearing diacylamine branching sites. Under the preparation conditions applied, the virtually immiscible polyamide components were dispersed on a molecular level before crystallization and phase separation set in. The above-mentioned transamidation reactions[5] between different polyamides are excluded so that phenomena associated with phase separation in crystalline and amorphous states can be studied with the products.

For comparison, binary PA6–PA12 blends were also prepared by the polymerization technique; up to 15 wt% of linear PA12 was dissolved in 6-hexanelactam, which was then polymerized.

EXPERIMENTAL

*Copolymers PA6-*block*-PA12 and PA6–PA12 blends*

The samples were prepared by the monomer casting–bulk polymerization method either in glass ampoules at 180°C (overheating by polymerization and crystallization heat was up to 5°C) or in an aluminium mould at 170°C (overheating 1–3°C). Shrinkage of the polymers and separation from the glass wall were observed in ampoules after 10–20 min of polymerization. Their basic characteristics are given in *Table 1*; for a detailed description see the previous paper[6].

Differential scanning calorimetry

D.s.c. measurements were performed in nitrogen atmosphere with a Perkin-Elmer DSC7 instrument interfaced with a computer data station and calibrated with indium. The samples were discs (diameter 4 mm, thickness 0.5–0.7 mm) turned from the product, which were freed of low-molecular-weight compounds and wet annealed in boiling water for 3 h, dried in vacuum at 60°C, enclosed in Al pans and heated from 30 to 250°C at a rate of $20^{\circ}\mathrm{C\,min^{-1}}$ (first scan), cooled to room temperature at $100^{\circ}\mathrm{C\,min^{-1}}$ and heated again (second scan) at $20^{\circ}\mathrm{C\,min^{-1}}$. Glass transition temperatures T_g were evaluated from the second scans. Some samples were, in addition to wet annealing, dry annealed by heating under an Ar atmosphere to 160°C for 24 h before enclosing in Al pans. The melting temperatures (T_m) and heats of fusion

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* To whom correspondence should be addressed

Table 1 Characteristics of samples: content of PA12 in extracted samples (PA12); casting temperature (*T*) and time (*t*); portion extractable in ethanol (*EP*); number-average molecular weight of PA12 ($\overline{M}_{12}$) and PA6 ($\overline{M}_6$) blocks in copolymers or homopolymers in blends

PA12 (wt%)	*T* (°C)	*t* (min)	*EP* (wt%)	$\overline{M}_{12}$ ($\times 10^{-3}$)	$\overline{M}_6$ ($\times 10^{-4}$)
Block copolymers					
5.3	170	30	5.4	2.4	8.3
10.4	170	30	3.8	2.4	4.1
15.8	170	30	5.2	2.4	2.5
21.2	170	30	5.6	2.4	1.7
9.4	180	40	3.6	2.6	2.1
9.5	180	15	4.4	0.6	1.0
9.5	180	40	4.0	4.1	7.3
9.7	180	30	4.0	1.9	1.1
10.7	180	30	4.7	5.1	3.0
11.1	180	20	17.1	2.6	4.3
15.0	180	60	2.8	2.6	3.0
15.7	180	30	4.7	2.7	1.1
15.9	180	30	5.5	5.1	1.9
16.2	190	60	6.9	4.0	4.1
16.6	180	20	9.7	2.7	2.7
PA6–PA12 blends					
0	170	30	2.7	–	6.2
5.1	170	30	2.8	9.9	5.1
10.3	170	30	2.9	9.9	3.9
15.4	170	30	2.4	9.9	3.6

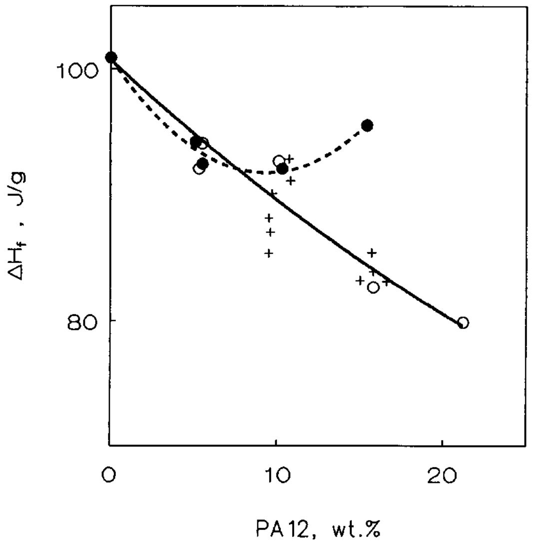

Figure 1 Total heats of fusion (ΔH_f, first d.s.c. run) as a function of the PA12 concentration in PA6-*block*-PA12 ((——, ○) mould cast at 170°C with the same initiator, (+) polymerization in glass with various initiators) and PA6–PA12 blends ((- - - -, ●) mould cast at 170°C)

(ΔH_f) obtained from the area of endothermic melting peaks were evaluated from the first scans.

Water sorption

Equilibrium sorption of water vapour was determined gravimetrically with extracted samples in the form of fine shavings, which were predried over P_2O_5 to a constant weight and then kept in air of relative humidity 65% (over 36% H_2SO_4) or 93% (over a saturated aqueous solution of KNO_3) at 23°C.

Morphology

Micrographs of thin sections of the non-extracted products were obtained with a polarizing microscope (Photomicroscope III, Zeiss-Opton).

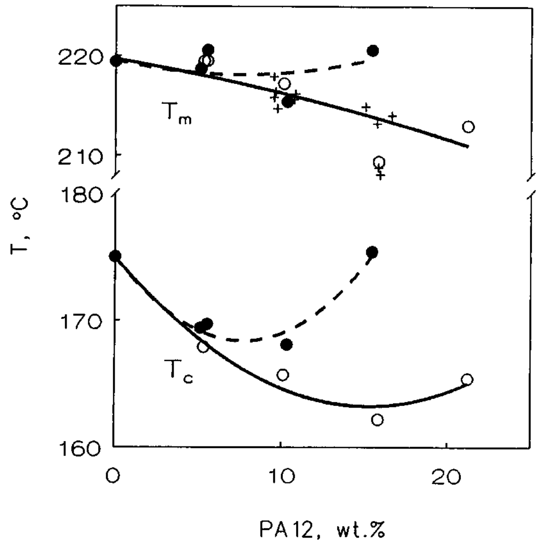

Figure 2 Melting (T_m, first d.s.c. run) and crystallization temperature (T_c) as functions of PA12 concentration in PA6-*block*-PA12 and PA6–PA12 blends; for symbols see *Figure 1*

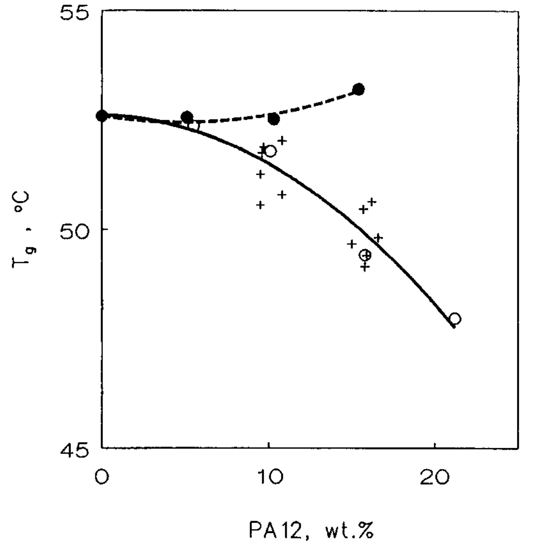

Figure 3 Glass transition temperature (T_g, second d.s.c. run) as a function of PA12 concentration in block copolymers and PA6–PA12 blends; for symbols see *Figure 1*

Mechanical properties

Mechanical properties were measured with dry and non-extracted specimens, cut from the plaques and milled to the required thickness, by standard methods: Shore D hardness °*ShD* at 23°C (DIN 53 479), flexural stress σ_0 by Dynstat at 25°C and the standard deflection of 15°. Specimen dimensions were $(10 \pm 0.5)\,\text{mm} \times (15 \pm 1)\,\text{mm} \times (1.5\text{–}4.5)\,\text{mm}$ (DIN 51 230). Flexural modulus of elasticity E_f was calculated from the relationship derived for the anionic PA6:

$$\ln E_f = 0.0777\ {}^{\circ}ShD + 1.8114$$

RESULTS AND DISCUSSION

D.s.c. study of block copolymers and blends

The d.s.c. measurements were carried out with the

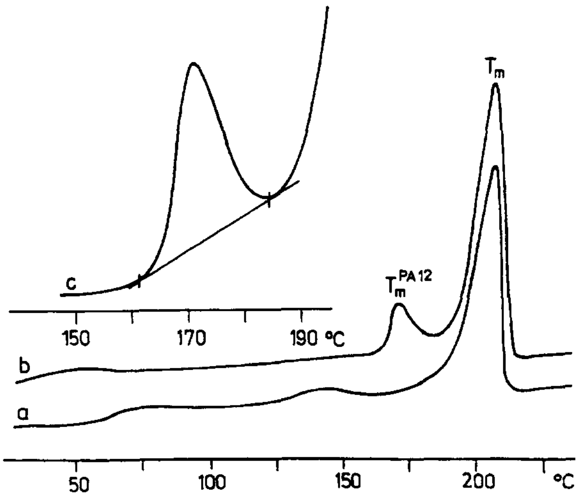

Figure 4 D.s.c. curves of the block copolymer containing 15.1 wt% PA12 blocks and homopolymer: first run of wet (a) and dry-annealed (b) sample, and (c) melting endotherm of PA12 (shoulder) and its integration

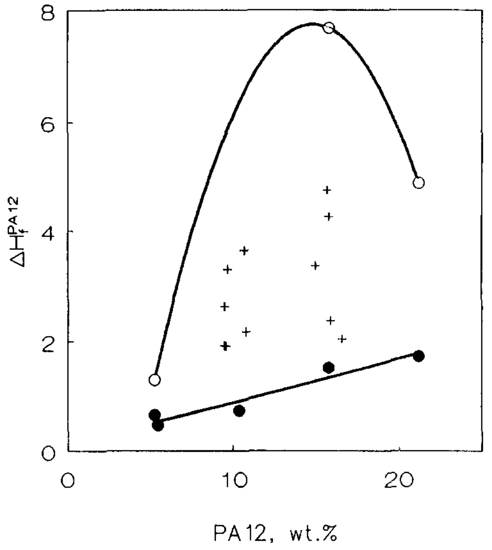

Figure 5 Heat of PA12 fusion (ΔH_f^{PA12}, shoulder area) in PA6-*block*-PA12 as a function of PA12 concentration: mould cast series after wet (●) and dry annealing (○); wet-annealed samples prepared under various conditions (+)

samples wet annealed during extraction of low-molecular-weight components in boiling water. Under these conditions, i.e. in swelling above T_g, crystallization of the PA6 phase should be practically complete and the samples show the highest endothermic effect in the first heating scan.

In the samples containing PA6-*block*-PA12 as the major component (88.8 to 98.0 wt%), the heat of fusion ΔH_f, corresponding to the total crystallinity, continuously decreases with the increasing content of the PA12 component (blocks and homopolymer) (*Figure 1*). The positions of the endothermic T_m peak in the first heating scans (*Figure 2*) have a similar tendency. This can be explained by the more pronounced formation of an amorphous interphase containing both PA6 and PA12 segments in the block copolymer, which decreases the total crystallinity and the size and perfection of PA6 crystals. However, the rate of crystallization of PA6 is facilitated by viscosity reduction in the presence of PA12 melt[4].

The values of ΔH_f, ΔH_c and T_c for PA6–PA12 blends show a shallow minimum at 5–10 wt% PA12, whereas T_m practically does not change and corresponds to that of PA6 homopolymer. In the blends, the interaction between chains of different polyamides is limited only to small amounts of PA12 present in the amorphous phase of PA6.

A similar effect can be seen even better in the dependence of T_g on the total content of PA12 blocks and/or homopolymer (*Figure 3*) where the formation of interphase clearly decreases T_g in the block copolymers. In the PA6–PA12 blends, the found T_g values are practically constant and correspond to the PA6 matrix.

The extent of crystallization of the minor PA12 phase in block copolymers strongly depended on the sample history, namely on the polymerization conditions, and was not reproducibly enhanced by the treatment in boiling water. The endotherm of PA12 melting was observed as a shoulder on the PA6 melting peak in most of the copolymers (*Figures 4b* and *4c*). Its area was evaluated as heat of fusion ΔH_f^{PA12}. A correlation between ΔH_f^{PA12} and the content of PA12 was found only in the series of block copolymers prepared under the same defined conditions[6], viz. by mould casting at 170°C (*Figure 5*, lower curve); the samples prepared at 180°C in a glass ampoule generally contained a higher proportion

Table 2 Comparison of thermal characteristics obtained in the first d.s.c. scan with PA6-*block* PA12 copolymers and PA6–PA12 blends after wet (W) and dry (D) annealing

PA12[a]	T_m (°C)[b]		T_m^{PA12} (°C)[c]		ΔH_f (J g^{-1})[d]		ΔH_f^{PA12} (J g^{-1})[e]	
(wt)	W	D	W	D	W	D	W	D
Block copolymers								
5.3	219.5	219.9	182.5	185.5	92.1	93.3	0.7	1.3
15.8	209.4	211.6	167.7	185.4	82.7	85.5	1.5	7.7
21.2	213.0	213.4	169.5	174.3	78.9	82.6	1.7	4.9
Blends								
5.1	220.6	217.9	–	185.6	92.5	93.7	–	0.5
15.4	220.6	215.8	–	172.2	95.6	101.1	–	4.1

[a] Content of PA12—blocks and homopolymer
[b] Main melting endotherm
[c] Shoulder (PA12 endotherm)
[d] Total heat of fusion
[e] Heat of fusion of the separated PA12 (area of the shoulder)

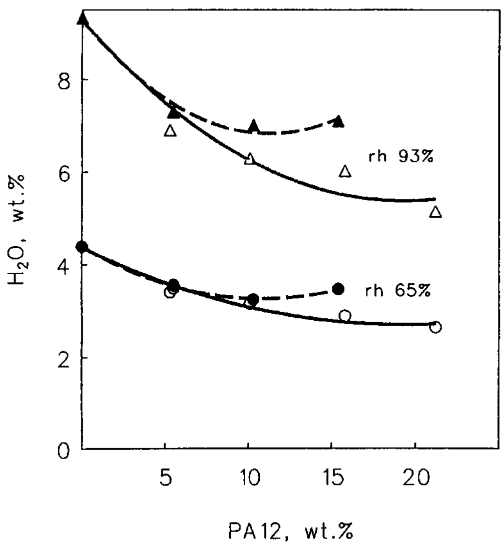

Figure 6 Sorption of water in PA6-*block*-PA12 (○, △) and PA6–PA12 blends (●, ▲) as a function of PA12 concentration at relative humidity of 65% and 93%

of crystalline PA12. Shorter casting times and faster cooling in the metal mould leads to lower PA12 crystallinity than obtained for a slower cooling in the glass ampoule. Surprisingly, the crystallization of PA12 in the PA6–PA12 blends prepared by mould casting did not occur after polymerization and wet annealing.

The effect of dry annealing at 160°C for 24 h was followed with selected samples of block copolymers and PA6–PA12 blends and is presented in *Table 2*. The block copolymers prepared by mould casting[6] at 170°C markedly enhanced their PA12 crystallinity by annealing. This is manifested in the increase of shoulder area (ΔH_f^{PA12} in *Figure 4*, upper curve in *Figure 5*) and total crystallinity (ΔH_f) and in the shift of the shoulder maximum (T_m^{PA12}) to higher temperature. In the dry-annealed PA6–PA12 blends, a small peak or shoulder of PA12 melting also separates from the main melting endotherm and the total crystallinity (ΔH_f) also increases.

The difference found in the crystallization behaviour of block copolymers and PA6–PA12 blends may also be ascribed, in addition to the occurrence or absence of a compatibilization effect, to the difference between the number-average molecular weights of the PA12 blocks ($\overline{M}_b \sim 500$–5000) and the linear PA12 homopolymer in the blends ($\overline{M}_h \sim 10\,000$) because PA12 with higher $\overline{M}_h$ crystallizes less easily. The shortest PA12 blocks of copolymers are obviously soluble in PA6 phase and could contribute more to the formation of an amorphous interphase. The molecular weights of PA6 blocks and/or homopolymer as the main component are much higher indeed (10 000–83 000).

Sorption of water vapour

It is known that water does not penetrate into the

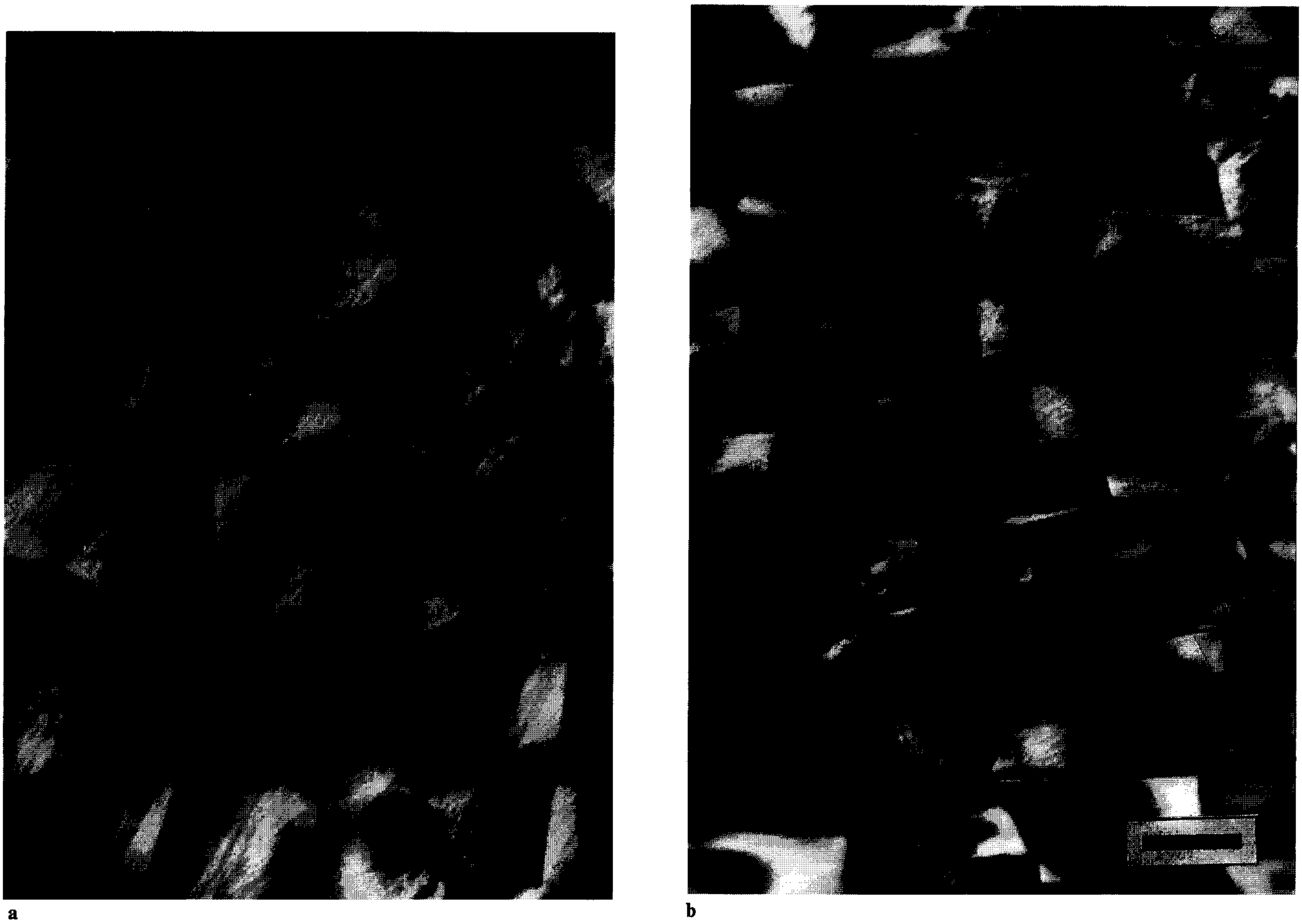

Figure 7 Micrographs of thin slices between crossed polarizers: (a) block copolymer (21.2% PA12); (b) PA6–PA12 blend (15.4% PA12); scale bar 20 μm

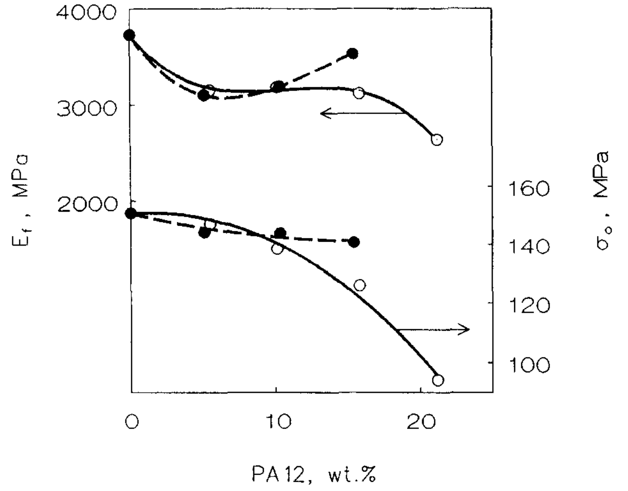

Figure 8 Flexural modulus (E_f) and flexural stress (σ_0) of mould cast block copolymers (○) and PA6–PA12 blends (●) as functions of PA12 concentration

crystalline regions of polymers and that amide groups in non-crystalline regions of PA12 absorb three times less water[7] than those in PA6. The equilibrium amounts of water absorbed from air of relative humidity 65% and 93% by water-extracted samples of block copolymers and PA6–PA12 blends are plotted in *Figure 6* as a function of the total content of PA12. It is obvious that the blends, though more crystalline, absorb more water than the block copolymers. This means that, in the block copolymers, the less absorbing PA12 is concentrated in the amorphous phase. In the blends, the sorption capacity is almost independent of the PA12 content.

Morphology

The size of spherulites observed in thin slices is similar in the block copolymers and PA6–PA12 blends (*Figures 7a* and *7b*). However, a different preference in the location of the amorphous phase can be seen in these two cases. While the marked contour lines between spherulites indicate the location of amorphous phase also in the interface of spherulites in the blend, the more marked fine lamellar structure of spherulites is evidence of the amorphous phase occurring mainly between lamellae in the block copolymers.

Mechanical properties

The purpose of this study was to confirm our conception of polymerization blending and compatibilization, but special properties of the product composed of two crystalline polyamides had not been expected. Polymeric modifiers improving the application properties of PA6, particularly its impact resistance, should have a low T_g value and form domains of separated elastomeric phase in the PA6 matrix. This requirement cannot be met by PA12.

Flexural modulus of elasticity E_f and flexural stress σ_0 of PA6-*block*-PA12 samples and PA6–PA12 blends are mainly affected by the total crystallinity of the samples. Therefore, the dependences of these properties on the content of the PA12 component (*Figure 8*) have a similar shape as those of the total crystallinity (*Figure 1*). This similarity may be somewhat distorted by the presence of various amounts of residual monomer (6-hexanelactam) in the non-extracted specimens for mechanical testing. The lactam acting as a plasticizer is also responsible for the differences in Dynstat notched impact resistance, which ranged from 4.1 to 8.4 kJ m^{-3} for various block copolymers and blends without a direct link to their composition.

CONCLUSIONS

The described systems consist of two separately crystallizing incompatible polyamide chains, either in the form of homopolymers or as blocks linked in the copolymer. Their main difference is the formation of a mixed amorphous phase from linked structural units of PA6 and PA12 blocks and the shortest blocks of PA12 which are soluble in PA6. This phase causes a decrease in T_g and in water sorption of block copolymers. In spite of the fact that PA12 is dissolved in 6-hexanelactam in the preparation of the PA6–PA12 blend, the polyamide phases are separated during polymerization to a higher extent than in the block copolymers, which is apparent also from the morphology resulting in blends.

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