ELSEVIER

Polymer 40 (1999) 4811–4819

polymer

Compatibilization of poly(ethylene terephthalate)/polyamide-6 alloys: Mechanical, thermal and morphological characterization

Costas K. Samios, Nikos K. Kalfoglou*

Department of Chemistry, University of Patra, 26500 Patra, Greece

Received 22 April 1998; received in revised form 29 September 1998; accepted 29 September 1998

Abstract

An acrylic-modified polyolefin type ionomer (Ion., Zn^{2+}), was successfully applied to compatibilize poly(ethylene terephthalate) (PET)/polyamide-6 (PA-6) blends. Melt-mixed blends were prepared at various PET/PA-6 ratios and at constant main component ratio, with various amounts of Ion., Zn^{2+}. The techniques applied to characterize compatibilization were tensile testing, dynamic mechanical analysis, d.s.c. and morphology of cryofractured and etched specimens using electron microscopy (SEM). The effects of thermal history and physical ageing were also examined. Compatibilization was attained at Ion., Zn^{2+} levels higher than 10 wt%. Good tensile and impact properties were obtained in quenched blends, while in annealed samples crystallization of main components reduced ductility drastically. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyamide-6 polymer alloys; Poly(ethylene terephthalate) polymer alloys; Compatibilization by ionomer

---

1. Introduction

Compatibilization of incompatible blends leading to useful polymeric alloys is an attractive route to polymer property improvement and diversification [1]. In this work the compatibilization of poly(ethylene terephthalate) (PET) with polyamide-6 (PA-6) is examined using a methacrylic-acid modified olefinic ionomer (Ion., Zn^{2+}), as a compatibilizer. A compatibilized PET/PA-6 alloy offers certain advantages since depending on the composition ratio of the main constituents, the stiffness (modulus) and strength of PA-6 may be increased as well as the impact strength of both components at low compatibilizer levels. Also, the presence of the olefinic compatibilizer may reduce moisture sensitivity of the final product.

The choice of the ionomer – a low cost commercial product – was dictated by the possibility for trans-reactions with PET [2,3] and its strong interactions with the amide groups of PA attributed to metal–ion coordination and specific forces; ion–dipole and H-bonding interactions [4–7]. The binaries PET/PA-6 [8], PET/PA-66 [9], Poly(butylene terephthalate) (PBT)/PA-6 [10] are incompatible at ambient temperature. However, mixing at melt temperatures may lead to compatibilization owing to formation at the interphase of a polyester–polyamide copolymer through an ester–amide interchange reaction [11,12]. This process requiring prolonged mixing time may also lead to property deterioration owing to thermal degradation and extensive copolymer formation [13]. Pillon and Utracki inferred good interphase interactions for non-compatibilized melt-mixed PET/PA-66 blends on the basis of rheological measurements and the applicability of the time–temperature superposition principle. The same workers examined [15] the extent of ester–amide interchange reactions for the same blend, using high resolution NMR to determine the structure of polymers obtained after melt-mixing. Compatibilization via crystallite interpenetration at the interface of uncompatibilized PET/PA-66 oriented specimens was invoked [16] to expain the good mechanical performance of the blend. Recently, Weiss et al. [17] reported on the compatibilization of an aromatic liquid crystalline polyester (LCP) with PA-66 or with PC, using as a compatibilizer the zinc salt of sulfonated polystyrene (Zn-SPS). Compatibilization of the LCP/Zn-SPS/PA-66 blend was attributed to strong intermolecular attractive interaction between the sulfonate and amide groups, while the ionomer/LCP miscibility was explained as the result of intramolecular repulsive interactions along the ionomer molecules. During the course of this investigation Moore and coworkers [18,19] reported on the compatibilization of binary blends of a sulfonated polyester type ionomer with PET and with PA-66 as a preliminary step to PET/PA-66 compatibilization. Compatibility assessment based on thermal and morphology examination

---

* Corresponding author. Tel.: 0030 61 997102; fax: 0030 61 997122.

0032-3861/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(98)00709-5

Table 1
Tensile properties of blends[a]

PET/PA-6/Ion., Zn^{2+}	σ_y (Mpa)	σ_b (MPa)	ϵ_b (%)	E_b (J/cm^3)
100/0/0	39 ± 5	46 ± 2	587 ± 41	156 ± 11
0/100/0	25 ± 2	36 ± 2	423 ± 31	135 ± 4
50/50/0	35 ± 1	42 ± 4	396 ± 43	128 ± 14
48.5/48.5/3	24 ± 1	26 ± 2	279 ± 27	65 ± 6
47.5/47.5/5	30 ± 2	32 ± 4	357 ± 60	88 ± 3
45/45/10	31 ± 1	33 ± 2	333 ± 48	86 ± 6
42.5/42.5/15	23 ± 0	33 ± 3	420 ± 38	101 ± 5
37.5/37.5/25	20 ± 2	34 ± 2	452 ± 22	99 ± 11
33.3/33.3/33.3	18 ± 1	35 ± 5	481 ± 54	117 ± 9
66.7/33.3/0	30 ± 3	37 ± 3	413 ± 31	108 ± 6
56.7/28.3/15	25 ± 1	38 ± 3	486 ± 65	127 ± 9
33.3/66.7/0	24 ± 2	47 ± 5	505 ± 53	149 ± 19
28.3/56.7/15	21 ± 1	30 ± 2	347 ± 46	72 ± 7

[a] Quenched at 0°C, conditioned for 1 day at 25°C, R.H. 60%.

indicated miscibility. As of today no results on the ternary system were reported.

In the present work melt-mixed blends of PET/PA-6 were prepared at different component ratios and compatibilizer levels. Properties examined were, tensile, dynamic mechanical (d.m.a.), thermal and morphological (SEM). Physical ageing effects during storage on properties of blends were also examined, since it was observed that these seriously affect the mechanical properties of the non-compatibilized PET/PA-6 blend and accentuate the importance of compatibilization in stabilizing blend performance.

2. Experimental

2.1. Materials and specimen preparation

PET was extrusion grade obtained from Akzo Plastics b.v. (Arnite DO2 300). It was reported to have predominantly terminal hydroxyl groups, an $\bar{M}_n = 23\,500\ \mathrm{gmol}^{-1}$, $T_m = 252°\mathrm{C}$ and an amorphous product density of $1.34\ \mathrm{gcm}^{-3}$. PA-6 obtained from BDH, was found to have $[n] = 0.778\ \mathrm{dlg}^{-1}$ in 85% formic acid at 25°C and $\bar{M}_v = 20\,600\ \mathrm{gmol}^{-1}$. The amount of amine end groups was estimated by titration to be 52.5 equiv./106g. The ionomer, Zn^{2+} (Surlyn 9020) from Du Pont de Nemours Co, is a random ethylene–methacrylic acid–isobutylacrylate terpolymer with a molar concentration of 78 : 10 : 12, respectively and a degree of neutralization of ca. 70%. $\bar{M}_n = 25000\ \mathrm{gmol}^{-1}$, density $= 0.96\ \mathrm{gcm}^{-3}$ and MFI 1.0 g per 10 min (190°C, 2160 g).

Table 2
Tensile properties of blends during physical ageing[a]

PET/PA-6/Ion., Zn^{2+}	50/50/5	47.5/47.5/5	42.5/42.5/15
σ_b (MPa)			
1 day	35 ± 1	31 ± 3	33 ± 3
1 week	36 ± 9	22 ± 5	31 ± 7
2 weeks	41 ± 1	24 ± 2	32 ± 2
1 month	40 ± 3	20 ± 4	33 ± 2
ϵ_b (%)			
1 day	396 ± 43	323 ± 56	420 ± 38
1 week	373 ± 34	25 ± 9	373 ± 31
2 weeks	327 ± 28	25 ± 14	402 ± 47
1 month	17 ± 3	15 ± 7	420 ± 30
E_b (J/cm^3)			
1 day	128 ± 14	88 ± 3	101 ± 5
1 week	103 ± 10	2 ± 1	82 ± 6
2 weeks	94 ± 8	1 ± 0	95 ± 7
1 month	3 ± 1	1 ± 0	118 ± 6

[a] Originally quenched to 0°C. Stored at 25°C, R.H., 60%.

PET was dried at 150°C for 12 h *in dynamic vacuo*. This ensures that moisture levels are limited to less than 0.01 wt% so that the hydrolytic stability of PET is not impaired during the melt mixing. Both PA-6 and Ion., Zn^{2+} were dried at 60°C for 24 h. Blends were prepared by melt mixing at 285°C in a home made stainless steel bob-and-cup type of mixer previously described [21]. The mixing cup was blanketed under an argon atmosphere. Based on tensile property optimization, specifically the ultimate elongation ϵ_b, mixing time employed was 10 min at 285°C; ϵ_b was shown in the past to be a sensitive mechanical property indicator of compatibilization of polymeric alloys. One blend was prepared in a CSI Lab mini extruder (model CS-194AV), where mixing time is ca. 0.5 min.

Compositions of PET/PA-6/Ion., Zn^{2+} prepared were; 50/50/0, 48.5/48.5/3, 47.5/47.5/5, 45/45/10, 42.5/42.5/15, 37.5/37.5/25, 33.3/33.3/33.3, 66.7/33.3/0, 56.7/28.3/15, 33.3/66.7/0 and 28.3/56.7/15. Films were obtained by compression moulding between Teflon sheets at 275°C and 10 MPa for 1.0 min, followed by quenching to 0°C.

2.2. Apparatus and procedures

Tensile tests were performed at a crosshead speed of $10\ \mathrm{cm\ min}^{-1}$ and at 23°C, according to ASTM D882 using a J J Tensile Tester type 5001 and rectangular strips measuring $6.0 \times 0.65 \times 0.25\ \mathrm{cm}^3$.

The d.m.a. data storage modulus E', loss modulus E'' and loss angle $\tan\delta$ were obtained at 10 Hz with the RSA II dynamic mechanical spectrometer of Rheometric Scientific Ltd. Specimen dimensions were $2.3 \times 0.5 \times 0.015\ \mathrm{cm}^3$.

The d.s.c. measurements were carried out using the DSC (SP) equipped with the AutoCool accessory from Rheometric Scientific Ltd. Nominal weight was 10 mg and heating/cooling rate $10°\mathrm{C\ min}^{-1}$. The thermal cycling applied was quenching at $50°\mathrm{C\ min}^{-1}$ to $-50°\mathrm{C}$, heating to 300°C (1 min), followed by quenching to $-50°\mathrm{C}$ and applying a second heat to 300°C. Etching of specimens to remove PA-6 was performed with 50% formic acid; immersion time was 5 min at ambient temperature.

SEM was carried out on a JEOL model JSM-500 instrument. Cryofractured or etched surfaces were examined at a tilt angle of 30°.

Table 3
Effect of mixing protocol and annealing on tensile properties[a]

PET/PA-6/Ion., Zn^{2+}	Mixing temperature (°C)	Mixing time (min)	σ_y (MPa)	σ_b (MPa)	ϵ_b (%)	E_b (J/cm^3)
47.5/47.5/5	285	10	30 ± 2	32 ± 4	357 ± 60	88 ± 3
47.5/47.5/5	285	15	31 ± 3	35 ± 4	323 ± 56	91 ± 18
42.5/42.5/15	285	10	23 ± 0	33 ± 3	420 ± 38	101 ± 5
42.5/42.5/15[b]	285	1	22 ± 1	20 ± 4	119 ± 34	28 ± 14
42.5/42.5/15[c]	285	10	22 ± 1	31 ± 3	368 ± 38	93 ± 8
Annealing (T = 100°C, t = 30 min)						
50/50/0	285	10	—	32 ±	7 ± 5	—
47.5/47.5/5	285	10	—	17 ± 2	4 ± 2	—
42.5/42.5/15	285	10	—	33 ± 3	15 ± 2	—
42.5/42.5/15[c]	285	10	—	36 ± 3	18 ± 8	—

[a] Originally quenched to 0°C, conditioned at 25°C, R.H. 60%.

[b] Mini extruder.

[c] Adding PA-6 to premixed PET/Ion., Zn^{2+}.

3. Results

3.1. Tensile properties

In Table 1 the results on tensile properties of quenched blends are summarized after conditioning for 24 h at 25°C and 60% R.H. The quantities of interest are yield stress σ_y, strength σ_b, ultimate elongation ϵ_b% and energy to tensile failure E_b. The last quantity is determined from the area under the stress–strain curve and gives a measure of the impact strength. The data show that for several days after specimen preparation the non-compatibilized blends at the three component ratios (1/1, 2/1, 1/2), maintain their good mechanical properties. Thus one might infer that the binary blend is mechanically compatible. The effect of compatibilization is demonstrated after physical ageing for 1 month. The results in Table 2 show very limited increase in strength for the uncompatibilized blend but all other ultimate properties are reduced to levels typical of an incompatible system. In contrast, the presence of the compatibilizer at the 15 wt% level stabilizes these properties. The results in Table 1 show that increasing the PET/PA-6 ratio at constant compatibilizer level (15 wt%) increases strength, while increasing compatibilizer levels at constant components ratio increases ductility (ϵ_b%) and impact strength. PA-6 has a higher ductility and a lower stiffness than PET when conditioned at ambient humidity levels. This raises σ_b at increased PET/PA-6 ratios. The stiffness increase is also supported by d.m.a. results; see Fig. 2. Increasing the amount of the compatibilizer – a low T_g, high ductility modified polyolefin, is expected to raise ϵ_b and E_b of the blends.

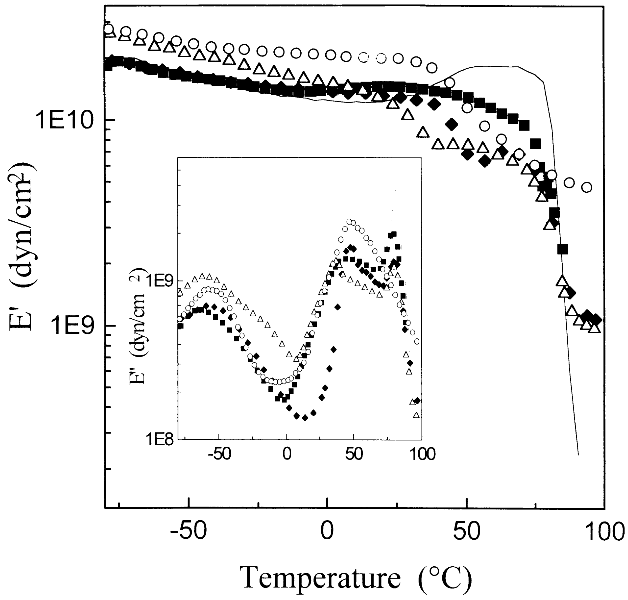

Fig. 1. Temperature dependence of storage modulus of PET/PA-6/Ion., Zn^{2+} blends: (—), PET; (◆), 50/50/0; (■), 48.5/48.5/3; (△), 42.5/42.5/15; (○), PA-6. Inset: loss modulus at corresponding compositions.

The effects of mixing time, mixing protocol and annealing are summarized in Table 3. Inspection of the results of mixing time on ultimate elongation (a property most sensitive to interfacial adhesion) suggests that 10 min is adequate to attain compatibility though a more efficient industrial mixer could reduce this time. Regarding mixing protocol, addition of all three components together yields improved properties. The other option of initially combining PA-6 with Ion., Zn^{2+} was not tested since it is documented [4] that this would preferentially attach the ionomer onto PA-6 leading to poor compatibilization when the third component (PET) is added. The result of annealing is devitrification and embrittlement owing to crystallization of PET, leading to drastic ductility reduction, while the compatibilized blend retains an edge over the uncompatibilized product.

3.2. Dynamic mechanical analysis

Fig. 1 shows the loss modulus spectra E'' at various compatibilizer levels at a constant PET/PA-6 ratio. Main relaxations at 82°C (α) and at − 68°C (β) for PET [22] as well as those of PA-6 [23] at ca. 49°C (α) and at − 56°C (β) are present, though modified with the addition of the ionomer affecting PA-6 more strongly. The olefinic ionomer

Table 4
Main visoelastic transitions and thermal properties of blends

PET/PA-6/Ion., Zn^{2+}	T_g (°C) (PET)	T_g (°C) (Pa-6)	T_m (°C) (PET)	T_m (°C) (PA-6)	T_m (°C) (Ion., Zn^{2+})	T_c (°C) (PET)	T_c (°C) (PA-6)	T_c (°C) (Ion., Zn^{2+})	x_c[a] (°C) (PET)	x_c[b] (°C) (PA-6)	x_c[c] (°C) (Ion., Zn^{2+})
100/0/0	82	—	252	—	—	212	—	—	27.6	—	—
0/100/0	—	49	—	221	—	—	194	—	—	32.1	—
50/50/0	81	48	251	220	—	212	190	—	29.9	31.3	—
48.5/48.5/3	80	45	253	220	—	210	188	—	32.5	30.9	—
47.5/47.5/5	—	—	251	219	—	214	189	—	30.9	34.5	—
45/45/10	—	—	252	220	86	213	188	—	27.6	34.7	—
42.5/42.5/15	80	37	251	219	80	214	190	50	33.1	33.5	13.1
37.5/37.5/25	—	—	252	220	85	211	189	50	29.8	28.4	13.8
66.7/33.3/0	—	—	251	220	—	210	189	—	23.1	38.7	—
56.7/28.3/15	80	57	252	219	82	211	185	49	26.5	26.9	12.2
33.3/66.7/0	—	—	250	221	—	209	192	—	23.4	29.4	—
28.3/56.7/15	80	30	252	220	84	217	191	57	23.6	35.4	12.3

[a] $\Delta H_f = 33.5$ cal g^{-1}.
[b] $\Delta H_f = 45.9$ cal g^{-1}.
[c] $\Delta H_f = 66.0$ cal g^{-1}.

with a main transition at −17°C, in the binary PA-6/Ion., Zn^{2+} was found [24] to reduce regularly the T_g of PA-6, while its relaxation shifted upwards. In the ternary at the 1/1 PET/PA-6 ratio, increasing the ionomer content again causes a T_g reduction of PA-6 as well as that of PET (see also Table 4). This is evidence of component interaction since the T_g of the PA-6 shifts downwards by ca. 12°C with the addition of 15 wt% ionomer in the ternary. The effects on PET are smaller; a T_g reduction of ca. 2°C. This shows a preferential partition of the ionomer among the two components. In the ternary the T_g of the ionomer cannot be detected clearly because it overlaps with the secondary relaxation of PA-6 (see Fig. 2). Moduli E' data in Fig. 1 show that addition of the ionomer (3 wt%) leads to stiffening of PA-6, while at higher compatibilizer levels E' though decreased maintains a satisfactory value.

The effects of changing the PET/PA-6 ratio at constant ionomer content are shown in Fig. 2. Increasing the amount of PET gives a stiffer alloy (higher E') while the lower T_g of PA-6 reduces stiffness at increased polyamide ratios. Loss moduli E'' maxima variation shows that the T_g of PET is little affected by changing the main components ratio, while that of PA-6 shifts upwards owing to interphase mixing with PET. At increased amounts of PA-6, its interaction with the ionomer predominates shifting the polyamide main relaxation to 30°C (see Table 4).

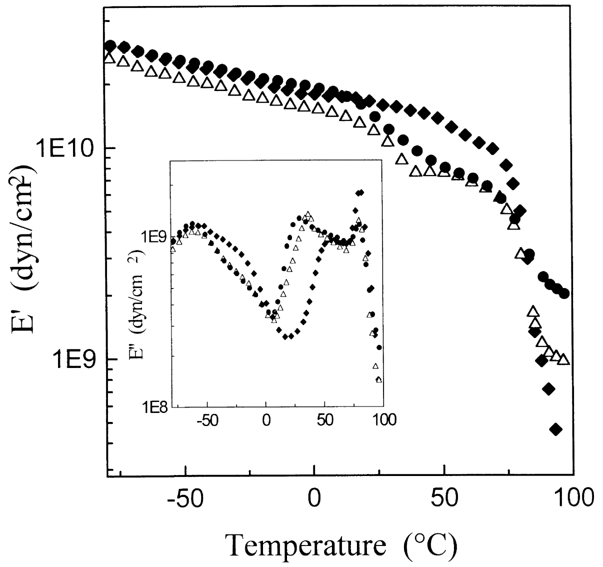

Fig. 2. Temperature dependence of storage modulus of PET/PA-6/Ion., Zn^{2+} blends. Effect of PET/PA-6 ratio: (◆), 56.7/28.3/15; (△), 42.5/42.5/15; (●), 28.3/56.7/15. Inset: loss modulus at corresponding compositions.

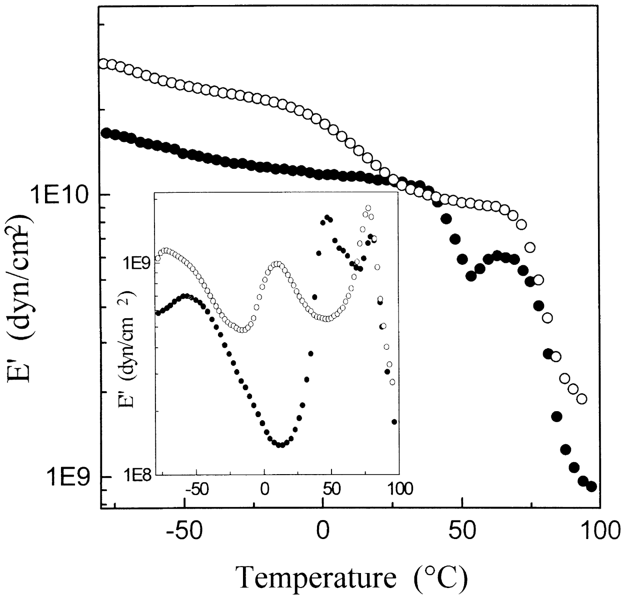

Fig. 3. Temperature dependence of storage modulus of PET/PA-6 (50/50) blends. Effect of ageing: (●) after 1 day; (○) after 1 month. Inset: loss modulus.

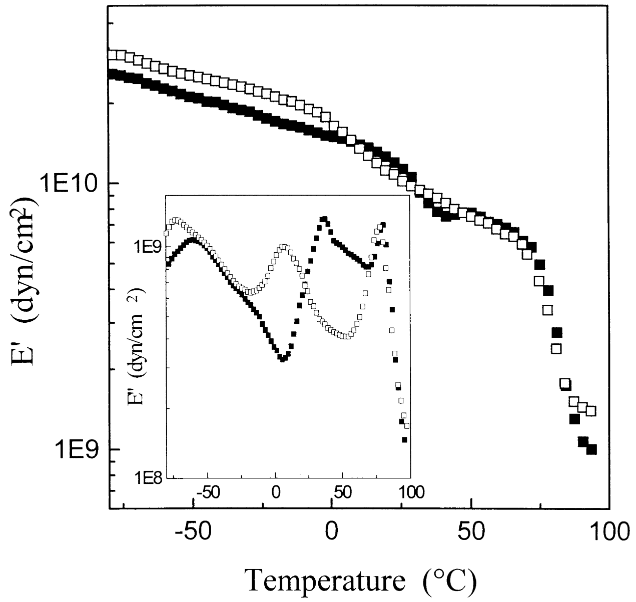

Fig. 4. Temperature dependence of storage modulus of PET/PA-6/Ion., Zn^{2+} (42.5/42.5/15) blends. Effect of ageing: (■) after 1 day; (□) after 1 month. Inset: loss modulus.

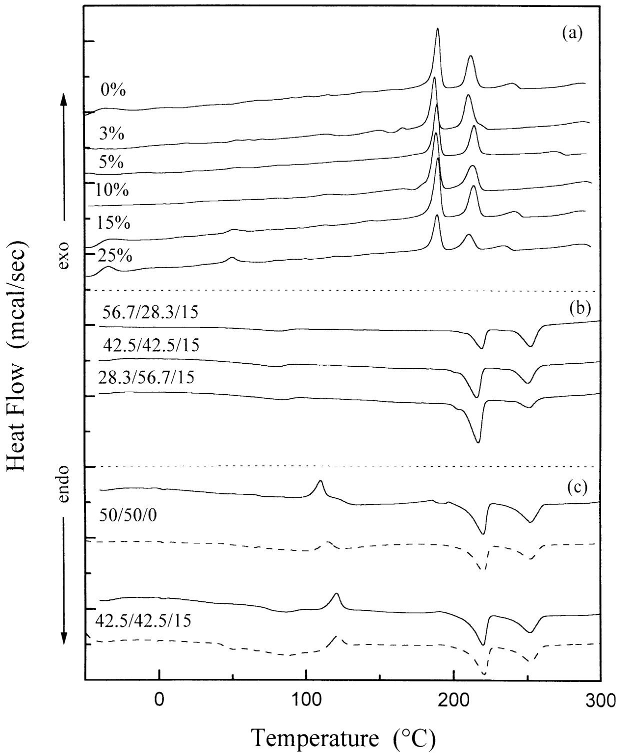

Fig. 5. The d.s.c. thermograms of PET/PA-6/Ion., Zn^{2+} blends: (a) Effect of increasing compatibilizer content (indicated) at PET/PA-6 ratio 50/50 during cooling. (b) Effect of changing PET/PA-6 ratio (indicated) at constant ionomer content 15 wt% – Second heat. (c) Effect of ageing on non-compatibilized (50/50) and compatibilized blend (42.5/42.5/15): (—), 1 day; (–), 1 month – First heat.

The effects of ageing are shown in Fig. 3 and Fig. 4 for the uncompatibilized and compatibilized blend, respectively. The former shows a modulus increase with ageing attributed to a crystallinity increase and possibly to PET densification [25]. Loss moduli maxima become well separated and a reduction of the relaxation strength in between the main component T_g's is observed. It is not clear whether this reflects a reduction of interphasial material or the result of moisture absorption. Addition of the compatibilizer, see Fig. 4, reduces the effects of ageing on modulus, however, the E'' thermomechanical spectra are little affected compared to the uncompatibilized blend. This indicates that the crystalline phase may be determinant to ageing effects observed in the tensile behaviour.

3.3. Thermal properties

The d.s.c. thermograms were obtained to examine the effect of raising compatibilizer levels on crystallization temperatures T_c (Fig. 5a), the effect of PET/PA-6 ratio on melting transitions (Fig. 5b) and the effect of ageing within 1 month (Fig. 5c). The results from these and other thermograms [24] not included in this work, are reported in Tables 4 and 5 which also include main viscoelastic transitions and bulk crystallinities of the main components in compatibilized and non-compatibilized blends. The crystallization exotherm of PET (cold crystallization) (see Fig. 5c) is observed only during the first heat. Ageing affects PA-6, raising both crystallinity and T_m and to a lesser extent PET (see Table 5). Thermal data in Table 4 reveal no significant T_m variation or trend and this has also been observed [24] for the binary PA-6/Ion., Zn^{2+} blends. Thus in compatibilized blends interface interactions and transreactions involve primarily the amorphous phase. The T_c of PET passes through a maximum as the amount of compatibilizer increases (see Table 4). Increasing amounts of the ionomer facilitate crystallization of PET. This may be attributed to the nucleating activity of the ionomer which may take place even in melt [26]. This was documented for the sodium ionomer of a similar copolymer [26]. It is proposed that the same mechanism is applicable in the present case. At high ionomer contents (25%), its efficiency may drop owing to ‘‘flocculation’’ [4]. The T_c of PA-6 in the ternary blend is little affected when the ionomer content is increased. This was not the case for the binary PA-6/Ion., Zn^{2+} where a regular reduction of T_c of the polyamide was observed [24]. This effect is offset in the ternary since PET ‘‘cold’’ crystallizing before PA-6, may facilitate its crystallization by heterogeneous nucleation. Bulk crystallinity of PET is slightly increased in compatibilized blends. Again, this may be the result of the ionomer acting as a nucleating agent [26]. However, crystallinity is also affected by the PET/PA-6 ratio. In the case of PA-6, increased crystallinity may be attributed to heterogeneous nucleation owing to PET. This is in line with the observation that the higher T_c

Table 5
Effect of physical ageing on thermal properties of blends

PET/PA-6/Ion., Zn^{2+}	T_m (°C) (PET)	T_m (°C) (PA-6)	x_c (%) (PET)	x_c (%) (PA-6)
After 1 day				
50/50/0	250.3	216.0	29.9	31.3
42.5/42.5/15	250.3	215.8	33.1	33.5
After 1 month				
50/50/0	251.6	219.7	34.3	39.3
42.5/42.5/15	251.7	220.5	35.6	36.8

of PET leads to increased PET crystallinity leading to a correspondingly enhanced level of PA-6 crystallinity.

3.4. Scanning electron microscopy

Scanning electron micrographs of cryofractured surfaces and of microtomed and etched specimens to extract the PA-6 component are given in Figs. 6 and 7, respectively. The micrographs (Fig. 6a and b) compare a non-compatibilized and a compatibilized alloy at the 1/1 PET/PA-6 ratio. Fig. 6b shows features of ductile fracture. Increasing the PA-6 content enhances this feature but in the case of the compatibilized blend (Fig. 6d) the surface is qualitatively different from Fig. 6c in that the former shows craters left when the PET component was pulled out during fracture. Apparently the increased amount of PA-6 because of its stronger interaction with the ionomer, effectively reduces the amount available for the compatibilization of PET. This feature is absent from the uncompatibilized blend which however showed good mechanical properties before ageing. Fig. 6e and f, shows the effect of ageing (after 1 month) for compositions corresponding to Fig. 6a and b. The uncompatibilized blend shows considerable coarsening and loss of the uniform texture compared to the non-aged specimen. In the case of the compatibilized alloy the two-phase structure becomes more prominent (compare Fig. 6b and f) notwithstanding the stability of its mechanical properties observed.

In the case of etched specimens where the PA-6 was removed, the ‘‘fresh’’ samples lack the fibrillation observed; compare Fig. 7a and c (non-compatibilized) and Fig. 7b and d (compatibilized) blends. Comparison of non-compatibilized and compatibilized alloys at equivalent times of ageing do not give any clear evidence explaining the superior performance of the compatibilized alloy except that this specimen has a higher degree of PET fibrillation compare micrographs in Fig.7a and d, and 7c and d.

4. Discussion

The results of tensile testing and evidence from d.m.a. support the view that the PET/PA-6 blend is compatibilized by the Ion., Zn^{2+} when added at the appropriate level (15 wt%). The good mechanical properties maintained for a considerable length of time by the incompatible PET/PA-6 is suprising. Assuming that the solubility parameter concept holds for these polar polymers, calculation of δ at an extended temperature range using relation [27]

$$\frac{\partial \ln \delta}{\partial T} \cong -\alpha$$

where α is the coefficient of cubic expansion, gives the data in Fig. 8. δ values in the glassy state were calculated [28] using Hoy’s constants; $\delta_{PET} = 11.60\ (\mathrm{cal\ cm^{-3}})^{1/2}$ and $\delta_{PA-6} = 11.18\ (\mathrm{cal\ cm^{-3}})^{1/2}$. According to Fig. 8, there is a crossover in the viscoelastic state. At mixing temperatures, δ’s diverge and there is conclusive morphological evidence [8] that melt-mixed components phase separate at ambient temperature. Good mechanical properties reported by Fakirov, coworkers [12] refer to a system specially processed (drawn) and heat-treated. In the present case the good properties may be attributed to limited fibrillation of PET during film preparation, as shown by the etched SEM specimens, the resulting composite ensuring mechanical integrity. Another contributing factor promoting interface adhesion is the physical interlocking of components when PA-6 melt penetrates the initially crystallized PET at their interface during melt cooling, in line with previous findings on PET/PA-66 blends [16]. This process is followed by PA-6 crystallization when temperature is further reduced. Varma [8] presented X-ray evidence for mutual component nucleation and proposed that PET crystallites may be arranging themselves in the intercrystaline regions of PA-6 reinforcing specific lattice planes. During ageing the metastable system reverts to its most stable condition; a gross phase separated blend. Also, differences in expansion coefficients [29], the PA-6 with $\alpha_g = 2.40 \times 10^{-4}$°$C^{-1}$ contracting more than PET with $\alpha_g = 1.95 \times 10^{-4}$°$C^{-1}$, set up interface stresses eventually leading to debonding and brittleness.

Morphology evidence obtained with SEM show a more ductile cryofracture surface for the ternary alloy with PET embedded in the PA-6 matrix. The non-compatibilized binary blend has a more even fracture surface, probably the result of the lesser ductility of crystalline domains. During ageing the surfaces for both uncompatibilized and compatibilized blends become coarser; components relax and owing to different expansivities the ridges in fracture surfaces are accentuated. However, in the case of compatibilized alloys the ionomer ensures interface bonding stabilizing mechanical behaviour.

Though several papers were published on binary PET/

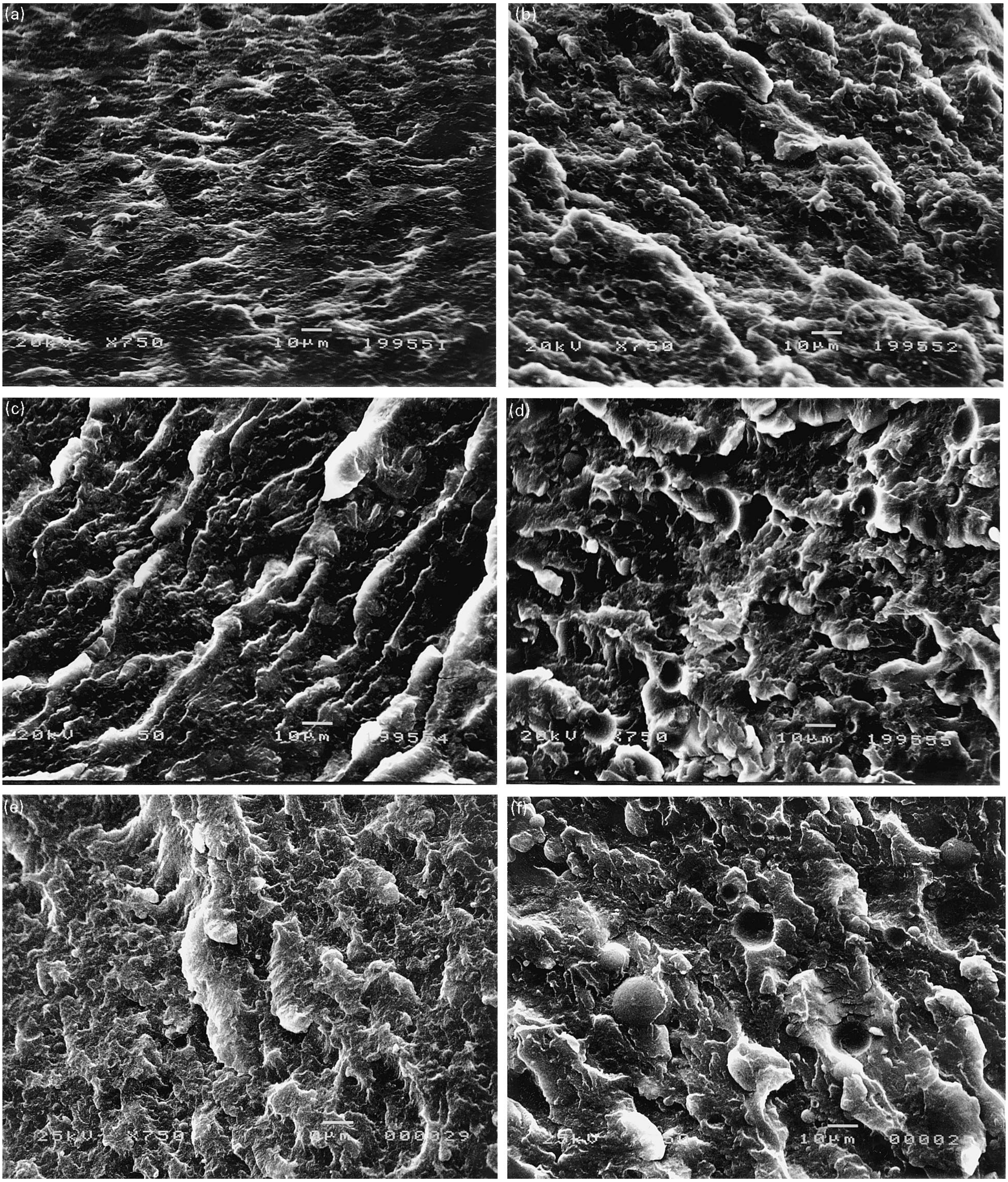

Fig. 6. SEM micrographs of cryofractured PET/PA-6/Ion., Zn^{2+} blends: (a) 50/50/0; (b) 42.5/42.5/15; (c) 33.3/66.7/0; (d) 28.3/56.7/15; (e) 50/50/0 after ageing for 1 month; (f) 42.5/42.5/15 after ageing for 1 month.

ionomer [2,3], PA-6/ionomer [5,6] and PET/compatibilizer/polyolefin [20,30] blends, very little was found in the literature on the compatibilization of the particular ternary. It is possible that the good mechanical properties reported on the uncompatibilized PET/PA-66 blends dissuaded investigators from pursuing research on the compatibilization of PET/PA-6 blend. The effects of ageing on the non-compatibilized PET/PA-66 are not known. In this work it is demonstrated that the non-compatibilized PET/PA-6 blend shows deterioration of mechanical properties within approximately a month owing to physical ageing; therefore compatibilization is necessary. To the best of our

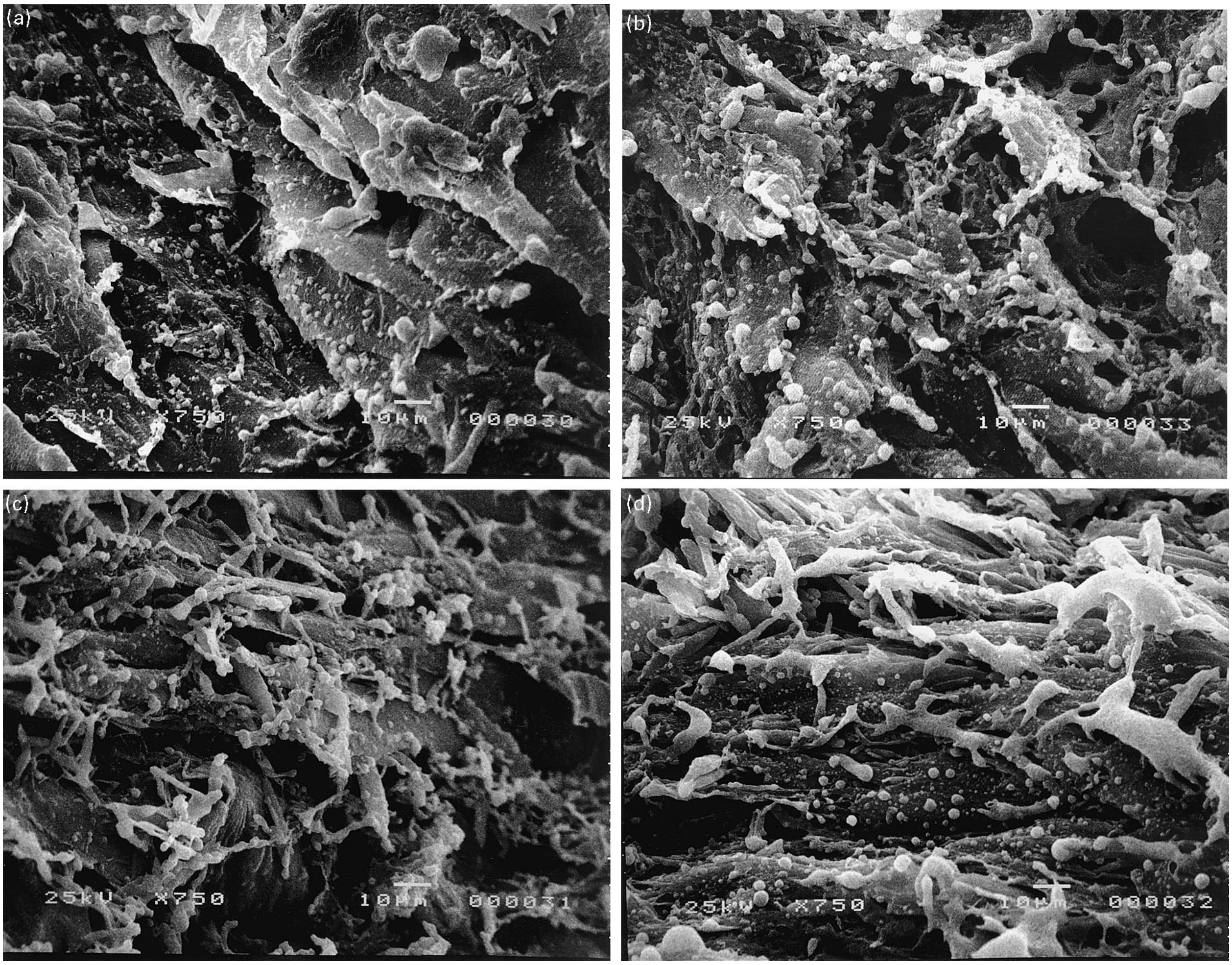

Fig. 7. SEM micrographs of etched PET/PA-6/Ion., Zn^{2+} blends: (a) 50/50/0; (b) 42.5/42.5/15; (c) 50/50/0 after ageing for 1 month; (d) 42.5/42.5/15 after ageing for 1 month.

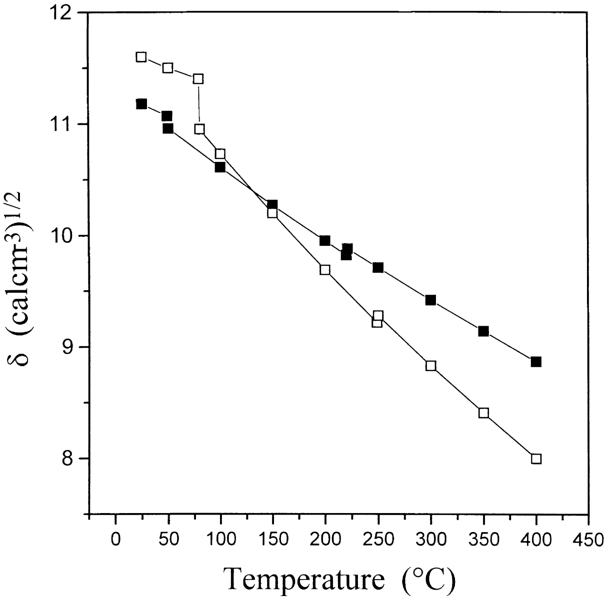

Fig. 8. Temperature dependence of solubility parameter δ of PET (□) and PA-6 (■).

knowledge the only literature related to the present work is the report by Weiss et al. [17] which differs in the type of polyester and compatibilizer used (see Section 1). In particular, the structure of the compatibilizer is radically different from the ionomer used in our work. Thus while the PA/Zn-SPS interactions though stronger do not differ in character, the modified olefinic compatibilizer used in the present work offers the possibility of compatibilizing the polyester via a different mechanism [3,31]. A different approach was used by Montaudo et al. [32] to compatibilize the related PC/PA-6 blend. They synthesized PC-b(PA-6)-PC triblock and PC-b(PA-6) diblock copolymers and compared their compatibilizing efficiency examining the morphology of the ternary blends. It was found that the diblock was more efficient than the triblock copolymer and very low levels (ca. 2 wt%) were required. The mechanism of this type of compatibilization is different from our system in that the compatibilizer acts as an ‘‘emulsifier’’ concentrating at the interface and reducing interfacial tension. In the present system the compatibilizing action of the ionomer may be traced to acidolysis [3] and transesterification reactions [31] with PET, since both acid and ester functionalities are present in both components. Transesterification reactions ordinarily require prolonged melt-mixing [31]. Time required depends on the particular blend. Pillon and Utracki [33] report a time of 5–30 h at 220°C–290°C to promote ester–amide exchange reactions, for PET/PA-66 blend in the absence of catalyst. However it was suggested [19] that the Zn^{2+} of the ionomer may serve as a catalyst. With regards to PA-6, the capability of the ionomer to enter into chemical and physicochemical interactions is supported by the findings of MacKnight et al. [34] who reported on the compatibilization of binary alloys of PA-6/ethylene methacrylic acid copolymers, by Subramanian and Mehra [35] and by Willis et al. [4,5] who used Ion., Zn^{2+} to compatibilize PA-6/Polyolefin blends. More recently we have used this ionomer to compatibilize polyurethane(PU) [36] and PU/HDPE blends [37]. As to the active groups participating, depending on mixing conditions (mixing time and temperature) these may be terminal amide groups of PA-6 and the acid functionality of Ion., Zn^{2+} in line with the findings of MacKnight et al. [34] and/or complexation reactions of the Zn^{2+} with the basic NH group as well as dipole–dipole interactions, as relevant work cited in Section 1 has demonstrated.

5. Conclusions

1. Melt-mixed blends of PET/PA-6 require compatibilization so that stability of mechanical properties against physical ageing is ensured.
2. The acrylic-modified polyolefin, Zn^{2+} ionomer is an effective compatibilizer at the 10–15 wt% level. Lesser amounts are insufficient because of the uneven partition of the compatibilizer among the main blend components.
3. Compatibilization is attributed to strong PA-6/ionomer association and the PET/ionomer interchange reactions.

Acknowledgements

This work was supported in part with a grant of the General Secretariat of Research and Technology (ΠΕΝΕΔ-95, code no. 96), administered by the University of Patra. Thanks are also due to Prof. P.Koutsoukos for the use of the SEM facility, to Ms. D. Sotiropoulou for obtaining the micrographs and Ms. E. Koulouri for PA-6 characterization.

References

[1] Utracki LA. Polymer alloys and blends. Munich: Hanser, 1989.
[2] Subramanian PM. Polym Eng Sci 1987;27:1574.
[3] Kalfoglou NK, Skafidas DS. Eur Polym J 1994;30:933.
[4] Willis JM, Favis BD. Polym Eng Sci 1988;28:1416.
[5] Willis JM, Favis BD, Lavallée CJ. Mater Sci 1993;28:1749.
[6] Feng Y, Schmidt A, Weiss RA. Macromolecules 1996;29:3909.
[7] Molnar A, Eisenberg A. Macromolecules 1992;25:5774.
[8] Varma DS, Dhar VK. J Appl Polym Sci 1987;33:1103.
[9] Kamal MR, Sahto MA, Utracki LA. Polym Eng Sci 1982;27:1913.
[10] Watanabe K, Izuka A, Sumita K, Kita M. Compalloy ‘90, 1990 (cited in Ref. [14]).
[11] Evstatiev M, Fakirov S. Polym Networks Blends 1994;4:25.
[12] Fakirov S, Evstatiev M, Schultz JM. Polymer 1993;34:4669.
[13] Huang C-C, Chang F-C. Polymer 1997;38:2135.
[14] Utracki LA. Polymer alloys and blends. Munich: Hanser, 1989 p. 213.
[15] Pillon LZ, Utracki LA. Polym Eng Sci 1984;24:1300.
[16] Utracki LA. Polymer alloys and blends. Munich: Hanser, 1989 p. 128.
[17] Datta D, Weiss RA, He J. Polymer 1996;37:429.
[18] Boykin TL, Ciacco J, Moore RB. Polymer Preprints 37(1), ACS Meeting, New Orleans, Louisiana, March 1996, p. 717.
[19] Boykin, T.L., Ciacco, J., Moore, R.B., Polymer Preprints 38(2), ACS Meeting, Las Vegas, Nevada, September 1997, p. 179.
[20] Kalfoglou NK, Skafidas DS, Kallitsis JK, Lambert J-C, Van der Stappen L. Polymer 1995;36:4453.
[21] Papadopoulou CP, Kalfoglou NK. Polymer 1997;38:4207.
[22] McCrum NG, Read BE, Williams G. An elastic and dielectric effects in polymeric solids. New York: Wiley, 1967 p. 501.
[23] McCrum NG, Read BE, Williams G. An elastic and dielectric effects in polymeric solids. New York: Wiley, 1967 Chapter 12.
[24] Samios CK, work in progress.
[25] Tant MR, Wilkes GL. J Appl Polym Sci 1981;26:2813.
[26] Dekoninck JM, Legras R, Mercier JP. Polymer 1989;30:910.
[27] Sanchez IC. In: Paul DR, Newman S, editors. Polymer blends, 1. New York: Academic Press, 1978 Chapter 3.
[28] Sanchez IC. In: Paul DR, Newman S, editors. Polymer blends, New York: Academic Press, 1978 Chapter 2.
[29] Guide to plastics. McGraw-Hill Inc, New York, 1985.
[30] Carté TL, Mòet A. J Appl Polym Sci 1993;48:611.
[31] Porter RS, Wang L-H. Polymer 1992;33:2019.
[32] Montaudo G, Puglisi C, Samperi F, La Mantia FP. J Polym Sci Part A Polymer Chemistry 1996;34:1283.
[33] Utracki LA. Polymer alloys and blends. Munich: Hanser, 1989 p. 127.
[34] MacKnight WJ, Lenz RW, Musto PV, Somani RJ. Polym Eng Sci 1985;25:1124.
[35] Subramanian PM, Mehra V. Polym Eng Sci 1987;27:663.
[36] Papadopoulou CP, Kalfoglou NK. Polymer 1998;39:7015.
[37] Papadopoulou CP, Kalfoglou NK. Polymer, to be published.