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Characterization of melt-mixed blends of poly(ether–ester) with various polyamides

E.G. Koulouri, E.C. Scourlis, J.K. Kallitsis*

Department of Chemistry, University of Patras, 265 00 Patras, Greece

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Abstract

Mechanical properties of binary melt mixed blends of various polyamides (Nylon 11; 6,6; 6,10; 6,12) with a block copolyetherester (PEE) were investigated. All the blends prepared had very good mechanical properties and in some cases even better than those of the respective pure polyamides. Two of the systems (Nylon 11/PEE and Nylon 6,12/PEE) were selected to be studied further in terms of morphology, viscoelastic and thermal properties. These blends showed two distinct but mutual shifting T_g's and low extracted amount of PEE during extraction experiments, supporting the view that a very good interfacial grafting had been achieved in these two-phase systems. This assumption was further evaluated on the cryofractured and selectively etched blends where the existence of the grafted PEE was justified by Fourier transform infrared as well as by micro-Raman spectroscopy. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blends; Poly(ether–ester); Polyamides

1. Introduction

Segmented thermoplastic poly(ether–ester)s (PEE) have attracted much interest as thermoprocessable high performance elastomers combining desired physical and mechanical properties such as solvent resistance, thermal stability, elastic recovery and energy absorption [1,2]. These are two-phase materials, consisting of two types of long chain segments, possessing both thermoplastic and rubbery nature, the former resulting from the crystalline hard segments and the latter from the soft blocks with low glass and melting transition temperatures.

A literature survey shows that blends of PEE with various polymers were studied not only because of scientific interest but also in order to obtain products with improved characteristics of physical/processing properties and optimum cost performance. Among others, blends of PEE with PVC were used in engineering applications [3–6]. Other blends of PEE with polymers such as chlorinated polyethylene [7], poly(butylene terepthalate) [8–12], poly(ethylene terepthalate) [13], polycarbonate [14], polyurethanes [15] and polyamides [16,17] were also studied. Most of the blends described earlier are physical mixtures of PEE but in cases where the second polymer is a polyester, blending under reactive conditions has also been reported, [10–12,13,14].

Concerning mixtures of PEE with polyamides, beside the patent literature, only few studies dealing with the physical blending of the two polymers were published [16,17]. According to these studies the system was characterized as not miscible but it was found that a transcrystallization process is induced by the previously crystallized polyamide spherulites on the crystallizable phase of the PEE. Recently we have reported on the reactive mixing of PEE with Nylon 6 [18]. In general, reactive blending of different Nylons with rubber-like copolymers was adopted as a method for the toughening of polyamides [19–23]. Grafting of a thermoplastic material like PEE onto polyamide matrix would be a good solution to the improvement of the impact strength of polyamides, particularly at low temperatures.

In the present work we report on the melt-mixing behavior of PEE blends with various Nylons and the subsequent characterization of the obtained mixtures using dynamic mechanical analysis (d.m.a.), tensile testing, differential scanning calorimetry (d.s.c.), scanning electron microscopy (SEM), extraction experiments, Fourier transform infrared (FT*ir*) as well as micro-Raman spectroscopy.

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* Corresponding author. Tel.: +00-3061-997121; fax: +00-3061-997122.

E-mail address: j.kallitsis@upatras.gr (J.K. Kallitsis)

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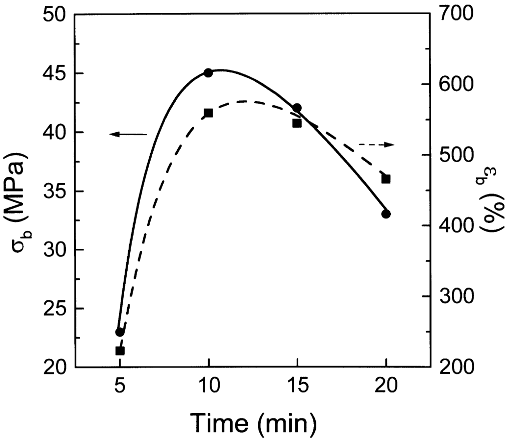


Fig. 1. Optimization of mixing conditions for the blend Nylon 11/PEE 75/25 at 230°C.

2. Experimental

2.1. Materials and specimen preparation

Poly(ether–ester) (Hytrel, type 4056 with ca. 44 wt% poly(tetramethylne ether glycol terepthalate units) was supplied by the Elastomers Department, DuPont (UK) Ltd. Nylons 11; 6,6; 6,10 and 6,12 were obtained from BDH. All materials were dried in vacuum oven at 80°C for 48 h to remove sorbed water.

Blends were prepared by melt-mixing in a stainless steel home-made batch mixer, consisting of a cylindrical rotor, rotating into a thermostated cylindrical cup at about 100 rpm. The base of the rotor was tapered into a flat cone (2°C). Mixing was carried out under a blanket of inert gas (Ar) and the maximum amount produced per batch was ca. 10 g. Mixing temperature was 230°C (265°C for Nylon 6,6 blends) and the mixing time 10 min.

Nylons/PEE compositions prepared under these conditions were 95/5, 85/15, 75/25, 50/50. Films were made by compression molding between Teflon sheets at 250°C and 70 kg cm^{-2}, pressure release and quenching at 0°C.

2.2. Apparatus and procedures

Dynamic mechanical analysis was performed in a solid state Analyzer RSA II, Rheometrics, at 10 Hz. Specimen dimensions were $3.0 \times 0.5 \times 0.01$ cm^3.

The d.s.c measurements were carried out in an inert atmosphere using the DSC plus of Rheometrics Scientific. The sample weight was ca. 10 mg and the heating rate was 10°C min^{-1}. The samples were heated up to 250°C, quenched at − 50°C followed by heating to 250°C. The second heating run was recorded.

Tensile tests were performed according to ASTM D882 at 23°C using a J.J. Tensile Tester type 5001 with a crosshead speed of 10 cm min^{-1}. Specimen dimensions were $4.0 \times 0.65 \times 0.025$ cm^3.

The FT*ir* spectra were recorded using a Perkin Elmer 1600 spectrometer.

SEM was carried out on cryofractured specimens etched or not, using a Jeol model 6320-Field Emission Scanning Electron Microscope.

Raman spectra were excited with the 514.5 nm line of a Spectra Physics (Stabilite 2017-055 model, USA) water cooled Ar^+ laser and analyzed with a T-64000 (Jobin Yvon, France) micro-Raman system in the single spectrograph configuration. The spectral resolution was of about 7 cm^{-1}. The micro-Raman set-up used was described in detail elsewhere [24].

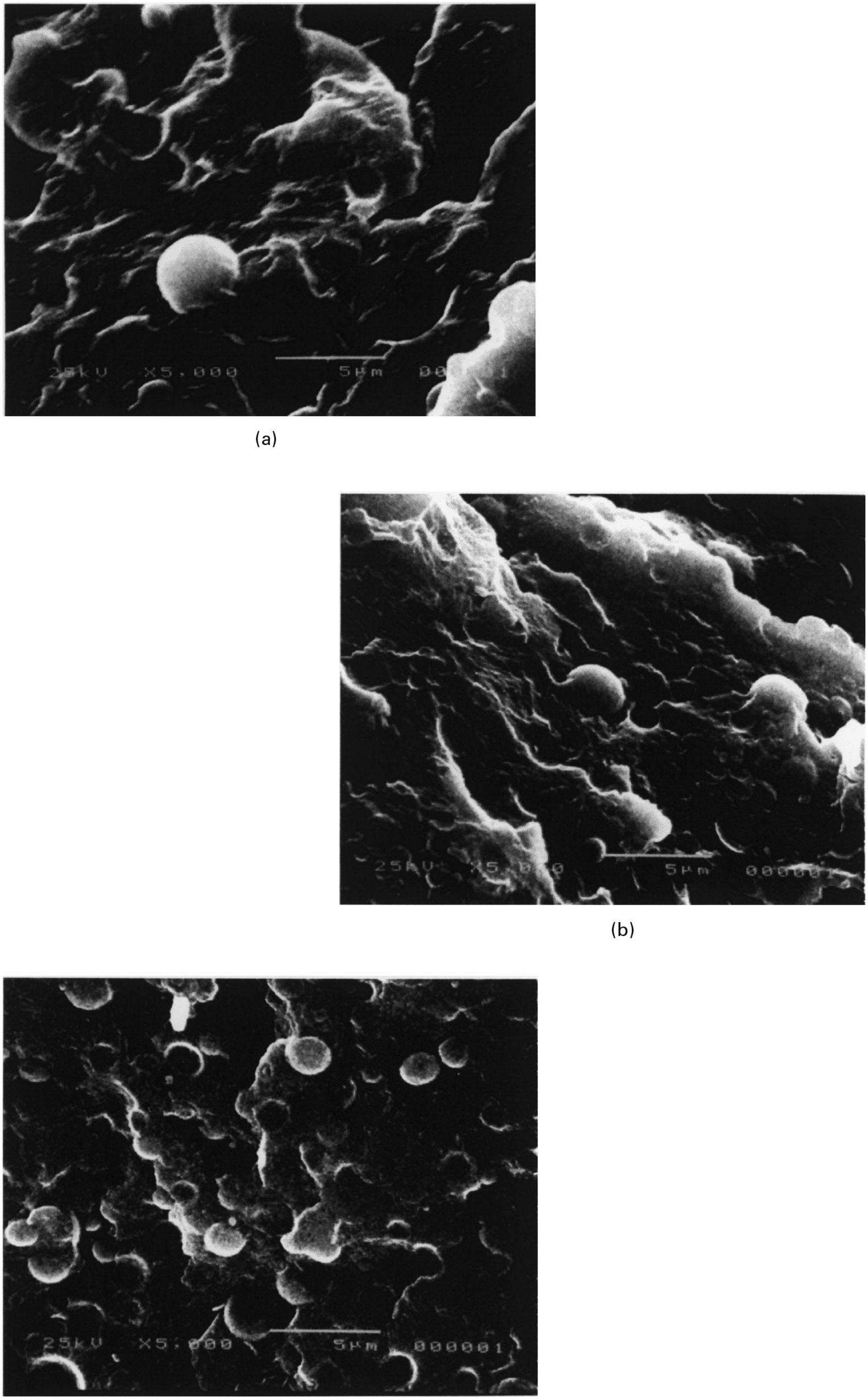
Extraction experiments were performed in chloroform at room temperature for 24 h in order to remove the unreacted poly(ether–ester). The extraction time was adopted after a series of extraction experiments which revealed that even after 15 days the extracted amount of PEE was the same. The films after the extraction were dried in vacuum oven at 100°C for 24 h. In the case of Nylon 6,6 blends these films were further treated with formic acid at room temperature for 24 h to remove the ungrafted Nylon 6,6 but it was not possible to isolate the pure copolymer from the formed suspension.

3. Results and discussion

3.1. Tensile testing

Tensile properties, tensile strength (σ_b) and in particular ultimate elogation (ϵ_b) were used as a criterion to optimize compatibilization conditions, since large deformation behavior is governed by good component adhesion at the interface. Fig. 1 gives the ultimate properties as a function of mixing time for the Nylon 11/PEE blend at the composition of 75/25. The temperature of 230°C was selected based on our previous experience on the reactive compatibilization of different Nylons [18,22,23]. It is well known that both ϵ_b and σ_b show a maximum at 10 min reaction time. Although there is no big difference on the mechanical properties of the blend prepared at 10 min and of that at 15 min, the shorter reaction time was adopted since longer reaction time contributes to partial decomposition of the polymeric blend as it is evident for 20 min reaction where the mechanical properties are significantly reduced. Cryofractured samples of the blends prepared at different mixing times were also examined by scanning electron microscopy. The micrographs taken (Fig. 2) reinforce the view that 10 min is the optimum mixing time. The dimensions of the minor phase not only decreased but also attained a more uniform distribution in the blend of 10 min mixing time in comparison to blend prepared at 5 min. Further increase in mixing time (20 min) does not show any significant change in the morphology of the cryofractured sample whereas a deterioration of its mechanical properties is observed (Fig. 1).

It is known from the literature that interchange reactions



(a)

(b)

(c)

Fig. 2. Scanning electron micrographs of cryofracture Nylon 11/PEE blends 75/25 at 230°C: (a) 5 min mixing time, (b) 10 min mixing time, (c) 20 min mixing time.

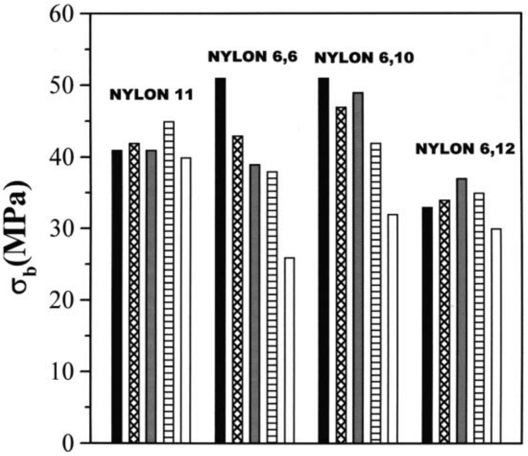


Fig. 3. Composition dependence of ultimate stress of PEE blends with various polyamides: (■), Nylon; (▦), 5% PEE; (■), 15% PEE; ▤, 25% PEE; and (☐) 50% PEE.

may occur during melt state mixing of polyamides with polyesters [25]. Such reactions are expected to lead either in a homogeneous system or in a two-phase system with good interface adhesion. Mechanical properties under large deformation can also be used to evaluated the effectiveness of the reactions mentioned earlier and for the systems studied the results are summarized in Figs. 3 and 4. It is seen that in most systems the 50/50 composition which is usually less favorable to miscibility and/or interface adhesion, has ϵ_b values well above those of the respective pure polyamides. In some cases, σ_b is also comparable to that of the pure polyamides (Nylon 11 and Nylon 6,12). In the case of Nylon 11 and Nylon 6,12, in all compositions examined, the σ_b values remain constant at the pure polyamide level, despite the presence of the ‘‘soft’’ component. For these blends also the ϵ_b values are comparable with those of the pure polyamides, supporting the view that a

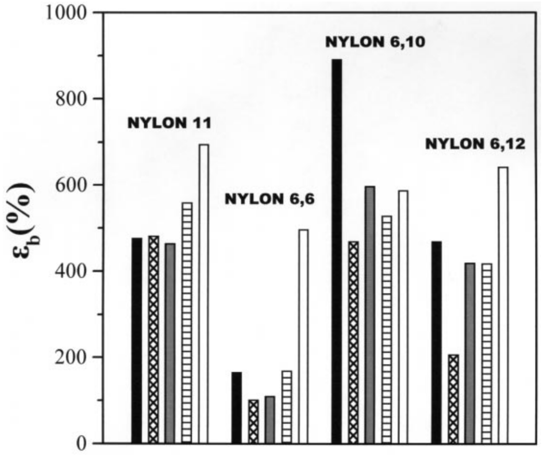


Fig. 4. Composition dependence of ultimate strain of PEE blends with various polyamides: (■), Nylon; (▦), 5% PEE; (■), 15% PEE; (▤), 25% PEE; and (☐), 50% PEE.

Table 1
Extracted amount after treatment with chloroform at room temperature

Blend composition	Nylon 11		Nylon 6,6		Nylon 6,10		Nylon 6,12	
	Total reduction (wt%)	Removed PEE (%PEE)	Total reduction (wt%)	Removed PEE (%PEE)	Total reduction (wt%)	Removed PEE (%PEE)	Total reduction (wt%)	Removed PEE (%PEE)
95/5	1	20	1	20	1	20	1	20
85/15	4	27	5	33	6	40	6	40
75/25	12	48	7	28	7	28	8	32
50/50	46	92	46	92	43	86	43	86

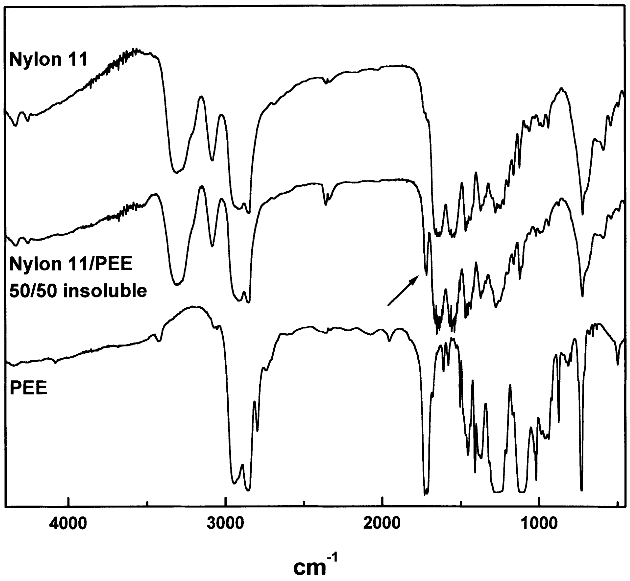


Fig. 5. FT*it* spectrum of the Nylon 11/PEE 50/50 blend, after the extraction of PEE with chloroform at room temperature, in comparison with the pure polymers.

very good interfacial adhesion in these two-phase systems was achieved. Owing to the fact that the blend prepared at 5 min had much worse properties than the respective blend at 10 min (Fig. 1) we can say that the good mechanical properties can possibly be attributed to a transesteramidation reaction which needs adequate time to be performed.

3.2. Extraction experiments

Solubility tests of the blends studied testify the occurrence of interchange reactions under the processing conditions. The extraction experiments were carried out by dissolving the unreacted PEE of the blends in chloroform at room temperature and the results are shown in Table 1. As shown in Table 1, blends with compositions of PEE less than 50 wt% show low extracted amount, 20%–48%, of the total PEE concentration. At the 50/50 composition, in all examined systems, a much higher extract (86%–92% of the expected) was observed. Since this composition appears to have very good mechanical properties as described before, it is possible that the amount of PEE that was grafted onto the polyamide phase, acts as compatibilizer for the non-reacted PEE phase. The presence of the PEE in the insoluble fraction was evaluated by means of FT*ir* for the case of Nylon 11/PEE and Nylon 6,12/PEE blends; see Figs. 5 and 6 respectively. Indeed, the absorption at $\sim 1720\ \mathrm{cm}^{-1}$ owing to the carbonyl group of PEE is present in the FT*ir* spectra of the blends after the extraction of the ungrafted PEE. It is accepted that an ''in situ'' formed compatibilizer is much more effective since the reacted amount of both phases is well dispersed through the interface. One possible reason for the lower grafting efficiency in 50/50 composition could be a phase inversion at this composition resulting in a PEE matrix and thus in its easier removal. Another possibility is based on the fact that the amount of available reactive end-groups of the polyamide, which is reducing with the composition, leads to a lower degree of grafting as the percentage of PEE is increasing.

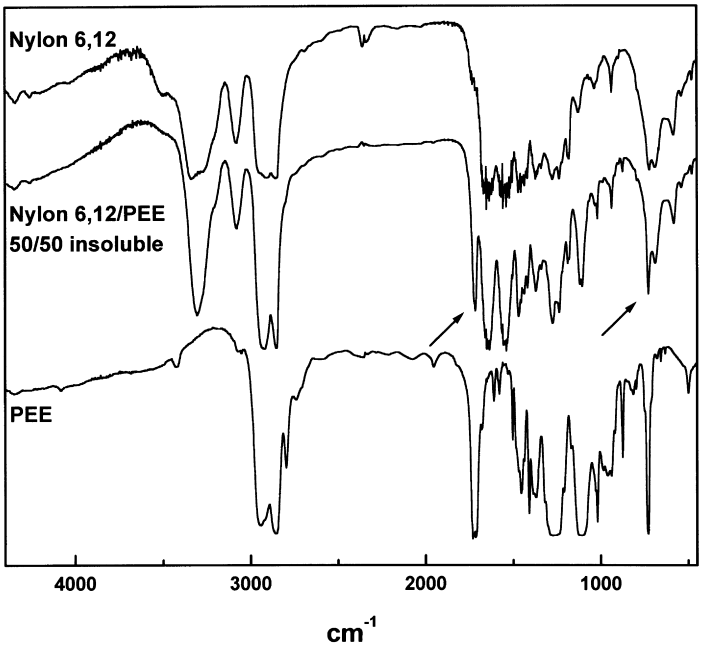


Fig. 6. FT*ir* spectrum of the Nylon 6,12/PEE 50/50 blend, after the extraction of PEE with chloroform at room temperature, in comparison with the pure polymers.

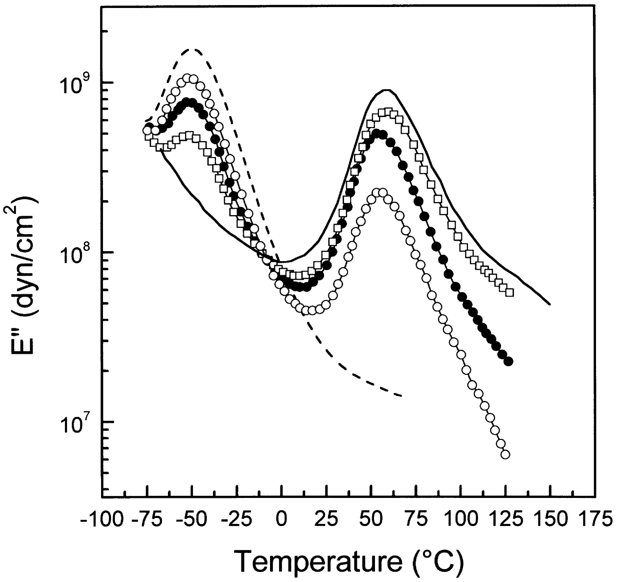


Fig. 7. Temperature dependence of the loss modulus (E'') of Nylon 11/PEE blends: (—), Nylon 11; (--), PEE; (-□-), 85/15; (-●-), 75/25; and (-○-), 50/50.

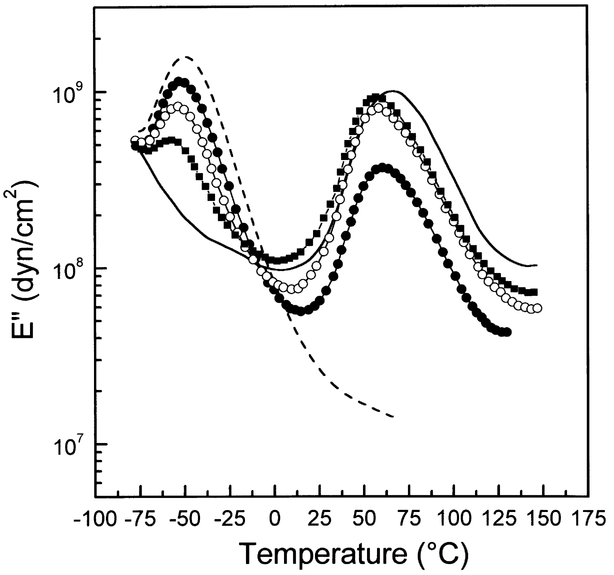


Fig. 8. Temperature dependence of the loss modulus (E'') of Nylon 6,12/PEE blends: (—), Nylon 6,12; (--), PEE; (-■-), 85/15; (-○-), 75/25; and (-●-), 50/50.

Based on the tensile properties, the systems Nylon 11/PEE and Nylon 6,12/PEE seem to have the best mechanical properties in all the examined compositions. These systems were selected for further examination of their morphology as well as their dynamic mechanical and thermal properties.

3.3. Dynamic mechanical properties–thermal properties

The dynamic mechanical behavior of the systems Nylon 11/PEE and Nylon 6,12/PEE is shown in Figs. 7 and 8. As we can see there is a relaxation of PEE at − 49°C while Nylon 11 and Nylon 6,12 show a T_g at 58°C and 66°C (10 Hz), respectively, as shown by the temperature dependence plots of the loss modulus E''. The temperature dependence of the storage modulus E' reveals that in both cases two-phase systems are obtained. The T_g of PEE appears to shift to lower temperatures with the composition. Since this is a β relaxation and since the β relaxation of Nylon is also located at temperatures lower than − 60°C it is not possible to interpret such a shift. The T_g's of Nylon 11 and Nylon 6,12 are also shifted to lower temperatures. Such a small T_g shift is attributed to interface mixing or partial miscibility. In order to discriminate which of these two possibilities is valid in the examined cases, the dynamic mechanical properties of the 50/50 blend composition were studied before and after extraction experiments. Thus, the 50/50 composition of Nylon 6,12/PEE shows smaller T_g displacement compared to the blend with a lower PEE content, see Table 2, but after the extraction of the non-bonded PEE, the remaining blend appears to have two relaxations, one at − 57°C and another at 58°C (Fig. 9). Based on the PEE

Table 2
Viscoelastic and thermal properties of the blends

Blend composition	Nylon 11/PEE		Nylon 6,12/PEE			
	T_g (°C)[a] of PEEs	T_g (°C)[a] of Nylon 11	T_g (°C)[a] of PEEs	T_g (°C)[a] of Nylon 6,12	T_m (°C)[b] of Nylon 6,12	x_c (%) of Nylon 6,12
100/0	—	58	—	66	217.8	36
85/15	− 52	58	− 57	57	216.6	37
75/25	− 51	55	− 54	58	216.5	35
50/50	− 51	55	− 52	60	216.4	40
50/50[c]	BT[d]	54	− 57	58	216.7	—
0/100	− 49	—	− 49	—	—	—

[a] Results obtained from d.m.a.

[b] Results obtained from d.s.c.

[c] After the extraction of PEE with chloroform at room temperature.

[d] BT: Broad transition.

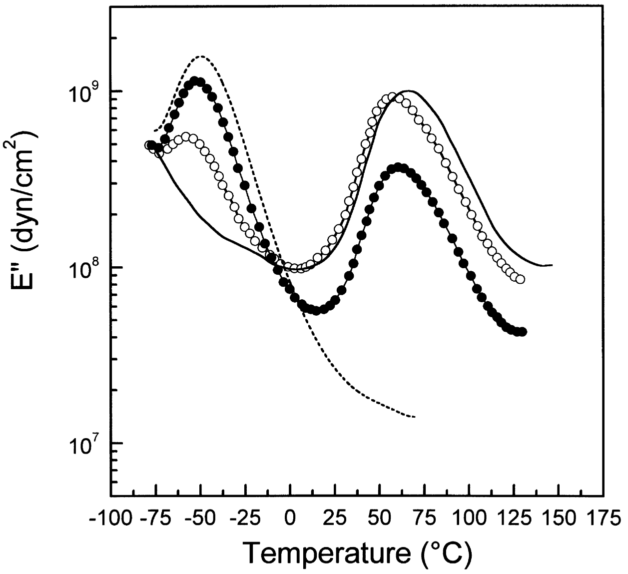


Fig. 9. Influence of the extraction of the non-grafted PEE on the loss modulus (E$''$) of Nylon 6,12/PEE 50/50 blends: (—), Nylon 6,12; (--), PEE; (-●-), blend before extraction; and (-○-), blend after extraction.

extracted amount, see Table 1, the calculated composition for Nylon 6,12/PEE (grafted) is 88/12 and the mechanical properties of such a blend are expected to be similar to those of a blend with composition 85/15 wt%, which is obviously happening in this case. Analogous results were also obtained for the Nylon 11/PEE 50/50 blend.

Taking into account the improved properties of the 50/50 composition, the fact that 86%–92% of the initial PEE content is removed during the extraction process, the two-phase behavior as well as the small T_g's shift of the pure components (as it is indicated by the d.m.a. analysis of the blends) gives the conclusion that interfacial mixing takes place and the blend with the composition of about 85/15 acts as a very efficient compatibilizer. Such ''in situ'' formed compatibilizers have the advantage that amphiphilic species are created and stay at the interface. This explains the low amount of PEE needed to obtain good mechanical properties.

In order to elucidate whether a phase inversion takes place or not at the 50/50 composition, we tested Kerner's mechanics model [26] for the system Nylon 6,12/PEE to correlate the moduli of the blends with those of their pure components. The complete equation is

$$|E^*| = |E_c^*|\cdot\frac{[\phi_d|E_d^*|/(7-5\nu_c)|E_c^*|+(8-10\nu_c)|E_d^*|] + \phi_c(15(1-\nu_c))}{\phi_d|E_c^*|/[(7-5\nu_c)|E_c^*|+(8-10\nu_c)|E_d^*|] + \phi_c(15(1-\nu_c))}.$$

Values used for density (d) and Poison ratio (v) were: $d_{(\text{Nylon 6,12})} = 1.04$ g cm^{-3}, $d_{(\text{PEE})} = 1.17$ g cm^{-3}, $\nu_{(\text{Nylon 6,12})} = 0.4$ and $\nu_{(\text{PEE})} = 0.44$. Fig. 10(a) gives the calculated and determined complex moduli $|E^*|$ at the 85/15 composition and

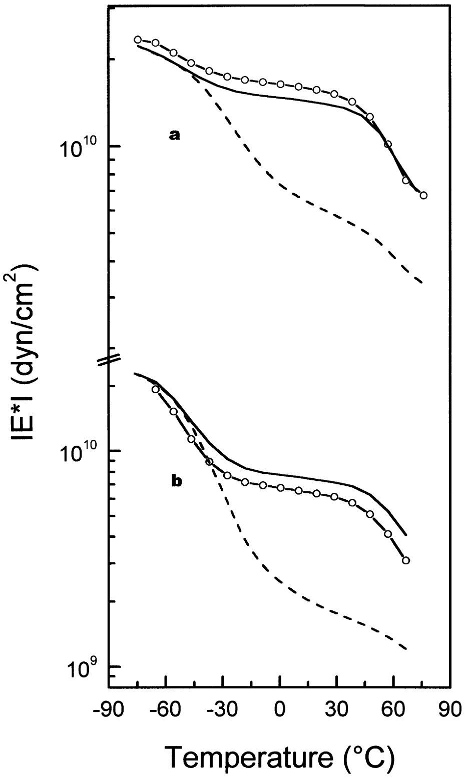


Fig. 10. Prediction of the temperature dependence of complex modulus $|E^*|$ using Kerner's model: (a) for Nylon 6,12/PEE 85/15 blend: (—), Nylon 6,12 matrix; (--), PEE matrix; (-○-), experimental. (b) For Nylon 6,12/PEE 50/50 blend: (—), Nylon 6,12 matrix; (--), PEE matrix; (-○-), experimental.

the prediction is satisfactory. The complex modulus $|E^*|$ determined is greater than the calculated, meaning that the blend is slightly stiffer despite the incorporation of an elastomer. The model also predicts that at the 50/50 composition. Nylon 6,12 serves as the matrix and phase inversion does not take place (Fig. 10(b)). This is supported also by the fact that 50/50 films does not disintegrated during the extraction experiments. This has also been observed before [27,28] in blends where the matrix polymer has a lower viscosity than the dispersed polymeric phase. Additionally, the success of the model indirectly supports the excellent adhesion between phases, since this is a necessary assumption for its applicability.

The thermal properties of the systems Nylon 11/PEE and Nylon 6,12/PEE do not give any further information as the T_g's of the components cannot be clearly detected and the T_m values of the polyamides in these blends do not show any significant depression. The very small T_m depression of Nylon 6,12/PEE blends in Table 2, is considered negligible and may probably

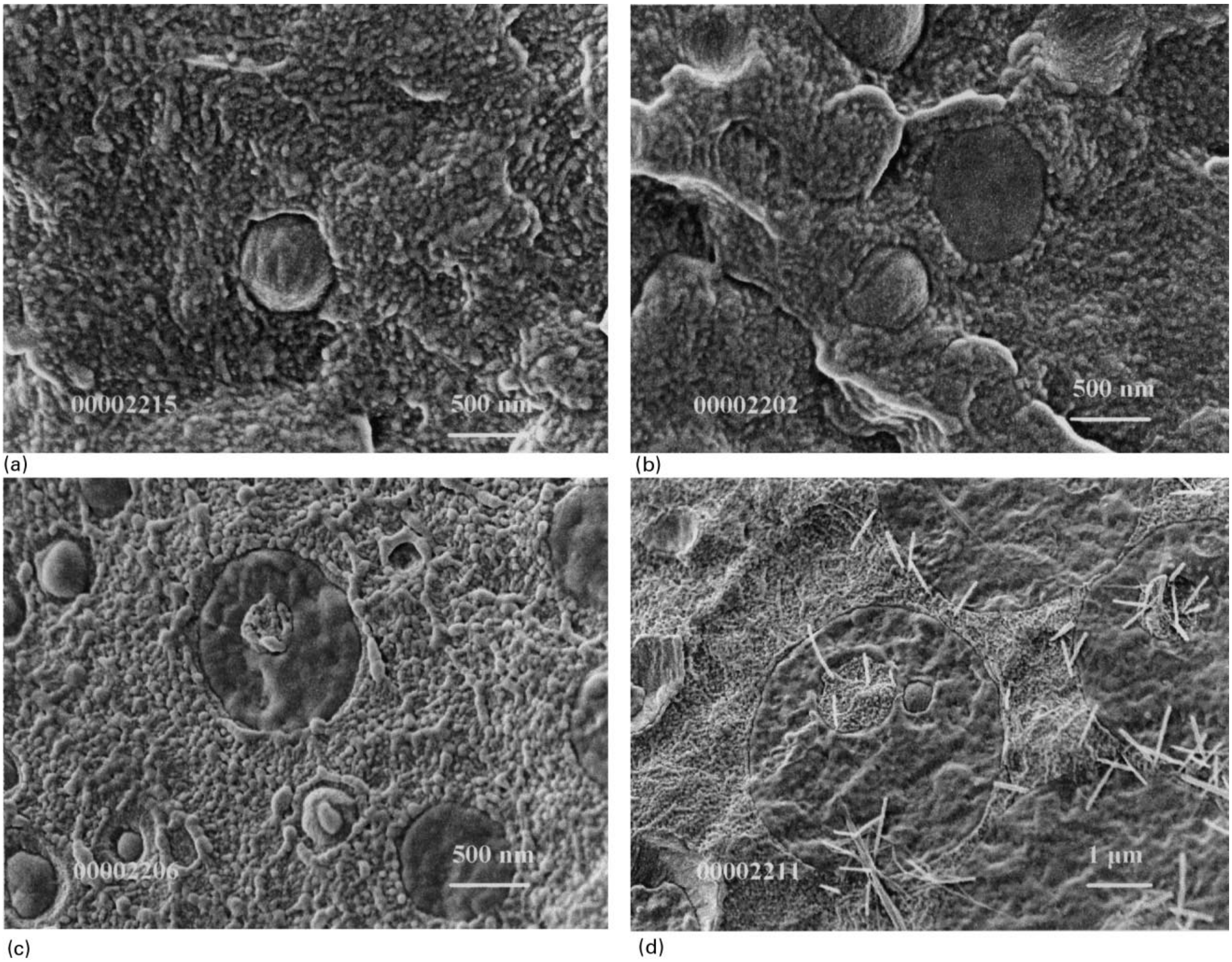


Fig. 11. Scanning electron micrographs of cryofractured Nylon 11/PEE blends: (a) 95/5; (b) 85/15; (c) 75/25; and (d) 50/503.

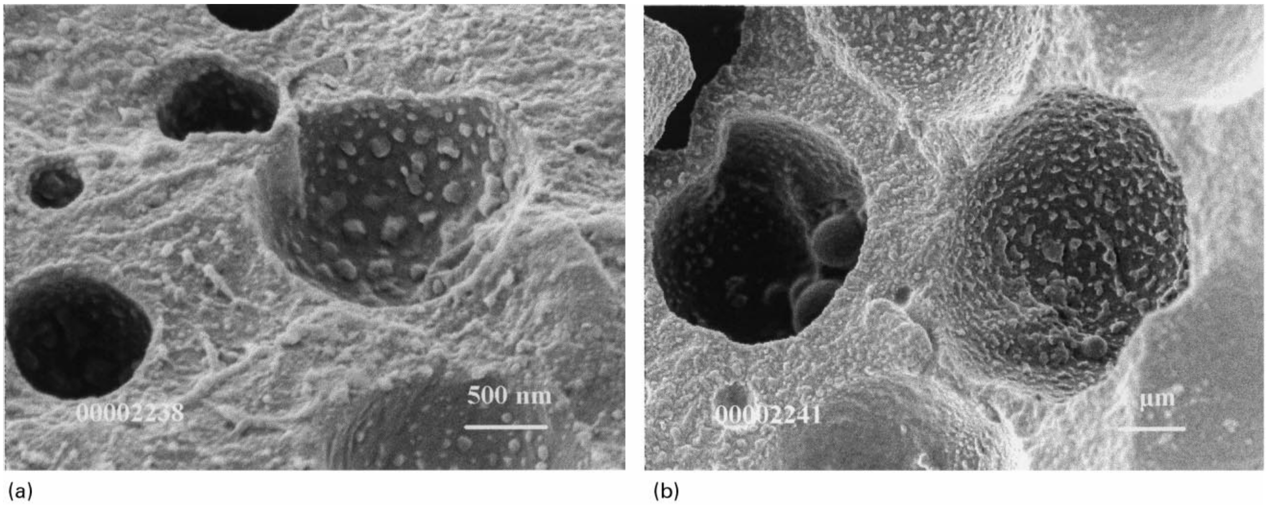


Fig. 12. Scanning electron micrographs of cryofractured and etched Nylon 11/PEE blends with chloroform at room temperature: (a) 75/25 and (b) 50/50.

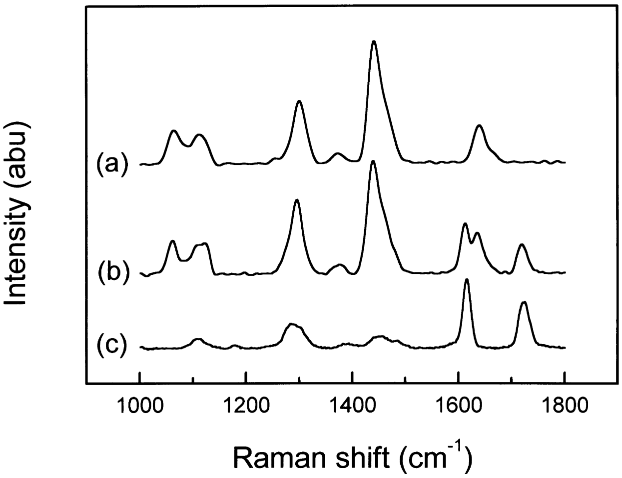


Fig. 13. Micro-Raman spectrum of the Nylon 11/PEE 50/50 cryofractured and selectively etched surface (b); in comparison with the spectra of the pure components: Nylon 11 (a) and PEE (c).

be attributed to morphological reasons. Crystallinity also remains rather constant with the composition.

3.4. Morphology

Blends of Nylon 11/PEE were further characterized with scanning electron microscopy. The micrographs taken (Fig. 11) reveal a fine dispersion of PEE into the polyamide matrix as the dispersed PEE particles range in size from ~ 0.5 μm for the compositions 95/5, 85/15 and 75/25 to ~ 2.5 μm for the intermediate composition. The fine dispersion of PEE, even in the intermediate composition, explains the very good mechanical properties that were observed. In all cases deformation of the matrix during fracture is evident indicating interpenetration of the two phases. The good adhesion between phases is also supported by the examination of the etched cryofractured surfaces by chloroform in order to remove the minor phase (PEE). The removal of PEE left holes which can be seen in the micrographs of Fig. 12. The 50/50 composition does not disintegrate and also the size of the holes formed after the extraction is quite small, proving the fine dispersion of PEE into the Nylon matrix. This is a further confirmation that Nylon is the matrix at this composition, also implied by Kerner's model. In all cases within the holes formed some specks are evident which are probably remnants of PEE ''chords'' formed when the physical separation occurs during fracture.

The presence of the PEE in the insoluble fraction was also evaluated by means of micro-Raman spectroscopy (Fig. 13). This technique was applied on the surface of the specimens after the extraction in order to evaluate the presence of PEE not only in bulk (proved by FT*ir*, Fig. 5) but on the surface as well. The spectrum clearly confirms the existence of PEE on the surface of the cryofractured and selectively etched sample as the carbonyl group peak at ~ 1730 cm^{-1} present. This is in agreement with the results of the extraction experiments which show that a significant amount of the available PEE for extraction remains attached to the matrix.

4. Conclusions

Binary melt-mixed blends of various polyamides with a polyetherester (PEE) had good mechanical properties and in some cases even better than the respective polyamides. Based on these results two of the initial systems. Nylon 11/PEE and Nylon 6,12/PEE, were selected for further examination. The dynamical mechanical analysis of these blends revealed two-phase systems but with a mutual displacement of their T_g's, implying some kind of interactions at the interphase probably random transesteramidation reactions between the components. The extraction experiments that were performed showed that the required amount of PEE for the compatibilization was low supporting the view that PEE can be used for the compatibilization of polyamides with other polymers which are compatible with PEE. The microscopic examination of Nylon 11/PEE blends revealed that in all the compositions examined, spherical PEE inclusions were formed, deformation of the matrix occurred during fracture and the remnants of PEE after the extraction were evident as specks within the holes formed. The presence of PEE on the cryofractured and selectively etched blends was confirmed using micro-Raman spectroscopy. Finally bearing in mind the very good mechanical properties and the phase behavior of the 50/50 blend the perspective of using common plastics like polyamides to reduce the cost of PEE can be considered.

Acknowledgements

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