

# *In situ* compatibilization of poly(ethylene-co-ethyl acrylate)/nylon 6 blends

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Blends of poly(ethylene-co-ethyl acrylate) (PEEA)/nylon 6 were found to have good mechanical properties when melt-mixed without added catalyst at optimum conditions. Characterization studies based on tensile testing, dynamic mechanical analysis, differential scanning calorimetry, Fourier transform infra-red spectroscopy and morphological evidence using optical and scanning electron microscopy, support the view that an *in situ* compatibilization of the two components takes place via aminolysis reactions. Compositions studied covered the complete composition range and the best mechanical properties were obtained at low amounts of PEEA (~15% w/w). Copyright © 1996 Elsevier Science Ltd.

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## INTRODUCTION

Certain advantages of aliphatic polyamides, e.g. good processability, impact strength and solvent resistance, may be further enhanced and complemented with the addition of polyolefins (PO) which increase stiffness and notched impact resistance, and reduce moisture absorption. The two classes of polymers are incompatible; however, reactive processing may overcome this problem<sup>1</sup>.

The present work aims at the *in situ* compatibilization of poly( $\epsilon$ -caprolactam) (nylon 6) via an aminolysis reaction with poly(ethylene-co-ethyl acrylate) (PEEA). The resulting modified polyamide (or polyolefin copolymer) may play the role of a compatibilizer in binary nylon 6/PO blends. In addition to property diversification of polyamides, compatibilization of this type may prove practical in recycling mixtures of nylons/PO into useful materials when their separation proves uneconomical.

Various compatibilization reactions pertaining to the above class of polymers have recently been summarized by Xanthos and Dagli<sup>2,3</sup> covering the period up to 1990. Compatibilizers most frequently quoted as suitable for polyamide/PO blends contain anhydride or carboxyl functionality to form amide linkages. Recent work includes the findings of Paul and co-workers<sup>4</sup> where a comparison of the toughening effectiveness on nylon 6 is made between a maleic anhydride (MA) grafted hydrogenated SBS (SEBS-*g*-MA) and a maleic anhydride modified ethylene-propylene elastomer (EPR-*g*-MA). In another report Paul and co-workers<sup>5</sup> investigated the effectiveness of the previous compatibilizers as impact modifiers as well, for nylon 6/polypropylene (PP) blends. Toughening of various polyamides has also been made by blending with SEBS-*g*-MA. Their mechanical behaviour and blend morphology were reported recently<sup>6</sup>. Armat and Moet<sup>7</sup> analysed the compatibilization of

nylon 6/low density polyethylene (LDPE) using SEBS-*g*-MA in terms of morphology changes during deformation. Rosch and Mulhaupt<sup>8</sup> compared the compatibilizing effectiveness of SEBS-*g*-MA and EPR-*g*-MA in nylon 6/PP blends (at high PP contents) and concluded that the modified styrenic block copolymer was more effective, in agreement with the findings of other workers<sup>4</sup>. Most recently Dagli *et al.*<sup>9</sup> carried out an analysis of the kinetics and of the reactive compatibilization process of nylon 6/PP blends using acrylic acid grafted PP (PP-*g*-AA) as a compatibilizer. Process parameters examined were temperature, mixer rotor speed and component feeding sequence. Finally, Lamba and co-workers<sup>10,11</sup> studied the transesterification and aminolysis reactions of alkyl acrylate copolymers using low molecular weight alcohols and amines. In all cases the presence of catalyst was required as its absence resulted in slow rates of reaction. The effect of the different catalysts on the reaction kinetics was examined as well as the dependence of the kind of alkyl acrylate copolymer on the degree of conversion.

In the present system compatibilization of PEEA/nylon 6 is believed to proceed via an aminolysis reaction. This bears analogy to an interchange reaction reported before<sup>12</sup> between poly(ethylene terephthalate) (PET) and PEEA. PEEA/nylon 6 blends were prepared by reactive mixing, without the presence of any catalyst, after optimizing temperature and mixing time. The techniques used for characterization were tensile testing, dynamic mechanical analysis (d.m.a.), optical and scanning electron microscopy (SEM), differential scanning calorimetry (d.s.c.) and Fourier transform infra-red spectroscopy (FTi.r.).

## EXPERIMENTAL

### *Materials and specimen preparation*

Nylon 6 obtained from BDH, was found to have

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$[n] = 0.778 \text{ dl g}^{-1}$  in formic acid 85% at 25°C and  $M_v = 20\,600$ . The amount of amine end groups was estimated by titration to be 52.5 equiv/10<sup>6</sup> g. PEEA with 18% w/w acrylic ethyl ester was obtained from Aldrich. Both nylon 6 and PEEA were dried in a vacuum oven at 60°C for 24 h to remove sorbed water before processing.

Blends were prepared by melt-mixing in a small glass vessel equipped with stirrer, under an inert atmosphere. Temperature was controlled to within  $\pm 3^\circ\text{C}$  using a suitable thermostatically controlled aluminium block. Tensile properties, tensile strength ( $\sigma_b$ ) and in particular ultimate elongation ( $\epsilon_b$ ) were used as criteria to optimize compatibilization conditions, since large deformation behaviour is governed by good component adhesion at the interface. Table 1 gives ultimate properties as a function of mixing time and temperature. Optimum

mixing conditions were determined to be 230°C and a mixing time of 25 min. Blending experiments were repeated at least twice to ensure that the blending procedure was reproducible.

Compositions prepared under these conditions were 15/85, 25/75, 50/50, 75/25 (w/w) PEEA/nylon 6. Films were made by compression moulding between Teflon sheets at 250°C and 70 kg cm<sup>-2</sup>, then releasing pressure and quenching to 0°C.

#### Apparatus and procedures

Morphology was studied on melt-pressed thin films using the phase contrast arrangement with oil immersion in a bright field and an Olympus BH-2 microscope.

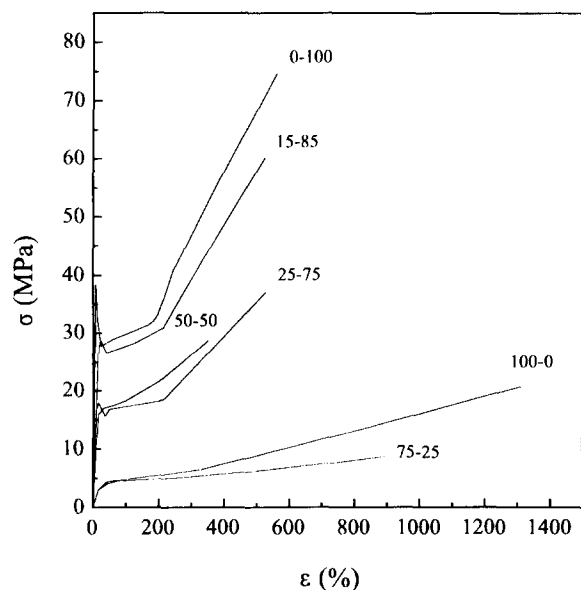
Extraction experiments were performed in boiling toluene for 4 h. The soluble fraction was obtained after

**Table 1** Optimization of mixing conditions<sup>a</sup>

Temperature (°C)	Time (min)	$\sigma_b$ (MPa)	$\sigma_y^b$ (MPa)	$\epsilon_b$ (%)	$E_b$ (J cm <sup>-3</sup> )
230	10	25	—	53	10.05
230	15	29	—	197	42.49
230	25	49	23	524	172.21
250	25	41	31	415	117.95

<sup>a</sup> Blend PEEA/nylon 6 15/85 quenched to 0°C

<sup>b</sup> Yield stress

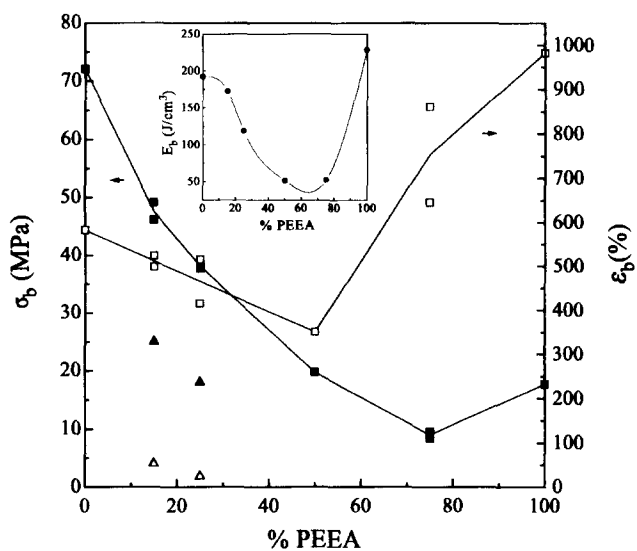


**Figure 1** Stress-strain properties of PEEA/nylon 6 quenched blends at the indicated compositions

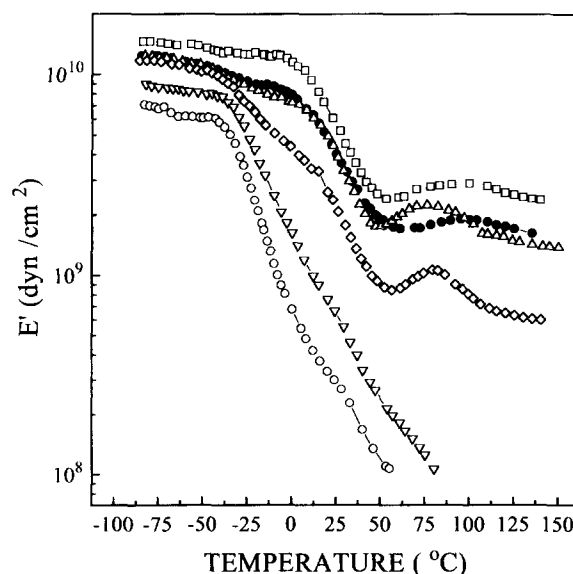
**Table 2** Tensile properties

Blend (PEEA/nylon 6)	$\sigma_b$ (MPa)	$\sigma_y^a$ (MPa)	$\epsilon_b$ (%)	$E_b$ (J cm <sup>-3</sup> )
0/100	72 ± 7	35 ± 4	583 ± 72	192.31
15/85	49 ± 6	23 ± 1	524 ± 61	172.21
25/75	39 ± 3	19 ± 1	515 ± 10	118.73
50/50	20 ± 1	—	351 ± 25	51.38
75/25	10 ± 1	5 ± 0.2	861 ± 54	51.79
100/0	18 ± 0.5	—	982 ± 69	228.38

<sup>a</sup> Yield stress



**Figure 2** Composition dependence of ultimate properties—stress  $\sigma_b$  (■) and elongation at break  $\epsilon_b$  (□)—of blends prepared under optimum conditions: (▲)  $\sigma_b$  and (△)  $\epsilon_b$  for 10 min reaction time. Inset: composition dependence of energy to tensile failure  $E_b$  of blends



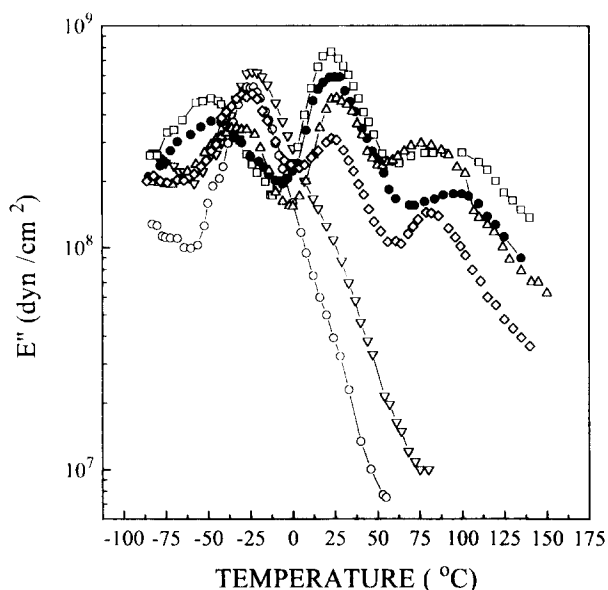
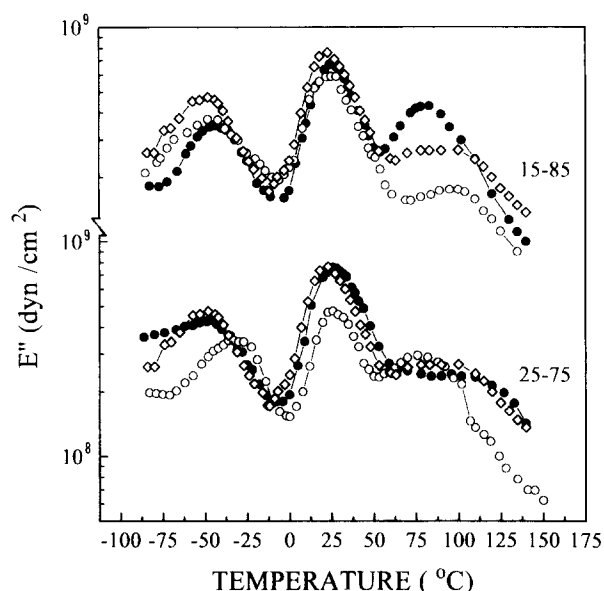
**Figure 3** Temperature dependence of the storage modulus of PEEA/nylon 6 blends: (□) 0/100; (●) 15/85; (△) 25/75; (◇) 50/50; (▽) 75/25; (○) 100/0

**Table 3** Transitions and thermal properties of blends<sup>a</sup>

Blend (PEEA/nylon 6)	$E''_{\max}$		$T_m$ (°C)		Blend crystallinity	Crystallinity of nylon 6 <sup>b</sup>
	$\beta$	$\alpha$	nylon 6	PEEA		
0/100	-50	23	216			37.0
15/85	-45	25	215	94	31.5	37.1
15/85 <sup>c</sup>	-43	25	218	94		
25/75	-35	26	215	96	27.8	37.0
25/75 <sup>c</sup>	-46	26	216	— <sup>d</sup>		
50/50	-27	25	215	95	21.2	42.3
75/25		-23	214	95	8.1	32.2
100/0		-25		95		

<sup>a</sup> Quenched to 0°C

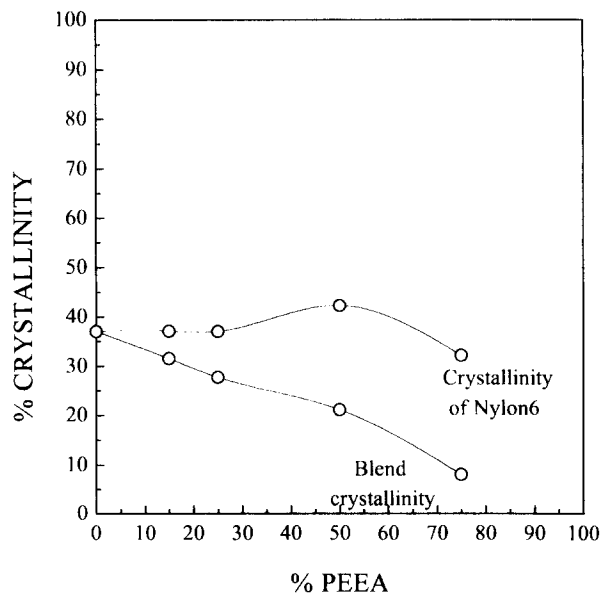
<sup>b</sup>  $\Delta h_f = 45.9 \text{ cal g}^{-1}$ 
<sup>c</sup> After extraction of non-grafted nylon 6 and PEEA

<sup>d</sup> Weak transition

**Figure 4** Temperature dependence of the loss modulus of PEEA/nylon 6 blends: (□) 0/100; (●) 15/85; (△) 25/75; (◇) 50/50; (▽) 75/25; (○) 100/0

**Figure 5** Temperature dependence of the loss modulus of 15/85 and 25/75 PEEA/nylon 6 blends before and after the extraction experiments: (◇) nylon 6, before (○) and after (●) extraction

evaporation of the solvent and drying at 100°C for 24 h. The insoluble films that remained were dried under the same conditions. After the removal of the non-grafted PEEA the remaining films were further treated with formic acid at room temperature for 24 h. The insoluble fraction was filtered and washed with formic acid and methanol. The soluble fraction was precipitated with water and received after filtration. Both fractions were dried at 100°C for 24 h in a vacuum oven.

SEM was carried out with a Jeol model JSM-500 instrument. Cryofractured and etched surfaces were examined at a tilt angle of 30°. D.s.c. measurements were carried out in an inert atmosphere using a DuPont 910 calorimeter system coupled with a 990 programmer recorder. Calibration was carried out with indium standard. Sample weight was ~10 mg and the heating rate was 20°C min<sup>-1</sup>. The samples were heated up to 250°C, quenched to -80°C followed by heating to 250°C. The second heating scan was recorded.

Tensile tests were performed according to ASTM D882 at 23°C using a J.J. Tensile Tester type T5001 and film strips with dimensions 4.0 cm × 0.65 cm × 0.025 cm.


**Figure 6** Composition dependence of blend crystallinity and of crystallinity of nylon 6 in the blends

Data reported were obtained at a crosshead speed of 10 cm min<sup>-1</sup>.

The d.m.a. data, loss tangent (tan δ) and complex modulus |E\*| were obtained at 110 Hz using a direct-reading viscoelastometer (Rheovibron model DDV II-C). Specimen dimensions were 3.0 cm × 0.20 cm × 0.02 cm.

FTi.r. spectra were obtained using a Perkin-Elmer 1600 spectrometer.

## RESULTS AND DISCUSSION

### Tensile properties

Stress-strain ( $\sigma$ - $\epsilon$ , %) properties of quenched blends prepared at optimum conditions are given in *Figure 1*. The curves in *Figure 1* are the average of five to eight tests. In view of the incompatibility of the starting materials as well as of the blends prepared at lower reaction times,  $\sigma_b$  and  $\epsilon_b$  of the compatibilized binary system are very good. Some reduction is seen at the intermediate composition and this is to be expected because of the lower grafting efficiency as shown by the extraction experiments. Ultimate properties  $\sigma_b$ ,  $\epsilon_b$ , yield strength  $\sigma_y$ , and energy to tensile failure  $E_b$  are summarized in *Table 2* and *Figure 2* for various compositions. For comparison purposes, data for the

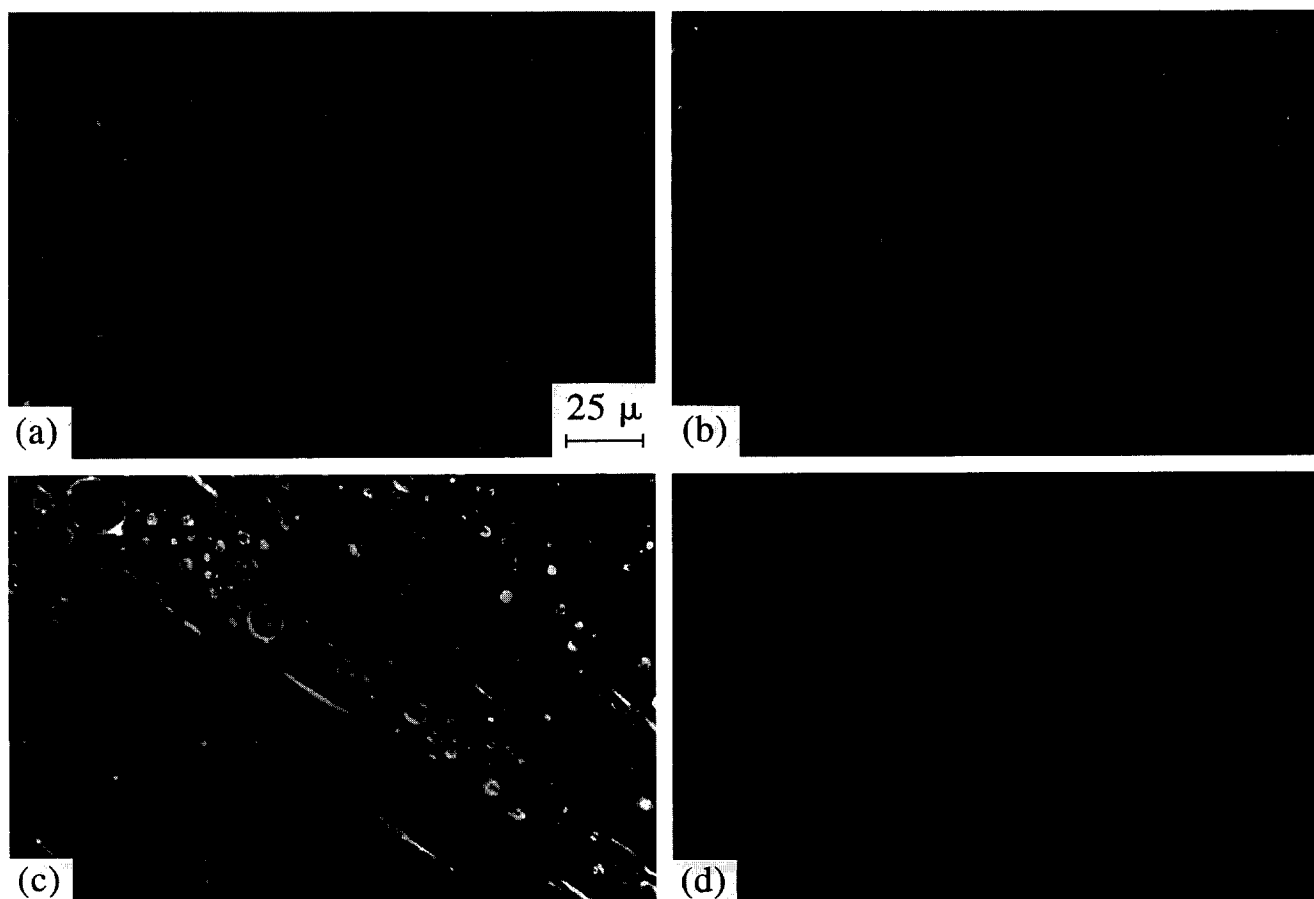
**Table 4** Extraction of PEEA by hot toluene

Blend (PEEA/nylon 6)	Mixing time (min)	Weight loss (%)	PEEA weight loss (%)
15/85	10	4.8	32.0
15/85	15	2.5	16.7
15/85	25	0.3	2.0
25/75	10	8.1	32.4
25/75	25	6.3	25.2
50/50	25	45.4	90.8
75/25	25	- <sup>a</sup>	

<sup>a</sup> Disintegrates immediately

**Table 5** Results of the extraction of PEEA (by toluene) and of nylon 6 (by formic acid) for blends prepared under optimum conditions

Blend (PEEA/nylon 6)	[NH <sub>2</sub> ]/[COOEt]	Toluene		Formic acid	
		soluble (%)	insoluble (%)	soluble (%)	insoluble (%)
15/85	0.165	0.5	99.5	76.5	23
25/75	0.088	6.5	93.5	73.5	20



**Figure 7** Phase contrast micrographs of blends: (a) 15/85; (b) 25/75; (c) 50/50; (d) 75/25

uncompatibilized binary have also been included in *Figure 2*. No synergism<sup>13</sup> has been observed as in the case of PEEA/PET compatibilized blend<sup>12</sup>.

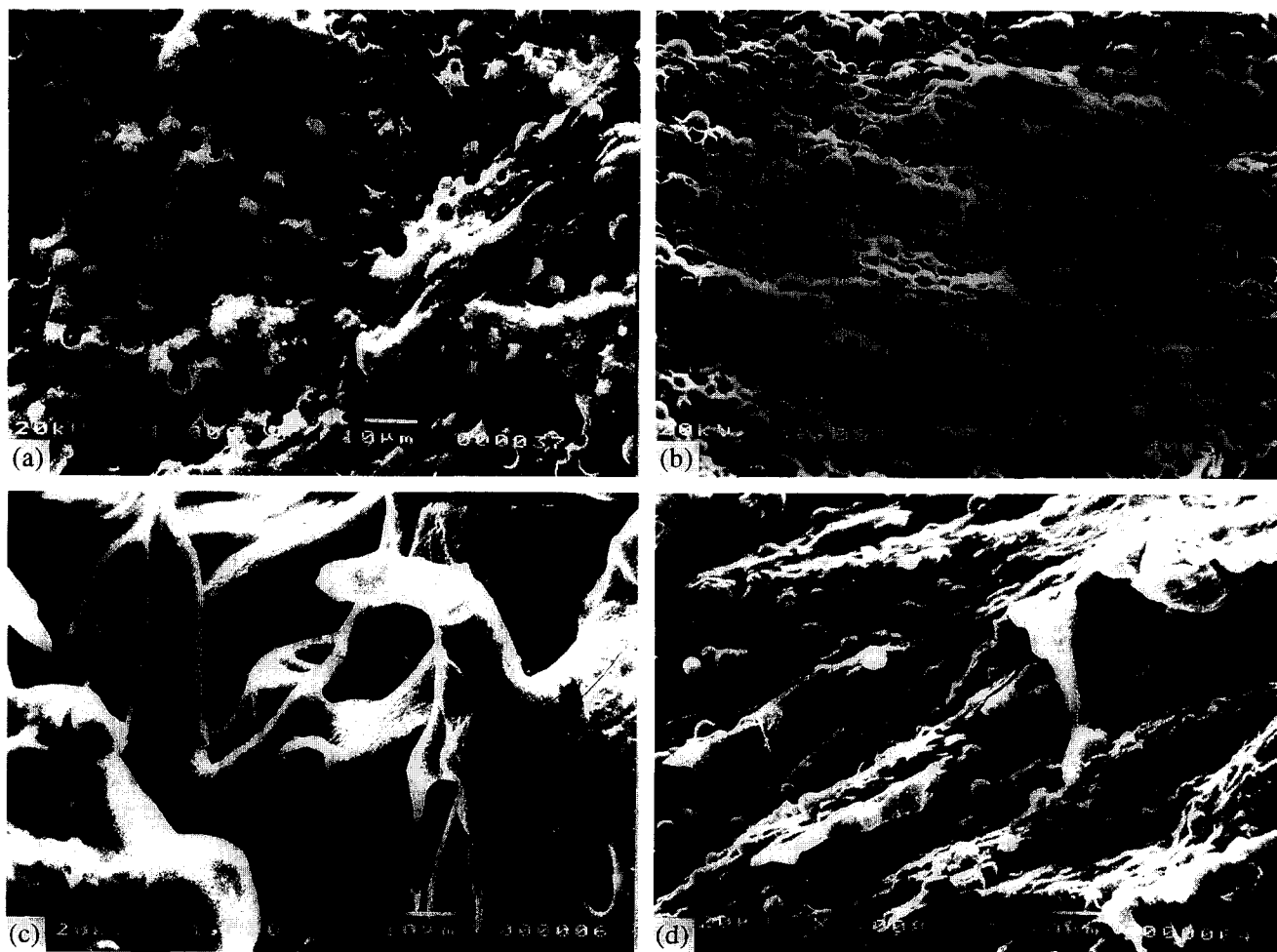
#### Dynamic mechanical properties

Dynamic mechanical properties are reported in *Table 3* and in *Figures 3* and *4*, in terms of the temperature dependence of the storage modulus  $E'$  and loss modulus  $E''$ , respectively, for the quenched blends. In *Figure 3* storage modulus, characterizing stiffness, drops regularly as the PEEA content increases. The small increase above  $\sim 50^\circ\text{C}$  is attributed to recrystallization during the thermal scan and has been observed for quenched polyamides<sup>14</sup> and PET<sup>15</sup>. This is also evident in the  $E''$  relaxation spectra, see *Figure 4*. The main relaxations of nylon 6 were detected at  $\sim 23^\circ\text{C}$  ( $\alpha$ ), (identified as the glass transition temperature  $T_g$ ) and at around  $-50^\circ\text{C}$  ( $\beta$ ). The shift to lower temperatures has been attributed to moisture plasticization. It was reported<sup>16</sup> that the first 1% of moisture may cause a  $T_g$  shift as large as  $30^\circ\text{C}$ . Both relaxations were reported<sup>17</sup> to involve the amorphous phase, increasing in strength with its content. In the blends the  $E''$  spectra do not indicate any  $T_g$  shift for the polyamide component while the secondary relaxation shifts with composition; see also *Table 3*. Secondary subambient temperature relaxations may be more sensitive to mixed interphase formation since they involve no large-scale main-chain movements hence

they are affected by the local short-range environment<sup>18</sup>. This seems to be the case for the nylon 6 component where the  $\beta$  relaxation has been attributed<sup>17</sup> to carbonyl groups hydrogen bonded to water molecules. Characteristically, after selective extraction of blends with toluene to remove non-grafted PEEA and formic acid to dissolve the unreacted nylon 6, the remaining copolymer gives d.m.a. spectra that differ.

Comparison of the  $E''$  spectra of nylon 6 and the 15/85 blend before and after extraction is shown in *Figure 5*. Before extraction the  $\beta$  relaxation of nylon 6 shifts to  $-45^\circ\text{C}$  due to the presence of the copolymer. This shift remains after the removal of the non-grafted polymers, where only the copolymer is present. The difference of the  $E''$  spectra obtained at higher temperatures (above  $50^\circ\text{C}$ ), where a new peak appears in the case of the copolymer, can be attributed to the crystallization processes during the heating scan.

For the 25/75 blend the  $E''$  spectra before and after extraction are also shown in *Figure 5*. The blend before extraction shows a significant shift of the  $\beta$  relaxation, probably due to the overlapping of the  $\beta$  relaxation of nylon 6 with the  $\alpha$  relaxation of PEEA. After the removal of both non-grafted nylon 6 and PEEA the copolymer shows only a small shift of the  $\beta$  relaxation compared with nylon 6. This is due to the lower grafting efficiency as the amount of nylon 6 is decreased. The lower PEEA content of the copolymer



**Figure 8** Scanning electron micrographs of cryofractured surfaces of blends: (a) 15/85; (b) 25/75; (c) 50/50; (d) 75/25

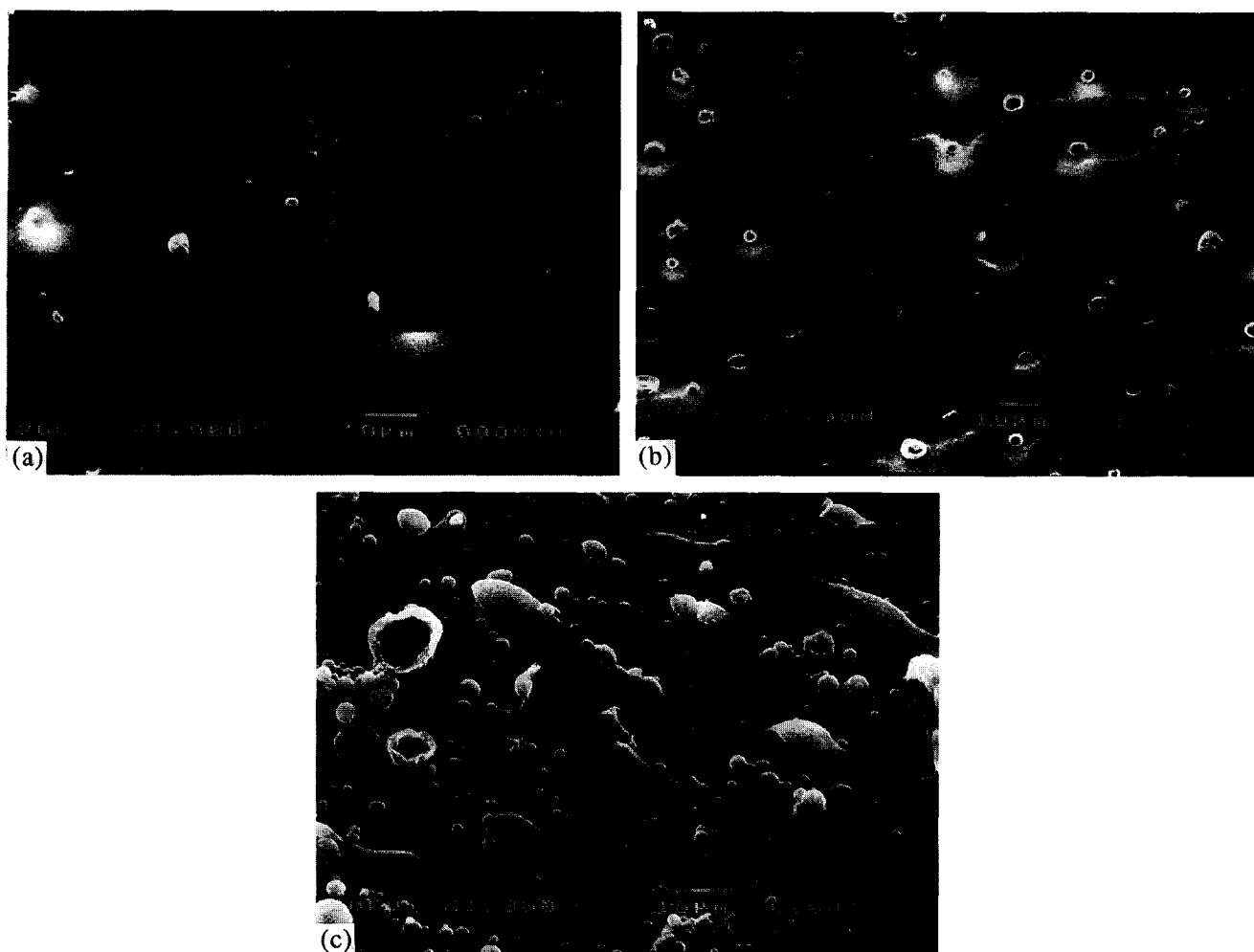


Figure 9 Scanning electron micrographs of blends selectively etched in boiling toluene: (a) 15/85; (b) 25/75; (c) 50/50

formed in the case of the 25/75 blend is also supported from the FT i.r. spectra.

#### Thermal properties

Inspection of Table 3 does not indicate any systematic or significant melting temperature ( $T_m$ ) depression that would suggest component miscibility. Also the level of nylon 6 crystallinity in the blend at various compositions (as shown in Figure 6) suggests that it crystallizes independently of the PEEA component. This is reasonable since the polyamide crystallizes in the molten PEEA. This is not the case for the latter component since during quenching it crystallizes in the presence of nylon 6 crystals. Some interference is therefore expected, but the PEEA melting endotherm is located close to the  $T_g$  of nylon 6 and hence it is difficult to determine it accurately.

#### Extraction experiments

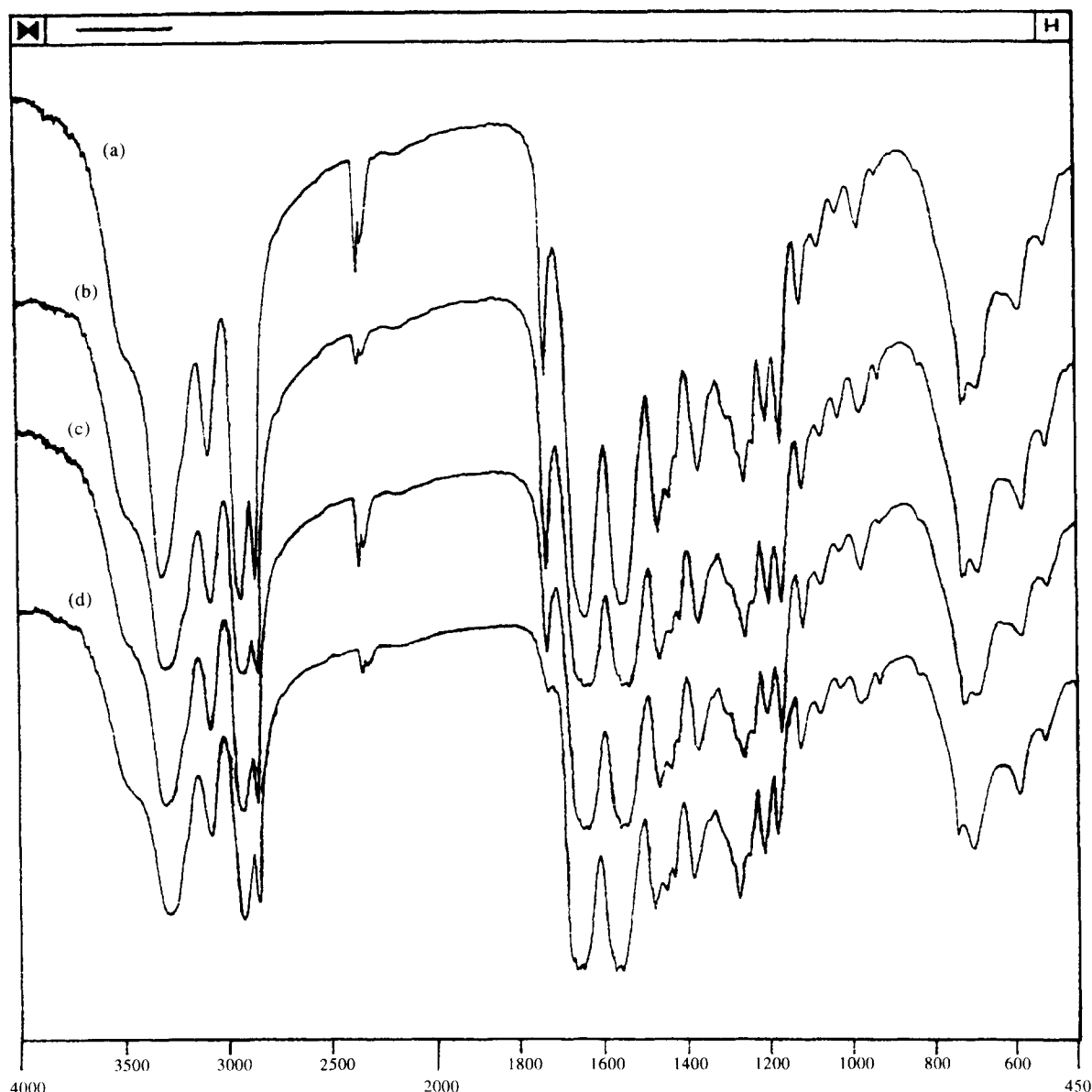
The grafting efficiency of nylon 6 onto PEEA chains can be easily proved by an extraction study performed in boiling toluene. The results are recorded in Table 4. They show that in all examined cases the removal amount of PEEA, which is soluble in toluene, is decreased as the reaction time is increased. In cases such as the 15/85 blend, for a 25 min reaction time, only 2 wt% of the initial amount of PEEA was removed, indicating that the reaction led to a very effective grafting of the two

polymers. The increase of the extracted PEEA percentage with increasing PEEA blend content is easily understood since as the amount of the amine end groups is reduced, effective grafting is reduced too.

The grafting efficiency was higher in this system compared with that obtained for the PEEA/PET<sup>12</sup>. Even in the 50/50 blends, where previously disintegration was reported<sup>12</sup>, in the present case more than 5 wt% PEEA remained on the nylon 6 films.

For the 15/85 and 25/75 blends most of the used PEEA was grafted onto nylon 6. In these cases, further extraction with formic acid was performed to remove the non-grafted nylon 6. The results of this second extraction procedure showed that 25% of the total blend weight was found to be insoluble in both solvents, as shown in Table 5. This fact proves that a copolymer composed of nylon 6 and PEEA chains was formed during the reactive blending of these two polymers under the prescribed conditions.

Tensile properties of the 15/85 and 25/75 blends after extraction with toluene were examined and the results were compared with those of the initial blend. For the 15/85 blend there was no significant difference in the tensile properties after the extraction procedure as was expected from the very low amount of the extracted PEEA. For the 25/75 blend a small decrease of the  $\epsilon_b$  value was observed while the  $\sigma_b$  and  $\sigma_y$  values remained almost the



**Figure 10** Infra-red spectra of 15/85 PEEA/nylon 6 blends: (a) initial blend; (b) insoluble fraction after extraction with hot toluene; (c) insoluble fraction after treatment with formic acid at room temperature; (d) soluble in formic acid at room temperature

same. The observed reduction in the  $\epsilon_b$  value after removal of the non-grafted PEEA could be attributed to the lower degree of grafting compared to that of the 15/85 blend.

#### Morphology

Phase contrast micrographs in *Figure 7* show an inhomogeneous phase distribution at all compositions, with finer structure in blends with low PEEA content. More information on morphology was obtained using SEM. Cryofractured surfaces of blends are shown in *Figure 8*. The 15/85 and 25/75 blends, having good mechanical properties, appear to have a finer dispersion of the spherical particles attached to the matrix. *Figure 9* shows the micrographs from surfaces etched with boiling toluene. These results are in agreement with those obtained from extraction studies. In the 15/85 blend, which gave a very low soluble fraction, the surface appears to be homogeneous, while in the 25/75 blend small 'holes' are formed, showing the higher amount of

the extracted PEEA. In the 50/50 blend the etched surface shows a higher degree of PEEA removal without disintegration of the film. Comparison of the etched surfaces observed in this work with those reported previously for PEEA/PET<sup>12</sup> clearly shows the higher grafting efficiency obtained in the present case. The absence of the specks observed previously<sup>12</sup> can be attributed to the higher degree of grafting (proved by the extraction studies) and also to the different behaviour of the nylon 6 matrix compared to that of PET.

#### FTi.r. spectroscopy

An FTi.r. examination was performed using the blends after the extraction. For the 15/85 blend, the FTi.r. spectra of the initial blend, the blend after extraction with toluene and the two fractions obtained after extraction with formic acid are shown in *Figure 10*. The carbonyl bond of PEEA at  $1732\text{ cm}^{-1}$  was present after the extraction with toluene, and also in the fraction that was insoluble in formic acid (copolymer). In the

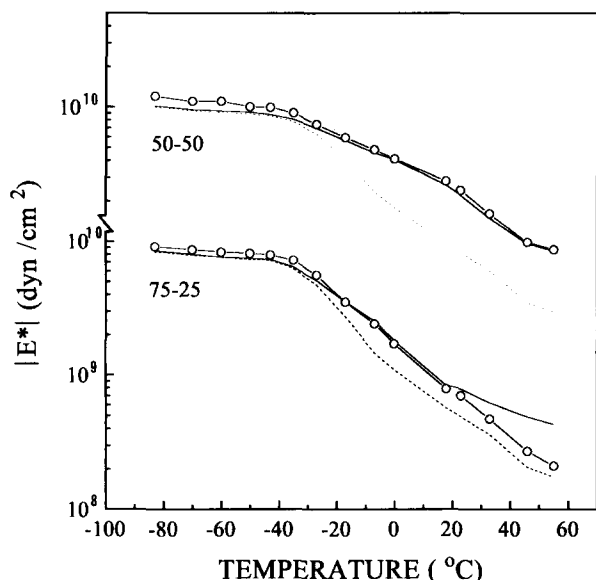
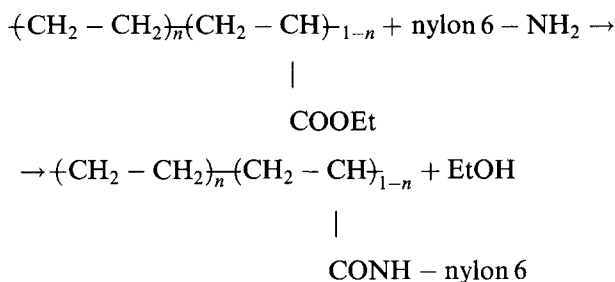


Figure 11 Prediction of the temperature dependence of complex modulus  $|E^*|$  using Kerner's model, for the indicated compositions: (—○—) experimental; (—) nylon 6 matrix; (---) PEEA matrix

formic acid soluble fraction, nylon 6 was the predominant material but even here a small fraction of PEEA was detected. The same trends were also observed for the 25/75 and 50/50 blends.

Combination of the FTi.r. results with those obtained from extraction experiments supports the view that reaction between the amine end groups of nylon 6 and the pendent ester groups of PEEA proceeds as shown in the following reaction:



$n = 0.94$ .

#### Mechanics models

The spherical shape of the dispersed PEEA phase in blends with good mechanical properties (low PEEA content)—a fact that also supports the very good adhesion—led us to test Kerner's mechanics model<sup>19</sup> to correlate the moduli of the blends with those of their pure components. The complete equation is given elsewhere<sup>20</sup>. Values used for density ( $d$ ) and the Poisson ratio ( $\nu$ ) were:  $d(\text{nylon 6}) = 1.138 \text{ g cm}^{-3}$ ;  $d(\text{PEEA}) = 0.93 \text{ g cm}^{-3}$ ;  $\nu(\text{nylon 6}) = 0.4$ ; and  $\nu(\text{PEEA}) = 0.49$ . Figure 11 gives the calculated and determined complex moduli  $|E^*|$  at various compositions and the prediction is satisfactory. The model correctly predicts that at the 50/50 composition phase inversion does not take place, which is also supported by the fact that 50/50 films do not disintegrate during the extraction experiments. Phase inversion takes place over the 75/25 composition,

predicted by the model and shown by the extraction experiments. This has also been observed before<sup>21</sup> in blends where the matrix polymer has a lower viscosity than the dispersed polymeric phase. The success of the model indirectly supports the excellent adhesion between phases, since this is a necessary assumption for its applicability.

#### CONCLUSIONS

Nylon 6 may be reactively compatibilized with PEEA at elevated temperatures and prolonged mixing time, without the addition of any catalyst. This is the result of an aminolysis reaction between the amine end groups of nylon 6 and the pendent ester groups of PEEA. The significant grafting efficiency of the blends with low (up to 25 wt%) PEEA content was proved by the high  $\epsilon_b$  values in combination with the low amount of the extracted PEEA.

Additionally, FTi.r. analysis shows that PEEA is present even after extraction with toluene, which leads to the conclusion that PEEA is chemically attached to the nylon 6 matrix. D.m.a. and FTi.r. data of samples extracted with both toluene and formic acid support the view that a copolymer is formed under the compatibilization conditions described.

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