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In situ compatibilization of poly(ethylene terephthalate)/poly(ethylene-*co*-ethyl acrylate) blends

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Blends of poly(ethylene terephthalate) (PET)/poly(ethylene-*co*-ethyl acrylate) were found to have good mechanical properties when melt-mixed at optimum conditions, i.e. at ~290°C for 25 min. Characterization studies based on tensile testing, dynamic mechanical analysis, differential scanning calorimetry and Fourier transform infra-red spectroscopy of blend extracts and morphological evidence using optical and scanning electron microscopy, support the view that an *in situ* compatibilization of the two components takes place via transesterification reactions. Compositions studied covered the complete range and best mechanical properties were obtained when PET formed the blend matrix.

(Keywords: compatibilization; blends; transesterification)

INTRODUCTION

Reactive blending has recently opened a new avenue for polymer modification[1–3]. Using this type of polymer–polymer processing not only may a new polymeric product be obtained, but also a potential compatibilizer for the two starting homopolymers. This is so because the polymeric product thus prepared combines structural features from both its parent homopolymers.

In this report the properties of poly(ethylene terephthalate) (PET) melt-blended with poly(ethylene-*co*-ethyl acrylate) (PEEA) are examined. PET was chosen because of its applicability as an engineering resin and its availability at low cost via recycling, and PEEA because of the potential reactivity of its ester group with the terminal hydroxyl group of PET in a transesterification reaction[4], as demonstrated by Hu *et al.*[5]. In that work, the kinetics and efficiency of the transesterification reaction of various polyethylene acrylate esters in the melt and in solution with a low molecular weight alcohol was investigated. More recently, the reactive compatibilization of a PET copolymer with ethylene vinyl acetate copolymer via catalysed transesterification reactions was reported[6].

In the present work, the influence of the reaction time and temperature during melt mixing was examined and optimized on the basis of the tensile properties of the products obtained. In addition, these blends were characterized using dynamic mechanical analysis (d.m.a.), differential scanning calorimetry (d.s.c.) and optical and scanning electron microscopy (SEM) before and after selective etching. Had reactive compatibilization been successful, the modified PET obtained could in principle be used to compatibilize PET/polyolefin blends, as mentioned above. Indeed, preliminary work in this direction is encouraging[7]. To this end, research work was published recently involving PET modification in binary and ternary blends using polyethylene acrylate terpolymers having a pendent epoxy functionality. Thus Subramanian[8] and How[9] reported on the mechanical and processing characteristics of PET melt-blended with poly(ethylene-*co*-isobutyl methacrylate-*co*-methacrylic acid) Zn^{2+} ionomers and poly(ethylene-*co*-vinyl acetate-*co*-glycidyl methacrylate) terpolymers.

More recently, Akkapeddi and Van Buskirk[10,11] investigated mechanical properties of the reactively blended PET/poly(ethylene-*co*-glycidyl methacrylate) (EGMA) and its efficacy as a compatibilizer of PET/polyolefin blends. Good tensile properties were reported for low density polyethylene (LDPE) and ethylene–propylene copolymer, and moderate for high density polyethylene (HDPE), at increased levels of PET and moderate levels of the compatibilizer. Thermal ageing effects on mechanical properties were also examined. A related work examining reactive blending of poly(butylene terephthalate) with poly(ethylene-*co*-ethyl acrylate-*co*-glycidyl methacrylate) (E/EA/GMA) and with E/EA/maleic anhydride (MA) copolymers was also published by Hert[12]. Impact behaviour was related to morphology and blend composition.

EXPERIMENTAL

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 and $M_n = 23\,500\,g\,mol^{-1}$. PEEA with 18% w/w acrylic ethyl ester was obtained from Aldrich. PET was dried at 150°C and PEEA at 80°C, both for 12 h *in vacuo*. Blends were

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prepared by melt mixing in a small glass vessel equipped with stirrer, under an inert atmosphere (Ar). Temperature was controlled within ± 3°C using a suitable thermostatically controlled aluminium block. Temperature and blending time were varied to obtain improved ultimate tensile properties, i.e. ultimate strength σ_b and elongation at break ε_b, see *Table 1*. Optimum mixing conditions were determined to be 290°C and a mixing time of 25 min. Blending experiments were repeated at least three times to assure that the blending procedure was reproducible.

Compositions prepared under these conditions were 5/95, 15/85, 25/75, 50/50, 75/25 PEEA/PET (w/w). Films were prepared by compression moulding between Teflon sheets at ~280°C and 50 kg cm^{-2}, pressure release and quenching at 0°C.

Apparatus and procedures

Morphology was studied on melt-pressed thin films using the phase contrast arrangement with oil immersion in bright field and an Olympus BH-2 microscope. These films were also examined under crossed polars.

SEM was carried out on a Jeol model JSM-500 instrument. Cryofractured and etched surfaces were examined at a tilt angle of 30°C. 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^{-1}. The heating cycle applied was 25°C→285°C (5 min)→−70°C→285°C. Thermal data were obtained during the second heating.

Tensile tests were performed according to ASTM D882 at 23°C using a J.J. Tensile Tester type T5001 and film strips with dimensions 6.0 cm × 0.50 cm × 0.025 cm. Data reported were obtained at a crosshead speed of 10 cm min^{-1}. Tensile tests were repeated five to eight times and the values reported (see *Figures 3* and *4*) are the average of these tests.

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

*FT*i.r. spectra of blend extracts were obtained using a Perkin–Elmer 1600 spectrometer.

RESULTS

Dynamic mechanical properties

Results are summarized in *Figures 1* and *2* in terms of the temperature dependence of the storage (E') and loss (E'') moduli respectively. Variation of modulus with composition shows an abrupt change at the 50/50 blend. Noticeable also is the stiffening effect of pure PET beyond 120°C, due to its cold crystallization. This was also observed in the case of the 5/95 blend (not included for clarity). The relaxation spectra in *Figure 2* do not show any shift of the main PET relaxation α at ~90°C, whose origin, as well as that of β, has been attributed to the amorphous component[13] and is strongly dependent on crystallinity. In blends, β relaxation at −50°C is shifting towards the main PEEA relaxation at −20°C. Thus at the 15/85 and 25/75 compositions, an intermediate value of −30°C is obtained; see *Table 2*. Overall, the spectra do not indicate any extensive miscibility of the two components.

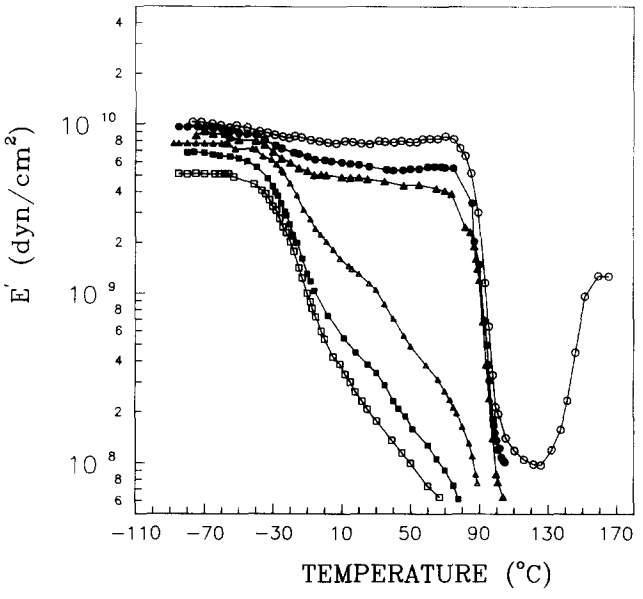

Figure 1 Temperature dependence of the storage modulus of PEEA/PET blends: (○) 0/100; (●) 15/85; (▲) 25/75; (△) 50/50; (■) 75/25; (□) 100/0

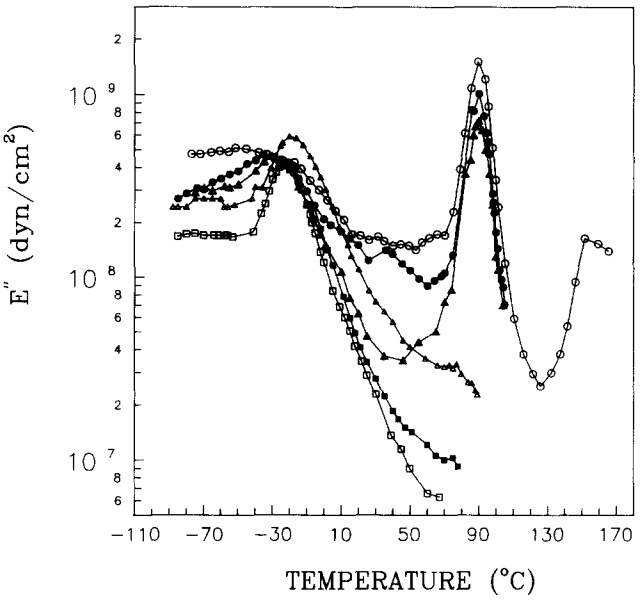

Figure 2 Temperature dependence of the loss modulus of PEEA/PET blends: (○) 0/100; (●) 15/85; (▲) 25/75; (△) 50/50; (■) 75/25; (□) 100/0

Table 1 Optimization of mixing conditions[a]

Temperature (°C)	Time (min)	σ_b (MPa)	σ_y[b] (MPa)	ε_b (%)
260	25	8	8	9
290	10	8	12	6
290	15	13	14	7
290	25	44	35	650
290	50	9	10	10

[a] Blend 15/85 quenched to 0°C
[b] Yield stress

Tensile properties

Results are given in *Figures 3* and *4* in terms of stress–strain and ultimate properties, respectively. Blends with low PEEA contents (up to 25 wt%) show improved mechanical properties compared to PET. In particular the 15/85 composition shows a maximum in ultimate strength σ_b and elongation at break ε_b (see *Figure 4*). At high PEEA contents, ductility is high since PEEA becomes the matrix. A minimum in mechanical properties is obtained at the intermediate composition (50/50). There is experimental evidence that at this composition range matrix inversion is initiated (see the Discussion). Mechanical properties, in particular ultimate elongation, are adversely affected by thermal ageing (see *Figure 3*). This has also been observed for impact behaviour in the case of compatibilized PET/EGMA and PET/GMA blends[11] and may be attributed to embrittlement caused by the crystallization of PET. Similarly, ultimate elonga-

Table 2 Transitions and thermal properties of blends[a]

Blend (PEEA/PET, w/w)	E''_{blend}	T_m(°C) PET	T_m(°C) PEEA	T_c^b (°C)	PET[c] crystallinity (%)
0/100	−50[d]	257	–	149	33.2
5/95	s[e]	255	96	140	36.3
15/85	−32	255	96	140	42.4
25/75	−32	254	96	133	43.5
50/50	−20	254	97	129	44.0
75/25	−20	254	97	124	46.0
100/0	−20	–	104		

[a] Quenched to 0°C
[b] Temperature of maximum crystallization exotherm
[c] ΔH_f(PET) = 33.5 cal g^{-1}
[d] For PET, β relaxation only reported
[e] Shoulder

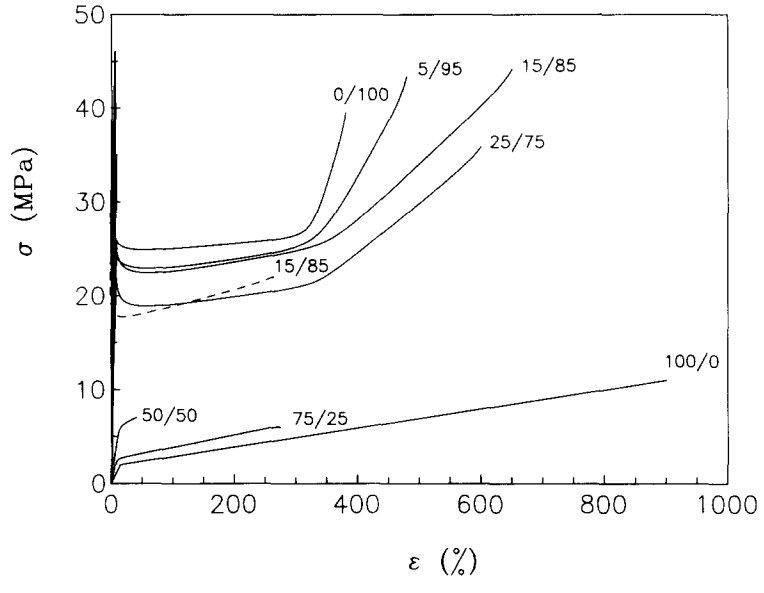

Figure 3 Stress–strain properties of PEEA/PET quenched blends at the indicated compositions, (– –) Blend annealed for 3 h at 90°C

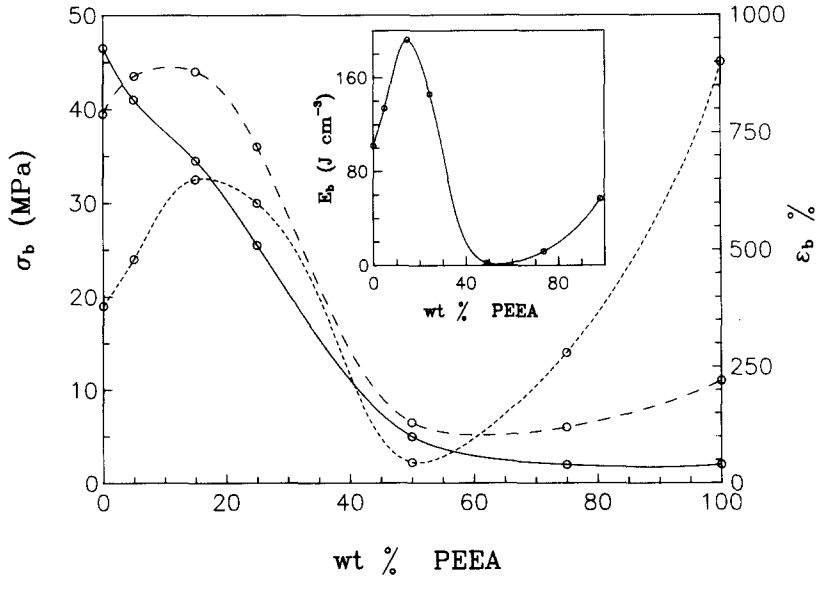

Figure 4 Composition dependence of ultimate stress σ_b (– –), strain (. . .) and yield stress (——) of blends. Inset: composition dependence of energy to tensile failure E_b of blends

tion was found to decrease by ~50% in PET/linear LDPE blends compatibilized by an ethylene–acrylic acid copolymer[14]. Since both ultimate properties σ_b and ε_b pass through a maximum at ~15 wt% PEEA, the energy to tensile failure E_b, obtained as the area under the stress–strain curve, should also exhibit a maximum in the same composition range (see inset in *Figure 4*). This quantity, combining the strength and the elongational properties of materials, shows significant mechanical property improvement compared to pure components, and is often related to impact strength.

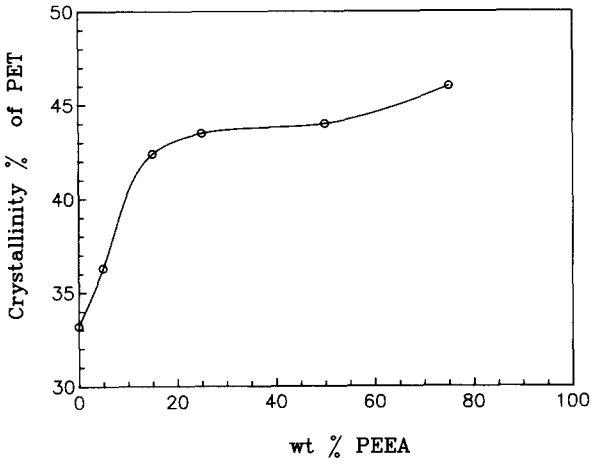

Figure 5 Composition dependence of PET crystallinity in the blends

Thermal properties

Total blend crystallinity could not be determined since the PEEA melting endotherm at ~104°C is close to the PET crystallization exotherm depending on composition peaks in the range 124–140°C (see *Table 2*). However, crystallinity of the PET component could be determined and the results are shown in *Figure 5* and *Table 2*, where additional data on thermal transitions are recorded. *Figure 5* shows that the crystallinity of PET in the blend is enhanced by the presence of the acrylate copolymer. It has been reported[15] that poly(methyl methacrylate) facilitates crystallization of PET. This is further corroborated by the data in *Table 2* which show that cold crystallization is also facilitated by the presence of PEEA. It is suggested that during quenching in the d.s.c. run, PEEA is crystallized in the supercooled PET amorphous matrix, providing nuclei for its subsequent crystallization during the final heating scan when crystallinity is determined. *Table 2* also indicates a detectable T_m depression of PET and a considerably higher one for the PEEA component. This is another indication of strong interface interactions between components, modifying crystal perfection and/or purity.

Morphology

Phase contrast micrographs in *Figure 6* show an inhomogeneous phase distribution at all compositions. Since PET has a higher refractive index ($n_D^{23} = 1.64$) than the copolymer ($n_D^{23} = 1.49$–1.50), at positive phase contrast,

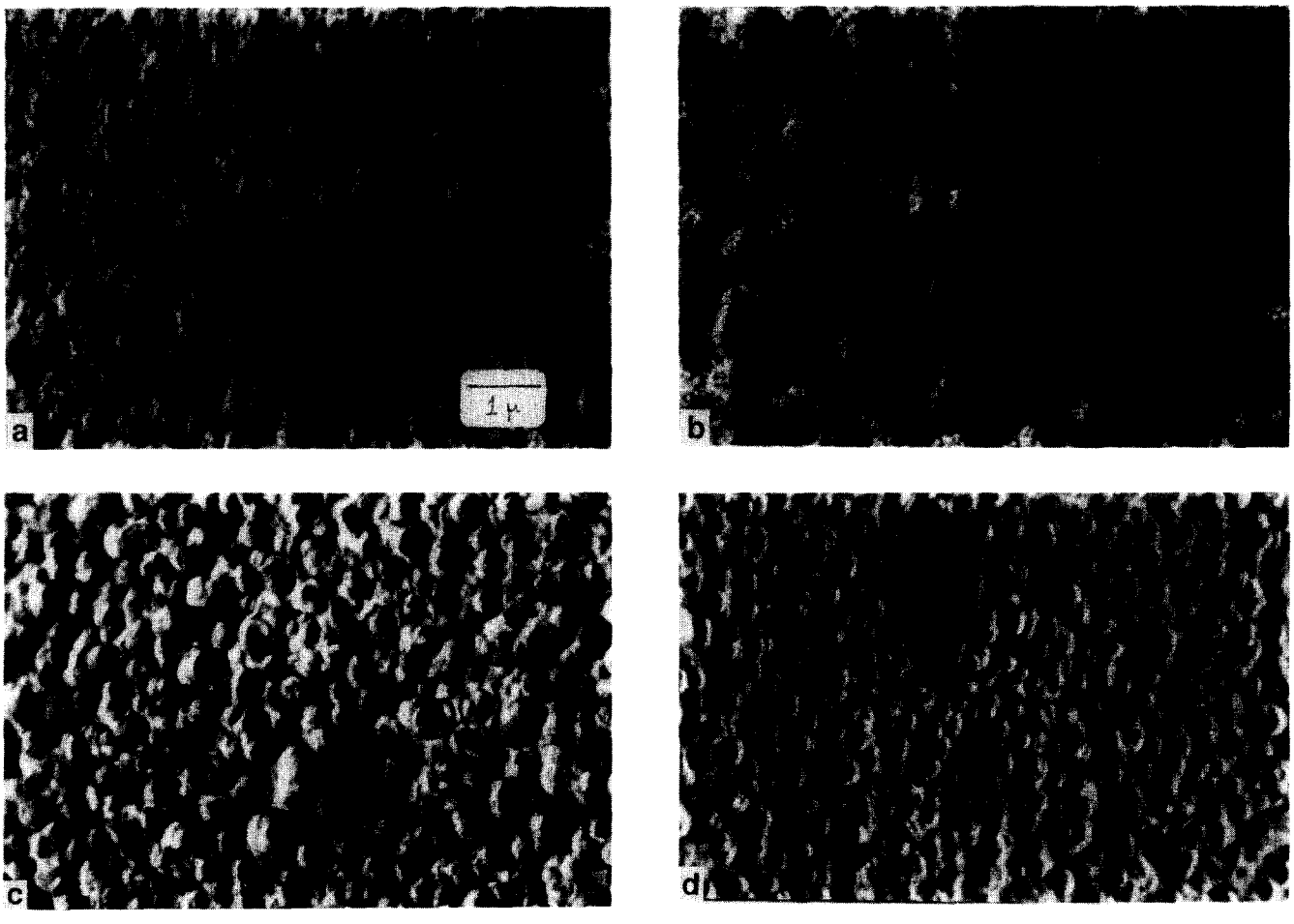

Figure 6 Phase contrast micrographs of blends: (a) 15/85; (b) 25/75; (c) 50/50; (d) 75/25

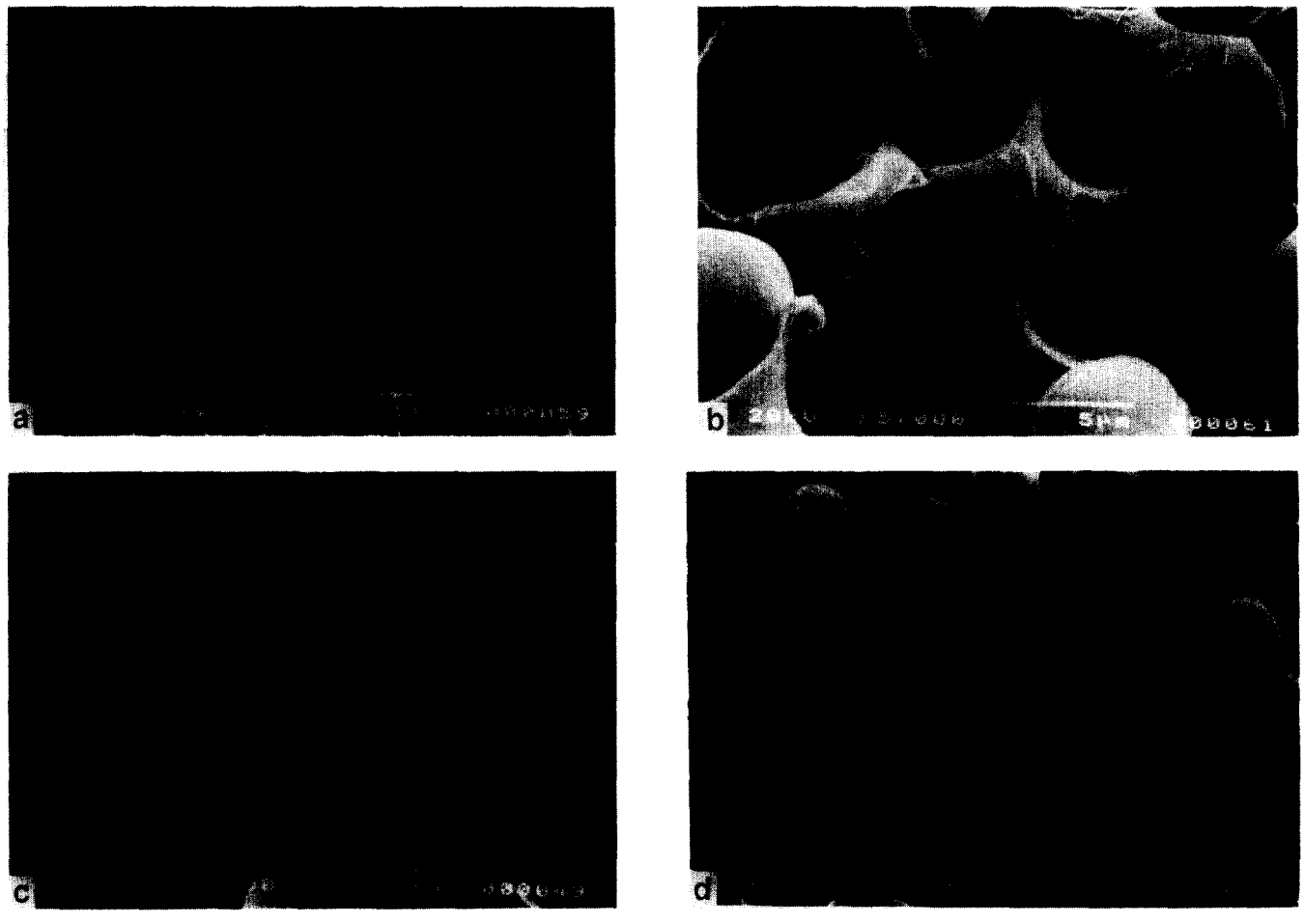

Figure 7 Scanning electron micrographs of cryofractured surfaces of blends: (a) 15/85; (b) 25/75; (c) 50/50; (d) 75/25

dark areas correspond to the PET phase. More accurate information on morphology was obtained using SEM. In *Figure 7* cryofractured surfaces of blends show a finer dispersion of particles in compositions having good mechanical properties. This is to be expected since the surface-to-volume ratio is increased in finely dispersed blends, providing the geometric requirement for good adhesion. In *Figure 7* the distinction between 25/75 and 50/50 in terms of phase sizes is less evident, however while in the latter blend, components are more clearly separated in the 25/75 composition there seems to exist a higher degree of phase interpenetration. *Figures 8* and *9* are micrographs from surfaces that were fractured and microtomed then etched with toluene (selectively removing PEEA) at room temperature (*Figure 8*) and at reflux (*Figure 9*). In the former case, the characteristic specks seen in *Figure 9*, attributed to PEEA grafted onto the PET matrix, causing its deformation during fracture, are not visible. In both cases grafting is present (explaining the good mechanical properties of blends); however, in *Figures 8a* and *b* these are 'buried' within the interfacial region, which is not removed owing to mild etching conditions. Thus the specks are remnants of PET 'chords' formed when the physical phase separation occurs during fracture, which deforms the matrix. These findings are in agreement with SEM morphology results reported recently on PET/HDPE blends compatibilized with maleic anhydride grafted hydrogenated styrene–butadiene–styrene copolymer[16]. Etching the 50/50 composition with boiling toluene led to the disintegration of specimens. As shown by mechanics models (see below), phase inversion takes place at this intermediate composition; however, there is no matrix continuity to provide sufficient strength. This explains the low ultimate properties at the 50/50 composition (see *Figure 3*) and the sudden modulus E' drop (*Figure 1*).

DISCUSSION

The fact that certain optimum conditions in terms of blending time and temperature are required to obtain blends with improved mechanical properties, supports the view that the blends studied had been reactively compatibilized. Given the functionalities of the blend components, and on the basis of the recent work of Lambla and co-workers[5], it is proposed that at the blending conditions employed a transesterification reaction takes place between the acrylate ethyl ester group of PEEA and the terminal OH and COOH groups of PET, with reaction (1a) predominating and effective in grafting blend components at the interface:

$$\begin{aligned} &\text{—}(CH_2\text{–}CH_2)_n\text{—}(CH_2\text{–}CH)_{1-n} + \text{PET–OH} \\ &\qquad\qquad\qquad\qquad\quad | \\ &\qquad\qquad\qquad\qquad\quad COOEt \\ &\rightarrow \text{—}(CH_2\text{–}CH_2)_n\text{—}(CH_2\text{–}CH)_{1-n} + EtOH \qquad (1a) \\ &\qquad\qquad\qquad\qquad\quad | \\ &\qquad\qquad\qquad\qquad\quad COO\text{–PET} \end{aligned}$$

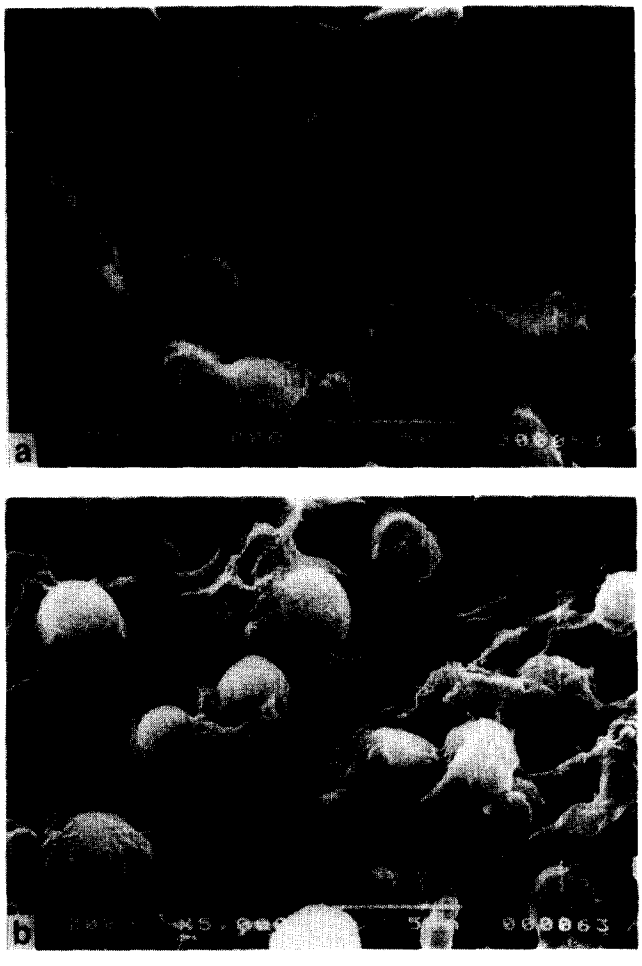

Figure 8 Scanning electron micrographs of blends microtomed and selectively etched at room temperature: (a) 25/75; (b) 50/50

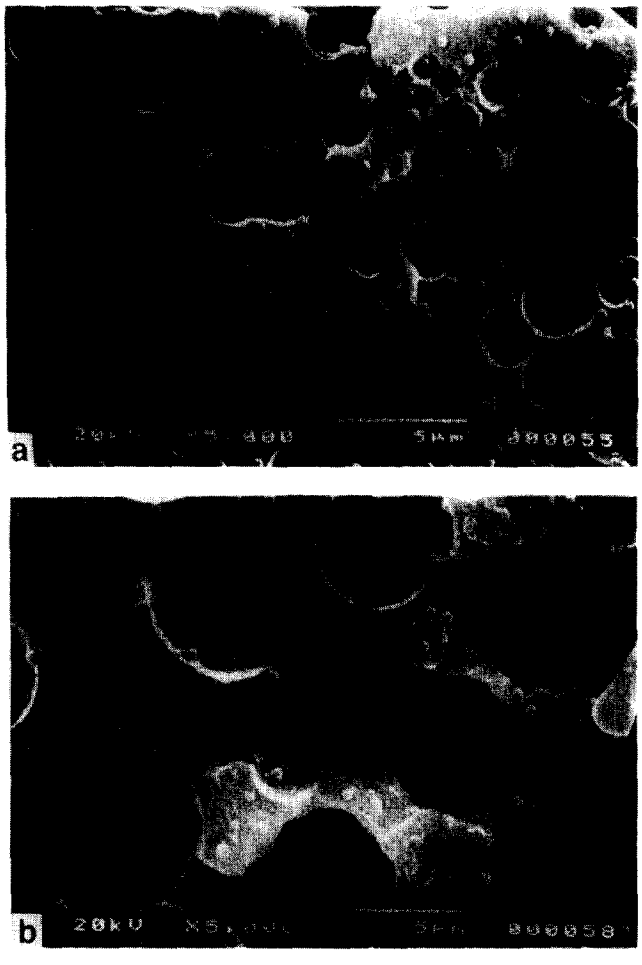

Figure 9 Scanning electron micrographs of blends microtomed at room temperature and selectively etched with boiling toluene: (a) 15/85; (b) 25/75

$$-(CH_2-CH_2)_n-(CH_2-\underset{\underset{COOEt}{|}}{CH})_{1-n}+PET\text{–}COOH$$

$$\rightarrow -(CH_2-CH_2)_n-(CH_2-\underset{\underset{COOH}{|}}{CH})_{1-n}+PET\text{–}COOEt \quad (1b)$$

In the present study, no catalyst has been added but the presence of residual catalyst in the starting polymers cannot be excluded.

The subject of blend compatibilization via trans-esterification reactions has been reviewed recently[4]. The interpolymer reactions (1a) and (1b) lead to grafting at the interface of PET/PEEA. This explains the good mechanical properties of blends and the morphological findings. It is well documented in the literature that ultimate properties, and especially ε_b, are very sensitive to phase adhesion or partial miscibility at the interface of blend components in phase separated systems[17,18]. Direct *FT*i.r. evidence for such interchange reactions cannot give unambiguous results since both reactants and products belong to the same class of compounds. However, indirect evidence provided by the *FT*i.r. examination of extracts of blends is given below. It is logical that reactive compatibilization should depend on mixture composition determining the stoichiometric ratio [OH]/[COOEt] of the two components. When this ratio is close to unity, grafting efficiency is increased and the amount of material extracted with boiling toluene is lower. Extraction experiments gave the results presented in *Table 3*. As shown in *Table 3*, the extracted material in all blends is less than the amount of PEEA used in their preparation. This is an indication that the 'missing' PEEA has been grafted onto PET.

Table 3 Results of extraction experiments

Blend	[OH]/[COOEt]	Material extracted (wt%)
5/95	1.05	1
15/85	0.315	5
25/75	0.166	20
50/50	0.055	disintegration

The results are in the right direction, and the higher amount of material removed at stoichiometric ratios other than unity, in combination with d.m.a. and tensile property results, indicates that a small quantity of PEEA is adequate to bond the two blend components by grafting at the interface. Toluene extracts of blends were examined with *FT*i.r.

The extracts contained both PEEA and traces of PET since the spectra showed the C–O absorption of PEEA at 1176 cm^{-1} and the C–O absorption of PET[19] at

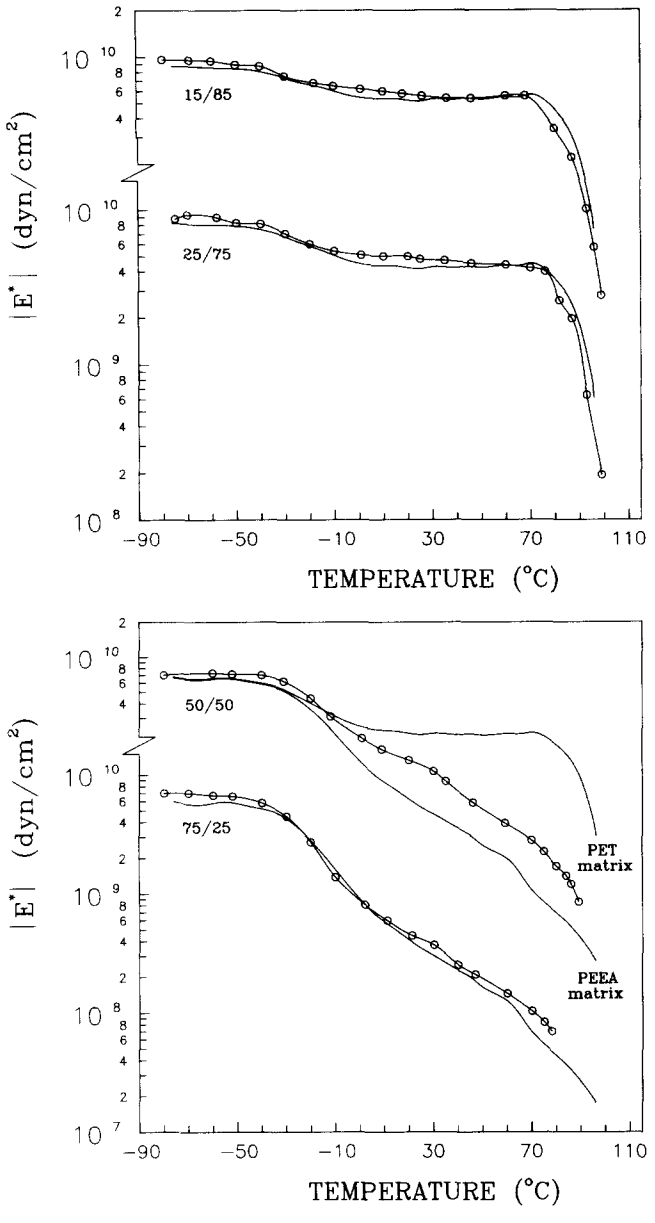

Figure 10 Prediction of the temperature dependence of complex modulus $|E^*|$ using Kerner's model, equation (2), for the indicated compositions: (○) experimental; (—) calculated. For the 75/25 blend, PEEA was assumed to be the matrix

1266 cm^{-1} and 1098 cm^{-1}. The C–H bending of the terephthalic unit at 794 cm^{-1} (used as an internal standard by Padbjo and Ward[20]) shifted to 807 cm^{-1} in the difference spectrum of the blend extract minus PEEA component. This may indicate that extracts contain not only a mixture of PEEA and PET oligomers but also graft products of the two blend components.

The spherical shape of the dispersed particles shown by SEM and their excellent adhesion established by the tensile testing led us to believe that Kerner's mechanics model[21] could be tested to correlate the moduli of the blends with those of their pure components. The complete equation is given by[22]:

$$E = E_c\left[\frac{\phi_d E_d}{(7-5\nu_c)E_c+(8-10\nu_c)E_d}+\frac{\phi_c}{15(1-\nu_c)}\right]\Bigg/\left[\frac{\phi_d E_c}{(7-5\nu_c)E_c+(8-10\nu_c)E_d}+\frac{\phi_c}{15(1-\nu_c)}\right] \quad (2)$$

where ϕ is volume fraction, ν is the Poisson ratio, E is the complex modulus of the blend $|E^*|$, and indices c and d signify the continuous (matrix) and dispersed phases, respectively. Values used for density (d) and ν were; d(PET) = 1.40 g cm^{-3}, d(PEEA) = 0.93 g cm^{-3}, ν(PET) = 0.33 and ν(PEEA) = 0.45. *Figure 10* 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 takes place. The success of the model indirectly supports the excellent adhesion between phases, since this is a necessary assumption for its applicability.

CONCLUSIONS

PET may be reactively compatibilized with PEEA at elevated temperatures and prolonged mixing time. This is the result of a transesterification reaction and leads to mechanically compatible heterophase blends with excellent tensile properties at low (5–25 wt%) PEEA (acrylate) contents. At the other end of the composition range, flexible blends with spherical PET inclusions are formed.

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