S0032-3861(96)00617-9

Polymer Vol. 38 No. 5, pp. 1057–1064, 1997

0032-3861/97/$17.00 + 0.00

Property–composition dependence of poly(ethylene terephthalate)/poly(ether ester) blends

Dimitrios S. Skafidas and Nikos K. Kalfoglou*
Department of Chemistry, University of Patra, 26500 Patra, Greece
(Received 12 February 1996; revised 27 May 1996)

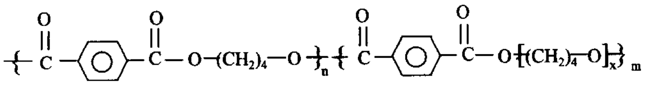
The compatibility of melt-mixed blends of poly(ethylene terephthalate) (PET) with two types of poly(ether esters) (PEE) was studied over the complete composition range. The PEE used had a low (PEE-s) or a high (PEE-h) content of hard butylene glycol terephthalate (4GT) sequences. The techniques applied were dynamic mechanical analysis (d.m.a.), d.s.c., tensile testing and optical microscopy. Both blend series showed good tensile properties and this was attributed mainly to the miscibility of the segregated $(4GT)_n$-domains in PEE with PET. As the d.m.a. study indicated, miscibility was higher in PET/PEE-h than in PET/PEE-s blends. Depending on blend composition, the PET/PEE-s system showed a wide spectrum of tensile properties spanning thermoplastic, at high PET contents, to self-reinforcing elastomeric behaviour at the other end of the scale of compositions. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: PET; poly(ether ester) blends; compatibility of PET)

INTRODUCTION

Poly(ether ester) (PEE) copolymers consisting of soft segments of polyethers and hard crystalline segments of polyesters have been classified as block copolymers[1–4], the implication being that there is phase separation into crystalline and soft domains, the former providing thermolabile physical crosslinks. This concept was later modified since experimental evidence indicated a structure characteristic of semicrystalline copolymers[5]. These engineering self-reinforcing thermoplastics have gained considerable applicability since, depending on the polyether–polyester ratio, they exhibit a wide range of elastoplastic mechanical behaviour combined with solvent resistance, thermal stability and ease of melt processability[4].

A typical PEE can be considered as being formed by randomly joining soft poly(tetramethylene ether glycol terephthalate) $(PTMEG\text{-}T)_m$ and hard poly(tetramethylene glycol terephthalate) $(4GT)_n$ segments, as follows:



In the context of blend compatibility the above structure of PEE offers some interesting possibilities via the electron donor capability of the carbonyl and ether groups, leading to donor–acceptor intermolecular interactions[6] with other ‘complementary dissimilar’ polymers.

In addition, the partial segregation of crystalline $(4GT)_n$ domains may lead to athermal mixing with the related poly(butylene terephthalate) (PBT) and possibly with poly(ethylene terephthalate) (PET), the latter via π-electron interactions[7] between the terephthalate residues present in both blend components.

Previous work on PEE blends includes the study of PEE/PVC[8,9] and PEE/chlorinated PE (CPE)[10], in which the acidic α-hydrogen of the chlorine-containing polymer led to miscible compositions with PEE of low $(4GT)_n$ contents and with CPE of high chlorine contents. PEE/PBT blends have been studied by numerous workers[11–14]. Of interest to this work is the report by Runt *et al.*[15] who studied the miscibility of PEE/PBT blends using PEE with different $(4GT)_n$ contents. Miscible compositions were obtained at high crystalline $(4GT)_n$ contents. On the basis of thermal and spectroscopic evidence, this was attributed to cocrystallization of components due to structural similarity. Most recently the compatibility behaviour of melt-mixed PEE/poly(carbonate) (PC) blends was investigated[16] with differential scanning calorimetry (d.s.c.) and dynamic mechanical analysis (d.m.a.). In addition to the high PEE compositions (80 wt%), blends were reported to be miscible in the melt and when quenched to room temperature; the latter was attributed to kinetic factors hindering phase segregation. This report quotes additional studies on PEE blends with polyamides (nylon-6) and hydrogenated styrene–butadiene–styrene copolymer (SEBS).

The present study covers the compatibility behaviour of PET/PEE blends using two grades of PEE differing in their $(4GT)_n$ content. The choice of the binary system was based on considerations related to polymer–polymer miscibility (see above) and the study covered the complete composition range. If mechanically compatible, the soft PEE would improve the impact properties of PET. An

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* To whom correspondence should be addressed

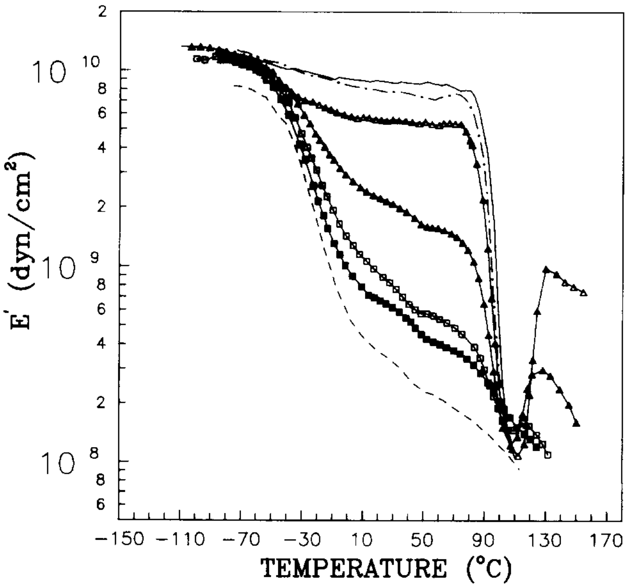

Figure 1 Temperature dependence of storage modulus E' of PET/PEE-s blends: (—) 100/0; (– · –) 90/10; (△) 75/25; (▲) 50/50; (□) 25/75; (■) 10/90; (– –) 0/100

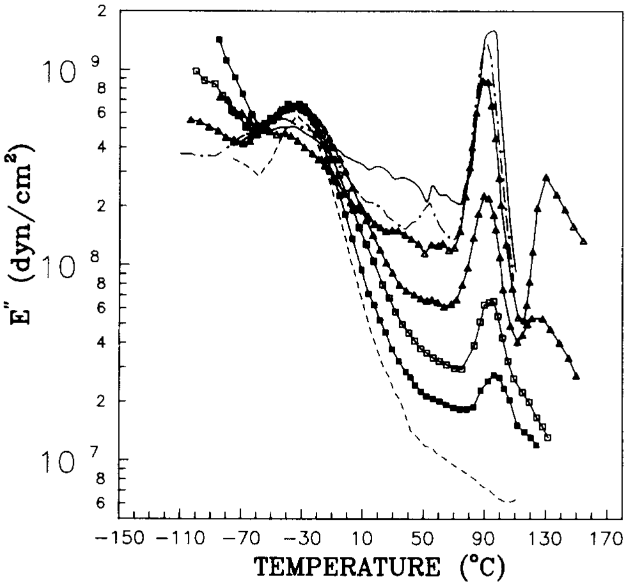

Figure 2 Temperature dependence of loss modulus E'' of PET/PEE-s blends: (—) 100/0; (– · –) 90/10; (△) 75/25; (▲) 50/50; (□) 25/75; (■) 10/90; (– –) 0/100

additional incentive was to find new avenues for the utilization of PET which is increasingly available as a recycled thermoplastic. Melt-mixed blends were studied with d.s.c., d.m.a., tensile testing and optical microscopy.

Table 1 Temperatures (°C) of main relaxations of PET/PEE blends[a]

Composition	PET α	PET β	PEE β
PET/PEE-s			
100/0	94	−40	–
90/10	92	−44	–
75/25	92	−41	–
50/50	92	−34	−33
25/75	93	–	−34
10/90	96		−34
0/100		–	−32
PET/PEE-h			
75/25	85	−60	38
50/50	84	−50	43
25/75	–		41
0/100		–	34
50/50[b]	89	−50	40
25/75[b]	89		38

[a] Melt-mixed at 285°C and quenched at 0°C
[b] Melt-mixed at 265°C

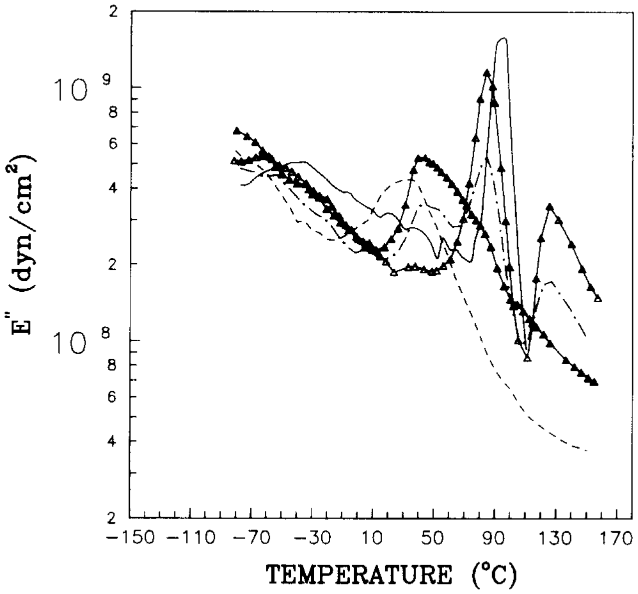

Figure 3 Temperature dependence of loss modulus E'' of PET/PEE-h blends: (—) 100/0; (△) 75/25; (– · –) 50/50; (▲) 25/75; (– –) 0/100

EXPERIMENTAL

Materials and preparations

PEE ('Hytrel') was supplied by the Elastomers Department, Du Pont (UK) Ltd. The 'hard' grade (PEE-h) contained ca 84 wt% and the 'soft' grade (PEE-s) *ca* 44 wt% $(4GT)_n$ units. $M_n = 2.5\text{–}3.0 \times 10^4\,\mathrm{g\,mol^{-1}}$. In PEE-s, in both $(4GT)_n$ and $(PTMEG\text{-}T)_n$ segments (see above), terephthalate units were replaced by isophthalate to the extent of 15 wt%. PET was extrusion grade, obtained from AKZO Plastics b.v. (Arnite D02 300). It was reported to have predominantly terminal hydroxyl groups and an $M_n = 24\,000\,\mathrm{g\,mol^{-1}}$. Materials were dried for 12 h *in vacuo* at 105°C (PEE) and 150°C (PET).

Blends were prepared by melt-mixing at 285°C using a CSI Max Mixing Extruder, Model CS-194 AV at *ca* 100 rpm. PET/PEE-s compositions (w/w) prepared under these conditions were 0/100, 10/90, 25/75, 50/50, 75/25, 90/10 and 100/0; for PET/PEE-h blends, compositions were 0/100, 25/75, 50/50, 75/25 and 100/0; two of the latter, 50/50 and 75/25, were also prepared at a lower temperature (265°C) to ascertain the influence of this parameter.

Films were prepared by compression moulding between Teflon sheets at *ca* 285°C and $50\,\mathrm{kg\,cm^{-2}}$, followed by pressure release and quenching at 0°C.

Apparatus and procedures

Optical micrographs were obtained with an Olympus BH-2 microscope. Specimens were prepared by melt

Table 2 Thermal properties of PET/PEE blends

Composition PET/PEE-s	T_m (°C) PET	T_m (°C) PEE	Crystallinity (%) PET	Crystallinity (%) PEE
100/0	255	–	19.6	–
90/10	252	–	25.6	0.0
75/25	252	150	24.7	1.6
50/50	251	150	19.9	4.8
25/75	250	148	10.1	8.3
10/90	250	148	3.4	10.7
0/100	–	150	–	12.3
PET/PEE-h				
75/25	252	218	22.0	7.2
50/50	252	218	19.8	13.4
25/75	251	217	7.3	20.6
0/100	–	220	–	32.1

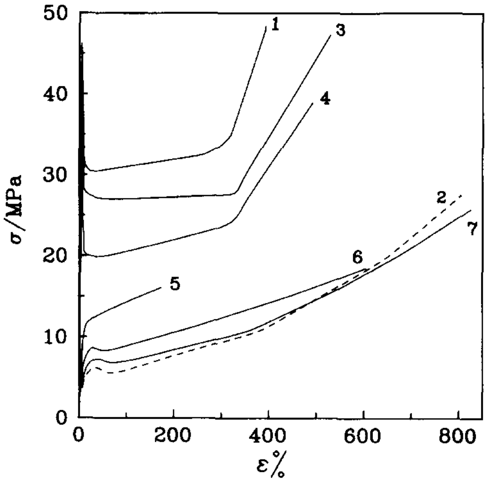

Figure 4 Stress–strain properties of PET/PEE-s blends: 1, PET; 2, PEE-s; 3, 90/10; 4, 75/25; 5, 50/50; 6, 25/75; 7, 10/90

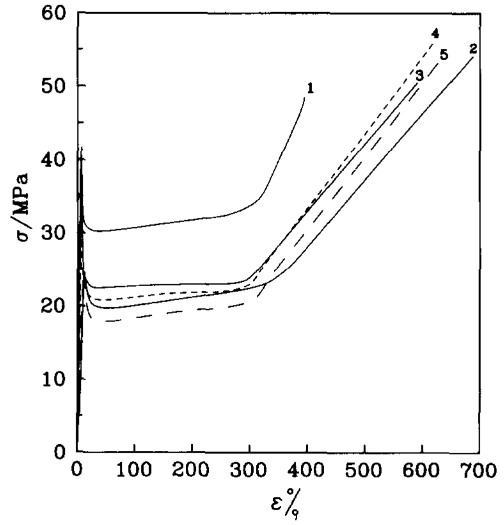

Figure 5 Stress–strain properties of PET/PEE-h blends: 1, PET; 2, PEE-h; 3, 75/25; 4, 50/50; 5, 25/75

pressing blends between the cover glass and microscope slide and quenching to 25°C. D.m.a. data complex modulus $|E^*|$ and $\tan\delta$ were determined at 110 Hz between *ca* −100 and 120°C using a Rheovibron Model DDVII-C, Toyo Baldwin.

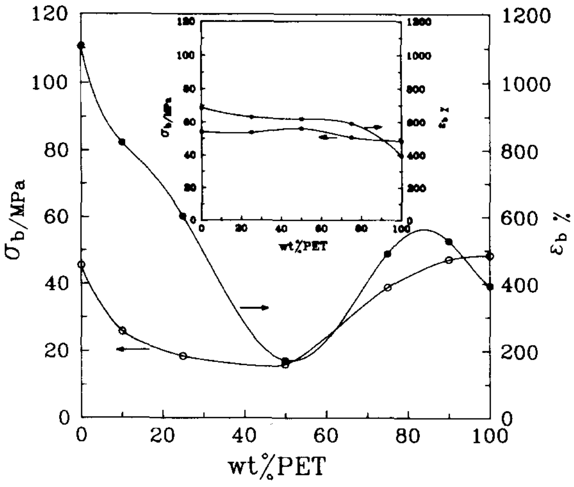

Figure 6 Composition dependence of ultimate properties of PET/PEE-s blends. Inset: PET/PEE-h blends

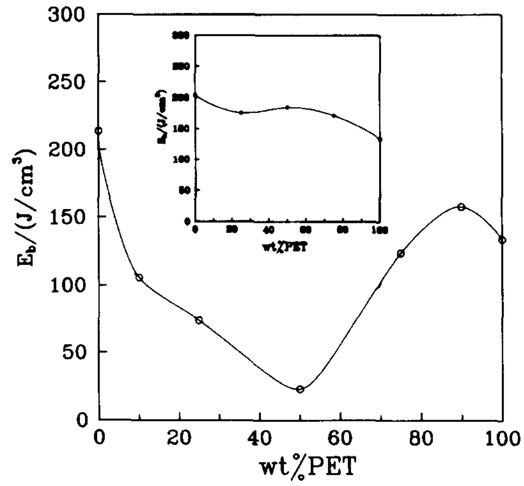

Figure 7 Composition dependence of energy to tensile failure of PET/PEE-s blends. Inset: PET/PEE-h blends

Specimen dimensions were 30 × 3 × 0.4 mm^3.

D.s.c. measurements were performed with a Du Pont 910 calorimeter coupled with a 990 programmer recorder. Nominal weight was *ca* 10 mg. Heating rate was 10°C min^{-1} for T_g and T_m determination and 20°C min^{-1} for crystallinity measurements. The heating cycle applied was: 25°C → 280°C (1 min) → −90°C → 290°C. T_g and T_m were determined during the last heat scan.

Tensile tests were performed at a crosshead speed of 10 cm min^{-1}, at 23°C, according to ASTM D 882, using a J.J. Tensile Tester type T5001 and rectangular strips measuring 40 × 6.5 × 0.5 mm^3.

RESULTS

Dynamic mechanical analysis

The dynamic mechanical behaviour of PEE is well documented[17,18]. The main T_g relaxation (β) is attributed to soft phase shifts to higher temperatures as the $(4GT)_n$ content increases; T_g of PEE-s and PEE-h is at −32°C and 34°C, respectively. Annealing of PEE-h was observed[17] to cause a new peak to appear at *ca* 150°C due to crystallization and extensive segregation of the $(4GT)_n$ sequences.

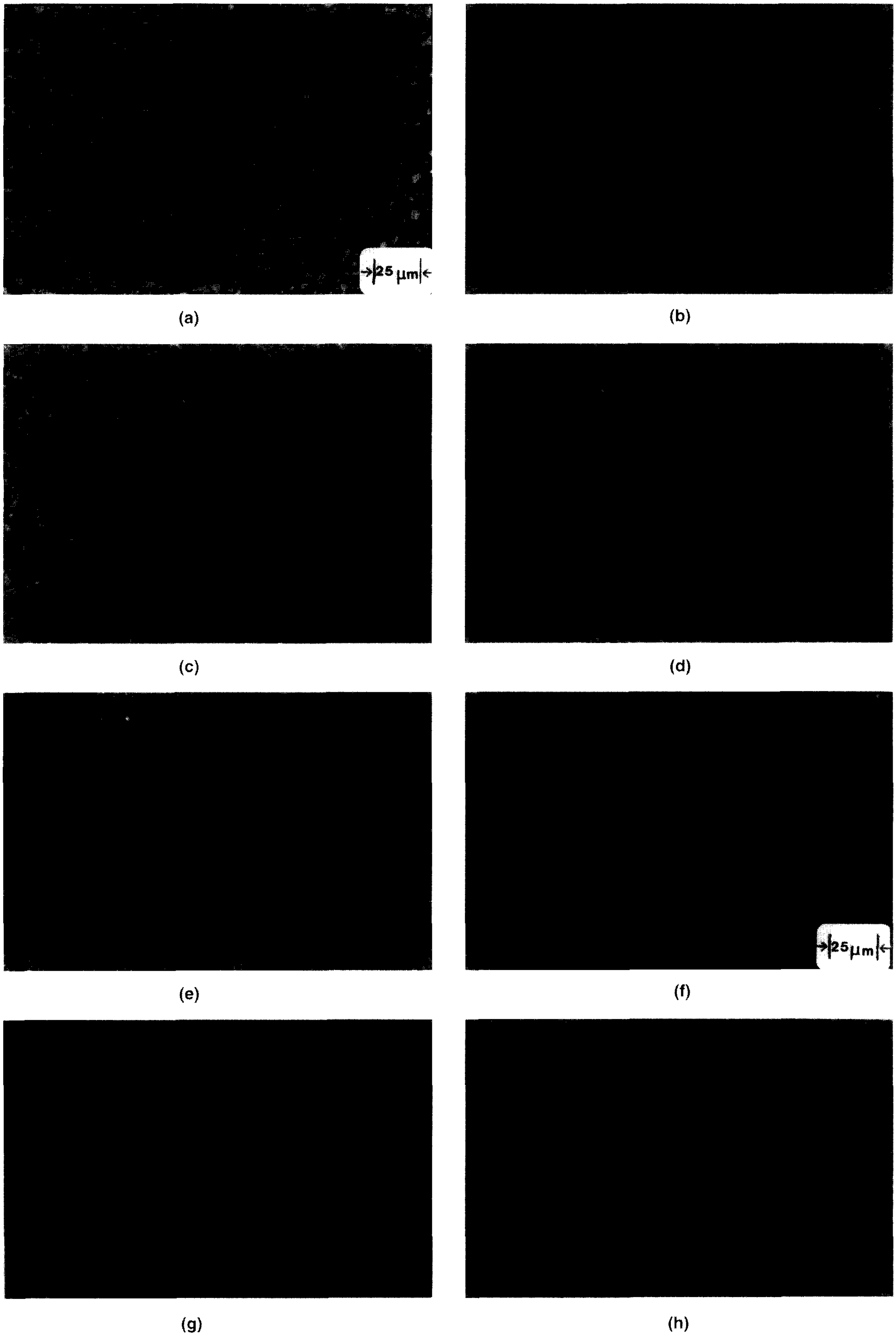

Figure 8 Phase-contrast micrographs of PET/PEE-s blends: (a) 90/10; (b) 75/25; (c) 50/50; (d) 25/75; (e) 10/90. PET/PEE-h blends: (f) 15/25; (g) 50/50; (h) 25/75

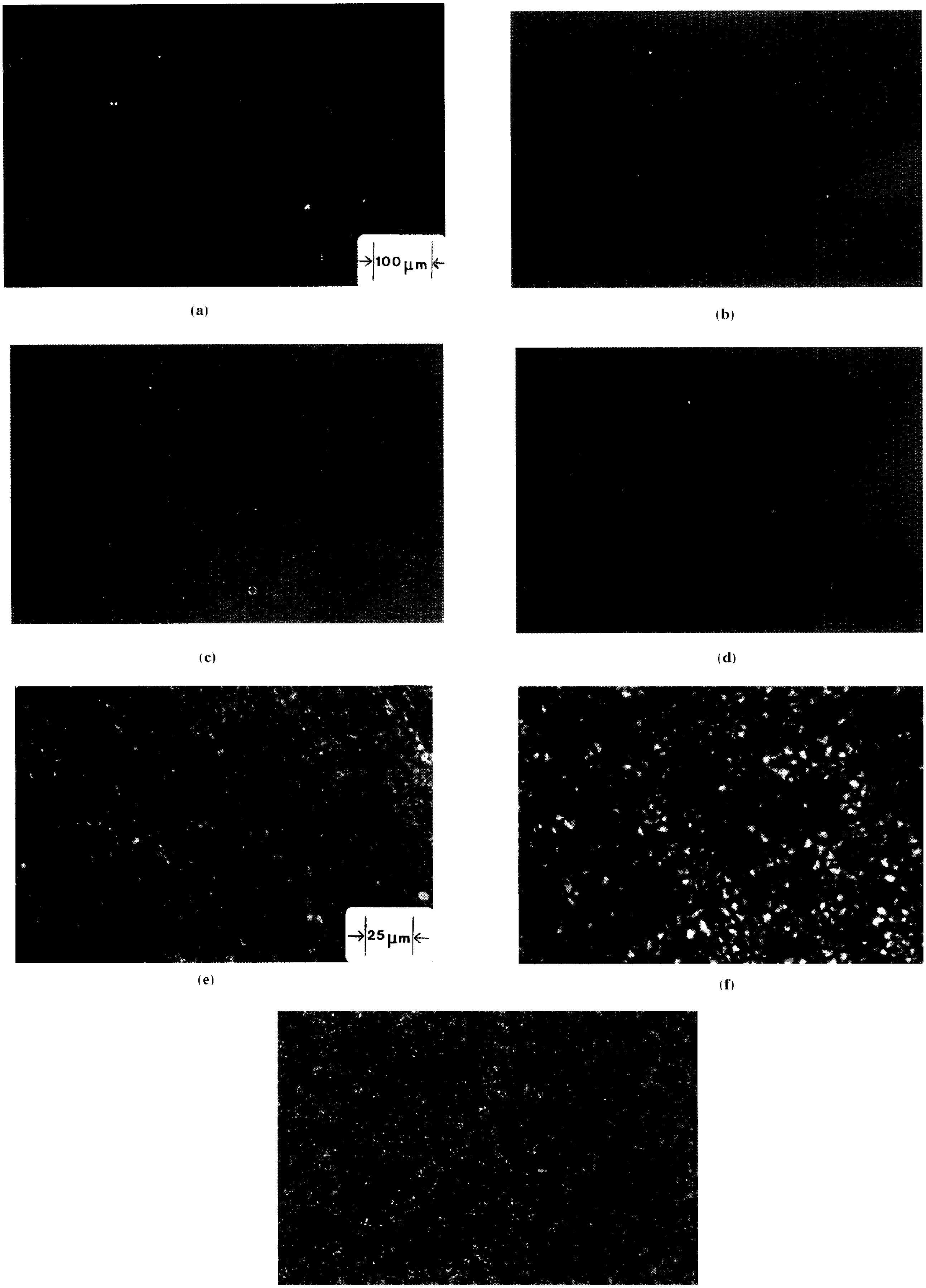

Figure 9 Optical micrographs with crossed polars of PET/PEE-s blends: (a) 90/10; (b) 75/25; (c) 50/50; (d) 25/75. PET/PEE-h blends: (e) 75/25; (f) 50/50; (g) 25/75. (Each blend series at the same magnification)

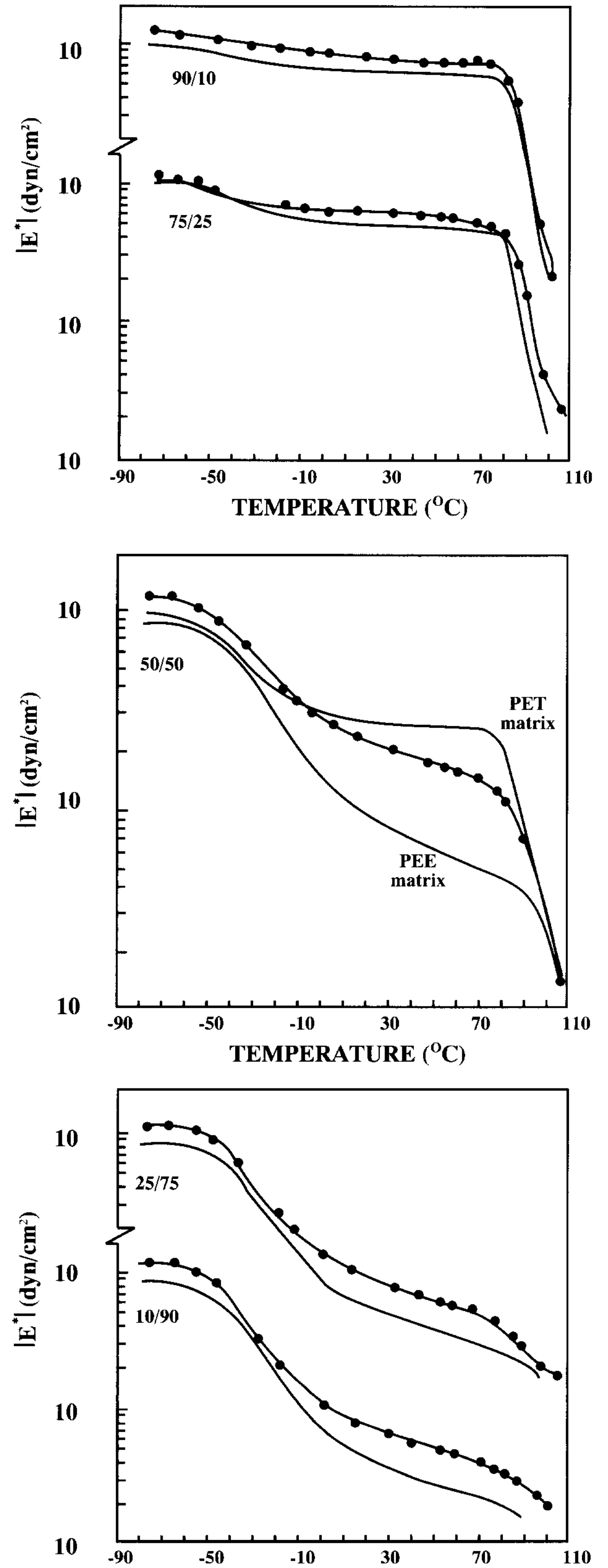

Figure 10 Prediction of the temperature dependence of complex modulus $|E^*|$ of PET/PEE-s blends using Kerner's model, for the indicated compositions: (O) experimental; (—) calculated. For 25/75 and 10/90, PEE-s was assumed to be the matrix

D.m.a. data of PET have been reviewed in detail[19]. Both the T_g (α) and β relaxations have been attributed to the amorphous component and are affected by the degree of crystallinity. A small relaxation preceding the α peak has been attributed to an orientation effect[20]. *Figures 1* and *2* summarize the results in terms of the temperature dependence of the storage E' and loss modulus E'', respectively, of PET/PEE-s blends. *Table 1* lists the temperatures of the main relaxations observed for all the blends studied.

Increasing the amount of polyester in the PET/PEE-s blend (see *Figure 1*) causes a gradual modulus decrease typical of 'plasticization'. The appearance of a 'hump' above *ca* 110°C is due to cold crystallization of the PET component during the heat scan and has been observed under similar conditions in other PET blends[21]. Inspection of *Figure 2* does not reveal blend miscibility since both pure component relaxations retain essentially their original position in the temperature scale; see also *Table 1*. However, the small mutual shift of the β relaxations signifies limited mixing of the amorphous components in the blend. Though the proximity of the β peaks does not allow a more definitive statement, it is significant to note that only one β peak is discernible in these blends. A significant degree of miscibility, possibly at the components' interphase, is observed in PET/PEE-h blends where both main relaxations approach each other (see *Figure 3* and *Table 1*), and at the 25/75 composition a single relaxation is observed. However, its non-symmetric and broad shape—the result of two peaks nearly merging—is typical of a nearly but not completely miscible blend.

In the case of PET/PEE-h blends mixed at a lower temperature (265°C), the temperature shifts of the main relaxations at the corresponding compositions are smaller (see *Table 1*), attesting to the significant effect of the mixing temperature (see last section).

Thermal properties

T_m and crystallinity data are summarized in *Table 2*. The non-linear dependence of crystallinity of each component on blend composition suggests significant crystalline–crystalline interactions. The data show a significant crystallization synergy of PEE-s towards PET. Apparently, during the thermal scan of quenched blends, PEE-s in small amounts serves as a nucleating agent for PET. Larger amounts of each component hinder crystallization of the other blend partner. *Table 2* shows a systematic T_m depression of PET with composition in PET/PEE-s blends, tentatively attributed to morphological factors.

Tensile properties

Large deformation behaviour is quite sensitive to interphase adhesion[22,23] and the results are summarized in *Figures 4* and *5*, in terms of stress–strain properties, for the PET/PEE-s and PET/PEE-h, respectively. *Figure 4* differs in character from *Figure 5* in that the former shows a wide spectrum of tensile behaviour typical of self-reinforcing block copolymer for rich PEE-s blends and the thermoplastic character of PET-rich blends at the other extreme. In the case of PET/PEE-h blends, tensile behaviour is bracketed by that of their pure components. In *Figure 6* the composition dependence of ultimate properties shows a minimum at the 50/50 composition—typical of a phase-separated system; however, the level of properties even at this composition is satisfactory, indicating good interphase adhesion. Of significance is the improvement of tensile properties at low PEE-s levels. In the case of PET/PEE-h blends (see *Figure 6* inset) properties vary almost linearly with composition—a behaviour typical of miscible blends. Note that some synergism in the energy to tensile failure E_b at low PEE-s contents is observed in *Figure 7*. This quantity is obtained as the area under the stress–strain curve and was plotted as a function of blend composition. Frequently E_b may give a measure of impact strength; hence, PEE-s, when added in small amounts, is expected to improve the impact properties of PET.

No such behaviour was observed for PET/PEE-h blends (*Figure 7* inset); nevertheless, the E_b level of PET-rich blends is improved due to the self-reinforcing elastomeric character of the PEE-h component.

Morphology

Optical microscopy results are given in *Figures 8* and *9* with the phase-contrast and crossed-polars arrangement, respectively, for both blend series. Given the higher refractive index of PET compared to PEE, at positive phase-contrast, the dark areas in *Figure 8* should correspond to the former component. PET/PEE-s (see *Figures 8a–e*) are phase separated and phase distribution becomes coarser at the 50/50 composition where matrix inversion takes place (see last section) and at high PEE contents (10/90 blend), where PET is dispersed into the PEE matrix (*Figures 8c* and *8e*, respectively). A more uniform dispersion is obtained with PET/PEE-h blends (see *Figures 8f–h*). Examination with crossed polars (see *Figure 9*) indicates that even in quenched blends crystallinity develops in PEE-s (see *Figure 9a*). This provides nuclei for PET crystallization (see above). At increased PEE-s contents (*Figures 9b*, *d*), sample crystallinity is drastically reduced except for the 50/50 composition (*Figure 9c*)—the result of a coarse phase distribution facilitating limited crystallinity development. In PET/PEE-h blends (*Figures 9e–f*), crystallization is extensive and the Maltese cross is discernible at the 50/50 composition.

DISCUSSION

In both series of PET/PEE blends studied, d.m.a. results suggest a phase-separated system, especially for the PET/PEE-s blend. The mutual displacement of the main viscoelastic relaxations indicate a mixed phase formation (or partial miscibility) for the PET/PEE-h system, where increased amounts of $(4GT)_n$ sequences are available. In these PEE copolymers these sequences (which are equivalent to the basic repeat unit of PBT) are to some extent segregated. Therefore it is reasonable to adopt the view that miscibility between PET and $(4GT)_n$ takes place in the same sense that this happens in the PET/PBT blend. The latter system shows miscibility[24,25] in the complete composition range and this has been attributed to weak intermolecular π-electron interactions. Increase of the $(4GT)_n$ content of PEE leads to an increased degree of partial miscibility, as shown by the increased shift of the d.m.a. spectra in the PET/PEE-h blends. Consequently, in both blend series, the PET–$(4GT)_n$ interaction leads to good interface adhesion, leading in turn to good tensile properties. Of relevance is the application of the technique proposed by Rellick and Runt[26] to the PET/PEE-h blends, yielding the amount of each component that 'migrated' through miscibility into the other phase, using the d.m.a. spectra displacement. Calculation showed that in PET/PEE-h blends, at the 75/25 and 50/50 compositions, the PET phase contains 12 wt% and 14 wt% PEE-h, respectively.

Another possibility that should be considered as a possible cause for partial miscibility is the compatibilization brought about by possible transesterification reactions during melt mixing according to the following scheme:

$$\begin{aligned} &\text{PBT-CO}\!+\!\text{O(CH}_2)_4\text{O}\!+\!\text{PTMEGT} \\ &+\text{PET-CO}\!+\!\text{O(CH}_2)_2\text{O}\!+\!\text{PET}' \\ &\rightleftharpoons \text{PBT-CO}\!+\!\text{O(CH}_2)_2\text{O}\!+\!\text{PET}' \\ &+\text{PET-CO}\!+\!\text{O(CH}_2)_4\text{O}\!+\!\text{PTMEGT} \end{aligned}$$

This may take place to some extent, as the results on the temperature dependence of mixing on the d.m.a. spectra shifts of the PET/PEE-h blends indicate (see *Table 1*). However, these results could also mean a more efficient mixing. Given the high mixing temperature (285°C), one referee has suggested that ester exchange reactions may not be excluded, since this has been observed[27] among PET chains at comparable heating times. Though one cannot exclude this possibility, we have to consider the behaviour of a related binary blend, e.g. PET/PBT. The available data are reviewed by Porter and Wang[28] and support the view that longer mixing times are required for transesterification to take place to an appreciable extent. However, lower temperatures of mixing were reported. Avramova[25], in her study of melt-mixed PET/PBT blends at 310°C for 30 s (comparable to our mixing time), reported no interchange reactions. Since direct *FT* i.r. evidence for such interchange reactions cannot give unambiguous results, because both reactants and products belong to the same class of compounds, we have to rely on the thermal transitions observed (*Tables 1* and *2*). T_m depression of components was negligible in PET/PEE-h blends where miscibility (based on T_g shift) was greatest. In the case of PET/PEE-s, transesterification is more limited since the main viscoelastic transition of PET was unaffected by the change in blend composition. Also, as a result of the decreased amount of $(4GT)_n$ sequences, miscibility is less favoured, and it is reported[28] that transesterification is facilitated when the blend partners are initially compatible. It is therefore suggested that interchange reactions, if any, take place to a very small extent.

An attempt to apply the homopolymer–copolymer theory[29] in order to interpret miscibility gave results incompatible with the experimental findings[30]. This is attributed to the non-random character of PEE copolymers.

Given the phase-separated nature of PET/PEE-s blends, and to confirm the good interphase adhesion, we successfully applied Kerner's model[31] assuming a spherically dispersed phase. The results (see *Figure 10*) correctly predict blend moduli when PET is the matrix at compositions ϕ (PEE-s) < 0.50; where ϕ is the volume fraction of the dispersed phase. At the 50/50 composition, matrix inversion takes place and at higher PEE concentrations the PEE-s serves as the matrix. This is in agreement with tensile properties (see *Figure 7*), which pass through a minimum at the 50/50 composition. At high and low PET contents, blends deform in a manner determined by their matrix; correspondingly, they are like thermoplastics or self-reinforced elastomers.

CONCLUSIONS

(1) Melt-mixed PET/PEE blends show a wide spectrum of mechanical properties which depend on PEE structure and blend composition.

(2) Differentiation between PEE types (PEE-s vs PEE-h) is caused by their differing $(4GT)_n$ content influencing the degree of component miscibility.

(3) Miscibility between the segregated $(4GT)_n$ sequences and PET causes partial blend miscibility, leading to good tensile properties. This is also supported by the d.m.a. results.

ACKNOWLEDGEMENT

This work was supported in part by a Brite–Euram 0430-CT91 grant.

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