Compatibility of poly(ether ester) block copolymers with chlorinated polyethylene

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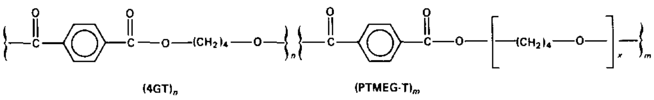
The compatibility of chlorinated polyethylene containing 48 and 25 wt% Cl (CPE 48 and CPE 25) with a poly(ether ester) block copolymer (PEES) was studied over the complete composition range. The compatibility of CPE 48 with poly(butylene terephthalate) (PBT) at the 50/50 composition was also studied. The techniques used were dynamic mechanical analysis (d.m.a.), differential scanning calorimetry (d.s.c.) and tensile testing. Fire retardancy tests were also performed on PEES/CPE 48 blends. The results indicated miscibility of PEES/CPE 48 at all compositions and allowed the determination of the LCST. CPE 25 was partially miscible while the crystalline component of PBT was immiscible with CPE 48. Thus, miscibility can be traced to amorphous polyether and polyester groups interacting with proton-donating CPE. Tensile properties of PEES/CPE 48 blends are good and constant beyond the 25 wt% CPE level. These blends are self extinguishing at high CPE levels. Miscibility of blends was rationalized using the copolymer–copolymer miscibility theory in combination with solubility theory.

(Keywords: miscibility of blends; compatibility; poly(ether ester); thermoplastic; chlorinated polyethylene; poly(butylene terephthalate); blend miscibility prediction)

INTRODUCTION

Poly(ether ester) block copolymers comprising soft, long polyether segments and hard, short polyester blocks can be classed as thermoplastic elastomers[1–3]. The easily crystallizable polyester domains provide thermolabile physical crosslinks in analogy to other classes of block copolymers[4–6]. These polyether esters (PEES) can be considered as being formed by randomly joining head to tail poly(tetramethylene ether) glycol terephthalate (PTMEG-T) and hard 1,4-butanediol terephthalate (4GT) segments, as follows:



Due to the ester group, one might anticipate possible miscibility with chlorine-containing polymers[7,8]. Indeed evidence was presented by Nishi *et al.*[9] for partial miscibility with poly(vinyl chloride) (PVC). In that work, due to the slow cooling of melt-mixed blends to ambient temperatures, phase separation was inadvertently induced. (The same workers reported an upper cloud point beyond *ca.* 130°C). The present work examines the compatibility behaviour of a similar elastomeric PEES with chlorinated polyethylenes (CPE) which have certain advantages compared with PVC; they are thermally more stable, problems associated with PVC crystallinity can be avoided and at high chlorine contents their thermomechanical spectrum is simpler (lack of the β PVC relaxation). Another matter of interest is the question whether miscibility in these blends arises from the ester group and/or the poly(alkylene oxide) segment of the PEES[10]. In a recent study[11] involving linear poly(alkylene oxide)–PVC blends a considerable degree of compatibility was detected.

From the practical viewpoint, CPE is a commodity thermoplastic and possible compatibility with PEES would give a cheaper product, with enhanced fire resistance and without impairment of its elastomeric properties, since the CPE used had a T_g near ambient temperatures.

Blends were studied in the complete composition range using a CPE containing 48 (CPE 48) and 25 wt% Cl (CPE 25). A 50/50 poly(butylene terephthalate) (PBT)/CPE 48 blend was also studied to obtain information on the contribution to blend miscibility of the hard segment containing a higher amount of the ester group.

In the present study, films were prepared using a suitable procedure to avoid phase separation. Blends subjected to suitable thermal treatment were examined using the dynamic mechanical (d.m.a.), tensile testing and differential scanning calorimetry (d.s.c.) techniques.

EXPERIMENTAL

Materials and procedures. CPE 48 was obtained from Aldrich, Europe. G.p.c. measurements in tetrahydrofuran (THF) gave $\bar{M}_w/\bar{M}_n = 1.5$, $\bar{M}_n = 60\,000\ \mathrm{g\,mol^{-1}}$ and d was $1.25\ \mathrm{g\,cm^{-3}}$. D.s.c. measurements indicated that it was amorphous. CPE 25 had a 20–25% bulk crystallinity, $\bar{M}_w = 10^5\ \mathrm{g\,mol^{-1}}$ and $d = 1.08\ \mathrm{g\,cm^{-3}}$. The PEES (Hytrel®) was supplied by the Elastomers Department, DuPont (UK) Ltd. The M_w of PTMEG-T was reported to be *ca.* $1120\ \mathrm{g\,mol^{-1}}$ and that of 4GT $220\ \mathrm{g\,mol^{-1}}$. The copolymer consisted of 30 wt% 4GT units (68 mol%) and in both segments terephthalate units were replaced by isophthalate to the extent of 15 wt%; $\bar{M}_n = 2.5$–$3.0 \times 10^4\ \mathrm{g\,mol^{-1}}$ and $d = 1.17\ \mathrm{g\,cm^{-3}}$. PBT was obtained from Aldrich, Europe; $\bar{M}_n = 2.0$–$4.0 \times 10^4\ \mathrm{g\,mol^{-1}}$, $d = 1.31\ \mathrm{g\,cm^{-3}}$ and $T_m = 227°\mathrm{C}$.

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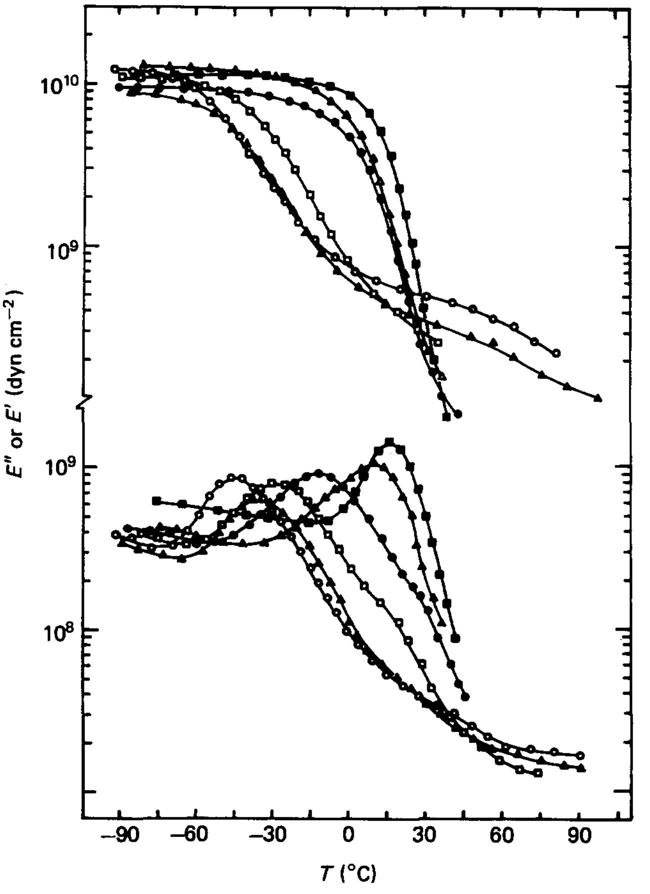


Figure 1 Thermomechanical spectra of PEES/CPE 48 blends: ○, 100/0; ▲, 90/10; □, 75/25; ●, 50/50; △, 25/75; ■, 0/100

Blends from PEES/CPE were prepared by dissolving in a common solvent (dichloromethane for CPE 48 and dichloroethane for CPE 25). Dibutyl tin dilaureate was added (2 wt%) as a thermal stabilizer. After solvent removal at room temperature with slow evaporation, films were dried in a vacuum oven at 60°C until constant weight. Two sets of films were tested; those prepared as above, and films obtained after compressing between Teflon sheets at 180°C and 15 MPa followed by quenching at 0°C. The latter procedure was needed for CPE 25 since complete dissolution was not obtained. For CPE 48/PBT, blends were prepared by dissolving each component separately in *N*-methyl pyrrolidone with heat (100°C for CPE 48, 160°C for PBT), and subsequently applying the procedure described in the literature[10]. Films were prepared by compression moulding at 240°C and quenching to 0°C.

For d.s.c. measurements specimens were tested after annealing at the desired temperature for 5 or 24 h, followed by quenching to *ca.* −70°C and heating to 180°C. This was followed by quenching to 0°C and a second heat scan.

The following compositions were studied for PEES/CPE 48: 100/0, 90/10, 75/25, 50/50, 25/75, 0/100; for PEES/CPE 25: 100/0, 75/25, 50/50, 25/75, 0/100; for PBT/CPE 48: 100/0, 50/50 and 0/100. (The second numeral denotes the percentage by weight of CPE.)

Apparatus. G.p.c. measurements at 25°C were carried out with a Waters Associates instrument (model 201). $\bar{M}_n$ was determined with a membrane osmometer (Knauer and Co.). D.s.c. data were obtained in a nitrogen atmosphere with a DuPont 910 calorimeter system coupled with a 990 programmer recorder. Calibration was made with indium standard. Sample weight was *ca.* 18 mg, heating rate 20°C min^{-1}. Dynamic viscoelastic data, mechanical loss tan δ and complex tensile modulus $|E^*|$, were obtained at 110 Hz. Specimen dimensions were $3 \times 0.30 \times 0.07$ cm^3. Tensile properties were obtained at room temperature using a J.J. tensile testing machine model T5001. Film strips measuring $60 \times 12 \times 0.6$ mm^3 were used at a crosshead speed of 420 mm min^{-1}. Flammability tests were carried out in a controlled mixture of oxygen–nitrogen according to ASTM D-2863-70 with specimen dimensions $7.0 \times 0.6 \times 0.3$ cm^3.

RESULTS

Dynamic mechanical properties

CPE 48 blends. The thermomechanical spectra in terms of storage (E') and loss modulus (E'') at isochronous conditions are given in *Figure 1*. The main relaxations for PEES have been studied before[12,13] and their origin has been described in the literature[14]. The main relaxation associated with T_g is located at *ca.* −47°C and arises from segmental motions within the soft phase, possibly the motion of the ether group of the PTMEG segment. Data on CPE48 are also in essential agreement with previous work[15]. By using solvent cast films of blends prepared at room temperature or melt pressed and rapidly quenched, phase separation induced by slow cooling through the LCST was avoided. Such a case was reported by Nishi *et al.*[9] for PEES/PVC blends. (In that work LCST was named as UCST contrary to conventional nomenclature.) D.m.a. results in *Figures 1* and *2* indicate miscibility between the amorphous components in the blend in the complete composition range. To verify whether a LCST exists for this system and if so locate it, d.m.a. spectra were also obtained at three compositions after annealing at various temperatures.

Indeed it was established that annealing at an elevated temperature induces phase separation and the results for

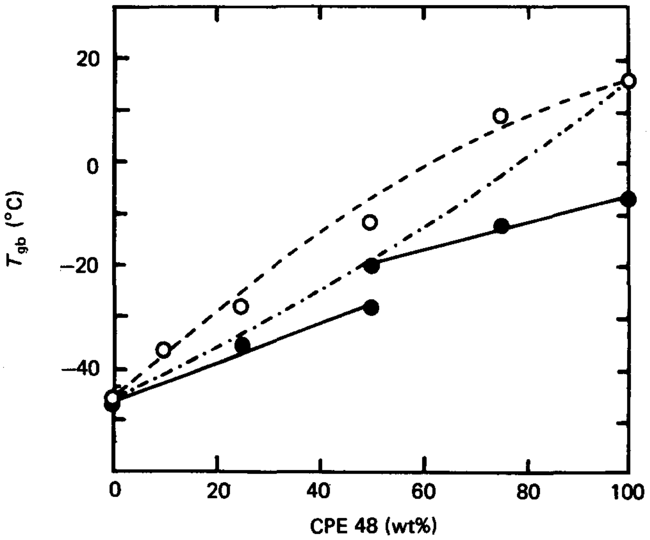


Figure 2 Composition dependence of T_{gb} of PEES/CPE48 (○) and PEES/CPE25 (●) blends: —·—, Fox relationship, $1/T_{gb} = W_1/T_{g1} + W_2/T_{g2}$; ---, Jenckel–Heusch and Kwei relationships (see text)

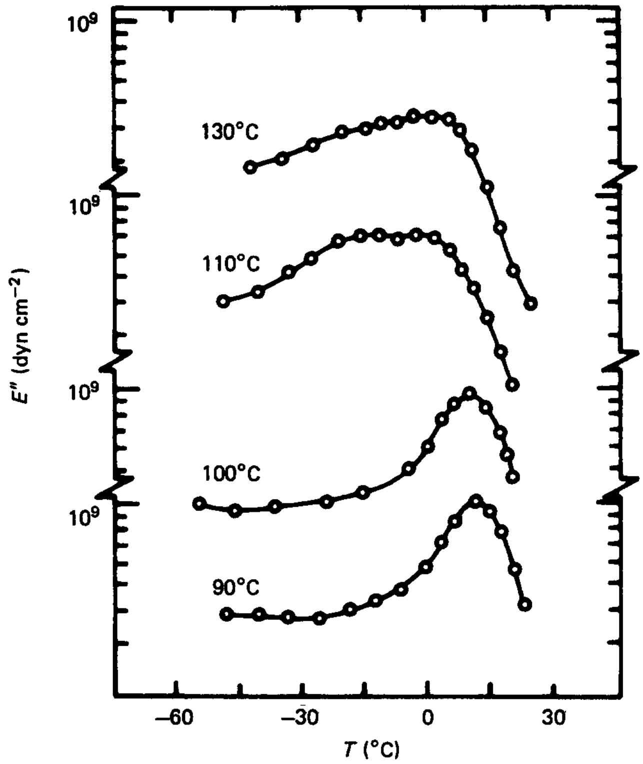


Figure 3 Effect of annealing on the thermomechanical spectrum of PEES/CPE 48 blend 25/75

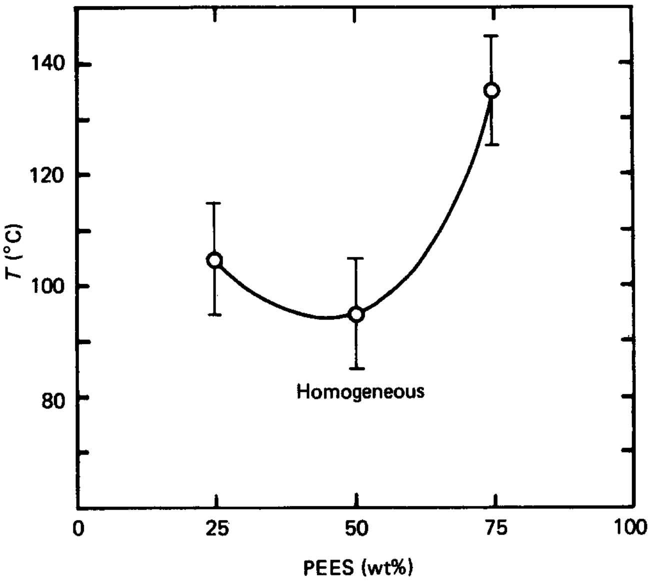


Figure 4 LCST of PEES/CPE 48 blends

one composition are given in *Figure 3*. These measurements allowed the determination of the LCST for this system (*Figure 4*). The curve is asymmetric with respect to composition. The technique, though laborious, is quite sensitive to polymer demixing at the segmental level[16] and can probe phase separation down to *ca.* 100 Å. It is also useful in cases where the optical method cannot be applied (semicrystalline specimens). Since no phase separation was detected when films were quenched to ambient temperature from melt, it is inferred that blends are also miscible in the melt.

CPE 25 blends. The data on these blends (*Figures 2* and *5*) suggest miscibility only at the extremes of composition. The 50/50 spectrum is characteristic of a partially miscible blend.

PBT/CPE 48 blends. The results from the 50/50 blend on tan δ indicate an incompatible system while E'' data are less discriminating (*Figure 6*). It is known that while tan δ values are in general influenced by crystallinity, E'' data are sensitive to the amorphous phase. These considerations support the view that while the amorphous phases have limited miscibility (both component peaks are discernible), the crystallizing portion of PBT does not mix with CPE 48. This is further supported by the negligible T_m depression of PBT by the CPE amorphous diluent.

Thermal properties

PEES homopolymer. To examine the effect of annealing, thermograms were obtained after annealing at various temperatures (*Figure 7*). At least one of the endotherms (T_2) is strongly influenced in position and magnitude by thermal history. The low temperature peak (T_1) in the vicinity of 40°C is most probably associated with the melting of the poly(tetramethylene oxide) (PTMO) segment. For low M_w PTMO, T_m was determined[11] to vary between 40°C (annealed) and 30°C (quenched) specimens. Low melting endotherms attributed to the PTMO sequence have been also reported for segmented polyurethanes[17]. Other endotherms (with increasing temperature) are identified as T_2'' (65°C), T_2' (82°C), T_2 (112°C), T_3 (135°C), T_4' (155°C) and T_4 (166°C). The T_2 shifts with annealing temperature and this can be explained if recent views on the morphology of PEES are taken into account[3,18,19]. Thus there exists a large variety of crystallizable species (segments of various lengths) within the soft domains, each having an optimum annealing temperature to

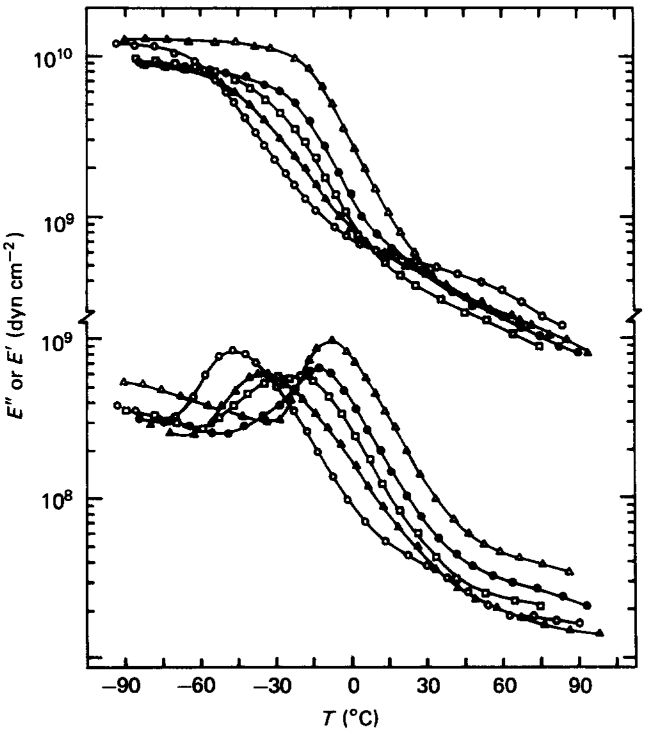


Figure 5 Thermomechanical spectra of PEES/CPE 25 blends: ○, 100/0; ▲, 75/25; □, 50/50; ●, 25/75; △, 0/100

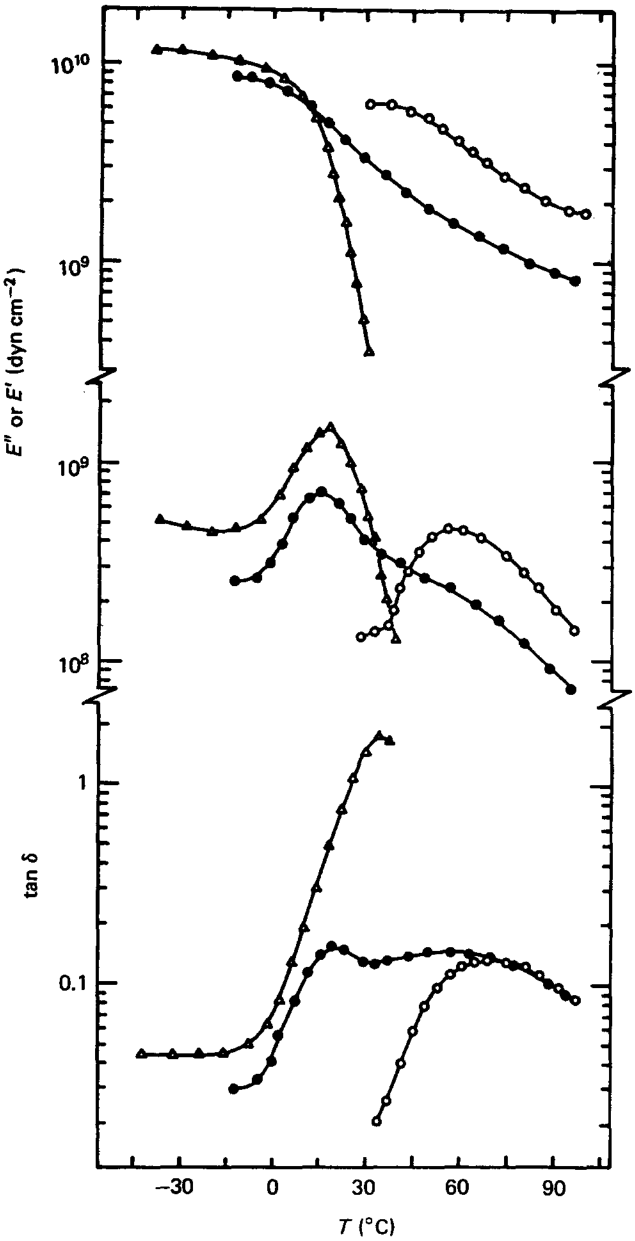


Figure 6 Thermomechanical spectra of PBT/CPE 48 blends: ○, 100/0; ●, 50/50; △, 0/100

develop. In addition various species can be perfected by recrystallization, e.g. $T_4' \rightarrow T_4$. The larger fraction of these corresponding to an average hard segment length of *ca.* 3 units melt at *ca.* 166°C in agreement with literature[2]. The situation is further complicated by the existence of isophthalate units which crystallize much slower than the regular terephthalate[17].

Quenching in liquid N_2 fractionates out the more imperfect crystals, thereby perfecting the T_4 peak (*Figure 7*).

When sufficient time is allowed for crystal perfection the amount of the original crystals formed (peak T_3) increases and concurrently crystals with T_4' reorganize to T_4 (*ca.* 166°C) (*Figure 7*).

The effect of scan speed (*Figure 7* (insert)) is to increase the T_4' peak while T_3 endotherm decreases. Thus it is to be concluded that the double peak (T_3, T_4') is not the result of crystal reorganization and corresponds to different crystallite distributions.

CPE 48 blends. In general the high temperature T_3 endotherm decreases with the addition of CPE 48 up to 50 wt%, when high annealing temperatures are used. Addition of the diluent also causes the appearance of multiplicity in peaks (*Figure 8*). These are usually observed when recrystallization is impeded because of a reduction of the diffusion coefficient due to miscibility[20,21]. It is significant that the most perfect crystals increase in concentration at increased CPE levels. It is suggested that CPE 'scavenges' (through miscibility)

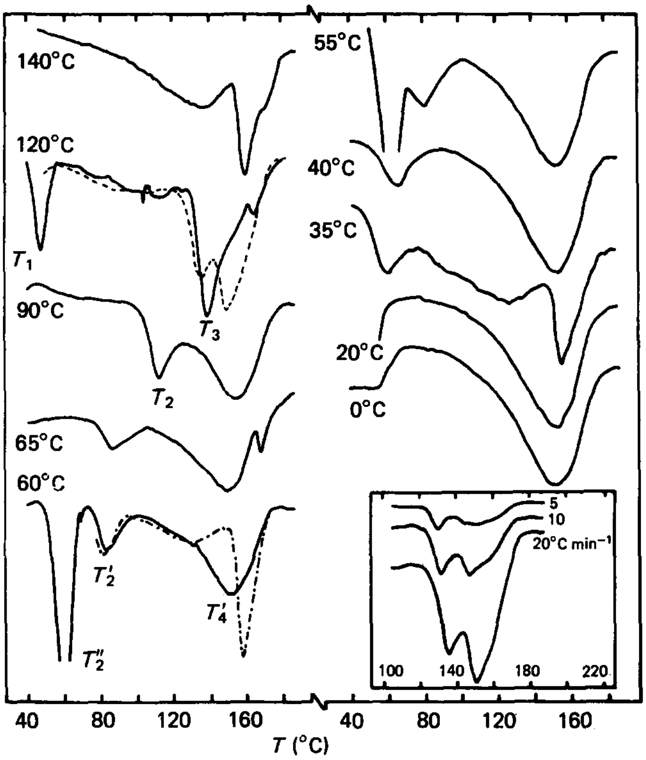


Figure 7 Thermograms of PEES annealed for 24 h at the temperatures indicated. – – –, Effect of annealing time; –·–·–, effect of liquid N_2 quenching. Insert: effect of scanning rate

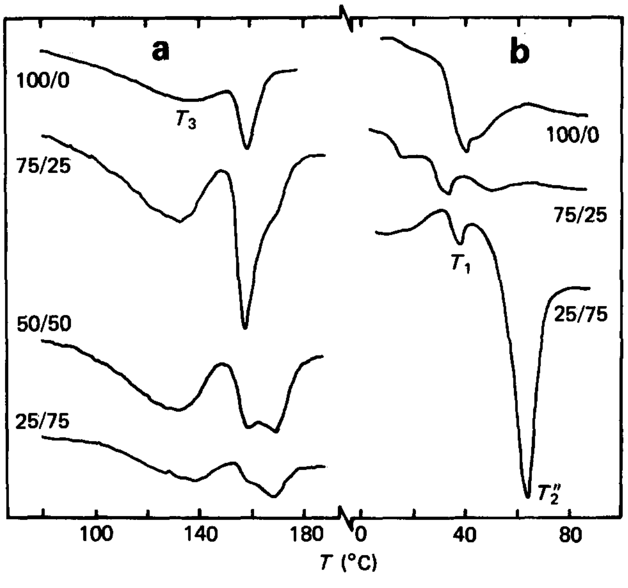


Figure 8 Thermograms of PEES/CPE 48 blends: a, high temperature; b, low temperature endotherms. Blend composition indicated next to d.s.c. traces

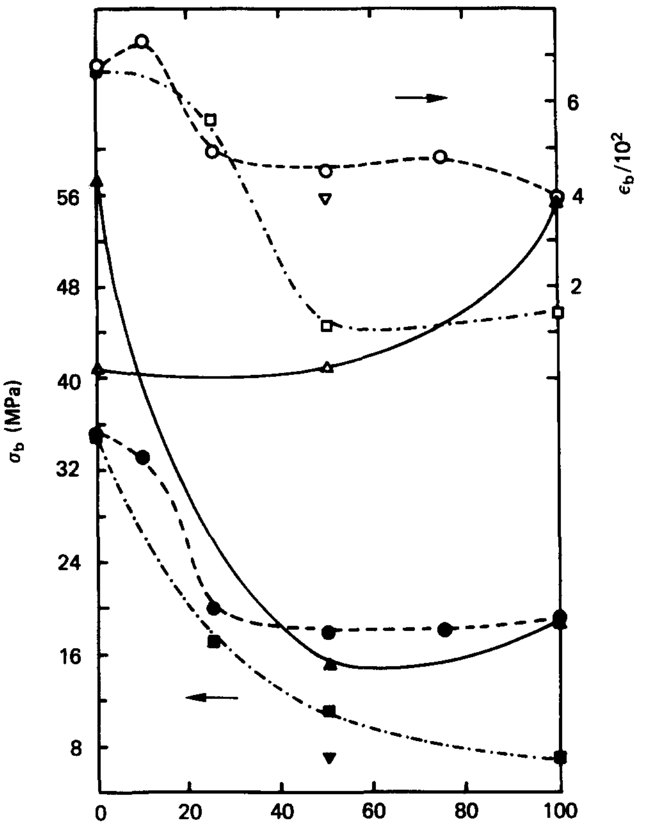


Figure 9 Ultimate tensile properties of blends: ○, PEES/CPE 48; □, PEES/CPE 25; △, PBT/CPE 48; ▽, PEES/CPE 48 annealed at 130°C. (Filled symbols tensile strength)

the melt from material that crystallizes less readily, (see reduction of the T_3 peak in *Figure 8a*), thus allowing a more perfect development of the crystallizing material. This has been observed, for example, by Martuscelli and coworkers[22] for blends of isotactic poly(propylene) with ethylene–propylene rubber and by Challa *et al.*[20], for poly(vinylidene fluoride)/it-poly(ethyl methacrylate) blends. An analogous situation involving the T_1, T_2'' peaks is observed for the low melting material. Thus addition of CPE 48 decreases the T_1 peak (up to 25 wt% diluent) and at the same time the T_2'' is better resolved (*Figure 8b*). It is pertinent to note that partial miscibility of PTMO with PVC has been observed[11] at low polyether content. Overall however, thermal data were not reproducible to a sufficiently high degree to apply the Hoffman–Weeks analysis[23].

Tensile properties

Figure 9 summarizes ultimate stress, σ_b, and strain, ε_b, of the blends studied. For CPE 48 blends, σ_b drops as the amount of the amorphous component increases up to the 25 wt% level. Further addition of the diluent does not cause significant reduction in strength. Retention of good elongation properties for this system is also observed. CPE 25 blends show a continuous drop of σ_b with composition while the PBT/PEES shows a minimum at the median composition. The latter systems have rather poor elongational properties at these compositions which are evidently the result of phase separation.

Fire retardancy

As expected fire retardancy continuously increases with CPE 48. At the 75 wt% CPE level, blends are self-extinguishing. This could be of practical value since at these compositions blends retain their useful ultimate properties, especially ε_b (*Figure 10*).

DISCUSSION

The experimental evidence presented supports the view that CPE 48 is miscible with PEES at all compositions at ambient and moderate temperatures defined by a LCST. CPE 25 is partially miscible. PBT shows partial miscibility confined to the amorphous phases of the blend constituents. T_g variation of CPE 48 blends shows only moderate interaction between blend partners; see *Figure 2* where data are analysed using the Jenckel–Heusch[24] and the Kwei[25] relationships. The former is given by:

$$T_{gb} = W_A T_{gA} + W_B T_{gB} + bW_A W_B(T_{gB} - T_{gA}) \qquad (1)$$

and the latter by:

$$T_{gb} = \frac{W_A T_{gA} + kW_B T_{gB}}{W_A + kW_b} + qW_A W_B \qquad (2)$$

where W_i, T_{gi}, is the weight fraction of component i and its T_g, respectively, and k is the ratio of the volume expansion coefficient difference in the viscoelastic and glassy state of the pure polymers. Since $qW_A W_B$ is proportional to the interaction between components, parameter q may be assumed[25] to give a measure of the specific interactions in a blend. Analysis of the data gives a value of $b = 0.502$ and for $k = 1.0$, $q = 31.0$. As to the specific sites providing for interaction, results of this and of another study[11] suggest that both polyether and polyester amorphous segments (mode rate proton acceptors) may serve as a complementary dissimilar partner to the α-hydrogen of the chlorinated polymers.

The experimental procedure applied accurately defined the LCST and indicates that the phase separation

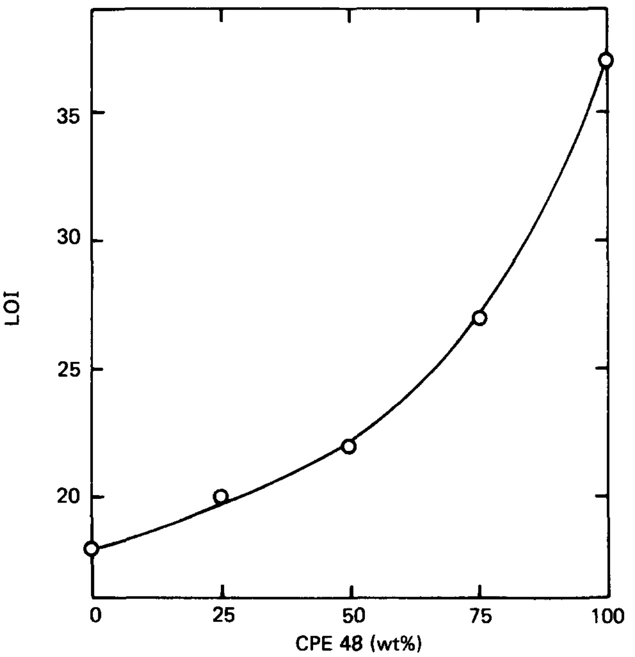
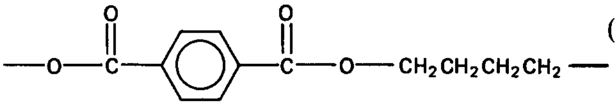


Figure 10 Limiting oxygen index (LOI) *versus* composition of PEES/CPE 48 blends

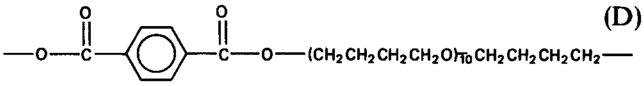
reported[9] in previous work was the result of an insufficiently rapid cooling of the test specimens.

As in previous work[11,26], a predictive scheme applicable to random copolymer–copolymer blends was tested. CPE was assumed to be a statistical copolymer consisting of $-CH_2-$ (A) and $-CHCl-$ (B) units and PEES of



(C)

and



(D)

moieties. For high degrees of polymerization the following basic relationship[27,28] yields χ_b the blend interaction parameter in terms of χ_{ij} the segmental interaction parameters and the compositions in volume fraction, x,y, of the two copolymers $(A_xB_{1-x})_n$ and $(C_yD_{1-y})_n$

$$\chi_b = xy\chi_{AC} + (1-x)y\chi_{BC} + x(1-y)\chi_{AD} + (1-x)(1-y)\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD} \quad (3)$$

χ_{ij} can be obtained as suggested by Krause[29] using the concepts of the solubility theory[29,30] and molar attraction constants F_i, the relevant equations being

$$\chi_{ij} = V_r(\delta_i - \delta_j)^2/RT \quad (4)$$

and

$$\delta = \rho\Sigma(F_i/M) \quad (5)$$

where V_r is a reference volume taken to be close to the molar volume of the smallest repeat unit, δ_i the solubility parameter of homopolymer with units i, each of molar mass M and whose density is ρ. In the case of 'unknown' homopolymers, density was obtained by the scheme proposed by Askadskii[31], the particular values being:

$$\rho_{An} = 0.92, \qquad \rho_{Bn} = 1.72$$
$$\rho_{Cn} = 1.29, \qquad \rho_{Dn} = 1.18$$

Solubility parameter values determined using equation (5) were

$$\delta_{An} = 8.74, \qquad \delta_{Bn} = 10.54$$
$$\delta_{Cn} = 10.59, \qquad \delta_{Dn} = 9.09$$

Use of these data in equations (3) and (4) yields at constant temperature (25°C) χ_b data which define in a composition–composition plot a zone of compatibility where $\chi_b \leq 0$; see shaded area in *Figure 11*. The scheme correctly predicts that blends with PVC 48 are miscible. It is less accurate with respect to PEES/CPE 25 where experiment showed it to be semi-compatible.

Though the scheme used is not rigorous and has not been adequately tested yet, it may serve as a preliminary guide to screen potential miscible blends. It has the advantage of taking into account inter- as well as intramolecular[32] interactions and it was found to be successful[26] even in polymer pairs where specific forces were expected to be present. (It is known that solubility theory is valid in systems where dispersion forces are prevalent[33].)

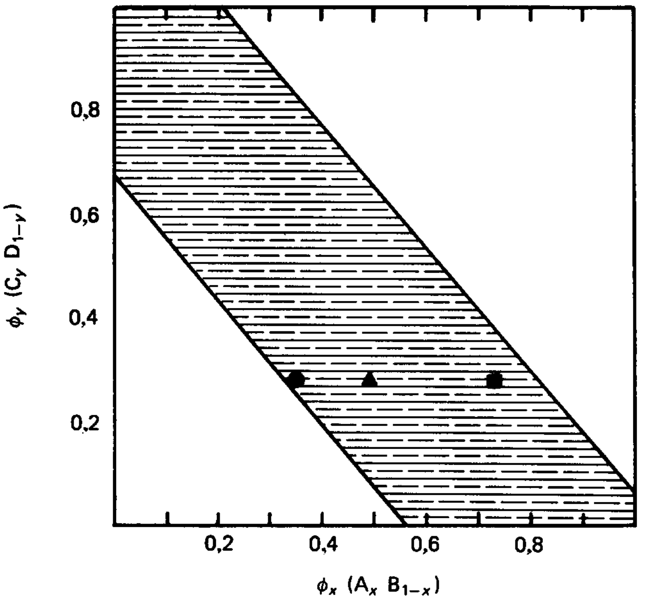


Figure 11 Miscibility map of PEES/CPE blends at 25°C: ●, PEES/PVC; ▲, PEES/CPE 48; ■, PEES/CPE 25

CONCLUSIONS

Sufficiently chlorinated polyethylene (wt% Cl≥48) is miscible with poly(ether ester) elastomers. The miscibility region is bounded by a LCST asymmetric with respect to composition with a minimum at *ca.* 50 wt% CPE 48.

Thermal behaviour (fairly complicated even for the pure PEES) is strongly dependent on thermal history, reflects the internal organization of the semicrystalline thermoplastic and in the case of blends indicates the effect of miscibility in scavenging imperfectly developed crystalline matter.

Mutual miscibility can be traced to amorphous polyether and polyester segments interacting with the proton-donating CPE and could be predicted by a scheme based on the copolymer–copolymer and solubility theories.

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