Dynamic mechanical and microcalorimetric studies on the phase structure in blends of two multiblock copolymers:
1. Poly(ether–ester) and poly((ether–carbonate)–urethane) blends

Zbigniew Rosłaniec
Technical University of Szczecin, Institute of Materials Engineering, Al. Piastów 17, 70-310 Szczecin, Poland
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The physical properties and phase structure of blends of the multiblock poly(ether–ester) elastomer (PEE) and the multiblock poly((ether–carbonate)–urethane) elastomer (PUC) have been investigated using the methods of differential scanning calorimetry and dynamic mechanical analysis. The blends were prepared in the melt. The system is characterized by one glass transition temperature (T_g) for the soft phase, which points to the occurrence of partial miscibility. The blends appear to possess two hard phases, a polyester phase and a polyurethane phase, with glass transition temperatures and melting points close to the temperatures of the initial copolymers. Suggestions have been made regarding the possibility of occurrence of an intermediate phase conspicuous by extra glass transition and crystallization temperatures.

(**Keywords: polymer blends; copoly(ether–ester); copoly((ether–carbonate)–urethane); phase structure**)

INTRODUCTION

The possibility of obtaining a homogeneous (one-phase) structure of blends of two or more polymers is limited because most macromolecular components are immiscible. By the classic Flory–Huggins–Scott theory, the high molecular weights and the difference in chemical structures of the polymers are the deciding factors[1]. A system is compatible when one of its components is a diblock (AB) or a triblock (ABA) copolymer in which one of the blocks has the same structure as the other component (homopolymer A or B). Many experimental and theoretical studies[2–4] have been devoted to solution of this problem.

A specific microphase structure is shown by block copolymers, which have in the chain two kinds of segments distinctly varying in chemical structure, determined as 'soft' and 'hard' segments[5]. Such polymer materials, called thermoplastic elastomers, exhibit a unique combination of strength, flexibility and processability.

In a multiblock copolymer $(AB)_n$ the polymer chain is formed by alternately repeating the soft and hard segments. Such a structure occurs in, for example, poly(ether–ester)[6], poly(ester–urethane), poly(ether–urethane)[7] and poly(carbonate–ester)[8].

A literature survey shows that one can gather reliable information about the correlation between the physical properties and the phase structure of multiblock copolymers by studying mixtures of those copolymers with homopolymers or random copolymers with physical properties similar to those of one of the segments, such as polarity, crystallizability, etc. The co-crystallization of copoly(ether–ester) with poly(butylene terephthalate) (PBT)[9] and of copoly(ether–amide) with polyamide[10] has been investigated, among others.

The present work examines the phase structure of multiblock poly(ether–ester) elastomer (PEE) and multiblock poly((ether–carbonate)–urethane) elastomer (PUC) blends. There is no literature information known to the author on the properties of such systems.

EXPERIMENTAL

Materials

Copoly(oxytetramethylene-*b*-butylene terephthalate) (trade name, Elitel 4450, Elana, Poland) was used as PEE. It was prepared by polycondensation in the melt[11] with a small fraction of the star structure[12]. PEE contains 50 wt% of polyether soft segments with $M_w = 1120$ g mol^{-1}. The intrinsic viscosity of PEE in the solvent mixture phenol/trichloroethylene (40/60 wt%, 30°C) was $[\eta] = 1.43$ dl g^{-1}, density $d = 1.15$ g cm^{-3}, hardness $H = 47$–48 Sh D.

As PUC, a commercial product, Desmophan 786 (Bayer AG), was used. The intrinsic viscosity of this polymer in phenol/trichloroethylene (40/60 wt%, 30°C) was $[\eta] = 1.20$ dl g^{-1}, density $d = 1.16$ g cm^{-3}, hardness $H = 87$ Sh A. Its poly(ether–carbonate) soft-segment content was about 65 wt% (evaluated by i.r. spectroscopic method).

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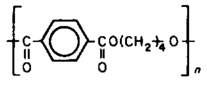
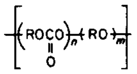
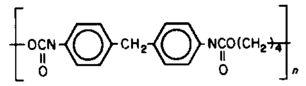
Table 1 The chemical structure and physical characteristic of polymer segments

Polymer segment	Chemical structure	Symbol	Average degree of polymerization, *n*	Density (g cm^{-3})	V_u[a] (cm^3 mol^{-1})	Solubility parameter (MPa$^{1/2}$) Calc.[b]	Solubility parameter (MPa$^{1/2}$) Other[c]	Glass transition temperature (°C)	Melting point (°C)
Poly(tetramethylene oxide)	$\left(O-CH_2CH_2CH_2CH_2 \right)_n$	PO4	14	0.98[d]	73.5	16.5	17.5[21] 16.6[16]	−85[24]	–
Poly(tetramethylene terephthalate)		PBT	~5	1.31[e]	168	22.8	21.6[32] 23.1[22]	50[13] 60[9]	227[13]
Poly(ether alkyl carbonate)	 $\left[\left(RO\overset{}{\underset{\underset{O}{\Vert}}{C}}O \right)_n \left(RO \right)_m \right]$	PC	–	1.08	138[b]	22.1	–	–	–
Polyurethane		PU	~2.5	1.29	274[b]	22.6	22.4[21] 27.0[23]	110[14]	241[25,f] 206[26,g]

[a] Molar volume of structural unit

[b] Calculated from Van Krevelen[18] and Barton's handbook[20]

[c] From other papers

[d] For amorphous state[18]

[e] For semicrystalline forms[19]

[f] For $n = 6$

[g] For $n = 3$

Blending

Polymer blends were prepared by a two-stage process. In the first stage, polymers in the form of very small granules were mixed and homogenized in the molten state in a Plastograph Plasticorder (Brabender OHG) mixer (nitrogen atmosphere) for 5 min. In the second stage, the samples were subjected to homogenization in a laboratory extruder (Brabender), $L = 25D$, and granulated.

The homogenization temperature in the mixer or in the third extruder zone, for most of the blends, was 5°C higher than the melting point (determined using a Böetius apparatus) of the more fusible component.

The initial copolymers have been prepared in the same way.

Sample preparation

The samples for d.s.c. and dynamic mechanical examination were prepared as films by compression moulding between poly(tetrafluoroethylene) (PTFE) plates. Compression moulding was carried out at a temperature 20–25°C higher than the Böetius melting point. Samples were placed in the press for 3 min, quenched at a rate of approximately 15°C min^{-1} and stored in an inert-gas atmosphere at room temperature for about a month.

Differential scanning calorimetry analysis

Calorimetric testing was carried out using a Perkin–Elmer DSC-2 scanning microcalorimeter. The samples were rapidly quenched in liquid nitrogen to a temperature of −100°C and then examined in a triple cycle 'heating–cooling–heating' in the temperature range −100 to +230°C. The heating and cooling rates were 10°C min^{-1}. Calibration was based on indium and synthetic sapphire standards. The weight of the samples was 24.5 to 28.1 mg.

The glass transition temperatures of the blends in the low-temperature range (T_{g1}) have been determined from the d.s.c. diagram at half of the heat capacity total change. The T_{g2} transition temperature has been determined as the temperature corresponding to the upper inflection point (or maximum) of the curve. The interpretation of the T_{g2} phase transition for poly(tetramethylene terephthalate), its copolymers and polyurethanes has been given in many papers[9,13–15]. The ΔC_p for the soft phase has been measured[16] at T_{g1}.

The melting point (T_m) and crystallization temperature (T_c) have been determined as the temperature of maximum endothermic or minimum exothermic effect, respectively.

Dynamic mechanical testing

The tests were performed using a Rheovibron viscoelastometer (DDV-IIc model, Toyo Baldwin). The measurements were carried out at a frequency of 3.5 Hz, over the temperature range of −100 to +230°C. The storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) have been determined.

The temperatures of E''_{max} and $\tan \delta_{max}$ have been measured from Rheovibron data in non-logarithmic coordinates.

RESULTS AND DISCUSSION

On account of the block structure of the copolymers involved in the blends, the properties of the system of interest should be considered to be the result of interactions between the four polymers that form the blocks. *Table 1* shows the chemical structures and physical characteristics of the polymer blocks under study.

The miscibility criterion taken as a decrease in the free energy of mixing ($\Delta G_m < 0$) for a system of two polymers (A and B) is determined by the necessity to minimize the Flory–Huggins interaction parameter (χ_{AB}), which can be expressed in terms of the solubility parameters (δ)[1,17]:

$$\chi_{AB} = V_u(\delta_A - \delta_B)^2/RT \qquad (1)$$

where V_u is the molar volume of a structural unit.

For PEE and PUC, the difference between the solubility parameters for hard and soft segments ($\delta_H - \delta_S$) is so great that χ_{HS} exceeds the boundary value and microphase separation is observable[23]:

$$\chi_{HS} \simeq \tfrac{1}{6}(\delta_H - \delta_S)^2 > (\chi_{HS})_{crit} = \tfrac{1}{2}(1/n_H^{1/2} + 1/n_S^{1/2})^2 \qquad (2)$$

where n_S and n_H are the degrees of polymerization of soft and hard segments.

Hence, the system should possess a four-phase structure. Considering the solubility parameters (*Table 1*), an interaction between PBT and PU, between PBT and PC or between particular microphases is expected to occur. Such an interaction for soft microphases manifests itself in segregation rate changes for soft segments involved in the system and linear change of T_g. The specific-heat change is generally used to estimate the phase segregation rate[21]:

$$SR_S = (\Delta c_p^{obs}/w_S)/\Delta c_{pS} \qquad (3)$$

where SR_S is the soft-segment segregation rate, $\Delta c_p^{obs}/w_S$ is the observed change in heat capacity per gram of soft segment in the copolymer, and Δc_{pS} is the heat capacity of the soft-segment material.

The glass transition temperature (T_g) in a system of miscible polymers is expressed (among others) by the Kwei equations[27]:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + q w_1 w_2 \qquad (4)$$

$$T_g = \frac{w_1 T_{g1} + K w_2 T_{g2}}{w_1 + K w_2} + q w_1 w_2 \qquad (5)$$

where w_1, w_2 and T_{g1}, T_{g2} are the mass fractions and the glass transition temperatures of the two components, and K and q are constants.

The d.s.c. measurements showed the PEE/PUC blends to be characterized by two ranges of glass transition temperature, from −67 to −35°C for T_{g1} and from 36 to 65°C for T_{g2}.

Figure 1 shows the low-temperature thermograms for the blends, whereas *Table 2* shows the readings of the glass transition temperature values (T_{g1}) and the specific-heat changes (Δc_{p1}) taken from the thermograms.

The blends are characterized by a single glass transition temperature for the soft phase, confined within the glass transition temperature values for the initial components and varying nearly monotonically. On the other hand, Δc_p changes irregularly. That irregularity may be caused by the change in microphase segregation rate.

Some changes related to relaxation can be observed in the character of curve 1 (*Figure 1*) for PEE above the glass transition range. The inflection apparent at point T_3 can be interpreted as the glass transition temperature of the totally amorphous rigid segment (PBT) (about −25°C)[13]. Occurrence of these transitions (curves 3 and 4) may influence the Δc_{p1} and T_{g1} values.

Figure 2 shows the d.s.c. thermograms of the PEE/PUC blends in the second range of glass transition temperature. The effects observed in the curves correspond to rotational freedom, relaxation and change in arrangement of part of the chains in the hard segments as well as to a partial change in arrangement of the non-crystalline and slightly crystalline areas formed by the segments[23]. In most papers, all of the effects are attributed to the glass transition temperature of PBT and polyurethane (4,4′-diphenylmethane diisocyanate–butanediol, MDI–BD) hard segments (T_{g2})[13,28]. *Table 2* shows the results from measurements of T_{g2}. A glass transition temperature characteristic for PEE (T_{g2} = 46°C) and that for PUC (T_{g2} = 65°C) occur in the thermograms of blends of 30% or more of the second component (T_5, T_6; *Figure 2*). An additional effect,

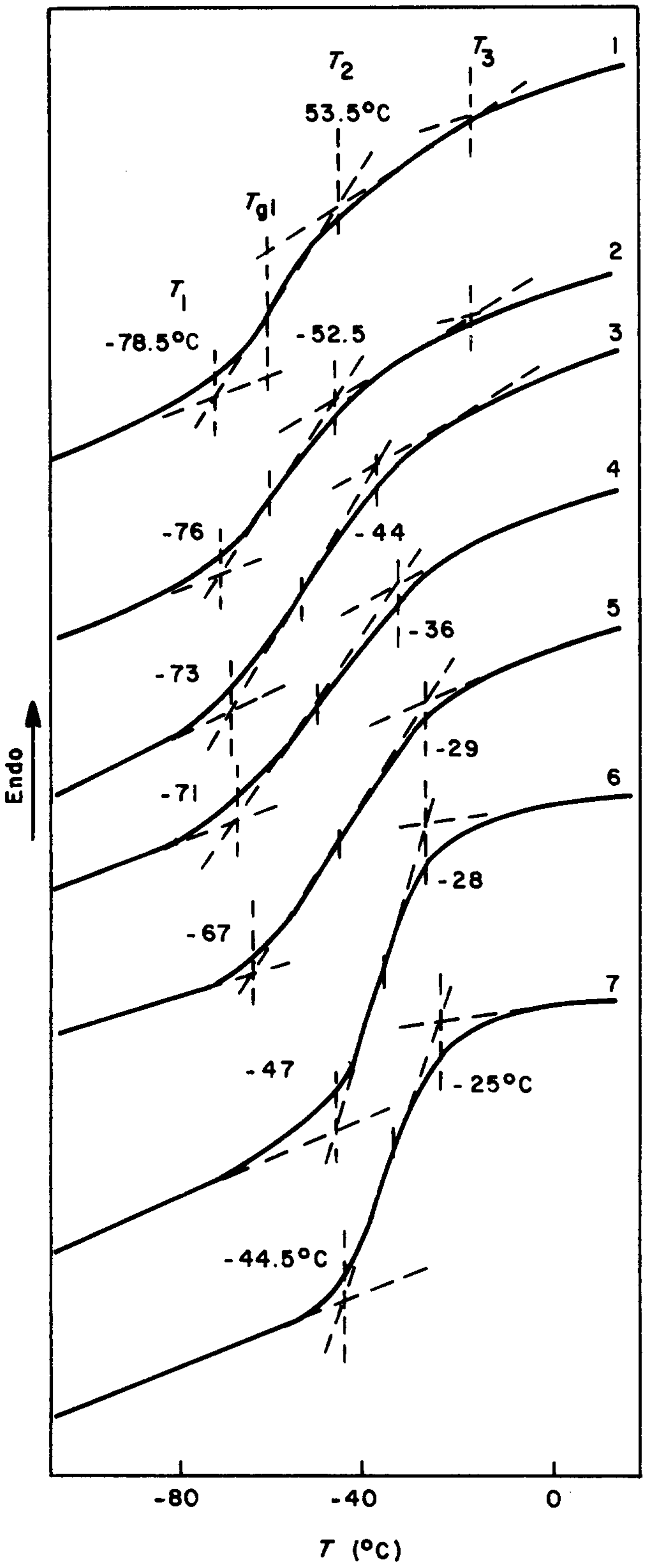


Figure 1 D.s.c. thermograms for the low-temperature region of PEE/PUC blends. Rate 10°C min^{-1}. Contents of PUC: (1) 0%, (2) 10%, (3) 30%, (4) 50%, (5) 70%, (6) 90%, (7) 100%

denoted as T_4, occurs in blends of 10, 30 and 90% of PUC (*Figure 2*, curves 2, 3 and 6). Temperature T_4 lies below temperatures T_5 and T_6.

Relaxation in block copolymers is apparent due to changes in the d.s.c. thermogram depending on the conditions of crystallization and annealing[6,29]. The conditions of crystallization of the PEE/PUC blends were established when they were cooled at a rate of 10°C min^{-1}. *Figure 3* shows the thermograms of the cooled samples, and *Table 2* shows the crystallization temperature (T_c) and the total heat of crystallization (ΔH_c). The crystallization temperature of blends containing above 50% of PEE differs insignificantly from the T_g of the predominant component (154°C). In blends with 70 and 90% of PUC, two crystallization temperatures occur close to T_g of the initial components. For blends with 30 and 50% PUC content, one can observe additional exothermic effects at 121 and 119°C, respectively (T_6 in *Figure 2*). ΔH_c varies with the change in composition of the blends in a way resembling an additive one.

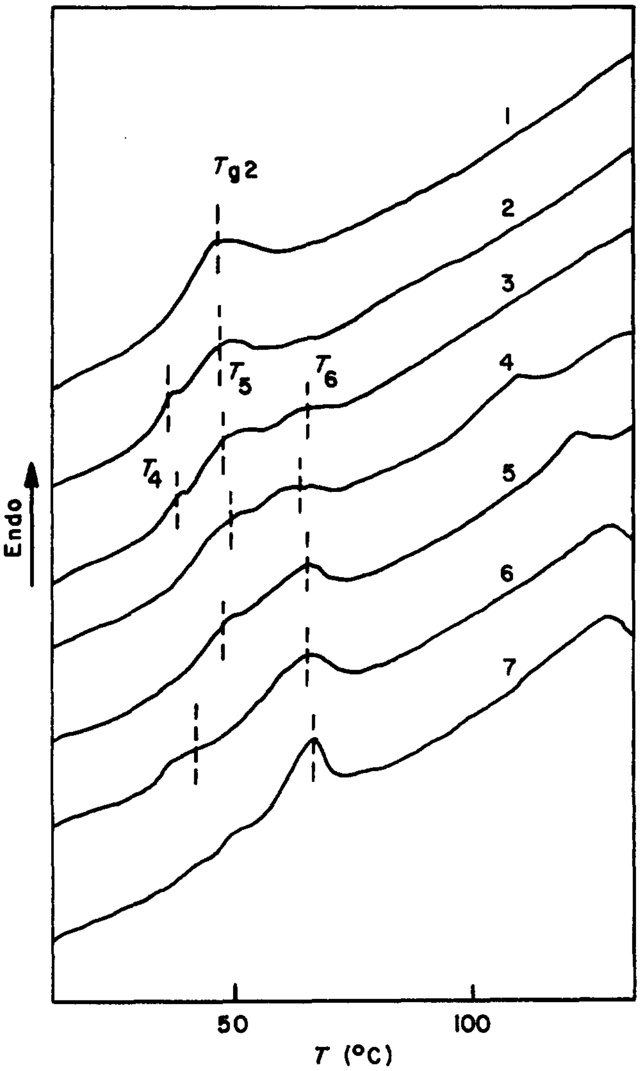


Figure 2 D.s.c. thermograms of PEE/PUC blends for T_{g2} region. Notation as in *Figure 1*

For mixtures of polymers with one crystallizing component, a measure of molecular interaction can be the depression of melting point[30]:

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{RV_{u2}}{\Delta H_u V_{u1}} \chi_{12} \phi_1^2 \qquad (6)$$

where T_m° is the melting point of the pure crystalline polymer, T_m is the melting point in the presence of a diluent, V_u is the volume per mole of repeat units of the constituents 1 or 2, ϕ is the volume fraction, and ΔH_u is the heat of fusion per mole of repeat units of the crystalline component.

It has been shown earlier that an aliphatic polycarbonate affects the depression of melting temperature of the crystalline PBT segment more than polyether[8], hence its influence on the PEE/PUC system.

Figure 4 and *Table 2* show the results from the d.s.c. studies on the melting temperature range. They have been recorded from the second heating accomplished in the cycle 'heating–cooling–heating'. With PEE, one observes the main melting endotherm of the crystalline phase (T_8) at 191°C and two minor endotherms connected with the conditions of crystallization (T_7) at 155°C and recrystallization (T_9) at 204°C[6]. For PUC there occur three endotherms (T_{10}, T_{11}, T_{12}) connected with disorganization of the pseudocrystalline structure (hydrogen bonding) of the hard phase formed from polyurethane segments[31]. The thermograms of the blends are an approximate superposition of the initial component thermograms, the main endotherms of PEE

Table 2 D.s.c. study results for PEE/PUC blends

PEE/PUC (wt%)	T_{g1} (°C)	Δc_{p1} (J g^{-1} °C^{-1})	T_{g2} (°C)	T_m (°C)	ΔH_m (J g^{-1})	T_c (°C)	ΔH_c (J g^{-1})
100/0	−67	0.262	46	155, 191, 204	29.5	154	30.2
90/10	−66	0.318	36, 47	154, 189, 203	27.1	155	26.7
70/30	−62	0.285	37, 47, 65	105, 154, 188, 202	25.2	121, 154	23.9
50/50	−53	0.305	49, 64	114, 187, 202	21.4	119, 152	20.9
30/70	−44	0.503	47, 65	122, 178, 188, 202	15.9	101, 153	16.8
10/90	−37	0.523	41, 65	124, 178, 188	12.2	103, 153	14.2
0/100	−35	0.484	65	126, 175, 191	8.9	101	9.3

T_{g1}, glass transition in low-temperature region
Δc_{p1}, heat capacity change in T_{g1}
T_{g2}, relaxation and disruption of ordered non-crystalline (or slightly crystalline) hard segment (second glass transition)
T_m, melting points of the hard segment domains
ΔH_m, total heat of fusion
T_c, temperatures of crystallization
ΔH_c, total heat of crystallization

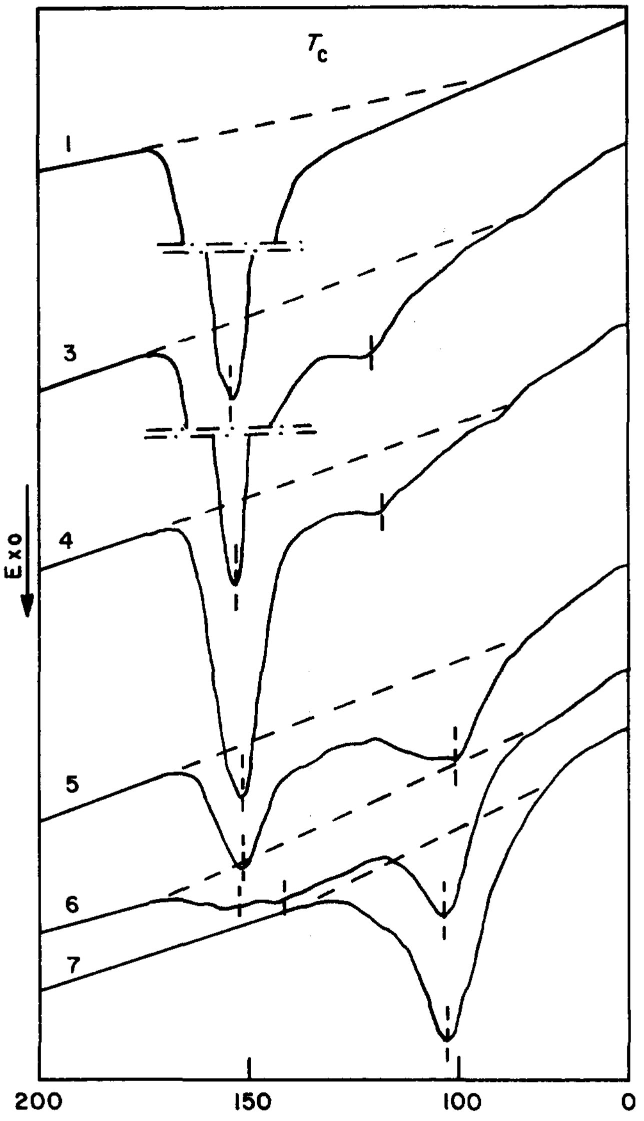


Figure 3 D.s.c. thermograms of PEE/PUC blends for cooling cycle. Rate 10°C min^{-1}. Notation as in *Figure 1*

(T_8) and PUC (T_{11}, T_{12}) taken as the softening point of copolymers and blends (T_m) having similar values. The heat of fusion (ΔH_m) varies nearly linearly.

Block copolymers showing microphase segregation are conspicuous in that, between the glass transition temperature of the soft phase (matrix) and the melting temperature of the hard phase, there occurs a low elastic modulus 'plateau'. The modulus value in that range depends on the length and content of individual segments in a copolymer[5,17]. For PEE/PUC, the storage modulus (E'), loss modulus (E'') and loss tangent ($\tan\delta$) were studied between −100 and 200°C. The temperature dependence is typical of thermoplastic elastomers (*Figures 5–8*). At low temperature E' is increasing with increase of the PUC content in the blends, but at elevated temperature the relation appears to be the inverse. At −20°C, E' is approximately constant (the intersection point of the curves: *Figure 5*, plot 2 in *Figure 6*). The relaxation temperature (T_β) defined by the dependence $E'' = f(T)$ (*Figure 7*), which may be interpreted as the glass transition temperature of the soft phase, is decreasing with increase in the PEE content in the blends. *Figure 9* shows a comparison of the relation between the phase transition temperature (T_{g1} from d.s.c., T_β from E'') and the composition of the blends determined at low temperature by a variety of methods. The dependence shows a considerable deviation from linearity. There is a suggestion of reaching a good correlation with the modified Kwei equation (4):

$$T_g = w_{1c}T_{g1} + w_{2c}T_{g2} + q w_{1c} w_{2c} \qquad (7)$$

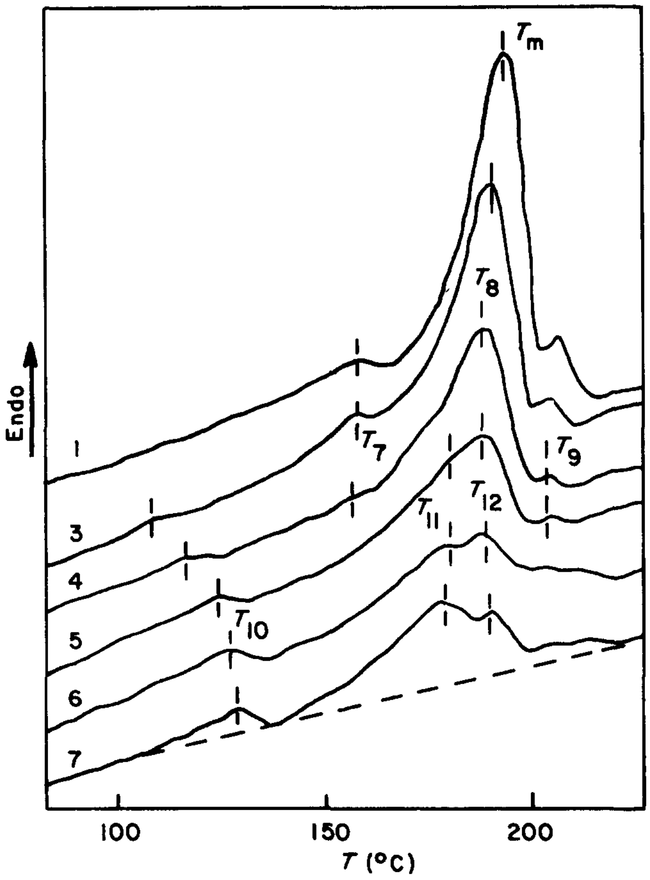


Figure 4 The melting region of d.s.c. traces for PEE/PUC blends. Second heating cycle. Rate 10°C min^{-1}

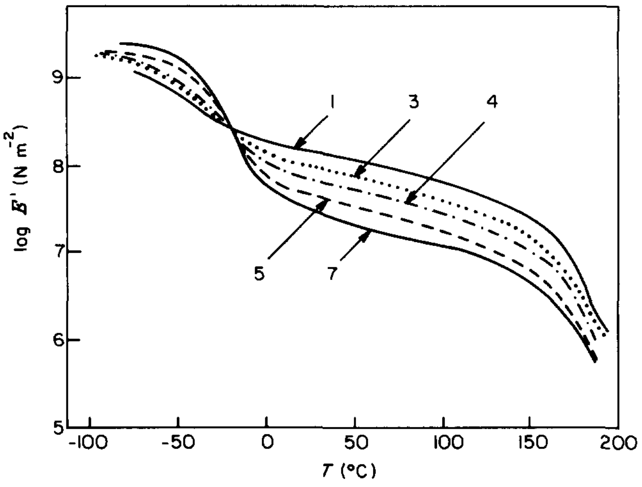


Figure 5 The storage modulus (E') of PEE/PUC blends vs. temperature (T). Notation as in *Figure 1*

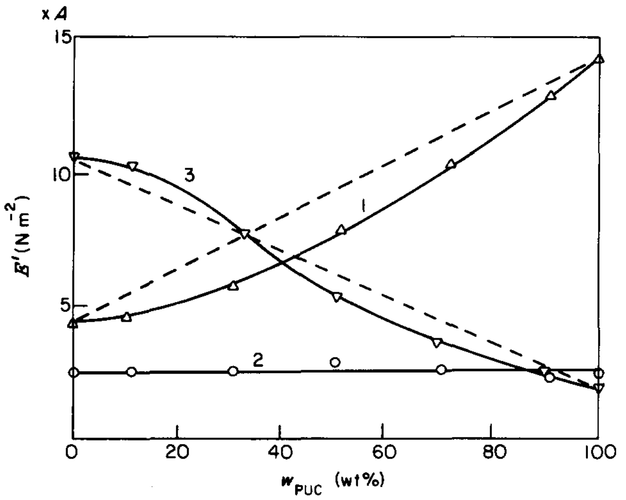


Figure 6 Dependence of dynamic mechanical storage modulus (E') on PUC weight fraction (w_{PUC}) in copolymer blend and temperature: (1) −40°C, $A = 10^8$; (2) −20°C, $A = 10^8$; (3) +60°C, $A = 10^7$

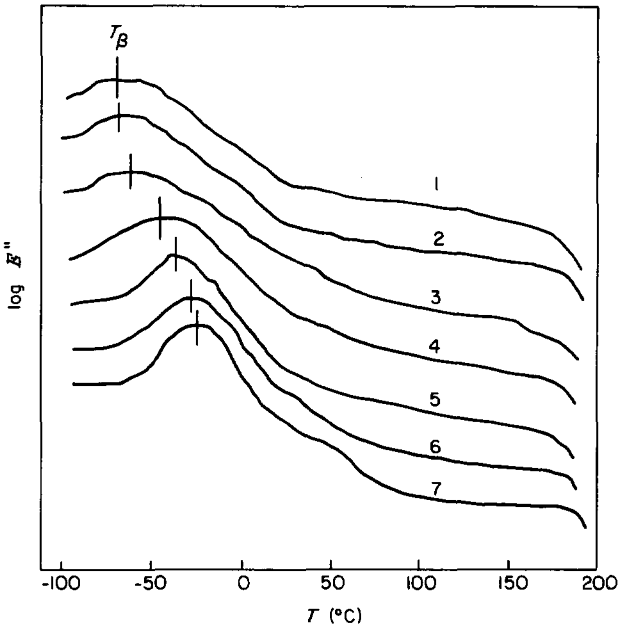


Figure 7 The loss modulus (E'') of PEE/PUC blends vs. temperature (T). Notation as in *Figure 1*

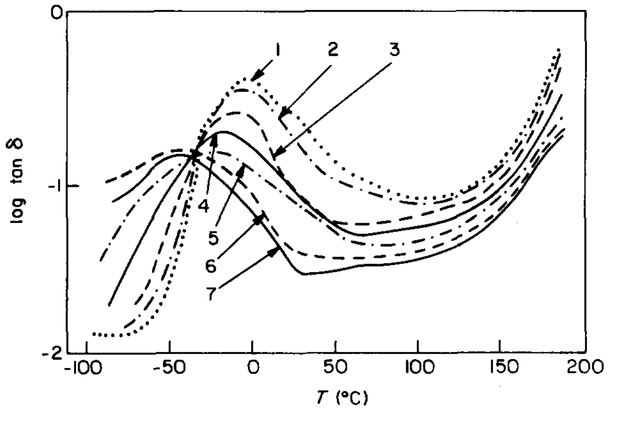


Figure 8 The loss tangent (tan δ) of PEE/PUC blends vs. temperature (T)

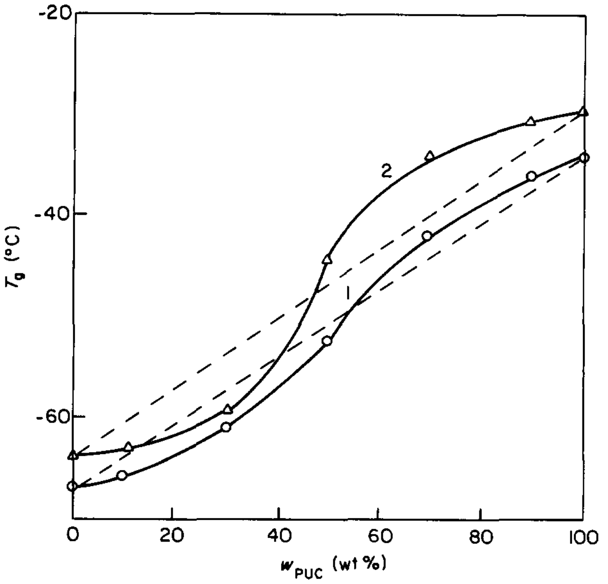


Figure 9 The glass transition temperatures (T_g) of PEE/PUC blends vs. weight fraction of PUC (w_{PUC}): (1) T_{g1} from the low-temperature d.s.c. curves; (2) T_β from E''_{max} peaks

where

$$w_{1c} = w_1/(w_1 + Kw_2)$$

$$w_{2c} = Kw_2/(w_1 + Kw_2)$$

$$K = \Delta C_{p2}/\Delta C_{p1} \qquad q = -25$$

On account of the micro-heterophase structure of the initial components (PEE, PUC), it is not to be expected that their blends will be one-phase. A single glass transition temperature of blends in the low-temperature region may be interpreted as the result of:

(a) one soft phase;

(b) overlapping of d.s.c. curves and E''_{max} peaks as a result of the small difference between T_g of the initial components ($T_g >$ 30–40°C, MacKnight *et al.* in ref. 17); and

(c) small size of microdomains in soft microphase structure.

For the investigated copolymers T_{g1} is smaller than 40°C. On this point one soft phase or small microdomain size can be accepted. In the second case, broadening E''_{max} and tan δ_{max} peaks for middle compositions may be the result of increasing microdomain size of co-continuous soft phases. Hence, the partial miscibility shown by a single T_g in the low-temperature region is to be related exclusively to soft phases. A possible molecular interaction may manifest itself by the lack of tendency to macrophase segregation.

CONCLUSIONS

In a system of two multiblock copolymers, such as PEE or PUC, one glass transition temperature (T_{g1}) has been found to exist in a range relevant to soft phases, which points to conditions more advantageous to their miscibility than would follow from the value estimated of (values for) the solubility parameters δ. The hard microphases segregate to completion, giving rise to the occurrence of two glass transition temperatures (T_{g2}) characteristic of each of the components. No melting temperature depression has been found. This fact implies lack of additional interaction of the soft segments of one component with the hard phase of the other copolymer. Nevertheless, the appearance of additional effects within the range of the glass transition temperature (T_{g2}) and the crystallization temperature (T_c) may result from formation of an interphase in some blends. The melting points of the hard phases of both copolymers are too close in value to be used for evaluating the phase interaction.

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