Characteristics of multiblock terpoly(ester-ether-siloxane) elastomers

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The structure and physical properties of multiblock terpoly(ester-ether-siloxane) elastomers (EES) have been examined by differential scanning calorimetry, dynamic mechanical analysis, optical microscopy and other standard physical methods. Terpolymers consisted of poly(butylene terephthalate) (PBT), poly(oxytetramethylene) (PO4) and poly(dimethylsiloxane) (PDMS) segments. The content and length of segments was changed at a constant PBT:PO4 mass ratio of 45:55. At PDMS content above 10% terpolymers were characterized by three glass transition temperatures. EES was characterized by two temperature ranges of elastic state. The characteristic of terpolymers results from their multimicrophase structure and is very specific for thermoplastic elastomers.

(Keywords: terpoly(ester-ether-siloxane)s; thermoplastic elastomers)

INTRODUCTION

Block copolymers that contain chain segments distinctly differing in chemical structure and physical properties, show phase-separated microstructure. Such a structure is characteristic of polymeric materials exhibiting the combined properties of vulcanized rubbers and plastics; such materials are referred to as thermoplastic elastomers[1-3]. The regions formed of soft segments with a low glass transition temperature impart flexibility to such materials. Hard-segment-rich microdomains resulting from intermolecular actions (e.g. crystallization, hydrogen bonds) form so-called physical crosslinks and guarantee good mechanical strength[4,5]. The change of Gibbs free energy is a thermodynamic condition of microphase separation which depends, among other things, on differences in the Hildebrand solubility parameters for particular components[6].

Widely known thermoplastic elastomers include two-(AB) and triblock (ABA) diene-styrene and ethylene-propylene copolymers and multiblock $(AB)_n$ ester-urethane, ether-urethane, ether-ester and ether-amide copolymers[3]. This paper deals with multiblock ester-ether-siloxane terpolymers (EES).

Other systems which have previously been synthesized and investigated include ether-siloxane-urethane[7], carbonate-siloxane-urethane[8], ester-siloxane[9-11] terpolymers and series copolymers containing siloxane blocks[12-16].

EXPERIMENTAL

Synthesis

EES was obtained by transesterification and two-stage polycondensation in the melt. Dimethylterephthalate and 1,4-butanediol were heated in the temperature range 150–200°C in the presence of magnesium hydrohexabutoxy-*o*-titanate as a catalyst till more than 90% of the stoichiometric amount of methanol had been evaporated. At the first stage of polycondensation at 200–220°C and under reduced pressure, oligo(butylene terephthalate) (PBT) was synthesized. During the second stage α,ω-dihydroxypoly(oxytetramethylene) (PO4, Terathane 1000, Du Pont) and α,ω-dihydroxypoly(dimethylsiloxane) (PDMS, Polastosil, Sarzyna, Poland) along with catalyst and amine antioxidant were added. The polycondensation was carried out at 260°C and 0.4–0.5 mmHg till the product of highest melt viscosity in such conditions was obtained. The polymers were extruded and granulated. A detailed description of this synthesis is given in an earlier paper[17]. The terpolymers with segment content from 0 to 40 wt% and a constant mass ratio of PBT:PO4 segments of 45:55 (samples 1–5) were obtained. Samples 6 and 7 were synthesized using 40% dimethylsiloxane diols differing in their viscosities and in molecular weight[18]. For comparison a terpolymer of different PBT and PO4 segment ratio (sample 8) and copolymers PBT-PDMS and PBT-PO4 (samples 9 and 10) were synthesized (*Table 1*). The polymers were characterized by determining the limiting viscosity number $[\eta]$ at 30°C from one point in the solution of phenol–trichloroethylene–toluene (1:1:2 vol).

Sample preparation

Samples for strain–stress, hardness and resilience testing were obtained by injection moulding and those for dynamic mechanical and microcalorimetric determination by compression moulding. Injection moulding was carried out at ~50 MPa in a form heated to 40–60°C. Compression moulding was performed at 5 MPa at a temperature 20–25°C higher than the melting point determined with Böetius apparatus (*Table 1*).

Examination

The microcalorimetric examinations were performed with Perkin–Elmer (DSC-2) apparatus. The samples were rapidly quenched to a temperature below −150°C

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Table 1 Segment content and some physical properties of EES

Sample	Segment content (wt%) PBT	PO4	PDMS	η_{PDMS} (mPa s)	$[\eta]_{PDMS}$ (dl g^{-1})	$[\eta]_{EES}$ (dl g^{-1})	T_t (°C)
1	45	55	–	–	–	1.41	202
2	43	52	5	166	0.0843	1.57	199
3	40.5	49.5	10	166	0.0843	1.60	198
4	36	44	20	166	0.0843	1.43	198
5	27	33	40	166	0.0843	1.12	196
6	27	33	40	310	0.1004	1.16	196
7	27	33	40	1862	0.1950	1.15	198
8	48	12	40	310	0.1004	1.04	220
9	70	–	30	1862	0.1950	0.82	226
10	80	20	–	–	–	1.03	223

η_{PDMS}, viscosity of PDMS-diols at 25°C
$[\eta]_{PDMS}$, PDMS-diols limiting viscosity number at 25°C with one point in toluene
$[\eta]_{EES}$, EES limiting viscosity number at 30°C with one point in phenol–trichlorethylene–toluene (1:1:2 vol.)
T_t, melting point of EES with Böetius apparatus

and examined in a triple cycle 'heating–cooling–heating' in the temperature ranges −150 to +250°C and −100 to +250°C. The rate of heating and cooling was 10°C min^{-1}. The calibration was based on indium and synthetic sapphire. The glass transition temperatures of terpolymers (T_{g1} and T_{g2}) were determined from temperature diagrams as the temperature at which half of the total change in heat capacity occurred. The glass transition temperature T_{g3} was determined as a temperature corresponding to the upper inflection point or maximum of the curve. The melting point (T_m) and crystallization temperature (T_c) were determined as corresponding to the maximum of the endothermic curve and the minimum of the exothermic curve respectively.

The glass transition temperatures were also determined by the method based on maximum of loss modulus E'' (T''_{g2}). The dynamic mechanical characteristic was performed on a Rheovibron DDV II-c viscoelastometer (Toyo Baldwin Co.) in the temperature range from −140 to +240°C at 35 Hz. The storage modulus (E'), loss modulus (E'') and loss tangent (tan δ) were determined.

Uniaxial stress–strain data were collected at room temperature with an Instron 1161 tensile tester using a crosshead speed of 100 mm min^{-1}.

Hardness measurements were performed using Shore D apparatus (Carl Franc GmbH) according to ASTM D-2240. The resilience and melt flow index (MFI) were determined according to ASTM D-638 and ASTM D-1238, respectively.

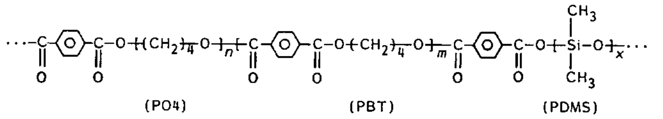
The water sorption of the terpolymer was determined by the method reported in ASTM D-570.

Thin films (10 μm) prepared by melt pressing and quenching were examined under a phase contrast microscope.

RESULTS AND DISCUSSION

A series of multiblock EES elastomers, with the general formula shown in *Scheme 1*, has been synthesized and examined.

The charge of components into reactor has been calculated to obtain terpolymers of determined weight fraction of PBT, PO4 and PDMS. The weight compositions and preliminary characteristics of EES are given in *Table 1*.



where n = 14, m and x are variables

Scheme 1

The results of d.s.c. examination are presented in *Figures 1–3* and *Tables 2* and *3*. The d.s.c. examination revealed that EES containing more than 10 wt% PDMS are characterized by three glass transition temperatures denoted respectively T_{g1}, T_{g2} and T_{g3}. T_{g1} values are observed in the vicinity of −130°C (143 K) and refer to PDMS[19]. For samples 4–7 a change in value of T_{g1} from −134 to −126°C has been observed. This probably results from an increase of the PDMS segment length as observed for block poly(siloxane-carbonate)s investigated by Hedrick *et al.*[20]. Stoichiometric calculation shows that the longer the PDMS segment, the higher is the polycondensation degree m (*Scheme 1*) of PBT segment at the same mass composition of terpolymer. It might be possible that changes observed in T_{g1} are caused by superposition of low temperature (< −100°C) γ-relaxation effects originating from the phase containing PBT and PO4[21,22]. The T_{g1} transformation does not appear directly on d.s.c. curves for the samples of low PDMS segment content (samples 2 and 3) although the greater slope of the curve in the range from −130 to −60°C has been observed (*Figure 1*, sample 3).

T_{g2} refers to the glass transition of the phase rich in PO4 and has been determined in the temperature range from −69 to −60°C. For copolymers of constant PBT:PO4 mass ratio of 45:55 the differences in T_{g2} are rather small (−69 to −66°C) and only slightly dependent on PDMS content. On the other hand the dependence of T_{g2} on PO4 content in terpolymer can be observed (*Table 2*, sample 8, T_{g2} = −60°C). T_{g2} values taken from d.s.c. results may be influenced by the endothermic effects of a PDMS melting phase appearing in the vicinity in the form of two characteristic peaks (*Figure 1*). The d.s.c. characteristics of cooling from +250 to −100°C were also performed. The respective low temperature glass

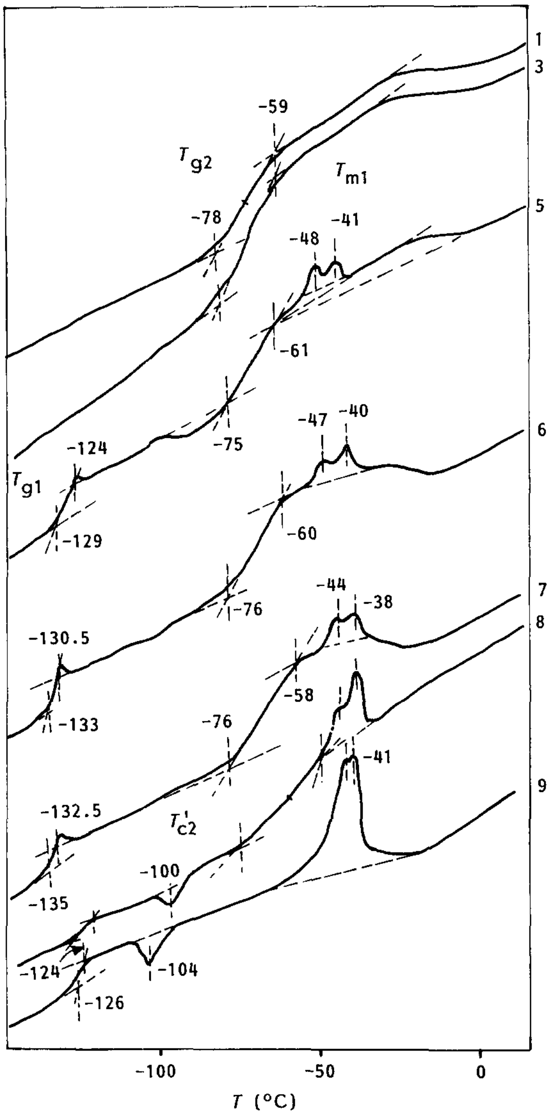


Figure 1 D.s.c. curves obtained during heating at 10°C min^{-1}. Numbered curves refer to sample numbers. Temperatures are in °C

transition is clearly seen on the curves for samples 1–7 (*Figure 2b*). The values of glass transition temperatures T_{g2} (*Table 2*) are close to those determined on heating.

T_{g3} appears on the d.s.c. diagrams for all samples only during the first stage of heating (*Figure 3*). This transition refers to the phase rich in PBT. For semicrystalline PBT homopolymer the glass transition temperature determined by Cheng *et al.*[23] was 37–52°C depending on crystallization conditions. Owing to only slight inflection of the curve, T_{g3} values were taken from the maximum observed and ranged from 46 to 51°C for the samples investigated. On cooling sample 9, the glass transition could also be observed at about −25°C (*Figure 2*, T'_{g3}) which according to Cheng may be attributed to totally amorphous PBT.

Low temperature glass transitions of the investigated samples were verified by readings of relaxation temperatures (T_β and T_γ) from loss modulus curves E''. From these two values only T_β may be interpreted as a glass transition temperature of the phase rich in PO4 ($T_\beta = T''_{g2}$). T_γ refers to rotation release of $-CH_2-$ and $-COO-$ groups in PBT and PO4 segments. It should not be connected with the glass transition temperature of PDMS[22].

For the investigated EES samples one or two melting and crystallization transitions were observed. The d.s.c. curve shows an endothermic effect in the range from −50 to −40°C (*Figure 1*) which is identical to that of PDMS

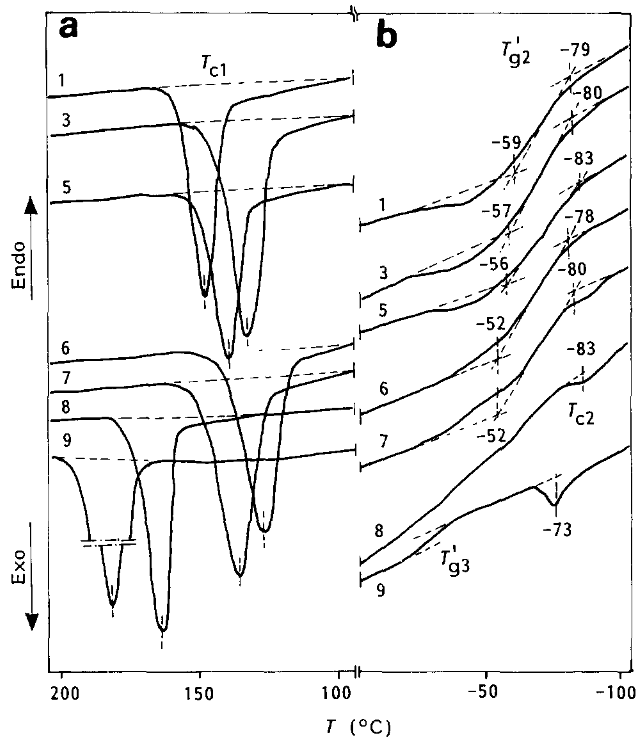


Figure 2 D.s.c. curves obtained during cooling at 10°C min^{-1}. (a) Crystallization range; (b) glass transition and low temperature crystallization range. Numbered curves refer to sample numbers. Temperatures are in °C

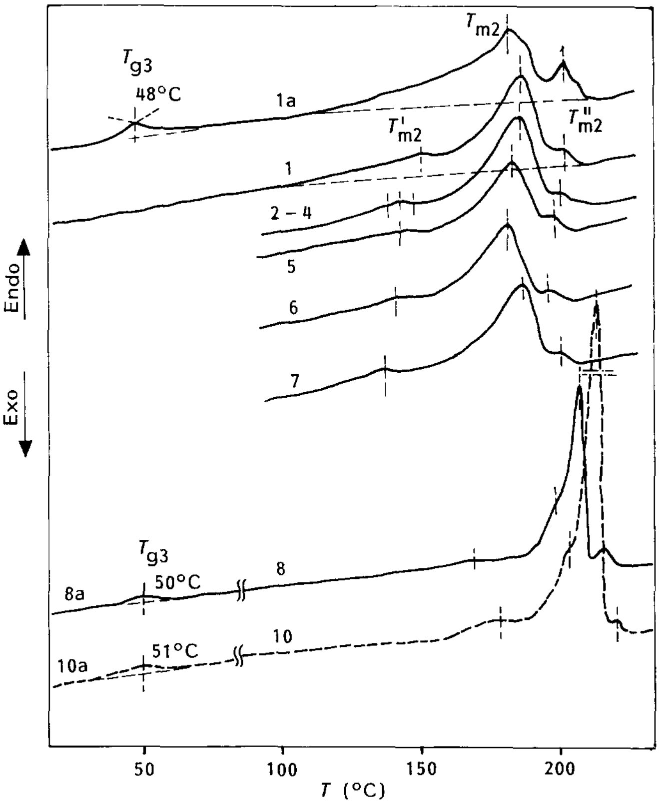


Figure 3 D.s.c. curves obtained during heating. Numbered curves refer to sample numbers: 1a, 8a and 10a refer to first heating; other curves refer to second heating

Table 2 Glass transitions and heat of melting of EES in low temperature region

	D.s.c.						E''_{max}	
Sample	T_{g1} (°C)	T_{g2} (°C)	T_{g3} (°C)	T_{m1} (°C)	ΔH_{m1} ($J g^{-1}$)	T'_{g2} (°C)	T_γ (°C)	T_β (°C)
1	–	−68	48	–	–	−69	–	−68
2	–	−66	49	–	–	−67.5	–	−66
3	–	−67	49	–	–	−68.5	–	−65
4	−126	−69	49	−48, −41	0.37	−68.5	−135	−62
5	−127	−68	48	−48, −41	0.69	−69.5	−134	−62
6	−132	−68	47	−47, −40	0.71	−65	−134	−62
7	−134	−68.5	46	−44, −38	0.69	−66	−135	−64
8	−125	−60	50	−46, −39	1.26	–	−134	−50
9	−126	–	51	−43, −41	3.64	–	−134	–

T_{g1}, T_{g2}, T_{g3}, glass transition temperatures from d.s.c. for heating sample (see *Figure 1*)
T_{m1}, melting point temperature for PDMS rich phase
ΔH_{m1}, heat of melting at T_{m1}
T'_{g2}, glass transition temperature from d.s.c. for cooling sample (see *Figure 2*)
T_γ, T_β, temperature of γ- and β-relaxation determined by mechanical loss modulus (E'')

Table 3 Thermal properties of EES in high temperature region

Sample	T_{m2} (°C)	T'_{m2} (°C)	T''_{m2} (°C)	ΔH_{m2} ($J g^{-1}$)	T_{c1} (°C)	ΔH_{c1} ($J g^{-1}$)
1	187	151	202	29.4	149	27.3
2	186	145	200	28.0	141	24.9
3	186	138	200	25.9	136	23.1
4	186	143	200	23.2	141	21.5
5	184	143	199	17.6	142	20.4
6	182	129	198	21.5	130	20.5
7	188	138	202	19.9	138	21.1
8	209	171	217	21.1	169	20.9
9	224	212	–	41.8	186	37.3
10	214	179	220	49.8	177	45.3

T_{m2}, melting point of EES (with middle maximum)
T'_{m2} and T''_{m2}, other point at melting region (see *Figure 3*)
ΔH_{m2}, heat of fusion of EES
T_{c1}, crystallization temperature of EES
ΔH_{c1}, crystallization heat of EES

homopolymer[19]. The endothermic effect is revealed only at PDMS segment contents higher than 10 wt% in the terpolymer. The melting temperatures T_{m1} (doublet) increase with segment length (−48°C and −41°C for samples 4 and 5 and −44°C and −38°C for sample 7). The value of heat of fusion ΔH_{m1} (see *Table 1*) does not depend on the length of siloxane block but is distinctly dependent on its content in the terpolymer (samples 4 and 5) and polyether segment content (samples 6, 8 and 9). Thus the high content of PO4 makes the crystallization of PDMS more difficult.

The main melt transition of the investigated EES terpolymers occurs in the temperature range from 129 to 220°C. Three and sometimes four endothermic peaks (*Figure 3*) characteristic for copoly(ether-ester) and PBT homopolymer are observed. Stevenson and Cooper[24] and Yeh and Runt[25] proved that the intensity and position of those peaks on the d.s.c. curve depend on temperature and duration of crystallization. During the first stage of heating (*Figure 3*, curve 1a) repeatable results were not obtained. Thus the evaluation was based on the curves from the second heating of the sample in the cycle heating–cooling–heating at a rate of 10°C min^{-1}. The crystallization conditions were settled by cooling the melted polymer at the same rate (*Figure 2a*). Values of T_{m2} temperatures are significantly connected to crystallization temperatures T_{c1} (*Figure 3*). A decrease of T_{c1}, T_{m2} and T'_{m2} with increase in PDMS content in terpolymer is observed. As the T_{m2} values are less dependent on crystallization conditions[24] these values are more reliable. T''_{m2} (*Figure 3*) refers to the melting temperature of crystallites resulting from recrystallization at a temperature close to T_{m2}, therefore it is directly dependent on T_{m2}. The heat of fusion ΔH_{m2} and heat of crystallization ΔH_{c1} decrease approximately in proportion to the decreased PBT segment content in EES (*Table 3*). From a comparison of T_{m2} for samples 1, 8, 9 and 10 it is seen that PDMS does not cause such a melting temperature depression as is observed in the case of increasing PO4 content in copoly(ether-ester)s[26]. For ester-siloxane copolymer containing 30% PDMS, T_{m2} differs only slightly from the melting temperature of PBT homopolymer[22].

In the low temperature region, crystallization peaks probably derived from PDMS segments (*Figures 1* and *2*, T_{c2}, T'_{c2}) can be observed. These refer exclusively to the terpolymers with high content of PBT segments and low content of PO4 segments (samples 8 and 9). Due to the small length of segments in the phase rich in PO4, crystallization was not observed.

The results of dynamic examinations are presented in *Figures 4–7*. For samples 1–7 (*Figure 4*) in the temperature range from $\sim$130 to ~ -40°C a relatively flat course of storage modulus E' is observed. This is the range of elastic state limited by the previously discussed phase transitions. With increase in siloxane segment content in EES in the range from -70 to -120°C on E' curve the second plateau of elastic state is observed. It is characteristic that in both of these temperature ranges the greater change of modulus is observed for low contents of PDMS in the material (*Figure 5*). *Figure 6* shows that an increase in PDMS length and its content in terpolymer cause an increase in tan δ in the range from ~ -50 to $\sim$50°C and replacement of the β relaxation temperature maximum towards higher temperatures. On the basis of other works[21,27] it is known that an increase in PO4 segment content in copoly(ether-ester)s also causes the replacement of tan δ maximum but towards low temperatures. This effect can be extremely well observed by comparing curve 1 with 8 and 9 with 10 in *Figure 6*.

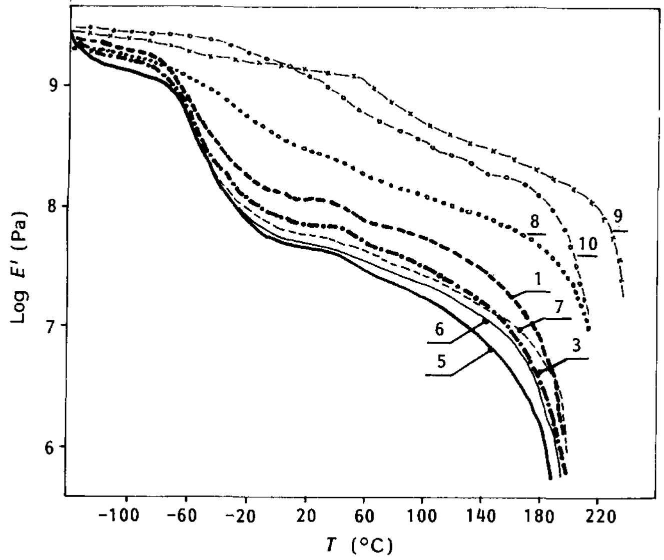


Figure 4 Dependence of dynamic mechanical storage modulus E' on temperature for EES. Frequency 35 Hz. Numbered curves refer to sample numbers

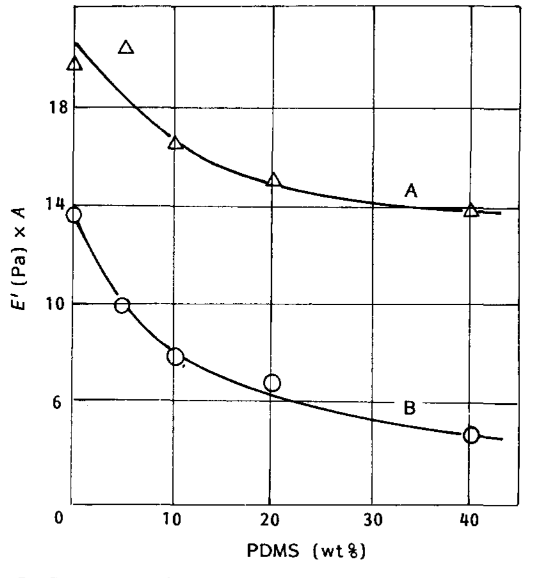


Figure 5 Storage modulus E' of EES *versus* content of PDMS segments. Curve A, $T = -100$°C, $A = 10^8$; curve B, $T = +20$°C, $A = 10^7$

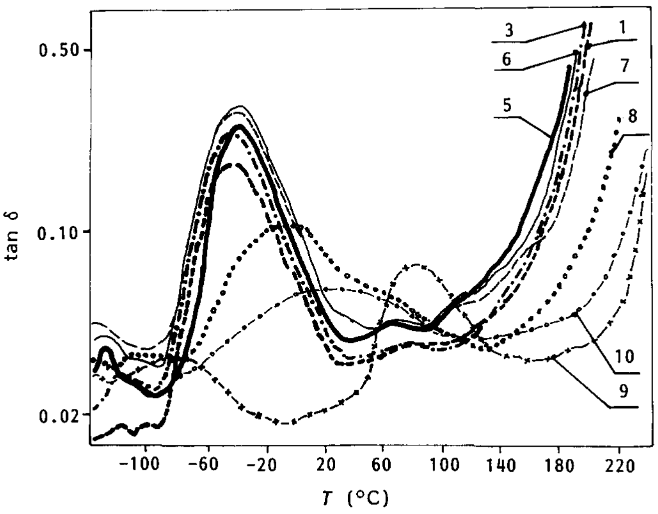


Figure 6 Dependence of tan δ for EES on temperature. Frequency 35 Hz. Numbered curves refer to sample numbers

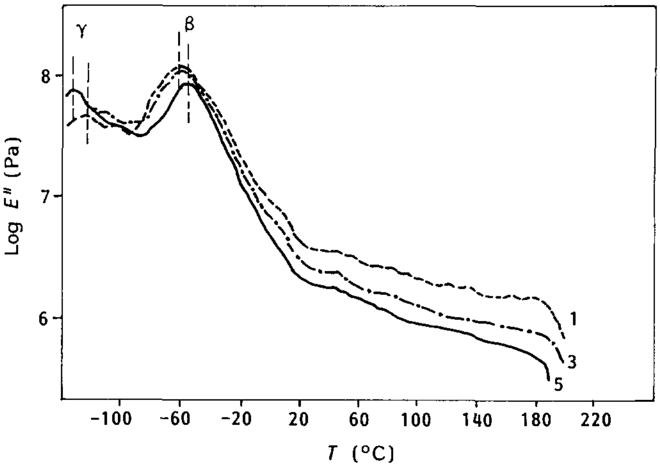


Figure 7 Dependence of dynamic mechanical loss modulus E'' for EES on temperature for samples 1, 3 and 5

The diagrams of loss modulus E'' enabled the determination of $T_\beta = T''_{g2}$ values and T_γ mentioned earlier (*Table 3*). Examples of changes in E'' as a function of temperature for samples 1, 3 and 5 are shown in *Figure 7*.

Figure 8 shows photomicrographs of EES thin films, obtained by press moulding. The domain–matrix microphase structure is characteristic of multiblock copolymers[28,29].

Some of the physical properties of EES are given in *Table 4*. *Figure 9* shows the relationship between stress and tensile strain. These data indicate that hardness,

Table 4 Physical properties of EES elastomers

Samples	Hardness (Sh D)	Resilience (%)	Water sorption (wt%)	Strength at break (MPa)	Elongation at break (%)	*d* (g cm^{-3})	MFI (g/10 min)
1	45	50	0.40	22	1100	1.150	4.04
2	41	50	0.38	25	1100	1.144	1.88
3	40	51	0.19	20	1000	1.128	1.43
4	37	50	0.12	17	900	1.120	1.91
5	27	48	0.15	13	800	1.098	6.02

d, density determined by gradient column method
MFI, melt flow index at 210°C

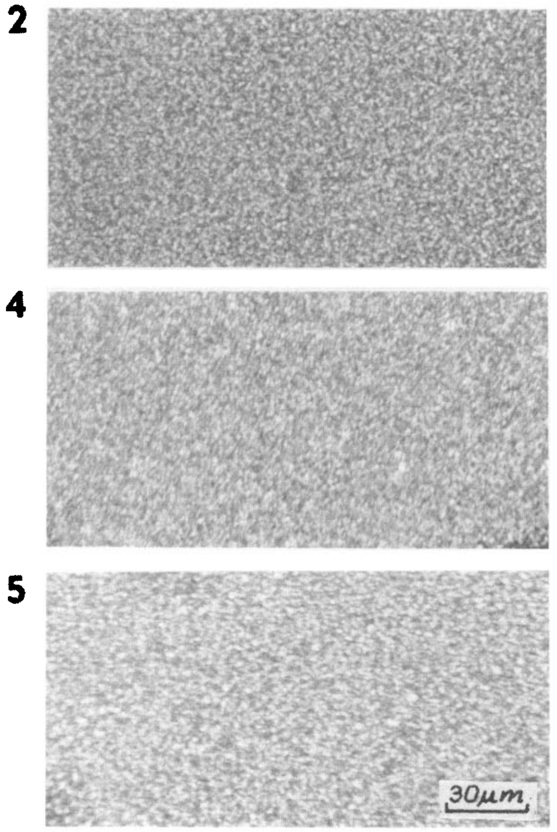


Figure 8 Photomicrographs of EES samples 2, 4 and 5

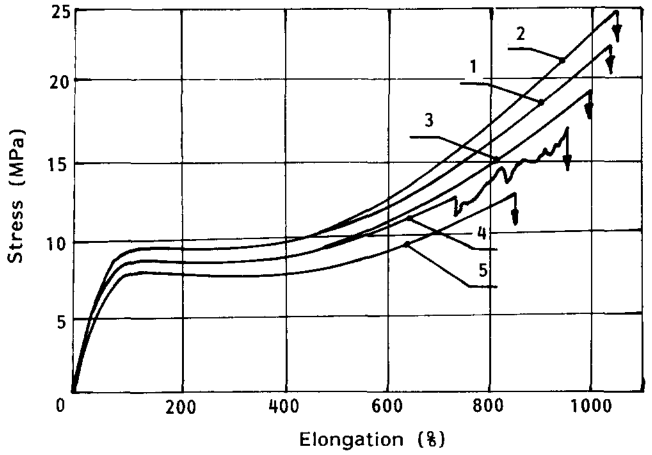


Figure 9 Stress–strain dependence for EES terpolymer samples 1–5

tensile strength and water absorptivity decrease with increase in PDMS segment content. The high elasticity and large elongation at rupture of the EES under investigation should be pointed out. The stress–strain plots are similar to those of thermoplastic elastomers[3,16,30,31].

CONCLUSION

A great difference between Hildebrand solubility parameters for PBT[13] ($\delta = 23.1\ \mathrm{J^{1/2}\ cm^{3/2}}$) and PO4[32] ($\delta = 17.5\ \mathrm{J^{1/2}\ cm^{3/2}}$) results in the immiscibility of those polymers. Block copolymers of such segment structure undergo microphase separation. The chemical composition of particular phases depends on the content of segments and their length, as for all such materials[33]. PDMS has one of the smaller solubility parameters in comparison with other organic polymers[12,34] ($\delta = 14.9$–$15.3\ \mathrm{J^{1/2}\ cm^{3/2}}$). Thus the incompatibility is expected for PBT-PDMS and PO4-PDMS systems assuming that interdispersion of the components, resulting from alternating multiblock structure of the macromolecules, does not play an important part. PDMS does not cause the depression of PBT melting temperature (sample 9) and its only very slight lowering is noticeable in the case of increased PDMS content in terpolymer (*Table 3*, samples 1–5). From T_{g1} and T_{m1} determinations at PDMS content up to 10% it follows that the separation of this phase from the system does not occur. This takes place at higher contents of polysiloxane segments; however, the separation probably does not proceed totally or the crystallization process would be considerably disturbed. This may be concluded from the lower values of fusion heat ΔH_{m1} for samples 4 and 5 than for sample 8 (in relation to PDMS). Microscopic observations did not reveal macrophase separation in the system.

Thus it can be expected that EES has a multimicrophase structure. In normal conditions, in an elastic (liquid) matrix consisting of a mixture of polyether and polyester segments rich in PO4, dispersed hard PBT domains exist with considerable content of crystalline structure and low content of tangled PO4 segments. In the polyether matrix the second liquid phase (microphase rich in more mobile PDMS segments) is emulsified. This emulsion is structurally stabilized by fixing of the segment ends in the polymer chain. The increase in length or content of PDMS segments probably influences the enlargement of these microphases. This leads to the decrease in hardness with simultaneous maintenance of good resilience and tensile strength, influenced by the PO4 matrix. This characteristic is based on the model composition of sample 5 (PBT:PO4:PDMS = 27:33:40). Obviously, due to varying compositions of particular phases the content of these segments in a material differs from stoichiometry. Up to ~ 10% PDMS content the segments are dispersed molecularly and do not form a separate phase, similarly to poly(ether-siloxane-urethane)s[7]. If the content of PDMS is increased it will act as an elastic matrix and material may lose its strength properties, as in the case of carbonate-siloxane copolymers[35]. If such a structure of EES terpolymers is confirmed then in the low temperature elastic region an increased (in comparison to ether-ester elastomers) impact strength of the material can be expected. On the basis of the above data EES block terpolymer appears to have a multiphase structure and physical characteristics of a thermoplastic elastomer.

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REFERENCES

1 Hofmann, V. *Kunststoffe* 1987, **77**(8), 767

2 Domininghaus, H. *Plastverarbeiter* 1989, **40**(1), 39; 1989, **40**(2), 42; 1989, **40**(3), 30

3 Folkes, M. J. 'Processing, Structure and Properties of Block Copolymers', Elsevier Applied Science, London, 1985

4 Quan, X., Bair, X. E. and Johnson, G. E. *Macromolecules* 1989, **22**, 4631

5 Stevenson, J. C. and Cooper, S. L. *Macromolecules* 1988, **21**, 1303

6 Walsh, D. J. and Rostami, S. *Adv. Polym. Sci.* 1985, **70**, 119

7 Shibayama, M., Inoue, M., Yamamoto, T. and Nomura, S. *Polymer* 1990, **31**, 749

8 Obolonkova, Ye. S., Levin, V. Yu., Zdanov, A. A., Slonimski, G. L. and Makarova, L. I. *Vysokomol. Soed.* 1985, **A-27**(9), 1886

9 Madec, P. J. and Marechal, E. *J. Polym. Sci.* 1978, **16**, 3157

10 Jap. Pat. 60245629, 1985; *Chem. Abs.* 1986, **105**, 44647g

11 Jap. Pat. 62285917, 1987; *Chem. Abs.* 1988, **108**, 156510a

12 Yilgor, I., Steckle, W. P., Yilgor, E., Freelin, R. G. and Riffle, J. S. *J. Polym. Sci., Polym. Chem. Edn.* 1989, **27**, 3673

13 Pukanszky, B. and Tudos, F. 32nd Microsymposium on Macromolecules, Prague, 17–20 July 1989, paper SL-9

14 Tang, S. H., Meinecke, E. A., Riffle, J. S. and McGrath, J. E. *Rubber Chem. Technol.* 1980, **53**, 1160; 1984, **57**, 184

15 Marsial, A. and Gallot, Y. *Makromol. Chem.* 1975, **176**(6), 164

16 Noshay, A. and McGrath, J. E. 'Block Copolymers', Academic Press, New York, 1977

17 Rosłaniec, Z., Pękala, S. and Wojcikiewicz, H. 2nd Symposium on Thermoplastic Elastomers, Szczecin, 21–22 May 1991, Prace Naukowe Politechniki Szczecinsksej (Science Reports of Technical University of Szczecin) 1991, Vol. 443, pp. 51–58

18 Hardman, B. and Torkelson, A. in 'Encyclopedia of Polymer Science and Engineering' (Ed. J. I. Kroschwiz), John Wiley, New York, 1989, Vol. 15, p. 246

19 Friedrich, J. and Rabolt, J. F. *Macromolecules* 1987, **20**, 1975

20 Hedrick, J. L., Haidar, B., Russell, T. P. and Hofer, D. C. *Macromolecules* 1988, **21**, 1967

21 Shen, M., Mechra, U., Niinomi, M., Koberstein, J. T. and Cooper, S. L. *J. Appl. Phys.* 1974, **45**, 4182

22 Castles, J. L., Vallance, M. A., McKenna, J. M. and Cooper, S. L. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 2119

23 Cheng, S. Z. D., Pan, R. and Wunderlich, B. *Makromol. Chem.* 1988, **189**, 2443

24 Stevenson, J. C. and Cooper, S. L. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 953; *Macromolecules* 1988, **21**, 1309

25 Yeh, J. T. and Runt, J. *J. Polym. Sci., Polym. Phys. Edn.* 1989, **27**, 1543

26 Schmidt, F. G. *Makromol. Chem.* 1983, **184**, 2669

27 Kalfoglou, N. K. *J. Appl. Polym. Sci.* 1977, **21**, 543

28 Chang, Y. P. and Wilkes, G. L. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 455

29 Lin, Y. G., Jin, P. W., Chien, J. C. W. and Winter, H. H. *Polymer* 1989, **30**, 831

30 Heineck, D. W. and Rader, C. P. *Plast. Eng.* 1989, **45**(3), 87

31 Fakirov, S. and Gogeva, T. *Makromol. Chem.* 1990, **191**, 603

32 Camberlin, Y. and Pascault, J. P. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 415

33 Xie, M. and Camberlin, Y. *Makromol. Chem.* 1986, **187**, 383

34 Van Krevelen, D. W. 'Properties of Polymers, their Estimation and Correlation with Chemical Structure', Elsevier, Amsterdam, 1976

35 Niznik, G. E. and Legrang, D. G. *J. Polym. Sci., Polym. Symp. Edn.* 1977, **60**, 97