Segmented block copolymers based on dimerized fatty acids and poly(butylene terephthalate)

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Segmented block copolymers based on dimerized fatty acids and poly(butylene terephthalate) (PBT) have been synthesized in the melt. Branched C_{36}, C_{44} and C_{70} dimerized fatty acids with a low degree of unsaturation were used. The fraction of PBT was varied from 50 to 100wt%. The resulting polymers were analysed with d.s.c. and d.m.a. The glass transition temperature (T_g) increased with increasing weight fraction of PBT. T_g decreased with increasing molecular mass of the dimerized fatty acid. The melting temperature increased with increasing weight fraction of PBT and increasing molecular mass of the dimerized fatty acid. The range of service temperatures of the thermoplastic elastomers can therefore be enlarged by using dimerized fatty acid with a high molecular mass. With increasing molecular mass of the dimerized fatty acid the storage modulus and the melting and crystallization enthalpy did not change significantly. The storage modulus can be described as a function of the volume fraction of crystalline PBT, but is not a function of the type of dimerized fatty acid.

(Keywords: dimer acid; dimerized fatty acid; segmented block copolymer; poly(butylene terephthalate); poly(ester ester); thermoplastic elastomer)

INTRODUCTION

Segmented block copolymers are polymers that consist of different types of segments that alternate along the polymer backbone. Each segment of the polymer backbone has its own properties and transition temperatures. When proper monomers are chosen segmented block copolymers can be synthesized with elastomeric properties. One segment (A) must possess a low elasticity modulus and a low glass transition temperature (T_g). This segment imparts elastomeric properties to the material and, therefore, is often called the soft phase. The other segment (B) is designed to undergo some sort of association with other B segments so that it can form physical crosslinks. This segment will then impart dimensional stability to the material and, therefore, is often called the hard phase. Since the crosslinks of the material are of a physical nature, the materials with elastomeric properties can be processed in the melt by thermoplastic moulding techniques. For this reason, the materials are called thermoplastic elastomers (TPEs).

An example of a commercial TPE that has been studied extensively in the literature[1] is the segmented block copoly(ether ester). Commercial block copoly(ether ester)s are usually based on poly(tetramethylene oxide) (PTMO) and poly(butylene terephthalate) (PBT) as the rubbery and semicrystalline components, respectively. These materials and their modifications are known under many tradenames such as Hytrel (DuPont), Arnitel (AKZO) and Pelprene (Toyobo). These materials couple interesting properties such as high melting temperature (T_m), low T_g, high tensile and tear strengths with ease of processing.

One of the disadvantages of PTMO in TPEs is that it is prone to oxidative degradation[2–5] and hydrolysis[5] at elevated temperatures. It also degrades at ambient temperatures in sunlight[6,7]. For these reasons commercial copoly(ether ester)s are stabilized with various stabilizers[2–5,7–10].

An alternative to polyethers in TPEs are saturated fatty acids. Hoeschele[11] synthesized segmented block copolymers with a C_{36} dimerized fatty acid as the soft phase. All the properties concerning degradation stability were improved while most other properties were not influenced significantly. The properties at lower temperatures, however, showed poorer results due to the higher T_g value. This is probably caused by the low molecular mass of the dimerized fatty acid.

Commercial dimerized fatty acids are usually synthesized by dimerization of unsaturated C_{18} fatty acids such as oleic, linoleic and linolenic acids. This yields mixtures of branched C_{36} dimerized fatty acids with a molecular mass of ~565 g mol^{-1}. Unichema Chemie BV (Gouda, The Netherlands) synthesized C_{44} dimerized fatty acid by employing C_{22} fatty acids[12]. Also, a C_{70} dimerized fatty acid was synthesized by coupling two C_{36} dimerized fatty acids[13]. These new types of dimerized fatty acid have a high purity and a low unsaturation level.

The aim of this work is to study the synthesis and properties of segmented block copolymers with PBT as the hard phase and dimerized fatty acids with different molecular masses as the soft phase.

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EXPERIMENTAL

Materials

Dimethylterephthalate (DMT), 1,4-butanediol (BDO) and tetrabutyl *o*-titanate (all synthetic grade) were purchased from Merck, Hohenbrunn, Germany. The dimerized fatty acids were obtained from Unichema Chemie, Gouda, The Netherlands.

Some properties of the dimerized fatty acids are given in *Table 1*. The iodine value is the number of unsaturated bonds present; the values indicate that a low number is present.

The purity of the dimerized fatty acids is also given in *Table 1*. Pure dimerized fatty acid would consist of 100% dimer. Some monomer remains in the material. Also, a portion of trifunctional trimer is formed as a by-product in the reaction. The intermediate fraction consists partly of monofunctional fatty acid ($>C_{18}$ fatty acid) and partly of bifunctional dimerized fatty acid ($<C_{36}$ dimerized fatty acid).

Synthesis of segmented block copolymers[11]

Batches of copolymer (50 g) were synthesized by placing BDO, DMT and dimerized fatty acid in an agitated round-bottom flask, fitted for distillation. A stainless steel stirrer with a paddle, cut to conform with the internal radius of the flask, was positioned a few millimetres above the bottom of the flask. Agitation was started while nitrogen was led into the flask. The flask was placed in an oil bath at 160°C, agitated for 5 min and then 0.1 wt% tetrabutyl *o*-titanate was added. Methanol distilled from the reaction mixture as the temperature was slowly raised to 240°C over a period of 1 h. At 240°C the pressure was reduced in 15 min to ~0.5–1 mm Hg to distil excess BDO from the reaction mixture. The reaction mixture was agitated for another hour and allowed to cool down slowly under vacuum to room temperature. A white polymeric product was produced.

Synthesis of amorphous polymers (dimerized fatty acid with BDO)

To determine the T_g of the pure amorphous phase two polyesters of C_{36} and C_{44} dimerized fatty acids with BDO were synthesized (no DMT). The same procedure was followed as described for the TPEs except that no vacuum was employed. The products were transparent viscous liquids.

Characterization

Viscometry. The logarithmic viscosity number (inherent viscosity) of $1\,g\,l^{-1}$ solutions of copolymer in *m*-cresol (Merck, analytical grade) was determined with an Ubbelohde viscometer at 25°C.

End group titration. The purely amorphous polyesters from dimerized fatty acid with BDO were titrated to determine the concentration of carboxyl end groups. The concentration was measured by dissolving 200 mg of product in freshly distilled benzyl alcohol followed by titration with potassium hydroxide in tertiary butanol. Titration was carried out with a glass calomel electrode under nitrogen, to minimize oxidation of benzyl alcohol, in a titroprocessor (Metron 636). All chemicals were analytical grade and obtained from Merck. The number-average molecular masses of the amorphous polyesters, as determined by end group titration, were 2100 ± 110 and $2470\pm90\,g\,mol^{-1}$ for the C_{36} and C_{44} polyesters, respectively.

WAXS measurements were performed on stretched samples of 1,6-hexane diamine–dimerized fatty acid polymers. Ni-filtered CuKα radiation was generated by a Phillips PW 1700 diffractometer. A scan was performed from 1.01 to 60°, at a speed of 25 s per degree.

D.s.c. Thermal properties were measured with a Perkin–Elmer DSC-7. Samples (4–8 mg) of the as-prepared copolymers were dried *in vacuo* at 100°C for 24 h prior to testing. D.s.c. curves were obtained using the following procedure (heating/cooling rate, $20^{\circ}C\,min^{-1}$): first heating run from 50 to 40°C above the T_m; equilibration for 8 min; cooling run to 50°C; second heating run to 40°C above the T_m.

The crystallization temperature (T_c) and T_m were taken as the maxima in the cooling and second heating runs respectively. The crystallization enthalpy (ΔH_c) and melting enthalpy (ΔH_m) were also taken from these runs. The absolute error in T_c and T_m was $\pm2^{\circ}C$. The absolute errors in ΔH_m and ΔH_c were ±4 and $\pm2\,J\,g^{-1}$, respectively.

D.m.a. Torsion bars (approximate dimensions $80\times9\times2$ mm) were prepared by compression moulding of the as-prepared copolymers. The copolymers were placed between the heating plates of a hydraulic press (Lauffer), compressed and kept at a temperature ~40°C above the T_m for 7 min, then the cooling of the heating plates was started. The bars were subsequently dried for 18 h *in vacuo* at 100°C. The test bars were heated from −100°C to the onset of melting at a heating rate of $\sim1^{\circ}C\,min^{-1}$ at a resonance frequency of 1 Hz. Torsion moduli were calculated with a computer-controlled Myrenne torsion pendulum. The maximum of the loss modulus was taken as the T_g. The absolute error in T_g was $\pm2^{\circ}C$. The relative error in the moduli was ± 5%.

The T_g of the pure amorphous polyesters (dimerized fatty acid–BDO) was determined by an indirect route. First, a piece of cloth with the right dimensions was cut. The piece of cloth was then impregnated with the polyester and dried at 40°C for 5 h. The specimen was measured under the same conditions as described above.

RESULTS AND DISCUSSION

Dimerized fatty acids

WAXS. The average number of carbon atoms directly between the carboxyl groups of the C_{36} dimerized fatty acid was determined with WAXS. The number of carbon atoms could not be determined for C_{44} and C_{70} dimerized fatty acid. The result is given in *Table 1*. For the C_{36} dimerized fatty acid 13 carbon atoms can be found directly between the carboxyl groups. The branched side groups therefore contain 21 carbon atoms.

Segmented block copolymers

Viscometry. The logarithmic viscosity numbers of all the synthesized block copolymers are given in *Table 2*. They compare well with the results of Hoeschele[2] on copolymers based on C_{36} dimerized fatty acid and PBT. In all cases, polymers were formed with a high enough molecular mass to allow torsion bars to be compression

Table 1 Properties of dimerized fatty acids

Dimerized fatty acid				Composition				WAXS	
Tradename/ laboratory code	Number of carbon atoms	[–COOH] (meq g^{-1})	Iodine value (mg I per 100 g)	Monomer (wt%)	Intermediate (wt%)	Dimer (wt%)	Trimer (wt%)	Repeating unit^a (Å)	C^b
Pripol 1008	36	3.46	3.8	0.1	0.5	99.0	0.5	25	13
UCN 83.033	44	2.97	<7	0.1	5.0^d	93.5	1.5	–	–
–^{c}	70	–	<7	4.0	–	96.0	–	–	–

[a] Repeating unit of amide of dimerized fatty acid with 1,6-hexanediamine
[b] Number of carbon atoms directly between COOH groups
[c] Dimethylester of C_{70} dimerized fatty acid
[d] Mainly other dimerized fatty acids

Table 2 Logarithmic viscosity numbers, d.s.c. data and torsional data of copolymers based on dimerized fatty acids and varying PBT fractions

Material acid	$W_{PBT}{}^a$	η_{inh} (dl g^{-1})	n^b	T_m (°C)	T_c (°C)	ΔH_m (J g^{-1})	$-\Delta H_c$ (J g^{-1})	$\alpha_{tot}{}^c$ (%)	$\alpha_{PBT}{}^c$ (%)	T_g (°C)	G'(30°C) (MPa)
PBT^d	1.00	1.66	–	223	190	55	–	40	40	50	2600
C_{36}	0.78	1.22	10.0	208	156	31	38	26	34	−3	153
C_{36}	0.70	0.96	6.6	203	153	29	36	25	36	−15	90
C_{36}	0.60	0.90	4.2	185	146	21	32	22	37	−26	58
C_{36}	0.50	0.46	2.8	171	116	16	22	15	30	−32	28
C_{44}	0.80	0.37	13.3	212	168	42	45	31	39	−12	168
C_{44}	0.60	0.44	5.0	194	143	26	32	22	37	−36	62
C_{44}	0.50	0.26	3.3	181	152	14	23	16	32	−40	42
C_{70}	0.81	0.25	21.3	217	178	45	45	31	38	−34	230
C_{70}	0.61	0.47	7.8	211	146	27	32	22	37	−37	60
C_{70}	0.51	0.50	5.2	199	142	18	24	17	33	−41	36

[a] Weight fraction of PBT
[b] $n = x/(1-x)$, where x = molar fraction of PBT repeating units
[c] $\alpha_{tot} = \Delta H_c/144.5$; $\alpha_{PBT} = \alpha_{tot}/W_{PBT}$
[d] From reference 25

moulded. As already predicted by Hoeschele, a few exploratory tests showed that the logarithmic viscosity number could be increased by post condensation. The as-prepared copolymers were used without post condensation for further tests.

D.s.c. D.s.c. data of the dried copolymers are given in *Table 2*. The T_ms of the copolymers are lower than that of pure PBT. The T_m is usually a function of the PBT block length[14,15]. In *Figure 1* the T_m of the copolymers based on dimerized fatty acids is plotted *versus* the number-average hard segment sequence length (n). Data on copoly(ether ester)s based on PTMO (PTMO-glycol 1000 g mol^{-1}) and PBT from reference 14 are also included. The average hard segment sequence length is calculated from the known molar fraction of PBT repeating units (x), according to $n = x/(1-x)$. The T_m is solely a function of the block length. This can be explained as being due to the change in thickness of the PBT lamellae. In the melting point depression of random copolymers the concentration and interaction parameter of the amorphous phase also play a role[16]. In our segmented block copolymers no effect of interaction parameters on T_m is observed (the nature of the amorphous phase does not influence T_m significantly; all data fit the line well). The block length is a function of the molecular mass of the amorphous phase and the weight fraction of PBT. The T_m can therefore be increased at a constant composition by increasing the molecular mass of the soft block.

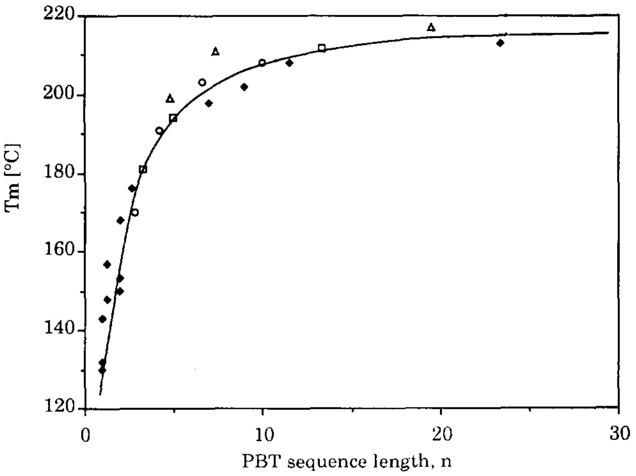

Figure 1 Melting temperature as a function of the sequence length of PBT segments. Copolymers based on PBT and: (○) C_{36} dimerized fatty acid; (□) C_{44}; (△) C_{70}; (▲) PTMO-glycol 1000 g mol^{-1} (data from ref. 14)

The T_c behaves much the same as T_m with different dimerized fatty acids and composition. Its value is usually some 40–60°C lower. This difference is larger than for pure PBT reflecting the increased difficulty to crystallize.

The ΔH_m and ΔH_c increase with increasing weight fraction of PBT. Strangely, ΔH_m and ΔH_c do not change significantly with the molecular mass of the dimerized fatty acids at a constant weight fraction of PBT. The enthalpy is influenced by composition only.

The calculated total weight fraction of crystalline material in the TPEs (α_{tot}) and the weight fraction of crystallized PBT segments (α_{PBT}) are also given in *Table 2*. They increase to the values for pure PBT at higher weight fractions of PBT: α_{tot} increases because the total amount of crystallizable material increases; α_{PBT} increases because the concentration of short PBT segments that do not crystallize decreases.

D.m.a. Figures 2–4 show storage and loss moduli of the dried copolymers based on PBT and dimerized fatty acids with different molecular masses. In *Table 2*, T_g and storage moduli above T_g are presented. The curves of the storage moduli show rubber plateaux that stay constant over long temperature ranges and decrease over a short range near the T_m. The loss moduli show a single sharp maximum (T_g) at lower PBT concentrations. At higher concentrations the maxima shift to higher temperatures and broaden considerably. The broadening is especially distinct when dimerized fatty acids with a higher molecular mass are used.

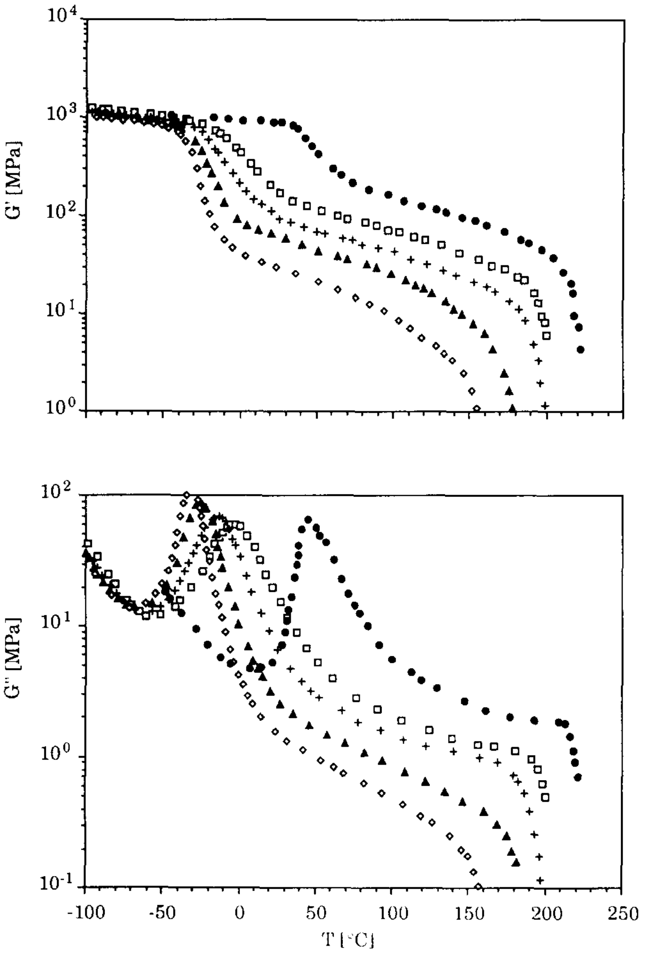

Figure 2 Torsional storage and loss moduli of copolymers based on C_{36} dimerized fatty acid and varying amounts of PBT (W_{PBT}): (●) 1.00; (□) 0.78; (+) 0.70; (▲) 0.60; (◇) 0.50

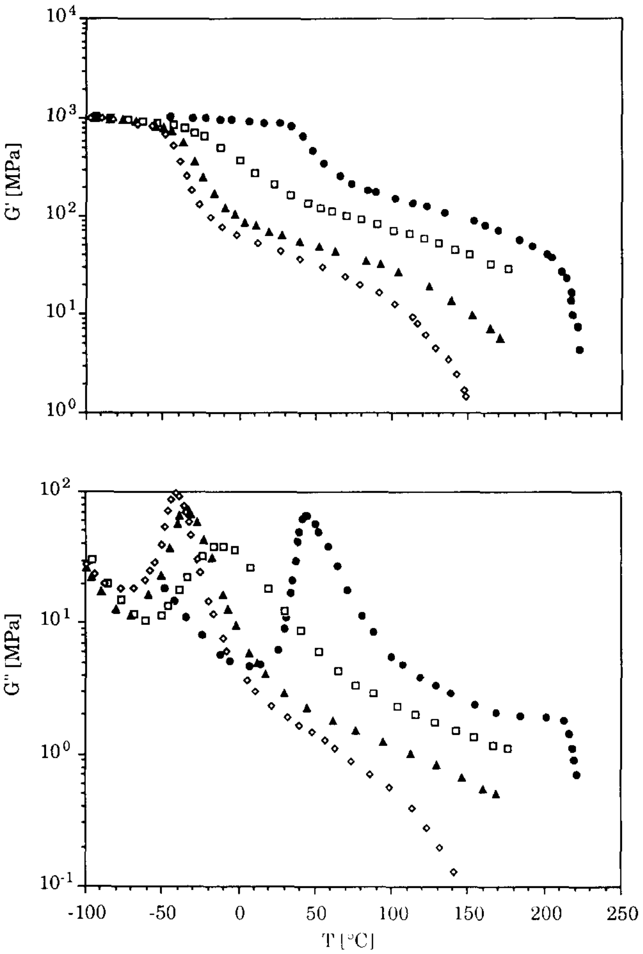

Figure 3 Torsional storage and loss moduli of copolymers based on C_{44} dimerized fatty acid and varying amounts of PBT (W_{PBT}) (●) 1.00; (□) 0.80; (▲) 0.60; (◇) 0.50

Lilaonitkul *et al.*[17] found a shift in the tan δ for PBT–PTMO-glycol 1000 g mol^{-1} polymers towards higher temperatures at higher concentrations of PBT. Also the peaks broadened significantly. They concluded that this was due to the formation of more than one amorphous phase in polymers with high PBT concentrations. The same can probably be concluded for TPEs based on dimerized fatty acids.

In *Figure 5*, T_g is plotted *versus* the weight fraction of PBT. For comparison, data on copoly(ether ester)s based on PTMO-glycol 650/1000 g mol^{-1} and PBT are also given. The copoly(ether ester)s were synthesized in our laboratory under the same reaction conditions as applied to the materials based on the dimerized fatty acids. The PTMO-glycol was purchased from BASF, Ludwigshafen, Germany. Data on the pure amorphous polyester (C_{36} or C_{44} dimerized fatty acid with BDO) are also given.

From the figure it can be seen that the T_gs of the purely amorphous phases at low weight fraction of PBT are close to each other. The T_gs of the purely amorphous polyesters of C_{36} and C_{44} dimerized fatty acids with BDO are −55 and −55°C, respectively. For PTMO-glycol 650 g mol^{-1} and PTMO-glycol 1000 g mol^{-1} the T_g is −65°C. The differences that occur at higher weight fractions of PBT must therefore be caused by differences in the molecular mass of the amorphous phases and

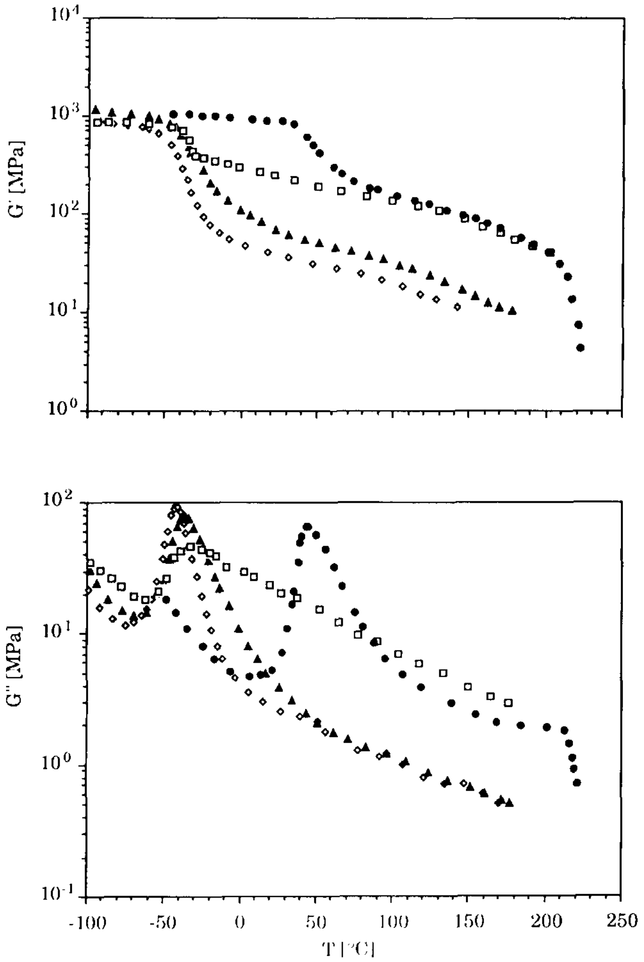

Figure 4 Torsional storage and loss moduli of copolymers based on C_{70} dimerized fatty acid and varying amounts of PBT (W_{PBT}): (●) 1.00; (□) 0.81; (▲) 0.61; (◇) 0.51

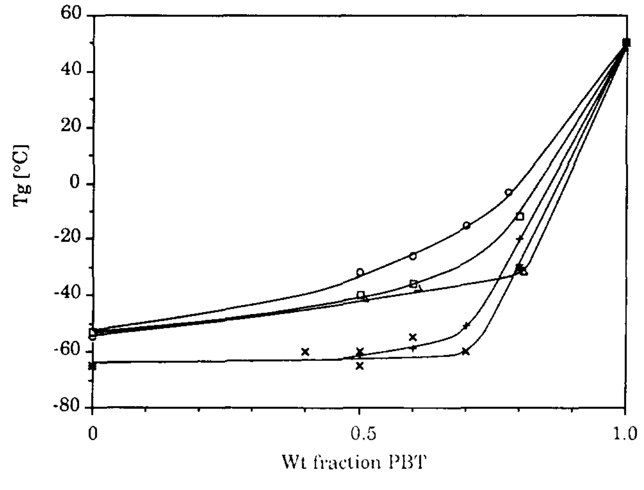

Figure 5 Glass transition temperature as a function of the weight fraction of PBT. Copolymers based on PBT and: (○) C_{36} dimerized fatty acid; (□) C_{44}; (△) C_{70}; (+) PTMO-glycol 650 g mol^{-1}; (×) PTMO-glycol 1000 g mol^{-1} (+ and ×, this work)

differences in the compatibility between the amorphous phase and PBT.

As can be seen from the figure, the T_g of the TPEs based on the C_{36} dimerized fatty acid is at a higher level than that of the PTMO materials. If these poor properties are in part due to the short length of the amorphous phase they can be improved by using dimerized fatty acids with higher molecular masses. Indeed, this can be concluded from the figure. In particular, the TPE based on C_{70} dimerized fatty acid shows a curve that stays at a low level at high weight fractions of PBT.

A final comment involves the curves of the PTMO materials. The figure shows a constant value for T_g with increasing weight fraction of PBT until, at a certain point, the T_g value climbs with a steep slope to the T_g of pure PBT. Cella[14] published a similar figure of T_g *versus* weight fraction of PBT for TPEs based on PTMO (1000 g mol^{-1}). He measured the T_g by d.s.c. This figure shows a much more gradual increase in T_g *versus* weight fraction of PBT. If the amorphous phase is indeed composed of one homogeneous mixture of amorphous PBT and PTMO this result is to be expected. Our results for the PTMO materials and the C_{70} copolymer show a different behaviour. Possibly due to heterogeneity the T_g might primarily be dictated by a portion of the amorphous phase that consists mainly of polyether (or dimerized fatty acid). Another portion, that consists mainly of PBT, might cause a broadening of the peak, especially at high weight fractions of PBT. The portion rich in polyether (or dimerized fatty acid) decreases rapidly at high weight fractions of PBT, which will cause the steep increase in T_g. As a result, peak broadening will then diminish at very high weight fractions of PBT. This can indeed be seen in *Figures 2–4*.

Other authors have also found evidence for a system with more than two phases. Perego *et al.*[18], for example, concluded that heterogeneity existed in copoly(ether ester)s according to deviations in electron density measurements by SAXS and WAXS.

In *Figure 6* the storage moduli of the copolymers based on dimerized fatty acids and PBT are plotted as a function of the volume fraction of crystalline PBT. The volume fraction of crystalline material can be calculated from the melting/crystallization enthalpy[19].

The storage moduli increase with increasing volume fraction of crystalline PBT. From *Table 2* it can be concluded that this volume fraction is influenced by the PBT content but seems to be independent of the type of dimerized fatty acid used. The phenomenon that the composition is the only factor that influences properties

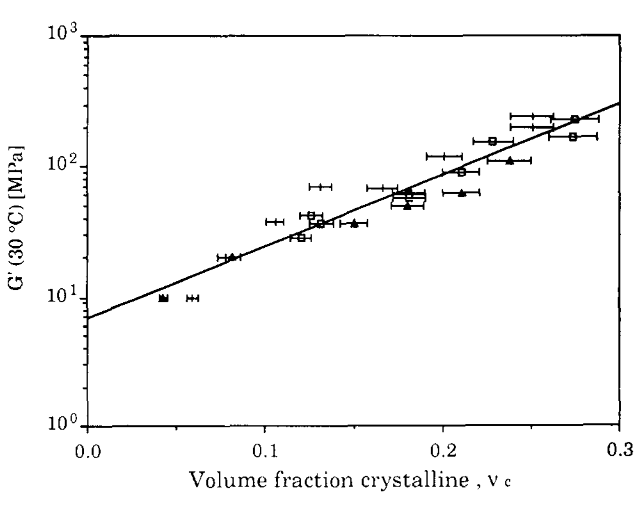

Figure 6 Storage modulus as a function of the volume fraction of crystalline PBT. Copolymers based on PBT and: (□) dimerized fatty acid; (+) PTMO-glycol 650/1000 g mol^{-1} (this work); (▲) PTMO-glycol 1000 g mol^{-1} (data from ref. 15)

like the modulus, stress–strain properties, enthalpies, hardness, etc., was also reported by van Berkel *et al.*[20]. Their work focused on TPEs based on different kinds of polyethers.

Zhu *et al.*[21] used an empirical relation between the volume fraction of crystalline material and the modulus:

$$\log E = v_c \log \frac{E_c}{E_a} + \log E_a$$

where E represents the modulus, v_c is the volume fraction of crystalline material, E_a is the modulus of the amorphous phase and E_c the modulus of the purely crystalline material. With the empirical relation (*Figure 6*) the values for G'_a and G'_c are calculated to be 6.9×10^6 and 2.2×10^6 MPa. If we assume that $E \sim 3G'$ this will yield $E_a = 20.7$ and $E_c = 6.6 \times 10^6$ MPa. For TPEs based on PTMO, Zhu *et al.* found $E_a = 29.5$ and $E_c = 1.95 \times 10^5$ MPa. The values for E_a are close to each other. This could be expected, because the data points lie close to the y axis. The calculated E_c values differ considerably and are much higher than can be expected for a randomly ordered 100% crystalline material. If a more realistic E_c value of 30 GPa is used, no good fit of the data points can be obtained. The empirical relation can fit the data points only with unrealistic values and is too simple for this system. It is probably better to describe the elastic properties of segmented block copolymers as if they were for a reinforced polymer system. The problem one then has is to know the form and size of the reinforcing phase (lamella) and whether there is interconnectivity in the reinforced phase. At low concentrations of reinforcing filler the logarithms of the moduli increase linearly with concentration[22], as in *Figure 6*.

CONCLUSIONS

In this work segmented block copolymers based on dimerized fatty acids and PBT were synthesized. The T_g and T_m could be controlled by variation of the weight fraction of PBT and the molecular mass of the dimerized fatty acid. With WAXS, the average number of carbon atoms directly between the carboxyl groups for C_{36} dimerized fatty acid is 13. The branched alkyl side groups contain 21 carbon atoms.

The T_gs of the TPEs based on the dimerized fatty acids are higher than the T_g of the TPEs based on PTMO. It is shown that T_g can be lowered by utilization of dimerized fatty acid with a higher molecular mass. The higher molecular mass is likely to reduce the compatibility of the PBT segments with the amorphous phase as well as to increase the average length of the PBT segments. These factors will decrease the PBT concentration in the amorphous phase. From the results it seems possible that an extra amorphous phase is formed which contains a higher PBT concentration. The T_g of the soft phase is thus lowered, but broadened by the amorphous phase with high PBT concentration. In the literature, the formation of extra phases with different T_gs for polyamide–polyether segmented block copolymers is often described[23,24]. With increased PBT block length the T_m is also increased. The complete rubber plateau is in this way enlarged.

It is also expected that the storage modulus and the melting enthalpy increase with increasing molecular mass of the dimerized fatty acids. The fraction of short, non-crystallizable PBT segments should decrease with increasing molecular mass of the dimerized fatty acids (increasing length of PBT segments). From the results, however, it can be concluded that the storage modulus and the melting enthalpy do not change significantly with molecular mass of the dimerized fatty acid.

A plot of the logarithm of the storage modulus *versus* the volume fraction of crystalline PBT of the TPEs based on the dimerized fatty acids and PTMO shows a linear relationship. Extrapolating these values to 100% crystallinity gives unrealistically high values. The segmented block copolymers can best be regarded as 'molecular composites' and the data fitted with composite equations.

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