Toughened thermoplastics: 1. The synthesis and use of maleate-modified poly(butylene terephthalate) in polyester/rubber blends

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The synthesis of poly(butylene terephthalate), PBT, which contains approximately 3.5 mol% of maleate groups is discussed. The polymer is used in conjunction with unmodified PBT to reduce the particle size of the elastomeric phase in certain polyester/unsaturated rubber blends. This results in an improvement in impact properties compared with control samples which either contain no modified polyester, or an unreactive rubber such as polybutadiene. Model compound experiments indicate that the electron-deficient maleate groups of the modified polyester can react with unsaturated groups in ethylene–propylene–diene terpolymers via an ene mechanism.

(Keywords: poly(butylene terephthalate); interfacial adhesion; polymer blend; impact strength; particle size; rubber toughening)

INTRODUCTION

The inclusion of a dispersed elastomeric phase in both thermoplastic and thermosetting polymers is a well established method of improving impact strength and other mechanical properties[1]. The theories to explain this phenomenon are not well developed, although it is generally accepted that energy can be absorbed by several mechanisms (often coexistent) which include crazing, plastic yielding of the matrix and the formation of shear bands. Brittle polymers such as polystyrene and poly(methyl methacrylate) tend to craze, whereas more ductile materials such as polyesters will generally yield plastically.

The rubber-toughening of semi-ductile, semi-crystalline thermoplastics such as polyamides[2], and to a lesser extent polyesters[3–5], has received considerable attention in recent years, and several commercial products have been developed. The fracture of these materials is characterized by stress whitening and the formation of a 'process zone' ahead of the propagating crack. Although crazing and shear banding are unlikely to occur in these ductile matrix materials, the origin of the stress whitening phenomenon has seldom been proved.

It is thought that the fracture behaviour of rubber-toughened thermoplastics is influenced by several factors such as the particle size and particle size distribution of the dispersed phase, the rubber type and the degree of interfacial adhesion between the dispersed and continuous phases. However, the exact role of these various factors, and the possibility of synergistic effects have not been conclusively demonstrated. For example, Wu[6] has introduced the concept of ligament length (the distance between the boundaries of adjacent rubber particles), which he believes is the overriding factor in determining the impact strength of rubber-modified polyamides. However, in a study of poly(butylene terephthalate) – ethylene propylene rubber (PBT–EPR) blends, Martuscelli and coworkers[7] concluded that interfacial adhesion is an important factor, provided that the particle size is below a critical value.

Particle size undoubtedly has some effect, but a sufficiently fine dispersion of the elastomeric phase is not always readily achieved. Several factors will influence the size of the rubber particles including the viscosity match of the two components[8–10], the degree of interfacial interaction (e.g. covalent[7,11–13], ionic[14–16], donor–acceptor[17,18]) and the use of compatibilizers[19,20] (e.g. block copolymers). An alternative approach which has been adopted for several commercial blends is the use of latex particles made by emulsion polymerization[21]. Using this procedure, it is possible to generate complex composite particles (e.g. core-shell morphologies) which can have a very narrow size distribution. Agglomeration of these rubber particles during the subsequent blending process can be a problem.

Chemical modification of the elastomeric phase (e.g. epoxidation[22] or grafting of maleic anhydride[23,24] onto unsaturated rubbers) to allow covalent reaction with the amino/carboxyl and hydroxyl/carboxyl end groups of polyamides and polyesters, respectively, is a well established procedure. However, the degree of interfacial reaction, and hence the particle size control, is limited by the concentration of end groups of the thermoplastic. In this paper we describe the synthesis and use of PBT

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which incorporates approximately 3.5 mol% of maleate groups (M-PBT). The electron-deficient carbon–carbon double bonds of this modified polyester are thought to react with unsaturated rubbers via ene or Diels–Alder cycloaddition reactions, as demonstrated by model compound reactions. Since two backbone sites are involved in the cycloaddition reactions, the degree of reaction between the rubber and polyester can be easily varied.

EXPERIMENTAL

Materials

The PBT (Arnite TO6 204) was provided by Akzo. The ethylene–propylene diene monomer (EPDM) rubbers (Keltans 820 and 714) and the polybutadiene (Buna CB35) were obtained from DSM and Bayer, respectively. Characterization data for these polymers are shown in *Table 1*. Diethylmaleate (ex. BDH), dicyclopentadiene (ex. BDH) and ethylidene norbornene (ex. Aldrich) were used without purification. Lindlar catalyst and neat diisobutylaluminium hydride were supplied by Lancaster Synthesis and Aldrich, respectively. Column chromatography was performed using Merck 7734 silica gel Kieselgel 60 and reagent grade solvents.

Instruments

^{1}H nuclear magnetic resonance (n.m.r.) spectra were recorded in $CHCl_3$ using a Jeol PMX 60 spectrometer and mass spectra were obtained on a Hewlett Packard 5995C combined gas chromatography (g.c.)/mass spectroscopy instrument. A Hitachi HU-11B microscope was used for transmission electron microscopy, and the samples were stained with osmium tetroxide. Infra-red (i.r.) spectra were recorded using a Nicolet MX-S Fourier transform spectrophotometer.

Differential scanning calorimetry (d.s.c.) thermograms were obtained using a Perkin Elmer Series 7 differential scanning calorimeter with a ramp rate of 10°C min^{-1}. Dynamic mechanical thermal analyses (d.m.t.a.) were performed using a Polymer Laboratories dynamic mechanical thermal analyser at a frequency of 10 Hz, a heating rate of 3°C min^{-1} and the single cantilever mode of clamping.

Synthesis of ethylidene norbornane

Lindlar catalyst (1 g) was added to a solution of ethylidene norbornene (13.4 ml, 0.1 mol) in methanol (200 ml), and the mixture was then stirred vigorously in an atmosphere of hydrogen. When g.c. analysis showed that complete reaction had occurred (*c.* 1.5 h), the solution was filtered to remove catalyst. The methanol was then removed *in vacuo* to give the product as a colourless oil (87.7 g, 71%) which was not purified further. Some of the product was lost due to codistillation with the methanol.

Table 1 Compositions of PBT/rubber blends

Blend	Rubber (type, wt%)	PBT (wt%)	M-PBT (wt%)
1	Keltan 714, 16.7	41.7	41.7
2	Keltan 820, 16.7	41.7	41.7
3	Keltan 820, 16.7	83.3	0
4	Buna CB35, 16.7	41.7	41.7
5	Keltan 714, 40.0	0	60.0
6	Keltan 714, 40.0	60.0	0

Synthesis of dihydrocyclopentadiene

A mixture of diisobutylaluminium hydride (17.82 ml, 0.1 mol) and dicyclopentadiene (12.34 ml, 0.1 mol) was heated at 80–100°C for 3 h, in an atmosphere of dry nitrogen. After cooling to room temperature, the colourless product was hydrolysed by pouring into a cooled (0°C) mixture of concentrated sulphuric acid (20 ml) and water (120 ml), under a blanket of nitrogen. After stirring for 2 h, the aqueous layer was extracted with three portions of pentane. The combined extracts were washed thoroughly with water and dried ($MgSO_4$). Distillation (109–110°C at 35 mmHg) gave the title compound (10.2 g, 76%) as a colourless oil.

Reaction of dihydrocyclopentadiene with diethyl maleate

A mixture of dihydrocyclopentadiene (1.34 g, 0.01 mol) and diethyl maleate (1.62 ml, 0.01 mol) was heated under reflux and the extent of reaction was monitored by g.c. After 9 h, the internal reaction temperature had risen to 215°C and g.c. analysis indicated approximately 40% loss of starting material. The reaction mixture was then cooled, and column chromatography (hexane–dichloromethane: 1/1) gave a mixture of cycloaddition products (four peaks by g.c.) as a colourless oil. Traces of unreacted maleate and fumarate esters were removed *in vacuo* to give 0.68 g (22%) of pure products: m/z 306(M^+), 261(M^+–EtO) and 260(M^+–EtOH); ν_{max} (thin film) 1750 cm^{-1}.

The ^{1}H n.m.r. spectrum was complex due to the mixture of diastereomers. However, integration of the signal at δ 5.5 (broad ABX pattern) relative to the rest of the spectrum showed that two alkene protons were present.

Reaction of ethylidene norbornane with diethyl maleate

Using the same procedure as above, ethylidene norbornane (1.22 g, 0.01 mol) and diethyl maleate (1.62 ml, 0.01 mol) gave a similar mixture of four diastereomers.

Synthesis of M-PBT

The copolyester was synthesized from 1,4-butanediol, dimethylterephthalate and diethyl maleate in a stainless steel autoclave using a standard polycondensation procedure[25], with tetrabutyltitanate as a catalyst. The initial product was then heated at 185°C under vacuum to give a solid state post-condensation reaction (relative solution viscosity 1.87 (1% in *m*-cresol)).

Blending procedures

Initial blending was carried out using a Werner and Pfleiderer ZSK-30 30 mm twin-screw extruder. The screw speed was 200 rev min^{-1} at a through-put of approximately 10 kg h^{-1} and a chopper rate of 30 m min^{-1}. The barrel was under reduced pressure, and at a temperature of 245–255°C. The temperature of the polymer melt varied from 285 to 295°C, and the pressure in the die head was approximately 50 bar.

The rubbers were ground in a mill and coated with powdered PBT to prevent agglomeration. This anti-sticking agent was removed by sieving immediately prior to use. The pre-dried polyesters and rubbers were mixed and metred to the extruder as a single feed.

A Brabender plastograph was used to remix the samples at a temperature of 240–250°C. The granules were melted using a screw speed of 10 rev $\min^{-1}$, and the material was then kneaded at a rate of 100 rev $\min^{-1}$ for 5 min.

Preparation of test specimens

Impact and tensile test pieces were prepared from the extruder blended samples using an Arburg allrounder injection moulding apparatus. The Brabender-blended samples were compression moulded into plaques from which test specimens were cut.

Impact testing

Impact experiments were performed on machine-notched test bars (105 × 10 × 4 mm) using a modified Rosand instrumented impact tester with a three-point bend loading geometry (span between supports = 50 mm). The mass of the impacter was 4.95 kg, the impact velocity was 3 m s^{-1} and the raw data were filtered using a frequency of 1 kHz. Samples were cooled in ice (0°C), or by adding solid carbon dioxide to methanol (−30°C), and were tested no more than 5 s after being removed from the coolant. The stress intensity factors (K_c) and strain release rates (G_c) reported are the average of four samples and were obtained using a computer program which calculates the geometrical correction factor (ϕ) from a series of linear interpolations.

Tensile testing

Tensile experiments were performed on a Nene MC3000 tensometer at 10 mm $\min^{-1}$ and at a temperature of 23°C, using crosshead displacement to measure strain. Measurements of Young's modulus were made in separate experiments using a strain rate of 1 mm $\min^{-1}$ and a Howden HE 25-50 contacting extensometer. Standard dumb-bell specimens were used for both types of experiment.

RESULTS AND DISCUSSION

Synthesis and characterization of M-PBT

The M-PBT polyester was prepared by a standard transesterification procedure[25] using 5 mol% of diethyl maleate. A ^{1}H n.m.r. spectrum of the product indicated that about 3.5 mol% of the maleate groups had been incorporated, of which some 30 mol% had isomerized into fumarate groups; and that the molecular weight ($\bar{M}_n$) of the polymer was approximately 20 000.

A d.s.c. thermogram recorded over the temperature range 25–260°C provided useful information concerning the melting point and crystallinity of the sample, although a glass transition temperature, T_g, was not observed. The melting point of the M-PBT (218°C) is approximately 8°C lower and is significantly sharper than that of pure PBT, possibly related to its somewhat lower molecular weight.

As would be expected the d.m.t.a. thermogram of M-PBT is very similar to that of PBT, although the T_g of 53°C is approximately 10°C lower than that of the pure PBT. Within the limits of experimental error, the storage modulus curve is the same as for pure PBT.

Model compound experiments

In order to prove that ene reactions can occur between M-PBT and the EPDM rubbers used in this work, model compound experiments were undertaken. Ethylidene norbornane and dihydrocyclopentadiene were chosen as models for the Keltan 714 and Keltan 820 EPDM rubbers, respectively, and diethylmaleate was used as the M-PBT model. The two EPDM models were synthesized by selective reduction of the corresponding dienes as shown in *Figure 1*.

Both model compounds were heated under reflux (approximately 220°C) with diethylmaleate and the reaction mixtures were monitored by g.c. Since the rate of interfacial reaction during blending of the polymers is likely to be markedly influenced by bulk diffusion processes, and by the distance between the reactive sites and the polymer backbone, it is not possible to predict the absolute rates of reaction in the polymeric systems from these model studies. However, the rate of the ethylidene norbornane reaction was significantly greater than that of the dicyclopentadiene model, as would be expected. In both cases the diethylmaleate slowly isomerized to diethylfumarate during the reaction as observed by n.m.r. spectroscopy in the M-PBT.

The reaction products were analysed by g.c./mass spectroscopy and in both cases, four diastereomers were formed (*Figure 1*), although it was not possible to separate these on a preparative scale. However, analysis of the mixture by ^{1}H n.m.r. spectroscopy confirmed that ene reactions were involved since alkene protons were present, which would not have been the case with the alternative (2 + 2) cycloaddition products.

Preparation and testing of M-PBT/rubber blends

Blends with the compositions shown in *Table 2* were prepared using a 30 mm twin-screw extruder, and the properties of the corresponding rubbers are shown in *Table 1*. Some of the blends were then remixed using a Brabender plastograph in order to investigate the variation of physical properties and blend morphology with reaction time.

Strain energy release rates and stress intensity factors obtained from notched bar impact tests are shown in

Table 2 Glass transition temperatures, T_g, and Mooney viscosities of rubbers

Rubber	Composition	T_g (°C) by d.s.c.	Mooney viscosity
Keltan 820	EPDM (4.5% DCPD)	−53	77
Keltan 714	EPDM (8% ENB)	−47	63
Buna CB35	Butadiene (high *trans* 1.4)	−97	35

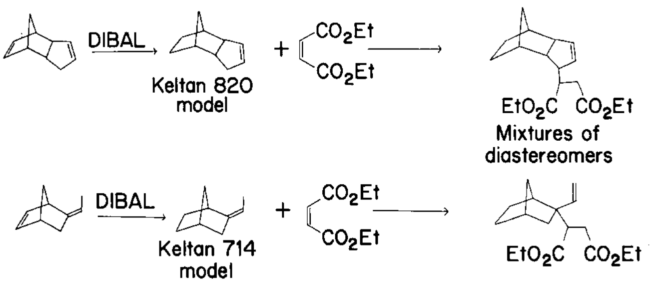

Figure 1 Model compound experiments

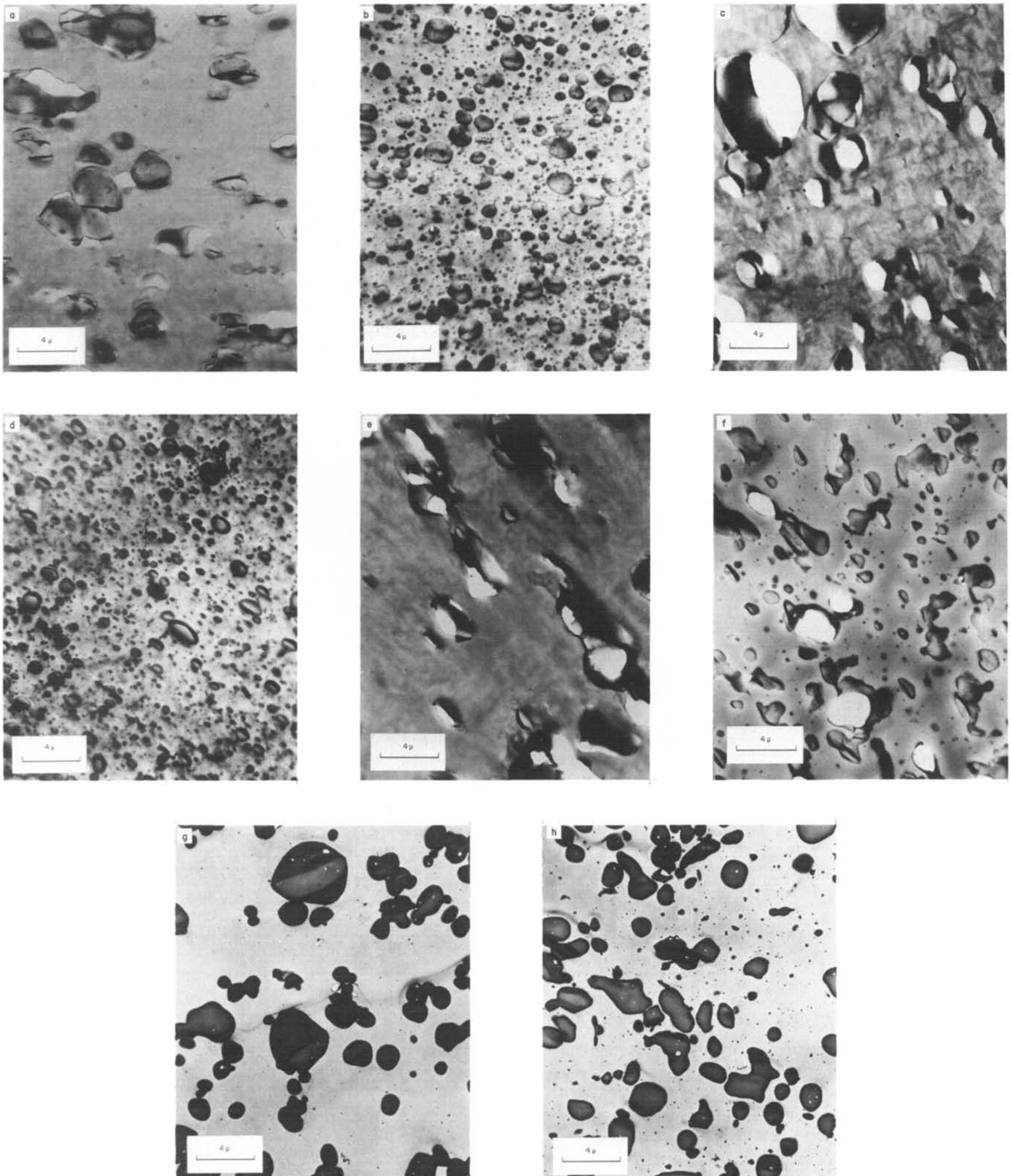

Figure 2 Transmission electron micrographs of PBT/rubber blends. Blend 1: (a) after initial extrusion; (b) after remixing. Blend 2: (c) after initial extrusion; (d) after remixing. Blend 3: (e) after initial extrusion; (f) after remixing. Blend 4: (g) after initial extrusion; (h) after remixing

Table 3 Stress intensity factors, K_c, and strain release rates, G_0, obtained at 3 m s^{-1}

Temperature (°C)	Blend	K_c (MN m$^{-3/2}$) Initial value	K_c (MN m$^{-3/2}$) After remixing	G_c (kJ m^{-2}) Initial value	G_c (kJ m^{-2}) After remixing
23	1	1.97	2.89	3.35	6.68
	2	1.52	2.66	2.37	5.75
	3	1.67	1.93	3.12	3.12
	4	2.21	2.20	3.95	3.85
0	1	1.97	2.59	3.41	4.49
	2	2.38	2.84	4.02	5.31
	3	2.17	2.05	4.02	3.77
	4	2.56	2.47	4.10	3.65
−30	1	2.21	2.12	3.29	3.15
	2	2.46	1.87	3.70	2.12
	3	1.72	1.92	2.41	2.57
	4	2.73	2.16	4.08	2.97

Table 4 Tensile data (6 mm min^{-1}) for PBT/rubber blends

Blend	Elongation (%)	Yield stress (MPa)	Toughness (J)	Modulus (MPa)
1	18.0	34.7	22.4	1800
2	23.3	33.7	29.0	1780
3	27.8	32.0	33.8	1740
4	38.8	33.4	48.3	1740
5	15.0	23.2	11.8	980
6	15.3	15.6	8.3	680

Table 3. It should be emphasized that since these materials do not fracture in a perfectly linear elastic manner, the values of K_c and G_c are not true material parameters. However, treatment of the impact data using linear elastic fracture mechanics (LEFM) theory provides a useful measure of the relative toughness of the blends. Although all the test bars failed via a brittle mechanism, with no stress whitening behind the fracture surface, differences in fracture energy and fracture toughness were observed. At 0°C and 23°C, the impact properties of the two EPDM/M-PBT blends are significantly improved by remixing in the Brabender, whereas blends 3 and 4 show no such improvement. However, this increase in impact strength is not observed at −30°C. Blend 3 is obviously 'unreactive' because it contains no M-PBT, and it is believed that the 1,4-polybutadiene rubber in blend 4 will be unable to participate in ene reactions with M-PBT since two backbone sites would be involved.

Further evidence for reaction between the components in blends 1 and 2 is provided by transmission electron microscopy (TEM) as shown in *Figure 2*. Remixing of the 'reactive' blends leads to a marked reduction in average particle size, whereas the morphology of the 'unreactive' blends is not significantly altered. Although the impact properties of blends 1 and 2 are considerably enhanced after remixing, it is not possible to say whether the improvement is a result of the change in particle size *per se*. It is possible that the increase in interfacial reaction which accompanies the reduction in particle size is the critical parameter.

At room temperature, the increases in the K_c and G_c values for blend 2 are significantly greater than those for blend 1. This observation is contrary to the model compound experiments in which the ethylidene norbornane was found to be more reactive than the dicyclopentadiene towards diethylmaleate. A possible explanation for this discrepancy is the steric hindrance associated with the two diene functionalities. Although the dicyclopentadiene group is the more electron deficient and therefore, electronically less reactive, the carbon–carbon double bond in Keltan 820 is significantly further from the polymer backbone than that in Keltan 714. The conformational constraints on polymer–polymer reactions are considerably more severe than for monomeric reactions and the relatively minor change in stereochemistry could well account for the observed reactivities.

The difference between 'reactive' and 'unreactive' systems is also clearly illustrated by the tensile properties of blends 5 and 6, as shown in *Table 4*. Even after the initial extrusion, the yield stress and Young's modulus of the 'reactive' blend are substantially greater than those of the 'unreactive' system. The same effect is seen, to a lesser extent with blends 2 and 3, although in both cases, the 'reactive' blends have a lower elongation to break, which indicates that the presence of M-PBT does not have a beneficial effect on the post-yield behaviour of the materials.

CONCLUSIONS

It has been shown that PBT can be modified with a few per cent of maleate groups to give a polymer which has thermal and mechanical properties which are comparable to those of the unmodified polyester. The use of M-PBT in PBT/EPDM blends provides a convenient way to reduce the particle size of the dispersed elastomeric phase if the reaction time is sufficiently long. It is believed that the increased interfacial adhesion in the reactive blends is due, at least in part, to ene reactions between the M-PBT and the EPDM rubbers. Modification of the rubbers, which often results in instability and cross-linking, is not necessary, and the degree of reaction between the two components of the blend can be varied.

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REFERENCES

1 Bucknall, C. B. 'Toughened Plastics', Applied Science, London, 1977

2 Borggreve, R. J. M. *Ph.D. Thesis*, University of Twente, 1988; and references therein

3 Laurienzo, P., Malinconico, M., Martuscelli, E. and Volpe, M. *Polymer* 1989, **30**, 835

4 Pilati, F. *Polym. Eng. Sci.* 1983, **23**, 750

5 Subramanian, P. M. *Polym. Eng. Sci.* 1987, **27**, 1574

6 Wu, S. *J. Appl. Polym. Sci.* 1988, **35**, 549

7 Cimmino, S., D'Orazio, I., Greco, R., Maglio, G., Malinconico, M., Mancarella, M., Martuscelli, E., Palumbo, R. and Ragosta, G. *Polym. Eng. Sci.* 1983, **23**, 380

8 Wu, S. *Polym. Eng. Sci.* 1987, **27**, 335

9 Favis, B. D. and Chalifoux, J. P. *Polym. Eng. Sci.* 1987, **27**, 1591

10 Fortelny, I., Kamenicka, D. and Kovar, J. *Angew. Makromol. Chem.* 1988, **164**, 125

11 Ide, F. and Hasegawa, A. *J. Appl. Polym. Sci.* 1974, **18**, 963

12 Chen, C. C., Fontan, K. M. and White, J. L. *Polym. Eng. Sci.* 1988, **28**, 69

13 Pierola, I. F., Caceres, M., Caceres, P., Castellanes, M. A. and Nunez, J. *Eur. Polym. J.* 1988, **24**, 895

14 Hara, M. and Eisenberg, A. *Macromolecules* 1987, **20**, 2160

15 Hara, M. and Jar, P. *Macromolecules* 1988, **21**, 3187

16 Hsieh, K. H., Chou, L. M. and Chiang, Y. C. *Polym. J.* 1989, **21**, 1

17 Pugh, C. and Percec, V. *Macromolecules* 1986, **19**, 65

18 Rodriguez-Parada, J. M. and Percec, V. *Macromolecules* 1986, **19**, 55

19 Xanthos, M. *Polym. Eng. Sci.* 1988, **28**, 1392

20 Howe, D. V. and Wolkowicz, M. D. *Polym. Eng. Sci.* 1987, **27**, 1582

21 Hobbs, S. Y., Dekkers, M. E. J. and Watkins, V. H. *J. Mater. Sci.* 1988, **23**, 1219

22 General Electric Company. Eur. Pat. Appl. 0 149 192

23 Cimmino, S., D'Orazio, I., Greco, R., Maglio, G., Malinconico, M., Mancarella, M., Martuscelli, E., Palumbo, R. and Ragosta, G. *Polym. Eng. Sci.* 1984, **24**, 48

24 Hert, M., Geurdoux, L. and Lebez, J. *Angew. Makromol. Chem.* 1987, **154**, 111

25 Sorenson, W. R. and Campbell, T. W. 'Preparative Methods of Polymer Chemistry', Interscience, New York, 1968