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Toughened thermoplastics: 3. Blends of poly(butylene terephthalate) with (butadiene-*co*-acrylonitrile) rubbers

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The preparation of a series of blends containing poly(butylene terephthalate) (PBT) and nitrile rubbers of varying acrylonitrile contents is reported. The nitrile rubbers form a dispersed phase within the polyester matrix to give blends with enhanced fracture resistance. The tensile and fracture properties of the materials are related to the blend morphologies as determined by transmission electron microscopy. It is suggested that the effectiveness of nitrile rubbers in the toughening of PBT may result from the relatively close match of the cohesive energies of the two components, or from the irregular shape of the rubber particles.

(Keywords: poly(butylene terephthalate); polymer blend; rubber toughening)

Introduction

The rubber toughening of semiductile thermoplastics[1] is a well established procedure of considerable commercial interest. It is generally accepted that in order to achieve the maximum toughening effect, the particle of the dispersed, elastomeric phase should be submicrometre in diameter[2]. Small rubber particles reduce the yield stress of the matrix and induce plastic flow of the material in the shear plane[3,4]. However, a sufficiently fine dispersion of rubber particles is not readily obtained by simple mechanical blending of the components, and one of two procedures is routinely adopted to produce a suitable morphology. The interfacial tension may be reduced by covalent reaction between the components, which is typically achieved by grafting maleic anhydride onto ethylene, propylene, diene monomer (EPDM) rubber or ethylene–propylene rubber (EPR)[5,6]. Alternatively, the required morphology can be obtained by the use of latex particles[7] which can be synthesized with precise control of particle size.

Although the relationship between morphology and impact properties has been investigated in many polymer blends[8,9], relatively little is known about the role of other factors, such as interfacial adhesion[10] and the type of rubber[11], in determining the mechanical strength of the blend. For example, most previous studies on engineering thermoplastics have involved functionalized EPR or EPDM rubber as the elastomeric component, and to our knowledge, the use of poly(butadiene-*co*-acrylonitrile) rubbers for the toughening of polyesters and polyamides has not been reported. This is rather surprising, since it is known that carboxylic acids (polyester and polyamide end groups) can react with nitriles[12], at elevated temperatures, to form imides. In this paper, the synthesis and characterization of a series of poly(butylene terephthalate)/nitrile rubber blends is reported.

Experimental

Materials. The poly(butylene terephthalate) (PBT) (Arnite T06 204) and maleate-modified polyester[10] were provided by Akzo. Breon N28C60 (28% acrylonitrile), Krynac 1965 (19% acrylonitrile) and Hycar 1095 (15% acrylonitrile) were obtained from British Petroleum, Polysar and Goodrich, respectively. The solubility parameters of the three rubbers were calculated using data from Briston and Watson[13] and are shown, together with the measured glass transition temperatures (T_g), in *Table 1*.

Blending procedures. Blends were prepared using a Berstorff ZE-25 25 mm twin-screw extruder, operated at a screw speed of 200 rev min^{-1} and a reduced pressure of approximately 20 mbar. 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, and the pre-dried polyester and rubber were mixed and metered to the extruder as a single feed. All the blends were passed through the extruder at a throughput of 4.5 kg h^{-1}, dried under reduced pressure and re-extruded at 1.8 kg h^{-1}. In each case the temperature of the polymer melt was approximately 260°C. Impact and tensile test pieces were injection-moulded using an Arburg Allrounder injection-moulding apparatus.

Instruments. Transmission electron micrographs were obtained using a Hitachi HU-11B microscope and specimens were stained with osmium tetroxide before sectioning. 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. Standard dumb-bell-shaped speci-

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Table 1 Solubility parameters and glass transition temperatures of the nitrile rubbers used for blending with PBT

Rubber type	Acrylonitrile content (wt%)	Solubility parameter[a] $(\mathrm{J\,cm^{-3}})^{1/2}$	T_g (°C)
Hycar 1095	15	17.4	−53
Krynac 1965	19	18.0	−46
Breon N28C60	28	19.6	−28

[a] Solubility parameter of PBT = 21.9 $(\mathrm{J\,cm^{-3}})^{1/2}$

Table 2 Blend compositions

Blend number	Composition (w/w)[a]
1	16.7% Hycar 1095, 16.7% M-PBT
2	16.7% Krynac 1965, 16.7% M-PBT
3	16.7% Breon N28C60, 16.7% M-PBT
4	16.7% Krynac 1965

[a] Remainder is Arnite TO6 204 grade PBT

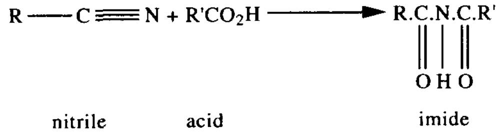
$$\mathrm{R{-}C{\equiv}N + R'CO_2H \longrightarrow R.\underset{\overset{\|}{O}}{C}.\underset{\overset{|}{H}}{N}.\underset{\overset{\|}{O}}{C}.R'}$$

Figure 1 The reaction between nitrile and carboxylic acid groups

mens with a cross-sectional area of approximately $4 \times 10^{-5}\,\mathrm{m^2}$ were used, and the values given in *Table 5* are the average of at least three tests.

Charpy impact experiments were performed on machine-notched, injection-moulded test pieces, and the instrumented fracture tests were carried out using machine-notched test bars (105 mm × 10 mm × 4 mm) at velocities of $3\,\mathrm{m\,s^{-1}}$ or $10\,\mathrm{mm\,min^{-1}}$. A Rosand impact tester was used for the high-speed impact experiments and a modified Nene MC3000 tensometer (operated in compression mode) was used for the experiments at the lower strain rate. Identical wedge-shaped strikers were fitted to the two instruments, and the span between supports was 50 mm in each case. The data obtained from the impact tester were filtered using a frequency of 1 kHz.

Stress intensity factors (K_c) and strain release rates (G_c) are the average of at least four samples and were obtained using a computer program which calculates the geometrical correction factor (ϕ) from a series of linear interpolations. Values of initiation energy (G_i) and tearing modulus (T_a) were obtained from a least-squares analysis of the Vu Khanh equation[14], using 22 samples for each blend with notch depths ranging from 1.0 to 6.0 mm.

Table 3 Data obtained from Charpy impact tests and three-point bend experiments performed at $3\,\mathrm{m\,s^{-1}}$

Blend number	K_c $(\mathrm{MN\,m^{-3/2}})$	G_c $(\mathrm{kJ\,m^{-2}})$	Charpy energy $(\mathrm{kJ\,m^{-2}})$
1	3.3 ± 0.1	7.9 ± 0.2	5.44 ± 1.20
2	3.2 ± 0.1	7.1 ± 0.4	13.79 ± 5.49[a]
3	3.2 ± 0.1	7.8 ± 0.4	8.48 ± 2.64[a]
4	3.2 ± 0.1	7.1 ± 0.8	8.95 ± 0.76
PBT	1.8 ± 0.1	2.4 ± 0.2	2.94 ± 0.41

[a] Ductile fracture of some test pieces

Table 4 Data obtained from three-point bend experiments performed at $10\,\mathrm{mm\,min^{-1}}$ and analysed according to the Vu Khanh procedure[14]

Blend number	G_i $(\mathrm{kJ\,m^{-2}})$	T_a $(10^9\,\mathrm{J\,m^{-4}})$	Correlation coefficient
1	20.8	3.62	0.99
2	20.2	2.96	0.99
3	16.6	3.04	0.98
4	21.5	2.10	0.99

Table 5 Data obtained from tensile experiments performed at $10\,\mathrm{mm\,min^{-1}}$

Blend number	Yield stress (MPa)	Elongation (%)	Toughness (J)
1	32.8 ± 0.3	79 ± 4	99 ± 5
2	32.8 ± 0.2	62 ± 4	75 ± 5
3	34.2 ± 0.3	67 ± 10	83 ± 12
4	32.4 ± 0.5	54 ± 5	66 ± 7

Results and discussion

A series of PBT/nitrile rubber blends was produced using rubbers of different acrylonitrile contents, as shown in *Table 2*. As mentioned in the Introduction, covalent reaction between the carboxylic acid end groups of the polyester and the acrylonitrile groups should lead to the formation of graft copolymers containing imide linkages during the blending procedure, as shown in *Figure 1*. Maleate-modified poly(butylene terephthalate) (M-PBT), which is known to react with unsaturated rubbers[10], was also added to three of the blends to provide additional interfacial adhesion between the rubber particles and the polyester matrix.

The blends all fractured in a brittle manner when notched bending bars (105 mm × 10 mm × 4 mm) were tested under high-velocity ($3\,\mathrm{m\,s^{-1}}$) impact conditions. The results of these experiments are shown in *Table 3*, and it can be seen that although the blends have better impact properties than unmodified PBT, there is no significant difference between the various compositions. It should be noted that although the samples all failed in a characteristically brittle manner, it is unlikely that the fracture process was perfectly elastic. However, the K_c and G_c values given in *Table 3* provide a useful indication of the relative strength of the blends under high-velocity impact conditions.

However, when the same blends were subjected to the Charpy impact test, in which the sample geometry tends to promote conditions of plane stress that are more conducive to ductile failure, significant differences in impact properties were observed (*Table 3*). Indeed, under these test conditions, blends 2 and 3 were in the region of the brittle–ductile transition and some test pieces failed in a ductile manner.

When the notched bending bars were fractured, using a three-point bend configuration, at the much slower strain rate of $10\,\mathrm{mm\,min^{-1}}$, all fractured in a ductile manner and absorbed considerably more energy than under the corresponding high-velocity impact conditions. By using the Vu Khanh procedure[14], in which test pieces with a range of notch depths are tested, it is possible to separate the contributions from the initiation

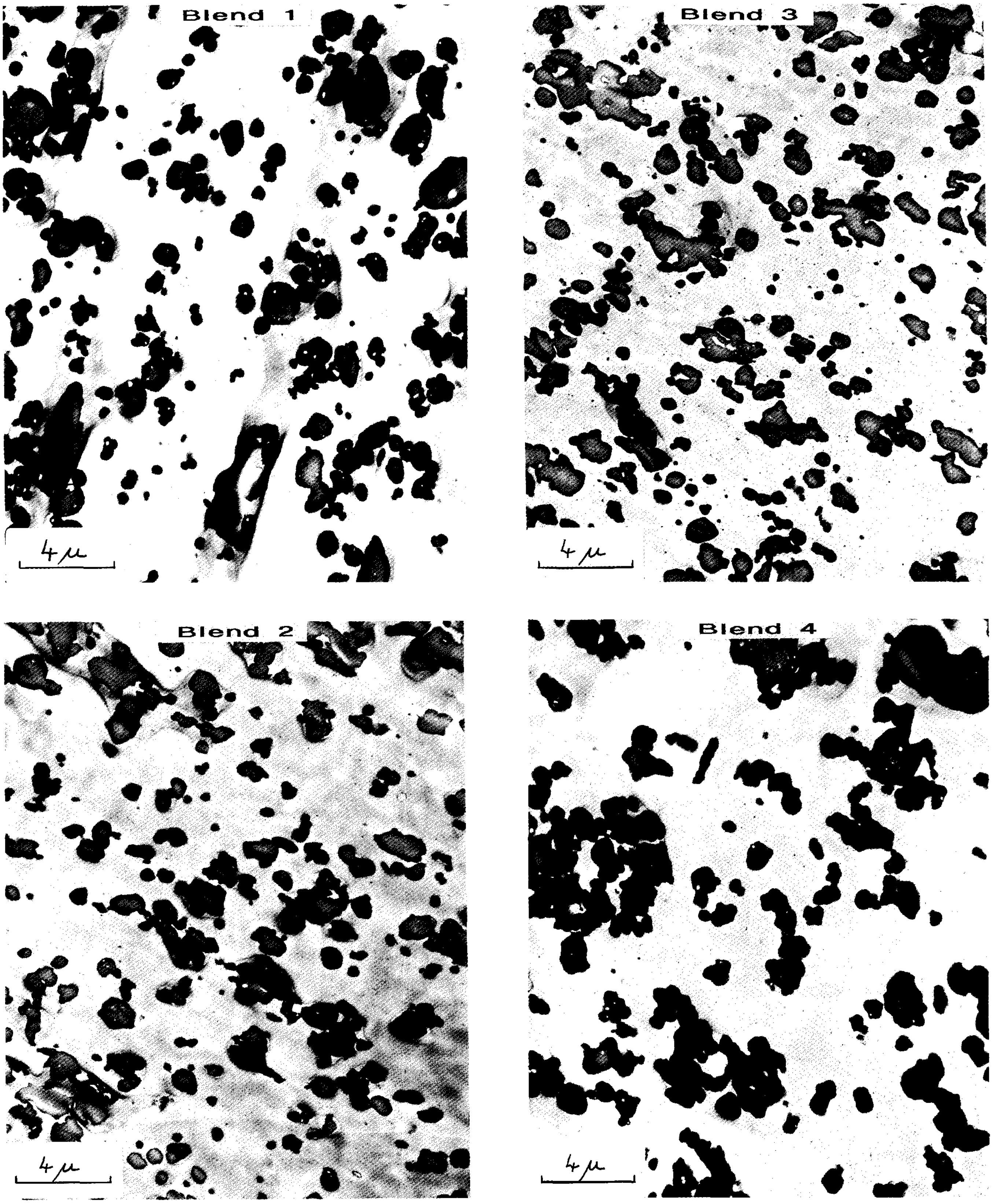

Figure 2 Transmission electron micrographs of PBT/nitrile rubber blends

and propagation stages of fracture to the overall energy absorption. Values of G_i and T_a are given in *Table 4* and, although there are significant differences between the blends, there is no correlation between G_i or T_a and the percentage of acrylonitrile in the rubber (note that corresponding values for unmodified PBT cannot be quoted since ductile failure is seldom observed under these conditions). It is also evident that there is no correlation between the G_i and T_a values, which suggests that different factors may influence the initiation and propagation stages of fracture.

The blends were also tested at the same strain rate of

10 mm min^{-1} under uniaxial tension, and the results of these experiments are shown in *Table 5*. It is interesting to note that there is a correlation between G_i values obtained from the three-point bend fracture tests and the yield stresses obtained under uniaxial tension at the same strain rate. As the tensile yield stress decreases, the energy absorbed during the initiation of fracture increases. In addition, the post-yield behaviour in the two types of experiment can be correlated, with T_a increasing in almost direct proportion to the toughness values obtained from the tensile tests (toughness index = integration of stress *versus* strain curve).

The morphologies of the four blends were investigated using transmission electron microscopy, and typical micrographs of each blend are shown in *Figure 2*. It can be seen that all three nitrile rubbers give irregular-shaped particles of comparable size. It is also apparent that the use of M-PBT does not significantly reduce the average particle size or particle-size distribution of the dispersed phase.

Conclusions

Nitrile rubbers give much tougher blends with PBT than do most other elastomers, although the reasons for this are not readily apparent. It is possible that the relatively close match of the cohesive energy densities of the rubber and polyester could account for this difference by increasing the extent of molecular mixing in the interfacial regions of the blends. However, the cohesive energies of the rubbers would then be expected to vary significantly with the percentage of acrylonitrile and, as mentioned earlier, there is no correlation between the mechanical properties of the blends and the rubber compositions. This is in contrast to the behaviour of a series of poly(vinyl chloride)/nitrile rubber blends in which Bramfitt and Heaps[15] demonstrated a correlation between impact strength and acrylonitrile content. It is possible that some other property of nitrile rubbers, such as their ability to cavitate under an applied triaxial stress, may be responsible for their superior toughening ability.

Another interesting feature of these blends is the irregularity in the shape of the rubber particles. Whereas most elastomers are dispersed in PBT as approximately spherical domains, it can be seen in *Figure 2* that this is clearly not the case with nitrile rubbers. As a consequence, the stress fields which develop around a strained nitrile rubber particle will be far more complex than those associated with spherical particles. This may explain why nitrile rubber particles are particularly effective in reducing the shear yield stress of the polyester matrix.

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