Rubber toughened polybutylene terephthalate: influence of processing on morphology and impact properties

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The toughening of polybutylene terephthalate (PBT) was achieved by adding to it a functionalized ethylene–propylene (EPR) random copolymer. Maleic anhydride molecules, inserted onto the rubber backbone, provided the functionalized sites with which the terminal PBT hydroxide groups could react. A graft copolymer made from an EPR backbone and by PBT branches acted as an interfacial agent between the matrix and the rubbery dispersed phase. The intensity of mixing, represented by the roller speed of the mixing equipment, was varied from 4 to 64 rpm. The morphological features as well as the mechanical impact performance improved with increasing the roller speed up to a value of 48 rpm. Beyond such a value the situation was reversed due to the mechanical degradation of the molten PBT. This induced a diminished internal interconnection of the matrix and hence a worse impact resistance. Dynamic mechanical analysis proved to be a very sensitive tool to detect the presence of interzones existing between the PBT matrix and the EPR rubbery particles. The extension of such zones represents the adhesion between the two components and was also detected by Charpy impact tests.

(Keywords: polybutylene terephthalate; toughening; dynamic mechanical analysis)

INTRODUCTION

The glass transition temperature (T_g) plays a crucial role in determining the end uses of polymeric materials. Non-crystalline polymers, such as polystyrene, polymethyl methacrylate, and semicrystalline ones, such as isotactic polypropylene, polyamides and PBT exhibit a brittle behaviour at room temperature (T_a) or below[1,2]. Their toughening has been generally obtained by adding to the brittle matrix a component having a T_g much lower than T_a. The dispersed rubbery particles act as stress concentrators favouring the dissipation of the impact energy. An optimum particle size, a low interfacial energy and a good adhesion to the matrix are the necessary requirements for efficient toughening[2]. In some cases this can be achieved by adding a component which is compatible to the amorphous regions of the brittle polymer. For isotactic polypropylene a random ethylene–propylene copolymer (EPR) can be a suitable additive[3,4]. In the case of polyamides and polyesters the same EPR can be used, but the rubber is very incompatible with the matrix. Therefore there is no adhesion between the phases. At this point one is facing the general problem of compatibilizing a system made of two incompatible polymeric components by adding a third one. The latter must be made of a block or a graft copolymer, whose segments have a chemical affinity for the two polymers. In this way the copolymer can act as an emulsifier, that is, as an interfacial agent, thus solving the problem.

Several examples are reported in literature: Locke and Paul[5,6] and Barentsen and others[7–10] used graft copolymers of polystyrene onto polyethylene in order to compatibilize atactic polystyrene with low density polyethylene or with ethylene–propylene rubber. Pilati and others[11,12] compatibilized poly(butyleneterephthalate) and ethylene–vinylacetate copolymer by a reactive processing, with an *in situ* formation of the graft copolymer. In our institute a series of papers[13–18] were published which showed evidences of a graft copolymer formed *in situ* when: a functionalized EPR was melt-mixed with nylon 6 (Ny-6)[12–14]; or the hydrolytic polymerization of ε-caprolactam occurred in presence of the above mentioned rubber[16–18]. The EPR was functionalized by inserting onto its chain backbone maleic anhydride (MAH) groups. The latter reacted with the amino terminal ones of Ny-6, giving rise to a graft copolymer made by the EPR chain and by Ny-6 branches. Fine dispersions of the rubber particles and good adhesion to the matrix yielded high impact resistant materials. A careful and suitable processing was used in both the cases. Furthermore, the functionalization degree (amount of MAH inserted onto EPR) was varied by keeping constant all the other variables (i.e. the mixing temperature and the roller speed in the Brabender-like apparatus).

In the present paper the toughening of a polyester, the poly(butylene terephthalate) (PBT) was considered. The above mentioned philosophy and techniques were extended to this new class of polymers. A functionalized EPR was melt-mixed in a Brabender-like apparatus with PBT in order to obtain the suitable graft copolymer *in situ*. In addition, with respect to the previous works, the effect of the mixing efficiency on the morphology and impact properties of system was analysed, the roller speed of the equipment was varied and all the other variables were kept constant.

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EXPERIMENTAL

Materials

The polybutylene terephthalate (PBT) used in this work was a commercial polymer (Pibiter TQ-13), having $[\eta] = 1.35\,dl/g$ in a 50 wt% mixture of phenol/1,1,2,2-tetrachloroethane at 25°C and MFI = 5.7 g/min at 250°C (load 2.16 kg). Before use the PBT was dried in a vacuum oven at 120°C for 6 h. The ethylene–propylene rubber (EPR) random copolymer is a commercial sample (Dutral CO/054) having a weight-average molecular weight (M_w) of 1.8×10^5, an ethylene content (C_2) of 67 mol% and a glass transition temperature (T_g) of −60°C. Both materials were supplied by Dutral S.p.A.

EPR-g-SA with a graft content of maleic anhydride of 2.3 wt% was prepared following the procedure already described elsewhere[13]. The solvents used, when required, were purified according to standard procedures.

Homopolymer processing and blend preparation

Pure PBT was processed at 240°C for 5 min at roller speeds ranging from 4 to 64 rpm in a Brabender-like apparatus (Rheocord, Haake Inc.). PBT/EPR and PBT/EPR-g-SA blends, all having an 80/20 w/w ratio were prepared at the same conditions as above, at roller speeds as illustrated in *Table 1*.

Specimen preparation

The materials coming from the mixer were compression moulded in a heated press, at a temperature of 240°C and a pressure 200 kg/cm², in order to obtain 3 mm thick sheets. From these sheets parallelepiped-shaped samples $(60 \times 6.0 \times 3.0\,mm^3)$ were cut to perform Charpy impact tests. The specimens were notched at the middle point of their length as follows: first a blunt notch was produced using a machine with a 'V' shaped tool and then a sharp notch 0.2 mm deep was made by a razor blade fixed on a microtome. The final value of the notch depth was measured after fracture, using an optical microscope.

Techniques

Morphological analysis. Microtomed surfaces of binary blends were exposed for 20 min to boiling xylene vapours and subsequently examined by a scanning electron microscope (Philips SEM 501), after coating them with a gold palladium alloy. It was observed that the xylene selectively dissolved the rubbery phase, leaving the PBT undissolved.

Impact fracture measurement. Charpy impact tests were carried out at an impact speed of $1\,m\,s^{-1}$, using a Ceast fracture pendulum. Samples with a notch depth-to-width ratio of 0.3 and a test span of 48 mm were fractured at different temperatures from −60°C to 20°C. The temperature was changed by means of a home-made liquid nitrogen apparatus.

Table 1 Roller speed values utilized for homopolymer processing and blend preparation

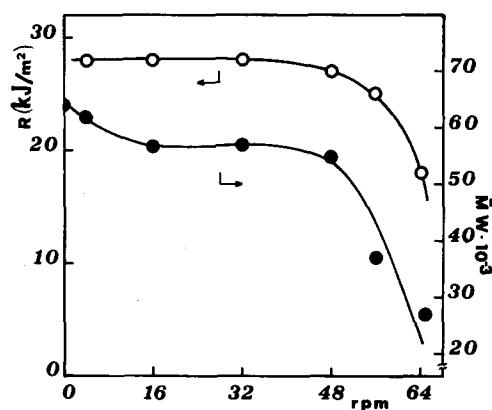| Materials	Roller speed (rpm)					
PBT	4	16	32	48	56	64
PBT/EPR	–	–	32	48	–	–
PBT/EPR-g-SA	4	16	32	48	–	64

Figure 1 Impact resistance (R) and viscometer molecular weight (MW) as a function of roller speed (rpm) for PBT homopolymer

Viscosity measurements. Viscosity measurements of processed pure PBT were performed with a Cannon-Ubbelohde 75E238 viscometer at $T = 25°C$ in phenol/ 1,1,2,2, tetrachloroethane 50/50 wt% $(C = 0.5\,g\,dl^{-1})$. The viscometric molecular weight (MW) was calculated by using the equation:

$$[\eta] = KMW^a$$

where: $[\eta]$ is the intrinsic viscosity; a and K are two constants whose values are $K = 9.31 \times 10^{-5}\,dl/g$ and $a = 0.871$.

Blend analysis. A chemical analysis of PBT/EPR-g-SA blends was carried out by selective extraction with dichloro acetic acid and xylene.

D.s.c. analysis. Thermal analysis was performed on 12 mg of samples recovered from selective extraction, by using a Mettler TA-3000 differential scanning calorimeter. The scanning rate was 20°C/min. The temperature and enthalpy calibrations were made, using indium as standard.

RESULTS

PBT homopolymer

The values of impact resistance, R, and viscometric molecular weight, MW, as a function of roller speed, rpm, are reported in *Figure 1*. Both the variables exhibit an analogous trend: they are almost constant up to a value of 48 rpm, then sharply decrease.

The behaviour can be attributed to the well known phenomenon of mechanical degradation, due to the intense shear and elongational stresses acting in the mixing chamber[19]. In particular Keller and co-workers[20–22] studied the behaviour of diluted and concentrated solutions of polystyrene and polyethylene oxide in elongation and simple shear flow. They found that at given critical values of strain rate the chains halved. In this way all the molecular weight distribution was altered and the weight average molecular weight was sharply reduced. Our system is quite different: the PBT is in a molten state, the molecular weight is much lower than in their case, the hydrogen bonding plays a role in determining the polymer viscosity. However, one can assume that an analogous behaviour takes place in our system. The 48 rpm represents a critical roller speed at which the strain rate, acting under the influence of very

complex fluid dynamics, reaches a value sufficient for a massive chain halving.

This effect monitored by the MW decrease is detected by the R trend as well. In fact when the MW is lowered the interconnection of the PBT is diminished and therefore also the resilience, which represents the resistance to crack initiation, must decrease.

PBT BASED BLENDS

Reactive blending

The functionalized rubber, (EPR-g-SA), bearing maleic anhydride groups, can react during the melt-mixing with the terminal hydroxide ones of PBT, as follows:
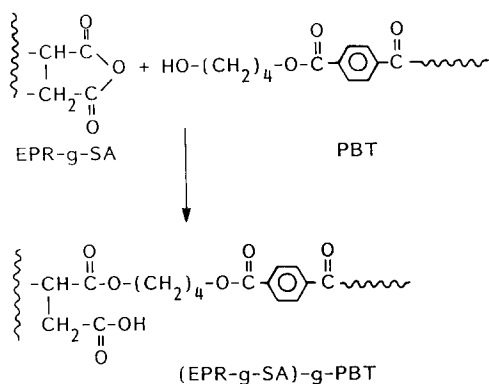
The reaction product is the graft copolymer (EPR-g-SA)-g-PBT. The above hypothesis of reaction is based on literature data[23]. In previous works, performed in this institute, it has been shown, in fact, that anhydride groups, grafted on EPR, can react with hydroxide groups giving an ester linkage[23]. The grafting reaction occurs at the interface between matrix and rubber. Hence only a small quantity of graft copolymer can be formed. This makes it rather difficult to recover such small quantities.

By means of selective extractions with DCA and xylene we made an attempt at isolating such a product, but only a small quantity of reticulate rubber, insoluble in xylene, was recovered. The presence of reticulate rubber can be explained by the reaction of EPR-g-SA with both the hydroxyl terminal groups of PBT.
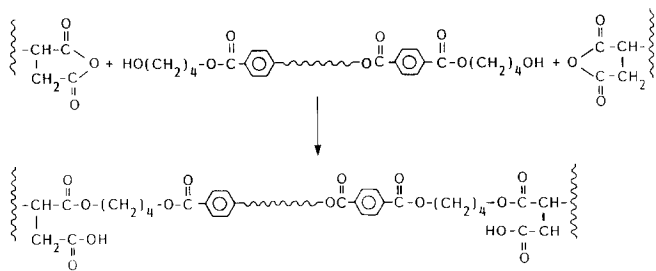
Unfortunately i.r. spectroscopy could not be performed on this type of cross-linked rubber because the material was not mouldable. Therefore we tried to characterize this product by a d.s.c. analysis. In *Figure 2* the d.s.c. trace of the insoluble fraction recovered from PBT/EPR-g-SA blend processed at 32 rpm is shown. It is possible to observe only a small peak in correspondence of the pure PBT melting point. The presence of this peak could be an indirect confirmation of our hypothesis about the formation of a graft copolymer (EPR-g-SA)-g-PBT.
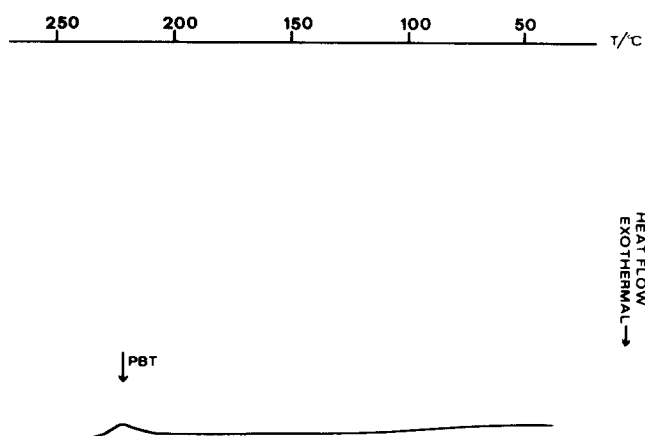
Figure 2 D.s.c. thermogram of the insoluble fraction recovered from PBT/EPR-g-SA blend

Morphology

A morphological investigation was performed by SEM on smoothed and etched surfaces of the blends. Electron micrographs of PBT/EPR blends at 32 and 48 rpm roller speeds are shown in *Figure 3*. The rubber particles appear to be very large with an average value of about $10 \mu m$. Almost no difference can be detected between the morphology of the two blends. Electron micrographs of nominal PBT/EPR-g-SA (80/20) blends, mixed at different roller speeds are shown in *Figure 4*.

The effect of the mixing conditions on these blend morphologies is very evident: the rubber particle dimensions decrease with enhancing the roller speed. At 4 rpm there is an inhomogeneous distribution of holes, representing the sites where the rubber particles were located prior to the etching. Very large holes with diameter of $20-30 \mu m$ are present, along with smaller holes of about $2-3 \mu m$.

At 16 rpm a more homogeneous distribution of rubbery domains of smaller sizes is obtained. The particle diameters range from $10 \mu m$ to $1 \mu m$. With increasing the rpm from 16 to 32 the mean particle dimensions further decrease, exhibiting a narrow size distribution. Beyond this value no further morphological variation can be observed.

Fracture and dynamical mechanical characterization

The impact resistance R, obtained by Charpy tests, as a function of temperature, is shown in *Figure 5* for plain PBT, processed at 32 rpm, for two PBT/EPR blends, processed at 32 and 48 rpm, for PBT/EPR-g-SA blends processed at 4, 16, 32, 48, 64 rpm and for a commercial toughened PBT (dashed curve) produced by Dutral S.p.A. The R values of pure PBT are constant and quite low at all temperatures. This is characteristic of a brittle material. An analogous trend is shown for PBT/EPR blends with a very small R improvement. For the PBT/EPR-g-SA blends one can distinguish two ranges of testing temperatures. At $T < -10°C$ all the alloys show a slightly increasing linear trend. R is still quite low and representative of a fragile behaviour. One can observe a certain influence of the roller speed, used in their processing, on the slopes of R versus T curves. Beyond $T > -10°C$ the 4 rpm blends still maintain low R values, whereas all the other blends become tougher and tougher with increasing the temperature.
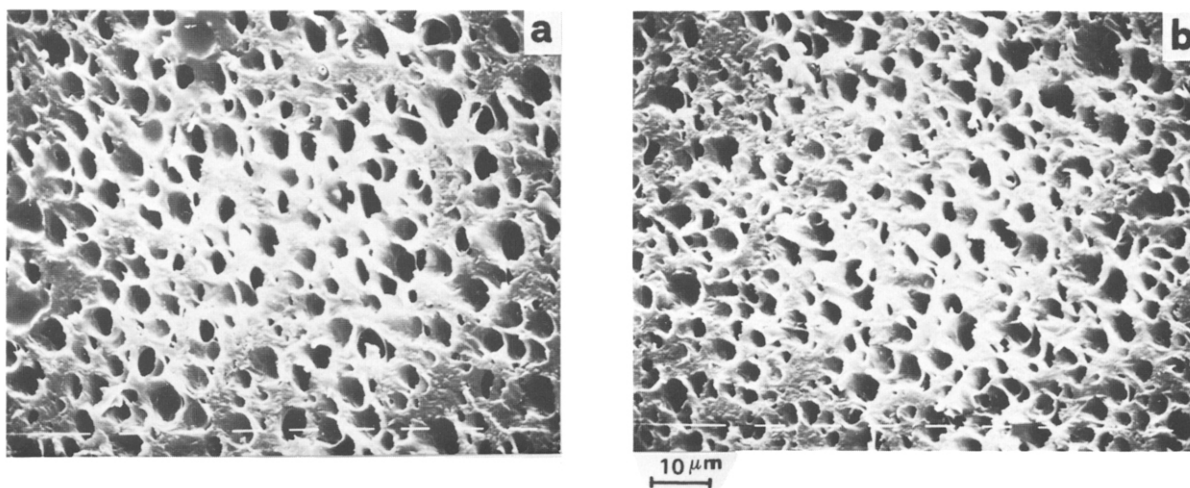
For each blend there is an upper temperature beyond

Figure 3 Scanning electron micrographs of PBT/EPR blends after etching: (a) roller speed 32 rpm; (b) roller speed 48 rpm
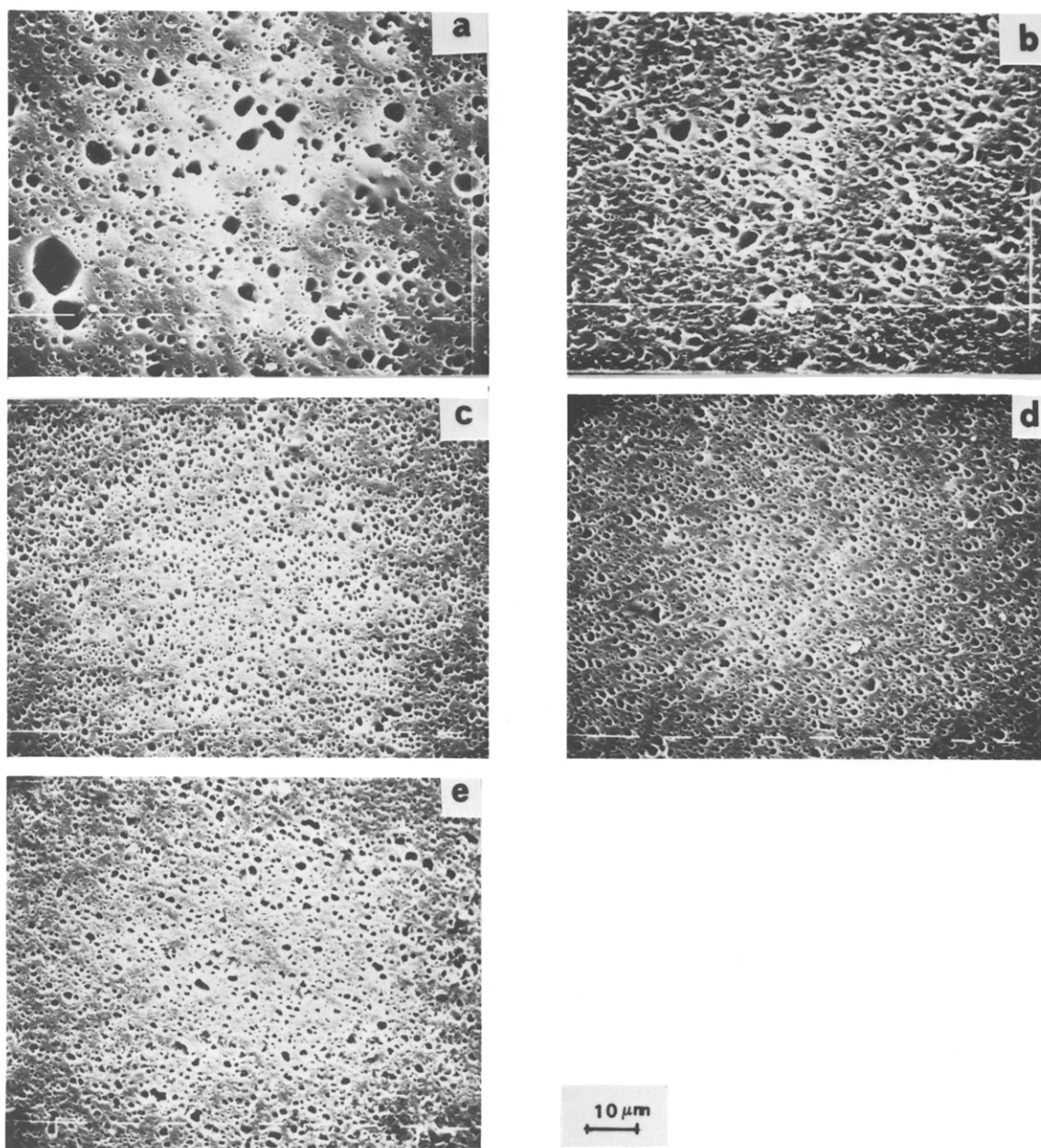

Figure 4 Scanning electron micrographs of PBT/EPR-g-SA blends after etching at different roller speeds: (a) 4 rpm; (b) 16 rpm; (c) 32 rpm; (d) 48 rpm; (e) 64 rpm
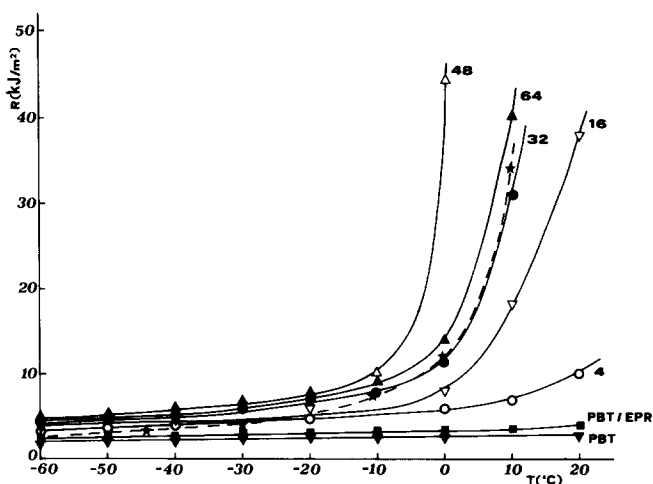
Figure 5 Impact resistance (R) for PBT and PBT/rubber blends as a function of testing temperature (at different roller speeds): ▼, PBT 32 rpm; ■, PBT/EPR 32 and 48 rpm; ○, PBT/EPR-g-SA 4 rpm; ▽, PBT/EPR-g-SA 16 rpm; ●, PBT/EPR-g-SA 32 rpm; ▲, PBT/EPR-g-SA 64 rpm; △, PBT/EPR-g-SA 48 rpm

the dispersed phase respectively, γ is the interfacial tension, r the radius of the rubbery dispersed phase and dv_g/dx the shear rate. Equation (1) is a very simplified expression valid for two Newtonian fluids in a shear flow when only viscous and interfacial forces are balanced (i.e.
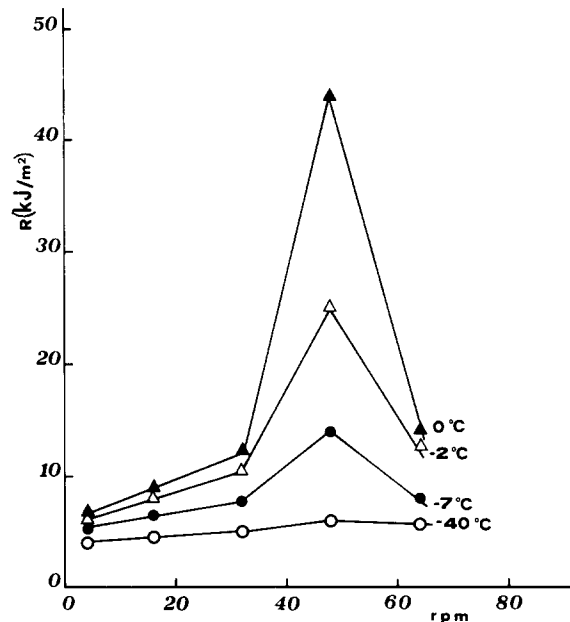

Figure 6 Impact resistance (R) as a function of roller speed (rpm) at different temperatures: ○, $-40°C$; ●, $-7°C$; △, $-2°C$; ▲, $0°C$
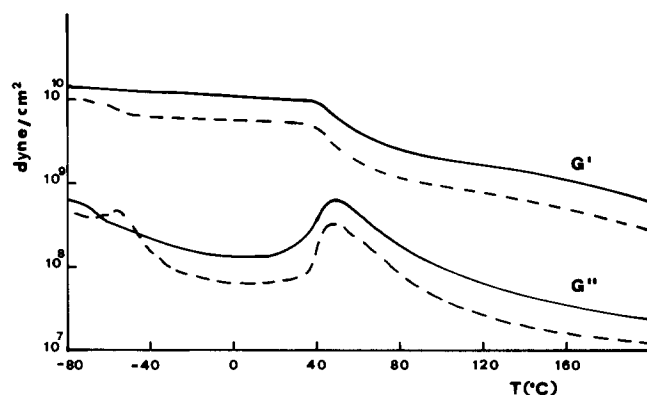
which no rupture is possible by our technique and R is no longer measurable. Note that the commercial high impact PBT curve is nearly equivalent to the 32 rpm curve. The specimens obtained at 48 rpm show much better values than the above mentioned material, indicating, by comparison, the higher performance of our blend. The dependence of the roller speed on the resilience R is better seen in *Figure 6*.

At very low temperature ($-40°C$) R initially changes rather slightly showing a broad maximum at 48 rpm. As the testing temperature increases the maximum becomes more and more prominent. This indicates that at this roller speed the reactive processing is more efficient than at any other ones.

Dynamical mechanical data are reported in *Figures 7* and *8*, where the storage modulus, G', and the loss modulus G'' are reported as a function of temperature, for plain PBT and for PBT/EPR-g-SA blend processed at 32 and 48 rpm.

For the plain PBT the peak relative to PBT T_g does not depend on the roller speed. This indicates that there is no variation of the matrix T_g with such a variable. For the blends it is possible, by comparison of the two figures, to detect a shift of the T_g values both of the matrix and of the rubbery phase. In fact the rubber T_g of the specimen processed at 48 rpm is higher by about 5°C than that of the one prepared at 32 rpm. Correspondingly the matrix T_g is lower than in the former case by about the same amount.

Discussion

The morphological and mechanical effects of this kind of processing are very complex. However the above results can be qualitatively explained as follows.

For PBT/EPR blends, processed at different roller speeds, the main effect on morphology is given by the shear field. In a very qualitative way one can refer to Taylor's expression[24–27]:

$$\left(\frac{\eta_m r \, dv_g/dx}{\gamma}\right) = f\left(\frac{\eta_d}{\eta_m}\right) \qquad (1)$$

where η_m and η_d are the viscosities of the matrix and of

Figure 7 Storage modulus (G') and loss modulus (G'') as a function of temperature for PBT homopolymer ( ), and for PBT/EPR-g-SA blend (– – –), at 32 rpm

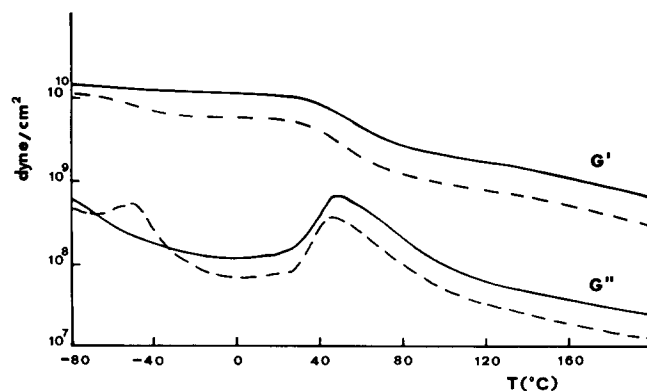**Figure 8** Storage modulus (G') and loss modulus (G'') as a function of temperature for PBT homopolymer (–), and for PBT/EPR-g-SA blend (– – –) at 48 rpm

neglecting inertial effects and the viscoelastic characteristics of polymeric materials).

In our case all the parameters except the shear rate are kept constant. The shear rate is seen in equation (1) to be inversely proportional to the particle radius. However, this effect is not very detectable at high roller speeds (cf. *Figure 2*) for two main reasons. Firstly, the roller speeds are too close to induce an observable change in the particle size distribution and secondly during the subsequent pressure moulding, coalescence phenomena can level off the differences that have arisen during the mixing process at the above indicated roller speeds.

What is far more interesting is the great difference in size and size distribution of these samples compared with the PBT/EPR-g-SA blend samples which show rubber particles of smaller size and of a narrow size distribution. This effect arises from a more complex situation in which the chemistry and the fluidynamics coexist. In fact, during the mixing, the reaction between SA and OH groups of PBT forms the graft copolymer (EPR-g-SA)-g-PBT, which acts as an emulsifier, reducing the interfacial tension γ. This parameter is directly proportional to r in equation (1). Therefore, at the same roller speed, the particles in this system are smaller than in the previous one (cf. *Figures 2* and *3*).

With an increase in the rpm in the mixer the efficiency of reaction is also enhanced. In fact, at a higher shear rate the rubber particle size decreases and the overall external surface increases. Therefore more SA groups are available to react with PBT, enhancing the amount of the graft formed. This, in turn, reduces again both γ and hence r. This mechanism will go on until the particle radii become so small that no further reduction can be obtained. At this point if the shear rate is increased the probability of contact between SA and OH groups, at equal reaction times, increases as well. Therefore, even though the morphology appears to be the same (at 32 and 48 rpm), the higher the roller speed the more graft is formed. More indirect evidence of this effect can be seen in the dynamic mechanical analysis data (*Figures 6* and *7*), where the T_g values of both the PBT matrix and the rubber phase shift to lower and higher temperature, respectively, with increasing roller speed. These shifts can be explained by the existence of interzones around the rubbery particles made of the interfacial agent (EPR-g-SA)-g-PBT. This copolymer is linked both to the matrix, which is softened, and to the rubbery particles, which are hardened improving the adhesion between these phases. The improved adhesion yields a better impact performance, as shown in *Figure 3*.

Beyond this optimum value of 48 rpm, the molten PBT undergoes a molecular degradation. The degree of molecular interconnection of the matrix is diminished and the impact properties are worsened. This effect is analogous to that previously discussed with reference to homopolymers.

CONCLUSIONS

In the present paper the toughening of PBT has been successfully achieved by adding to molten PBT a random EPR, functionalized by maleic anhydride molecules. The hypothesis of the *in situ* formation of a graft, (EPR-g-

SA)-g-PBT acting as an interfacial agent, has been indirectly demonstrated by dynamic mechanical data and by Charpy fracture tests.

The mixing intensity, determined by the roller speed, has a strong influence on the morphology as well as on the adhesion between the rubbery particles and the matrix. In particular with varying such a parameter both the shear field intensity and the reactivity of the system are enhanced, and the impact performances of the materials can be optimized. A limiting value of the roller speed is found to be determined by the mechanical degradation of the molten PBT.

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