Rubber modification of polybutyleneterephthalate by reactive blending concurrently with polymerization reaction

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Rubber modification of polybutyleneterephthalate (PBT) was accomplished by the addition of suitable functionalized ethylene–propylene copolymers (EPR) concurrently with the high temperature polycondensation of 1,4-butanediol and dimethylterephthalate. Ester and alcohol modified rubbers were tested in the polymerization process, and it was found that the type and amount of grafted groups can play a fundamental role because they determine mode and state of dispersion of the elastomeric phase inside the plastic matrix. An attempt was made to correlate the results obtained to the influence of the different kinds of grafted pendant groups on the polymerization equilibria of PBT.

(Keywords: polybutyleneterephthalate (PBT); rubber modification; polymerization)

INTRODUCTION

Polybutyleneterephthalate (PBT) is of growing interest as material for injection moulding. In fact, its rate of crystallization is lower than that of the other widely used linear polyesters such as polyethyleneterephthalate (PET). PBT shows a low impact resistance, particularly at low temperatures. For this reason the uses of PBT are limited. The usual method to overcome this limitation is to add a second elastomeric phase to the PBT matrix. Rubber modification of PBT has been realized by melt blending with preformed rubbers such as poly(ethylene-co-vinylacetate) (EVA) and poly(ethylene-co-vinylalcohol) (EVOH)[1].

A different method is based on the possibility of having block copolymers as a dispersed phase between PBT and elastomeric polyethers. The blends and the copolymers are obtained directly during the polymerization of PBT by dispersing the polyether, end capped with reactive groups, in the starting monomeric reactive mixture[2,3].

For both types of blends a good adhesion is observed between the dispersed phase and the matrix, mainly due to transesterification reactions, which occur at high temperatures. Nevertheless, it must be pointed out that the molecular architecture of the EVA-g-PBT or EVOH-g-PBT copolymers, which form during the processing and which are responsible for the interfacial activity, is very badly controlled.

Recently, a new method suitable to produce rubber-modified nylons with very high impact properties was investigated and developed in our Institute[4]. Blends between polyamide 6 (PA6) and functionalized ethylene–propylene rubber (EPR) were prepared concurrently with the polycondensation reaction of ε-caprolactame. Due to the presence along the EPR chains of reactive groups (–COOH; –COOR) able to react with the terminal –NH_2 groups of the growing PA6 molecules, graft copolymers of the type EPR-g-PA6 are formed[5,6]. We found that it was possible to tailor the mode and state of dispersion of the rubber component and the adhesion between the different phases and the final mechanical impact response by controlling the molecular structure of the starting functionalized rubber (grafting degree and chemical nature of the functionality) and the blending conditions (mainly, the viscosity of the medium, i.e., the time of polycondensation at which the reactive rubber is added)[7]. The excellent results obtained lead us to follow the same approach to improve the impact resistance of PBT.

In the present paper a method to prepare blends with good interfacial adhesion between PBT and a saturated ethylene–propylene rubber (EPR) opportunely functionalized with alcoholic or ester groups is reported. The blends obtained during the high temperature catalysed polymerization of 1,4-butandiol and dimethylterephthalate have been characterized by i.r. spectroscopy, differential scanning caloritmetery (d.s.c.) and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The starting EPR was a random copolymer Dutral COO54, 67 mol% in C_2, kindly supplied by Dutral S.p.A., $M_w = 1.8 \times 10^5$, Melt flow index (100°C) = 40 g/min. EPRs modified by insertion of succinic anhydride (EPR-g-SA) and dibutylsuccinate (EPR-g-DBS) were prepared, at different grafting degrees, by using a solution method of grafting previously described

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in reference 8. Dimethylterephthalate (DMT), Fluka reagent grade, was used without further purification. 1,4-butandiol (BDO), Fluka reagent grade, was purified under vacuum overnight. Titanium tetraisopropylate ($Ti(iP)_4$), an ICN Pharmaceutical product, was purified by distillation at a pressure of 1 mmHg and a temperature of 120°C. All the solvents used were of analytical grade and were purified according to standard procedures.

Standard preparation of EPR-g-ethanolsuccinimide (EPR-g-ESI)

10 g of EPR-g-SA 1.5% by weight of anhydride (15 mmol SA/100 g of EPR) were dissolved in 200 cc of xylene. 0·37 ml of ethanol-amine (EA), corresponding to an excess of 4/1 moles EA/moles SA, were added to the solution, together with 0.43 ml of triethylamine (TEA) as catalyst, at a temperature of 90°C. After 1 h, the reaction mixture was cooled to room temperature and precipitated in acetone, repeatedly washed and dried in a vacuum oven at a temperature of 60°C overnight.

Typical procedure for a binary 90/10 blend preparation

A mixture of 89.2 g (0.46 mol) of DMT, 82.8 g (0.92 mol) of BDO and 5.7 ml of a 0.5% by volume solution of $Ti(iP)_4$ in $CHCl_3$ (corresponding to a molar ratio ($Ti(iP)_4$/DMT of 1×10^{-4}/l) was charged into a cylindrical glass vial, equipped with mechanical stirrer and a distillation apparatus. The mixture was heated, using an oil bath, up to 200°C and left to react (transesterification step) for 4 h under N_2 while distilling methanol as by-product. The temperature was then raised to 255°C within 30 min and the pressure was gradually reduced to 0.5 mmHg. The polycondensation step was continued for 30 min. At this point, 11.2 g of rubber were added to the polymerizing mixture and the polymerization was further continued for 90 min. After cooling, the white reaction product was recovered and finely granulated in a laboratory mill. Codes and contents of rubber of the prepared blends are reported in *Table 1*.

Techniques of characterization

The i.r. spectra were obtained with a Nicolet 5DXB spectrophotometer at 4 cm^{-1} resolution (32 scans collected), using films compression moulded at 250°C.

Viscosity measurements were carried out using a Cannon–Ubbelhode viscosimeter, on solutions in a solvent mixture phenol/tetrachloroethane 60/40 wt/wt, at a temperature of 30°C.

Thermal analysis was performed with a Mettler system TA-3000 equipped with a control and programming unit (microprocessor Tc 10A) that manages the apparatus and permits the elaboration of the memorized data. The system is provided with a calorimetric cell DSC-30 which allows temperature scans from −170 to 600°C.

Table 1 Codes and compositions wt/wt of the prepared PBT/functionalized rubber blends

Code of blends	Rubber type and grafting degree	(%wt)	% by weight of rubber	% by weight of PBT
PBTEPR (90/10)	EPR	0	10	90
PBTDBS2 (90/10)	EPR-g-DBS	2	10	90
PBTDBS9 (90/10)	EPR-g-DBS	9	10	90
PBTESI0.5 (90/10)	EPR-g-ESI	0.5	10	90
PBTEPR (80/20)	EPR	0	20	80
PBTDBS2 (80/20)	EPR-g-DBS	2	20	80
PBTESI0.5 (80/20)	EPR-g-ESI	0.5	20	80

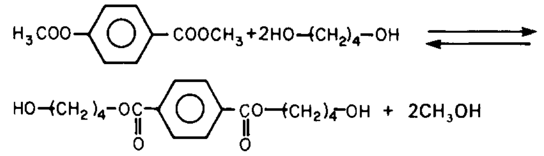
The morphological characterization of the prepared blends was carried out using a scanning electron microscope (SEM), Philips model 501. Micrographs of surfaces fractured in liquid N_2 and of microtome-faced surfaces of blends after exposure for 30 min to boiling xylene or *o*-dichlorobenzene vapours were obtained. Before the examination, samples were coated with gold-palladium.

RESULTS AND DISCUSSION

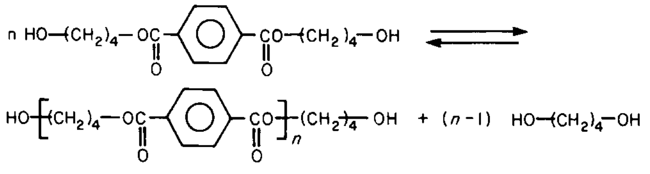
Polycondensation of PBT

It is known from the literature that the synthesis of PBT occurs according to the following scheme[9,10]:

Step I: transesterification reaction:

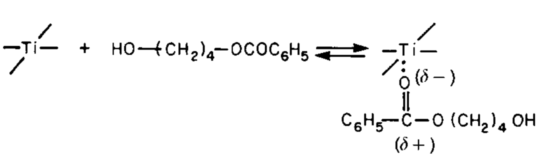


Step II: polycondensation reaction:



In the first step a prepolymer is formed and the conversion is kept high by removing methanol under a N_2 stream. At this stage, the molten reacting mixture has a very low viscosity due to the low M_w of the prepolymer. In the second step, the effective polycondensation occurs, and the equilibrium is shifted towards high M_w polymer by the removal of excess BDO at high temperature (255°C) and under reduced pressure (0.5 mmHg).

The influence of the catalyst on both steps of the reaction process is very high. In fact, the reaction is 100–1000 times faster in presence of a suitable catalyst. The catalysts used for synthesis of PBT are usually titanium esters or alcoholates. According to a proposed mechanism[10], the titanium can coordinate itself to the oxygen of the carbonylic function, facilitating the nucleophilic attack of the hydroxyl group of glycol to the carbonyl (see scheme):



The stoichiometric ratio between moles of $Ti(iP)_4$ and moles of DMT used in our synthesis is 1×10^{-4}/l. The resulting PBT is characterized by a crystallinity degree of about 40%, with a melting point of 225°C and a T_g of 51°C. The molecular weight has been obtained by viscosimetric analysis, using a semi-empirical relation between the intrinsic viscosity and M_n[11]:

$$\eta_{int} = 1.166 \times 10^{-4} M_n^{0.871}$$

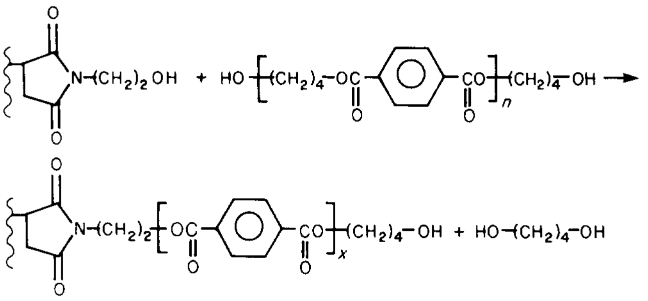
where $\eta_{\mathrm{int}} = \ln(t/t_0)/c$ has been measured in 60:40 phenol: tetrachloroethane at 30°C, at a concentration of 50 mg/10 cc. Applying this relation, we obtained a number average molecular weight M_n of 24000.

Preparation of blend concurrently with polymerization of PBT

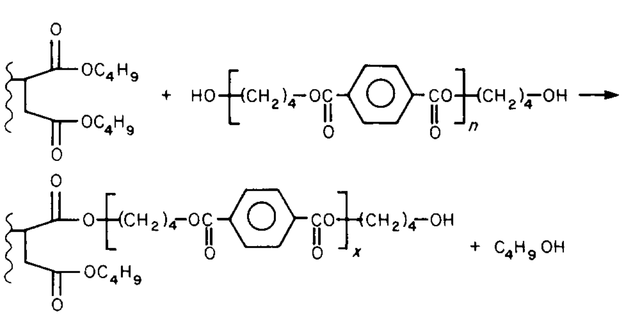
The addition of a rubbery phase during the polymerization of a monomer of a second polymer to obtain a rubber-modified thermoplastic material has two main advantages towards the melt-mixing process of high M_w preformed polymers. Firstly, the synthesis of the polymer and rubber modification are done in one step, saving time and reducing the machining of materials, which always produces some degradation. Secondly, the lower viscosity of the polymerization medium, at least when the rubber is added, allows a more favourable mixing with respect to the dispersion of the rubbery phase and makes it possible to obtain a better dispersion of one phase into the other.

Following this procedure, the preparation of blends PBT/functionalized EPR have been carried out by adding the rubbery component during the high temperature polymerization of butandiol and dimethylterephthalate. The functional groups grafted onto EPR must be able to participate in the transesterification equilibria occurring during the polycondensation. In this respect, the ester functionality of EPR-g-DBS or the alcoholic functionality of EPR-g-ESI are both interesting because they take part in the polycondensation equilibrium with the following reactions:

EPR-g-ESI



EPR-g-DBS



The problem which must be faced when preparing similar blends is when in the polymerization the second component must be added in order to obtain an optimal state and mode of dispersion of rubber. From our previous studies on the polyamide 6/functionalized rubber blends prepared directly during the caprolactame polymerization, we know that there are four critical factors which influence the attainable degree of dispersion of a functionalized rubber inside a polymerizing matrix: (1) the reactivity of grafted groups; (2) the grafting degree; (3) the length of the polymerizing chains at the moment the rubber is added and (4) the viscosity of the reaction medium at that time.

The first critical factor will be discussed later. With regard to the third and fourth critical factors, it must be considered that the grafting of a growing PBT chain onto a molecule of functionalized EPR is a heterogenous process which occurs at the interface between the two immiscible components. A PBT molecule, upon grafting, is at least partially segregated from the solution, so it will have less chance to grow. Furthermore, once a growing PBT chain has reacted with ester or alcoholic groups of functionalized EPR, it has only one residual alcoholic end group, so it is also intrinsically less able to polymerize via the transesterification reaction. In this respect, the degree of polymerization at the moment in which the rubber is added is very important for the emulsifying efficiency: chains which are too short will be segregated inside the rubber and fail to act as emulsifiers. On the other hand, if there is too high a degree of polymerization, the viscosity of the medium will increase very sharply, and the physical dispersion of the rubber inside the matrix will be very difficult to achieve. A compromise between these two opposite factors led us to choose 30 min for the polycondensation step as a suitable time for the addition of the rubber.

As a matter of fact, kinetic experiments have demonstrated that after 30 min the polymer has reached a M_n of 10000 while developing a good degree of crystallinity. Moreover, the viscosity of the molten polymer seems to be relatively low.

Some general observations concerning the preparation of some of the blends are discussed below.

Blends with EPR-g-ESI. It was observed that when an EPR-g-ESI having a high grafting degree (6.8% by weight) is used, the resulting PBT/EPR-g-ESI blends show a macroscopic phase separation of the rubber. On the other hand, blends containing an EPR-g-ESI at 0.5% grafting level are easily stirrable and the molecular weight of PBT at the end of reaction is rather large (21000). Moreover, the final material are characterized by a very fine distribution of rubber component. The macroscopic phase separation between rubber and PBT which occurs when an EPR-g-ESI at high grating degree is used can be interpreted on the basis of our previous experience on rubber toughened polyamide 6 (ref. 6). The alcoholic derivative of succinic anhydride, ESI, causes strong interactions between different grafted EPR chains, due to the occurrence of extended hydrogen bondings. When the outer shell of a rubbery particle has reacted with growing PBT chains, the weak shear forces of our single-blade stirrer are not sufficient to disrupt the entanglements of the rubbery domains, leading to a blend macroscopically phase separated.

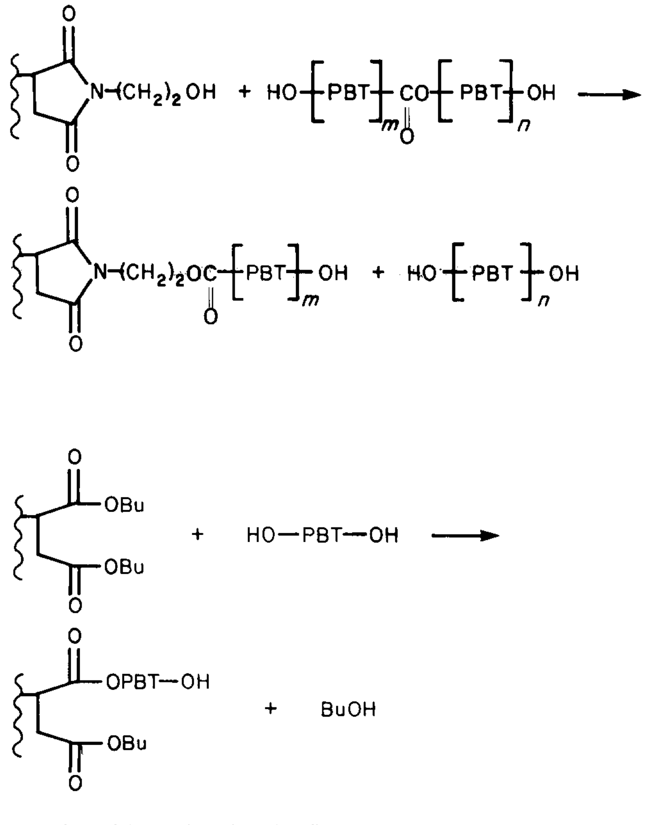
Blends with EPR-g-DBS. A different behaviour is shown by EPR-g-DBS. In fact, in this case we obtained good dispersion of the rubber even for a grafting degree of 9%. This difference is probably due to the lack of either hydrogen or polar interactions between the DBS groups and to the extensive degradation of the starting EPR backbone, which occurs during the grafting of DBS molecules[8].

Blend analysis

Selective extractions of blends with 10% rubber content by trifluoroacetic acid have been made in order to separate and characterize their components. By treatment with this solvent we obtained three phases in all cases: on the bottom a clear solution containing as solute pure PBT which is completely soluble in the acid; an opaque solution in the middle, mainly containing the copolymer functionalized EPR-g-PBT; and at the top a supernatant condensed rubbery phase.

The three phases have been separately analysed by i.r. and d.s.c. techniques. Furthermore, the pure PBT, recovered by vacuum stripping of the solvent from the clear solution, was characterized by viscosimetric analysis to determine its molecular weight.

The PBT recovered from PBTDBS9 has a molecular weight of 10 000, indicating that the addition of a rubber when there is a high content of diester groups plays a negative role on the homopolymerization of PBT. Instead, the PBTs recovered from PBTDBS2 and PBTESI0.5 have M_n around 20 000, suggesting that either a low content of esters or the presence of alcoholic functions do not hinder the polymerization of PBT. Because it was not possible to prepare a blend with EPR-g-ESI at high grafting degree having a fine dispersion of the rubber, we prepared a model experiment to show the influence of monohydroxyl molecules on the polymerization of PBT. We obtained a PBT at $M_n = 21\,000$ and added an amount of dodecylic alcohol equal to the amount which would be present to an EPR-g-ESI at 10% grafting degree. The different behaviour of esters and alcohols can be explained on the basis of the following scheme:



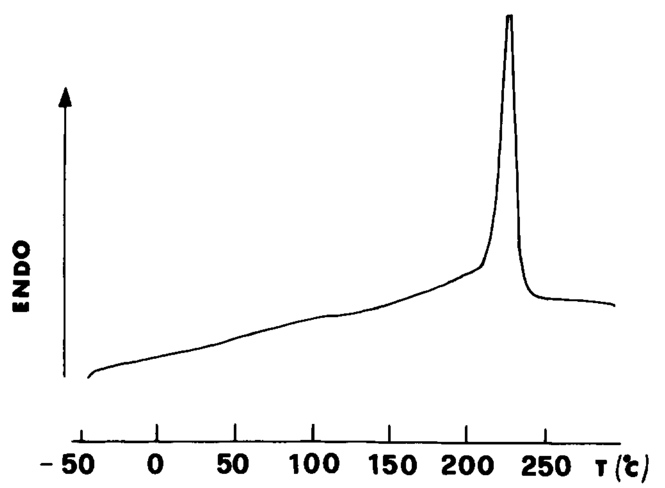


Figure 1 D.s.c. thermogram of PBT extracted from PBTDBS9 90/10; heating rate = 20°C/min

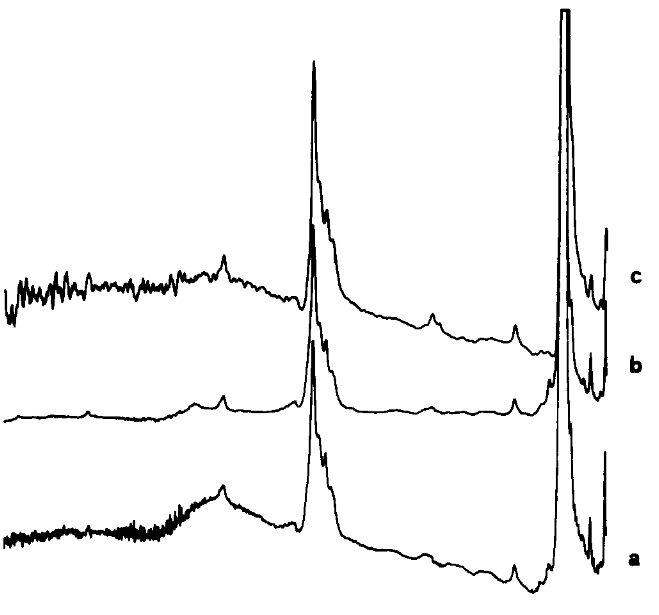


Figure 2 FTi.r. spectra of PBTs extracted from (a) PBTDBS9; (b) PBTESI0.5; (c) PBTEPR

It is evident that by the first process there is no loss of functionality in the homopolymeric phase, i.e., the number of hydroxyl end groups remains constant. On the other hand, in the second case, upon grafting the content of hydroxyl functionalities in the homopolymeric phase decreases, the kinetic of polymerization will be depressed as butanol is produced.

In the case of PBTEPR blend, the molecular weight of the extracted PBT is 24 000, identical to that obtained from the homopolymerization of PBT. The d.s.c. thermograms of extracted PBTs irrespective of blend composition all show the same values of T_g and T_m ($T_g = 51°C$, $T_m = 226°C$; see *Figure 1* as an example). In *Figure 2*, FTi.r. spectra related to some of the extracted PBT are reported. Their appearances are identical to commercial grade PBT. However, in the case of PBTDBS9 blend, the existence of a broad band at 3300 cm^{-1}, which has been attributed to a high concentration of –OH terminal groups, confirms the low molecular weight of the extracted PBT.

The copolymeric phases of PBTESI0.5, PBTDBS2 and PBTDBS9 blends have been recovered by centrifugation of the milky solutions. They represent only a small fraction of the total blend. Obviously, in the case of the

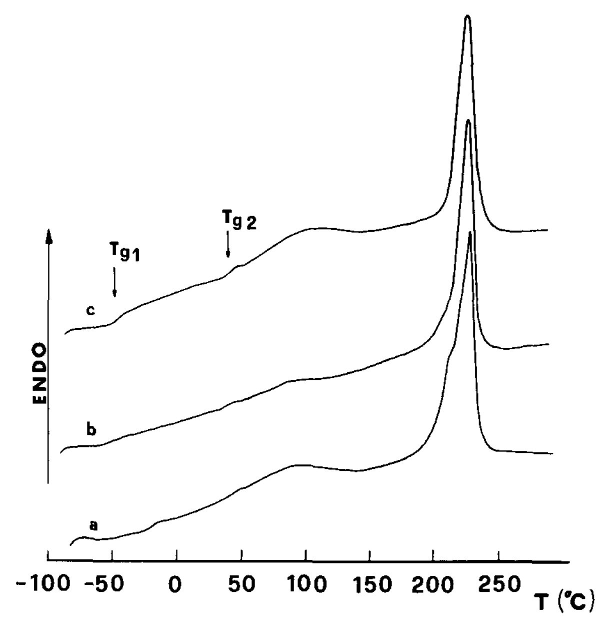


Figure 3 D.s.c. thermograms of copolymers extracted from (a) PBTESI0.5; (b) PBTDBS2; (c) PBTDBS9, heating rate = 20°C/min

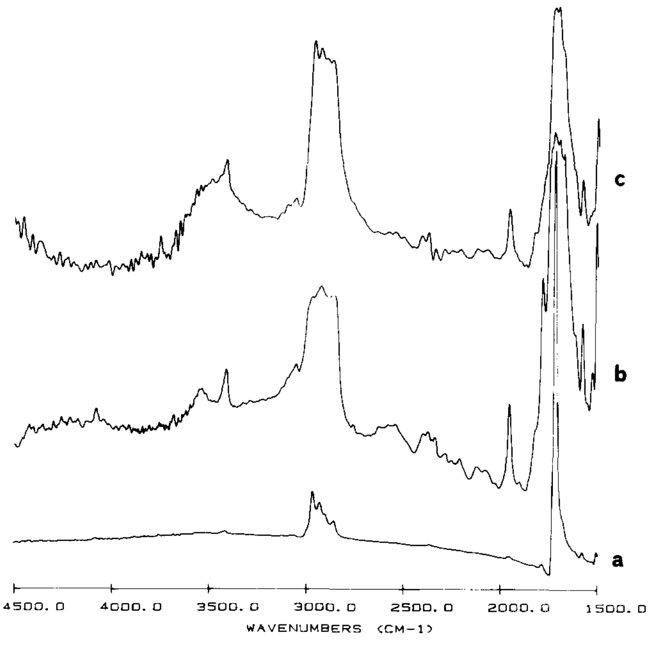


Figure 4 FTi.r. spectra of copolymers extracted from (a) PBTESI0.5; (b) PBTDBS2; (c) PBTDBS9

PBTEPR blend the intermediate copolymeric phase is absent because of the lack of chemical interactions between PBT and EPR. D.s.c. traces relative to these copolymers are reported in *Figure 3*. The copolymers extracted from the blends show an endothermic peak at 226°C, close to the melting point of plain PBT. Furthermore, the low temperature glass transition of the EPR backbone at $T = -43°C$ and the glass transition of PBT grafts at $T = 44°C$ are evident.

In *Figure 4*, i.r. spectra of the copolymers are reported. The spectrum (a) refers to the copolymer (EPR-g-ESI)-g-PBT. The presence of the rubbery phase is confirmed by the small band at 1784 cm^{-1}, corresponding to the secondary peak of imide group grafted onto the EPR. The spectra of (EPR-g-DBS)-PBT copolymers from PBTBS2 and PBTDBS9 blends (spectra (b) and (c) respectively) show an evident broadening of the ester band (1719 cm^{-1}), due to the overlapping of the band of residual unreacted dibutylsuccinate and terephthalate groups (1740 and 1716 cm^{-1}, respectively). It is worth noting the broad band at 3300 cm^{-1} which appears in the spectrum of the copolymer from PBTDBS9 blend, already present in the corresponding extracted PBT.

The i.r. spectra of the insoluble in trifluoroacetic acid, supernatant rubbery phases of PBTDBS9, PBTESI0.5 and PBTEPR blends are shown in *Figure 6*. The d.s.c. thermogram of the rubbery phase from the PBTESI0.5 blend is shown in *Figure 5*, as an example. It can be seen that both d.s.c. and i.r. analysis confirm that this rubber has the same characteristics of the starting functionalized EPR. Thus it may be concluded that the supernatant phase obtained after extraction of the blends with trifluoroacetic acid is mainly constituted by unreacted rubber.

Phase structure studies

Scanning electron microscopy has been utilized to

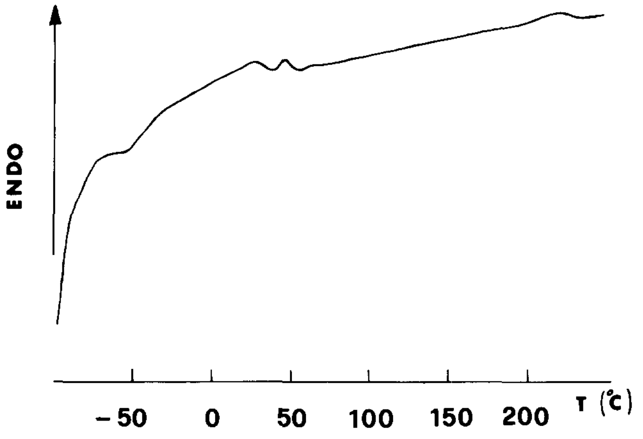


Figure 5 D.s.c. thermograms of EPR-g-ESI extracted from PBTESI0.5; heating rate = 20°C/min

Figure 6 FTi.r. spectra of rubbers extracted from (a) PBTDBS9; (b) PBTESI0.5; (c) PBTTEPR

Figure 7 SEM micrograph of fracture surface of PBT, 2500 x

investigate the morphology of fracture surfaces and smoothed surfaces after etching of samples of PBT and blends. Samples as obtained from polymerization have been first compression-moulded at 260°C and then fracturated in liquid N_2. Smoothed surfaces have been obtained by using a microtome and analysed after exposure to xylene or *o*-dichlorobenzene (blend PBTESI0.5) vapours.

Micrographs of fracture surfaces of 90/10 and 80/20 blends are shown in *Figures 8* and *9*. The micrograph relative to PBTDBS9 80/20 blend is lacking because this blend has not been prepared. The micrograph of the fracture surface of samples of plain PBT, for comparison, is shown in *Figure 7*.

The PBTEPR 90/10 blend shows a 'cheese-like' morphology. The presence of large spherical particles (about 5–10 μm) uniformly distributed in the PBT matrix without evidence of interfacial adhesion is observed (see *Figure 8a*). From the SEM examination of the fracture surfaces of PBTDBS2, PBTDBS9 and PBTESI0.5 (90/10) blends it emerges that in all cases a dispersed phase, almost spherical in shape, with dimensions lower than that of PBTEPR blend is present. Moreover, the average dimensions of such domains, as well as the adhesion to the PBT matrix, are strongly dependent upon the graft degree of the functonalized rubber and upon the chemical nature of the functional group.

In the case of PBTDBS blends, domains with lower average dimensions are obtained when an EPR-g-DBS rubber with a grafting degree of 2% is used (compare *Figures 8b* and *8c*). The adhesion of dispersed domains to the PBT matrix seems to be very low both in the case of PBTDBS2 and PBTDBS9 blends.

Fracture surfaces of PBTESI0.5 90/10 blend are characterized by the presence of a dispersed phase with a rather large size distribution (0.5–5 μm). Moreover, in such blends the domains show a strong adhesion to the matrix (see *Figure 8d*).

The SEM micrographs in *Figures 9a, b*, and *c* show the mode and state of dispersion of rubbery phase for PBTEPR, PBTDBS2 and PBTESI0.5 (80/20) blends. Examination of the micrographs clearly shows that a higher rubber concentration in the case of PBTEPR and PBTDBS2 blends only induces an increase in the average dimensions of the dispersed particle. In addition, the

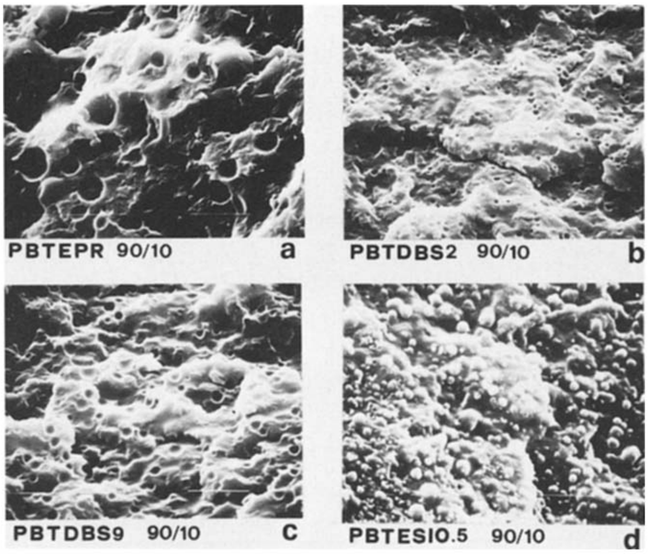


Figure 8 SEM micrographs of fracture surfaces of 90/10 blends (a) PBTEPR; (b) PBTDBS2; (c) PBTDBS9; (d) PBTESI0.5, 2500 x

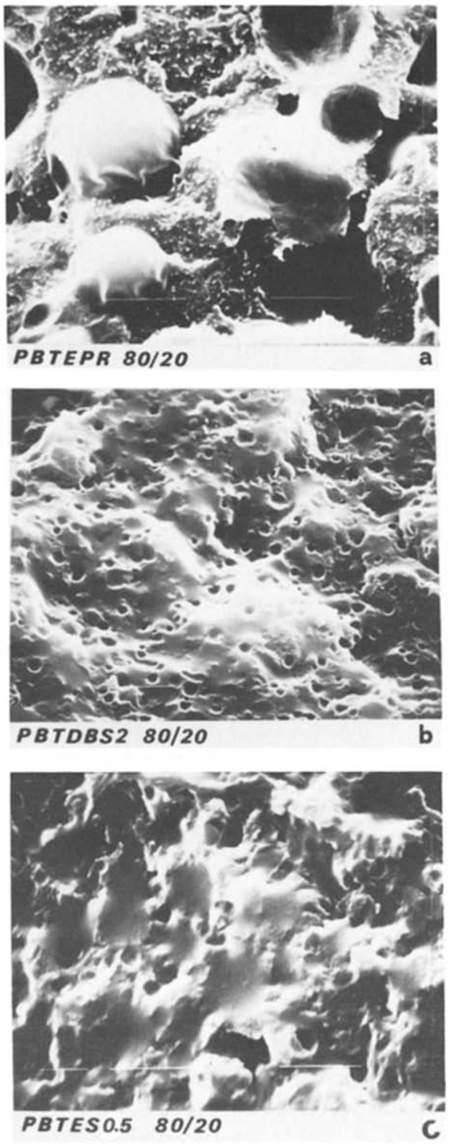


Figure 9 SEM micrographs of fracture surfaces of 80/20 blends (a) PBTEPR; (b) PBTDBS2; (c) PBTESI0.5, 2500 x

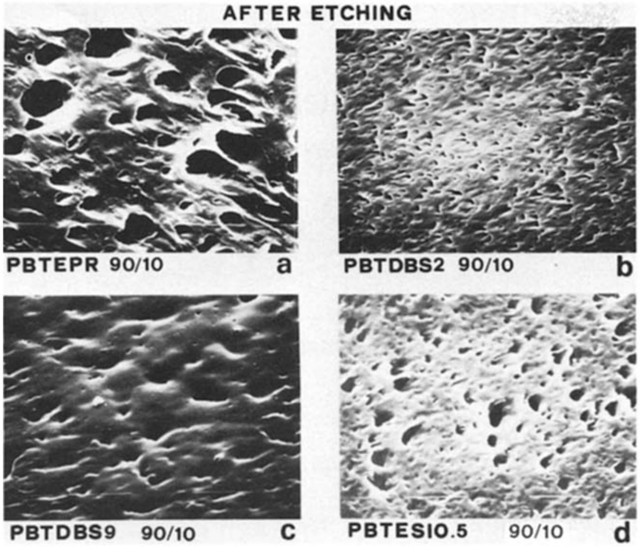


Figure 10 SEM micrographs of smoothed surfaces after etching of 90/10 blends (a) PBTEPR; (b) PBTDBS2; (c) PBTDBS9; (d) PBTESI0.5, 2500 ×

Table 2 Results of the thermal analysis by d.s.c. of the blends. Heating rate = 20°C/min; ΔH° = 31.5 kJ/mol (ref. 13)

Code blend	ΔH_f (J/g of PBT)	T_g (°C)	$T_m{}^n$(°C)	X_c of PBT phase (%)
PBT	58	51	225	41
PBTER 90/10	43	43	225	33
PBTDBS2 90/10	49	48	226	34
PBTDBS9 90/10	50	44	227	38
PBTESI0.5 90/10	49	47	226	36
PBTEPR 80/20	51	45	225	35
PBTDBS2 80/20	51	49	224	36
PBTESI0.5 80/20	45	45	224	32

PBTESI0.5 (80/20) blend shows larger domains than the corresponding 90/10 blend, but the adhesion of these domains to the matrix seems to be very strong. No almost free spherical particles emerging from the surface are found. The morphology observed in this blend is accounted for by assuming that the crack propagation front generates the rupture of the dispersed domains without causing any enucleation from the fracture surface. This last result probably indicates that the molecular structure of the graft copolymer PBT-functionalized EPR (i.e., number of graft per surface area unit, length of PBT grafts, etc.) is influenced by rubber concentration. This is especially evident in the case of PBTESI blends.

The SEM micrographs of the smoothed and etched surfaces of PBTEPR, PBTDBS and PBTESI (90/10) blends are shown in *Figures 10a, b, c* and *d*. A comparison with *Figure 8* indicates that a large part of the domains are etched out from the surfaces.

Thus it may be concluded that only a relatively small amount of rubber reacts with PBT preformed chains, when added during the polymerization, giving rise to the formation of EPR-g-PBT graft copolymers insoluble in xylene and *o*-dichlorobenzene.

Thermal analysis

Results of thermal analysis of samples of pure PBT and samples of as obtained blends are reported in *Table 2*. All experiments have been performed at a heating rate of 20°C/min. Only a single T_g was detectable, which is clearly attributable to the homoPBT-rich phase. The T_g of the rubbery phase is not observable, due to the low content of EPR in the blends. The T_g of PBT generally decreases in the blends: this effect can be attributed to some plasticization of the matrix due to the presence of the rubber.

No variations in the values of T_m are observed, while the crystallinity degree of blends seems to be lower than that of plain PBT. Similar results are consistent with previous studies on the crystallization behaviour of nylon 6/functionalized EPR blends and indicate that the presence in the melt of an elastomeric phase disturbs the crystallization process of the matrix[12].

CONCLUSIONS

The presence of EPR molecules bearing reactive groups during the PBT polycondensation reaction with alcoholic or ester functionalities at low grafting degree does not hinder the polymerization of PBT. Selective extraction of blends by trifluoroacetic acid reveals the existence of a copolymeric phase constituted by an EPR backbone grafted with PBT chains (functionalized EPR-g-PBT). Such graft copolymers show, together with the glass transition of the EPR, the glass transition and melting endotherm of PBT.

From the morphological analyses it emerges that the mode and state of dispersion of the rubbery phase depends on the blend composition, type and level of grafting degree of functionalized EPRs. In particular, the addition of an EPR bearing a very low content of alcoholic functionalities (EPR-g-ESI) leads to blends characterized by a high adhesion between the rubber and the PBT phase.

Work is in progress to characterize the mechanical and impact properties of the rubber-modified PBT, prepared according to the method described here.

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