Role of degree of grafting of functionalized ethylene–propylene rubber on the properties of rubber-modified polyamide-6

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An amorphous random ethylene–propylene rubber (EPR) copolymer and EPR-*g*-succinic anhydride (EPR-*g*-SA) graft copolymer have been used as rubbery components to obtain binary polyamide (PA6)/EPR or PA6/EPR-*g*-SA and ternary PA6/EPR/EPR-*g*-SA blends by melt mixing. The influence of degree of grafting (*DG*) or EPR-*g*-SA on the morphology and tensile and impact properties of such blends has been investigated. Finer and more homogeneous dispersions of the rubbery domains and better impact properties are obtained with increasing degree of grafting in the blends. At equal *DG* values and for the compositions used, the binary PA6/EPR-*g*-SA alloys show better behaviour than the ternary ones. These results are related to the presence of an (EPR-*g*-SA)-*g*-PA6 graft copolymer formed during melt mixing, which acts as an interfacial and emulsifying agent.

INTRODUCTION

In previous papers we have reported on the preparation and characterization of rubber-modified polyamide-6 (PA6) with improved impact properties. Such materials were prepared by melt mixing binary and ternary blends containing as rubbery component an amorphous ethylene–propylene rubber (EPR) random copolymer and/or a functionalized EPR copolymer with succinic anhydride (EPR-*g*-SA)[1].

The functionalization of the ethylene–propylene rubber was performed by solution grafting of maleic anhydride molecules promoted by radical initiators[2]. It was found that binary PA6/EPR-*g*-SA (80/20) and ternary PA6/EPR/EPR-*g*-SA (80/10/10) blends show at low temperature (−20°C) a significant improvement in Izod impact behaviour. Such a result was correlated with the mode and state of dispersion of the rubbery components. It was assumed that during mixing a graft copolymer of the type (EPR-*g*-SA)-*g*-PA6 is formed, following the reaction between the $-NH_2$ terminal groups of the PA6 and the anhydride groups of EPR-*g*-SA[1]. It was observed that PA6/EPR-*g*-SA and PA6/EPR/EPR-*g*-SA blends show a very fine distribution of the rubber in the PA6 matrix. Such an observation was accounted for by assuming that the EPR-*g*-SA graft copolymer is able to act as emulsifier and/or interfacial agent[1].

The isothermal crystallization and the thermal behaviour of PA6/EPR and PA6/EPR-*g*-SA blends were also investigated[3]. It was found that the addition of functionalized rubber influences drastically the primary and secondary nucleation process of PA6.

More recently[4] a finer morphology and even better impact properties were obtained in the case of PA6/EPR/EPR-*g*-SA ternary blends adopting a two-step melt-mixing procedure. According to this method, the EPR and EPR-*g*-SA components are first premixed at 130°C before the final mixing with PA6 at higher temperature in the same Brabender-like apparatus.

In all the studies reported so far, a functionalized rubber containing 2.9 wt% of grafted anhydride was used throughout.

The main goal of the present paper is to study the mode and state of dispersion of the minor component, the impact behaviour and the tensile mechanical response of some binary PA6/EPR-*g*-SA and ternary PA6/EPR/EPR-*g*-SA blends (prepared by the double-step mixing procedure) as functions of the degree of grafting of the functionalized EPR-*g*-SA rubber.

EXPERIMENTAL

Materials

The polyamide-6 (PA6) used in the present work was Sniamid ASN27/S produced by Snia Viscosa, with a number-average molecular weight ($\bar{M}_n$) of 2.3×10^4.

The ethylene–propylene rubber (EPR) random copolymer was Dutral CO/054 supplied by Dutral SPA, having a weight-average molecular weight ($\bar{M}_w$) of 1.8×10^5, an ethylene content (C_2) of 67 mol% and a glass transition temperature (T_g) of about −60°C.

EPR-*g*-SA with a graft content of maleic anhydride of 0.6, 2.4 and 4.5 wt% were prepared following the procedure already described elsewhere[1,2].

Before use the PA6 was kept under vacuum at 60°C for 48 h to eliminate the water content absorbed during industrial washing.

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Table 1 Initial blend composition

Blend code (PA6/EPR/EPR-*g*-SA)	PA6 (wt%)	EPR (wt%)	EPR-*g*-SA (wt%)	Degree of grafting, *DG* (wt%)
100/0/0	100	–	–	–
80/20/0	80	20	–	–
80/0/20	80	–	20	0.6
80/0/20	80	–	20	2.4
80/0/20	80	–	20	4.5
80/15/5	80	15	5	0.6
80/15/5	80	15	5	2.4
80/15/5	80	15	5	4.5

Blend preparation

Binary PA6/EPR and PA6/EPR-*g*-SA blends were prepared in a Brabender-like apparatus (Rheocord E.C. of Haake Inc.) by simultaneous melt mixing of the components at a temperature of 260°C with a mixing time of 20 min and a roller speed of 32 r.p.m. For the preparation of ternary PA6/EPR/EPR-*g*-SA blends, the EPR and EPR-*g*-SA were first premixed in the same Rheocord apparatus at 130°C for 10 min and at 32 r.p.m. The rubber mixture was then melt mixed with PA6 under the same operating conditions as for the binary blends.

The initial composition of all binary and ternary blends investigated are reported in *Table 1*.

Specimen preparation

The final blends from the mixer were compression moulded in a heated press (Wabash Hydraulic Press) at a temperature of 260°C and a pressure of 240 kg cm^{-2}, to obtain sheets 1 mm and 3 mm thick. The former were used to get dumbbell-shaped specimens for mechanical tensile tests. The latter were used to make parallelepid-shaped samples ($60 \times 6 \times 3.0$ mm^3) to perform Charpy impact tests. Such 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 and ternary blends were exposed for 30 min to boiling xylene vapour and subsequently examined by a scanning electron microscope (Philips SEM 501), after coating with gold–palladium alloy. It was observed that the xylene selectively dissolved the rubbery phase, leaving the PA6 undissolved.

Mechanical tensile tests. Stress–strain curves for all the blends examined were obtained by an Instron machine (model 1122) at room temperature and at a crosshead speed of 5 mm min^{-1}. Moduli, stress and elongation at break were calculated from such curves on an average of 10 specimens.

Prior to testing, all the specimens were conditioned in water at 90°C in order to obtain the same amount of absorbed water (about 3 wt %). The procedure is reported in a previous paper[1].

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 fractures at different temperatures from −50°C to 20°C. The temperature was changed by means of a home-made liquid-nitrogen apparatus.

Curves of resilience as a function of test temperature were obtained for all the blends investigated.

Prior to testing, the specimens were dried under vacuum at 90°C for 10 h.

RESULTS AND DISCUSSION

Mode and state of dispersion of rubbery components

SEM micrographs of microtomed surfaces, taken after etching, for the binary and ternary blends are shown in *Figures 1, 2* and *3*. In the case of PA6/EPR (80/20) binary blend (*Figure 1*), the rubber segregates from the PA6 matrix in spherically shaped domains regularly distributed throughout the whole sample. The dimensions of such domains are very large, the diameter ranging from about 10 μm to about 30 μm. The walls of the cavities left seem to be very smooth, indicating no adhesion between matrix and rubber.

The degree of grafting of EPR-*g*-SA plays an important role in determining the mode and state of dispersion of the rubbery components in both binary PA6/EPR-*g*-SA and ternary PA6/EPR/EPR-*g*-SA blends. From the micrographs of *Figures* 2 and *3* it emerges that:

(i) The dimensions of the etched domains and the relative distribution are much lower than in the case of blends containing unmodified EPR (compare *Figure 1* with *Figures* 2 and 3).

(ii) In both PA6/EPR-*g*-SA and PA6/EPR/EPR-*g*-SA systems, the dimensions of the etched domains drastically decrease with increase of the degree of grafting (*DG*) of the EPR-*g*-SA rubber. For PA6/EPR-*g*-SA with $DG = 0.6\%$ the diameter of the holes ranges from 1 μm to 5 μm while for $DG = 4.5\%$ the average diameter is less than 1 μm (compare *Figures 2a* and *2c*). It can be observed that for the same value of *DG* the average dimensions of the etched domains seem to be larger in the case of 80/15/5 ternary blends (compare *Figure 2* with *Figure 3*).

(iii) It can be noted that the amount of material etched, in the case of the PA6/EPR-*g*-SA binary blends containing rubber with $DG = 4.5\%$, seems to be smaller than in the other cases. Such an observation may be accounted for by the fact that in such a system a larger

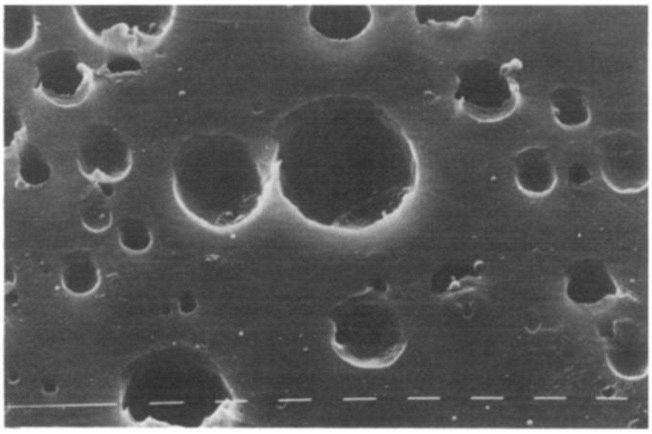

Figure 1 SEM micrographs of microtomed surface of binary PA6/EPR blend after etching (640×)

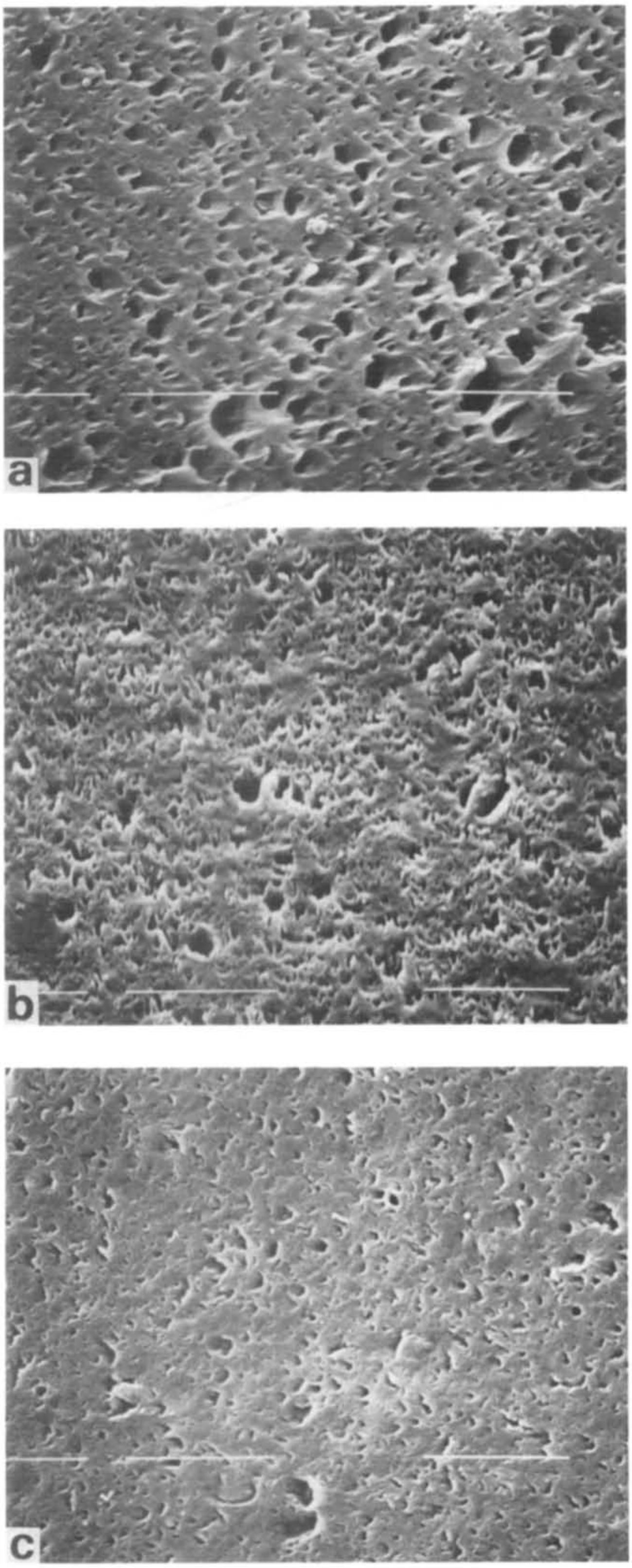

Figure 2 SEM micrographs of microtomed surfaces of binary PA6/EPR-*g*-SA blends at increasing degree of grafting (*DG*) after etching: (a) $DG=0.6\%$ (2500×); (b) $DG=2.4\%$ (2500×); (c) $DG=4.5\%$ (2500×)

concentration of unextractable (EPR-*g*-SA)-*g*-PA6 graft copolymer is formed. In fact the PA6 branches of the (EPR-*g*-SA)-*g*-PA6 graft copolymer are firmly fixed into the PA6 matrix. Therefore the rubber dispersed phase is less and less extractable the higher *DG*.

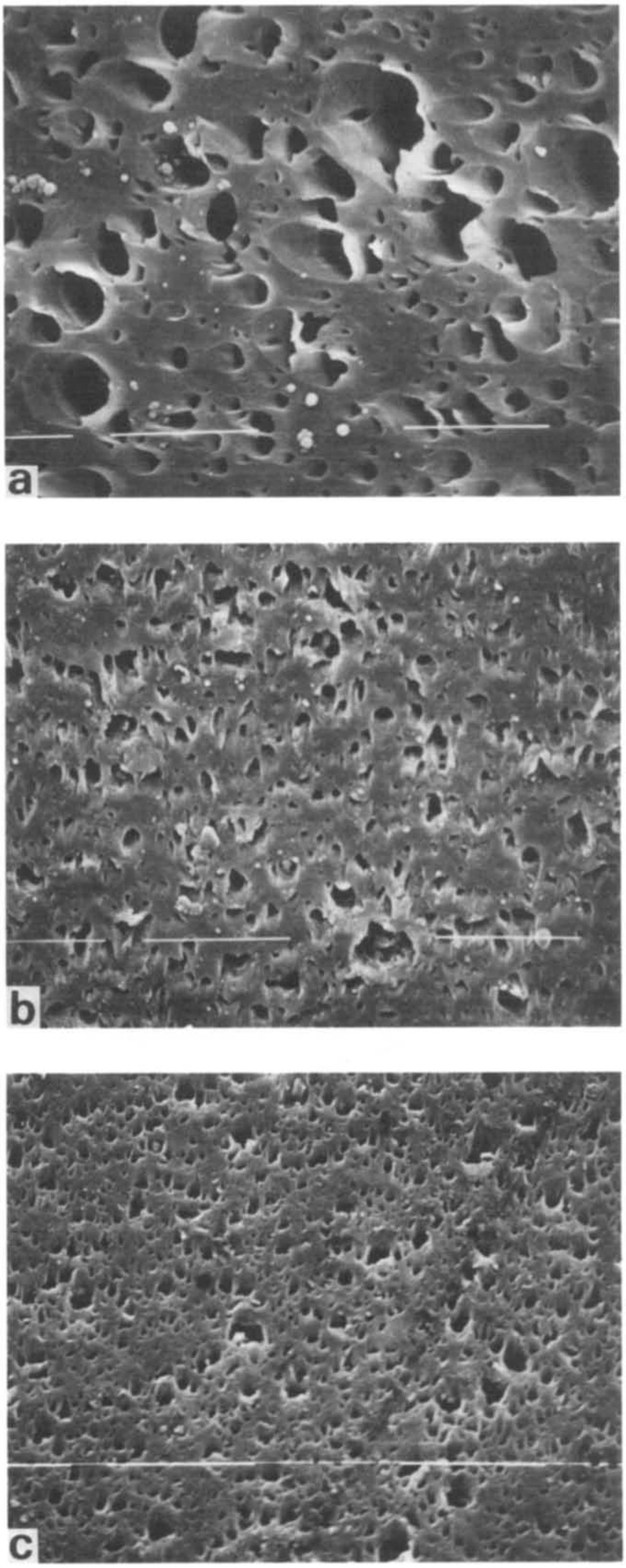

Figure 3 SEM micrographs of microtomed surfaces of ternary PA6/EPR/EPR-*g*-SA blends at increasing degree of grafting (*DG*) after etching: (a) $DG=0.6\%$ (2500×); (b) $DG=2.4\%$ (2500×); (c) $DG=4.5\%$ (2500×)

Mechanical tensile properties

Typical nominal stress vs. strain curves for PA6 homopolymer and for all the binary blends investigated are shown in *Figure 4*. The corresponding moduli (E) and

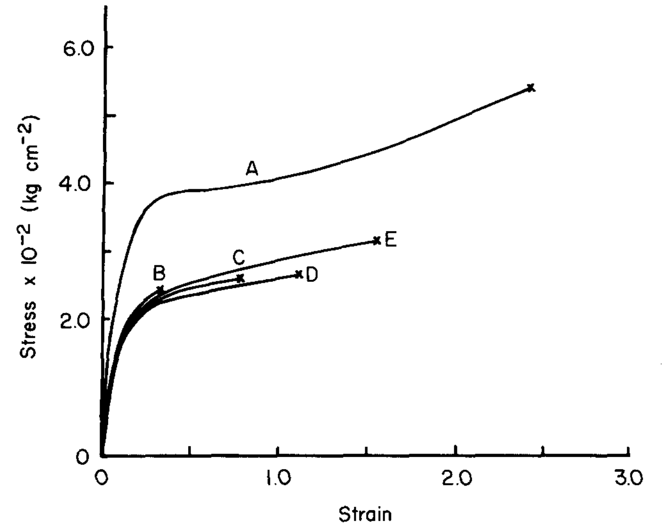

Figure 4 Stress–strain curves for PA6 homopolymer and for binary blends at increasing degree of grafting (*DG*): curve A, PA6; curve B, *DG*=0%; curve C, *DG*=0.6%; curve D, *DG*=2.4%; curve E, *DG*=4.5%

Table 2 Mechanical tensile properties of PA6 homopolymer and binary blends

Composition (PA6/EPR/EPR-*g*-SA)	*DG*	$E\times10^{-3}$ (kg cm^{-2})	$\sigma_b\times10^{-2}$ (kg cm^{-2})	ε_b
100/0/0	–	6.9±0.9	5.2±0.4	2.2±0.4
80/20/0	–	3.7±0.5	2.2±0.2	0.3±0.1
80/0/20	0.6	4.0±0.4	2.5±0.1	0.75±0.2
80/0/20	2.4	3.3±0.2	2.4±0.2	1.2±0.3
80/0/20	4.5	3.6±0.3	3.2±0.3	1.6±0.4

the ultimate properties such as the stress (σ_b) and the elongation at break (ε_b) are summarized in *Table 2*. As it is possible to see, the performance of PA6 (curve A) is strongly modified by rubber addition. The overall effect is a decrease in the values of all the above-mentioned parameters (see *Table 2*). The lowering of the modulus, however, seems to be scarcely influenced by the nature of the rubber (EPR or EPR-*g*-SA), whereas the more sensitive is the elongation at break. In fact, ε_b changes drastically depending on the type of rubber and the degree of grafting (*DG*) of the EPR-*g*-SA used. The very low ε_b value observed for the PA6/EPR blend (curve B) can be attributed essentially to the presence of very large EPR particles with a poor adhesion to the matrix, as shown by SEM micrographs (see *Figure 1*). These domains act as gross material defects, causing premature rupture of the specimen soon after the beginning of yield. Only a few whitened bands of microvoids are visible along the specimens, indicating an ineffective mechanism of craze termination since there is no adhesion of the rubber particles to the matrix.

As EPR is substituted with EPR-*g*-SA (curves C, D and E), the ability of the material to be plastically deformed is raised. In this case an intense stress-whitening phenomenon is observed on the blend specimens due to diffuse craze formation. This effect increases more and more with increasing degree of grafting of the EPR-*g*-SA. This finding is probably related to the presence of an (EPR-*g*-SA)-*g*-PA6 graft copolymer formed during mixing. This will act as an interfacial agent between the dispersed (unreacted EPR-*g*-SA) and continuous phases. As a matter of fact, a greater homogeneity with a finer dispersion of the rubber component (see SEM micrographs of *Figure 2*) is achieved with respect to the PA6/EPR blend. This overall morphology facilitates the formation of crazes as well as their termination, so that the material is able to sustain larger plastic deformation prior to fracture.

Passing to the ternary PA6/EPR/EPR-*g*-SA blends, the relative tensile properties are reported in *Table 3*. All the blends show, within the limit of experimental errors, the same ε_b values with varying degree of grafting, in contrast with their different morphologies (*Figure 3*). This disagreement is probably due to the presence of some defects created in the pressure moulding of the material during specimen preparation. Such features overcome the intrinsic morphological defects of the material constituted by the rubbery dispersed particles and cause a premature rupture of the specimens, therefore masking the real structure of the ternary blends.

Impact properties

The resilience *R*, obtained by a Charpy test, as a function of temperature is reported for binary and ternary blends in *Figures 5* and *6* respectively. The PA6 homopolymer is taken as the reference material in order to evaluate the improvement in impact properties of the blends.

As it is possible to see, the pure polyamide exhibits very brittle behaviour with very low *R* values, which remain unchanged over the whole investigated temperature range. A similar trend is observed for the PA6/EPR blend (*Figure 5*). Such behaviour is in agreement with the

Table 3 Mechanical tensile properties of ternary blends

Composition (PA6/EPR/EPR-*g*-SA)	*DG*	$E\times10^{-3}$ (kg cm^{-2})	$\sigma_b\times10^{-2}$ (kg cm^{-2})	ε_b
80/15/5	0.6	3.6±0.1	2.5±0.1	0.7±0.15
80/15/5	2.4	3.4±0.1	2.5±0.1	0.8±0.1
80/15/5	4.5	4.0±0.5	2.6±0.1	0.75±0.2

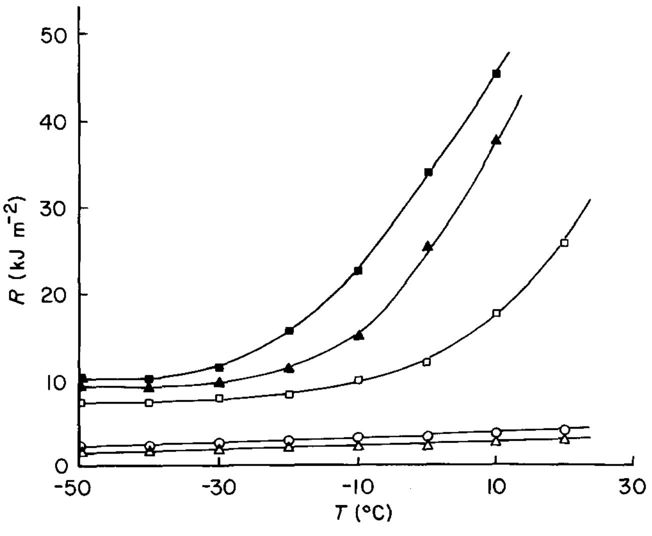

Figure 5 Charpy resilience (*R*) as a function of test temperature for PA6 homopolymer and for binary blends at increasing degree of grafting (*DG*): △, PA6; ○, *DG*=0%; □, *DG*=0.6%; ▲, *DG*=2.4%; ■, *DG*=4.5%

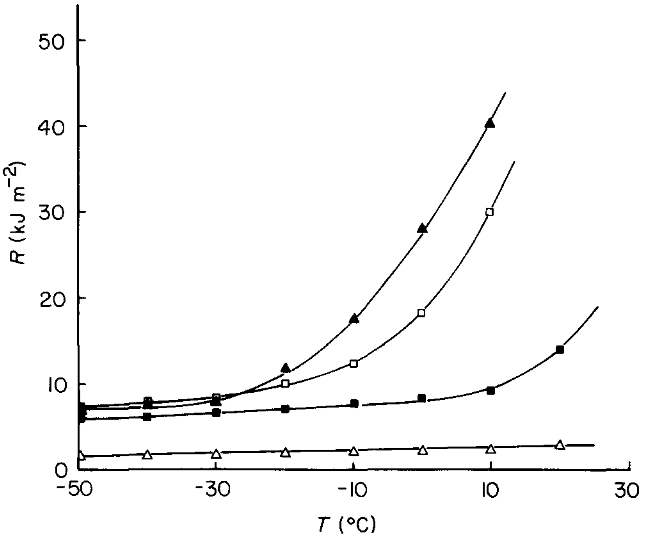

Figure 6 Charpy resilience (*R*) as a function of test temperature for PA6 homopolymer and for ternary blends at increasing degree of grafting (*DG*): △, PA6; ■, *DG*=0.6%; □, *DG*=2.4%; ▲, *DG*=4.5%

morphology of this blend in which large domains with a broad size distribution and no adhesion to the matrix are present.

For blends of the same composition but containing EPR-*g*-SA as rubbery phase and for ternary blends as well, a large enhancement of impact properties is observed with respect to pure PA6. From the trend of the curves, it emerges that *R* increases with increasing degree of grafting (*DG*) of the EPR-*g*-SA and that the binary blends show higher *R* values compared to those of the corresponding ternary blends. Furthermore, all these blends show a marked variation in *R* values over the temperature range in which the behaviour of the material changes from a brittle to a ductile mode of failure. The location of this transition temperature is a function of *DG* and blend composition. A shift towards lower temperature is observed with increasing *DG* value of EPR-*g*-SA and for the same *DG* passing from ternary to binary blends. All the above-mentioned features suggest that for these blends a good exploitation of (EPR-*g*-SA)-*g*-PA6 graft copolymer as an interfacial agent has been obtained. The extent of this effect for the blends, as demonstrated by the morphological analysis, is larger the higher *DG*. In fact, for a given blend composition, better homogeneity with smaller domain dimensions of the rubbery phase is achieved in the direction of an increase in the *DG* values. On the other hand, the finding that the investigated ternary blends exhibit lower impact properties than the corresponding binary ones can be related to a lower amount of (EPR-*g*-SA)-*g*-PA6 as interfacial agent, essentially due to the smaller initial percentage of EPR-*g*-SA. In fact, we have found in previous work[1,4] that by enhancing the EPR-*g*-SA content in the rubbery phase it was possible to get ternary blends with better impact properties than those of the corresponding binary blends. This finding suggests that, for the latter only, part of the EPR-*g*-SA can react to form graft copolymer with PA6, whereas the remainder plays a role similar to pure EPR in ternary blends.

CONCLUDING REMARKS

The possibility of improving the impact properties of polyamides by the addition of functionalized EPR has been confirmed in this paper for both binary PA6/EPR-*g*-SA and ternary PA6/EPR/EPR-*g*-SA initial blends. The formation of a graft PA6-*g*-(EPR-*g*-SA) copolymer, already previously suggested[4], and its effectiveness for toughening mechanisms, has received further support over a range of degrees of grafting from 0.6 up to 4.5 wt %. In the range investigated the morphology and impact properties are better the higher the *DG* for both the binary and ternary blends analysed.

From the data of the present work (restricted to one binary composition (80/20) and one ternary (80/15/5) one) and from those of previous work, obtained, however, under different experimental conditions, one could infer that the binary and ternary blends behave quite similarly with respect to impact mechanisms. In other words, the functionalized rubber added to PA6 (binary system) is only partially converted, during melt mixing, to form on the interface the PA6-*g*-(EPR-*g*-SA) copolymer responsible for PA6 toughening. The remainder, contained in the middle of the rubbery particles, behaves like pure EPR.

Therefore, work is in progress to analyse the effect on impact properties of changing the EPR/EPR-*g*-SA ratio in the rubbery phase of ternary blends and to compare those with the corresponding ones of binary systems.

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