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IMPACT IMPROVEMENT OF POLYAMIDE-6/RUBBER BLENDS VIA CONTROLLED DEGRADATION OF THE DISPERSED PHASE, USING ELECTRON BEAM IRRADIATION

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ABSTRACT

The influence of Electron Beam (EB) irradiation on the impact properties of Polyamide-6/Polyisobutylene (PA-6/PIB) blends has been investigated. Maleic anhydride modified PIB has been used. EB irradiation, which has been performed after the final processing step, results in controlled scission of the dispersed phase, i.e. lower cavitation stress of the PIB rubber. As a consequence, a decrease in brittle-to-tough transition temperature has been observed.

INTRODUCTION

The improvement of the impact properties of polyamides (PA), via the incorporation of small, homogeneously dispersed, rubbery particles has been studied extensively [1-12]. In order to obtain a small particle size and to assure sufficient interfacial adhesion, rubber grades containing polar groups, were used. For the PA/rubber blends a sharp Brittle-Tough (BT) transition was found to occur at a critical interparticle distance (CID) and the general condition for toughening is that the interparticle distance (ID) must be below this critical value [1-4]. This toughening criterion should be valid for all polymer blends which are toughened by increased shear yielding of the matrix. Several mechanisms have been proposed to explain the BT transition [1-4, 6-10]. An unambiguous explanation for this transition however, is still a matter of debate [9,10].

Provided that a minimum of adhesion between the phases is present, it was shown that a further increase in adhesion had no effect on the BT transition [4]. On the other hand a remarkable influence of the type of rubber used has been observed [4,11,12]. It has been suggested that enhanced cavitation of the rubber phase, causing a local change in stress-state, is favourable for good impact properties [4,11]. Gent has shown that the cavitation stress of rubbers is proportional to the modulus of the rubber [13]. Consequently, the best impact properties will be obtained with a low modulus, low molecular weight dispersed phase, provided that a homogeneous distribution of small particles can be induced. This latter condition however, is hard to fulfil, since such a fine dispersion can only be achieved when polymers are blended which possess approximately similar viscosities [14].

This contradiction might, in principle, be solved via Electron Beam (EB) irradiation. An optimum morphology for impact toughening can be induced using well-tuned mixing and processing equipment and choosing constituents with comparable viscosity. Subsequent irradiation should result in controlled scission of the dispersed phase, i.e. lower modulus and lower cavitation stress, whereas matrix and interfacial adhesion should remain unaffected. Moreover, via this method also the relation between impact strength and modulus of the dispersed phase can be revealed directly. In previous experiments, variations in modulus of the dispersed phase (using different types of rubber) were always accompanied by variations in morphology and interfacial adhesion [4,11]. Some preliminary results concerning EB irradiation of relatively inert Polyamide-6 (PA-6) and degradable Polyisobutylene (PIB) -rubber [15,16] will be presented.

EXPERIMENTAL

The matrix used was polyamide-6 (Akulon F135C, AKZO). The PIB rubber (Oppanol B100, BASF) was modified with maleic anhydride (MA), similar to the previously described method for EPDM-rubber [17], using Nourymix 914 (a 50/50 wt% masterbatch of MA on Polypropylene, AKZO) and Trigonox 101-50PP (a 50/50 wt% masterbatch of 2,5 dimethyl-2,5-bis (t,butylperoxy)hexane on Polypropylene, AKZO) as initiator.

Functionalization of PIB with MA is carried out in a Berstorff 25 mm corotating twin screw extruder at a temperature of 200 °C, using 4 wt% Nourymix and 0.8 wt% Trigonox. Free MA was removed by extracting the modified rubber with water (24 hours) at room temperature. Subsequently the PA-6/PIB blends were prepared in a 80 to 20 weight ratio in the same corotating twin screw extruder at an average barrel temperature of 240 °C. The blends were pelletized and subsequently injection moulded on an Arburg Allrounder into square plates with a length of 64 mm and a thickness of 3.2 mm. These plates were irradiated with various doses using a 3 MeV 'Van de Graaff' Electron Beam accelerator (IRI, Delft).

Test samples for notched Izod impact testing were prepared from the irradiated and non-irradiated plates, according to ASTM D256. Before testing at various temperatures, the samples were annealed at 80 °C during 24 hours.

Samples for Scanning Electron Microscopy (SEM) were first microtomed at liquid nitrogen temperature using a glass knife. Subsequently the samples were etched with an oxygen plasma and finally they were covered with an argon plasma induced gold layer.

Molecular weights were determined with size exclusion chromatography. For these measurements PA-6 was dissolved in hexafluorisopropanol and diol modified silica columns were used. The PIB samples were dissolved in THF and were measured on styragel columns.

RESULTS AND DISCUSSION

Figure 1a shows a SEM micrograph of an injection moulded PA-6/PIB 80/20 blend, prepared as described in the experimental section. For sake of comparison in Figure 1b the morphology of an injection moulded blend is shown using an unmodified PIB rubber. It is clear that modification of the PIB rubber results in a much smaller average particle size compared to the blend with pure PIB. However, compared to rubber particle sizes reported by Borggreve [3,4] and Wu [1], the weight average particle size in the PA-6/PIB (modified with MA) blend is still large, approximately 2 to 2.5 μm. Obviously MA modification is less effective for PIB rubber compared to EPDM rubber, due to the absence of double bonds in the PIB rubber.

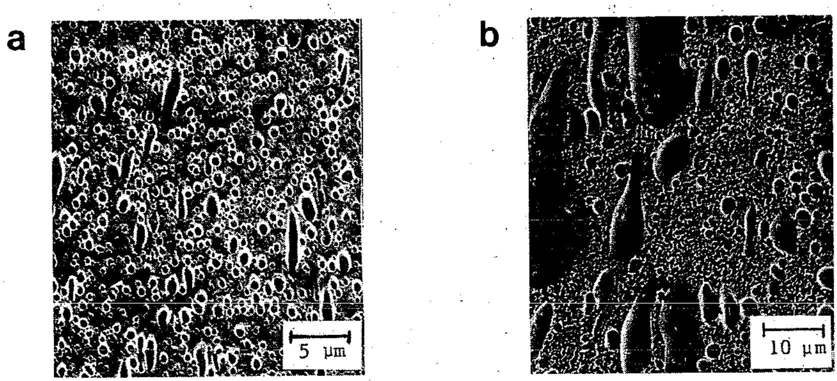

Figure 1. *SEM micrographs of injection moulded PA-6/PIB blends. a) PIB modified with MA, b) PIB unmodified*

The molecular weights of the PA-6 and PIB homopolymers are given as a function of the irradiation dose in table 1. It can be inferred that PA-6 is relatively inert towards EB irradiation and does not noticeably change up to doses of 80 kGy. For PIB on the other hand a rapid decrease in molecular weight is observed upon irradiation.

TABLE 1.

Molecular weights (M_n, kg/mole) of PA-6 and PIB homopolymers as a function of the irradiation dose.

dose (kGy)	PA 6	PIB
0	34	88
20	32	70
50	33.5	56
80	39	32

Figure 2 reflects the Izod values of the PA-6/PIB blends, irradiated with 0, 20 and 50 kGy, as a function of temperature. It is evident that there exists a BT transition for all blends, in the temperature range investigated. For the irradiated blends the BT temperature is lower than for the non-irradiated blend. Due to the relatively large particle size however, the absolute value of the BT temperature is still high compared to results reported by Borggreve and Wu for blends with much smaller rubber particles. The absolute values of the impact strength in the brittle region are not affected by irradiation.

For comparison, in Figure 2 also a curve for PA-6/EPDM is shown as obtained from Borggreve (figure 6 in ref [3]). This blend contains 20 wt% EPDM, with a weight average particle size of 1.94 µm and is the only blend reported by Borggreve which has a particle size and weight fraction comparable to the PA-6/PIB blend. It can be inferred that the BT transition for PA-6/PIB blends is approximately 25 °C lower than for the PA-6/EPDM blend. Probably the cavitation stress of the PIB rubber is already small compared to the cavitation stress of EPDM. A further reduction of the cavitation stress as a result of controlled scission of the dispersed phase might therefore not be as effective as expected.

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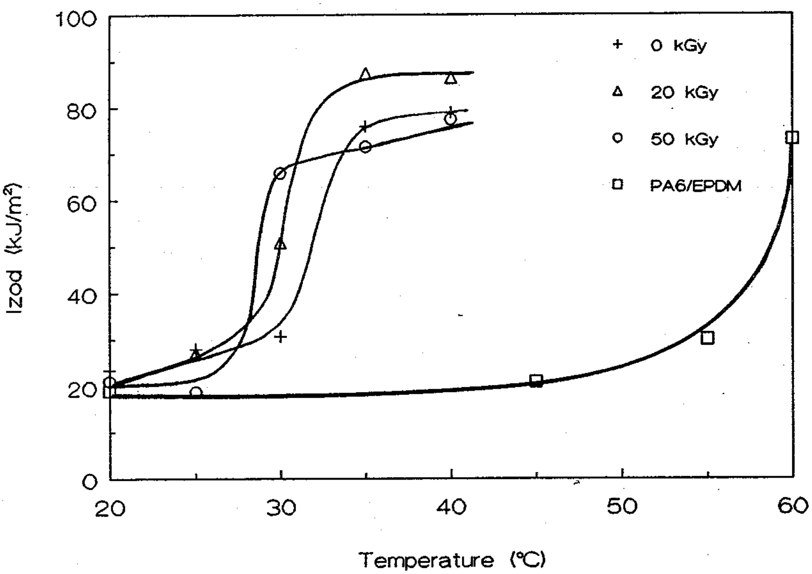

Figure 2. *Izod values of irradiated PA-6/PIB blends, PIB modified with MA, and homopolymers as a function of temperature. For comparison also a curve of PA-6/EPDM is shown as obtained from Borggreve, figure 6 from ref. [3]*

Summarizing, the particle size of the dispersed PIB phase in PA-6 is not optimized yet. Consequently, the absolute value for the BT transition is relatively high compared to results obtained for blends with much smaller rubbery particles. Nevertheless, the method of inducing a certain morphology and subsequent controlled scission of the dispersed phase via EB irradiation is proven. The lower molecular weight of the dispersed phase, i.e. a lower cavitation stress, results in a decrease in the BT transition temperature. Further research is focussed on inducing an optimum morphology in the PA-6/PIB blends to investigate the effectivity of the method in the low temperature region.