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Tensile properties and impact behaviour of poly(D(-)3-hydroxybutyrate)/rubber blends

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A random ethylene-propylene rubber copolymer with functional ester or anhydride groups and an ethylene vinilacetate copolymer modified by a partial transformation of acetate groups in alcoholic groups were used as minor components to obtain binary poly(D(-)3-hydroxybutyrate) blends by melt-mixing. The influence of the rubbery impact modifier on the morphology and on the tensile and high-speed fracture behaviour of such blends was investigated. Better properties were found when anhydride groups were present on the rubbery component. This was attributed to chemical interactions occurring between the dispersed phase and the matrix during the blending process.

1. Introduction

The results of investigations concerning mainly the crystallization and thermal behaviour, as well as the phase structure and the miscibility of poly(D(-)3-hydroxybutyrate) (PHB) based blends have been reported previously [1, 2]. The aims of the research were

(i) to find polymers which being miscible in the melt with PHB were able to lower its melting temperature and then the window of processability, and

(ii) to find rubbery polymers which were able to enhance the impact behaviour of PHB.

It was found that polymers such as poly(ethylene oxide) (PEO) and poly(vinylacetate) (PVAC) were melt compatible with PHB. Consequently, PHB/PVAC blends show a single glass transition temperature and drastic depression of equilibrium melting temperature [1, 2]. No melt compatibility was observed in the case of blends containing an ethylene–propylene random copolymer (EPR) as second component.

At relatively low undercooling the PHB spherulites grow in the presence of a two-phase melt. During crystallization the spherical domains of EPR are occluded in intraspherulitic regions following a mechanism already studied by Martuscelli *et al.* [3] in isotactic polypropylene-based blends.

Here, the results of an investigation concerning the tensile and high-speed fracture behaviour of PHB-based blends having different type of rubbers as second component, are reported. The rubbers were obtained by suitable reactions to activate EPR and vinylacetate copolymer (EVA) samples. The aim of the research was mainly to determine the interrelationships between the molecular structure of rubber, type of functional group and reactivity, mode and state of dispersion of the rubbery component in the PHB matrix, adhesion at the interface, mechanical tensile properties (mainly, strength and elongation to break) and impact behaviour.

2. Procedure

2.1. Materials

The starting polymers used in this work included:

(i) poly(D(-)3-hydroxybutyrate) (PHB) a polyester produced by ICI using a bacterial fermentation process [4] with $M_w = 400\,000$;

(ii) ethylene–propylene random copolymer (EPR) (trade name Dutral CO/054) supplied by Dutral S.p.A., having an ethylene content of 68 mol % $M_w = 180\,000$ and a glass transition temperature of about -60° C;

(iii) ethylene vinylacetate copolymer (EVA) (trade name Elvax 210) supplied by DuPont, having 30 wt % vinylacetate and an intrinsic viscosity $[\eta] = 0.54\,\mathrm{dl\,g^{-1}}$ in toluene at 30 °C.

2.2. Preparation of EPR-grafted copolymers

An EPR modified by insertion of 4.0 wt % succinic anhydride groups (EPR-g-SA) and an EPR functionalized by insertion of 7.0 wt % dibutylmaleate (EPR-g-DBM), were prepared following procedures already described in detail elsewhere [5, 6]. The structures of EPR-g-SA and EPR-g-DBM are reported in Table I.

2.3. Preparation of an EVA-modified copolymer (EVAL)

EVA was modified by a partial transformation of acetate groups in alcoholic groups. The modification reaction was performed following the procedure reported in [7]. The degree of modification was evaluated by infrared analysis, from which a vinyl alcohol content of 5% wt/wt was detected. The EVAL structure is reported in Table I.

2.4. Blend preparation

Binary PHB/EPR, PHB/EPR-g-SA, PHB/EPR-g-DBM, PHB/EVA and PHB/EVAL blends with a

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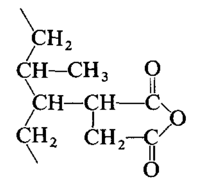
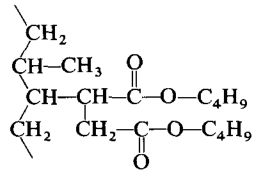
TABLE I Structures of EPR-g-SA, EPR-g-DBM and EVAL copolymers

(a)



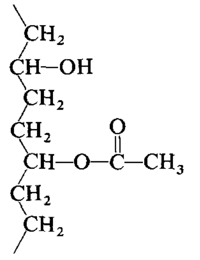
EPR-g-SA

(b)



EPR-g-DBM

(c)



EVAL

composition 80/20 wt/wt, were prepared by melt-mixing the two components in a Brabender-like apparatus at a temperature of 180 °C for a mixing time of 8 min and at a roller speed of 32 r.p.m.

Previous analysis had already established that under such processing conditions no appreciable thermomechanical degradative effects, especially for PHB, occurred.

2.5. Sample preparation

The premixed material was compression moulded to produce sheets of two different thickness (1 and 4 mm) at 180 °C and at a pressure of 150 bar (1 bar = 10^5 Pa) in a heated press. The 1 mm thick sheets were cut using a suitable hollow punch in dumb-bell-shaped specimens on which tensile mechanical tests were performed. The 4 mm thick sheets were cut using a mill to obtain rectangular specimens 6.0 mm wide and 60 mm long for performing Charpy impact tests. Such specimens were notched at the middle point of their length as follows: first a blunt notch was made using a machine with a V-shaped tool and then a sharp notch 0.2 mm deep was produced by a razor blade fixed on a micrometric apparatus. The final value of notch depth was measured after fracture using an optical microscope. Prior to testing the specimens were stored at room temperature for 48 h.

2.6. Mechanical tensile tests

Stress–strain curves for all the materials were obtained using an Instron machine (model 1122) at room temperature and at a cross-head speed of 2 mm min^{-1}. Moduli, stress and elongation at rupture were calculated from such curves on an average of eight specimens.

2.7. Impact fracture measurements

Charpy impact tests were carried out at an impact speed of 1 m sec^{-1} using an Instrumented Pendulum (Ceast Autographic Pendulum MK2). For all the materials examined a set of specimens with various crack lengths and a span of 48 mm were broken at different temperatures ranging from −80 to 20 °C. The temperature was changed by means of a homemade liquid-nitrogen apparatus. Curves of energy and load against time or displacement were recorded for each test temperature. The Charpy impact data were analysed using the concepts of the linear elastic fracture mechanics (LEFM) theory [8–10].

2.8. Fracture toughness parameters

Following the approach of LEFM, the critical stress intensity factor, K_c, was calculated using the equation

$$K_c = Y\sigma_c a^{1/2} \tag{1}$$

where σ_c is the nominal stress at the onset of crack propagation, a is the initial crack length, and Y is a calibration factor depending on the specimen geometry. The values of Y used here are those given by Brown and Srawley [11]. For single-edge notched three-point bend specimen the values of σ_c were evaluated from

$$\sigma_c = \frac{3F_c L}{2BW^2} \tag{2}$$

where F_c is the force at failure, L is the specimen span, B and W are thickness and width of the sample.

Using Equation 1, a plot of σ_c against $1/a^{1/2}$ gives a straight line with K_c as the slope. Graphs of this type were obtained from each material examined, and K_c determinated. An example of such an analysis is shown in Fig. 1 for PHB homopolymer.

To determine the critical strain energy release rate, G_c, the following equation was used

$$G_c = U/BW\Phi \tag{3}$$

where U is the fracture energy corrected from the kinetic energy contribution, and Φ is a calibration factor depending on the length of crack and size of the

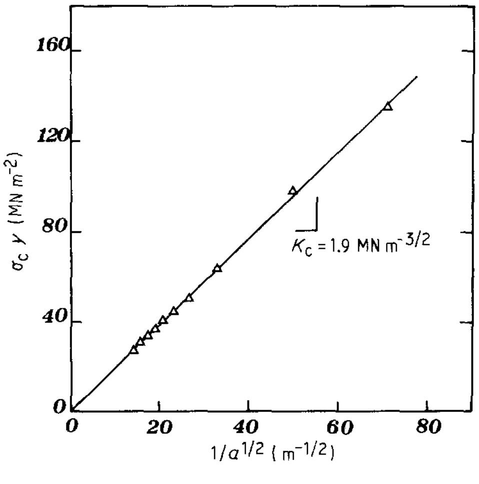


Figure 1 $\sigma_c Y$ as a function of $1/a^{1/2}$ for PHB homopolymer at 20 °C.

specimen. The values of Φ were taken from Plati and Williams [12]. Equation 3 predicts that a graph of U against $BW\Phi$ should give a straight line with G_c as the slope. An example of G_c so determinated is shown in Fig. 2 for PHB homopolymer.

2.9. Fractographic analysis

The fracture surfaces of notched specimens were examined by scanning electron microscopy (SEM). Before observation the samples were coated with a thin layer of gold–palladium alloy by vacuum deposition.

3. Results and discussion

3.1. Mechanical tensile properties

Nominal stress–strain curves obtained at room temperature and at a strain rate of 1.3×10^{-3} sec^{-1} for PHB homopolymer and for all the PHB/rubber blends investigated are shown in Fig. 3.

The plain PHB, unlike the other semicrystalline polymers which generally undergo fracture only after large amounts of drawing, exhibits at room temperature a stress–strain relation typical of a brittle polymer. The material extends linearly to a fracture strain of about 1.8%. This behaviour is related to the fact that PHB has a glass-transition temperature which is close to the testing temperature (20 °C determinated by dynamic mechanical analysis and 5 °C obtained by differential scanning calorimetry). As a consequence, the amorphous phase connecting spherulite and crystallite regions is unable to flow and so failure occurs at relatively low strain.

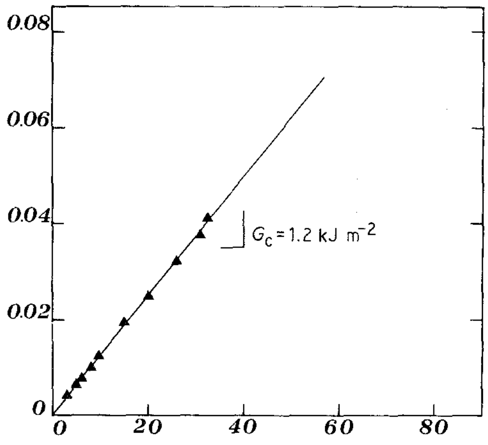


Figure 2 Impact fracture energy, U as a function of $BW\Phi$ for PHB homopolymer at 20 °C.

The stress–strain behaviour of blends is also approximately linear up to a stress of about 90 kg cm^{-2}, thereafter the trend becomes non-linear as the test proceeds and the final fracture occurs after a limited amount of strain. The corresponding modulus (E) and ultimate parameters such as the stress (σ_R) and the elongation at rupture (ε_R) calculated from the stress–strain diagrams are summarized in Table II. The overall effect of the rubber addition on the PHB tensile properties is a reduction of E and σ_R and an enhancement of ε_R. The lowering of E and σ_R, however, seems to be little influenced by the nature of the rubber and the type of reactive groups present on it. On the contrary, ε_R is found to be more sensitive to the above factors. In particular, an appreciable increases in ε_R, if compared to that of pure PHB, is observed when EPR-g-SA is used as rubbery component. This finding, as evinced by the fractographic analysis reported in the next section, can be essentially attributed to the fact that, for PHB/EPR-g-SA blend, a finer dispersion of the rubbery phase with improved adhesion to the matrix is achieved. This will induce local

TABLE II Modulus, E, stress, σ_R, and elongation, ε_R, at rupture for PHB homopolymer and for PHB/rubber blends

Sample	$E \times 10^{-3}$ (kg cm^{-2})	σ_R (kg cm^{-2})	ε_R (%)
PHB	2.1	290	1.5
PHB/EPR	1.5	170	2.0
PHB/EVA	1.6	175	2.0
PHB/EVAL	1.7	185	3.0
PHB/EPR-g-DBS	1.6	175	4.0
PHB/EPR-g-SA	1.6	180	6.5

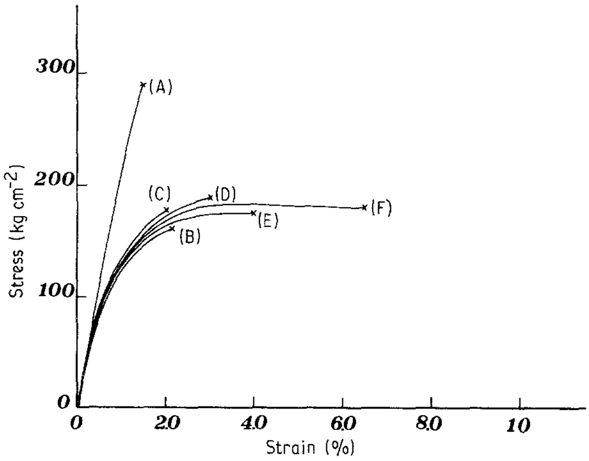


Figure 3 Stress–strain curves at 20 °C for PHB and PHB/rubber blends: (A) PHB, (B) PHB/EPR, (C) PHB/EVA, (D) PHB/EVAL, (E) PHB/EPR-g-DBM, (F) PHB/EPR-g-SA.

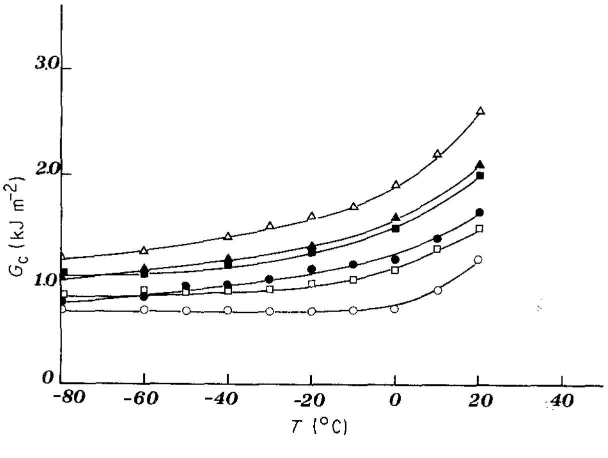


Figure 4 Critical strain energy release rate, G_c, as a function of temperature for PHB and PHB/rubber blends: (○) PHB, (□) PHB/EVA, (●) PHB/EPR, (■) PHB/EVAL, (▲) PHB/EPR-g-DMB, (△) PHB/EPR-g-SA.

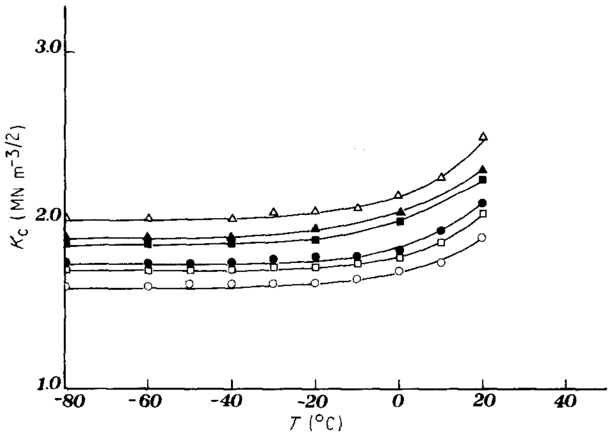


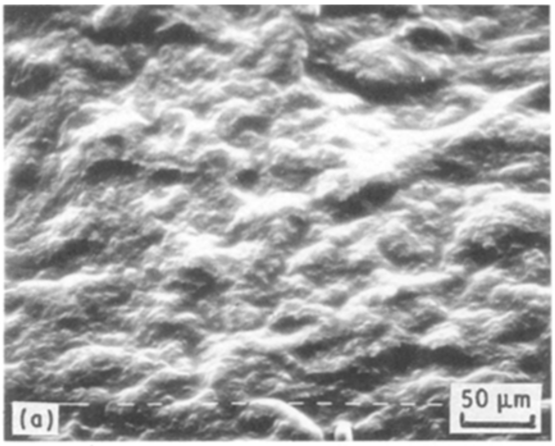
Figure 5 Critical stress intensity factor, K_c, as a function of temperature for PHB and PHB/rubber blends: (○) PHB, (□) PHB/EVA, (●) PHB/EPR, (■) PHB/EVAL, (▲) PHB/EPR-g-DBM, (△) PHB/EPR-g-SA.

yielding of PHB around the rubber particles, enhancing the capability of the material to be plastically deformed.

3.2. Impact fracture toughness and fractographic analysis

The critical strain energy release rate, G_c, and the critical stress intensity factors, K_c, for all the examined materials, calculated according to the procedure described in Section 2.8, are shown as a function of test temperature in Figs 4 and 5. As can be seen for PHB, G_c and K_c remain quite constant at low values up to about 0 °C. Beyond this temperature, due to the occurrence of the glass-transition in PHB, a slight enhancement of both parameters is achieved. The addition of unmodified EPR or EVA produces a certain improvement in the G_c and K_c values with respect to the PHB over the entire temperature range investigated. A more substantial enhancement of the toughness is obtained when EPR or EVA are replaced by a modified rubber. This effect is larger for the blend containing EPR-g-SA as rubbery phase. It must be stressed, however, that in all cases G_c seems to be more sensitive to rubber addition. The results on the fracture behaviour can be interpreted on the basis of the fractographic analysis performed by SEM on PHB/rubber materials. Figs 6 to 8 show scanning electron micrographs after impact failure at room temperature. All the pictures have been taken near the notch tip in the region of crack initiation.

The fracture surface of PHB (Fig. 6a) display features of a very brittle material. In fact, there is no evidence of localized defects in the form of crazes and/or shear bands from which crack development can take place, and consequently low fracture toughness values are achieved. The fracture surfaces of PHB/EPR (Fig. 6b) and PHB/EVA (Fig. 6c) blends are characterized by a morphology in which the rubbery phase is segregated in spherical domains dispersed in the PHB matrix. In both blends a rather broad size distribution of the rubbery domains is observed; small domains (3 to 5 μm) coexist with medium-size domains (10 to 20 μm) and very large ones (30 to 40 μm). Moreover, from these micrographs, it also appears that a large number of rubbery particles were pulled away during the fracture process indicating a poor adhesion at the PHB/rubber interface. This finding is further supported by the fact that the domains' surface and the surface of holes left by the rubbery particles are very smooth with no significant signs of plastic deformation around them. From this type of fracture morphology it emerges that the rubbery particles are probably not much better than cavities in controlling premature crack growth. In fact, even though most particles acting as stress-raisers inside the PHB matrix, may promote localized dissi-



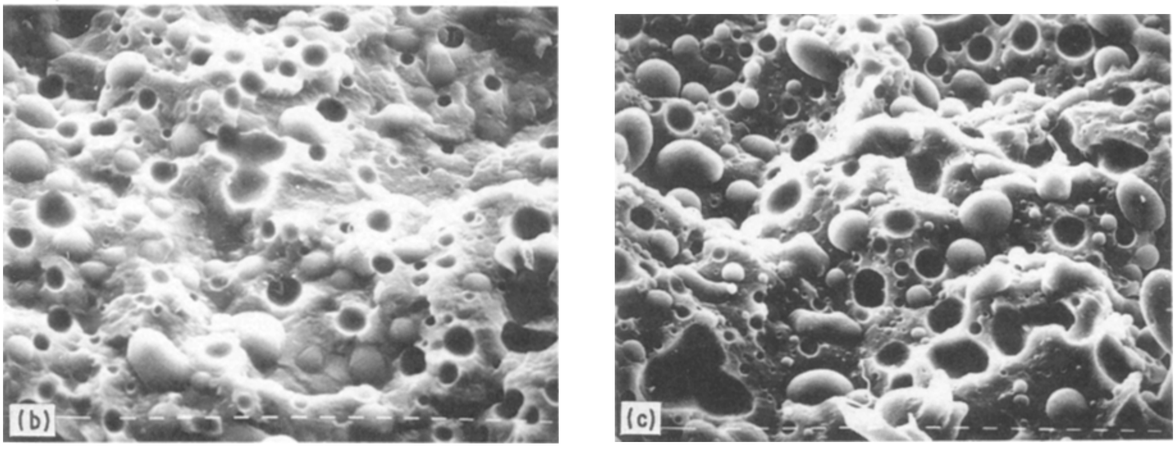


Figure 6 Scanning electron micrographs of Charpy fractured surfaces of PHB/rubber blends: (a) PHB, (b) PHB/EPR, (c) PHB/EVA.

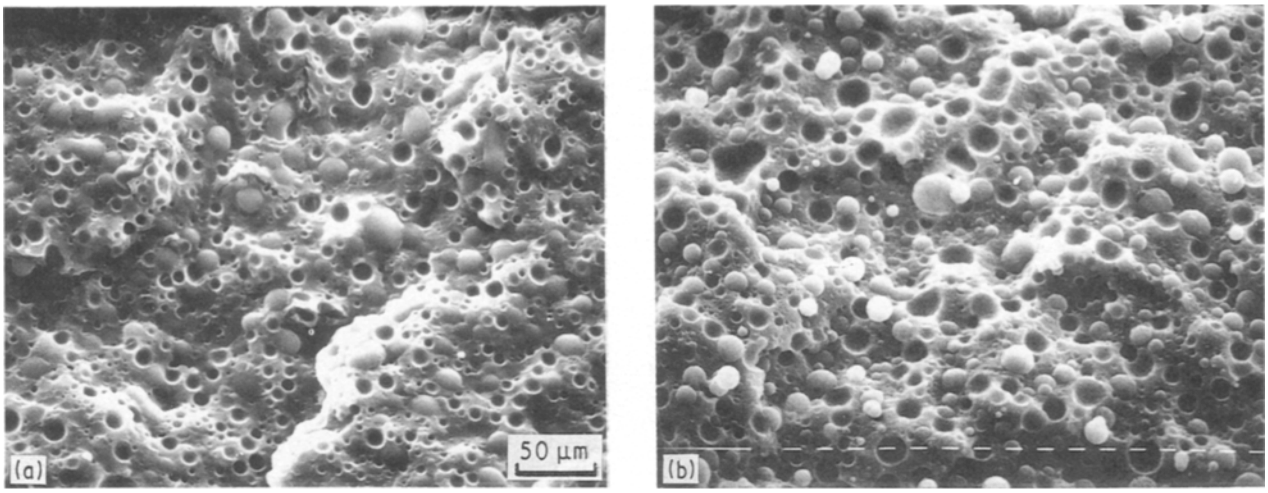


Figure 7 Scanning electron micrographs of Charpy fractured surfaces of (a) PHB/EPR-g-DBM and (b) PHB/EVAL blends.

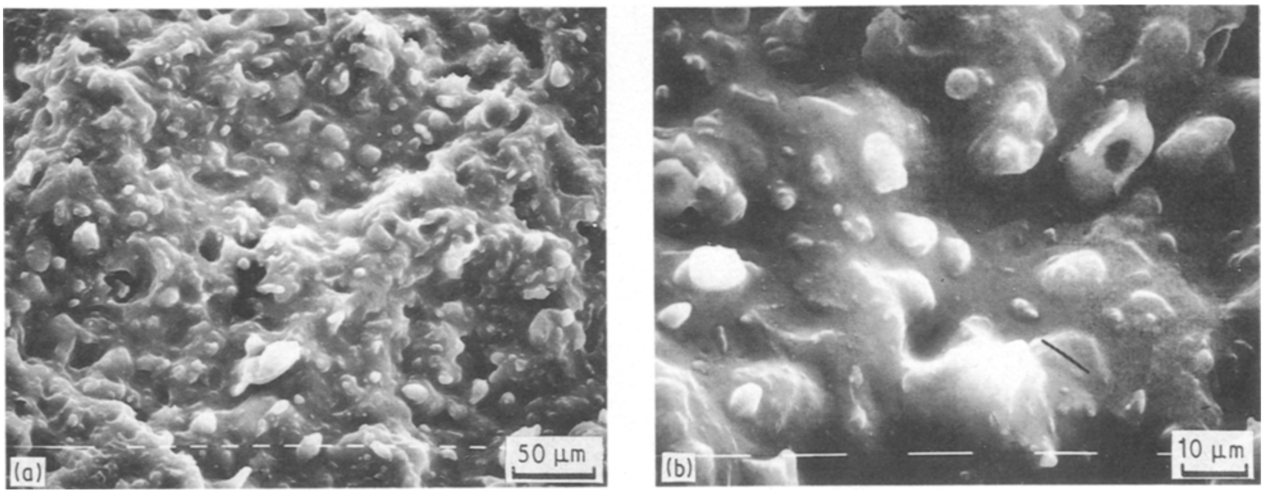


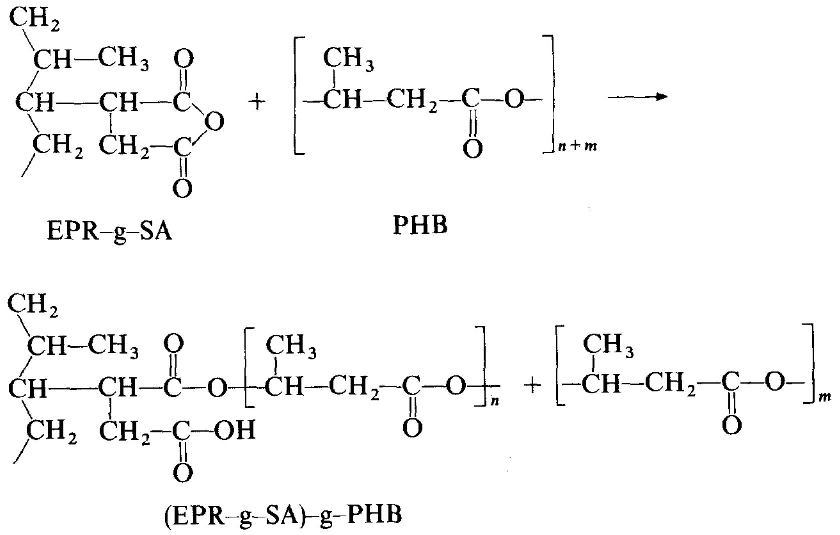
Figure 8 Scanning electron micrographs of Charpy fractured surfaces of PHB/EPR-g-SA blend.

pating mechanisms (crazing and/or shear yielding), they are unable to act efficiently as sites for their termination becuase they are weakly bonded to the matrix. Consequently, only a small amount of energy can be dissipated prior to the final fracture which accounts for the slight rises obtained in the values of G_c and K_c.

By replacing EPR with EPR-g-DBM (Fig. 7a) and EVA with EVAL (Fig. 7b), a more homogeneous and narrow size distribution of the rubbery particles is obtained. The particle diameter ranges from about 3 to about 10 µm. This effect can be ascribed to intermolecular interactions, taking place during the blending process, between the ester or the alcoholic functional group present on the rubber and the ester groups of PHB. It must be noted, however, that such blends still exhibit a poor interfacial adhesion.

Therefore, the reason for their better fracture toughness, compared to the previous blends, may be found in a more efficient use of the rubbery phase in promoting the toughening mechanisms. This is probably due to the presence of a larger number of rubber particles with an optimum size being effective in nucleating crazes or shear bands, so that the volume of material in which these dissipating mechanisms occur will be greater and the fracture toughness will be accordingly higher.

In the blend containing EPR-g-SA as rubbery component, the morphology of the fractured surface appears to be quite different, as can be readily seen from the micrographs of Fig. 8. In this case the rubbery domains do not show a well-defined shape and there seems to be evidence of domains finely dispersed and well embedded in the PHB matrix, indicating that the two phases are adequately bonded. Moreover, almost no free domains emerging from the surface are visible. These fractographic features suggest that, contrary to the other blends, for the PHB/EPR-g-SA system some kind of chemical interaction between the rubber and matrix must be taken into consideration. It is likely that during the blending process, part of EPR-g-SA may be involved in the formation of a certain amount of a graft copolymer of the type (EPR-g-SA)-g-PHB by means of a reaction in which the anhydride functional groups of EPR-g-SA may react with the ester functional groups of PHB according to Reaction 4.



(4)

Such a graft copolymer acts as an interfacial agent to improve the mode and state of dispersion of the rubbery phase, as well as its adhesion to the matrix, yielding a morphology more suitable for toughening mechanisms. Thus for PHB/EPR-g-SA blend the significant enhancement observed in the values of G_c and K_c can be attributed to an increased effectiveness of the well-bonded rubbery particles in controlling the growth and the termination of crazes or shear bands before they can develop into catastrophic cracks.

The hypothesis that for PHB/EPR-g-SA blend a grafting process may occur, is based on results obtained in a very similar blend system constituted by polybutylene-therephtalate (PBT) and EPR-g-SA. Evidence of a graft copolymer formed *in situ* has been found, when (i) EPR-g-SA was melt-mixed with PBT [13, 14] of (ii) the synthesis of PBT occurred in the presence of the above rubber [15, 16]. In the former, the grafting is obtained by means of reaction between the anhydride groups of EPR-g-SA molecules and the -OH end groups of PBT molecules, whereas in the latter the anhydride groups on EPR are able to take part to the transesterification equilibria occurring during the polycondensation, leading to the formation of a graft copolymer [16].

In the case of PHB/EPR-g-SA blend probably, as reported before, a transesterification reaction is responsible for the grafting process, because due to the high molar mass of PHB, the concentration of the -OH terminal groups should be very low. A systematic investigation is currently under way to verify this assumption.

4. Conclusion

The possibility of improving the mechanical and impact properties of PHB, which is very prone to brittleness, by melt-mixing with appropriately functionalized rubbers, has been investigated.

As already observed for other types of blend, a decrease in the particle size of the dispersed phase and an increased adhesion to the matrix yielded an improvement in the ultimate tensile properties, such as elongation to break and in the high-speed fracture toughness of these materials. The best results have been obtained when a EPR-g-SA was used as rubbery component. This finding is related to chemical interactions taking place between the two components during the blending process. Evidence mainly supported by morphological analysis suggests that for PHB/EPR-g-SA blend a graft copolymer is probably formed which can act as emulsifier and compatibilizing agent between the PHB matrix and the unreacted molecules of EPR-g-SA. However, the enhancement attained in the fracture toughness for the PHB/EPR-g-SA system, even if very significant, especially at room temperature, is not so high as to render such a blend a high-impact technological material. Therefore, more complex formulations and new methods need to be investigated in order to obtain rubber-modified PHB blends with very high impact properties, and work is in progress in our Institute in this direction.

Acknowledgements

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