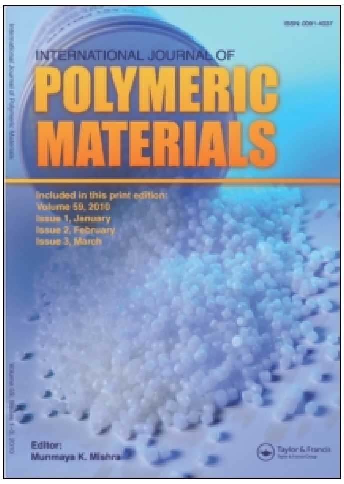

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Rubber Modification of Polyester Resins, 2-Impact Behaviour and Morphology

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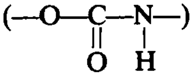
Brittle thermosetting polyester resins are blended with low molecular weight liquid polybutadiene rubbers. The morphology of the rubber modified resins was investigated as function of the nature of terminal groups of the polybutadiene, either hydroxyl or isocyanate and as function of composition. The concepts of the linear elastic fracture mechanism (LEFM) were applied to the prepared systems, to study their fracture behaviour. Interesting results were obtained when using a rubbery phase able to react with the base polyester leading to the formation of an A-B-A type block copolymer.

INTRODUCTION

In a previous paper the results of an investigation concerning the study of chemical reactivity between two samples of low molecular mass polybutadiene (PB), differing in the nature of the terminal functional groups (namely hydroxyls and isocyanates), with a commercial polyester resin (H35) were reported.[1] It was found that the isocyanate terminated polybutadiene (PBNCO) easily reacts with polyester prepolymer (PER) through a condensation reaction that leads to the formation of urethane  $(—O—\underset{\underset{O}{\|}}{C}—\underset{\underset{H}{|}}{N}—)$ linkages.

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In the course of the reaction mainly PER—PB—PER triblock copolymers are formed according to the following scheme:

$$\mathrm{OCN{-}R{-}NH{-}CO{-}O{-}PB{-}O{-}CO{-}NH{-}R{-}NCO}$$
$$+\,2\mathrm{HO{-}PER{-}COOH}$$

$$\mathrm{HOOC{-}PER{-}O{-}CO{-}NH{-}R{-}NH{-}CO{-}O{-}PB}$$
$$\mathrm{{-}O{-}CO{-}NH{-}R{-}NH{-}CO{-}O{-}PER{-}COOH}$$

where R = methyl phenyl.

The reaction is carried out, before curing, at 80°C simply by adding to the PBNCO the styrene solution containing the prepolymer. Under the same conditions no reaction was observed between the hydroxyl terminated polybutadiene (HTPB) and the base prepolymer.

The phase structure of H35/PBNCO and H35/HTPB blends was also investigated before and after the cure reaction. Small domains around 2 μm in size uniformly distributed all over the samples, strongly adherent to the matrix are present in H35/PBNCO blends. In the case of H35/HTPB blends dispersed domains with a larger distribution of dimensions scarcely adherent to the matrix were observed.[1]

From those results it was concluded that the mode and state of dispersion of the rubbery phase, as well as the thermal behaviour of the rubber modified resin are strongly dependent upon both the reactivity of the terminal groups of the rubber and the relative miscibility of the components before and after cure reaction.[1]

In the present paper the impact behaviour of the same rubber modified polyester resins is investigated. The results are then correlated with fractographic analysis performed on fracture surfaces developed in charpy impact test.

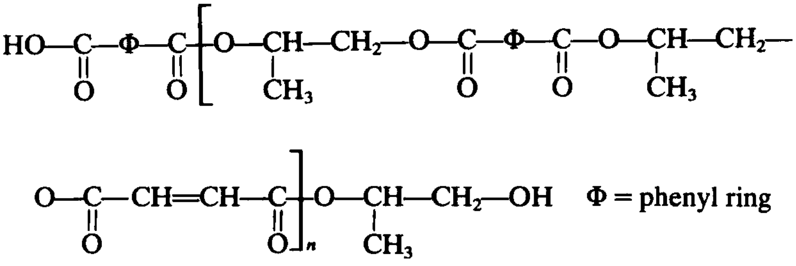
The main goal of the work is to find interrelations between chemical structure of rubbers, mode and state of dispersion of minor components and mechanism of crack formation and propagation in rubber modified polyester resins.

EXPERIMENTAL

1. Materials

i) *Base resin* Commercial samples of uncured unsaturated polyester resin were supplied by SNIAL (Colleferro–Roma–Italy) with the trade name of SNIATRON H35. The base resin is usually available as solution containing about 68 wt.% of a prepolymer dissolved in styrene monomer. The base prepolymer is normally prepared by the reaction of a saturated diol (propylene glycol) with a mixture of phthalic and maleic anhydride (mole ratios 1:0.7:0.3 respectively).

The so called "conventional unsaturated polyester prepolymer" is characterized by the presence, along the backbone chains, of randomly distributed ester groups and carbon–carbon double bonds. The molecular structure may be schematically represented as follows:



$$HO-\underset{\underset{O}{\|}}{C}-\Phi-\underset{\underset{O}{\|}}{C}\left[O-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-\underset{\underset{O}{\|}}{C}-\Phi-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-\underset{\underset{O}{\|}}{C}-CH{=}CH-\underset{\underset{O}{\|}}{C}\right]_n O-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$$

Φ = phenyl ring

The chains will be on average hydroxyl and carboxyl-terminated together with some minor fraction of di-hydroxyl and di-carboxyl terminated chains. The acid number of the prepolymer (defined as the mg of potassium hydroxide used for the titration of 1.0 g of prepolymer) ranges from 40 to 45.

The base prepolymer was characterized by using ^{1}H-NMR technique.[1] From this analysis a content of fumarate of about 95 wt% of total maleic anhydride used was calculated. Such a result indicates that double bonds along the chains are practically all in a trans configuration.

ii) *Low molecular mass rubbers*

a) As starting rubber a sample of hydroxyl terminated polybutadiene (HTPB) Mn = 1350, supplied by Polyscience, was used. The molecular structure of HTPB was determined by analysis of 270 MHz ^{1}H-NMR spectrum in $CDCl_3$ solution, using TMS as the internal standard.[1] It was found that about 70% of the units are arranged in a 1,2 enchainment and 30% in a 1,4 cis/trans enchainment. The hydroxyl number was determined by using the following procedure: first the hydroxyl end groups were quantitatively converted into isocyanate end groups (see later), then an excess of dibutylamine was added and finally the amine excess was titrated with 0.033 N HCl solution in *o*-dichlorobenzene/isopropanol 9/1 by volume. The resulting hydroxyl number: 1.2 meq/g, is in good agreement with an average functionality of HTPB molecules slightly lower than 2.

b) The isocyanate terminated polybutadiene (PBNCO) was obtained by reaction of HTPB with toluene diisocyanate (TDI). The TDI, supplied by Fluka, was a 80/20 mixture of 2,4 and 2,6 isomers; it was used without further purification. 10 g of HTPB were mixed to 1.78 ml of TDI (molar ratio TDI/HTPB 5% exceeding the stoichiometric 2:1 balance) for 10 min at 70°C under nitrogen atmosphere and mechanical stirring (the details of this reaction are reported in Ref. (1)).

2. Preparation of rubber modified polyester resins-cure conditions

The procedure for the preparation of cured rubber modified polyester resins (RMPER) was the following: first 10 g of HTPB or PBNCO rubber were dispersed in the styrene solution containing the polyester prepolymer by mechanical stirring for 30 min at 80°C (a polymerization reaction flask, capacity 250 cm^3, equipped with a mechanical stirrer and vacuum outlet was used); then the mixture was cooled to R.T. and air bubbles were removed under reduced pressure. At this point the catalyst was added under stirring; the mixture was poured into a mould consisting of either glass or metal glazing plates, separated by a flexible rubber gasket held by springs, and finally cured at 80°C for three hours. Methyl ethyl ketone peroxide (Butanox, 1 wt%) and Co-octoate (0.25 wt%) were used as catalyst and accelerator respectively (the first is available as 50% wt solution in dimethyl-phthalate while the second was already present in the starting formulation).

The codes and the compositions of RMPER materials investigated are given in Table I.

TABLE I

Codes and compositions[a] of rubber modified unsaturated polyester resins investigated

Sample code	Rubber content wt%	Base resin content wt%
H35	0	100
H35/HTPB-10	10	90
H35/HTPB-20	20	80
H35/PBNCO-10	10	90
H35/PBNCO-20	20	80

[a] The composition (wt%) refers to the base starting (H35) resin (prepolymer + styrene).

3. Fractographic analysis and morphological characterization

The morphology of the materials was investigated by scanning electron microscopy technique (SEM). The mode and state of dispersion of the minor component and the volume fraction were determined by scanning electron microscopy on fracturated surfaces of cured resins after metallization with AuPd alloy. A scanning Electron Microscope (Philips model 501) was used throughout. For a better resolution of the overall morphology an etching technique was used: fracture surfaces of blends were exposed for 2 min to boiling *n*-heptane vapours to remove preferentially the rubbery component. Such samples were subsequently prepared for SEM examination.

4. Impact TESTS

Charpy impact tests were performed by using a Ceast fracture pendulum at two different temperatures (−20°C and R.T.) (For details see next paragraph.)

RESULTS AND DISCUSSION

1. Fracture analysis

The fracture behaviour of unmodified and rubber-modified polyester resins was examinated by using the concepts of the linear elastic fracture mechanics (LEFM). From this approach two parameters can be determined which describe accurately the conditions for the onset of crack growth in brittle materials.[2]

One is the stress intensity factor (K), a parameter that determines the distribution of stress ahead of the crack tip. The fracture occurs when K achieves a critical value Kc given by:

$$K_c = \sigma y(a)^{1/2} \tag{1}$$

where σ is the failure stress, a is the initial crack length and y is a shape factor depending on the specimen geometry. The other parameter often used is the critical strain energy release rate (G_c), which represents the energy necessary to initiate the crack propagation. This can be expressed in terms of fracture energy by means of the equation:

$$G_c = U/BW\Phi \tag{2}$$

where U is the fracture energy corrected by the kinetic energy contribution, B and W are specimen thickness and width and Φ is a shape factor related to the specimen compliance (C) and to the crack length by the relationship:

$$\Phi = \frac{C}{dC/d(a/w)} \tag{3}$$

Φ can be calculated for any specimen geometry experimentally and theoretically.[3]

The fracture test used here for Kc and Gc determinations was the Charpy test conducted by means of an instrumented pendulum at an impact speed of 1 m/sec. For all the examined materials a set of specimens ($B = 6.0$ mm, $W = 6.0$ mm) with different notch lengths and test span of 48 mm were broken at room temperature and at −20°C. Therefore loads and energies as function of time were recorded. According to the equations 1 and 2 a plot of σy vs. $1/(a)^{1/2}$ and U vs. $BW\Phi$ should give a straight line with K_c and G_c as slope. The y values used to calculate K_c were those given by Brown and Srawley[4] and the failure stress σ was determined at the maximum load on load-time curves. For G_c calculation the Φ values were taken by Plati and Williams,[5] and the energies data were corrected by the kinetic energy contribution. An example of K_c and G_c determination is reported in Figures 1 and 2 for the pure

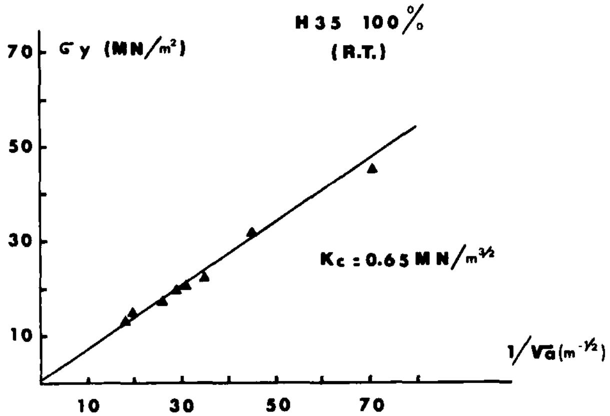


FIGURE 1 σy as a function of $1/(a)^{1/2}$ for unmodified resin H35 at room temperature.

polyester resin. Similar straight lines were obtained for both H35/PBNCO blends. Such result indicated that the approach followed is valid for all materials investigated.

The values of G_c obtained by energy measurements were also compared with those calculated using the equation: $G_c = K_c^2/E$ (plane stress condition) where E is the Young modulus.[4]

E values were determined by rebound test[6] performed on unnotched specimens at low impact speed ($0.2 \div 0.3$ m/sec.) using the same instrumented pendulum apparatus.

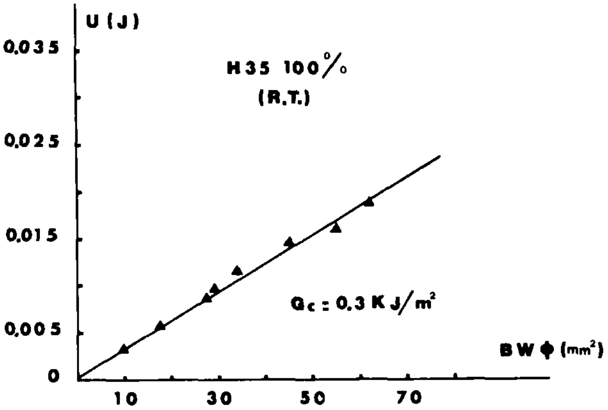


FIGURE 2 Impact fracture energy, U as a function of $BW\Phi$ for unmodified resin H35 at room temperature.

TABLE II

Modulus (E), K_c and G_c at room temperature and at −20°C[a]

	Room temperature				$T = -20°C$			
Materials	K_c MN/m$^{3/2}$	G_c(KJ/m^2) by energy measurement	E MN/m^2	$G_c = K_c^2/E$	K_c	G_c(KJ/m^2) by energy measurement	E (MN/m^2)	$G_c = K_c^2/E$
Pure resin H35	0.65	0.3	2630	0.2	1.0	0.35	3625	0.3
H35/HTPB (90/10)	0.5	0.20	2370	0.1	0.8	0.25	2910	0.22
H35/HTPB (80/20)	0.55	0.25	1780	0.15	0.7	0.28	2430	0.2
H35/PBNCO (90/10)	1.3	0.85	2470	0.7	1.6	0.8	3160	0.8
H35/PBNCO (80/20)	1.2	0.83	1815	0.8	1.5	0.8	2680	0.8

[a] Charpy impact tests were performed by using a CEAST fracture pendulum at two different temperatures (−20°C and R.T.).

The fracture toughness parameters and moduli for all the materials studied are collected in Table II.

As can be seen at room temperature the blends containing HTPB rubber show K_c and G_c values slightly lower than those of pure polyester resin, on the contrary a significative improvement in fracture resistance is achieved when the rubber is functionalized with isocyanate groups (PBNCO rubber). In fact the H35/PBNCO (90/10) and H35/PBNCO (80/20) blends show K_c and G_c values about twice and three times higher than the pure resin. Such an increase is accompanied by a slight decrease in the elastic modulus. Furthermore it can be observed that the decrease in the testing temperature (−20°C) causes only a slight enhancement in the K_c values, probably due to an increase of the modulus which yields a higher strength whereas the G_c values remain practically unchanged.

2. Morphological investigation on fracture surfaces

Scanning electron micrographies of broken surfaces of all the investigated blends, as obtained by the fracture tests at room temperature, are shown in Figures 3 to 8. The fracture surface of plane H35 samples (see Figure 3) is typical of a brittle polyester resin: the macro-cracks propagate linearly, leading to a rough stepped surface.

A comparison of the surface fracture of H35/HTPB and H35/

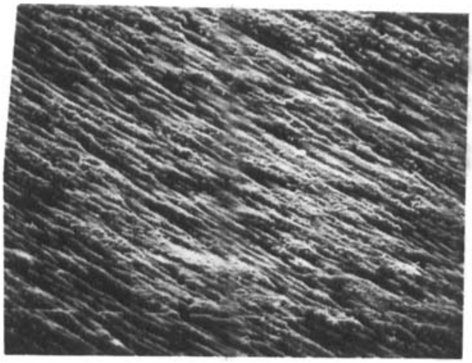


FIGURE 3 SEM micrograph of fractured surface of plane H35 Resin (Magnification 640×).

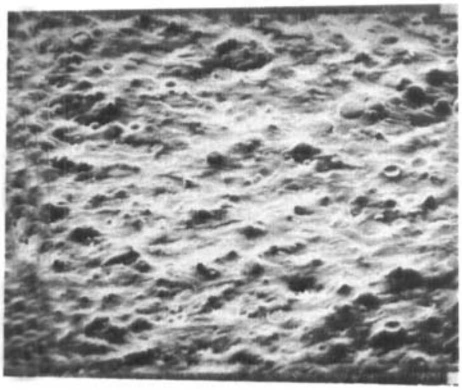


FIGURE 4 SEM micrograph of fractured surface of H35/PBNCO 90/10 blend (640×).

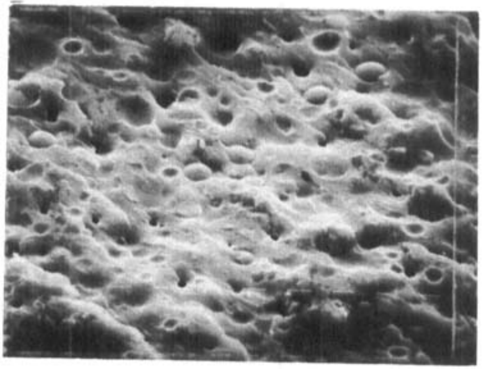


FIGURE 5 SEM micrograph of fractured surface of H35/PBNCO 80/20 blend (640×).

FIGURE 6 SEM micrograph of fractured surface of H35 PBNeO 90/10 blend (2500).

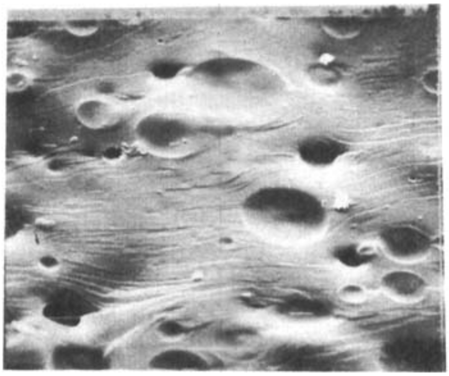


FIGURE 7 SEM micrograph of fractured surface of H35/HTPB 90/10 blend (640×).

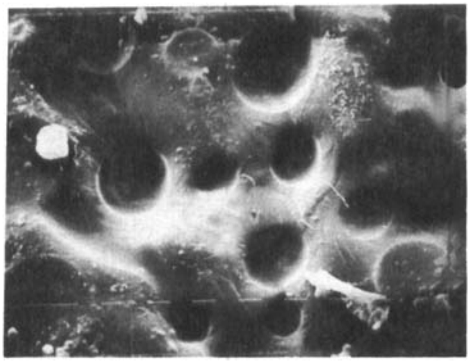


FIGURE 8 SEM micrograph of fractured surface of H35/HTPB 80/20 blend (640×).

PBNCO blends leads to the following observations:

i) The dimensions of the dispersed rubbery phase in the case of H35/PBNCO blends are much smaller (average diameter 5 μm in 90/10 blends) than those of H35/HTPB blends (average diameter 30 μm in 90/10 blends) compare Figures 4 and 7.

ii) The average dimension of the rubbery particles seems to increase, with increasing the content of rubber in both H35/HTPB and H35/PBNCO blends (see Figures 5 and 8).

iii) It can be observed that, on the broken surfaces of both blends (see Figures 6 and 7), the crack front interacts with the dispersed domains. Tails, or steps are formed at the rear of inhomogeneities due to the meeting of the two arms of the crack front from different fracture planes. According to Lange[7] such evidences led to a crack-pinning mechanism for the fracture propagation. According to this mechanism as a crack begins to propagate within the material the crack front bows out between the rubbery domains whilst still remaining pinned at all positions where it has encountered the dispersed particles. New fracture surfaces are formed while the length of the crack front is increased.

The overall amount of energy required and then the degree of toughness enhancement of the RMPER materials will be certainly dependent on factors such as volume fraction, particle size, interparticle distance, interface structure and adhesion between dispersed domains and matrix.

iv) The volume fraction of dispersed domains, as measured from SEM micrographies, results to be in the case of H35/HTPB larger than the calculated one (see data in Table III).

In order to know more about the nature of dispersed phase in H35/HTPB and H35/PBNCO blends the broken surfaces were, prior to SEM analysis, etched with *n*-heptane vapours.

It can be observed that in the case of H35/HTPB blends the dispersed domains are only partly etched by the solvent (see Figures 9 and 10): a sponge-like structure is obtained after etching. This

TABLE III

Calculated and measured volume fraction of rubbers domains for H35/HTPB and H35/PBNCO blends (For the calculation of the volume fractions the following density values were used H35 = 1.305 g/cm^3; HTPB = PBNCO = 0.897 g/cm^3)

Blend	Volume fraction calculated	Volume fraction measured
H35/PBNCO (90/10)	0.14	0.14
H35/PBNCO (80/20)	0.27	0.30
H35/HTPB (90/10)	0.14	0.20
H35/HTPB (80/20)	0.27	0.40

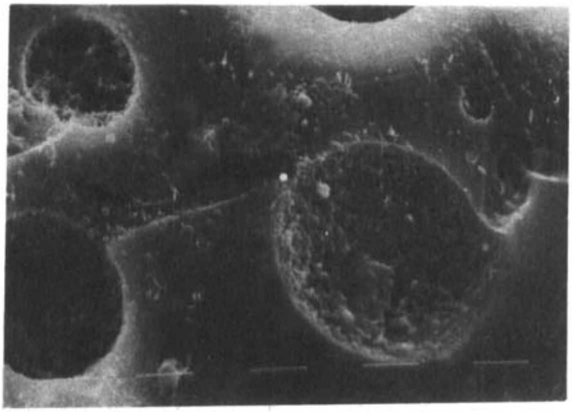


FIGURE 9 SEM micrograph of fractured etched surface of H35/HTPB 90/10 blend (1250×).

observation indicates that in such blends the dispersed domains, does not contain only rubber but also same inhomogeneities coming from the fact that during the blending and before the cure process a certain amount of styrene is likely occluded.

The above hypothesis could explain the larger volume ratio of dispersed domains measured for H35/HTPB blends. In the case of H35/PBNCO on the contrary the segregation of PB between the PER blocks in the ABA copolymers should avoid the occurrance of such phenomenon. As matter of fact almost no etched out materials

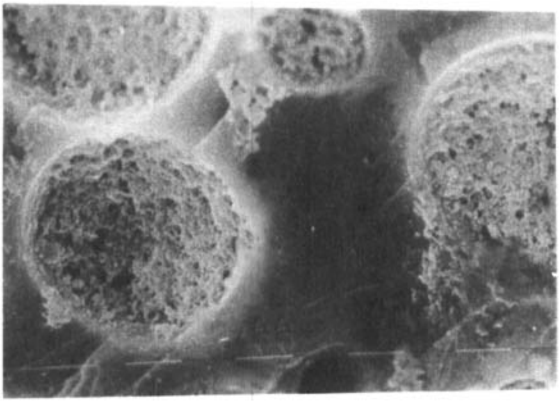


FIGURE 10 SEM micrograph of fractured etched surface of H35/HTPB 80/20 blend (1250×).

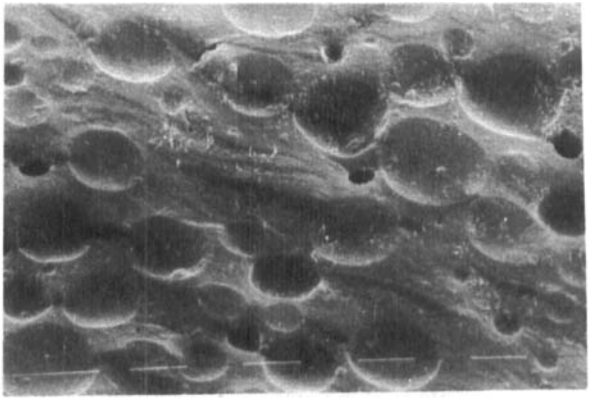


FIGURE 11 SEM micrograph ot fractured etched of H35/PBNCO 80/20 blend (1250×).

is found in the case of H35/PBNCO blends (see Figure 11). Such finding supports the idea that in those blends the rubbery domains are chemically bonded to the H35 matrix.

CONCLUDING REMARKS

It may be concluded that the better impact behaviour shown by H35/PBNCO blends is likely accounted for by:

a) the smaller dimensions of the dispersed domains

b) different nature and structure of the dispersed domains

c) the stronger adhesion between matrix and dispersed domains

d) the different mode and state of dispersion of rubbery component prior of the cure process.

The behaviour of H35/PBNCO and H35/HTPB blends is to be attributed to the functionalities of the rubbers.

The LEFM theory well applies to our systems revealing that both K_c and G_c parameters are positively influenced by the presence of PBNCO, while the impact properties of the blends containing HTPB show values of K_c and G_c slightly lower than those of pure H35. In the presence of the block copolymer A-B-A the dispersed phase is able to act as a barrier against the crack front propagation, so improving the impact response of the materials.

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