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## International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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**To cite this Article** Malinconico, Mario , Martuscelli, Ezio and Volpe, Maria Grazia(1987) 'Rubber Modification of Polyester Resins, 1. Rubber Reactivity and Blend Morphology', *International Journal of Polymeric Materials*, 11: 4, 295 – 315

**To link to this Article:** DOI: 10.1080/00914038708078668

**URL:** <http://dx.doi.org/10.1080/00914038708078668>

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# Rubber Modification of Polyester Resins, 1. Rubber Reactivity and Blend Morphology

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*(Received February 21, 1986)*

Thermosetting polyester resins obtained by polymerization of an unsaturated polyester and a vinyl monomer are known to suffer from certain disadvantages: for example, the impact strength of such materials is rather low. The impact behaviour of such resins may be significantly improved by the addition of suitable liquid rubbers bearing certain terminal chemical groups able to react with the base resin. We have found that the formation of polyester-rubber-polyester block copolymer is of determining importance, together with a very intimate dispersion of the rubbery domains, in the improvement of toughness. An investigation on the influence of formulation and composition, molecular mass of the rubber component, type of functional terminal groups, on the chemistry, morphology and curing behaviour of the prepared blends is reported.

## INTRODUCTION

The practical application of thermoset resins, epoxies and polyesters, is often limited because of their brittleness at room temperature. A method which has been adopted to overcome this limitation

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is based on the addition of reactive low molecular mass rubber to the brittle matrix.<sup>1</sup>

Low molecular weight polybutadiene and butadiene-acrylonitrile copolymers terminated with carboxyl, vinyl, amine, epoxy, phenol and hydroxyl groups have been widely used as toughening agents both for epoxy and polyester resins.<sup>2,3</sup> Thermally reactive isoprene-acrylonitrile and ethylacrylate-butylacrylate copolymers have been also used.<sup>2,3</sup>

According to Rowe<sup>3</sup> and Nichols *et al.*<sup>4</sup> in the case of epoxies and polyesters a liquid rubber is suitable for toughening if the following basic conditions are satisfied:

a) The rubber is compatible with the starting uncured base resin; it phase separates as small domains, during gelation process, distributed throughout the matrix;

b) the molecular structure of the rubbers is characterized by the presence of functional end groups which are able to react chemically with the base-resin.

The initial compatibility between rubber and uncured resin, their relative chemical reactivity and rate and nature of phase separation processes, during the cure reactions, mainly determine the mode and state of dispersion of separated rubber domains and consequently the mechanical response of the final cured rubber modified thermoset resin.

More recently Crosbie and Philips<sup>5,6</sup> investigated the toughening effect of several reactive liquid rubbers (carboxyl terminated butadiene-acrylonitrile, vinyl terminated butadiene-acrylonitrile, hydroxyl terminated polyether(polyepichlorohydrin) and an unspecified experimental reactive liquid rubber developed by Scott Bader Ltd.) on two different polyester resins: a flexibilized isophthalic-neopentyl glycol polyester resin, PVC compatible and an epoxy modified polyester resin, which is preaccelerated. The results of these studies are summarized as follows:

i) Three of the four liquid rubbers produced, upon curing, a dispersion of second-phase rubber-rich particles in the polyester

resin matrix, whereas the compatible rubber did not produce any detectable dispersion even at relatively high content.

ii) The mode and state of dispersion of particles were found to be highly dependent upon both rubber and resin formulation.

iii) Toughness increased generally with the presence of dispersed rubber phase.

We report in the present paper (the first of a series) the results of an investigation concerning studies of chemical reactivity between two samples of low molecular weight polybutadiene differing in the nature of the terminal functional groups with a commercial polyester resin.

Analytical techniques, including IR and DSC, were used to study the rubber-resin chemical reactivity. It was found that the reactive rubber, i.e. an isocyanate terminated polybutadiene, gives rise after cure to a modified resin characterized by comparatively smaller sized domains. Such domains, highly adherent to the matrix, are likely to contain triblock copolymers, such as unsaturated polyester-urethane rubber-unsaturated polyester formed before the cure process, after reaction between the prepolymer and the functionalized rubber.

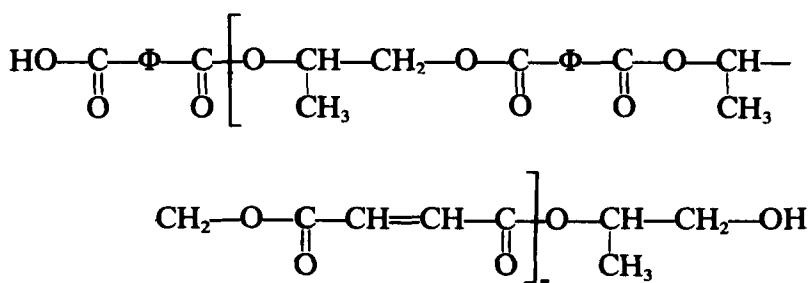
## EXPERIMENTAL

### 1. Materials

i) *Base resin* commercial samples of uncured unsaturated polyester resin (PER) are supplied by SNIAL (Collefero, Roma, Italy) with the trade name of 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 respectively 1:0.7:0.3).

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:-



$\Phi$  = 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  $^1\text{H-NMR}$  technique. The spectrum (see Figure 1) was obtained in  $\text{CDCl}_3$  solution using a  $^1\text{H}$  270 MHz BRUKER apparatus. From this analysis a content of fumarate of about 95 wt% of total maleic anhydride used was calculated (TMS was used as internal standard). Such a result indicates that double bonds along the chains are practically all in a trans configuration.

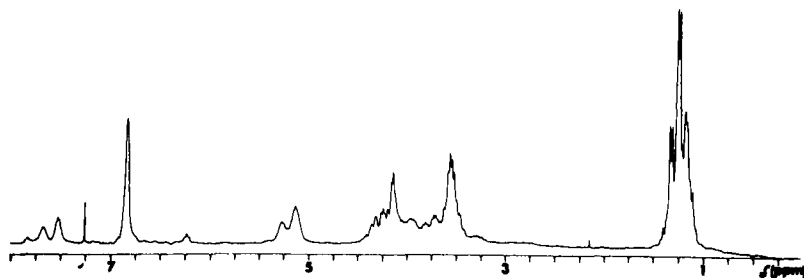


FIGURE 1  $^1\text{H-NMR}$  spectrum of PER resin.

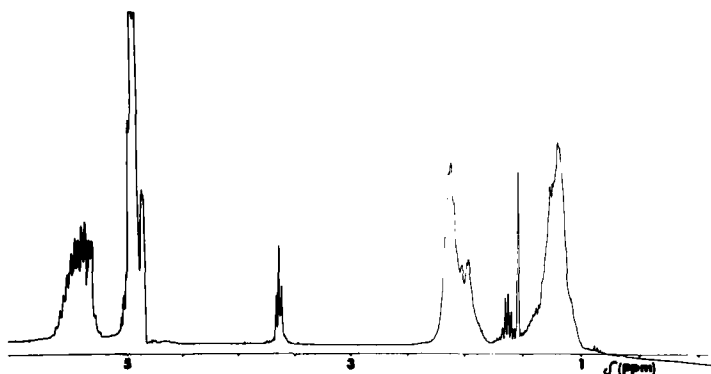


FIGURE 2  $^1\text{H}$ -NMR spectrum of HTPB rubber.

## ii) Low molecular mass rubbers

a) As starting rubber a sample of hydroxyl terminated polybutadiene (HTPB)  $M_n = 1350$ , supplied by Polyscience, was used. The molecular structure of HTPB was determined by analysis of 270 MHz  $^1\text{H}$ -NMR spectrum in  $\text{CDCl}_3$  solution, using TMS as the internal standard.<sup>7</sup> The spectrum is reported in Figure 2. 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) than 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.

## 2. Techniques of characterization

*i) Infrared spectroscopy* Infrared spectra in the range of 4000–400  $\text{cm}^{-1}$  were obtained by using a Nicolet 5 DX FTIR spectrophotometer. The resolution was of 4  $\text{cm}^{-1}$ . In the case of the resin and of the rubber modified resin, data were usually taken using films cured directly onto KBr or NaCl disks.

*ii) Differential scanning calorimetry* 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, was used. The system is provided with a calorimetric Cell DSC-30 which allows temperature scans from  $-170^{\circ}\text{C}$  to  $600^{\circ}\text{C}$ .

*iii) Morphological characterization* The morphology of the materials was investigated by optical (OM) and scanning electron microscopy techniques (SEM).

The phase separation was followed by means of a Leitz polarizing optical microscope with a Mettler hot stage. The mode and state of dispersion of the minor component and its volume fraction were determined by scanning electron microscopy on fractured surfaces after metallization with AuPd alloy. A scanning Electron Microscope (Philips model 501) was used throughout.

## 3. 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 HTPB or PBNCO rubber were dispersed in the styrene solution containing the polyester prepolymer by mechanical stirring for 30 min at  $80^{\circ}\text{C}$  (a polymerization reaction flask, capacity 250  $\text{cm}^3$ , 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 initiator 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  $80^{\circ}\text{C}$  for three hours.

TABLE I  
Code and compositions\* of rubber modified unsaturated polyester resins investigated

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

\* The composition (wt%) refers to the base starting (PER) resin (prepolymer + styrene + catalyst).

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, as naphthene solution).

The code and the composition of RMPER materials investigated are given in Table I.

## RESULTS AND DISCUSSION

*a) Preparation of isocyanate terminated polybutadiene (PBNCO)*  
The isocyanate-end capped polybutadiene (PBNCO) was prepared by a condensation reaction of diisocyanate with the hydroxyl terminal groups of rubber chains. In order to limit chain extension of HTPB through coupling reaction with TDI, a small excess of 5% with respect to the stoichiometric quantities of the latter was used. Larger excess are useless, as with an appropriate choice of the reaction temperature, only the isocyanate group in para position will react (8). The reaction was followed by DSC and I.R. spectroscopy.

The DSC thermograms obtained by heating the reaction mixture from R.T. to about 230°C with a scan rate of 20°C/min, show a large exothermal peak starting from R.T. (see Figure 3). The maximum observed at about 140°C is probably related to the fact that at this temperature the reaction involving mainly the terminal



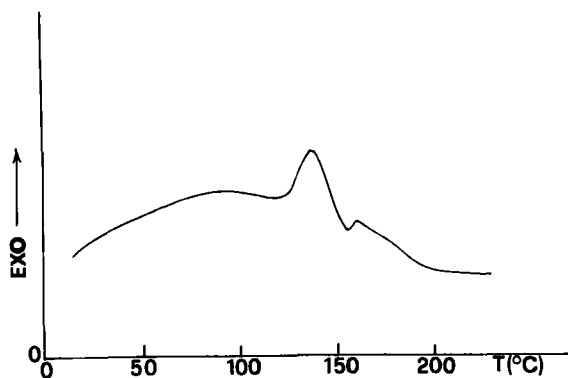
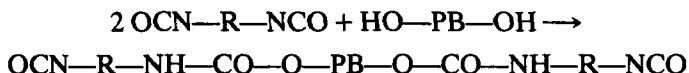


FIGURE 3 DSC thermogram of HTPB/TDI mixture.

groups of HTPB and the -NCO groups of 2,4 TDI in para position presents the highest rate of conversion. The small peak at about 160°C, is likely to be accounted for by the reaction between the -NCO groups in ortho position of 2,6-TDI and the terminal groups of HTPB. As matter of fact it is well known from literature,<sup>9</sup> that the reactivity of the isocyanate groups in the para position of 2,4 TDI is about eight times larger than the groups of 2,6 TDI. To promote the low temperature reaction only, and to avoid coupling, the experiments were effected at temperatures of 70°C. The scheme of the reaction is the following:



where R = toluene group and PB = polybutadiene chain.

The I.R. spectra of pristine TDI and HTPB are compared with that of the reaction product, mainly PBNCO, in Figure 4. The infrared spectra, after 10 minutes of reaction at 70°C, show a strong absorption band at 1710–1735  $\text{cm}^{-1}$ , corresponding to the stretching of the  $-\text{C}=\text{O}$  belonging to the  $(-\text{NH}-\text{C}(=\text{O})-\text{O}-)$  urethane groups of

the formed PBNCO molecules (see Figure 4c).

b) *Reaction of PBNCO with unsaturated polyester prepolymer* It was found that PBNCO and the unsaturated polyester prepolymer

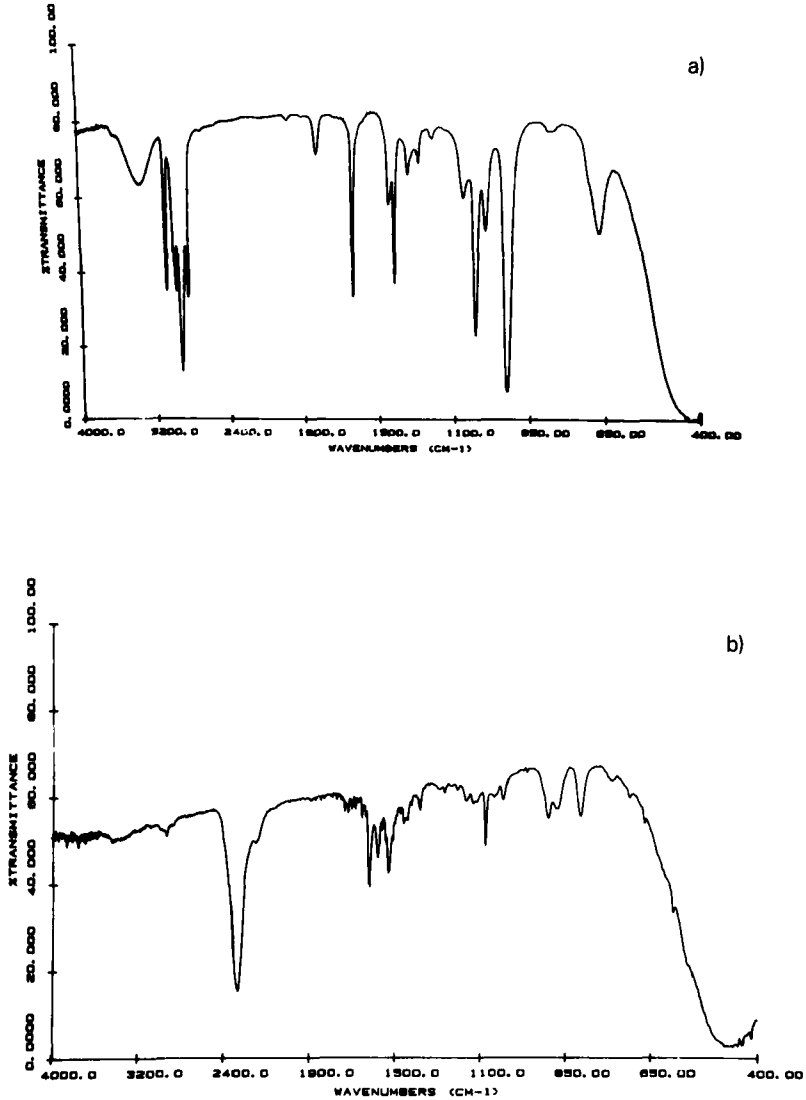
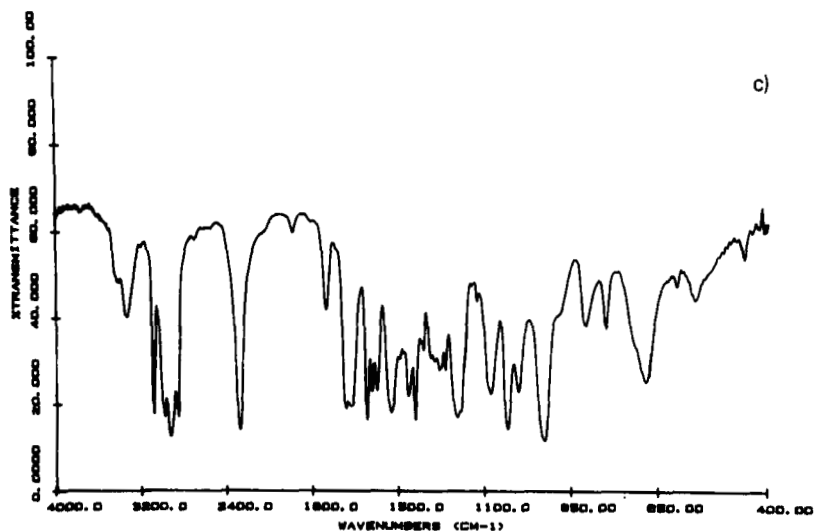
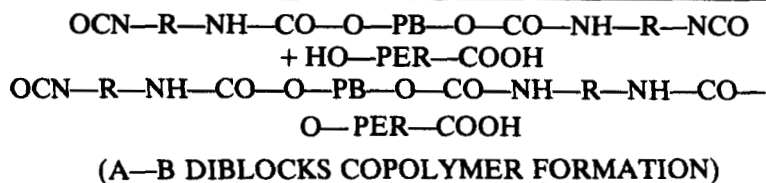
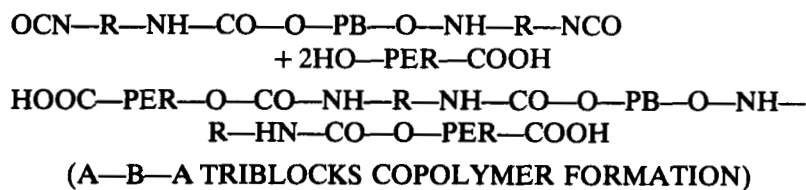


FIGURE 4 Infrared spectrum of: a) HTPB, b) TDI, c) HTPB/TDI mixture after reaction to give PBNCO.



easily react through a condensation reaction that leads to the formation of urethane ( $\text{—O—C(=O)—NH—}$ ) linkages. In principle, in

the course of the reaction diblock and triblock copolymers may form according to the following scheme:



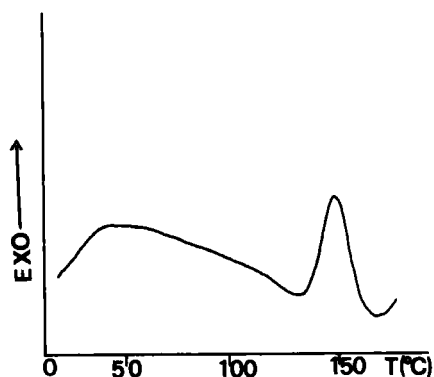


FIGURE 5 DSC thermogram of PER/PBNCO (90/10) mixture.

The reaction is carried out at 80°C under vigorous stirring adding to the PBNCO the styrene solution containing the prepolymer (base PER resin). The reaction was followed by DSC and I.R. As shown in Figure 5 the thermogram obtained by heating the reacting mixture (PBNCO—PER resin) from R.T. to 180°C is characterized by the presence of a broad exothermic peak centered at 60°C followed by a sharp peak centered at 145°C probably due to less reactive NCO groups). From the area of the first peak the heat generated resulted to be, for the 90/10 PER/PBNCO (wt/wt) composition about 143 KJ/mol of hydroxyl terminal groups, well according to literature data.<sup>8</sup>

On the contrary the DCS thermogram of HTPB/PER blends results to be flat indicating that in such case no reaction occurs, at least under our experimental conditions.

Infrared spectra of PBNCO/PER 80/20 blends before and after reaction are shown in Figure 6a and b respectively. From the analysis of the IR spectra it emerges that the band of —NCO isocyanate group at 2260 cm<sup>-1</sup> practically disappears after reaction, indicating that by the end of the reaction almost all the isocyanate terminated PB chains have been reacted. Thus it may be concluded that preferable A—B—A triblock type copolymers are formed.

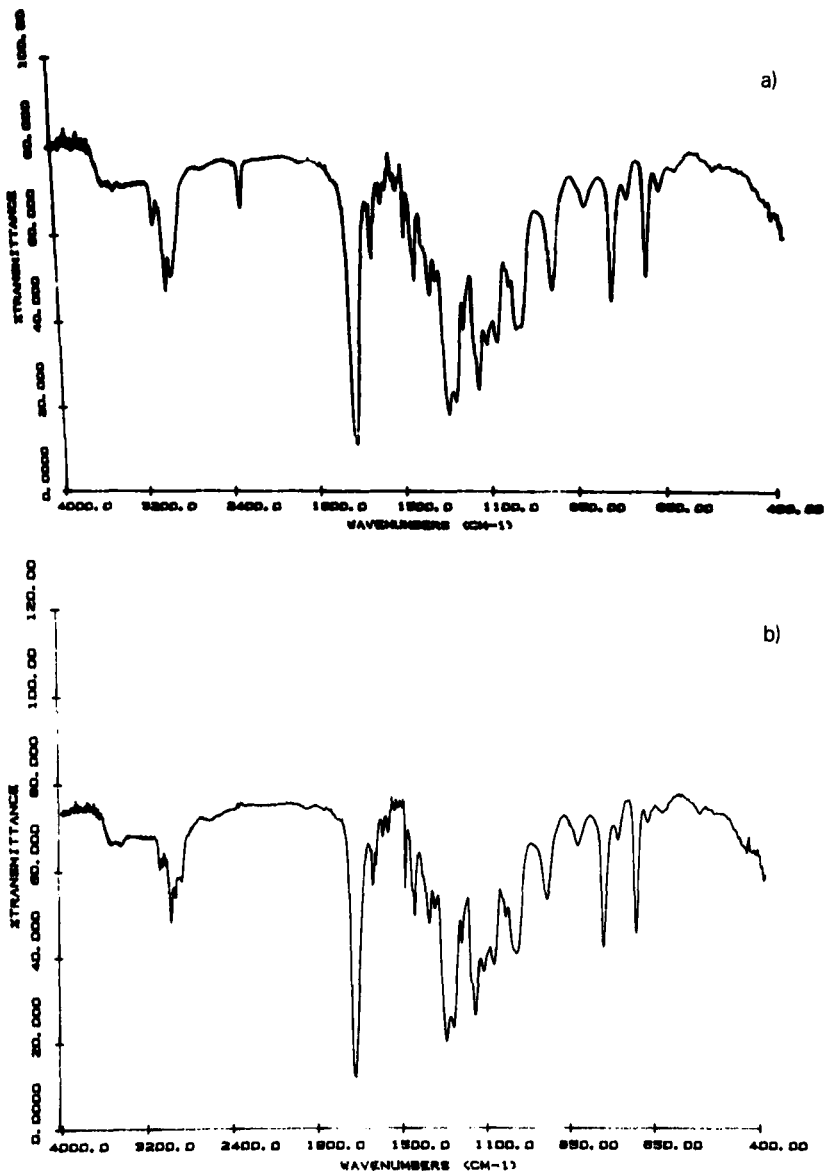
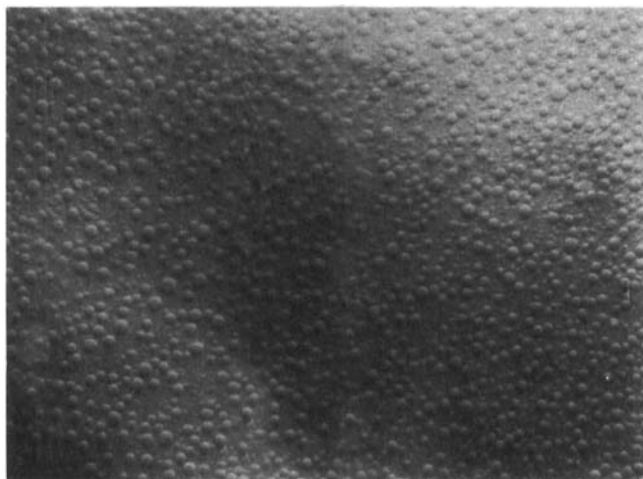


FIGURE 6 Infrared spectrum of: a) PER/PBNCO (80/20) mixture at R.T. before reaction, b) PER/PBNCO (80/20) mixture after reaction.



**FIGURE 7** Optical micrograph of PER/PBNCO (90/10) film before reaction and curing (100 $\times$ ).

*c) Morphology and phase separation studies in PER/PBNCO and PER/HTPB Blends*

*i) Phase structure before the curing process*

The phase structure of PER/PBNCO blends was investigated by optical microscopy by squeezing drops of the viscous mixture between two glass plates. The observations were first made after mixing at room temperature, when the rate of conversion related to the reaction of formation of A—B—A copolymer is very low, and then after storing the blend samples at about 80°C for 30 minutes, that is after completion of the reaction of copolymer formation.

It may be observed that before or at the early stage of copolymer reaction the PER/PBNCO mixture is separated in droplet-like domains (see Figure 7). On the contrary, the mixture at the end of reaction appears homogenous under optical microscope. It is interesting to point out that PER/HTPB 90/10 blends before curing show a morphology similar to that observed in PER/PBNCO blends before the formation of A—B—A copolymer (see Figures 7,8), with a clear phenomenon of separation of a rubbery-rich phase. On the

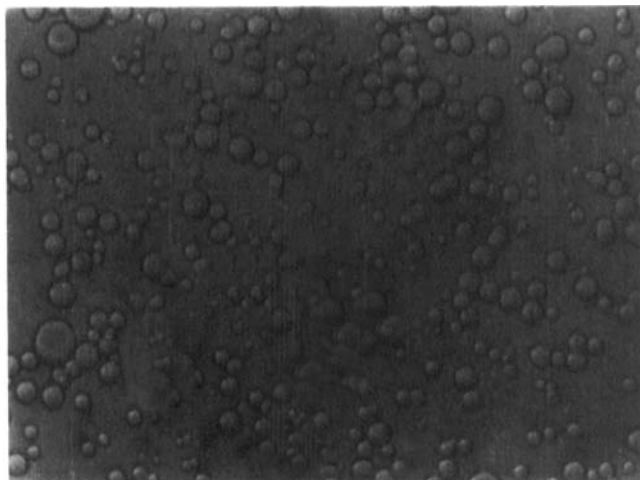


FIGURE 8 Optical micrograph of PER/HTPB (90/10) film before curing (100 $\times$ ).

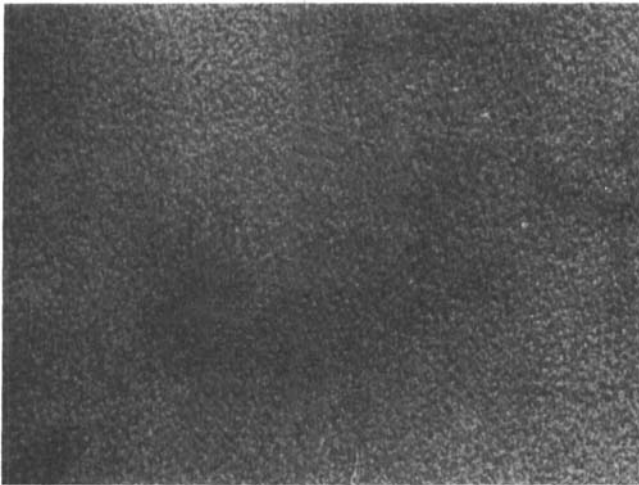
contrary, after the thermal treatment (30' at 80°C) the blend PER/PBNCO becomes transparent under the microscope, while the phase structure of PER/HTPB blends is not stable as coalescence processes induced by time and/or temperature are observed. This is a counterproof of the formation of a ABA block copolymer in the former blend, well emulsified inside the matrix. The mode and state of dispersion of the rubber component in the case of PER/HTPB 80/20 blends appears to be more complicated as domains of rubber with sub-inclusions of resin are observed (see Figure 9).

#### ii) *Phase structure after cure*

The phase structure of PER/PBNCO and PER/HTPB blends 90/10 and 80/20 (wt/wt) in composition, after the cure process was investigated by optical microscopy on thin films and by SEM observation of fractured surfaces. It can be seen that the starting of gelation causes the phase separation of the compatible PER/PBNCO blends, and small domains around 2  $\mu\text{m}$  in size, uniformly distributed all over the sample, strongly adherent to the matrix are visible (see Figure 10, 11 and 12). It can be seen (see Figure 11a and 11b) that the moving crack front seems to interact with the dispersed



**FIGURE 9** Optical micrograph of PER/HTPB (80/20) film before curing (100 $\times$ ).



**FIGURE 10** Optical micrograph of PER/PBNCO (90/10) mixture after reaction and curing process (100 $\times$ ).



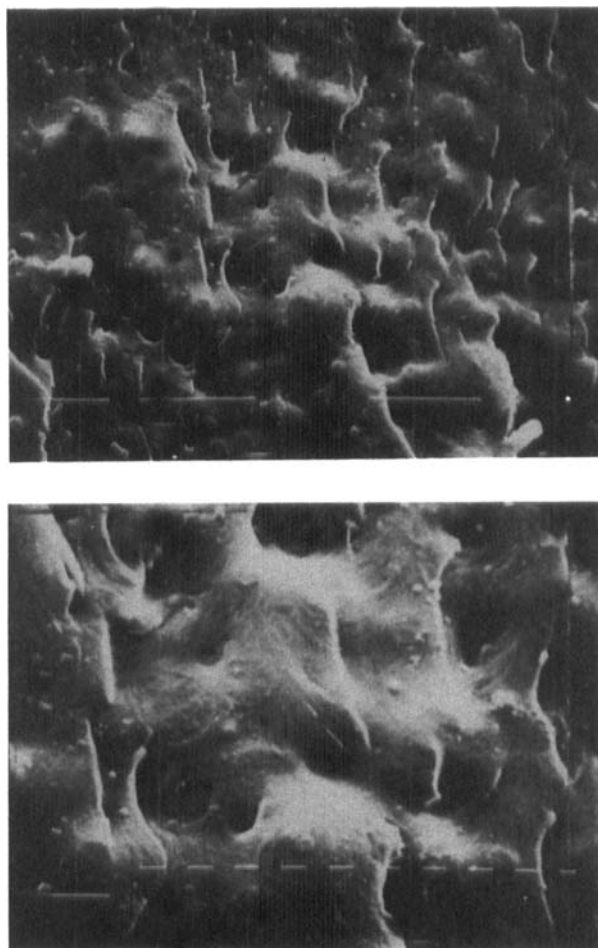
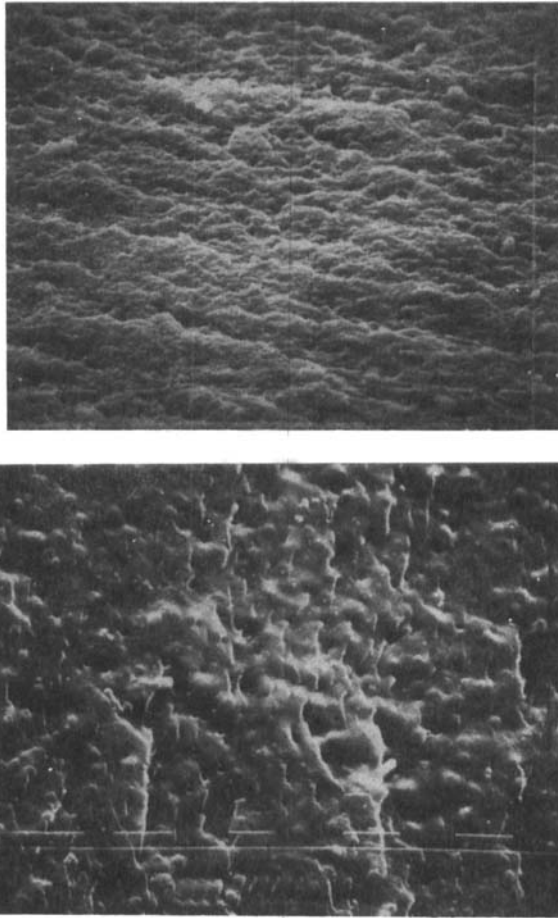


FIGURE 11 SEM micrographs of PER/PBNCO 90/10 mixture after rubber-prepolymer reaction and curing process at two different magnifications: a) 2500 $\times$  b) 5000 $\times$ .

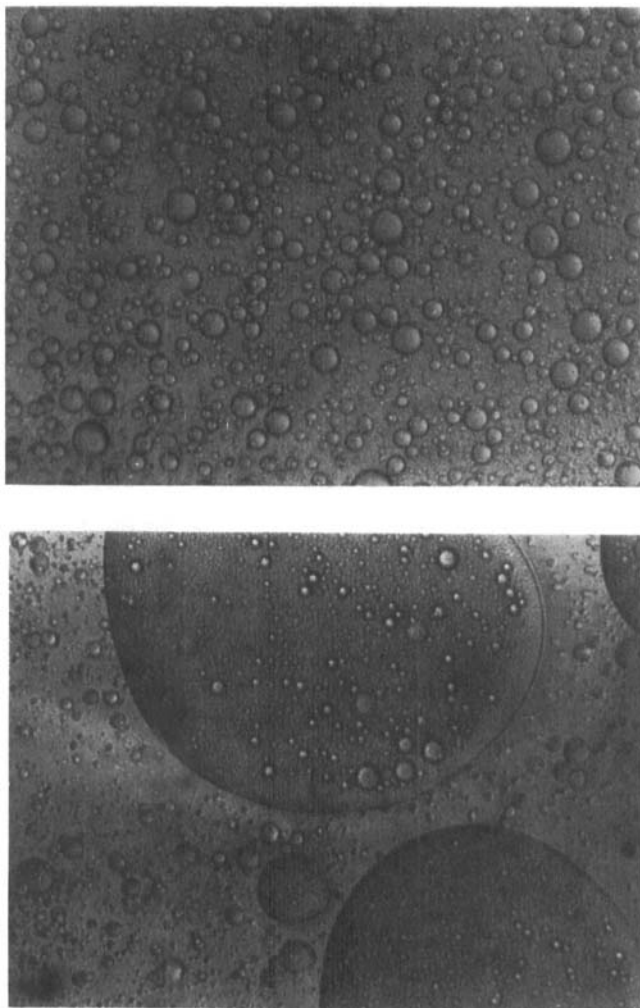
particles. Tails or steps are formed at the border of the inclusions. The phase structure of PER/HTPB blends is much more intricate. As shown by the optical micrographies of Figure 13 large rubbery domains, probably containing resin sub-inclusions, coexist with very small domains. The SEM analysis of fractured surfaces show the presence of dispersed domains with a dimension distribution much



**FIGURE 12** SEM micrographs of PER/PBNCO (80/20) mixture after rubber prepolymer reaction and curing process at two magnifications: a) 640 $\times$ ; b) 1250 $\times$ .

wider than in the case of PER/PBNCO blends. Moreover these domains seem to scarcely adhere to the matrix as holes with smooth walls are largely visible on the surface of the samples (see Figure 14).

It is interesting to observe that the crack front bores out between the domains, whilst still remaining pinned at all positions when it has encountered the particles (see Figure 14).



**FIGURE 13** Optical micrograph of a thin film of PER/HTPB blends after curing process (100 $\times$ ) a) (90/10); b) (80/20).

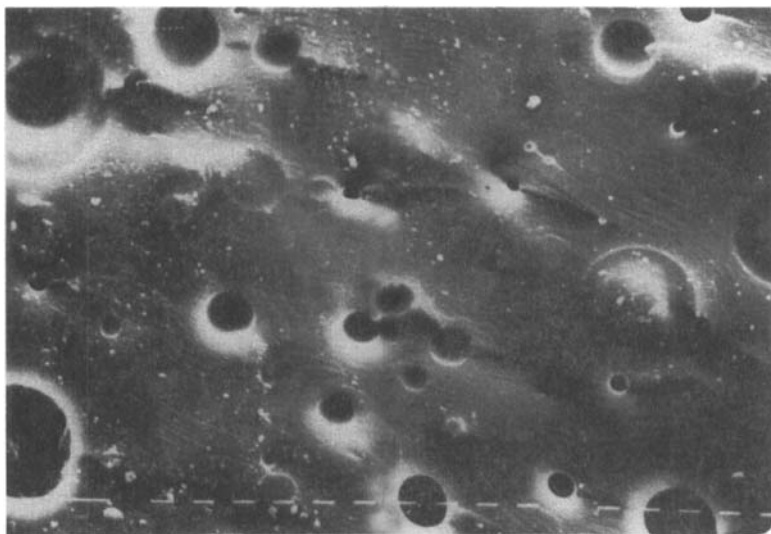


FIGURE 14 SEM micrographs of fractured surfaces of PER/HTPB (90/10) blend after curing process 320 $\times$ .

*d) Glass transition studies* The glass transition temperatures ( $T_g$ ) of pristine HTPB, PBNCO and PER and PER/HTPB and PER/PBNCO blends are reported in table II. From the figures of this table it emerges that:

a) the glass transition value of PBNCO is higher than that of HTPB ( $-9^\circ\text{C}$  and  $-16^\circ\text{C}$  respectively) probably related to the formation of urethane-type hydrogen bonding.

b) in both types of post cured blends i.e. PER/HTPB and PER/PBNCO two glass transition are observed, the one at lower temperature is attributable to rubber segments while that at high temperature belongs to the cured resin.

c) for PER/HTPB modified resins the  $T_g$  of rubber remains constant whereas the  $T_g$  of resin seems to decrease proportionally to the HTPB content (PER (100%):  $T_g = 66^\circ\text{C}$ ; Per (90%):  $T_g = 64^\circ\text{C}$  and Per (80%):  $T_g = 55^\circ\text{C}$ ).

This effect is likely due to uncomplete phase separation of the rubber inside the polyester matrix.

TABLE II  
Glass transition temperature of starting materials and of rubber modified post cured resins

Glass transition temperature (°C)		
Material (Code)		
HTPB	-16	
PBNCO	-9	
PER	66	
PER/HTPB (90/10)	-13	64
PER/HTPB (80/20)	-17	55
PER/PBNCO (90/10)	0	55
PER/PBNCO (80/20)	0	51

d) for PER/PBNCO modified resin the lowering in the T<sub>g</sub> of resin seems to be even larger; at the same time a substantial increase in the T<sub>g</sub> of rubber is observable.

The overall picture which emerges is that the presence of rubber influences the glass transition temperature of resin. The fact that the T<sub>g</sub> of the rubber for PER/PBNCO post cured resin is larger than that of pristine PBNCO may be accounted for by a reduction of free volume related to the formation of the A-B-A copolymer.

## CONCLUSIONS

From the study reported it may be concluded that the mode and state of dispersion of the rubbery phase, as well as the thermal behaviour of the rubber modified resin is to be drastically influenced

by the reactive attitude of the rubber added and by the relative miscibility of the components before cure reaction.

Partly supported by Progetto Finalizzato Chimica fine del C.N.R.

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