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Formulation, curing, morphology and impact behaviour of epoxy matrices modified with saturated rubbers

N. LANZETTA, P. LAURIENZO, M. MALINCONICO, E. MARTUSCELLI, G. RAGOSTA, M. G. VOLPE
Istituto di Ricerche su Tecnologia dei Polimeri e Reologia del CNR, Via Toiano, 6 Arco Felice, Napoli, Italy

New formulations of rubber toughening agents for difunctional and tetrafunctional commercial epoxies are attempted, on the basis of their increased thermal stability compared with classical unsaturated elastomers. Quite satisfactory results are obtained where a block copolymer of polydimethylsiloxane and polyoxyethylene elastomer or a functionalized poly (1-butene) in difunctional epoxy are used. On the other hand, poor results are obtained when the same elastomers are employed in tetrafunctional epoxies. A tentative explanation is given on the basis of the different networks obtained in the two matrix systems.

1. Introduction

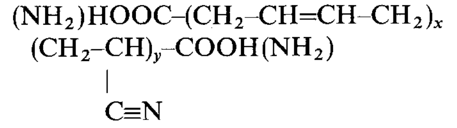
Epoxy resins, generally filled with a wide variety of reinforcing agents like fibres, are increasingly used as structural materials in areas with a high level of technological innovation (aerospace, advanced marine, transportation, building construction). These materials, mainly due to their cross-linked nature, offer the advantage of high moduli coupled with a good creep resistance [1]. Unfortunately, thermosetting resins in general suffer from low impact resistance and undergo fragile rupture as a consequence of the growth of defects and crazes, followed by their progressive propagation and, sometimes, by the catastrophic failure of structural parts. Typical values of fracture energy of epoxy fall in the range 80–200 $\mathrm{J\,m^{-2}}$. A general method to improve the impact properties of thermosetting, as well as thermoplastic, resins is to include reactive rubbers in the matrix polymer [2–5].

The procedure for the toughening of a thermosetting polymer can be summarized as follows:

(i) a low-M_w rubber bearing end-groups reactive towards the epoxy prepolymer is dissolved in the base resin;
(ii) the cross-linker is added to the solution;
(iii) the mixture is poured into a mould and pre-cured for a certain time, followed by a final cure at higher temperatures.

Several parameters can influence the entire process: type and M_w of the rubber and its functional end-groups, type and concentration of hardener, pre-cure and cure conditions.

The rubber normally separates during the cure process, leading to the formation of a discrete phase of spherical shape. By varying the temperature at which the cure is carried out it is possible to control the dimension and the number of rubbery particles. It must be stressed that the rubber precipitation has to be completed before the occurrence of gelation, when all the diffusion processes will essentially stop. The elastomers which have found extensive applications are low-M_w liquid copolymers of butadiene and acrylonitrile, carboxyl or amino-terminated, with the general formula:



$$\mathrm{(NH_2)HOOC{-}(CH_2{-}CH{=}CH{-}CH_2)_x(CH_2{-}\underset{\displaystyle C{\equiv}N}{\underset{|}{C}H})_y{-}COOH(NH_2)}$$

and an acrylonitrile content varying between 10 and 27 wt %.

The mechanism of toughening, although not yet completely understood, is related to the reactivity of the rubber towards the epoxy resin and to the domain size: spherical domains around 1 μm in size seem to impart better impact resistance, as they induce a combined mechanism of fracture propagation via multicraze formation and yielding. Concerning the reactivity, we have already found that, at least in the case of unsaturated polyester resins, only rubbers bearing functionalities reactive towards the matrix resin can improve the impact properties of the final material [6].

New formulations between bifunctional and tetrafunctional epoxy resins and liquid reactive elastomers are described. New types of rubber characterized by a higher thermal and photooxidative resistance when compared to polybutadiene-based elastomers have been used. The preparation of these rubber-modified epoxies, their morphology and the impact properties of the resulting materials are also described.

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2. Experimental procedure

2.1. Materials

The difunctional epoxy resin is a diglycidyl ether of bisphenol A (DGEBA) and is available from Shell Chemical Co. with the trade name Epikote 828. It presents an epoxy equivalent weight of 187 $\mathrm{g\,mol^{-1}}$. The tetrafunctional epoxy resin is a tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) and is available from Ciba-Geigy under the trade name MY720. It is characterized by a molecular weight of 530 $\mathrm{g\,mol^{-1}}$ and an epoxy equivalent weight of 123 $\mathrm{g\,mol^{-1}}$.

The hydroxyl-terminated liquid elastomer polydimethylsiloxane-co-polyoxyethylene (PDMSO-co-PEO) was kindly supplied by Dow. The M_w is 2400 $\mathrm{g\,mol^{-1}}$. The liquid elastomer saturated polyisobutylene Hyvis 10, having $M_w = 1000\ \mathrm{g\,mol^{-1}}$ and a single double bond at the extremity of the chain, was kindly supplied by BP Chemicals.

Maleic anhydride and di-benzoyl peroxide (Fluka reagents) were used for the functionalization of Hyvis. For the polymerization of DGEBA, 2,4,6-tris-(dimethylamino)methyl phenol (DMP 30, Fluka) was used as a catalyst without further purification. Reagent-grade isophorondiamine (IPDA) was used to cure the TGDDM systems. The codes and the compositions of the blends prepared are reported in Table I.

TABLE I Codes and composition of the prepared blends

Sample	Elastomer (wt %)	Catalyst (wt %)
EPON 828	0	2.5
EPON–PDMSO-co-PEO	8	2.5
EPON–PB-g-SA	8	2.5
TGDDM–IPDA	0	50[a]
TGDDM–IPDA–PB-g-SA	8	50[a]

[a] Hardener (wt %).

2.2. Preparation of Pb-g-SA

100 g of Hyvis 10 are dissolved in 100 ml of xylene. 10 g of maleic anhydride and 0.5 g of benzoyl peroxide (this last dissolved in xylene) are added on. The reaction is carried out at 120 °C for 2 h. The unreacted anhydride is removed by repeated washing with n-heptane which allows the precipitation of anhydride.

The final solution is filtered, dried under vacuum at 80 °C and stored under N_2. The i.r. spectrum of starting PB and of the functionalized PB-g-SA are reported in Fig. 1. An anhydride band at ~ 1790 $\mathrm{cm^{-1}}$ is evident in the spectrum of PB-g-SA.

2.3. Preparation of DGEBA-based blends

A mixture of DGEBA containing 8 phr of rubber is mechanically stirred in a flask for 20 min at 80 °C under N_2. 2.5 phr of DMP 30 are then added to the system. The blend is repeatedly degassed, then poured into a mould and cured for 12 h to 100 °C.

2.4. Preparation of TGDDM–IPDA-PB-g-SA blends

A mixture of TGDDM containing 8 phr of PB-g-SA is mechanically stirred and reacted at 80 °C for 10 min. 35 phr of IPDA are then added and the mixture is stirred at 120 °C for 10 min before degassing and pouring into a mould. The cure is carried out at 100 °C for 12 h, followed by a post-cure at 150 °C for 12 h more. Codes and compositions of prepared blends are reported in Table I.

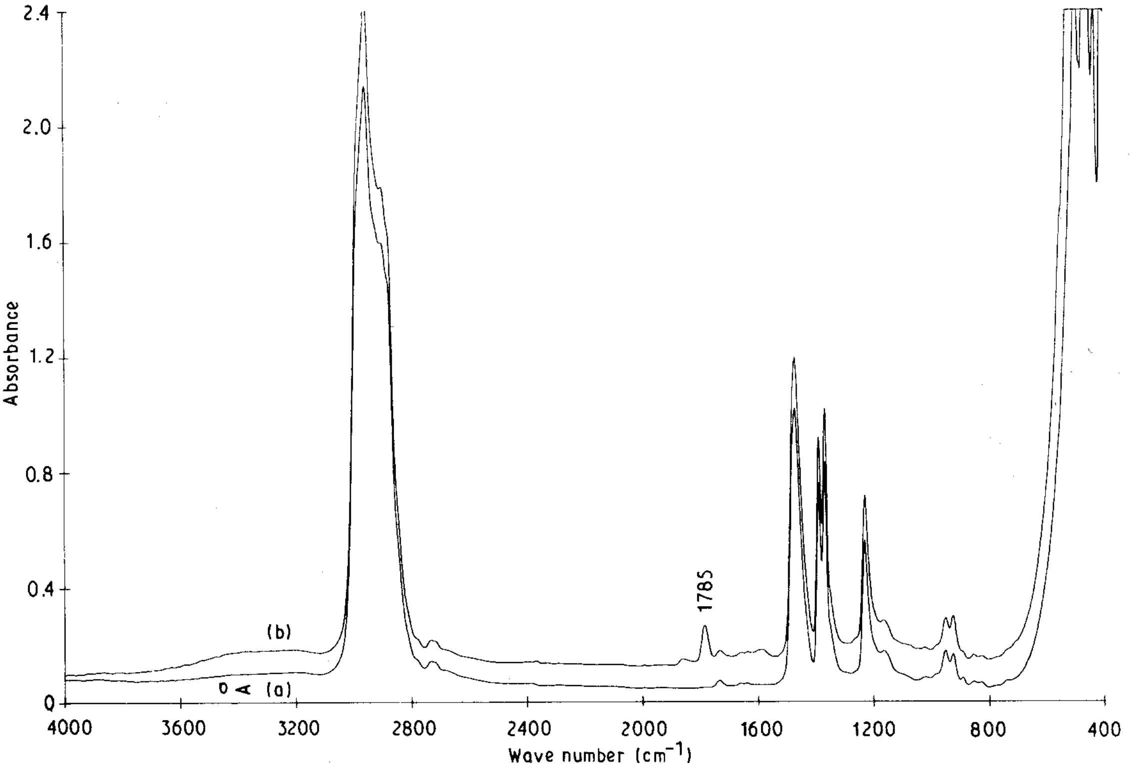


Figure 1 I.r. spectra of (a) starting PB, (b) functionalized Pb-g-SA.

2.5. Infrared spectra

The i.r. spectra were obtained with a Nicolet DxB FTIR spectrophotometer at 4 cm^{-1} resolution on KBr plates, equipped with a temperature control cell which allows scans of temperature from 200 to 250 °C (Specac 20–100).

2.6. Sample preparation for impact tests and SEM analysis

Plates 5-mm thick were milled to get 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.

2.7. Impact fracture measurements

Charpy impact tests were carried out at an impact speed of 1 m s^{-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 room temperature. Curves of energy and load against time or displacement were recorded.

2.8. Fractography

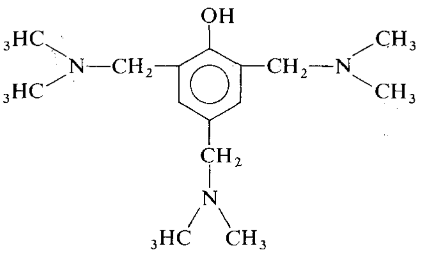
The fracture surfaces of both unmodified and rubber-modified epoxies were examined by scanning electron microscopy (SEM), using a Philips SEM 501. Before observation the samples were coated with a thin layer of gold–palladium alloy by vacuum deposition.

3. Results and Discussion

3.1. Rubber modification of bifunctional resin (DGEBA)

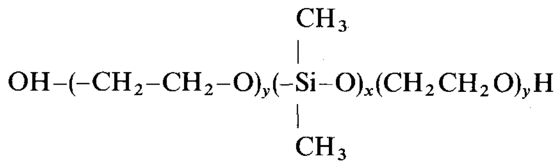
In the literature the curing of bifunctional epoxy resin [7] is normally obtained by using an aromatic amine, such as piperidine, in catalytic quantities (0.5 phr) as hardener. Unfortunately, this amine is volatile and toxic while other commonly used aromatic diamines are of suspect mutagen activity.

In order to avoid this problem we used a tertiary non-volatile aromatic amine in catalytic quantities. In particular, 2,4,6-tridimethylaminomethylphenol (DMP30) was used for the cure of DGEBA. The alcoholic function of DMP30 is able to take part in the network formation of the base resin, while the tertiary amine function exerts a strong catalytic influence. It is found that the gel time is a few minutes at 100 °C.



The cure reaction between DGEBA and DMP 30 (2.5 phr) was carried out by mixing epoxy resin with the catalyst at room temperature. After degassing at 60 °C, the mixture was poured into a mould and cured at 80 °C for 2 h, followed by a post-cure at 100 °C for 12 h. In these conditions we found that the residual heat of reaction, as measured by calorimetric methods, was zero.

Two kinds of elastomeric components were used: polydimethylsiloxane-co-polyoxyethylene (PDMSO-co-PEO) and saturated polybutene (PB). PDMSO-co-PEO is a liquid hydroxyl-terminated low molecular weight elastomer. It is composed of 30 wt % polydimethylsiloxane and 70 wt % polyoxyethylene units. The PEO blocks are located at both ends of the polymeric chain and the structure is as follows:

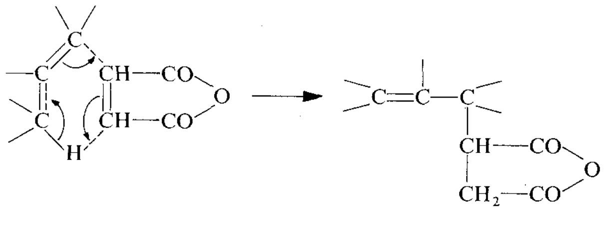


$$OH\text{-}(\text{-}CH_2\text{-}CH_2\text{-}O)_y(\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_x(CH_2CH_2O)_yH$$

The i.r. spectrum of PDMSO-co-PEO is reported in Fig. 2. The presence of the polyoxyethylene blocks improves the solubility of the conventional polydimethylsiloxane towards the epoxy resin and, at the same time, allows the chemical reaction with the epoxy groups.

The –OH terminal groups of the rubber can compete, in principle, with the –OH groups of DGEBA in the reaction of the epoxy rings during the curing process, leading to finer dispersion of the rubber particles in the matrix.

The liquid polybutene, PB, is used after functionalization with succinic anhydride (PB-g-SA) by a radical reaction. In fact, the PB is obtained by cationic polymerization and so possesses a single double bond at the end of the chain, due to the mechanism of termination of the cationic growing chain. This double bond can react in the allylic position with anhydride molecules during the radical functionalization reaction, leading to a PB-g-SA having a single molecule of SA on the chain:



In the i.r. spectrum obtained after repeatedly washing, there is a clear anhydride band at ~ 1790 cm^{-1}. (Fig. 1). The anhydride groups grafted on to the elastomeric backbone are able to react with the epoxy groups of the resins.

To follow this reaction, an infrared investigation was conducted by heating a sample of the mixture DGEBA–PB-g-SA (1 : 1 by weight) in a temperature cell from room temperature up to 200 °C as seen in Fig. 3; the anhydride band initially present at 1790 cm^{-1} slowly disappears during the course of reaction, while an ester band at 1730 cm^{-1} due to the

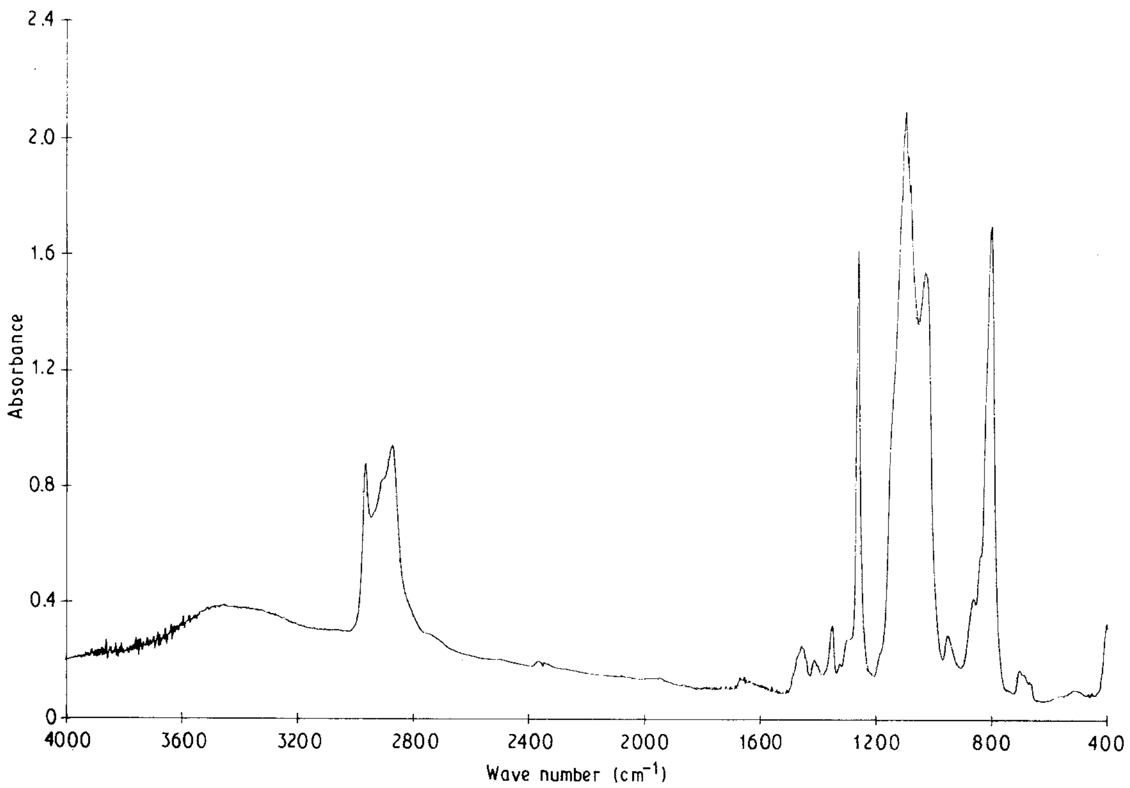


Figure 2 Infrared spectrum of PDMSO-co-PEO.

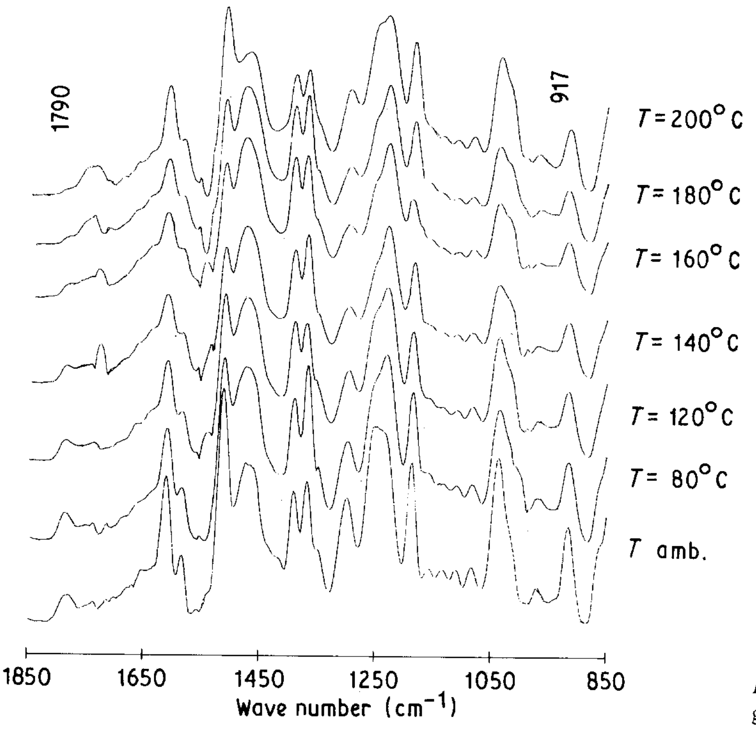


Figure 3 Infrared spectra of the mixture DGEBA–PB-g-SA (1 : 1) obtained by thermal scanning.

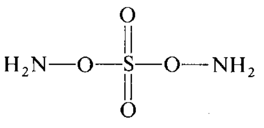
reaction of the anhydride groups with the alcoholic function of the resin increases proportionally. The spectra in Fig. 3 show that the esterification reaction between anhydride and epoxy groups starts at 80 °C. We therefore decided to keep the mixture of DGEBA and PB-g-SA at a temperature of 80 °C for 20 min before the addition of catalyst DMP 30, in order that the esterification reaction goes to completion before the curing process starts.

In this way, a graft copolymer (PB-g-SA)-g-DGEBA is formed, which is able to ensure a good adhesion between the two components in the final blend. In fact a thin layer of the mixture PB-g-SA–DGEBA observed under an optical microscope appears to be a fine emulsion of a rubbery phase in an epoxy matrix which is stable at room temperature even after several weeks of observation, whereas in the absence of the anhydride grafted groups PB and DGEBA delaminate completely in few minutes.

3.2. Rubber modification of tetrafunctional resin (TGDDM)

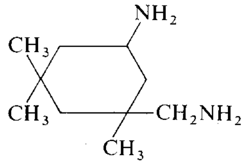
A similar study was performed on the tetrafunctional epoxy resin TGDDM. We used as curing agents both

DDS, normally employed in many commercial formulations [8], and an aliphatic diamine, IPDA, having the following formula:



$H_2N-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-NH_2$

DDS



IPDA

IPDA was chosen because of the toxicity and high post-cure temperature (~200 °C) of the aromatic DDS. In fact, IPDA is non-toxic, is soluble in the base resin at room temperature, and allows a post-cure temperature of 150 °C.

Two molar ratios of TGDDM to curing agent were used: 2 : 1 and 1 : 1 for TGDDM–DDS and TGDDM–IPDA systems, respectively. In the system TGDDM–IPDA 1 : 1 an excess of 20 wt % IPDA was used in order to reduce the resin homopolymerization and to compensate for the steric hinderance of IPDA. The curing conditions which led to final products with no residual heat were the following:

(i) TGDDM–DDS: cure at 150 °C for 12 h and post-cure at 180 °C for 2 h.
(ii) TGDDM–IPDA: cure at 100 °C for 12 h and post-cure at 150 °C for 2 h.

The same elastomers as those utilized for the bifunctional resin were used for TGDDM. However, it was impossible to prepare blends with PDMSO-co-PEO because it is completely insoluble in the base resin before the cure reaction, while it was possible to prepare blends with the PB-g-SA at 8 phr. Nevertheless, the decreased reactivity of the epoxy groups on TGDDM and, possibly, the poor solubility between TGDDM and PB-g-SA impede the obtaining of a solution or a stable emulsion as in the case of the difunctional resin.

3.3. Fracture toughness parameters

The Charpy impact data were analysed by using the concepts of linear elastic fracture mechanics (LEFM) theory [1]. Following this approach the critical stress intensity factor or fracture toughness, K_c, at the onset of crack growth was calculated from

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

where σ is the nominal stress at failure, a is the initial crack length and y is a dimensionless geometry factor. For single-edge notched bend specimens with a span length (S) to width (w) ratio of 8, as employed in the present study, the shape factor y is given by [7].

$$\begin{aligned} y = {} & 1.96 - 2.75(a/w) + 13.66(a/w)^2 \\ & - 23.98(a/w)^3 + 25.22(a/w)^4 \end{aligned} \tag{2}$$

On the grounds of Equation 1 a plot of σy against $1/a^{1/2}$ gives a straight line with K_c as the slope. A linear relationship between σy and $1/a^{1/2}$ was found for both neat and elastomer-modified epoxies. This result supports the use of the LEFM approach as a method for characterizing the impact resistance of epoxy polymers. An example of K_c determination is reported in Fig. 4 for the DGEBA resin.

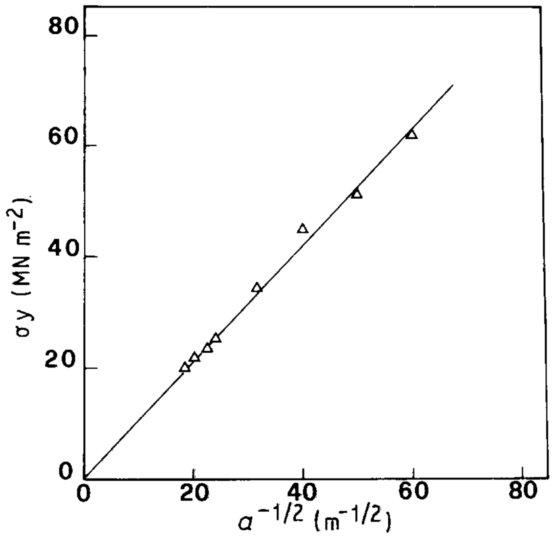


Figure 4 Plot for critical stress intensity factor (K_c) of DGEBA resin: $K_c = 1.1\ \text{MN m}^{-3/2}$.

An equivalent LEFM parameter is the critical strain energy release rate or fracture energy, G_c, needed to initiate the crack propagation. For the determination of G_c the following equation was used:

$$G_c = \frac{U}{Bw\Phi} \tag{3}$$

where U is the stored elastic strain energy in the specimen at the onset of crack growth, B and w are the thickness and width of the specimen and Φ is a dimensionless shape factor related to the specimen compliance (c) and to the crack length (a) by the relationship

$$\Phi = c\left(\frac{\mathrm{d}c}{\mathrm{d}(a/w)}\right)^{-1}$$

The value of Φ may be evaluated either from measuring the compliances as a function of crack length or more readily from published tables. In the present work the values of Φ for various crack length were taken from Plati and Williams [3]. Equation 3 predicts that a graph of U versus $Bw\Phi$ should give a straight line with G_c as the slope. An example of G_c so determinated is shown in Fig. 5 for the DGEBA resin. Graphs of this type were obtained for all the other materials investigated.

3.4. Fracture toughness and fractographic analysis

The fracture toughness for unmodified and rubber-modified DGEBA epoxy resin, as calculated from Equations 1 and 3, is summarized in Table II. A relatively small improvement in the impact toughness compared with the neat resin is observed for the material containing PDMSO-co-PEO as rubbery phase. A more substantial enhancement of the toughness is obtained when PDMSO-co-PEO is replaced by PB-g-SA.

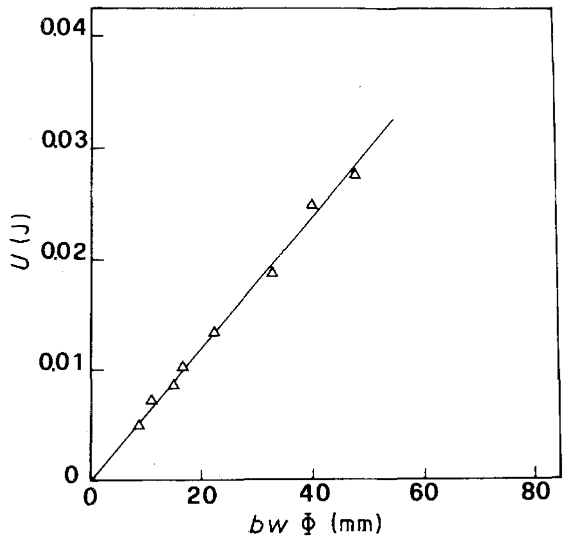


Figure 5 Plot for critical strain energy release rate (G_c) of DGEBA resin: $G_c = 0.6\ \mathrm{kJ\,m^{-2}}$.

TABLE II Critical stress intensity factor, K_c, and critical strain energy release rate, G_c, for unmodified and rubber-modified DGEBA resin at room temperature

Sample code	$K_c(\mathrm{MN\,m^{-3/2}})$	$G_c(\mathrm{kJ\,m^{-2}})$
Pure resin DGEBA	1.1	0.6
DGEBA-PDMSO-co-PEO	1.3	0.8
DGEBA-PB-g-SA	1.5	1.0

These toughness results can be interpreted on the basis of the fractographic analysis performed by SEM on such materials. In Fig. 6 are presented the SEM micrographs after impact failure at room temperature. All the pictures have been taken near the notch tip in the region of crack initiation. The micrograph of the unmodified resin (Fig. 6a), except for large fracture steps, does not show further fractographic features distinctive of an extensive plastic flow mechanism. The absence of significant plastic deformation such as shear yielding correlates well with the lack of toughness. The fracture surfaces of DGEBA–PDMSO-co-PEO (Fig. 6b) and DGEBA–PB-g-SA (Fig. 6c) are characterized by a morphology in which the rubber is segregated in spherically shaped domains dispersed in the DGEBA matrix. For the DGEBA–PDMSO-co-PEO system, the particle-size distribution is almost unimodal (mean diameter 1–2 μm) whereas for the DGEBA–PB-g-SA system the dispersed rubbery phase includes both small particles (< 1 μm diameter) and large particles (> 5 μm diameter). From the micrographs of Fig. 6b and c it is also evident that the crack growth, unlike that of the simple epoxy resin, is accompanied by large localized plastic shear deformations initiated by the rubbery particles. The extent of such deformations, which represent the main source of energy dissipation and increased toughness, appears to be greater for the material containing PB-g-SA as a second phase. This result may be ascribed either to a bimodal size distribution of the rubbery particles which, as shown by other authors [8], enhances epoxy polymer toughness more than a mono-dispersed formulation, or to a stronger chemical bond across the rubbery phase–resin matrix interface, due to the greater chemical reactivity of the anhydride functionality of PB-g-SA towards the epoxy groups.

In Table III are collected the toughness results for the TGDDM epoxy resin and for the same resin containing PB-g-SA as modifier. As can be seen, the type of hardener (DDS or IPDA) has little effect on the fracture parameters G_c and K_c. Furthermore, the data

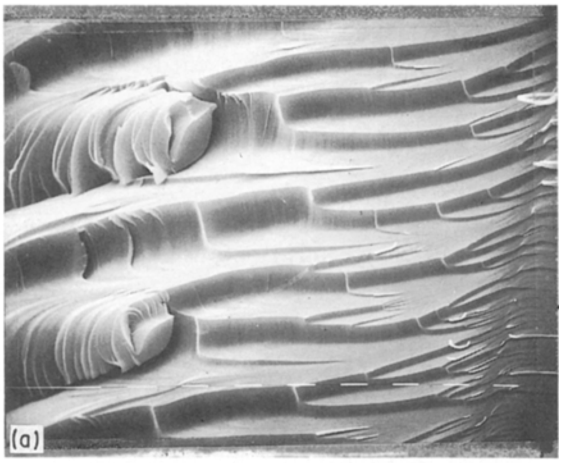
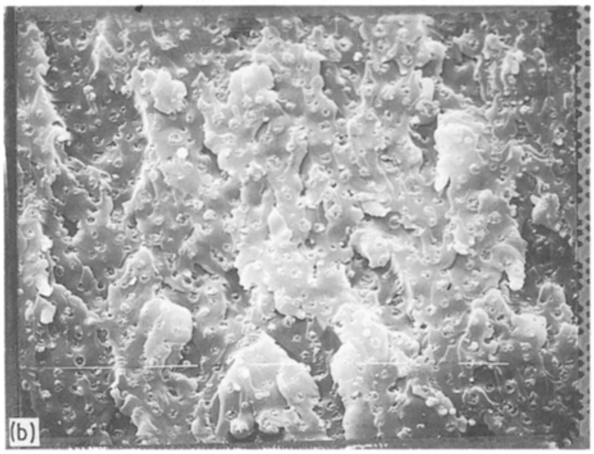
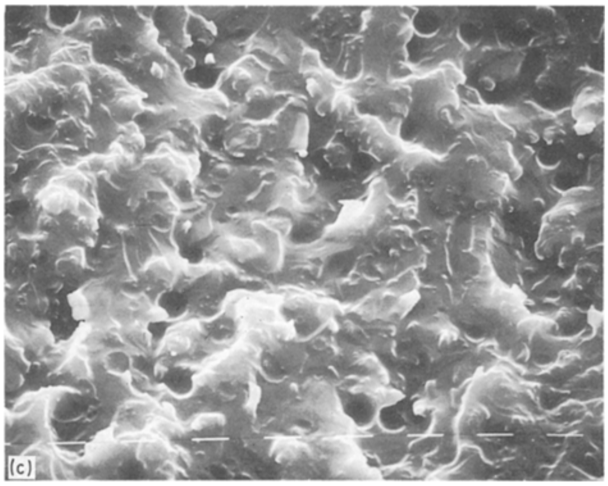


Figure 6 SEM micrographs (×640) after impact failure at room temperature of (a) unmodified resin DGEBA, (b) DGEBA–PDMSO-co-EVA blend, (c) DGEBA–PB-g-SA blend.





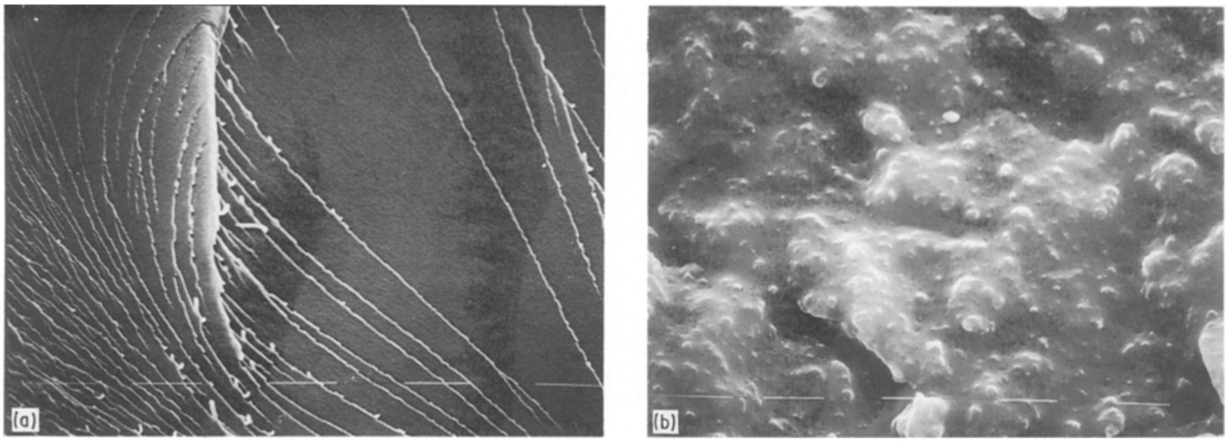


Figure 7 SEM micrographs (×1250) of the fracture surfaces of (a) unmodified TGDDM, (b) TGDDM–PB-g-SA blend.

TABLE III Critical stress intensity factor, K_c, and critical strain energy release rate, G_c, for unmodified and rubber-modified TGDDM resin at room temperature

Sample code	Hardener	$K_c(\mathrm{MN\,m^{-3/2}})$	$G_c(\mathrm{kJ\,m^{-2}})$
Pure resin TGDDM	DDS	0.5	0.1
Pure resin TGDDM	IPDA	0.40	0.1
TGDDM–PB-g-SA	IPDA	0.40	0.1

in Table III also show that the fracture toughness of TGDDM remains practically unchanged when PB-g-SA is added. The reason for this lack of toughening effect can be ascribed to the fact that the TGDDM resin is tightly cross-linked. In fact, when the cross-link density increases, the resin becomes more brittle and therefore its capacity to deform by shear yielding, which represents the principal mechanism to toughen thermosetting materials, is highly reduced. Consequently the contribution of the rubbery particles to enhance fracture toughness by promoting localized shear yielding in the matrix turns out to be very low. A close examination of the fractured surfaces of TGDDM (Fig. 7a) and TGDDM–PB-g-SA blend (Fig. 7b) effectively reveals that the yielding process of such materials is highly constrained.

Therefore for a tetrafunctional epoxy resin like TGDDM the conventional rubber-toughening procedure, which is effective for difunctional resins, does not achieve the desired result owing to the lack of ductility of the TGDDM. Currently an attempt to toughen tetrafunctional epoxy resins by using high-performance ductile thermoplastics as modifiers is under way in our Institute.

4. Conclusions

From our studies on the rubber-modification of bifunctional and tetrafunctional epoxy matrices by means of rubbers alternative to those normally emloyed in the literature, some relevant conclusions can be drawn:

1. The mechanism of fracture of bifunctional resins can be positively influenced by the addition of anhydride-grafted polybutene or PDMSO-co-PEO. On the other hand, for a tetrafunctional epoxy resin like TGDDM the same elastomer does not produce any improvement in the impact properties, owing to the lack of ductility of TGDDM.
2. The chemical reaction between elastomer and matrix DGEBA polymer must occur before the start of network formation in order to achieve the best morphological development of a disperse rubbery phase. This explain why PB-g-SA works better than PDMSO-co-PEO.
3. The modified polybutene employed, although interesting from the point of view of thermal and photo-oxidative stability, does not produce the effects reported in the literature for carboxy- or amine-terminated butadiene-co-acrylonitrile elastomers on the mechanical properties of epoxy matrices. We believe that this is mainly due to the low solubility of the polybutene in the base resin, even after chemical reaction with the epoxy matrix.

Acknowledgement

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