

Adhesive Properties of Epoxy Resin Modified by End-Functionalized Liquid Polybutadiene

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ABSTRACT: Adhesive properties of epoxy resin networks modified with different functionalized liquid polybutadiene were evaluated by using aluminum adherent. The end-functionalized polybutadiene rubbers were hydroxyl- (HTPB), carboxyl- (CTPB), and isocyanate-terminated polybutadiene (NCOTPB). The adhesive properties depend upon the morphology and the degree of interaction between the rubber-epoxy system. The most effective adhesive for Al–Al joint in both butt and single-lap shear testing was epoxy resin–NCOTPB system. This system presents stronger rubber-epoxy interactions and a higher degree of rubber particle dispersion with particle size diameter in the nanoscale

range. These characteristics were not important for improving the toughness of the bulk network but are fundamental for the improvement of adhesive strength. The effect of the pretreatment of the aluminum surface on the roughness was also evaluated by using profilometry analysis. The type of failure was also investigated by analyzing the adhered surfaces after fracture by scanning electron microscopy and profilometry. A proportion of cohesion failure higher than 90% was observed in all systems. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2370–2378, 2004

Key words: adhesives; compatibilization; thermosets

INTRODUCTION

Epoxy resins are one of the most widely used as a polymeric structural adhesive due to its technical versatility, good wetting ability, chemical resistance, and superior adhesive strength.¹ However, the high degree of crosslinking makes epoxy resin a brittle material, with weak peeling and impact strength, which limit their applications. An improvement of the adhesive strength can be achieved by using flexibilizers and/or toughening agents.^{2–3} The flexibilizer presents the disadvantage of reducing the bulk properties such as modulus and glass-transition temperature. The addition of suitable reactive rubbers constitutes one of the most promising ways to produce high-performance adhesives with optimum mechanical, thermal, and chemical properties.² For example, epoxy resins modified with carboxyl-terminated acrylonitrile-butadiene copolymer (CTBN),^{4–6} acrylate-based liquid rubber,⁷ and natural rubber grafted with poly(methyl methacrylate)⁸ were reported to present significant

improvement of adhesion properties. It is generally accepted that the improvement of impact and adhesive strength is due to the formation of two-phase morphology during the curing process by the controlled precipitation of rubbery particles from the initially compatible thermoset-elastomer mixture.⁹

In earlier investigations, liquid polybutadiene functionalized with different groups was used as modifier agents for epoxy networks.^{10–11} Polybutadiene is highly incompatible with epoxy matrix because of the difference in solubility parameters. However, its functionalization with suitable groups, such as carboxyl or isocyanate groups, increases the compatibility with the epoxy matrix because of the increase of interfacial adhesion promoted by chemical reactions between the reactive groups in both phases. Consequently, more uniform rubber phase dispersion with very small particle size was achieved, resulting also in better mechanical performance.

The aim of the present work was to examine the effect of the different end-functionalized liquid polybutadienes on the adhesive properties of epoxy resin in aluminum substrates. The adhesion performance of the modified epoxy resin was evaluated in terms of tensile properties by using both butt joint and single-lap shear configurations. A qualitative and quantitative evaluation of the type of failure in the adhesive joints was also performed by using both scanning electron microscopy and profilometry analyses.

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EXPERIMENTAL

Materials

The epoxy resin (ER) was a diglycidyl ether of bisphenol-A type (Shell Chemical Co., USA, EPON 828) with an epoxide equivalent of 192 g/equiv. The cure agent was a mixture of diethylenetriamine and triethylenetetramine (Shell Chemical Co., EPICURE 3140) with a number of amine groups corresponding to 378 g/equiv. Hydroxyl-terminated liquid polybutadiene (HTPB; trade name: Liquiflex H, Petroflex Ind. Com. S.A., Brazil) presents a number-averaged molecular weight (M_n) of 3000 and a hydroxyl number of 0.8 g/mequiv.

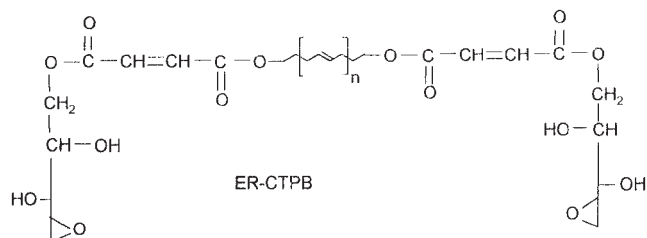
Carboxyl-terminated polybutadiene (CTPB) was an in-house product prepared by reacting HTPB with maleic anhydride, in a stoichiometric epoxy/anhydride molar ratio, as reported elsewhere.¹¹

Isocyanate-terminated polybutadiene (NCOTPB) was another in-house product prepared by reacting HTPB with a small excess (around 10%) of toluene diisocyanate (TDI) related to the amount of OH groups in the HTPB, in the presence of dibutyl tin dilaurate as a catalyst, as reported elsewhere.¹⁰

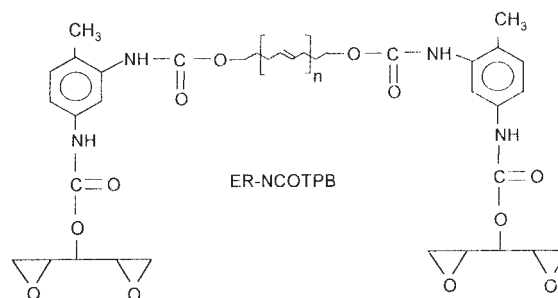
Modification and curing procedure of epoxy resin

All network polymers were prepared from stoichiometric mixtures of the ER and the hardener. Epoxy modified with HTPB (ER-HTPB) was prepared by mixing both components previously degassed for 60 min in a vacuum oven at 80°C. Then, the hardener was added and gently stirred for about 5 min to ensure proper dispersion of the hardener. The resulting mixture was degassed for 10 min, cast into molds, and cured at 100°C for 120 min.

Epoxy networks modified with CTPB (ER-CTPB) were prepared by pre-reacting the epoxy resin with different amounts of CTPB (5, 10, and 15 wt %) by using triphenyl phosphine (0.2 wt %) as a catalyst. The reaction was carried out at 80°C under nitrogen atmosphere for 24 h. During the process of pre-reaction, the carboxyl groups of CTPB react with the epoxy groups to produce the epoxy end-capped CTPB (Scheme 1).



Scheme 1 Structure of the reaction product between CTPB and epoxy resin.



Scheme 2 Structure of the reaction product between NCOTPB and epoxy resin.

After the pre-reaction, the hardener was added and the mixture was cast into molds and cured at 100°C for 120 min.

Epoxy networks modified with NCOTPB (ER-NCOTPB) were prepared by pre-reacting the epoxy resin with different amounts of NCOTPB (5, 10, and 15 wt %) by using dibutyl tin dilaurate as a catalyst, at 80°C for 120 min. During the process of pre-reaction, the isocyanate groups of NCOTPB react with the hydroxyl groups of the epoxy resin to produce the epoxy end-capped NCOTPB (Scheme 2). After the pre-reaction, the hardener was added and the curing process was performed as before.

Aluminum surface treatment

Aluminum alloy (2024T6) was used as substrate for measurement of Al–Al butt joint strength and single lap shear strength. The surface was submitted to mechanical and chemical treatments:

Mechanical treatment: The surface was roughened by using a glass microsphere-blast, washed with acetone in a ultrasonic bath for 5 min, and then washed with distilled water.

Chemical treatment: The surface previously treated by mechanical abrasion technique was submitted to chemical treatment, which consisted of the following steps:

1. The cleaned aluminum adherent was dipped into a water solution containing 38% $\text{Na}_2\text{B}_4\text{O}_7$, 12% Na_3PO_4 , and 50% water, for 5 min. After dipping, the substrate was washed with water for 5 min and preheated in an oven at 70°C for 5 min.
2. The surface was then dipped in a solution containing 155 mL H_2SO_4 , 112 g $\text{Fe}_2(\text{SO}_4)_3$, and 750 mL water at 65°C for 10 min. The chemically treated substrate was finally washed three times with distilled and deionized water for 5 min, dried in a forced air for 5 min, and stored in a dry camera.

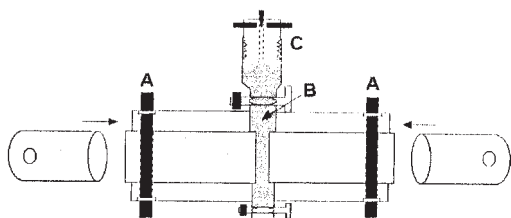


Figure 1 Homemade device used for the preparation of butt joints.

Preparation of adhesion test samples

The butt joints were prepared in a homemade device consisting of a Teflon cylinder containing a funnel with stop-cock for entrance of the adhesive, as illustrated in Figure 1. Two aluminum cylinders 12 mm in diameter and the surface previously treated were introduced into the mold, separated by a distance controlled by the two removable screws A. The thickness of the adhesive corresponds to the distance between the two substrates. The mold containing the aluminum substrates was put into an oven at 70°C for 10 min. Then, the air of the adhesion camera (B) was withdrawn by vacuum and the adhesive formulation was introduced into the camera with the help of a piston (C) located in the upper part of the mold, to completely fill the space between the substrates. The curing process was carried out by introducing the whole device in an oven at 100°C for 120 min. In all butt joints, the thickness of the adhesive corresponded to 0.01 mm.

For the single-lap shear joints, aluminum plates of 120 × 25 mm and a thickness of 1.8 mm were employed. The adhesive formulation was applied uniformly to both the surface portions of the adherent surface. The coating surface length corresponds to 25 mm. Curing was carried out in a hot-air oven at 100°C for 120 min by applying a pressure of ~ 0.5 MPa over the bonded specimens by using a lever press assem-

bly. The thickness of the adhesives in this lap shear testing corresponded to 0.03 ± 0.005 mm.

Testing of the bulk epoxy network

Flexural tests were performed by using an Instron 4204 testing machine fitted with a three-point bending fixture at a crosshead speed of 1 mm/min, according to ASTM D-790. The dimensions of the specimens were 75 × 25 × 2 mm and the span to thickness ratio was set at $L/D = 32$ in all cases. The values were taken from an average of at least five specimens.

The tensile tests were also performed in an Instron 4204 testing machine at a crosshead speed of 1 mm/min, according to ASTM D-638. The values were taken from an average of at least five specimens.

The impact strength of the notched specimens was determined in a Charpy Monsanto tensiometer, using rectangular specimens of 50 × 10 × 5 mm, according to ASTM D-256. The tests were carried out at room temperature and the values were taken from an average of at least 10 specimens.

Testing of the adhesive joints

The adhesive strength of the butt joints was determined in an Instron 4204 testing machine at a crosshead speed of 0.5 mm/min, according to ASTM D-2095 for cylindrical substrates.

The adhesive strength of the single lap shear joints was measured at the same conditions of the butt joint measurement, according to ASTM D-1002. All adhesion tests were carried out at room temperature and the values were taken from an average of at least 10 specimens.

Characterization of the adherent and adhesive surfaces

The wetting ability of the adhesive formulations on the aluminum surface was determined by measuring

TABLE I
Mechanical Properties of the Bulk Epoxy Networks Modified with Different End-Functionalized Polybutadiene

ER (%)	HTPB (%)	CTPB (%)	NCOTPB (%)	Impact strength (J/m ²)	Flexural yield stress (MPa)	Flexural modulus (MPa)	Tensile yield stress (MPa)
100	0	0	0	9.7 ± 0.4	83.8 ± 0.3	2536	54.3 ± 5.4
95	5	0	0	11.4 ± 0.4	72.0 ± 0.1	2385	50.2 ± 4.2
90	10	0	0	14.2 ± 0.4	62.2 ± 0.1	1912	50.4 ± 2.3
85	15	0	0	11.2 ± 0.4	60.0 ± 0.2	1860	46.0 ± 5.0
95	0	5	0	11.5 ± 0.3	92.0 ± 0.2	2350	90.4 ± 1.7
90	0	10	0	16.1 ± 0.4	82.0 ± 0.1	2300	84.1 ± 0.7
85	0	15	0	13.7 ± 0.3	66.0 ± 0.4	2166	63.5 ± 3.0
95	0	0	5	13.6 ± 0.3	67.0 ± 0.2	1753	70.0 ± 7.0
90	0	0	10	15.3 ± 0.4	70.0 ± 0.1	1776	52.6 ± 1.5
85	0	0	15	9.0 ± 0.9	62.3 ± 0.3	1523	45.0 ± 2.3

the contact angle between the adhesive drop and the aluminum surface. The measurements were performed in a Goniometer Ramé-Hart NRL, equipped with RHI 2001 imaging software, at 25°C and relative humidity of 45%. The values were taken from three analyses, performed in a period between 180 and 210 s.

Surface roughness parameters of the butt substrate and the adhesive joint after fracture were determined by using a Taylor Hobson profilometer with a 2 μm diameter stylus tip.

Scanning electron microscopy

The SEM micrographs of the bulk epoxy networks were obtained on a JEOL JSM-5610LV SEM with an electron voltage of 15 kV and secondary electron detector. The surface from the impact test was coated with a thin layer of gold before analyzing.

The SEM micrographs of the fracture surface of the adhesive joints were obtained by using backscattered electron and EDS detectors. The surface was coated with a thin layer of gold.

RESULTS AND DISCUSSION

Properties of the bulk epoxy networks

The impact strength, flexural and tensile properties of the bulk epoxy network modified with different end functionalized liquid polybutadiene rubbers are summarized in Table I. Except that containing 15% of NCOTPB, all other modified epoxy networks exhibit higher impact resistance than nonmodified ER. The best performance was normally achieved with 10% of rubber in all cases. Concerning the different epoxy-rubber systems, that corresponding to ER-CTPB network presented the best impact resistance and also the best tensile and flexural properties.

This different mechanical behavior was attributed to differences in the degree of dispersion of the rubber phase. As illustrated in Figure 2, ER-HTPB network displays wide particle size distribution, with large particle size diameters, in the range of 11–32 μm . ER-CTPB network is also heterogeneous but displays a more uniform rubber particle size distribution with small diameter, in the range of 0.5 to 3.0 μm . ER-NCOTPB network is visually transparent and homogeneous, indicating a single-phase system. In this case, the particle size is too small to be scattered by the light or detected by SEM. This feature was confirmed by atomic force microscopy, as previously reported.¹²

The best mechanical performance of ER-CTPB is related to the characteristic morphology with small rubber particle size homogeneously distributed in the

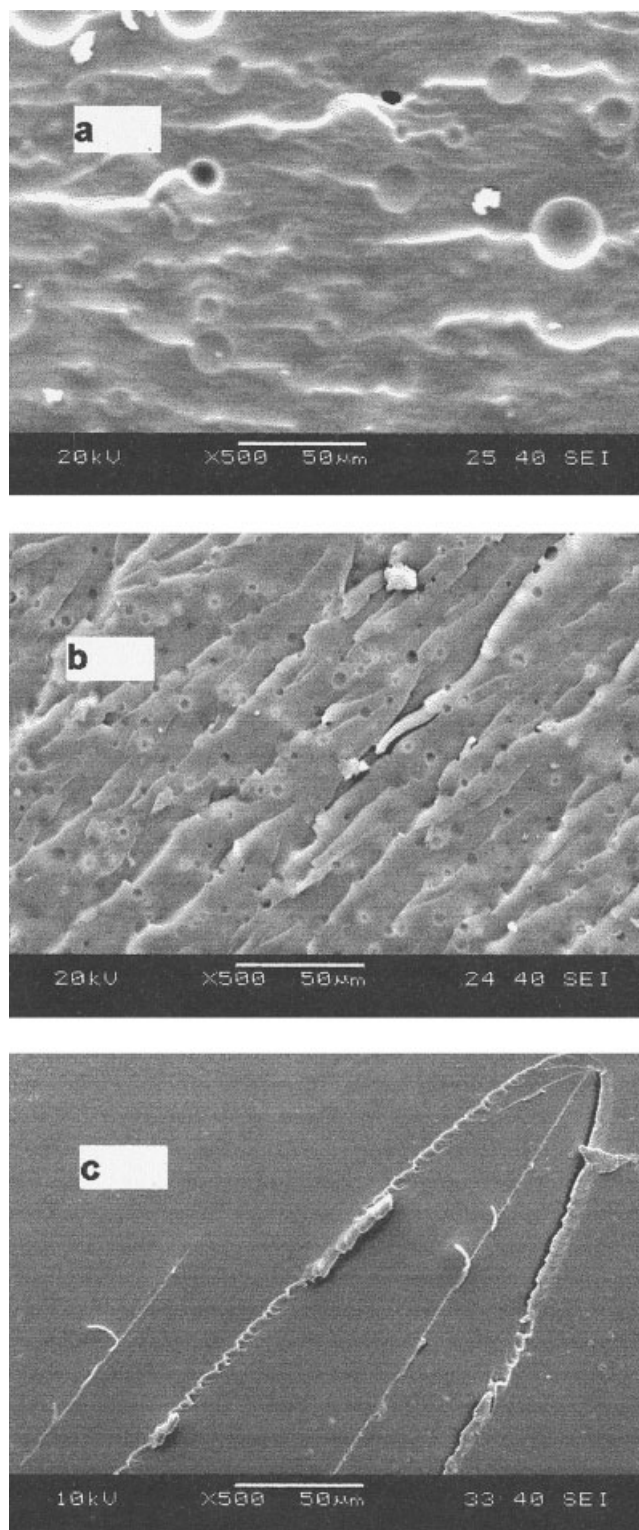


Figure 2 SEM micrographs of the bulk epoxy networks: (a) ER-HTPB, (b) ER-CTPB; and (c) ER-NCOTPB.

epoxy matrix and well adhered on it. In the case of ER-NCOTPB, the particles are also well adhered into the matrix but the particle sizes are too small to exert an effective toughening effect.

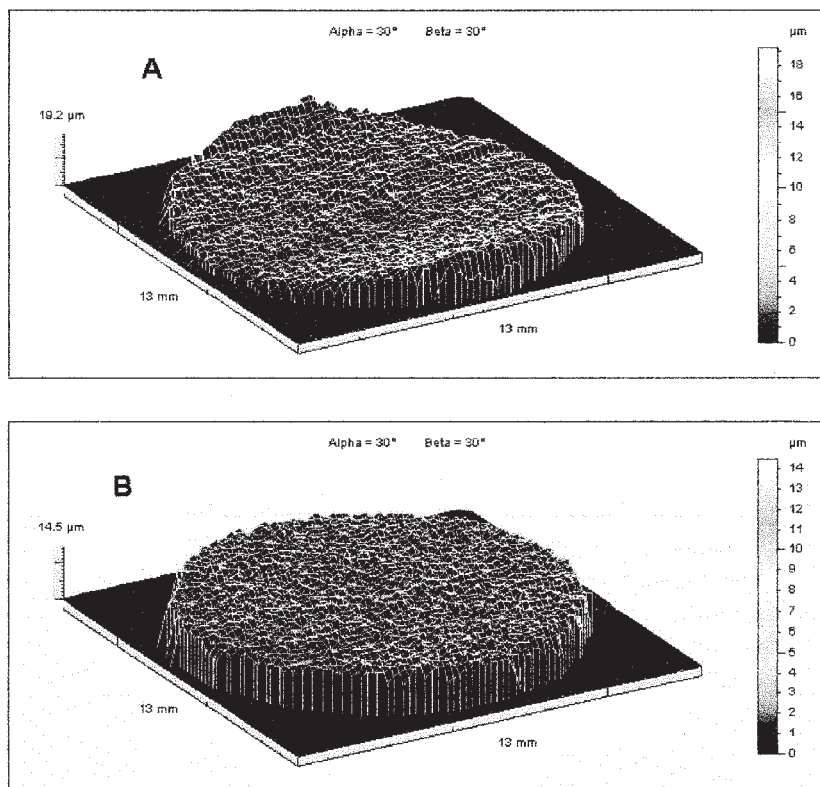


Figure 3 Profilometer images of the roughened aluminum surfaces submitted to (a) mechanical abrasion treatment and (b) mechanical and chemical treatment.

Characterization of aluminum surface

The metal surface pretreatment is of fundamental importance to provide a good surface to which the resin can strongly adhere.^{13–14} In this work, the aluminum surface of the substrates was first submitted to a mechanical abrasion technique, using glass microspheres, to remove any weak oxide layer. In a second stage, a chemical treatment was performed to create macro- and microdepressions that act as very good mechanical interlocking sites. In addition, this treatment gives rise to a chemically active surface to enable formation of chemical bonds between the adherent surface atoms and the compounds constituting the adhesive.⁶

Figure 3 compares the roughened surface images of the butt substrate, taken from the profilometer analysis. It can be seen that the subsequent chemical treatment is very important to provide a more uniformly roughened surface without significant waviness, as that observed in the surface submitted to a single mechanical treatment. A quantitative view of these surfaces is given in Table II, in terms of profile and area surface texture parameters. The last data give a better idea about the whole surface and are employed more and more to characterize a roughened surface.¹⁵ The mechanically/chemically treated substrate presented an average value of surface amplitude ($S_a = 0.67 \mu\text{m}$), less than that observed for the nonchemi-

cally treated substrate, suggesting a lower surface roughness of the former. The peak-to-valley parameter value ($St = 14.5 \mu\text{m}$) of the mechanically/chemically treated substrate is also lower, indicating a better homogeneity of the surface, as also observed in Figure 3(b).

An important parameter in the study of surface roughness is the skew parameter (S_{sk}), which is a measurement of density of peaks and valleys along the surface.¹⁵ The negative value of S_{sk} observed in the mechanically/chemically treated surface ($S_{sk} = -2.71 \mu\text{m}$) suggests that the density of valleys is

TABLE II
Profile and Area Surface Texture Parameters of Aluminum Surface Obtained from Profilometry Analysis

Parameters	Profile parameters (μm)		Area surface texture parameters (μm)		
	A	B	Parameters	A	B
Ra	0.18	0.16	Sa	2.50	0.63
Rq	0.28	0.30	Sq	3.19	0.91
Rt	1.36	3.40	St	19.20	14.50
Rsk	-0.29	2.57	Ssk	1.06	-2.71
Rz	0.62	0.52	Sz	19.20	14.50

(A) Mechanically treated aluminium surface; (B) mechanically/chemically treated aluminium surface.

TABLE III
Values of Contact Angle Measured Between a Drop of the Modified Noncured Epoxy Resin Deposited on the Aluminum Surface

Adhesive	Mechanically treated aluminum surface	Mechanically/chemically treated aluminium surface
ER	30	15
ER-HTPB	30	25
ER-CTPB	35	30
ER-NCOTPB	43	43

higher than peaks. This characteristic is very important for adhesive purposes because the liquid mixture containing the prepolymeric epoxy resin and the curing agent can penetrate into the cavities and pores, giving rise to a good adhesion by mechanical anchorage.

Besides mechanical anchorage, the adhesion promoted by chemical bond provides additional adhesion strength and gives more durability of the bonded joint or repair. The chemical affinity between adherent and adhesive is related to the wettability of the adhesive, which in turn can be estimated from measurements of the contact angle formed between the drop of the liquid phase deposited on a solid surface. Table III presents the values of contact angles measured when a drop of the modified noncured epoxy resin was deposited on the aluminum surface submitted to different treatment. The mechanically/chemically treated aluminum surface presented lower contact angle values, indicating an increase of wettability in these systems. The effect of the surface treatment was more pronounced when the pure epoxy resin was analyzed. This result suggests an increase of the metal surface polarity promoted by the chemical treatment.

The presence of liquid polybutadiene in the modified epoxy resin resulted in an increase of contact angle, which means a decrease of wettability. This phenomenon can be attributed not only to the decrease of affinity because of the nonpolar nature of the rubber component, but also to an increase of the viscosity of the liquid drop derived from the higher molecular weight of the polybutadiene component, related to the liquid epoxy prepolymer. Comparing

the modified epoxy resins, the contact angle increases in this order: ER-HTPB < ER-CTPB < ER-NCOTPB.

This result is somewhat intriguing because carboxyl and isocyanate groups provide an increase of polarity of the polybutadiene. According to previous work,¹² the different end groups in the polybutadiene rubber component result in different degrees of interactions between the epoxy matrix and the rubber particles, which also influence the degree of dispersion of the rubber particles (see Fig. 2). The morphological behavior associated with the different degrees of interactions between the epoxy–rubber components must influence the viscosity of the drop, resulting in unexpected contact angle results.

Evaluation of adhesive properties of modified epoxy networks

The adhesive properties were evaluated on aluminum–aluminum joints mechanically/chemically treated because of the more homogeneous roughness of this surface and because of the better wettability of the pure ER towards this treated surface. Regarding the modified resins, we have chosen those with 10% of liquid rubber because of the best impact and mechanical performance of this composition in bulk networks test (see Table I).

Table IV presents the adhesive properties of different epoxy systems obtained from butt joint test. ER-HTPB adhesive presented lower adhesion strength when compared to pure epoxy network. This behavior was also observed in tensile testing of the bulk networks. ER-CTPB adhesive presented little improvement on adhesive strength, whereas the ER-NCOTPB displayed a pronounced increase in ion adhesive strength. The toughness of this adhesive in butt joints, estimated from the area under the stress–strain curve, was also significantly improved. Figure 4 illustrates this behavior.

The adhesion ability of these modified epoxy networks was also evaluated in terms of lap shear strength, whose results are summarized in Table V. In this test, ER-HTPB also presented a decrease in tensile stress, whereas ER-CTPB displayed a little increase. In the last case, a pronounced deformation at break was observed, as better illustrated in Figure 5. Surprisingly, the adhesion strength of ER-NCOTPB in lap

TABLE IV
Adhesive Strength of Different Epoxy Systems Obtained from Butt Joint Test

Adhesive	Yield stress (MPa)	Elongation at break (%)	Young modulus (GPa)	Toughness (MPa)
ER	31.0 ± 6.7	0.7 ± 0.1	6.1 ± 0.4	0.14
ER-HTPB	26.0 ± 7.4	0.6 ± 0.1	6.4 ± 0.5	0.06
ER-CTPB	36.5 ± 2.4	0.7 ± 0.2	6.2 ± 0.3	0.12
ER-NCOTPB	50.0 ± 5.6	0.9 ± 0.1	6.2 ± 0.2	0.21

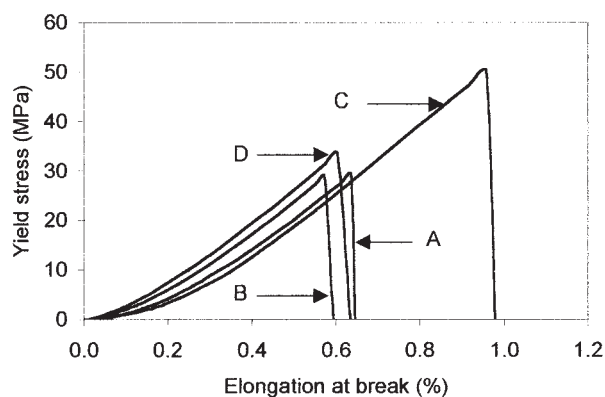


Figure 4 Stress–strain curves of (A) pure epoxy, (B) ER-HTPB, (C) ER-CTPB and (D) ER-NCOTPB adhesives in butt joints.

shear test was so strong that the fracture happened in the aluminum substrate plate and not through the adhesive layer.

The results obtained from testing on both joint configurations confirm the outstanding performance of ER-NCOTPB system as adhesive for aluminum–aluminum joints. The worst adhesion performance of ER-HTPB system is explained by the presence of large rubber particles, as observed in Figure 2. In addition, the HTPB particles are highly apolar and present weak interactions with the epoxy matrix. Such large nonadhered particles fail catastrophically during fracture, and hence, cause a diminution of adhesive properties.

In the ER-CTPB system, the rubber particles are well adhered to the epoxy matrix and present lower particle size with homogeneous distribution inside the matrix [see Fig. 2(b)]. These characteristics increase the toughness of the bulk network and also improve moderately the adhesion strength. In addition, the rubber phase contains some free carboxyl groups, which can exert some additional effect on the adhesion to metal surface.

The outstanding adhesion properties of the ER-NCOTPB system cannot be explained by an increase

TABLE V
Adhesive Strength of Different Epoxy Systems Obtained from Single Lap Shear Test

Adhesive	Load required to break (Ns)	Elongation at break (%)
ER	1100 ± 66	5.3 ± 0.5
ER-HTPB	1000 ± 71	5.4 ± 0.4
ER-CTPB	1200 ± 24	9.5 ± 0.8
ER-NCOTPB	1700 ± 24 ^a	10.0 ± 0.3 ^a

^a This value corresponds to the load to break the aluminum substrate plate, because the fracture did not happen through the adhesive layer.

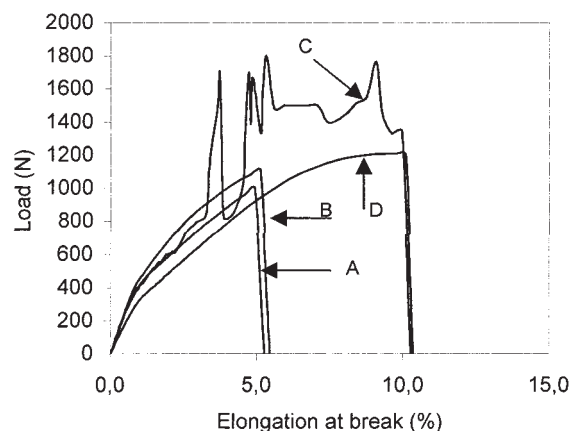


Figure 5 Stress–strain curves of (A) pure epoxy, (B) ER-HTPB, (C) ER-NCOTPB, and (D) ER-CTPB adhesives in single-lap shear joints.

in toughness of the cured network because the corresponding bulk crosslinked material presented lower impact resistance and tensile properties than ER-CTPB bulk network. However, this system presents the most homogeneous morphology among all modified epoxy resins studied in this work, with very small rubber particle size. The nonpolar rubber particles do not damage the adhesion ability of the epoxy matrix because they are present as nanoparticles. Because these particles are completely adhered to the epoxy matrix, there is no catastrophic fail during fracture. In addition, the urethane groups at the interface between epoxy and rubber cause this system to become more polar and can promote additional adhesion on the aluminum surface.

Inspection of the failure surface

The failure of the adhesive joint can occur inside the adhesive layer (cohesion failure—with adhesive residues on both surfaces) or at the interface between the adhesive layer and the adherent surface (adhesive failure), as illustrated in Figure 6. In this work, the type of failure was investigated by analyzing both surfaces of the butt joint after tensile fracture, using both profilometry and SEM analysis. Initially, the surfaces were analyzed by SEM microscopy by using backscattered electron detector, which can distinguish the regions containing atoms of different atomic number, as carbon and aluminum. The SEM micrographs of the fractured butt joints prepared with ER-CTPB



Figure 6 Types of failure in adhesive bonds.

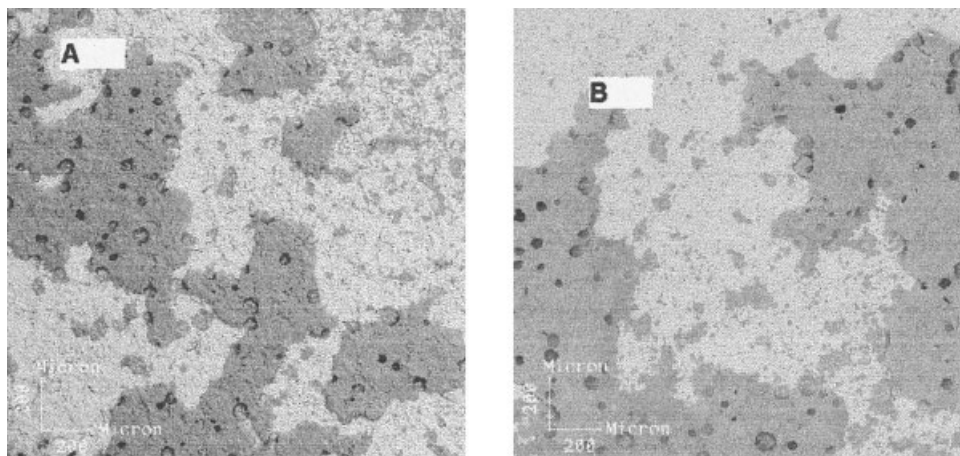


Figure 7 SEM micrographs of the fractured butt joints prepared with (a) ER-CTPB and (b) ER-NCOTPB.

and ER-NCOTPB are presented in Figure 7. The chemical composition of each region of the micrographs was determined by using an EDS detector, whose spectra are shown in Figure 8. The clear region corresponds basically to the aluminum surface and the darker region, containing predominantly carbon, is related to the epoxy adhesive layer. The presence of clear region indicates adhesion failure and the dark region indicates cohesion failure.

The adhesive failure region corresponds to the lowest depression region in the profilometry image. Thus, the proportion of the cohesion failure was considered to be all regions with some elevation. These results are summarized in Table VI. In all cases, a proportion of cohesion failure higher than 90% was observed, indicating good metal–epoxy adhesion. The modified epoxy adhesives resulted in a higher proportion of cohesion failure. The ER-NCOTPB, which has provided the best results in terms of adhesion strength, resulted in a lower amount of cohesion failure. The difference is not significant but suggests some problem during the joint preparation, probably because of the higher viscosity of this adhesive formulation.

CONCLUSION

Epoxy resins modified with different end-functionalized liquid polybutadienes present different adhesive

properties, which depend upon the morphology and the degree of interactions between the rubber particles and the epoxy matrix. ER-HTPB, which presents weak rubber–epoxy interactions and large rubber particle size, was ineffective in improving both adhesive properties and mechanical bulk properties, as expected. ER-CTPB presents a good rubber–epoxy interaction promoted by chemical reactions between carboxyl groups of rubber and epoxy groups of the matrix and also a two-phase morphology with small rubber particle size, which is normally claimed for good toughness. These characteristics resulted in a substantial improvement of bulk properties, as expected, but only marginal increase in adhesive strength.

The most effective adhesive for Al–Al joint in both butt and single-lap shear testing was the ER-NCOTPB system. This system presents a stronger rubber–epoxy interaction promoted by the reaction between isocyanate groups of the rubber and hydroxyl groups of the epoxy matrix, as previously reported.¹⁵ Such interactions result in a high degree of rubber particle dispersion with particle size diameter in the nanoscale range, giving rise to transparent material. These characteristics were not important for improving the toughness of the bulk network but are fundamental for the improvement of adhesive strength. Another important feature of this system is that, despite the increase in adhesive toughness, this material presents a glass-

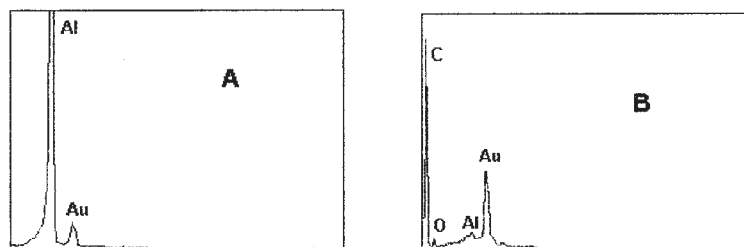


Figure 8 EDS spectra of (A) clear region and (B) dark region observed in SEM micrograph.

TABLE VI
Percentage of Cohesion Failure in the Fractured Butt
Joints as a Function of the Adhesive

Adhesive	Cohesion failure (%)
ER	92
ER-HTPB	97
ER-CTPB	97
ER-NCOTPB	94

transition temperature similar to the neat epoxy network.¹¹ All these results make ER-NCOTPB a very promising structural adhesive because of its outstanding adhesive performance and transparency without reduction of the glass-transition temperature.

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