

# Influence of Aliphatic Amine Epoxy Hardener on the Adhesive Properties of Blends of Mono-Carboxyl-terminated poly(2-ethylhexyl acrylate-co-methyl methacrylate) with Epoxy Resin

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**ABSTRACT:** The adhesive properties have been investigated in blends of mono-carboxyl-terminated poly(2-ethylhexyl acrylate-co-methyl methacrylate) with diglycidyl ether of bisphenol A and three different aliphatic amine epoxy hardener. The adhesives properties are evaluated in steel alloy substrate using single-lap shear test. The copolymers are initially miscible in the stoichiometric blends of epoxy resin and hardener at room temperature. Phase separation is noted in the course of the polymerization reaction. Different morphologies are obtained accord-

ing to the amine epoxy hardener. The most effective adhesive for steel-steel joints in single-lap shear test is the blends using 1-(2-aminoethyl)piperazine (AEP) as hardener. This system shows the biggest lap shear strength. However, the modified adhesives show a reduction in the mechanical resistance. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2762–2770, 2010

**Key words:** epoxy adhesive; aliphatic amine; lap shear; cohesive fracture; cavitation

## INTRODUCTION

Epoxy resins are some of the most important thermosetting polymers used for many applications like coatings, adhesives, insulation, and matrixes for composite materials because of good engineering properties. One major drawback is their poor resistance to impact and crack initiation. The fracture resistance of the epoxy network can be improved by using different types of modifiers.<sup>1</sup> Another possibility is to change the structure of the epoxy resin<sup>2–6</sup> or on the amine co-monomer.<sup>7–9</sup>

Liquid rubber-epoxy systems have been widely studied over 30 years ago. The aim is to increase the toughness of epoxy thermoset with a disperse rubber rich phase.<sup>1</sup> Particular attention had received reactive oligomeric compounds, such as carboxyl and

amino terminated butadiene-acrylonitrile with low molecular weight. Examples of these compounds include: statistical copolymers, telechelic acrylate copolymers and terpolymers, amine terminated polysiloxanes, and extended chain carboxyl-terminated perfluoro polyethers.<sup>10</sup> The liquid rubber that has received the most attention involves carboxyl-terminated butadiene-acrylonitrile (CTBN) liquid polymers.

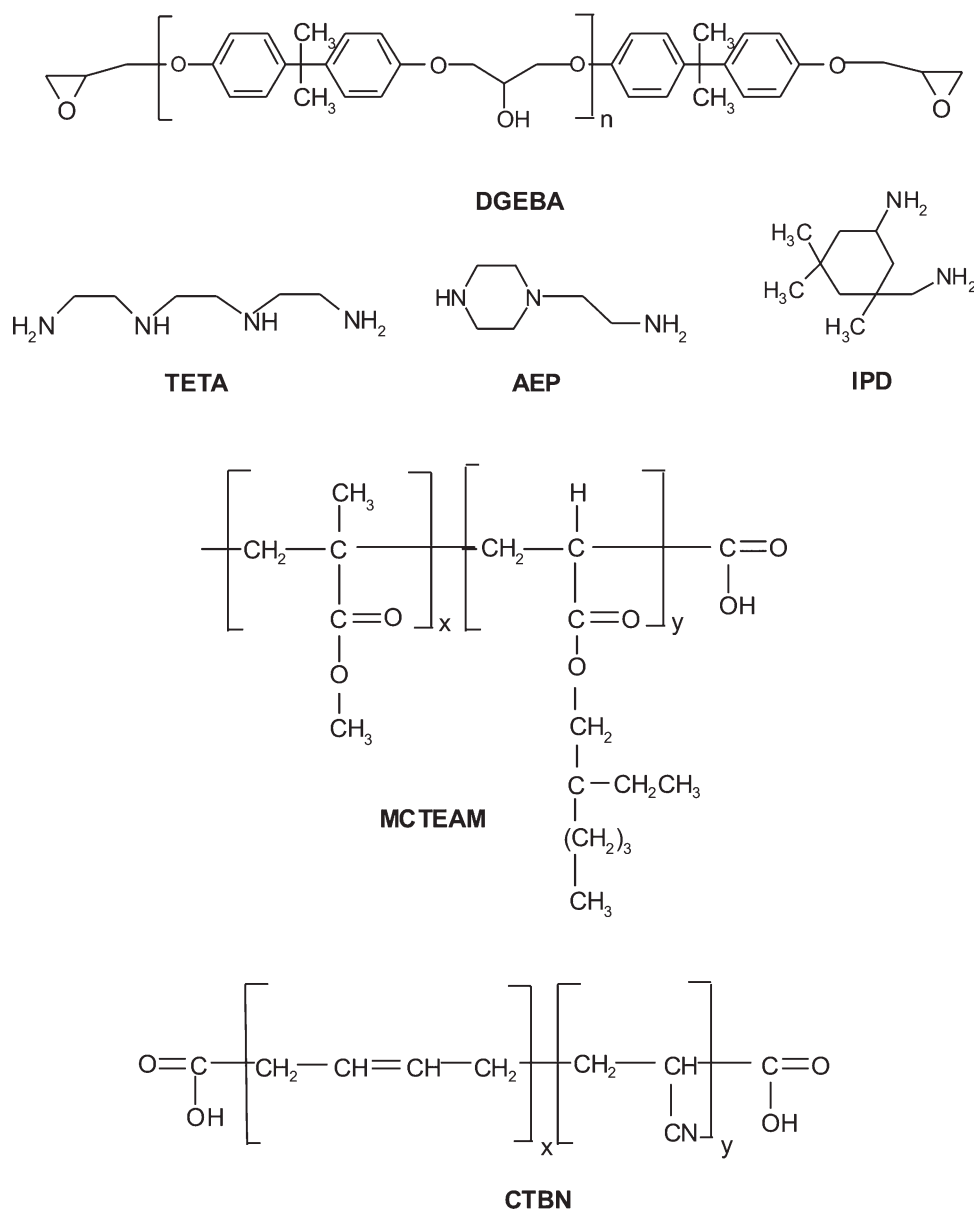
Recently, the adhesion behavior in blends of mono-carboxyl-terminated poly(2-ethylhexyl acrylate-co-methyl methacrylate) random copolymers (MCTEAM) with diglycidyl ether of bisphenol A (DGEBA), and TETA is evaluated as a function of the composition and concentration of the copolymer in steel alloy adherent.<sup>11</sup> In those copolymers, a phase-separation phenomenon induced by a polymerization reaction takes place. As expect, the size of the dispersed phase depends on the composition and the modifier concentration. The copolymer with 60% molar of methyl methacrylate showed the best adhesive properties. This behavior was related to the small average size of copolymer particle (5.0  $\mu\text{m}$ ) homogeneously distributed in the thermoset matrix.

In this way, the use of different aliphatic amine epoxy hardener on the adhesive properties of blends of mono-carboxyl-terminated poly(2-

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**Figure 1** Structure formulae, DGEBA, diglycidyl ether of bisphenol A; TETA, triethylenetetramine; AEP, 1-(2-aminoethyl) piperazine; IPD, isophorone diamine; MCTEAM, mono-carboxyl-terminated poly(2-ethylhexyl acrylate-*co*-methyl methacrylate; CTBN, carboxyl-terminated poly(butadiene)-*co*-poly(acrylonitrile).

ethylhexyl acrylate-*co*-methyl methacrylate) and epoxy resin is investigated. In our work, a random copolymer (60% molar of methyl methacrylate) (MCTEAM) and DGEBA are employed. The adhesive performance was evaluated in terms of tensile properties by using single-lap shear test. As previously demonstrated, the epoxy amine hardener affect both the miscibility during polymerization reaction and the reaction rate and consequently leads to different morphologies.<sup>12</sup>

In this study, three chemical structures of linear and cyclic aliphatic amine epoxy hardener, triethylenetetramine (TETA), 1-(2-aminoethyl)piperazine (AEP), and isophorone diamine (IPD) were select.

The epoxy/amine systems were characterized by rheological analyses aiming to investigate the influence of the hardener on the polymerization reaction. The metallic adherent surfaces were submitted to different treatments to investigate its influence on the adhesion behavior.

## EXPERIMENTAL

### Materials

Diglycidyl ether of bisphenol A (DGEBA, DER 331), supplied by Dow Chemical of Brazil S.A., with epoxy equivalent weight of 187 g eq<sup>-1</sup> determined by

**TABLE I**  
**Micro-Elemental Composition of Steel Adherent**  
**(Alloy A36)**

Element	C (%)	Mn (%)	P (%)	S (%)	Si (%)	Co (%)
Steel	0.041	0.162	0.008	0.009	0.001	0.006

acid titration,<sup>13</sup> was used as an epoxy prepolymer. Triethylenetetramine (TETA, DEH 24, from Dow Chemical of Brazil S.A.), 1-(2-aminoethyl)piperazine (AEP, from ACROS, São Paulo, Brazil), and isophorone diamine (IPD, from ACROS, São Paulo, Brazil) were used as epoxy amine hardeners, with amine hydrogen equivalent weight of 30.0, 43.0, and 42.5 g eq<sup>-1</sup>, respectively determined by potentiometric titration in aqueous media.<sup>14</sup>

Mono-carboxyl-terminated poly(2-ethylhexyl acrylate-*co*-methyl methacrylate) random copolymer with an average molecular weight number close to  $3.6 \times 10^3$ , 60% (molar) of methyl methacrylate,  $T_g = -28^\circ\text{C}$  and 0.9 eq g<sup>-1</sup> carboxyl groups content was selected as modifier. The synthesis and characterization of this copolymer have been recently described.<sup>15</sup> Carboxyl-terminated poly(butadiene-*co*-acrylonitrile) (CTBN, Aldrich, São Paulo, Brazil) random copolymer with an average molecular weight number  $3.5 \times 10^3$ , with 15 to 20% (weight) acrylonitrile content,  $T_g = -52^\circ\text{C}$  and 1.8 eq g<sup>-1</sup> average carboxyl functionality was also selected as modifier for comparative purposes. 1,1,1-trichloroethylene was used as analytical grade solvent. Figure 1 illustrates the structural formulae of the epoxy prepolymer, the epoxy amine hardeners, and the modifiers polymers.

### Modification of epoxy resin

Epoxy prepolymer was prereacted with each copolymer separately using a concentration of 10 phr (10 g of copolymer per 100 g of DGEBA) before curing. Epoxy resin (120 g) was prereacted with 12 g of copolymers by stirring in the presence of 0.18% by weight of triphenylphosphine. The reaction was carried out at 80°C under nitrogen atmosphere for 24 h. Afterward, the modified epoxy resin was degassed in a vacuum oven during 2 h at 80°C. The epoxy equivalent weight of the modified resins was determined by titration.<sup>13</sup> The unmodified and modified epoxy resins were cured by adding epoxy amine hardener in a stoichiometric amount (amino hydrogen equivalent weight to epoxide equivalent weight equal to 1). The cure schedule for each epoxy network was described previously.<sup>16</sup>

### Thermal analysis

Differential scanning calorimetry (Shimadzu, model DSC-60), was used to determine the glass transition

temperature ( $T_g$ ) of the cured unmodified and modified epoxy resins under nitrogen purge (samples with  $15 \pm 2$  mg), during a heating rate at  $10^\circ\text{C min}^{-1}$ .  $T_g$  was taken as the temperature corresponding to the middle of heat capacity base-line change.

### Rheological analysis

The rheological characterization of the epoxy/amine blends was carried out by using parallel plates of 25 diameter mm and thickness of 0.5 mm (Rheometer Anton Paar-Physica MCR 301; Germany). The rheological analyses was accomplished at isothermal conditions ( $40^\circ\text{C}$ ) using a constant oscillatory frequency of 1 Hz and tension of 100 Pa. The viscoelastic properties of the adhesives was monitored from measurements of the complex dynamic viscosity ( $\eta^*$ ), of the storage module ( $G'$ ), and the loss module ( $G''$ ).

### Steel surface treatment

Low-carbon alloy steel (alloy A36) was used as adherent for measurement of steel-steel joints using single-lap shear tests. The micro-chemical composition is listed in Table I. Before application of epoxy adhesive, the metallic adherent surfaces was submitted to solvent wiping, steel-grit abrasion, and chemical treatment.

#### Solvent wiping

1,1,1-trichloroethylene was used to degrease the adherent surfaces.

#### Steel-grit abrasion

The metallic surface was treated with dry abrasive jet with a pressure of  $6.5 \text{ kg cm}^{-2}$  using three types of steel-grit G80 (in the range of 0.125–0.180 mm), G40 (in the range of 0.300–0.425 mm) and G25 (in the range of 0.425–0.710 mm). Surfaces with different roughness were obtained by using various steel-grit abrasion. Subsequent to the abrasive treatment, the surface was dried with air.

#### Chemical treatment

The surface previously treated by steel-grit abrasion technique was submitted to chemical treatment, according to ASTM D 2651.<sup>17</sup> The surfaces were submerged by 5 min in acid solution ( $\text{HNO}_3$  5% v/v,  $\text{H}_3\text{PO}_4$  30% v/v and distilled water 65% v/v). The surfaces were washed with distilled water by 5 min, with acetone and immediately dried in flow air. The treated surfaces were kept in dry camera until joints preparation.

### Samples preparation and adhesion test

The adhesive properties were studied by single-lap shear test according to ASTM D 1002–01.<sup>18</sup> For the adhesive application, specific metallic mold was designed with the objective to control the thickness of the adhesive layer. After surface treatment, steel pieces (102 mm × 25 mm × 1.6 mm) were assembled into single-lap shear joints with adhesive area of 312.5 mm<sup>2</sup>. The applied contact pressure was always the same, which allows obtaining adhesive joints with the same uniform adhesive thickness, 0.18 ± 0.02 mm. To reduce the deviation of the adhesive layer respect to the tensile axis, chocks in the extremes of the samples in the lap shear tests were used. Before any test, the samples were stored at room temperature (22 ± 2°C) and relative humidity of 50 ± 5% during 48 h.

Single-lap shear strength was measured at room temperature after post-curing in a universal testing machine (Shimadzu Autograph AG-100) under a 100 kN load cell, with a crosshead speed of 1.27 mm min<sup>-1</sup>. The lap shear strength is expressed in MPa. All tests were carried out at 22 ± 2°C and relative humidity of 50 ± 5%. The values were taken from an average of at least 10 samples.

### Characterization of the adherent and epoxy resin surface

The wetting ability of the unmodified epoxy resin (without hardener) on steel surface was determined by measuring the contact angle between the unmodified epoxy resin drop and the steel surface treated. The measurements were performed in a Goniometer Ramé-Hart NRL, equipped with imaging software (RHI 2001), at 22.5°C and relative humidity of 45%. The values were taken from three analyses using drop of 0.04 ± 0.001 mm of radio (on time zero), performed in a period range of 0 to 120 s.

Surface roughness of the steel was determined by using tridimensional profilometer (Taylor Hobson Talyscan 150), equipped with a 2 μm diameter stylus tip. According to the protocol ISO 4288,<sup>19</sup> a scanning speed of 1000 μm s<sup>-1</sup> with reading data in the longitudinal direction using spacing of 1 μm in 1 μm was used. The same procedure was employed in intervals of 10 μm in 10 μm in the traverse direction. The measurements were carried out at 23°C and relative humidity of 50% and the Ra, Rt and Rsk parameters were determined.

### Scanning electron microscopy

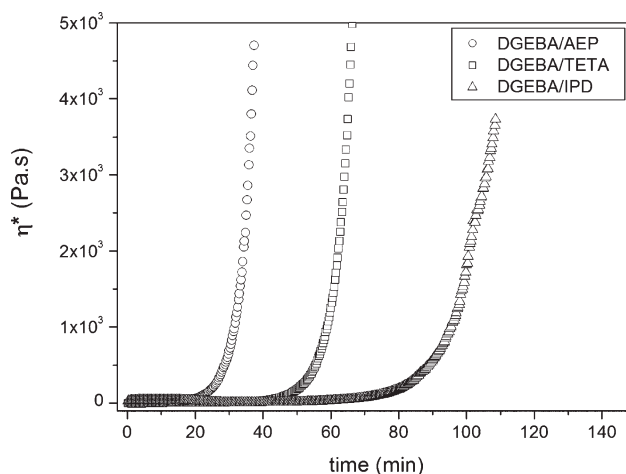
Small rectangular samples were broken and the surface fracture was coated with a thin layer of gold and then observed by scanning electron microscopy

(SEM), using a JEOL JSM-5610LV microscope. The SEM micrographies were obtained with an acceleration voltage between 5 and 15 kV and secondary electron detector. Five micrographies of each modified epoxy networks were considered. This analysis was represented by more than 400 particles of dispersed phase. The diameter of the each particle and the average diameter of polymer particles were determined using an image analyzer.

## RESULTS AND DISCUSSION

### Influence of aliphatic amine epoxy hardener on the polymerization reaction

Initially, the epoxy/amine systems based on three different cure agents was analyzed. Figure 2 presents the rheological analyses of the epoxy systems. Initially, the viscosity keeps constant while suddenly exponentially increases. This behavior is expected and can be attributed to the polymerization reaction. During polymerization, the conversion reaction increases and as a consequence improves functionality and reactivity. In this way, the growth of the molecules occurs in an unexpected way, giving place to the critical phenomenon known as gelation. This phenomenon comes from in only one molecule interconnected with the whole limit of the system. At this time, the viscosity increases to an infinite value ( $M_w$ ). During the polymerization, the material becomes elastic being constituted by a fraction insoluble denominated fraction gel and a soluble fraction. A simple complex dynamic viscosity ( $\eta^*$ ) measurements was not able to determine the exactly time where the gelation process occurs. However, 1-(2-aminoethyl)piperazine (AEP) reached the gelation in a shorter time while in the network based on



**Figure 2** Evolution of the complex dynamic viscosity ( $\eta^*$ ) as a function of reaction time at isothermal condition (40°C) for the DGEBA/AEP (o), DGEBA/TETA (□), DGEBA/IPD (Δ) systems.

isophorone diamina (IPD) the gelation occurred in a longer time. These statements are based on the complex viscosity evolution as a function of reaction time. The exponential increase in viscosity can be linked to what happens near to the gelation process.

The gelation phenomenon for the three epoxy systems can be explained by the different chemistry structures of these co-monomers which depend on the accessibility of the functional groups in the molecule, reactivity of the amine group and functionality. The 1-(2-aminoethyl)piperazine (AEP) manifested the gelation at shorter time. This molecule presents a combination of linear and cycloaliphatic structure, containing three active hydrogen atoms of the amine type (primary and secondary). The amine group presents relative accessibility for the chemical reaction. The TETA, which corresponds to an aliphatic polyamine, presents relative accessibility for the chemical reaction. However, AEP generally shows an increase of the reactivity, when compared with the aliphatic amines primary.<sup>20</sup> This fact is due to the largest reactivity of the primary amine group of AEP that induces gelation in a shorter period of time. In the isophorone diamina (IPD) the gelation occurs in a larger period of time. In this molecule, four active hydrogen atoms of the amine type exist (two amine primary groups). The two nitrogen atoms of the primary amine are chemically tied up in a different way. One of the atoms of amine nitrogenous is directly attached to the cyclic structure, and the other group through methylene group. This last amine group presents longer esteric impediment for the chemical reaction if compared with the amine group linked directly to the cycle. However, both functional groups present esteric hindrance due to the presence of three methyl groups in the molecule. This leads to a slower reaction and can be used to justify that the gelation process is reached in longer time. This process probably occurs at high conversion when compared with the other systems.

Later, the gelation times starting from the rheological analyses at 40°C are determined. The gelation time is considered as the crossing point among the storage module ( $G'$ ) with the loss module ( $G''$ ) as a function of time reaction.<sup>21-24</sup> In this case, the gelation times were 56.6, 84.6, and 122.3 minutes for the formulation with AEP, TETA, and IPD, respectively. These results corroborate that the gelation for the epoxy/amine systems occurs in the following order AEP > TETA > IPD, respectively.

### Morphological studies

The modified adhesives are transparent indicating that the copolymers were soluble in the epoxy adhesives. However, after a certain time they became cloudy. This phenomenon is a consequence of the

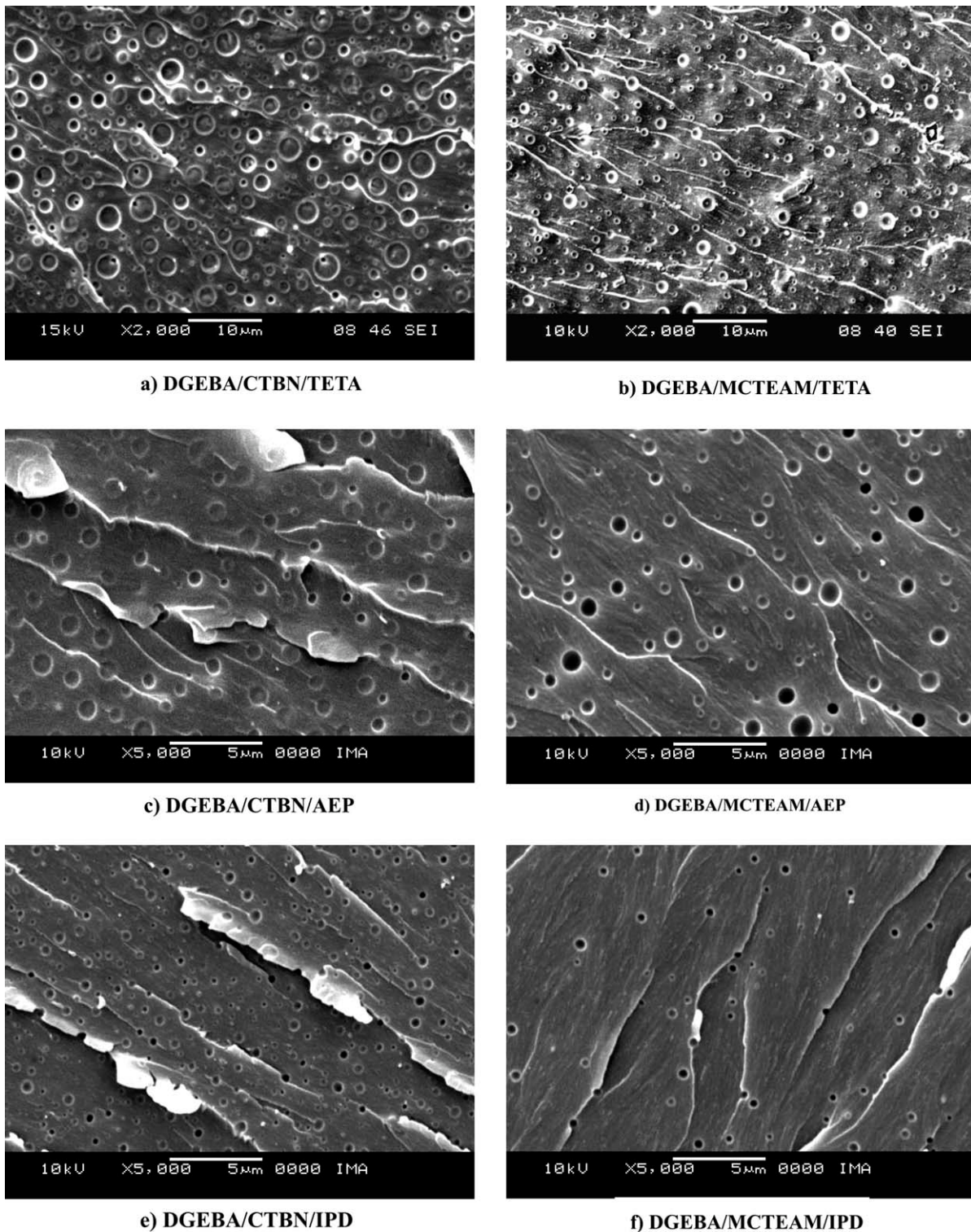
phases separation induced by the chemical reaction.<sup>25,26</sup>

SEM micrographies using different cure agents of the modified adhesives are shown in Figure 3. As can be seen, the morphology in all systems consists of dispersed/epoxy matrix phase. We noted a continuous phase with striated regions, and smooth areas, and other randomly dispersed phase consisting of white or black spheres. The white spheres were attributed to the phase modifier while the black's spheres were attributed to the holes. The epoxy blends with the copolymer based on butadiene (CTBN) originated a dispersed phase with larger diameters [Fig. 3(a)]. For the TETA system, the dispersed phase presents larger diameters originating a more polydispersed size distribution diameters in the range of 0.4 to 2.2  $\mu\text{m}$  with medium diameter of  $1.13 \pm 0.22 \mu\text{m}$  [Fig. 3(b)]. However, the acrylic copolymer (MCTEAM) led to a dispersed phase with a more uniform size distribution with smaller medium diameter ( $0.70 \pm 0.19 \mu\text{m}$ ). The micrographies of the AEP system reveal similar morphologic characteristics [Fig. 3(c,d)]. The medium diameters based on the butadiene copolymers and acrylic correspond to  $0.68 \pm 0.05 \mu\text{m}$  and  $0.56 \pm 0.10 \mu\text{m}$ , respectively. For the copolymer based on the butadiene, the size distribution was more uniform, with diameters in the range of 0.36 to 0.96  $\mu\text{m}$ . The IPD system presents the smallest diameter of particles [Fig. 3(e,f)]. This result is in agreement with gelation time data. The largest effect shown by these systems was evidenced by the larger conversions reaction when compared with the AEP and TETA systems. This seems to be related to a larger solubility of the modifiers and also to the polymerization rate.

A larger reaction time indicates that the viscosity limits the particles growth resulting in a minor size distribution. For the IPD, the medium diameters are quite similar  $0.33 \pm 0.06 \mu\text{m}$  and  $0.31 \pm 0.05 \mu\text{m}$  to the CTBN, and the modified MCTEAM, respectively. However, the copolymer based on the butadiene led to a dispersed phase with a larger size distribution (0.22–0.55  $\mu\text{m}$ ) whereas in the acrylic copolymer the size distribution was more uniform (0.20–0.49  $\mu\text{m}$ ). Other important aspect is the low concentration of the dispersed phase of the acrylic copolymer in the thermosetting matrix. These two factors indicate larger solubility of this copolymer in the adhesive. Also, the low concentration of the dispersed phase suggests that the content of acrylic copolymer is abundant in the epoxy matrix after the cure process.

### Characterization of steel surface

To obtain a strong interaction between the adhesive and the adherent is important to treat the surface of



**Figure 3** SEM micrographies of the fractured surface of the adhesive systems.

the substrate. The adherent surfaces contribute to the molecular mobility of the adhesive in the surface leading to a closed contact, which improves the adhesion intermolecular forces. The performance of this process is related to the capacity of the wetting ability of the adhesive in the adherent.

Tables II and III present the surface roughness of the adherents and the contact angle measured for a drop of epoxy resin without cure agent. As can be seen, the surface chemically treated with wiping solvent presents low surface roughness values ( $R_a$ ). This behavior was expected due the simple cleaning with

**TABLE II**  
**Profile Parameters of Steel Surface Obtained from Profilometry Analysis**

Treatment of steel surface	Profile parameters ( $\mu\text{m}$ )		
	$R_a$	$R_t$	$R_{sk}$
Solvent wiping	$1.39 \pm 0.24$	$9.99 \pm 0.53$	$-0.290 \pm 0.230$
Chemically treated	$2.20 \pm 0.18$	$14.75 \pm 1.50$	$0.244 \pm 0.079$
Mechanically with G80 steel-grit and chemically treated	$3.96 \pm 0.05$	$33.12 \pm 0.59$	$-0.120 \pm 0.168$
Mechanically with G40 steel-grit and chemically treated	$6.63 \pm 0.06$	$52.8 \pm 1.60$	$-0.271 \pm 0.047$
Mechanically with G25 steel-grit and chemically treated	$9.26 \pm 0.98$	$83.9 \pm 9.60$	$-0.339 \pm 0.040$

solvent. When the surface was chemically treated with posterior use of mechanical and chemical treatment, there was a significantly increase in the surface roughness. This occurs due to the increase of steel-grit particle size. The same behavior was noted for the  $R_t$  values. These parameters can contribute to the increase of the adhesion which proportionate nucleate sites for the mechanical anchorage of the adhesive. Nevertheless, the skew parameter ( $R_{sk}$ ) is important to characterize the surface characteristics due to the possibility to measure the profile symmetry starting from the relative medium line to the surface of the substrate. Due to the good wetting ability of the surface, an improvement in the adhesion behavior leading to an intimate contact and promoting attraction intermolecular forces was noted. This behavior was expected to improve better interaction between the adhesive and the substrate, which is necessary to create regions with macro and micro-roughness. However, there are not significant changes in the mechanical resistance when combinations of mechanical and chemical treatment using the steel-grit G80, G40, and G25 were employed.  $R_{sk}$  values are close to zero. Except for the surface chemically treated, the negative values observed for all specimens suggest the existence of valleys in the surface.

The substrates mechanically and chemically treated present the lowest angle values when compared to the surface chemically treated. This indicates that the combination of the mechanical and chemical treatment increases the ability of resin wetting. In this case, the wetting is increased by the use of steel-grit with particles size.

### Mechanical resistance of the joints treated with different adherents

The adhesion was evaluated by mechanical resistance test using a single-lap shear joints. The surface of the steel substrate was submitted to different treatments. The main idea is to connect the surface roughness of the substrate with the mechanical resistance. Table IV presents the mechanical resistance data of the adhesive performance.

The mechanical resistance increased for the substrate chemically treated. This behavior was expected since to improve better interaction between the adhesive and the substrate is necessary to create regions with macro and micro-roughness. However, there are no significant changes in the mechanical resistance when a combination of mechanical and chemical treatment using the steel-grit G80, G40, and G25 were employed. This means that the increase of the superficial roughness (Table II), and the slight increase of the resin wetting (Table III) have no strong effects on the mechanical resistance. Therefore, it seems that the adhesion process for mechanical anchorage has not promoted an increase in the adhesion, which can be explained by the same contact angle values. In this way, the adhesion process is guaranteed for the three surface treatments. Therefore, the adhesive resistance of the joints is connected with the cohesion process. This occurs after the cure process, which depends on the structure of the thermosetting networks. The relation between adhesive performance and the structure of the networks will be discussed in other work.<sup>27</sup>

**TABLE III**  
**Contact Angle Values Measured Between a Drop of the Epoxy Resin Deposited on the Steel Surface**

	Treatment of steel surface			
	Chemically	Mechanically with G80 steel-grit and chemically	Mechanically with G40 steel-grit and chemically	Mechanically with G25 steel-grit and chemically
Contact angle ( $^\circ$ )	19	15	16	10

### Thermal and mechanical resistance of the joints with the morphology

Table V shows the thermal and mechanical properties of the modified and unmodified adhesives. As can be seen, the thermal properties of the modified adhesives changed in an expect way. At the end of the polymerization reaction, a reduction in the glass transition temperature was noted. This is a result of a fraction of modified dissolved in the matrix. The adhesive with IPD was less effective in producing complete phase separation of the modifiers, due the reduction of  $T_g$  (decrease of 20°C). The reduction of  $T_g$  value for the adhesive that use the CTBN copolymer is explained by the smallest  $T_g$  value ( $T_g = -52^\circ\text{C}$ ) when compared the  $T_g$  value of the acrylic copolymer ( $T_g = -28^\circ\text{C}$ ). This result is in agreement with the SEM analyses data.

The unmodified and modified adhesives were analyzed with relationship to its mechanical resistance. As observed in the Table V, the mechanical resistance of the modified adhesives increased when compared with the unmodified adhesive. The increase in the mechanical resistance is a consequence of secondary phases, which is able to dissipate the tensions formed during the fracture process. Literature data indicate that the mechanism more appropriated for the increase of the toughening is plastic deformation. The dispersed particles in the matrix cause two effects; the formation of shear yielding and the growth of holes. This is the phenomenon present in rubber-modified epoxies well know as cavitation.<sup>28,29</sup>

The copolymers as independent modifiers of the epoxy adhesive were analyzed with relationship to its mechanical resistance as a function of the morphology. The most effective adhesive for steel-steel joints in single-lap shear test was the blends using 1-(2-aminoethyl)piperazine (AEP) as hardener. This system shows the biggest lap shear strength. However, the mechanical resistance for the modified adhesives is increased. In this case, the rupture tension of the epoxy modified when compared with the

**TABLE IV**  
Adhesive Strength of DGEBA/TETA System with Different Treated Steel Surface Obtained from Single-Lap Shear Test

Treatment of steel surface	Adhesive strength (MPa)
Solvent wiping	6.47 ± 0.82
Chemically	10.53 ± 1.28
Mechanically with G80 steel-grit and chemically	20.25 ± 1.02
Mechanically with G40 steel-grit and chemically	17.69 ± 1.47
Mechanically with G25 steel-grit and chemically	19.96 ± 1.50

**TABLE V**  
Thermal and Mechanical Properties of Different Epoxies System Obtained from Single-Lap Shear Test

Adhesive	$T_g$ (°C)	Adhesive strength (MPa)
DGEBA/TETA	124	16.6 ± 0.8
DGEBA/CTBN/TETA	118	17.5 ± 0.9
DGEBA/MCTEAM/TETA	119	18.1 ± 0.8
DGEBA/AEP	110	19.9 ± 0.8
DGEBA/CTBN/AEP	105	20.6 ± 0.7
DGEBA/MCTEAM/AEP	106	20.4 ± 0.8
DGEBA/IPD	155	17.5 ± 0.5
DGEBA/CTBN/IPD	134	20.2 ± 0.6
DGEBA/MCTEAM/IPD	138	18.0 ± 0.4

epoxy unmodified corresponded to 19.9 ± 0.8 MPa and 20.6 ± 0.7 MPa, respectively when uses the CTBN copolymer.

The adhesives modified with AEP show that the concentration of modifier and/or the cure conditions are not appropriated. Considering that the epoxy network is more flexible and presents the best initial toughenability, as expected, it can be considered that the network was modified in a correct way.<sup>30-32</sup>

The adhesive modified with the acrylic copolymer with TETA showed a slight increase in the adherence in the joints of single-lap shear. In this case, the tension rupture of the modified epoxy when compared with the unmodified epoxy corresponded to 18.1 ± 0.8 MPa and 16.6 ± 0.8 MPa, respectively. This represents an increment of 9% in the mechanical resistance. The best mechanical resistance behavior of the modified adhesive with the acrylic copolymer is related to the morphology generated by this adhesive. This behavior can be addressed to the morphologic characteristics based on the size distribution of particles with smaller medium diameter.

For the system that employs IPD with CTBN we noted a slight increase in the adherence of the single-lap shear. In this case, the tension rupture of the epoxy modified when compared with the unmodified epoxy corresponded to 20.2 ± 0.6 MPa and 17.5 ± 0.5 MPa, respectively. Therefore, the best mechanical resistance behavior of the modified adhesive with the CTBN copolymer is related to the morphology. For the modified adhesive, the high concentration of the copolymer in the matrix seems to increase the mobility and the flexibility of the chains. This improves the mechanical behavior of the modified adhesive, when compared with the unmodified adhesive.

In a similar way, the copolymers CTBN and MCTEAM improve the toughing of the epoxy systems. This justifies the application of the acrylic copolymer as toughing agent for thermosetting systems.



## CONCLUSIONS

In summary, adhesives properties of the modified and unmodified adhesive depend on the morphology and the hardener. The most effective adhesive for steel–steel joints in single-lap shear test were the blends using 1-(2-aminoethyl)piperazine (AEP) as hardener. The TETA acrylic copolymer presented the best performance as modified adhesive. The substrate chemically and mechanically treated showed increase in the mechanical resistance. Finally, the mechanical resistance of the adhesive joints depends on the structure of the thermosetting networks.

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