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## Durability of adhesives based on different epoxy/aliphatic amine networks

Filiberto González García<sup>a,\*</sup>, Maria Elena Leyva<sup>a</sup>, Alvaro Antonio Alencar de Queiroz<sup>a</sup>, Alexandre Zirpoli Simões<sup>b</sup>

<sup>a</sup> Departamento de Física e Química, Instituto de Ciências Exatas, Universidade Federal de Itajubá (UNIFEI), Av. BPS. No. 1303, 37500-903 Itajubá, MG, Brazil

<sup>b</sup> Departamento de Materiais e Tecnologia, Faculdade de Engenharia de Guaratinguetá, Universidade Estadual Paulista (UNESP), Av. Dr. Ariberto Pereira da Cunha No. 333, Pedregulho 12516-410, Guaratingueta, SP, Brazil

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## ABSTRACT

The mechanical and adhesives properties of epoxy formulations based on diglycidyl ether of bisphenol A cured with various aliphatic amines were evaluated in the glass state. Impact tests were used to determine the impact energy. The adhesive properties have been evaluated in terms single lap shear using steel adherends. Its durability in water at ambient temperature (24 °C) and at 80 °C has also been analyzed. The fracture mechanisms were determined by optical microscopy. It was observed a strong participation of the cohesive fracture mechanisms in all epoxy system studied. The 1-(2-aminoethyl)-piperazine epoxy adhesive and piperidine epoxy adhesive presents the best adhesive strength and the largest impact energy. The durability in water causes less damage to piperidine epoxy networks. This behavior appears to be associated with the lower water uptake tendency of homopolymerised resins due to its lower hydroxyl group concentration.

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## 1. Introduction

Epoxy resins are being widely used in industrial applications such as adhesives and matrixes for composite materials. High performances need to be achieved through the synthesis and processing of the materials; especially, a good mechanical behavior (stiffness and toughness) is expected. That is why a better understanding of the structure–processing–properties relationships is required. In the past decades, numerous papers have been treated to this topic, especially in the case of epoxy/amine networks.

The network structure can be modified in different ways by changing the crosslink density and/or the flexibility of chain between crosslinks. The crosslink density can be varied by changing the stoichiometric ratio of the reactants and the extent of cure [1–3]. In this case, the soluble fractions and/or the dangling chain alter the networks topology and the conclusions are not clear. A second way of modifying the crosslink density consists of changing the molar mass of the epoxy monomer [4,5], although a distribution of molar mass between crosslinks is also introduced. However, a more convenient method is to control the crosslink density by using a mixture of monoamines and primary diamine [6].

Another important physical characteristic of the epoxy network structure is the flexibility of the chains between the cross-linked chain segments. The flexibility of the epoxy network can be modified by the use of aliphatic epoxy prepolymer instead of the usual aromatic epoxy monomer [7]. Moreover; the nature of the amine comonomer can be changed [8].

In our previous work, the effect of the chemical structure of the comonomer on the thermal relaxations and mechanical properties of epoxy networks based on DGEBA and aliphatic amines were evaluated. [9]. It was observed that comonomers that operate at room temperature, such as primary amines, are suitable to be used as adhesive formulations.

Epoxy formulations are characterized as two components system. These monomers can be used at room temperature in the first stage on the cure schedule, allowing a better control of chemistry process. However, to obtain the best mechanical properties, it is necessary to ensure the stoichiometric ratios of the epoxy resin and comonomer and an optimized post cure stage. This allows obtaining the maximum glass transition temperature.

Adhesive joining is defined as the process of joining parts using a non-metallic substance (adhesive), which undergoes a physical or chemical hardening reaction causing the parts to join together through surface adherence (adhesion) and internal strength (cohesion). The significance of adhesive bonding as structure-joining technology is increasing because of its numerous advantages with other joining methods [10,11].

It is well known that to obtain resistant structures using adhesive joint is important to control the configurations, joint

\* Corresponding author. Tel.: +55 35 3629 1515; fax: +55 35 3629 1140.  
E-mail address: [filii@unifei.edu.br](mailto:filii@unifei.edu.br) (F. González García).

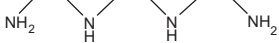

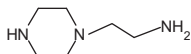
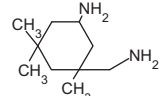
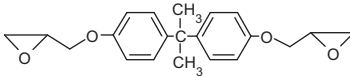
Name	Designation	Chemical structure	Functionality
Triethylenetetramine	TETA		6.0
Piperidine	Pip		1.0
1-(2-Aminoethyl)piperazine	AEP		3.0
Isophorone diamine	IPD		4.0
Diglycidylether of bisphenol A	DGEBA		2.0

Fig. 1. Chemical structure and monomers characteristics.

design and another important question of epoxy adhesive is the durability of the joint and the high capacity of water uptake. The structure-joining is optimized by a particular service [12–14]. However, it is convenient to study the durability and the one limits of application in water environment.

Although numerous studies have been published about the mechanical properties of epoxy polymers [15–17] and their adhesiveness [18,19], to our knowledge, no work has been undertaken about the relationship between the DGEBA network structure and their adhesive and durability properties. In this research, the effect of the chemical structure of the comonomer on the durability of the adhesive joint in water at ambient temperature (24 °C) and at 80 °C was investigated. The mechanical and adhesives properties of four DGEBA/aliphatic amine networks were studied.

In order to maintain a high functionality, a linear structure based on triethylenetetramine (TETA) was selected as comonomer. The three other comonomers are cycloaliphatic amines based on piperidine (Pip), 1-(2-aminoethyl)piperazine (AEP) and 5-amino-1,3,3-trimethylcyclohexanemethylamine (isophorone diamine, denoted IPD), having them cyclic structures. Fig. 1 shows the chemical structures of the monomers used in this work.

The mechanical properties of DGEBA/amine networks were evaluated with respect to impact tests. Adhesive properties of the epoxy networks were evaluated on steel alloy adherend while the adhesion performance of epoxy/amine networks was evaluated in terms single lap shear using steel adherends. The failure type in adhesive joints was analyzed by optical microscopy with imaging software.

## 2. Experimental

### 2.1. Materials

Diglycidyl ether of bisphenol A (DGEBA, DER 331 Dow Chemical, Brazil), with a weight per epoxy group, WPE=187 g, as determined by acid titration [20] was dried under vacuum at 80 °C before use. Aliphatic and cycloaliphatic epoxide amine hardeners such as,

triethylenetetramine (TETA, DEH 24 Dow Chemical, Brazil), piperidine (Pip, Aldrich São Paulo, Brazil, 99% purity), 1-(2-aminoethyl)piperazine (AEP, Aldrich, São Paulo, Brazil, 99% purity) and 5-amino-1,3,3-trimethylcyclohexanemethylamine, mixture of *cis* and *trans* (isophorone diamine, denoted IPD, Aldrich, São Paulo, Brazil, ≥ 99% purity) were used. The hardeners were used as received without further purification. Solvent such as 1,1,1-trichloroethylene (analytical grade) was used.

### 2.2. Specimens' preparation

The epoxy/amine adhesives were prepared by carefully weighing the hardener at the stoichiometric ratio (epoxy/amino-hydrogen  $e/a=1$ ). The mixture was poured into a mold and cured for 24 h at room temperature and later submitted to a post cure stage [9].

Piperidine formulation was prepared with 5 phr (5 g of piperidine per 100 g of DGEBA). In this case, the formulation was cured for 30 min at 60 °C and later submitted to a post cure state for 16 h at 120 °C. Specimens for the mechanical characterization were machined from the molded materials (rectangular), to reach final dimension and improve surface.

### 2.3. Thermal analysis

Glass transition temperature ( $T_g$ ) of the epoxy networks (sample weight  $15 \pm 2$  mg) was determined by differential scanning calorimetry (Shimadzu, model DSC-60) with a heating rate at  $10 \text{ }^\circ\text{C min}^{-1}$  under dry nitrogen ( $20 \text{ cm}^3 \text{ min}^{-1}$ ).  $T_g$  was recorded as the temperature corresponding to the middle of heat capacity base-line change.

### 2.4. Mechanical testing of the specimens

The Izod notched impact test was conducted in a (Tinius Olsen, model 892) pendulum-type impact tests with a striking velocity of  $3.46 \text{ m s}^{-1}$ , using rectangular specimens ( $62 \times 12.9 \times 6 \text{ mm}^3$ ). The rectangular specimens were machined out from the fully cured plates ( $190 \times 190 \times 12 \text{ mm}^3$ ). Care was taken to obtain

smooth and parallel faces. The impact test was carried out at  $20 \pm 2$  °C with impact energy given in  $\text{J m}^{-1}$ . Six specimens of each epoxy networks were tested and the average value reported.

The elastic modulus ( $E$ ) and yield stress ( $\sigma_Y$ ) of epoxy networks were determined at  $20 \pm 2$  °C from uniaxial compression tests. An EMIC DL 2000 universal testing machine was used. The uniaxial compression tangent elastic modulus ( $E$ ) was determined following ASTM standard at  $1 \text{ mm min}^{-1}$  with cylindrical specimens (length=20 mm, diameter=10 mm) machined out from cylinders of 60 mm length and 14 mm diameter. The yield point ( $\sigma_Y$ ) was recorded as the point when deformation ceased to be recoverable. The values were taken from an average of at least ten specimens.

### 2.5. Preparation of lap shear specimens

The adhesive behavior was evaluated for mechanical tests using single-lap shear joint. For this purpose, the adhesion test was carried out according to ASTM D 1002-01 [21]. The geometry of adhesive joint is shown in Fig. 2. The used metallic adherend was low-carbon alloy steel (alloy A36) with chemical composition shown in Table 1.

In order to increase its adhesive properties, the metallic adherend surfaces were prepared. The applied surface treatment consisted of the following steps: (1) Solvent wiping: single wiping of the steel surface with 1,1,1-trichloroethylene. (2) Steel-grit abrasion: the surface was abraded with steel-grit GH40B under a pressure of  $6.5 \text{ kgf cm}^2$  and speed of  $600 \text{ km h}^{-1}$ . The grain size of steel-grit abrasive was in the range from 0.30 to 0.42 mm. (3) Drying: the surface was clean with dry air. The treated surfaces were stored in dry chamber until the preparation of the adhesive joints.

In this work, the surface treatment was more simplified comparing to the recent study [22]. This can be explained by the non-dependence of surface roughness on mechanical resistance of steel–steel joints using single-lap shear test. In this way, the surface treatment of the metallic adherend can be simplified. This will allow evaluating the effect of the network structure of epoxy/amine system on the adhesive properties.

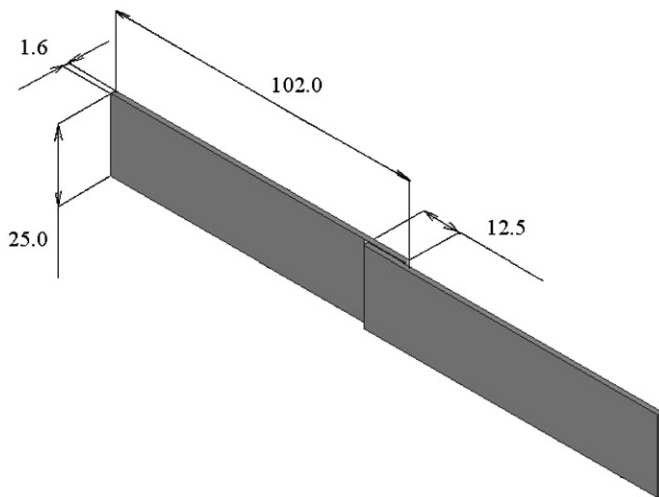


Fig. 2. Dimensions of the adhesives joints of single lap shear using steel adherend (measured in mm).

Table 1

Elemental composition of steel adherend (Alloy A36).

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

For the adhesive applications, specific metallic mold was designed for adhesive joint. The design of the mold allows control of the adhesive exactly layer thickness. After surface treatment, metallic pieces were assembled for adhesive single-lap shear joint. The epoxy adhesives were prepared by carefully weighing the epoxy amine hardener at the stoichiometric amount (ratio epoxy to amino-hydrogen  $e/a=1$ ). All mixtures were stirred for 1 min at room temperature to ensure the homogeneity of the prepared formulation.

The epoxy adhesive was applied uniformly on both surfaces of the adherend with the sample introduced in the specific metallic molds. The applied contact pressure was always the same, which allows obtaining specimens with uniform adhesive thickness,  $0.18 \pm 0.02 \text{ mm}$ . The specimens in the molds were cured according to the same schedules as the neat epoxy system. To reduce the deviation of the adhesive layer, respect to the tensile axis, chocks in the extremes of the specimens were used. Before any test, the specimens were stored at room temperature  $22 \pm 2$  °C and relative humidity of  $50 \pm 5\%$  during 48 h.

### 2.6. Testing of the adhesive specimens

The adhesive strength of the single-lap shear joints was measured at room temperature in a universal testing machine (Shimadzu Autograph AG-100) under a 100 kN load cell. A cross-head speed of  $1.27 \text{ mm min}^{-1}$  was employed. The lap shear strength is expressed in MPa. The adhesion tests were carried out at  $22 \pm 2$  °C and relative humidity of  $50 \pm 5\%$ . The average values were taken from at least eight specimens.

### 2.7. Water environment test

The water environment test consisted in submerging the specimens in water distilled at ambient temperature or at 80 °C and later to remove them at different times. The specimens were soaked in water distilled after post cure step. The water environment test consisted in submerging the specimens in water distilled at ambient temperature or at 80 °C and later to remove them at different times. Then, before each mechanical test the specimens were mechanically dry with cotton cloth and air.

### 2.8. Evaluation of the failure surface

The failure types of the different adhesive joints were determined by optical microscopy (Topcon) with software of imaging analysis. The fracture surfaces were observed by optical microscopy. The images were transmitted by a video camera to a personal computer. The dark regions were attributed to cohesive failure while the clear regions were attributed to adhesive failure. The percentage of the cohesive failure was determined by the quotient of the area of the dark region and the total area of the metal substrate multiplied by 100.

## 3. Results and discussion

### 3.1. Thermal and mechanical properties

The results of thermal, impact and uniaxial compression tests are shown in Table 2. The DGEBA/IPD system exhibits highest values of the glass transition temperature and yield stress than the DGEBA/TETA, DGEBA/AEP and DGEBA/Pip networks. However, DGEBA/AEP and DGEBA/Pip systems show the best impact resistance and the lowest values of the glass transition temperature. Lowest values of the  $T_g$  can be related to lower crosslink density [6]. In this way, we observe that the  $T_g$  depends on both crosslink density and chain

stiffness, although the yield strength should be better associated to the  $T_g$  value rather than to the crosslink density. The elastic modulus is almost the same for all epoxy networks.

### 3.2. Adhesive properties

The adhesive properties were evaluated in terms single lap shear using steel adherends mechanically treated. Table 3 shows the adhesive properties of different epoxy polymers obtained from single lap shear joints tests. The  $T_g$  of the DGEBA networks presents large influence on the mechanical behavior of the adhesive joints. This result is similar to the mechanical behavior previously discussed. As expected, the DGEBA/AEP and DGEBA/Pip systems exhibit the best adhesive properties.

The AEP and Pip systems exhibits lower values of the  $T_g$  than the other DGEBA networks. This can be related to lower crosslink density. On the other hand, the TETA and IPD systems show the biggest values of the  $T_g$ . However, the TETA structure exhibits more flexibility when compared to the rigid structure of the latter, leading to a relative high- $T_g$ .

The performance of the adhesive properties is related to different structure of the epoxy networks. This comes from the fact that the networks involved are “closed” networks, resulting from a single step polymerization mechanism and also that stoichiometric ratios of monomers are reacted until attaining the maximum value of  $T_g$ . In the DGEBA/Pip system, its different two curing processes were carried out for epoxy crosslinking, by polymerization steps and homopolymerization allowing into generating polyether chains with flexible structure. In those circumstances, the flexible epoxy network chains exhibit lower crosslink density and a smaller value of  $T_g$ .

With the results of this work it is possible to relate the mechanical properties and adhesives properties to the changes in the chemical structure of the amine comonomer what provoke changes in the networks structure.

### 3.3. Water environment test

The durability of lap shear joints with different epoxy adhesives under water environments at ambient temperature (24 °C) and at 80 °C was analyzed. Fig. 3 shows the adhesive properties of different lap shear joints using different epoxy networks obtained from water environment at ambient temperature. A slight

decrease of the adhesive strength is observed when the time increased until reaching a stable value. This behavior can be related to the water adsorption for the epoxy networks in the joints. In all investigated cases, the adhesive strength decreases. On the other hand, similar behavior was observed for the durability of lap shear joint using different epoxy polymer under water environments at 80 °C (Fig. 4).

It is important to notice that in all cases, the water environment causes a decrease in the adhesive strength. The magnitude of damage is not same for epoxy networks studied in this work. The decrease in the adhesive strength of DGEBA/Pip system is smaller for all epoxy networks. This result may be caused by the homopolymerised epoxy resin, due to its low tendency to absorb water as consequence of the epoxy networks structure, whose hydroxyl concentration is negligible. The presence of hydroxyl groups is an important factor for water uptake ability [23].

### 3.4. Characterization of the adherend surface

Fig. 5 illustrates the different failure type in the adhesive joints. The failure can occur inside the adhesive layer (cohesive failure—with adhesive residues on both surfaces) or at the interface between the adhesive layer and the adherend surface (adhesive failure). The images of the joint after fracture reveal dark and clear regions. The dark region corresponds to the adhesive surface and the clear region corresponds to the metallic

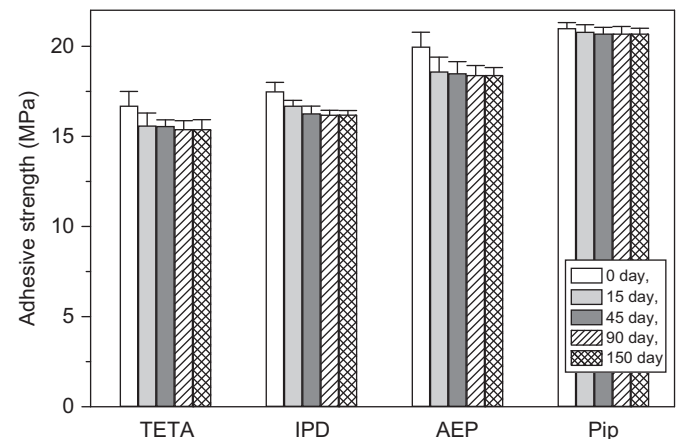


Fig. 3. Adhesive strength of different epoxy adhesive under water environments at ambient temperature.

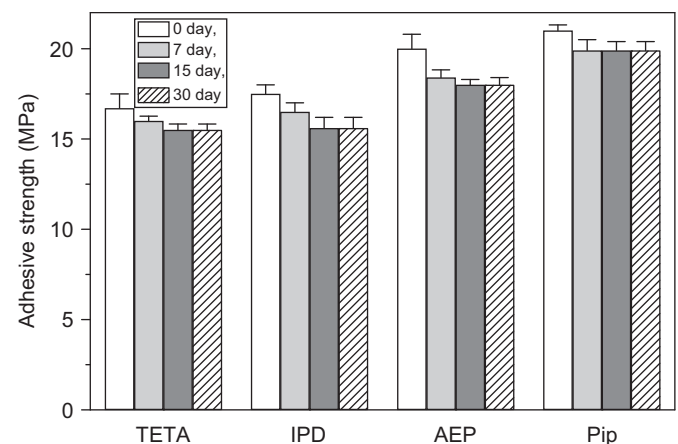


Fig. 4. Adhesive strength of different epoxy adhesive under water environments at 80 °C.

Table 2  
Thermal and mechanical properties of the epoxy/amine systems.

Adhesives	$T_g$ (°C)	Impact energy (J m <sup>-1</sup> )	Elastic modulus (GPa)	Yield stress (MPa)
DGEBA/TETA	124	36.2 ± 6.1	3.10 ± 0.1	49.2 ± 0.1
DGEBA/AEP	115	70.1 ± 4.4	2.87 ± 0.1	47.3 ± 0.1
DGEBA/Pip	80	49.8 ± 3.4	2.62 ± 0.1	46.8 ± 0.1
DGEBA/IPD	155	33.8 ± 2.8	3.77 ± 0.1	60.2 ± 0.1

Table 3  
Thermal and adhesive properties of different epoxy/amine adhesives obtained from single lap shear tests.

Adhesives	$T_g$ (°C)	Adhesive strength in lap shear joints (MPa)
DGEBA/TETA	124	16.6 ± 0.8
DGEBA/AEP	115	19.9 ± 0.8
DGEBA/Pip	80	21.0 ± 0.4
DGEBA/IPD	155	17.5 ± 0.5

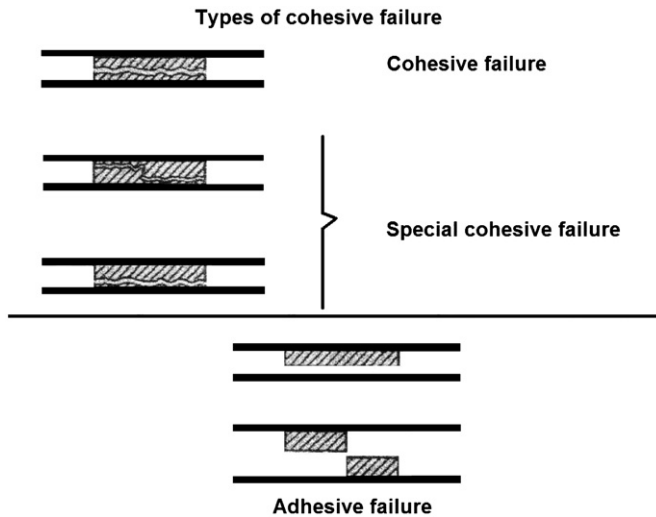


Fig. 5. Types of failure in adhesive bonds.

Table 4

Percentage of cohesive failure in the fractured joints as a function of the adhesive.

Adhesives	Cohesive failure (%)
DGEBA/TETA	75
DGEBA/AEP	82
DGEBA/IPD	78

surface. These results are shown in Table 4. As expected, the cohesive failure dominates in the epoxy adhesives [19,24].

#### 4. Conclusions

In summary, the mechanical and adhesive properties of the epoxy networks depend of the chemical structure of the amine comonomer. The DGEBA/IPD system exhibits highest values of the glass transition temperature and yield stress than the other epoxy systems studied in this work. However, DGEBA/AEP and DGEBA/Pip epoxy shows the best impact resistance and the lowest glass transition temperature values and also the best adhesive

properties. The water environment causes a decrease in the adhesive resistance in all investigated systems. The decrease in the adhesive strength of DGEBA/Pip system is smaller for all epoxy networks due to its low tendency to absorb water as consequence of the epoxy networks structure, whose hydroxyl concentration is negligible. Finally we noted that the epoxy adhesives dominate the cohesive failure.

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#### References

- [1] Gupta VB, Dizal LT, Lee CYC. *Polym Eng Sci* 1985;25:812.
- [2] Jordan C, Galy J, Pascault JP. *J Appl Polym Sci* 1992;46:859.
- [3] Amdouni N, Sautereau H, Gerard JF, Pascault JP. *Polymer* 1990;31:1245.
- [4] Misra SC, Manson JA, Sperling LH. *Adv Chem Ser* 1979;114:137.
- [5] Vaskil U, Martin GC. *J Appl Polym Sci* 1992;46:2089.
- [6] Pascault JP, Sautereau H, Verdu J, Williams RJJ. *Thermosetting polymers*. New York: Marcel Dekker; 2002.
- [7] Urbancewski E, Galy J, Gerard JF, Pascault JP, Sautereau H. *Polym Eng Sci* 1991;31:1572.
- [8] Grillet AC, Galy J, Gerard F, Pascault JP. *Polymer* 1991;32:1885.
- [9] González García F, Soares BG, Pita VJRR, Sánchez R, Rieumont J. *J Appl Polym Sci* 2007;106:2047.
- [10] Higgins A. *Int J Adhes Adhes* 2000;20:367.
- [11] Pearce P, Ennis BC, Grabovac I, Morris C. *J Adhes* 1994;47:123.
- [12] Taib AA, Boukhili R, Achiou S, Gordon S, Boukehili H. *Int J Adhes Adhes* 2006;26:226.
- [13] Da Silva LFM, Adams RD. *Int J Adhes Adhes* 2002;22:202.
- [14] Li W, Blunt L, Stout KJ. *Int J Adhes Adhes* 1997;17:303.
- [15] Crawford E, Lesser AJ. *Polym Eng Sci* 1999;39:385.
- [16] Cook WD, Mayr AE, Edward GH. *Polymer* 1998;39:3725.
- [17] Yang G, Fu SY, Yang JP. *Polymer* 2007;48:302.
- [18] Lapique F, Redford K. *Int J Adhes Adhes* 2002;22:337.
- [19] Hu X, Huang P. *Int J Adhes Adhes* 2005;25:296.
- [20] American Society for Testing and Materials, ASTM, Specification D1652. Standard test methods for epoxy content of epoxy resins, 1997.
- [21] American Society for Testing and Materials, ASTM D, 1002-01. Standard test methods for apparent shear strength of single-lap-joint adhesively bonded metal specimens by tension loading (metal-to-metal), 2004.
- [22] González García F, Soares BG, Leyva ME, Simões AZ. *Appl Polym Sci*, in press.
- [23] Prolongo SG, Del Rosario G, Ureña A. *Int J Adhes Adhes* 2006;26:125.
- [24] Barcia FL, Soares BG, Sampaio E. *J Appl Polym Sci* 2004;93:2370.