

Influence of Chemical Structure of Hardener on Mechanical and Adhesive Properties of Epoxy Polymers

Filiberto González García,^{1,2} Maria Elena Leyva,¹ Marcia Gomes Oliveira,³
Alvaro Antonio Alencar De Queiroz,¹ Alexandre Zirpoli Simões²

¹Laboratório de Biomateriais, Departamento de Física e Química, Instituto de Ciências Exatas, Universidade Federal de Itajubá (UNIFEI), Av. BPS. No. 1303, Itajubá 37500-903, MG, Brazil

²UNIFEI-Campus Itabira, Rua São Paulo No. 377, Itabira 35900-373, MG, Brazil

³Instituto Nacional de Tecnologia, Divisão de Processamento e Caracterização de Materiais, Avenida Venezuela, 82 sala 106 Centro, Rio de Janeiro 20081-312, RJ, Brazil

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ABSTRACT: The mechanical and adhesive properties of epoxy formulations based on diglycidyl ether of bisphenol A cured with various aliphatic amines were evaluated in the glass state. Impact and uniaxial compression tests were used to determine the impact energy, elastic modulus and yield stress, respectively. The adhesion tests were carried out in steel–steel joints using single-lap shear, T-peel, and impact adhesive joints geometry. The better mechanical and adhesive behavior of the networks is obtained when exists high flexibility of chain between

crosslink and/or high elastic modulus. The 1-(2-aminoethyl)piperazine epoxy network presents the best adhesive properties, high flexibility, and the largest impact energy. However, it possesses low elastic modulus and yield stress. Also, exhibits increases in peel strength and impact energy while reductions in lap shear strength. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2213–2219, 2010

Key words: epoxy adhesive; adhesive joint; epoxy/amine networks

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 articles have been treated to this topic, especially in the case of epoxy/amine networks.

The molecular architecture can be modified 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. A second way of modifying

the crosslink density consists of changing the molar mass of the epoxy comonomer,^{4,5} and the distribution of molar mass between crosslinks. A better method is to control the crosslink density by using a mixture of monoamines and primary diamine.⁶

The other important characteristic of the network architecture is the flexibility of the chains between the crosslinks. This can be modified by using aliphatic epoxy prepolymer instead of the usual aromatic epoxy monomer.⁷ Moreover; the nature of the amine comonomer can be changed.⁸

Recently, we have evaluated the effects of the amine comonomer on the thermal relaxations and mechanical properties.⁹ Amine comonomers that operate at room temperature, such as primary amines, are suitable to be used as adhesive. Epoxies formulations of general purpose are known as two components system. These comonomers 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 guarantee the stoichiometric ratios of the epoxy resin and comonomer, and the use of an optimized post cure stage. This allows obtaining the maximum glass transition temperature.

The significance of adhesive bonding as structure-joining technology is increasing because of its numerous advantages with other joining methods.^{10,11} To obtain resistant structures using adhesive

Correspondence to: F. González García (fili@unifei.edu.br).

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joint is important to control the configurations and joint design. The structure joining is optimized by a particular service.^{12–14} In this way, the evaluation of the adhesive joint to different mechanical efforts can be measured by adhesion tests. The main goal is to simulate the work conditions that the adhesive joint will be submitted. Evaluation of the adhesive joint can be carried out using different adhesive joints geometry, such as single-lap shear, T-peel, bar and rod specimens, impact, etc.

Although numerous studies have been published about the mechanical properties of epoxy polymer^{15–17} and adhesives,^{18,19} to our knowledge, no work has been undertaken about the relationship between the molecular architecture of the epoxy networks and their adhesive properties. In this way, we report in this article the effects of the comonomer structure on the mechanical and adhesives properties of epoxy/aliphatic amine networks.

To maintain a high functionality, a linear structure based on triethylenetetramine (TETA) was selected as comonomer. The two other comonomers are cycloaliphatic amines based on 1-(2-aminoethyl) piperazine (AEP) and 5-amino-1,3,3-trimethylcyclohexanemethylamine (isophorone diamine, denoted IPD), having both cyclic structures. In this case the combination of the linear and cyclic structures in 1-(2-aminoethyl)piperazine has a more flexibility of the chains between the crosslinks when compared to the cyclic structure in isophorone diamine.

The mechanical properties of three epoxy/amine networks were evaluated with respect to impact and uniaxial compression tests. Adhesive properties of the epoxy networks were evaluated on steel alloy adherend while the adhesion performance of epoxy/

amine networks was evaluated by tensile, T-peel, and impact properties. The wetting ability of the metallic surface was determined by measuring the contact angle between the epoxy network drop and the metallic adherend surface. The failure type in adhesive joints was determined by optical microscopy with imaging software.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA, DER 331 Dow Chemical, Brazil), with an epoxide equivalent weight of 187 g eq⁻¹²⁰ was degassed in a vacuum oven during 2 h at 80°C. Aliphatic and cycloaliphatic epoxide amine hardeners such as, triethylenetetramine (TETA, DEH 24 Dow Chemical, Brazil), 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. Figure 1 illustrates the chemical structures of the amine hardeners and epoxy monomer. Solvent such as 1,1,1-trichloroethylene (analytical grade) was used.

Specimens preparation

The epoxy/amine networks were prepared by carefully weighing the hardener at the stoichiometric ratio (amino-hydrogen to epoxy equal to 1). The mixture was poured into a mold and cured for 24 h at room temperature and later submitted to a post cure

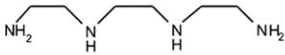
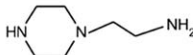
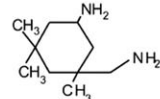
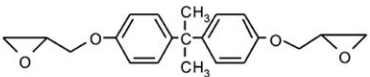
Name	Designation	Chemical structure	Functionality
Triethylenetetramine	TETA		6.0
1-(2-Aminoethyl)piperazine	AEP		3.0
Isophorone diamine	IPD		4.0
Diglycidylether of bisphenol A	DGEBA		2.0

Figure 1 Chemical structure and monomers characteristics.

stage.⁹ Specimens for the mechanical characterization were machined from the molded materials (plates or cylinders), to reach final dimension and improve surface.

Thermal analysis

Glass transition temperature (T_g) of the fully-cured epoxy networks (sample weight 15 ± 2 mg) was determined by differential scanning calorimetry (Shimadzu, model DSC-60) with a heating rate at $10^\circ\text{C min}^{-1}$ 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.

Dynamic mechanical measurements

Dynamic mechanical properties of the epoxy networks were obtained using a TA Instruments DMA 2980. The samples were shaped using a silicone cavity mold yielding the specimen geometry of approximately $60 \text{ mm} \times 12.5 \text{ mm} \times 2.5 \text{ mm}$. The α transition and the modulus were studied using the apparatus in double cantilever bending mode, between -110 and 180°C at a heating rate of 2°C min^{-1} and a frequency of 1 Hz.

Mechanical testing of the specimens

The Izod notched impact test was carried out using a (Tinius Olsen, model 892) pendulum-type impact tests with a striking velocity of 3.46 m s^{-1} , using rectangular specimens ($62 \text{ mm} \times 12.9 \text{ mm} \times 6 \text{ mm}$). The rectangular specimens were machined out from the fully-cured plates ($190 \text{ mm} \times 190 \text{ mm} \times 12 \text{ mm}$). Care was taken to obtain smooth and parallel faces. The impact test was carried out at $20 \pm 2^\circ\text{C}$ with impact energy given in Jm^{-1} . Six specimens of each epoxy networks were tested and the average value reported.

The elastic modulus (E) and yield stress (σ_Y) of fully-cured epoxy networks were determined at $20 \pm 2^\circ\text{C}$ 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 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 (σ_Y) was recorded as the point when deformation ceased to be recoverable. The values were taken from an average of at least 10 specimens.

Preparation of adhesion test samples

The adhesive behavior was evaluated for different mechanical tests using different adhesive joints geometry as such, single-lap shear, T-peel, and

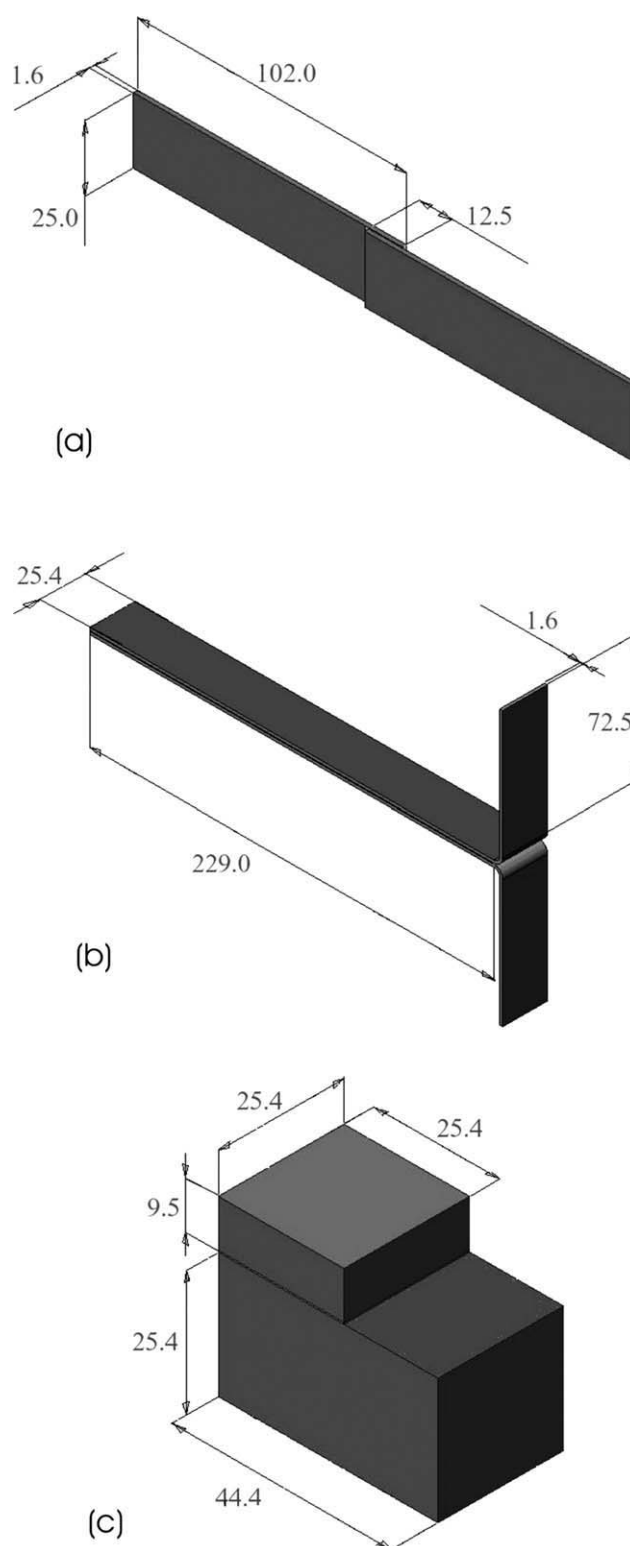


Figure 2 Geometry and dimensions of the adhesives joints of steel-steel (measured in mm). (a) single-lap shear joint, (b) T-peel joint, (c) impact joint.

impact. For this purpose, three adhesion tests were carried out according to ASTM D 1002-01,²¹ ASTM D 1876-01,²² and ASTM D 950-72,²³ respectively. The geometry of adhesive joints is shown in Figure 2.

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

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

The used metallic adherend was low-carbon alloy steel (alloy A36) with micro-chemical composition shown in Table I.

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 kgf cm² and speed of 600 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 is more simplified comparing to the recent study.²⁴ This can be explained by the nondependence 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 molecular architecture of epoxy/amine networks on the adhesive properties.

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

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 samples with uniform adhesive thickness, 0.18 ± 0.02 mm for single-lap shear joint, 0.20 ± 0.05 mm for T-peel joint, and 0.12 ± 0.05 mm for impact joint. The molds were cured using the same schedules of the epoxy networks specimens. To minimize deviation of the adhesive layer, 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.

Testing of the adhesive samples

The adhesive strength of the single-lap shear joints and T-peel joints were 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 and 254 mm min⁻¹ was employed. The lap shear strength is expressed in MPa. T-peel strength corresponds to the load required to break the adhesive joint (in newtons). The impact joints were broken in a pendulum-type impact tester machine (VEB RDA, model PS 30) with a hammer speed impact equal to 5.6 ms⁻¹. The impact energy was reported in kJ m⁻². All adhesion tests were carried out at 22 ± 2°C and relative humidity of 50 ± 5%. The average values were taken from at least eight samples.

Characterization of the adherend surface

The wetting ability of the epoxy/amine networks on steel surface was determined by measured contact angle between the adhesive epoxy drop (recently prepared) and pretreated steel surface. The measurements were performed on a Goniometer Ramé-Hart NRL, equipped with imaging software (RHI 2001), at 22.5°C and relative humidity of 45%. All epoxy adhesives recently prepared were gently stirred for 1 min at room temperature to ensure hardener dissolved. The values were taken from three analyses using drop of 0.04 ± 0.001 mm radio (for time zero, which was considered the mixture agitation at 1 min), performed in a period from 0 to 120 s. The short time used to measure the wetting angle was considered due the fast reaction cure.

Evaluation of the failure surface

The failure types of the different adhesive joints were determined by optical microscopy (Topcon) with imaging software. 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 adhesion failure. The percentage of the cohesion failure was determined by the quotient of the total area of the metallic substrate and the area of the dark regions multiplied by 100.

TABLE II
Physicochemical, Thermal, and Mechanical Properties of the Epoxy/Amine Adhesive

Networks	T_g (°C)	Contact angle (°)	Impact energy (J m ⁻¹)	Elastic modulus (GPa)	Yield stress (MPa)
DGEBA/TETA	124	20.5	36.2 ± 6.1	3.10 ± 0.1	49.2 ± 0.1
DGEBA/AEP	115	14.5	70.1 ± 4.4	2.87 ± 0.1	47.3 ± 0.1
DGEBA/IPD	155	21.9	33.8 ± 2.8	3.77 ± 0.1	60.2 ± 0.1

RESULTS AND DISCUSSION

Mechanical properties of the specimens

Results of physicochemical, thermal impact, and uniaxial compression tests are summarized in Table II. The DGEBA/IPD system exhibits highest values of the glass transition temperature and yield stress. However, DGEBA/AEP epoxy shows the best impact resistance and the lowest values of the glass transition temperature. This is due to the flexibility of chain between crosslinks. In this way, we observe that the T_g depends on both crosslink density and chain flexibility, although the yield strength should be better associated to the T_g value rather than to the crosslink density.

Concerning the different epoxy networks, the DGEBA/AEP system presents lower contact angle as a consequence of different viscosity, indicating better wettability of this adhesive. This is due the existence of molecular attraction forces among the molecules on the surface of the substrate and adhesive. As a consequence, there is an increase in the interfacial area, which improves adhesion, and as a result the formation of strong adhesive joints. The elastic modulus in the glassy state, which depends on the cohesive energy density and the intensity of sub-glass transition,⁶ is almost the same for all epoxy networks.

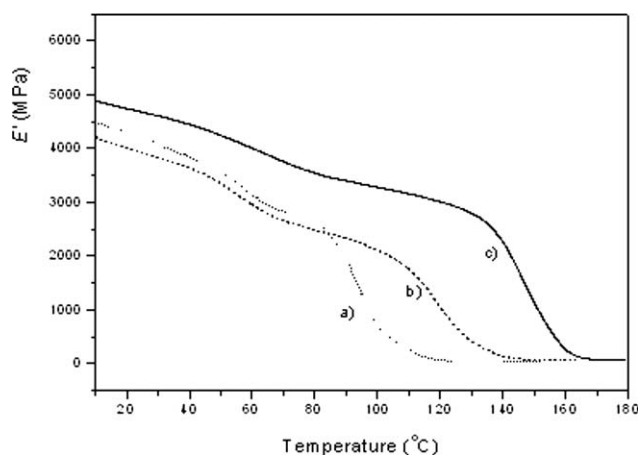


Figure 3 Storage modulus versus temperature plot of epoxy networks (a) DGEBA/AEP, (b) DGEBA/TETA, (c) DGEBA/IPD.

Dynamic mechanical measurements

Dynamical mechanical analyses were performed for the different epoxy/networks. Figure 3 shows the dependence of storage modulus E' on temperature. The different DGEBA/AEP, DGEBA/TETA, and DGEBA/IPD samples displays a sudden fall in the modulus at a temperature around 88°C, 113°C, and 139°C, respectively. These temperatures correspond to the glass–rubber transition of different epoxy/networks system and are equivalent to the ones summarized in Table II. The lowest values of the glass transition temperature was noted in the DGEBA/AEP system due to the higher flexibility of chain between crosslinks.

The epoxy/networks DGEBA/AEP, DGEBA/TETA show similar storage modulus, however an increase of modulus can be observed at DGEBA/IPD. This result is in perfect agreement with elastic modulus values shown in Table II. The DGEBA/IPD system has higher T_g and storage modulus due to rigidity of chain between crosslinks.

The dependence of mechanical loss tangent ($\tan \delta$) on temperature between -110 and 180°C for these systems is shown in Figure 4. As expected for an epoxy system, the different networks displays two

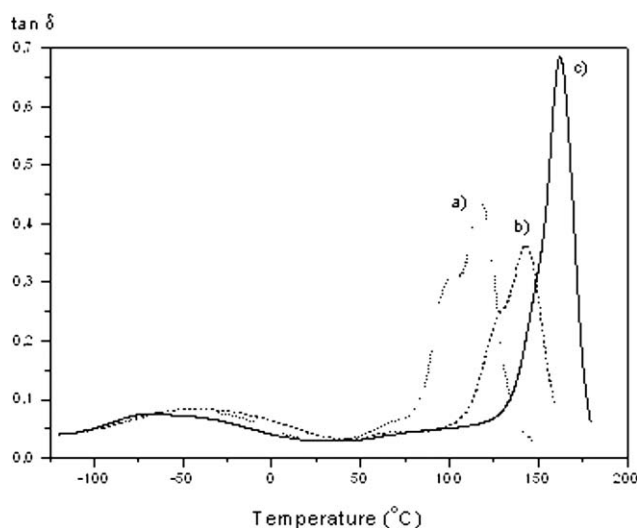


Figure 4 $\tan \delta$ as a function of temperature for epoxy networks (a) DGEBA/AEP, (b) DGEBA/TETA, (c) DGEBA/IPD.

TABLE III
Thermal and Adhesive Properties of Different Epoxy/
Amine Networks Obtained from Three Adhesion Tests

Networks	T_g (°C)	Adhesive strength in lap shear joints (MPa)	Load to break in T-peel joints (N)	Impact energy in impact joints (Jm^{-2})
DGEBA/TETA	124	16.6 ± 0.8	146 ± 16	11.7 ± 2.0
DGEBA/AEP	115	19.9 ± 0.8	218 ± 15	18.1 ± 3.2
DGEBA/IPD	155	17.5 ± 0.5	148 ± 11	12.8 ± 2.7

distinct transitions: one at -50°C , which corresponds to secondary relaxation due to short molecular segmental motion and the other at around 118°C , 142°C , and 163°C , related to the glass-rubber transition of the DGEBA/AEP, DGEBA/TETA, and DGEBA/IPD, respectively.

The DGEBA/IPD system shows higher tan delta peak height of the T_g transition than the others epoxy network system. This result confirms the lower mobility of the DGEBA/IPD epoxy network as a consequence of the increase in the rigidity of chain between crosslinks.

Adhesive properties

The adhesive properties were evaluated on steel-steel joint mechanically treated. Different mechanical tests using various adhesive joints geometry such as, single-lap shear, T-peel, and impact were performed. Table III illustrates the adhesive properties of different epoxy polymers obtained from different joints tests. The T_g of the epoxy networks presents large influence on the mechanical behavior of the adhesive joints. This result is similar to the mechanical behavior previously discussed. The DGEBA/AEP system exhibits the best adhesive properties. The value of the load to break in T-peel joints is 47% superior than for the other systems. Although our data were obtained at room temperature, the networks originated by AEP have similar adhesive behavior when compared to the networks with low crosslink density observed at high temperatures.²⁵

Figure 5 shows the chemical structures of the corresponding epoxy networks. The AEP system exhibits high flexibility and low- T_g epoxy network. The TETA and IPD systems show high crosslinking density. However, the TETA structure exhibits more flexibility when compared to the rigid structure, leading to a (relative) high- T_g .

The performance of the adhesive properties is related to different structure of the epoxy polymers. 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 to full conver-

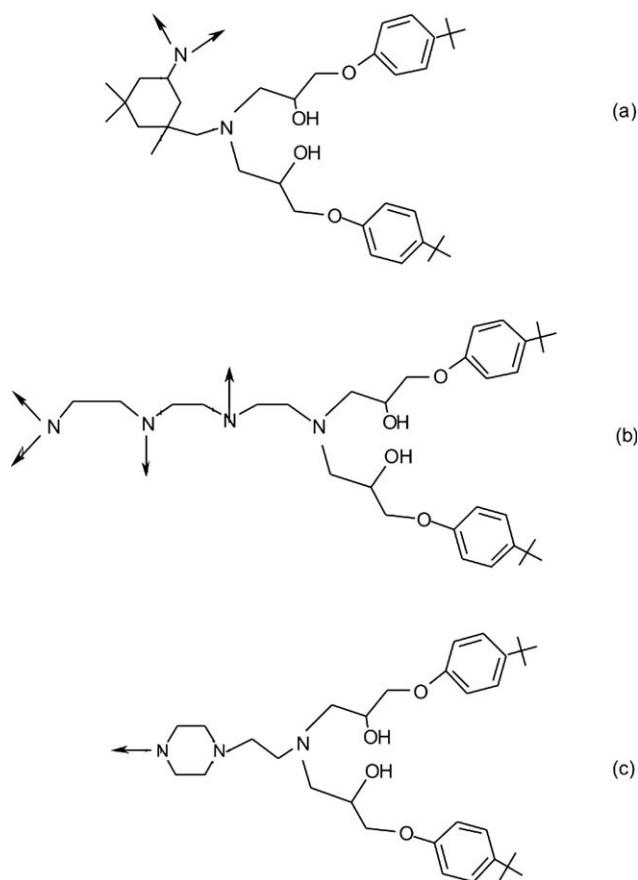


Figure 5 Chemical structures of the networks. (a) with isophorone diamine (IPD), (b) with triethylenetetramine (TETA), and (c) with 1-(2-aminoethyl)piperazine (AEP).

sion. In this case; it is possible to relate the mechanical properties and adhesives properties to the molecular architecture of the epoxy networks.

Characterization of the adherend surface

Figure 6 illustrates the different failure type in the adhesive joints. The failure can occur inside the

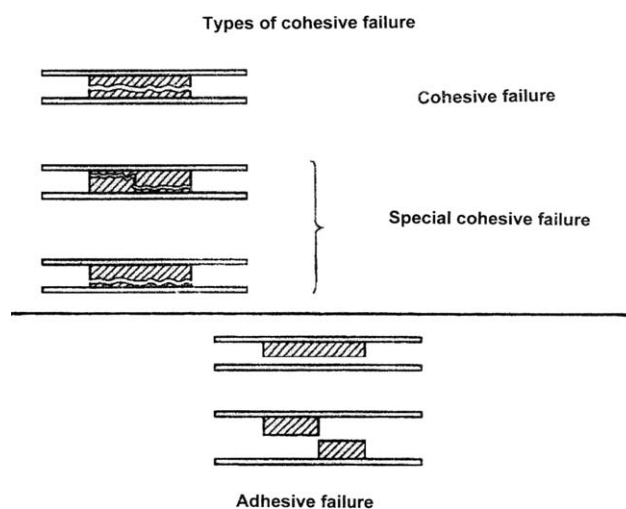


Figure 6 Types of failure in adhesive bonds.

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

Adhesive	Cohesion failure (%)
DGEBA/TETA	75
DGEBA/AEP	82
DGEBA/IPD	78

adhesive layer (cohesion 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 surface. These results are summarized in Table IV. As expected, the cohesive failure dominates in the epoxy adhesive.²⁶

CONCLUSIONS

In summary, the mechanical and adhesive properties of the epoxy networks depend on the molecular architecture. The DGEBA/IPD system exhibits highest values of the glass transition temperature and yield stress. However, DGEBA/AEP epoxy shows the best impact resistance and the lowest glass transition temperature values and also the best adhesive properties. The best mechanical resistance and impact joints were observed for the T-peel joints. Finally, we noted that the epoxy adhesives dominate the cohesion failure.

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