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Variation of the Adhesive Properties of an Epoxy Resin Modified by End-Functionalized Liquid Polybutadiene as a Function of Temperature and Water Absorption

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Variation of the Adhesive Properties of an Epoxy Resin Modified by End-Functionalized Liquid Polybutadiene as a Function of Temperature and Water Absorption

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The adhesive behavior of a diglycidyl ether of bisphenol-A epoxy resin modified by end-functionalized liquid polybutadiene was evaluated as a function of the temperature and of the time of immersion in distilled water. The neat epoxy and three modified systems were analyzed. Butt joints and single-lap joints were tested using an API X60 steel as substrate. The monophasic system obtained by reacting the epoxy monomer with hydroxyl-terminated polybutadiene (HTPB) functionalized with isocyanate groups (EPI) showed the best performance. The results show that this system is stable in respect to water degradation, but changes when exposed to temperature. Under the set of experimental parameters of time and temperature used, however, the adhesive strength increased with the temperature. For all epoxy formulations analyzed the fracture mode observed was of the adhesive type.

Keywords: Adhesive joints; Ageing; Epoxy resins; HTPB

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INTRODUCTION

Nowadays, adhesive bonding is being used in many industrial applications, including repair of pipes used for the transport of crude oil and other offshore applications [1–3]. Epoxy resins are among the most used structural adhesives due, partially, to the many epoxy formulations that can be prepared, and that show a large range of properties. Epoxies are also fairly easy to handle and can be manipulated with minimal hazard. Despite these good characteristics, epoxies are brittle materials [4] and can readily absorb water from the environment [5,6]. To increase the toughness of brittle thermoset polymers, like epoxies, elastomeric [7–11] and even thermoplastic polymers [12] can be used as additives. The use of hydroxyl-terminated compounds, like hydroxyl-terminated polyurethanes [13], hydroxyl-terminated polyesters [14,15], or hydroxyl-terminated poly(butadiene-coacrylonitrile) [16] proved to be very effective. Another possible way to improve the toughness of brittle polymers is introducing flexible segments on the macromolecular network [17,18].

Also, the use of hydroxyl-terminated polybutadiene (HTPB) to modify the macromolecular structure of the diglycidyl ether of bisphenol-A (DGEBA) epoxy formulations were shown to produce epoxy systems with a convenient set of properties [19,20]. The complete description of the modifications produced by the direct incorporation of HTPB and functionalized HTPB adducts on the macromolecular structure of the DGEBA based epoxy has been done in previous works [19,20]. In short, three different epoxy systems were developed: a biphasic DGEBA/HTPB blend (EPH); a biphasic system where the epoxy monomer was reacted with HTPB functionalized with carboxyl groups (EPA), and a monophasic system obtained by reacting the epoxy monomer with HTPB functionalized with isocyanate groups (EPI). The EPH blend is characterized by the presence of large elastomeric spherical domains ranging from around 11 to 32 μm in diameter while for the EPA system, the elastomeric domains are around 0.5–3 μm in diameter [20]. The EPI system, which is referred to here as monophasic, is a translucent and homogeneous material, with no observable elastomeric domains under scanning electron microscopy (SEM) examination [20]. However, previous dynamic mechanical analysis (DMA) indicates that phase separation can be occurring in this system [20]. Therefore, it could be that nanosize particles are being formed.

In this work, the feasibility of using these novel epoxy formulations as adhesives was analyzed. The structural API X60 steel, commonly used for oil transportation, was used as adherent. Single-lap and butt

joints were tested, and the effect of water absorption and temperature on the strength of the joints was evaluated.

EXPERIMENTAL

The API X60 is a high strength structural steel largely used by the gas and oil industry. Its average chemical composition is shown in Table 1 (the balance iron) [21].

The butt joints were manufactured according to the ASTM D-2094 standard. Figure 1a shows the geometry and dimensions of half of the joint, highlighting the 5 mm diameter hole used to fix the joint to the grips of the testing machine. The surface to be adhesively joined was mechanically cleaned using a jet of steel grit (GH 40B, Sinto Brazil, São Paulo, Brazil). The experimental set-up of the equipment used was: jet speed of 600 km/h and jet pressure of 7 kg/cm². The surface was then chemically cleaned using a nitro-phosphoric solution, as recommended by the ASTM D-2561 standard.

The roughness of these mechanically and chemically treated surfaces was determined using a surface roughness tester (Mitutoyo, Surf test 211, Mitutoyo Sul Americana, Suzano, Brazil) prior to joining. The average value, R_a , between the highs and depths of all valleys and peaks along eight different profiles was determined in this work. The contact angle between the different epoxy formulations and the treated surface of the API X60 steel was also evaluated. A Ramé-Hart goniometer (Ramé-Hart, Polimate Ltd., Porto Alegre, Brazil) was used and the tests were conducted at 25°C and 45% RH. Three measurements were made for each of the epoxy systems analyzed.

The joints were mounted using the unmodified epoxy resin (EP) and the HTPB modified formulations (EPH, EPA and EPI). The hardener used was the amine based EPICURE 3140 (HCl, São Paulo, Brazil), consisting of a mixture of diethylenetriamine and triethylenetetramine with the number of amine groups corresponding to 378 g/equiv. equiv. The HTPB used in the EPH blend and also used to prepare the HTPB adducts has a $\overline{M}_n = 3000$, and a hydroxyl number of 0.8 g/mequiv.

TABLE 1 Typical Chemical Composition of the API X60 Steel (wt%)*

C_{\max}	Mn_{\max}	P_{\max}	S_{\max}	Ti_{\max}
0.24	1.40	0.025	0.015	0.04

*Product specification level 2 (PSL 2) for seamless products.

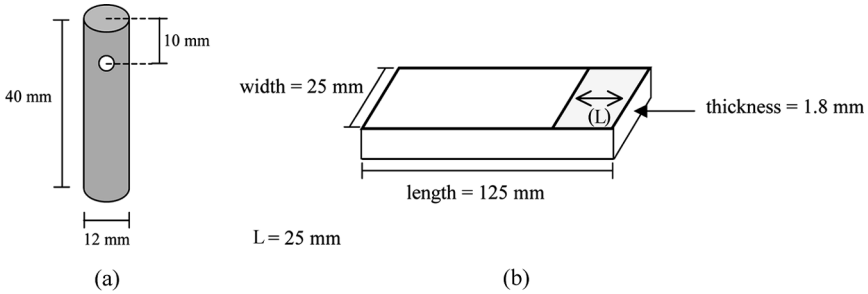


FIGURE 1 Geometry and dimensions of the adherents (a) butt joint and (b) single-lap joint.

The proper adhesive was applied using the brushing technique. Care was taken to avoid the entrapment of air bubbles and to obtain an adhesive layer with uniform thickness. The joints were held vertically in an alignment jig under a pressure of 0.1 MPa until the cure of the epoxy adhesives was completed. The final adhesive preparation is fully described elsewhere [20]. In short, the proper amount of epoxy monomer was first degassed for 60 min at 80°C and then the appropriate component (HTPB or functionalized HTPB adducts) was added and the mixture was stirred for 5 min. For the adhesive joints analyzed in this work the cure cycle used was 2 h at 70°C and 6 h at 100°C.

The single-lap joints were prepared following the same procedure described above. The dimensions of each of the steel strips used are shown in Figure 1b.

Before both types of joints were tested, the thickness of the adhesive layer was evaluated measuring the thickness of each test specimen, respectively, for the butt joint and the single-lap joint. Since the dimensions of each half of the joint were known, the adhesive layer thickness was obtained by difference. The measurements were made within ± 0.001 mm using a profile analyzer. Three values were measured for each test specimen.

The joints were aged following two different procedures: i) they were immersed in distilled water at room temperature and removed for test after 45 and 90 days, and ii) they were conditioned in an air-circulating oven for 7 days at 80°C and 150°C. The choice of these experimental conditions was based on the expected service use of the adhesives. Namely, room temperature humid environments or, at most, contact with steel parts transporting oil with a maximum expected temperature of 60°C. Therefore, the experimental parameters were aimed to observe the behavior of the adhesives under accelerated aging conditions.

After aging, the joints were tested on a mechanically driven test machine (Instron, Instron Brazil, São Paulo, Brazil) with capacity of 50 kN, at room temperature, and at 0.5 mm/min, according to the ASTM standards D-2095, for the butt joints, and D-1002, for the single-lap joints. Ten specimens were tested per joint configuration, test condition, and epoxy system.

The fracture surface of the single-lap joints was analyzed by SEM. The analysis was performed with secondary and backscattered electrons, at a beam voltage of 15–20 kV on samples covered with a conductive layer of sputtered carbon.

EXPERIMENTAL RESULTS AND DISCUSSION

The surface roughness of the adherents was $R_a = 9.92 \pm 0.76 \mu\text{m}$. From the low standard deviation obtained one could infer that the treatment performed was reliable enough to produce a homogeneous surface.

Figure 2 shows the evolution of the contact angle with time for the unmodified epoxy and for the three HTPB modified formulations. It can be seen that after 200 s a steady behavior was obtained and, therefore, the contact angles listed in Table 2 were measured at 220 s, well into the steady region of the contact angle *vs.* time curve. It is readily apparent from these results that the HTPB modified epoxy

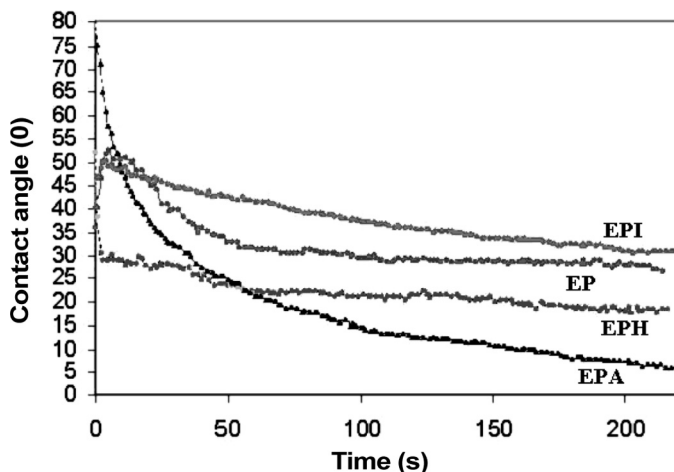


FIGURE 2 Variation of the contact angle with time.

TABLE 2 Values of the Contact Angle 220 s After the Adhesive Drop is Placed

Adhesive	Angle(°)
EP	26
EPH	18
EPA	6
EPI	31

formulations have a different behavior from that of the unmodified resin. The biphasic systems (EPA and EPH) show lower values for the contact angle than the neat epoxy, indicating that these systems have a better ability to wet the steel substrate. To the contrary, the monophasic EPI formulation has a higher contact angle than the unmodified epoxy resin, although the difference is not large.

The transient region, where the contact angle varies with time, reflects the differences of viscosity between the various formulations, and the shorter the time to reach a steady state the lower the viscosity. The curves show that the EPI formulation has the highest viscosity among the formulations analyzed, followed by EPA and EPH. To which extent a higher, or a lower, viscosity is a desirable characteristic depends on the adhesive use. For an adhesive joint, for example, a compromise between the ease of its application and the avoidance of adhesive flow from the joint must be found. Therefore, the results shown in Figure 2 do not exclude, *a priori*, the EPI formulation, although it has a lower wetting capability in respect to the steel substrate. In fact, a good wetting behavior of this formulation with an aluminum substrate was obtained after heating the EPI formulation for 5 min at 70°C [22].

The average thickness of the adhesive layer of both single-lap and butt joints was 0.10 mm but, despite the careful procedure used to apply the adhesive, a large range of values—from 0.02 to 0.18 mm—was obtained. This result raises a point of concern, since the strength of an adhesive joint is strongly dependent on the thickness of the adhesive layer [23]. Another protocol for laboratory control could be implemented to reduce this variation but, in fact, in real situations when the adhesive will be applied *in-situ* at a pipeline, even using microspheres as fillers in the adhesive to control the minimum thickness of the adhesive layer, variations in the thickness of the adhesive layer could be expected. Therefore, variations of the joint strength must be accounted for when the adhesive joints are being evaluated.

The results obtained for the strength of the butt joints are listed in Table 3. For the as-fabricated joints (immersion time = 0), there are no clear advantages of using HTPB modified formulations over the unmodified epoxy. A minor increase in the tensile strength was obtained with the EPI formulation but the difference relative to the unmodified epoxy, and even to the EPH blend, is not statistically significant. The EPA system was the only one with a statistically different result, but the level of strength obtained with this adhesive formulation was lower than that of the unmodified epoxy and the difference of the mean values is not high, $\Delta\sigma = -14.6\%$.

The minor variations observed in the values of the strength for these joints can be attributed to the complex stress state to which the adhesive layer is submitted on a butt joint. In fact, the stress varies from pure hydrostatic at the center of the joint to plane stress state at its periphery, where the normal stress acting perpendicularly to the adhesive/adherents interface is a maximum [24]. The triaxial stress state restrains the deformation capacity, and promotes brittle failure, thus inhibiting any toughening effect caused by the HTPB modifications.

The relevant difference of behavior was found when the butt joints were immersed in water (Table 3). The results show that water absorption strongly degrades the tensile strength of all but the EPI joint, indicating that this formulation has a stronger resistance to water effects. In fact, the EPI formulation has the smaller diffusion coefficient between the epoxy formulations analyzed here [25]. It could be that this behavior is due to the inferred presence of nanosize particles [20], since the barrier properties of polymer based nanomaterials are greatly increased over the unmodified matrix, due to the increase in the free path for water transport within the material [26]. The behavior shown by the EPI joint is very attractive from a practical point of view, since the test performed here is much more severe than the usual conditions found by a repair joint in service. These joints will

TABLE 3 Adhesive Strength of the Butt Joints in MPa, as a Function of the Immersion Time in Distilled Water

Epoxy formulation	Immersion time (days)		
	0	45	90
EP	22.69 ± 1.23	3.47 ± 1.13	2.43 ± 0.87
EPH	21.55 ± 5.11	0.88 ± 0.12	0.88 ± 0.30
EPA	19.37 ± 2.68	0.82 ± 0.24	0.37 ± 0.08
EPI	24.08 ± 4.11	26.06 ± 4.77	19.73 ± 4.43

certainly be in contact with humidity, but it is seldom that they will be immersed in water.

Exposure of the butt joints to temperature caused a “strengthening” effect, with significant increase of the tensile strength for all systems, and particularly for the EPA and EPI formulations (Table 4). Since the joints were already post-cured before this temperature aging experiment, these results indicate that further temperature driven reactions are occurring. From a practical point of view, nevertheless, the results are in fact better than if the adhesive were stabilized by the post-cure treatment. The temperature of crude oil being transported is about 60°C. Therefore, joints prepared with these formulations, that already have an “as-fabricated” adequate strength level, will strengthen with the time, becoming safer during operation.

It is clear, however, that aging for longer times has yet to be analyzed in order to establish a time interval for which the properties of the adhesive are improved. Moreover, the toughness of these joints must also be determined in order to determine the effects of this increase of tensile strength on their fracture behavior. Why the properties of the post-cured structures occurred is an open question. But, since the reaction of common bisphenol-A epoxy resins with phosphoric acid produces epoxyated phosphate oligomers with chemical groups capable of reacting both with the steel surface and with the polymer functional groups, and promote better adhesion [27], it is speculated here that the observed increase on the joint strength could be related to a temperature driven reaction of the acidic surface and the epoxy resin.

In the single-lap joint configuration, the two strips of the substrate overlap and the tensile load applied generates shear and tear stresses in the adhesive and at the joined surface of the substrates [28–30]. The shear stresses, in particular, have a parabolic distribution, with peak values at the edge of the lap joints. A complete description of the

TABLE 4 Variation of the Adhesive Strength of the Butt Joints, MPa, After Being Exposed for 7 Days to Temperature

Epoxy formulation	Temperature (°C)		
	23	80	150
EP	22.69 ± 1.23	30.28 ± 7.53	33.27 ± 4.71
EPH	21.55 ± 5.11	31.76 ± 5.82	28.31 ± 6.73
EPA	19.37 ± 2.68	39.74 ± 4.87	46.47 ± 5.39
EPI	24.08 ± 4.11	53.10 ± 7.92	48.13 ± 3.52

calculation of these stresses must take into account the thickness of the adhesive layer and the rigidity of the assembly [28]. These calculations are, nevertheless, beyond the scope of this work and only the average shear stress acting at the joints, τ_m , is presented here. τ_m is simply calculated by dividing the maximum load sustained by the single-lap joint by the area of adhesion. The values obtained for the as-fabricated single-lap joints as a function of the adhesive epoxy formulations are shown in Table 5. Similar to butt joints, EPI based adhesive showed the higher average value, although it is not statistically different from that of the unmodified EP. EPH and EPA formulations showed statistically significant lower values.

As shown in Table 5, immersion for up to 90 days did not cause such a strong effect as observed for butt joints. The results show, however, that the EPI formulation has once again the best performance with τ_m remaining almost constant. This behavior indicates good environmental stability of this adhesive, as already observed for butt joints (Table 3). The marked difference between the aging behavior when butt joints and single-lap joints are compared should be due to the externally imposed stress state. At the butt joints, as already said, one can expect a triaxial stress state to be developed at the adhesive layer, inhibiting any plasticizing effect caused by immersion in water. On the other hand, the stress state of a single-lap joint favors shear stresses, and any macromolecular change due to water absorption can be more accommodated at the joint.

Exposure to temperature (Table 6) brought changes in the average shear stress and in the majority of the cases, once again, to the safe direction, *i.e.*, shear stress tended to increase when the joint was exposed to a hot environment.

Figure 3 shows a typical fracture surface of the single-lap joints in the as-fabricated condition. Adhesive fracture was always observed, and one can see that the crack jumped from one interface to the other.

TABLE 5 Adhesive Strength of the Single-Lap Joints, τ_m (MPa)

Epoxy formulation	Immersion time (days)		
	0	45	90
EP	18.7 ± 2.4	13.2 ± 0.8	17.1 ± 1.2
EPH	12.4 ± 1.8	12.5 ± 0.8	18.6 ± 1.5
EPA	15.5 ± 1.5	14.2 ± 1.0	14.0 ± 1.6
EPI	19.7 ± 2.4	17.6 ± 1.6	18.2 ± 2.2

TABLE 6 Adhesive Strength of the Single-Lap Joints, τ_m (MPa), After Exposure for 7 Days to Temperature

Epoxy formulation	Temperature (°C)		
	23	80	150
EP	18.7 ± 2.4	12.9 ± 0.9	16.0 ± 1.7
EPH	12.4 ± 1.8	19.6 ± 1.1	23.4 ± 1.3
EPA	15.5 ± 1.5	16.3 ± 1.0	20.6 ± 1.6
EPI	19.7 ± 2.4	16.1 ± 1.6	24.6 ± 1.4

This latter aspect is due to the stress distribution imposed on the joint [30].

CONCLUSIONS

The modification of the basic diglycidyl ether of bisphenol-A epoxy monomer by end-functionalized liquid polybutadiene produces epoxy adhesives with differing adhesive properties and wetting characteristics in relation to the API X60 steel used as a substrate.

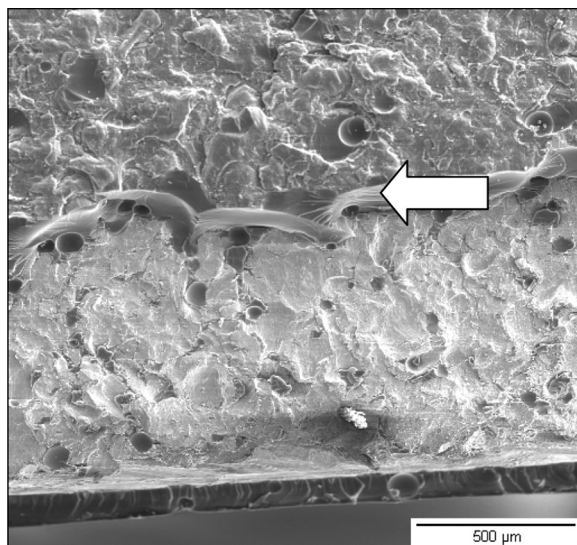


FIGURE 3 Adhesive fracture of the single lap-joints. A step (\leftarrow) is observed at the fracture surfaces, jumping from one metal-to-adhesive interface to the other.

Immersion in distilled water, combined with a triaxial tensile stress state in the butt joints, causes a strong decrease in the adhesive strength of the basic, unmodified, epoxy and of the biphasic systems, EPA and EPH.

The EPA biphasic system, where the epoxy monomer was reacted with HTPB functionalized with carboxyl groups, has the best wetting behavior among the systems analyzed in respect to the steel substrate. The adhesive strength of the butt joints and of the single-lap joints obtained with this adhesive is, however, smaller than that of the unmodified epoxy resin.

The adhesive properties of the monophasic EPI system, where the epoxy monomer was modified with HTPB functionalized with isocyanate groups were higher than that of the unmodified epoxy. Moreover, this system showed a good environmental stability in respect to immersion in water, being a promising candidate to be used in repairs of steel pipes.

Exposure to temperature caused an initial increase in the adhesive strength of the HTPB modified systems. This effect is desirable, but raises concerns about stability of the systems analyzed. Changes in toughness of these systems are of special concern, and must be measured.

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