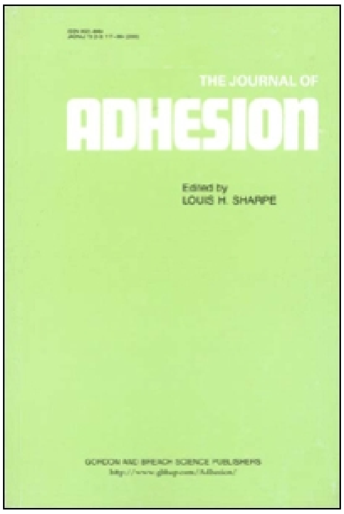

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Amino-*p*-benzoquinone Adducts and Polymers as Adhesion Promoters for Steel*

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Phenolic and quinonoid compounds are widely studied in biological sciences because of their ability to chelate heavy metals like iron and copper and recently have found new applications in synthetic macromolecules. Amino-*p*-benzoquinone polymers, poly[(2,5-hexamethylenediamino)-1,4-benzoquinone] and poly{[2,5-(2,2′-bistrifluoromethyl)-4,4′-biphenylenediamino]1,4-benzoquinone}, were synthesized and evaluated as adhesion promoters for steel/epoxy joints. An improvement in the torsional shear strength of these joints was observed when these polymers were used as adhesion promoters. The durability of the adhesive bond was also improved after boiling water treatment, relative to untreated and silane-treated joints. The improvement in adhesion could be attributed to the formation of a chelate between the polyaminoquinone (PAQ) and the iron surface and a chemical reaction between the PAQ and the epoxy resin. A low molecular weight model compound, bis[2,5-(4-methylanilido)]-1,4-benzoquinone, was also used to study coupling between the epoxy adhesive and the steel surface. Electron spin resonance (ESR), atomic absorption spectroscopy and infrared spectroscopy were used to document the epoxy-coupling agent reaction and the chelate formation.

Keywords: Polyaminoquinones; coupling agent; adhesion promoter; moisture; durability; epoxy/steel; torsional joint; adhesion

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INTRODUCTION

The durability of adhesives is affected by environmental factors. In a harsh environment they easily undergo degradation and fail to perform. Water is one of the most important causes of failure of adhesives, sealants and coatings [1]. Diffusion of water into the interfacial region can reduce the strength of polymer/metal adhesion systems by a number of different mechanisms [2–4]. A coupling agent or adhesion promoter is usually a di- or poly-functional compound, capable of forming a bond between the substrate surface and the adhesive through a true chemical interaction. Polymeric coupling agents are thought to present several advantages compared with low molecular weight coupling agents: they should be tougher and more hydrophobic, depending upon the polymer structure [5]. Another crucial factor one should take into account in designing an adhesive or coupling agent for use in a hostile environment is thermal and thermo-oxidative stability. Presently, several polymers, such as cyanates, bismaleimides, nadic end-capped and phenylethynyl end-capped aromatic polyimides have been investigated for high temperature applications. However, the sensitivity of these polymers after several hydrothermal cycles prevents long term use in humid environments at elevated temperatures. The introduction of trifluoromethyl or perfluoroalkyl groups has been shown to improve solubility and thermal stability of these polymers, while lowering the moisture uptake at the same time [6–9].

Although water is the worst enemy for synthetic adhesives, surprisingly it presents little or no problem to some natural adhesives secreted by mussels and barnacles [10]. These natural adhesives have been characterized and find use in some bioapplications [1]. Phenolic and quinonoid compounds are widely studied in biological sciences because of their ability to chelate transition metals like iron and copper and recently have found new applications in synthetic macromolecules [11–13]. A true chemisorption process has been proven to occur between these two classes of compounds and metallic surfaces [14–18].

There have been many reports in the literature which show that naturally-occurring catecholic protein polymers [19, 20], synthetic aliphatic amino-*p*-benzoquinone polymers [21–23], benzoquinone-amine modified polyurethanes [24–26] and heterocyclic benzoquinone polymers [27] form corrosion-resistant coatings on steel and iron surfaces. The theory proposed is that the polyaminoquinones (PAQ's) displace water from the metal surface [21] to form a strong bond to this surface either by chemisorption or by complexation of the iron by the amino-quinone ligand donor groups [16, 17].

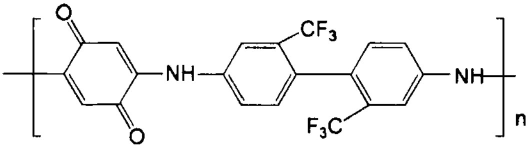
Adhesive bond measurements of the catecholic proteinaceous adhesive of living barnacles have been made by attachment of a solid cotton thread to the barnacle shell and measuring the force required to pull the barnacle off in a vertical direction from the surface [28–30]. A mean adhesive force of 24.5 MPa (3,500 psi) was measured for barnacle adhesive failure. This result clearly demonstrates the effectiveness of this natural adhesive made under seawater. No adhesive bond measurements have been made on the synthetic amino-quinone corrosion inhibitors.

Due to the lower water absorption and good thermostability of fluorinated polymers, fluorinated amino-quinone polymers were selected as potential candidates for coupling agents and adhesives. In the present paper, a novel fluorinated aromatic amine-*p*-benzoquinone polymer, an aliphatic amine-*p*-benzoquinone polymer and a diadduct of *p*-benzoquinone and *p*-toluidine (Fig. 1) were evaluated for their ability to promote adhesion to stainless steel surfaces, and to form a durable, moisture-resistant adhesive bond. Results of the interaction of the model compound bis[2,5-(4-methylanilido)]-1,4-benzoquinone diadduct to react chemically with the epoxy adhesive are also presented. Iron (III) complexes with poly{[2,5-(2,2′-bistrifluoromethyl)-4,4′-biphenylenediamino]1,4-benzoquinone} and bis[2,5-(4-methylanilido)]-1,4-benzoquinone were isolated and characterized. The amino-quinone/epoxy study and complex formation are directed toward developing an understanding of the adhesion mechanism.

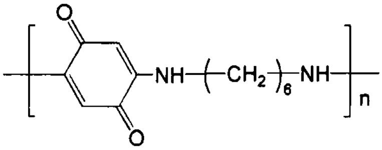
EXPERIMENTAL

Materials

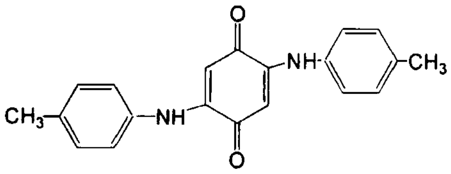
All the chemicals were purchased from either Aldrich or Fisher (unless otherwise specified) and used without further purification.



Poly{[2,5-(2,2'-bistrifluoromethyl)-4,4'-biphenylenediamino]1,4-benzoquinone}



Poly[(2,5-hexamethylenediamino)-1,4-benzoquinone]



Bis [2,5-(4-methylanilido)]-1,4-benzoquinone

FIGURE 1 Structures of polymers and model compound.

2,2′-Bistrifluoromethyl-4,4′-biphenylene diamine (TFMB) was purchased from Ken Seika Corp., Rumson, NJ, USA and used without further purification.

The structures of the starting reagents are shown in Figure 2.

Shear Strength of Neat Epoxy Resin

Epon 828® (Shell) was cured with a stoichiometric amount of 4,4′-methylenedianiline (4,4′-MDA).

Dog-bones specimens (gage section, 20 mml × 2 mmw × 1.0–0.5 th) of Epon® 828 cured with MDA were cast in a mold at 120°C for 1 hr followed by 150°C for 2 hr. The samples were then tested in tension in an Instron with a load cell of 100 lb (500 N), at a cross head speed of 5 mm/min, according to the ASTM D638 standard. The epoxy

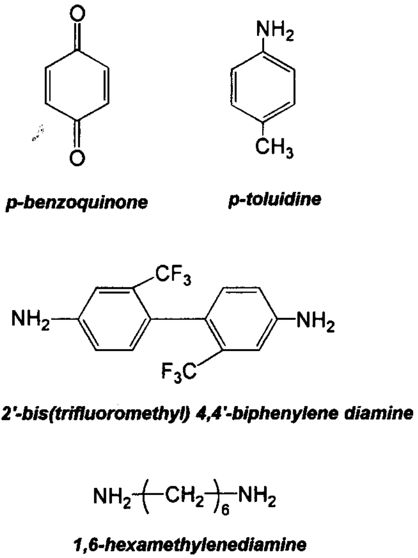


FIGURE 2 Starting materials for the synthesis of amino-*p*-benzoquinone polymers and model compound.

specimens were tested at room temperature and after exposure to boiling water for 24 and 96 hr. The shear strength (τ_{max}) was then calculated from the tensile strength at break (σ_{break}), using the equation

$$\tau_{\mathrm{max}} = \sigma_{\mathrm{break}} \cos\theta \sin\theta.$$

Polymer Synthesis

Several polymers have been synthesized from *p*-benzoquinone (*p*-BQ) and various aliphatic and aromatic diamines for testi as adhesion promoters [31–33]. However, only the adhesive results of two polymers derived from *p*-BQ and two diamines, 2,2′-bis(trifluoromethyl)-4,4′-biphenylene diamine (TFMB) and 1,6-hexamethylenediamine, will be described in this paper.

Poly{[2,5-(2,2′-bistrifluoromethyl)-4,4′-biphenylenediamino] 1,4-benzoquinone}, BQ012 and BQ007

This material was synthesized from *p*-BQ (0.09 mol, 9.78 g) and TFMB (0.03 mol, 9.60 g) in *N*,*N*′-dimethylacetamide at refluxing conditions for 3 hr. The product was precipitated by the addition of the reaction solution to an ice/water mixture (50/50), filtered, washed first with water, then with toluene and then dried at 70°C in vacuum for 48 hr. A dark brown solid (m.p. $\geq$ 300°C) was obtained in 87% yield.

FT-IR: 3238 cm^{-1} (N—H), 1624 and 1508 cm^{-1} (C=O).

Elemental Analysis: Calc.: C = 56.61%, H = 2.37%, N = 6.60%, F = 26.90%; Found: C = 57.03%, H = 2.11%, N = 6.21%, F = 27.45%.

Poly[(2,5-hexamethylenediamino)-1,4-benzoquinone], BQ128

p-BQ (0.06 mol, 6.47 g) was dissolved in 65 mL tetrahydrofuran (THF). A solution of 1,6-hexamethylendiamine (0.02 mol, 2.32 g) in 25 mL THF was added dropwise over a time period of 20 min to the BQ solution. The resulting solution was stirred at room temperature for 3.5 hr. The color turned from bright yellow to dark brown. The product was precipitated in ice/water (50/50), washed with ethanol and vacuum-dried in oven for 20 hr at 60°C. Yield = 95%.

FT-IR: 3231 cm^{-1},(N—H), 1629 and 1516 cm^{-1} (C=O).

Elemental Analysis: Calc.: C = 65.43%, H = 7.32%, N = 12.72%; Found: C = 65.40%, H = 7.50%, N = 11.90%.

Bis[2,5-(4-methylanilido)]-1,4-benzoquinone, MC04

p-BQ (16.2 g, 0.15 mol) was dissolved in 100 mL THF. A solution of *p*-toluidine (5.36 g, 0.05 mol) in THF (50 mL) was added dropwise at room temperature over a period of 20 minutes, then allowed to stir at RT for 4 hr. The reaction solution was added to an ice/water mixture (50/50). The product, which precipitated, was filtered, washed thoroughly with ethanol and then vacuum dried at 60°C overnight to yield a black compound in 57% yield (m.p. = 313°C, determined by DSC).

FT-IR: 3238 cm^{-1} (N—H), 1635 and 1564 cm^{-1}(C=O).

Elemental Analysis: Calc.: C = 75.45%, H = 5.69%, N = 8.80%; Found: C = 75.60%, H = 5.76%, N = 8.36%.

Complex Formation

Iron (III) chelates of the diadduct bis[2,5-(4-methylanilido)] *p*-benzoquinone and the polymer poly{[2,5-(2,2′-bistrifluoromethyl)-

4,4′-biphenylene diamino]1,4-benzoquinone} were formed by stirring an aqueous solution of $FeCl_3 \cdot 6H_2O$ (metal concentration = 2.0 mM) with a known amount of polymer or model compound (both insoluble in water) for 24 hr at room temperature, according to a published procedure [10–13]. The suspension was filtered and the colloidal solid was washed thoroughly with deionized distilled water and then with hot ethanol. The difference between initial and final concentration of the metal in the filtrate was measured by Atomic Absorption Spectroscopy. The polymer- and model compound-metal complexes were then analyzed by solid state Electron Spin Resonance (ESR) and DSC.

Characterization of the Amino-quinone/Epoxy Reaction

A thin film of a stoichiometric mixture of Epon 828® epoxy resin and bis[2,5-(4-methylanilido)] *p*-benzoquinone was spread on a pure KBr crystal. The FT-IR spectrum of the film was recorded. The disappearance of the epoxide band at 1250 cm^{-1} as a function of time at constant temperature (150°C) was recorded over a 1.5 hr period.

Characterization of Amino-*p*-benzoquinone Polymers and Adducts

Fourier Transform Infrared (FT-IR) spectroscopy was carried out on a Nicolet 605X FT-IR spectrometer. Samples were incorporated in a dry KBr pellet, unless otherwise specified.

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC7, using aluminum pans.

Joint Preparation and Adhesion Measurements

1018 steel/1018 steel torsional joints (Fig. 3) were prepared and measured according to a published procedure [34, 35]. The surface of the joints was machine polish and then etched by immersion in an aqueous solution of citric acid (3%), neutralized with ammonium hydroxide for 15 min at 70°C. The etching was followed by two rinsing steps: (1) distilled water and (2) methanol. The coupling agent was then applied from a 0.1%w/v THF solution (unless otherwise

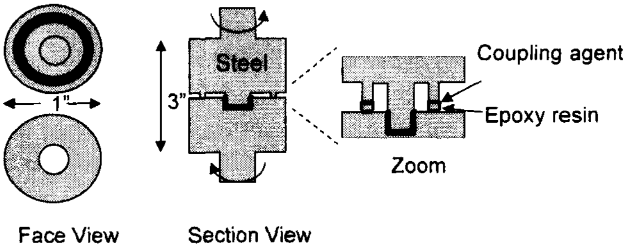


FIGURE 3 Schematic of steel torsional joint.

specified) by immersion of the joint surface in the solution for 15 min. The excess of material was removed by a final rinsing with THF. For the control joints (epoxy/4,4′-MDA only) the treatment was the same but, obviously, the coating step was omitted. After this pre-treatment, a measured quantity of premixed Epon 828® and 4,4′-MDA (44 ± 1 mg) was smeared onto the joint surface, the joints were mated and twisted to produce an air-free film between the surfaces, and then cured in a programmable oven at 120°C for 60 min and at 150°C for 120 min. The joints were then tested in shear with a modified Instron machine (speed: 1.27 cm/min) at room temperature under ambient conditions and after boiling water exposure.

Durability Tests

Durability tests were performed by immersing the joints in boiling distilled water for various time periods, followed by torsional shear testing.

Pure Iron Wire Test

One end of a pure iron (99.9995%) wire was coated by immersion in a 1% solution of bis[2,5-(4-methylanilido)] *p*-benzoquinone in THF for 15 min. After evaporation of the solvent, the wire was inserted into a Micarta® (phenolic resin+canvas) solid cylinder holder containing a hollow section for bonding the wire with epoxy resin as shown in Figure 4. A stoichiometric epoxy/4,4′-MDA mixture was then applied to the reservoir to bond the wire to the holder and the assembly was then cured at 150°C for 3 hrs. The holder served the

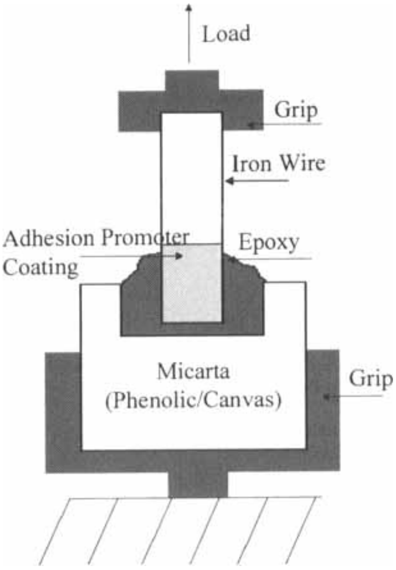


FIGURE 4 Schematic of the mounting of iron wire into sample holder.

purpose of filling the gap between the wire and the Instron grip (Fig. 4). The iron wire specimen obtained (diameter = 1 mm, 0.039 in, length = 6.3 mm, 0.24 in) was tested in an Instron at an (engineering) strain rate of 2.4% in a 1.5 min period, in liquid nitrogen (−197°C).

RESULTS AND DISCUSSION

Adhesion

Room Temperature Results

Room temperature adhesion strength data on stainless steel torsional joints for the control (no adhesion promoter), silane (γ-glycidoxypropyltrimethoxysilane), the hexamethylenediamine-*p*-benzoquinone polymer (BQ128), the fluorinated aromatic *p*-benzoquinone polymer (BQ012) and the *p*-toluidine-*p*-benzoquinone diadduct (MC04) are summarized in Table I. The torsional shear strength data for the control (no adhesion promoter) epoxy adhesive measured at different occasions varies considerably, from a low of 44.0 MPa (6328 psi),

TABLE I Room temperature torsional shear strength (σ) of stainless steel/stainless steel joints

System	σ, *MPa*	σ, *psi*	*Standard deviation*, %
Control	44.0	6,378	16.3
Control	56.5	8,190	8.9
Control	49.6	7,188	4.0
Control	58.8	8,533	10.0
Silane[a]	56.0	8,127	9.2
BQ128[b]	59.7	8,658	5.8
BQ007[c]	67.3	9,766	6.0
BQ012[c]	59.9	8,684	6.3
BQ012	72.9	10,567	1.0
BQ012	64.6	9,371	2.8
BQ012	61.0	8,852	2.7
MC04[d]	62.9	9,125	4.3

[a] γ-glycidoxypropyltrimethoxysilane.
[b] Poly(hexamethylenediamino-*p*-benzoquinone).
[c] Poly(trifluoromethyl-4,4′-biphenylenediamino-*p*-benzoquinone).
[d] Bis-[2,5-(4-methylanilido)]-*p*-benzoquinone.

to a high of 58.8 MPa (8533 psi), with a standard deviation from 4 to 16.3%. The mean strength for the silane adhesion promoter is 56.0 MPa (8127 psi), with a standard deviation of 9.2%. For the hexamethylene diamine-*p*-benzoquinone polymer (BQ128), a mean strength of 59.7 MPa (8658 psi) was attained, with a standard deviation of only 5.8%. Finally, for the fluorinated aromatic amine-*p*-benzoquinone polymer (BQ007 and BQ012), shear strengths ranged from 59.9 MPa (8684 psi) to 72.9 MPa (10567 psi), with a standard deviation from 4.0 to 6.3%. The shear strength derived from the diadduct adhesion promoter bis[2,5-(4-methylanilido)] *p*-benzoquinone (MC04) is 62.9 MPa (9125 psi) ±4.3%. Clearly, the room temperature torsional shear data suggest that wetting of the stainless steel surface by the epoxy resin or by the silane adhesion promoter is not as effective as the aminoquinone polymers or *p*-benzoquinone diadduct.

Boiling Water Results

The real test of the effectiveness of the adhesion promoter is the retention of torsional shear strength after boiling water immersion for several hours. Only the BQ012 aminoquinone polymer was tested under these conditions. The data for the BQ012 PAQ are shown in

Table II and Figure 5. It should be pointed out that the data scatter after this test is considerably higher than the scatter for the room temperature tests. However, the wet shear strength data for the fluorinated aromatic aromatic PAQ adhesion promoter after 72 hr water boil is 29.5 MPa (4281 psi) ± 14.5% and 25.6 MPa (3720 psi) ± 29.9% after 96 hours, while the data for the epoxy control for the same time period are 18.8 MPa (2735 psi) ± 22.4% and 17.5 MPa (2538 psi) ± 22%, respectively. Despite the large scatter in the data, the aminoquinone system is clearly more effective in maintaining good adhesion after this stringent test. The standard deviation for the aminoquinone series is smaller than for the epoxy series. Moreover, the shear strength of the epoxy resin adhesive after 24 hr boiling water exposure, calculated from tensile measurements, is around 4000 psi (see Tab. III). This value is very close to the value measured in the BQ012 joints after 24 hr exposure to boiling water, while the remaining

TABLE II Effect of boiling water on torsional shear strength for steel/steel joints

System	0 *hr* *MPa* (*psi*)	24 *hr* *MPa* (*psi*)	48 *hr* *MPa* (*psi*)	72 *hr* *MPa* (*psi*)	96 *hr* *MPa* (*psi*)
Control	49.4 (6378) ± 16.2%	24.1 (3496) ± 18.2%	15.3 (2216) ± 39.2%	18.8 (2735) ± 22.4%	17.5 (2538) ± 22.0%
BQ012	59.8 (8684) ± 6.2%	29.3 (4252) ± 14.3%	28.7 (4170) ± 14.1%	29.5 (4281) ± 14.5%	25.6 (3720) ± 29.9%

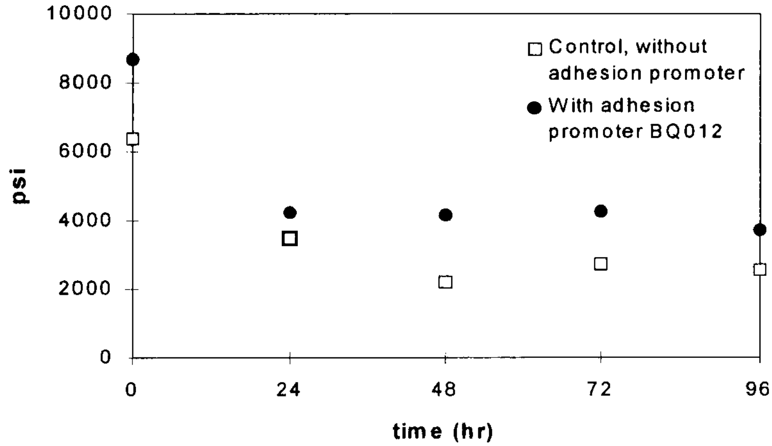


FIGURE 5 Shear strength of torsional joints *vs.* boiling water exposure time.

TABLE III Shear strength of the Epon828®/MDA system at room temperature and after exposure to boiling water

Time, hr	*psi*	*MPa*	*Standard deviation, %*
0	3730	28.9	12.3
24	4081	31.6	14.1
96	6136	47.5	9.6

strength of the control joints, after 24 hr, is as low as 17.2 Mpa (2500 psi). This strongly suggests that the epoxy/adhesion promoter/steel interfacial region is stronger than the epoxy/steel interfacial region. After an initial strength degradation in the first 24 hr, probably due to removal of low molecular weight material and/or plasticization of the resin, both systems achieve an equilibrium moisture uptake. In the joints without promoter, the hot water is more likely to diffuse through the epoxy film and epoxy/steel interface, significantly degrading the mechanical properties in the first 24 hr. In the case of the joints containing adhesion promoter, moisture diffuses in the epoxy film but meets a barrier at the epoxy/steel/adhesion promoter interface, thereby causing failure in the epoxy region of the adhesive joint. Therefore, the strength retained is very close to the shear strength of solid, thick epoxy specimens, even though in the adhesive joint the epoxy layer has a thickness of only 250 μm. This explanation is also corroborated by the smaller standard deviation, which is a possible indication of better interfacial control.

The increase in the epoxy shear strength after 96 hr in boiling water may be explained as a postcure effect caused by the combined actions of heat and moisture. Assuming that equilibrium occurs across the joint diameter (2.54 cm) and joint thickness (250 μm), failure might be taking place at the adhesion promoter/resin interface region rather than in the epoxy adhesive layer itself.

Long-term immersion can result in very complex stress states at the various boundaries, and considering that the epoxy is still postcuring, the weakest point in the joint cannot be precisely determined without more sophisticated tests. Failure modes of the fractured joints as determined by visual observation also reinforce these conclusions by revealing the nature of the fracture. Joints containing no adhesion promoters failed adhesively and mostly at the metal/epoxy interface region. Joints containing adhesion promoters failed mostly cohesively in the epoxy region. Exact identification of the fracture initiation point requires additional studies to arrive at a more definitive conclusion.

Evidence for Coupling of the Adhesion Promoter to the Epoxy Adhesive

An adhesion promoter theoretically should create a strong bond to the surface and to the adhesive matrix. The formation of iron complexes and the corrosion resistance of aminoquinone-coated steel surfaces provide evidence that a strong bond forms between the metallic surface and the aminoquinone moiety. The presence of secondary amino-groups in the aminoquinone provides a method for direct bond formation to the epoxy adhesive, by reaction with the epoxide functionality. We have investigated this possibility by monitoring the reaction between the model compound bis[2,5-(4-methylanilido)]-1,4-benzoquinone (MC04) and the epoxy resin using infrared spectroscopy, as shown in Figure 6, where the disappearance of the epoxide band (1250 cm^{-1}) as a function of time was recorded. At 150°C, over a period of 90 min, a gradual decrease of the epoxide band at 1250 cm^{-1} and the secondary amine band at 3240 cm^{-1} are noted, until the amine-epoxide reaction is completed. Clearly, this reaction provides a chemical link between the adhesion promoter and the epoxy adhesive.

Evidence for Bonding to Metal Surface

As described above, the improvement in the durability of the adhesive joints, containing either the amino-*p*-quinone diadduct (MC04) or polymer (BQ012) adhesion promoters, can be attributed to a chemisorption process between the steel surface and the electron donor groups on the aminoquinone moiety or the π-electrons on the quinone ring [14–18]. It has been demonstrated that the mode of absorption of amino-substituted quinones and hydroquinones is mixed, that is, the absorption on the metal surface is due to both π electrons on the rings and unshared pairs on amino or carboxylic moieties [14]. Some evidence to this effect was demonstrated by many reports on the excellent corrosion resistance of naturally-occurring

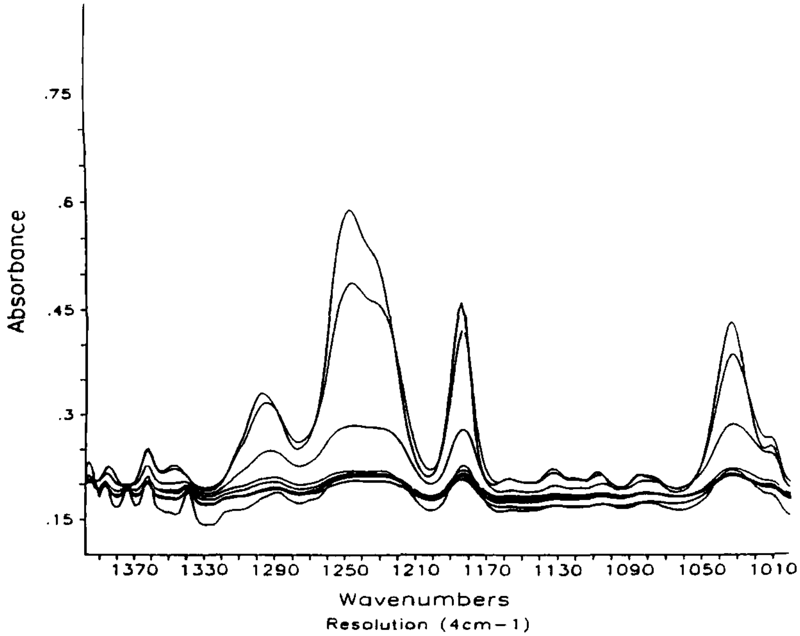


FIGURE 6 FT-IR stacked plot of the 1250 cm^{-1} band *vs.* reaction time for bis[2,5-(4-methylanilido)]-1,4-benzoquinone and epoxy.

catecholic proteins [19, 20], synthetic amino-quinone polyurethanes [24–26] and an amino-*p*-quinone polymer [27]. This evidence suggests that complex formation occurs between the metallic surface and the catecholic or aminoquinone moieties of the polymers. The evidence for complex formation raises the question of whether complexes can be isolated between amino-quinone compounds or polymers and metals, such as iron. In this connection, we have subjected ferric chloride to two systems: the amino-quinone diadduct (MC04) and the fluorinated aromatic BQ012 polymer. The materials isolated were analyzed for metal and organic content and by electron spin resonance (ESR) spectroscopy and DSC. Atomic absorption analysis of ferric chloride solutions, before and after exposure, was also carried out.

From the atomic absorption data it is possible to determine the chelating capacity, chelating efficiency and the ligand density, from which the stoichiometric ratio of ligand to iron (III) can be estimated, as summarized in Table IV. The chelating efficiency can be calculated as follows:

$$\text{Chelating Efficiency} = 100\,\frac{\text{moles of Fe(III) absorbed}}{\text{theoretical moles of Fe(III)}}\ \text{stoichiometric ratio}$$

For the polymer, given a ligand density of 9.43 mmol/g (calculated as the ratio of chelating groups to the molecular weight of the repeat unit) and a chelating capacity of 3.09 mmol/g, one can infer that the ratio of ligand density to chelating capacity is 3.05 or, in other words, that the stoichiometry of the chelate is 3.05 moles of ligand per mole of iron (III). For the model compound, the ligand density is 12.56 mmol/g and the chelating capacity 3.94 mmol/g. The chelate stoichiometric ratio is, therefore, 3.18.

ESR Spectra of MC04 and BQ012 iron complexes, run at 10 K (−263°C), showed two resonances, at $g = 1.99$ and $g = 4.40$, and $g = 2.00$ and $g = 4.40$, respectively (Fig. 7). The signal at $g = 4.40$ is typical of Fe^{3+} high-spin rhombic splitting, while the resonance at around $g = 2.0$ is attributed to low-spin signals, and it is the only resonance for MC04 and BQ012 alone in the ESR spectra run at 10 K (Fig. 8). The $g = 4.40$ signal has been attributed to high-spin iron (III) ions in distorted octahedral structures [12, 13]. These results are corroborated by the data obtained by Atomic Absorption measurements, that yield a stoichiometry of about 3 moles of ligand per mole of iron (III) (Tab. IV), which is consistent with an octahedral structure of the type shown in Figure 9.

DSC scans of MC04 before and after exposure to Fe^{3+} solution showed the disappearance of the melting peak of the organic ligand

TABLE IV Chelation results based on atomic absorption spectroscopy

Sample	*Ligand density, mmol/g*[a]	*Chelating capacity, mmol/g*[b]	*Chelating efficiency, %*	*Ratio ligand/Fe^{3+}*[c]
MC04	12.56	3.94	94	3.19
BQ012	9.43	3.09	98	3.05

[a] Defined as the number of ligands divided by the repeat unit molecular weight for polymer and molecular weight for the model compound.

[b] Defined as the ratio of mmol absorbed iron (III) to *g* of polymer or model compound.

[c] Defined as the ratio ligand density/chelating capacity.

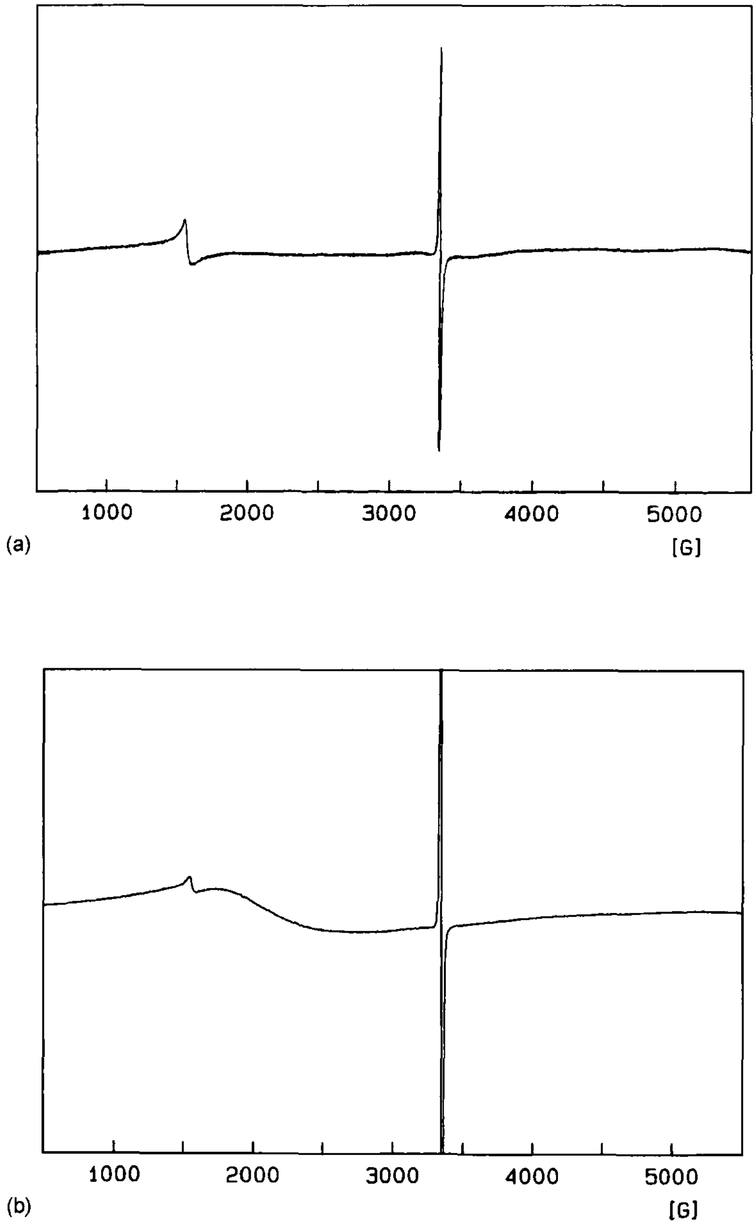


FIGURE 7 ESR spectra of (a) bis[2,5-(4-methylanilido)]-1,4-benzoquinone (MC04)/Fe chelate and (b) poly{[2,5-(2,2′-bistrifluoromethyl)-4,4′-biphenylenediamino]1,4-benzoquinone} (BQ012)/Fe chelate.

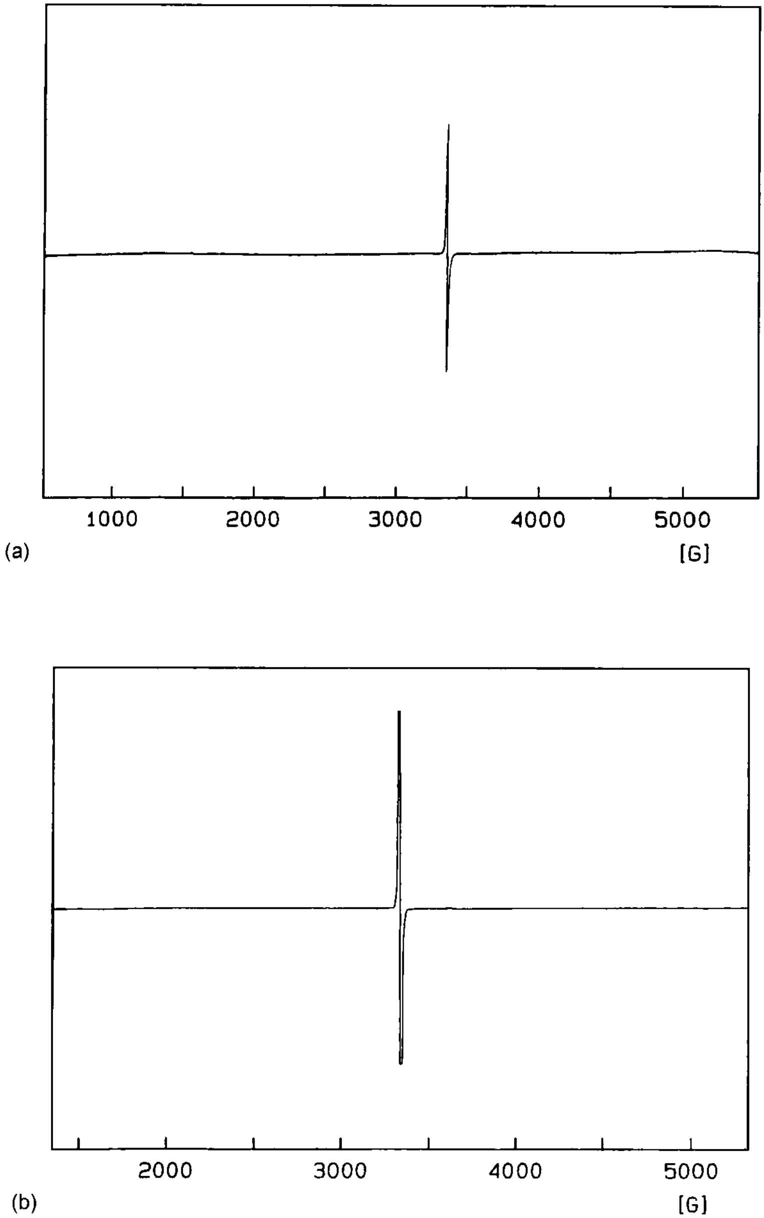


FIGURE 8 ESR spectra of (a) bis[2,5-(4-methylanilido)]-1,4-benzoquinone, MC04 and (b) poly{[2,5-(2,2′-bistrifluoromethyl)-4,4′-biphenylenediamino]1,4-benzoquinone}, BQ012.

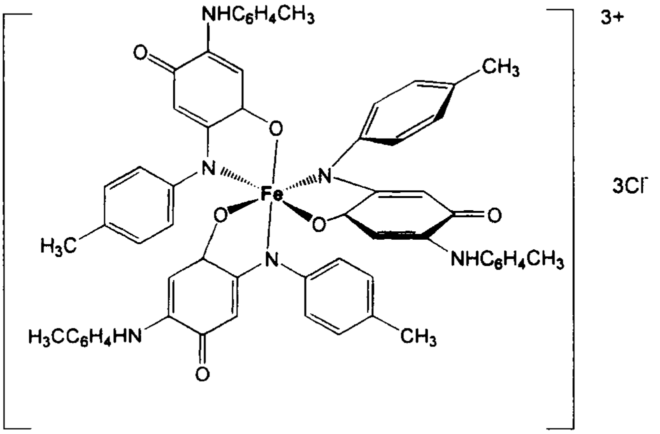


FIGURE 9 Proposed octahedral structure for the bis[2,5-(4-methylanilido)]-1,4-benzoquinone (MC04)/Fe chelate.

(313°C), suggesting that an iron complex with a high melting point may be formed.

Low Temperature Results on Pure Iron

The adhesion results for the pure iron wire also suggest that MC04 can bond to metal (iron) surfaces. The effect of our adhesion promoter and a commercial silane (γ-glycidoxypropyltrimethoxysilane) were compared in a tensile experiment. As shown in Table V, in two thirds of the tests with the adhesion promoter, failure occurred in the wire itself, whereas without adhesion promoter or with silane, failure occurred at the iron/epoxy interphase, resulting in the debonding of

TABLE V Pure iron wire tensile test results, $T = 76\,\mathrm{K}$ (−197°C)

Adhesion promoter	*Failure load (lb)*	*Failure mode*
None	86.9	Pull Out[a]
None	54.8	Pull Out
MC04/THF, 1%w/w	92.9	Wire[b]
MC04/THF, 1%w/w	89.4	Wire
MC04/THF, 1%w/w	61.4	Pull Out
Silane[c]/THF, 1%W/W	66.4	Pull Out
Silane/ THF, 1%w/w	33.1	Pull Out

[a] The failure happens at the iron/epoxy interface.
[b] The iron wire fails, the interface holds.
[c] γ-glycidoxypropyltrimethoxysilane.

the wire from the matrix. It should be mentioned that, as the iron wire samples were tested for tensile strength, all the other samples were tested in shear. Therefore, the numerical values of these different experiments are not directly comparable. Yet, the pure iron results provided additional understanding of the phenomena occurring at the metal/aminoquinone/epoxy interphase.

CONCLUSIONS

Two polymers, poly{[2,5-(2,2′-bistrifluoromethyl)-4,4′-biphenylenediamino]1,4-benzoquinone} and poly[(2,5-hexamethylenediamino)-1,4-benzoquinone] and a model compound, bis[2,5-(4-methylanilido)]-1,4-benzoquinone, were synthesized and tested as adhesion promoters for the stainless steel/epoxy/stainless steel joint system. Additional testing was carried out on pure iron wire specimens, bonded to epoxy adhesive and tested at liquid nitrogen temperature. The stainless steel joints were tested in shear, and the pure iron specimens were tested in tension. Results showed that aminoquinone materials, both polymeric and monomeric, can improve the durability of metal/epoxy/metal joints. The improvement is likely caused by the formation of a strong bond between available amino-carbonyl functionalities of the aminoquinone ligands and the metal surface, which can be attributed to chemisorption or chelation of the aminoquinones by the metals. Also, we have shown that the secondary amine functional groups present in these adhesion promoters react with the epoxy resin, providing the chemical coupling required for stable bond formation.

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