

# Quinone-Amine Polyurethanes: New Coupling Agents for the Steel-Epoxy System

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**ABSTRACT:** A new series of quinone-amine polyurethanes (QAPs) were synthesized using toluene diisocyanate, polytetrahydrofuran, and an amine-quinone monomer (AQM1). The AQM1 was synthesized and characterized using spectroscopic techniques (UV, IR, NMR). The QAP synthesis involved a two-step process and yielded block copolymers. These polymers were characterized using infrared spectroscopy, thermal analysis methods (thermogravimetric analysis and differential scanning calorimetry) and gel permeation chromatography. Steel coupons were treated with dilute solutions of the QAPs and analyzed using surface spectroscopic techniques (X-ray photoelectron spectroscopy, infrared reflection spectroscopy). These tests indicate that the polymer shows chemical interactions with the steel surface. The QAPs were tested for their efficiency as polymeric coupling agents to enhance the adhesion of steel to epoxy. The coupling agent treated epoxy-steel torsional joints were tested in shear. They demonstrated 10–15% dry strength improvement when compared to steel-epoxy controls. The QAPs can serve as very effective coupling agents for the steel-epoxy system. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1338–1350, 2000

**Key words:** adhesion; steel; epoxy; quinone-amine polyurethane; polymeric coupling agent

## INTRODUCTION

Steel is one of the most versatile materials known to mankind. It is used in a variety of structural and other applications. In many of these applications it is exposed to the atmosphere. This results in undesirable rusting, which weakens the structure made using the steel. The popular methods to prevent corrosion are painting, galvanizing, electroplating, etc. There are widely used toxic chemical processes, e.g., chromic acid etching, that are very effective in corrosion inhibition as

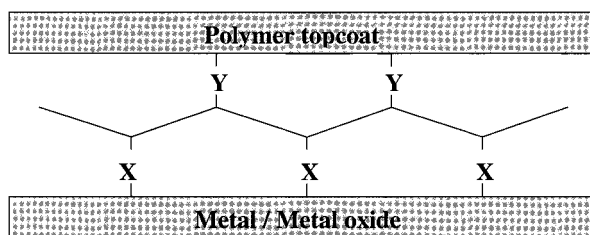
well as in hardening of the steel. Organic coatings can provide an effective and less toxic route to metal protection. The predominant need of modern metal-polymer adhesion science and technology is for the development of strong and durable protective coatings and structural adhesive joints.

Chemical coupling agents are di/polyfunctional compounds with reactive groups that chemically bond a polymer topcoat to fillers/fibers/matrices or inorganic substrates (Fig. 1). Such agents are normally applied to the metal substrate from a dilute solution as a final pretreatment step. By varying the number of reactive groups in a coupling agent, one can vary a number of interfacial properties of the same basic adhesion system.<sup>1</sup>

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**Figure 1** Metal–polymer adhesion enhancement using a polymeric coupling agent.

Coupling agents are different from primers. They have a true chemical reaction with the surface, while the primers enhance wetting. The thickness of application is also different in the two cases, being in the order of microns for primers, as opposed to 100–150 Å for the coupling agents.<sup>2</sup>

Until the present time, the effectiveness of coupling agents in increasing the durability of a metal–polymer system has been limited either by the low cohesive strength of the coupling agent layer or by the poor stability of the interfacial bonds formed. By directing efforts toward improving the strength and stability of the coupling agent region and the interfacial bonds formed to water and other corrosion products, it is believed that this durability limit can be significantly increased.

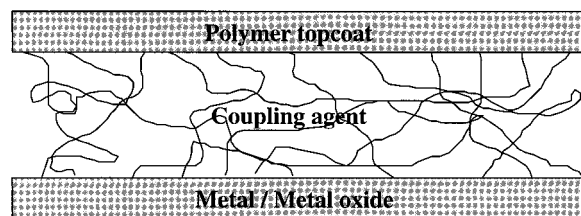
Polymeric coupling agents behave very differently from low molecular weight coupling agents. The inherent strength of a polymeric coupling agent and the entanglements of the coupling agent with itself as well as with the polymer topcoat leads to strength enhancement of the metal–polymer system.<sup>2</sup> Hence, unlike low molecular weight coupling agents, the polymeric coupling agents do not form the weak interface in a multilayer system.<sup>3</sup> Low molecular weight coupling agents are normally quite hydrophilic and promote the infiltration of water into the interfacial region. A polymer overcomes this difficulty. The viscoelastic nature of the polymeric coupling agents enable them to dissipate the mechanical, thermal, and other stresses encountered in a metal–polymer system.<sup>4</sup> Stresses develop primarily during the postcure cooling of the thermoset due to the thermal expansion coefficient mismatch between the metal and the polymer.<sup>5–8</sup> Epoxy resins have thermal expansion coefficients that exceed that of steel by an order of magnitude.<sup>6</sup> Excessive internal stress has been cited as the cause of failure in a number of adhesion systems.<sup>5,6,9–13</sup> To make a polymeric coupling agent,

the hydrophobic polymer backbone is tailor-made to have specific pendant functional groups. Some of these groups interact with the metal/metal oxide surface, others with the polymer topcoat. The adhesion enhancement of a metal–polymer system using a polymeric coupling agent is shown in Figure 2.

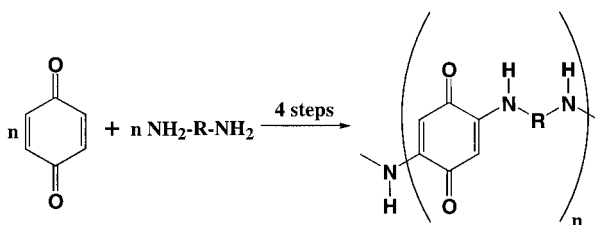
Gent has reviewed various chemical coupling agents and has concluded that chemical bonding at the interface of an adhesion system can definitely act as a strengthening feature. In addition, he has also reported that the most successful coupling agents have been those that are long and extensible molecules.<sup>14–17</sup>

There is experimental evidence for the localization of a block copolymer at the interface between two phases in a manner that minimizes their differences in surface energy.<sup>18</sup> Thus, a low energy block will diffuse to the surface against a low energy substrate. In a diblock copolymer, a reduction of interfacial tension<sup>19</sup> and improvement of mechanical properties<sup>20</sup> are observed as well. Thus, a block copolymer has the potential to be a very effective coupling agent for a metal–polymer system.

One of the most important factors to be taken into account in the metal–polymer systems is the surface of the metal. For optimum adhesive bonding, the metal surface must be pretreated to remove adsorbed impurities, weak contaminants, and loose oxide layers.<sup>21</sup> Adhesion scientists work toward optimization of these pretreatments and finding new means of treating surfaces so that the enormous potential of the metal–polymer systems can be utilized effectively. Some of the more promising durability-enhancing methods are (1) use of chemical coupling agents,<sup>22–43</sup> (2) employment of metal surface pretreatments to develop pores and cavities and thereby promote the mechanical adhesion,<sup>44–49</sup> (3) prevention of corrosion-induced delamination at the metal surface,<sup>50,51</sup> and (4) use of adsorption type corrosion inhibitors.<sup>52,53</sup>



**Figure 2** Mechanism of adhesion enhancement by a polymeric coupling agent.



**Figure 3** Synthesis of quinone-amine polymers. (from ref. 56).

Epoxy resins are excellent polymer topcoats for many coated metal applications. Epoxy resins have excellent adhesion to pretreated steel in a dry environment. In the presence of water, however, displacement of epoxy by water leading to a negative work of adhesion<sup>54</sup> and localized corrosion<sup>55</sup> cause strength loss of the metal-polymer system.

Quinone-amine polymers adhere to metals with sufficient affinity to displace water from a rusty steel surface after chemical or thermal curing of the topcoat.<sup>56,57</sup> These can be made resin compatible if designed properly. The synthesis (Fig. 3) and uses of quinone amine polymers in corrosion protection are well documented.<sup>56-62</sup> The synthesis of quinone-amine polymers was first reported by Erhan et al.<sup>56</sup> The main problems with Erhan's quinone-amine synthesis schemes (like the one shown in Fig. 3) are that they give very little polymer. The typical reaction product of this scheme is a poorly defined mixture of oligomers. This has been observed both at the University of Connecticut and at the University of Alabama. There are several other groups that describe synthesis of quinone-amines, but the work describing a well-defined and completely characterized set of polymers and oligomers is that of L. Mathias and co-workers.<sup>63</sup> One synthetic scheme that his group has adopted is shown in Figure 4.

## EXPERIMENTAL

### Quinone-Amine Polyurethanes

The quinone-amine polyurethanes used for the study were synthesized at the Center for Materials for Information Technology of the University of Alabama at Tuscaloosa. The synthesis involves a two-step process (discussed in detail below). The first step gives a prepolymer with a hard block, to which a soft segment diol is reacted subsequently

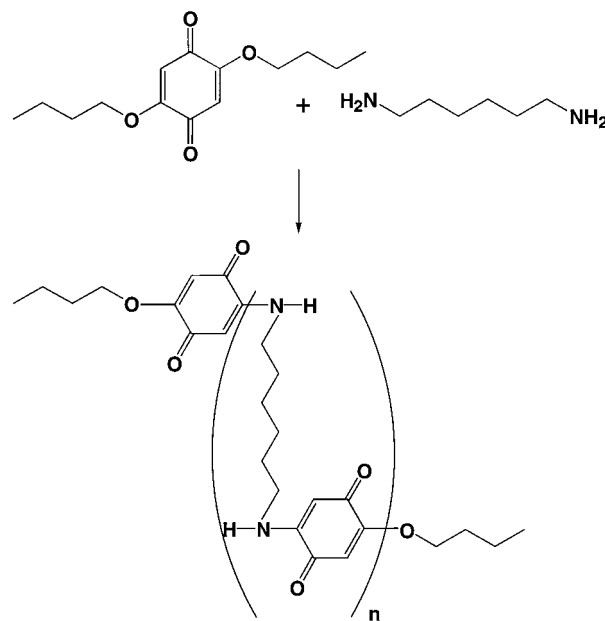
to give the block copolymer. These new copolymers are expected to be reactive with epoxy resins through their amine groups.

### Monomer Synthesis

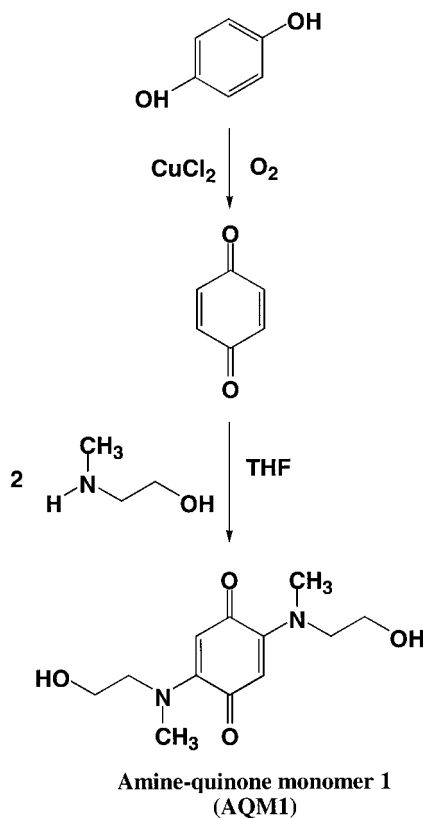
An amine-quinone monomer (AQM1) was made from 1,4-benzoquinone and 2-(N-methylamino) ethanol (Fig. 5). The scheme used was as follows: In a 500 mL three-necked round-bottom flask equipped with an addition funnel and a magnetic stirrer, 150 mL of tetrahydrofuran, 14.6 g of 1,4-hydroquinone, and 1.79 g of copper (II) chloride hydrate were added. After the green-colored solution was stirred for 5 min at room temperature, 2-(N-methylamino) ethanol was added dropwise through the addition funnel, over a period of 10 min with continued stirring. The color of the solution in the flask changed from green to red. After 1 h of continued stirring, red particles of AQM1 started forming in the flask. The reaction was taken to completion with continued stirring over a 24 h period at room temperature. The resulting crude product was collected by vacuum filtration. The AQM1 was recrystallized from ethanol and dried in a vacuum oven at 40°C for 2 days. All the chemicals used were reagent grade and purchased from Aldrich Chemical Company.

### Polymer Synthesis

The three quinone-amine polyurethane block copolymers (QAPs) that have been used as coupling



**Figure 4** Synthesis of quinone-amine polymers. (from ref. 63)

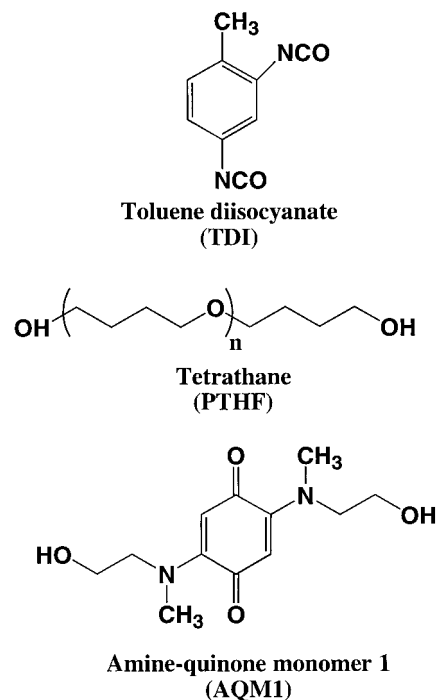


**Figure 5** Synthesis of AQM1.

agents for the epoxy–steel system are QAP-1B, -2B, and -3B. The QAP-1B, -2B and -3B contain 40, 20, and 30%, respectively, of the AQM1 (Table I and Fig. 6) and stoichiometric amounts of toluene diisocyanate and Tetrathane 650 (polytetrahydrofuran of mol wt 650). The hard segment contents of these segmented polyurethanes were 67, 34, and 51%, respectively. The polymers were made by a two-step process. The first step was a condensation reaction of the TDI with AQM1. This resulted in a brown-colored compound that was isocyanate terminated (observed using infrared spectroscopy). This was used as the prepoly-

**Table I** Ratios of Monomers Used to Make the QAP Series

| Polymer | AQM-1 Content (mol %) | TDI Content (mol %) | PTHF Content (mol %) |
|---------|-----------------------|---------------------|----------------------|
| QAP-1B  | 40                    | 50                  | 10                   |
| QAP-2B  | 20                    | 50                  | 30                   |
| QAP-3B  | 30                    | 50                  | 20                   |



**Figure 6** Monomers used to make the QAPs.

mer for the further condensation reaction with the chain extender Tetrathane 650. Thus, blocks of hard segments separated by soft segments of Tetrathane chain extenders were obtained in the QAPs (observed using X-ray diffraction).

#### Other Coupling Agents

For comparison, commercially available silanes (aminopropyltriethoxy silane and glycidoxypropyltrimethoxy silane) were tested for their effectiveness as coupling agents for the steel–epoxy system. These chemicals were purchased from the Aldrich Chemical Company.

#### Steel

SAE 1010 cold-rolled carbon steel coupons from Q-Panel Company (Cleveland, Ohio) and 1018 mild steel torsional butt joints were used as the steel substrates for this study. The chemical composition of the steel substrates is as follows: manganese, 0.30–0.60%; carbon, 0.08–0.20%; phosphorus, 0.04%, and sulfur, 0.05%. Both 1010 and 1018 fall under the category of steels that are known as mild steel. Mild steel was chosen for this study because it has no chromium, zinc, or other metallic pretreatments that can inhibit the corrosion of steel—in other words, mild steel is

very prone to corrosion. Several surface treatments were tested with the 1010 carbon steel coupons and the 1018 mild steel torsional butt joints. These included conventional grit blasting, sanding, detergent washing, etc. Satisfactory polymer coatings were not obtained (there were islands of exposed metal surface) on substrates cleaned by these methods. An ammoniacal citric acid etch<sup>41</sup> was found to be a satisfactory pretreatment. This treatment is detailed below:

The steel coupons/joints were machine polished with 600 grit sandpaper to give a smooth surface to isolate the effects of mechanical interlocking from the chemical adhesion. The coupons/joints were then immersed for 20 min in a 3% citric acid aqueous solution (with its pH adjusted to 7 using ammonium hydroxide) maintained at a temperature of 70°C, followed by quick immersions (2 min) at room temperature in distilled water and methanol.<sup>44</sup>

### Characterization

The polymers to be used as coupling agents were characterized using infrared spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and gel permeation chromatography (GPC). These experiments helped us in determining the molecular weights (GPC) of the synthesized polymeric coupling agents, functional groups present in them (IR spectroscopy), and their thermal stability (TGA and DSC).

The surface of a coupling agent treated steel coupon that was washed with copious quantities of solvent (tetrahydrofuran) was analyzed using X-ray photoelectron spectroscopy (XPS), infrared reflection spectroscopy, and reflection absorption infrared spectroscopy (RAIRS). These experiments helped us to study the interaction of the coupling agent with the steel surface.

The steel-epoxy adhesive joint was characterized using modified tubular butt joint for adhesion testing. The testing of the tubular butt joints was conducted on an Instron® Universal Testing Machine.

### Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra for the polymer coatings were taken using a Nicolet 60 SX FTIR spectrometer with a deuterated triglycine sulfate detector and a germanium/KBr beam splitter. Samples were prepared either by (1) coating a solution of the sample on a NaCl disk

and drying off the excess solvent or (2) preparing KBr pellets (after making a homogeneous powdery blend of the polymer in KBr by means of a Wig-L-Bug Amalgamator) using a Carver lab press (model C). The pellet or disk was placed in appropriate plastic holders designed to allow the passage of infrared light through the sample. The spectra were recorded using 32 scans and the resolution was 4 cm<sup>-1</sup>. FTIR was used to determine the incorporation of the various functional groups in the QAPs.

### Thermal Analysis

A TA Instruments differential scanning calorimeter (DSC—model 2920) and thermogravimetric Analyzer (TGA—model 2950) were used for the thermal analysis of the QAPs. Before the DSC runs, the instrument was precalibrated using indium and tin standards. Fifteen to twenty gram samples were placed in aluminum pans and scanned from 30 to 250°C at a heating rate of 10°C/min, in a nitrogen environment. A midpoint method was employed to estimate the  $T_g$  of the polymers. The TGA runs were done using 15–20 g samples at a heating rate of 2°C/min, in a blanket of nitrogen.

### Gel Permeation Chromatography

The molecular weights of the various polymers were estimated using a Waters 550C-150 Gel Permeation Chromatography system with a Waters 410 differential refractometer and ultrastyrigel columns (500, 10<sup>4</sup>, 10<sup>5</sup>, 10<sup>6</sup> Å). A universal calibration curve was constructed using monodisperse polystyrene standards of molecular weights ranging from 500 to 500,000 g/mol. QAP samples for study were prepared by dissolving 10–15 mg of polymer (depending on the molecular weight range of the sample) in 5 mL of solvent (tetrahydrofuran). All the samples were passed through a 0.2 mm Teflon filter. The molecular weight was calculated on the basis of the calibration curve constructed using the elution time of monodisperse polystyrene standards as described above and without using the Mark-Houwink constants of the polymer systems investigated (not available). Hence, the molecular weights obtained are not absolute, but only approximate in nature.

### Infrared Reflection Spectroscopy

The surface of a polished and pretreated steel coupons (SAE 1010 cold-rolled carbon steel cou-

pons purchased from Q-Panel Company) were analyzed after applying the coupling agent (and washing off the excess with tetrahydrofuran) by infrared reflection spectroscopy (Nicolet 60 SX FTIR spectrometer). The same experiments were repeated with coupling agent coatings of various thickness. The spectra of these coatings can be obtained directly in the reflection mode of the spectrometer. The spectra were obtained using 128 scans and at a resolution of  $4\text{ cm}^{-1}$ . The pure coupling agent was studied in the transmission mode.

### X-ray Photoelectron Spectroscopy

XPS is a nondestructive, highly surface sensitive technique for determining the composition of the uppermost atomic layers of a sample. When the surface of a solid is irradiated with high energy photons (e.g., X-rays), core level electrons can be ejected from the elements near the surface if the photon energy is greater than the binding energy of the electron plus the spectrometer work function. The binding energy of the photoelectrons may be correlated to the element from which each originated. Alteration of the chemical state of the parent atom through the formation of chemical bonds result in a shift of the binding energy of the electrons. This shift, in some cases, allows compound identification. Due to the limited mean free path of electrons in solids, some depth profiling is possible through varying the angle between the electron energy analyzer and the sample surface. When this angle is large (i.e., just grazing the surface), the effective electron path is long and only the electrons near the surface are detected. Conversely, small (i.e., near normal) exit angles result in the detection of electrons that originate from deeper within the sample. The mean free path for photoelectrons in metals, oxides and polymers is about 5–20 Å, 15–40, and 40–100 Å, respectively.<sup>64</sup>

A pretreated bare metal surface and the coupling agent treated metal surface (washed with an excess of pure solvent) were studied using a Perkin-Elmer X-ray photoelectron spectrometer (model PHI 5300). Soxhlet-extracted coupling agent treated surfaces were also studied in a similar fashion. These results coupled with the IR spectroscopy results provide a good insight into the chemical interactions of the coupling agent with the steel surface.

### Reflection Absorption Infrared Spectroscopy

RAIRS is a technique for obtaining the infrared spectra of extremely thin films on reflecting substrates. The method involves reflecting infrared radiation that is polarized parallel to the plane of incidence from the surface at large grazing angles ( $80^\circ$  or more) of incidence. Here, the dominant signal is from the *p*-polarized component of the beam, so the vibrational modes perpendicular to the surface alone are detected. Under these conditions, the incident and reflected waves combine to form a standing wave at the surface with considerable amplitude. On fairly good specular reflectors such as polished metals, evaporated metal films, or silicon wafers, the technique allows reasonable spectra to be obtained from an absorbing film of approximately monomolecular coverage. Under these conditions, the signal intensity at the metal–polymer interface is enhanced due to constructive interference between the incident and reflected beams.<sup>65</sup>

RAIRS was used to confirm the presence of the coupling agent on the surface of the steel coupon in a coupling agent treated, solvent washed, soxhlet extracted steel coupon.

### Adhesive Joint Characterization

Steel–epoxy adhesive joints were made using the different coupling agents for adhesion testing. After the surface pretreatment, the steel joints were immersed in a dilute solution (0.2–2.0% by weight of the coupling agent) in an appropriate solvent (THF for QAPs and BFPs (beta-diketone functionalized polymers); methanol–water for silanes; methanol for PETM (pentaerythritol tetra 3-mercaptopropionate)) for 20 min. The excess coupling agent was washed off using pure solvent and the joints were dried. The amount of 44 ( $\pm 0.1$ ) mg of a stoichiometric mixture of Epon-828 epoxy resin (Shell Chemical Company) and methylene dianiline (Eastman Chemical Company) curing agent (Fig. 7) was used in making each modified tubular butt joint for adhesion testing. The resin weight was measured accurately by weighing the male half of the joint containing the raised annular ring prior to and after application of the epoxy resin. The joint assemblies were cured ( $120^\circ\text{C}$  for 1 h followed by  $150^\circ\text{C}$  for 2 h) and tested using a torsional testing method,<sup>42,66,67</sup> which measures the shear strength of the joint (Fig. 8). These results were compared to control values obtained from joints not treated with the coupling agent. The main advantage of this method as compared

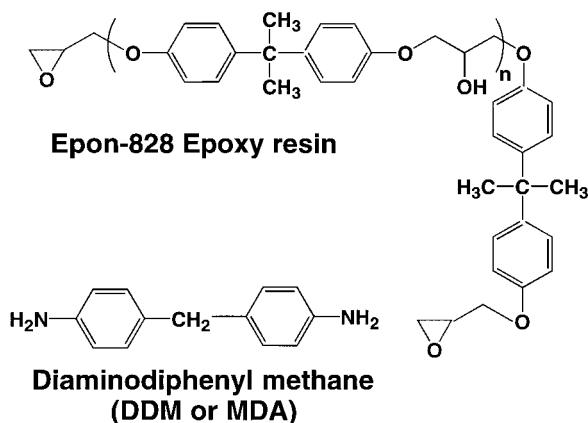


Figure 7 Epoxy resin and MDA curing agent.

to other adhesion testing methods is that the applied stress is very nearly simple shear. Hence, 5–7 torsional butt joint samples (per data point) are sufficient to obtain a value of shear strength with very good reproducibility.<sup>66</sup> Also, the torsional joints eliminate the geometric dependence of the data due to complex applied stresses. Finally, another advantage arises due to the reproducibility in the data due to (1) the very small contact area between the adhesive and the substrate allowing rapid equilibration in water and (b) the same quantity of adhesive being used each time.

The testing of the tubular butt joints was conducted on an Instron Universal Testing Machine, Model TM-S. Torque was applied to the joint assembly using an Instralab torsional device. A 1000 lb reversible load cell was used to measure the force at break. The cross-head speed used for the tests was 0.2 in/min. The applied torque  $M_t$  is related to the maximum shear stress  $t_{\max}$  using the following equation:

$$t_{\max} = (16M_t D_o) / [\pi(D_o - D_i)]$$

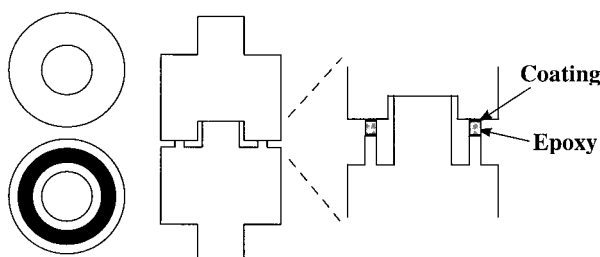


Figure 8 Schematic diagram of tubular butt joint (1018 carbon steel) (from ref. 66).

Table II Physical Properties of the QAPs

| Polymer | AQM-1 Content (mol %) | Physical Property of the Solid |
|---------|-----------------------|--------------------------------|
| QAP-1B  | 40                    | Hard and brittle               |
| QAP-2B  | 20                    | Soft and flexible              |
| QAP-3B  | 30                    | Brittle                        |

where  $D_i$  and  $D_o$  refer to the inner and outer diameter of the raised annular ring respectively.

The QAPs were studied using this method both after dip coating of the joints in a stationary coupling agent solution as well as in a stirred coupling agent solution. This experiment helped us to determine if the mass transfer of the coupling agent onto the metal surface was diffusion related.

## RESULTS AND DISCUSSION

### Quinone-Amine Polyurethanes

Three quinone-amine polyurethanes (QAP-1B, -2B, and -3B) were made containing, respectively, 40, 20, and 30% of the AQM1 and stoichiometric amounts of toluene diisocyanate (always 50%) and Tetrathane 650 (polytetrahydrofuran of mol wt 650). The physical properties of the QAPs are shown in Table II.

### Monomer Characterization

The details of the AQM1 synthesis have been described earlier in the experimental section. The main concern here was the confirmation of the incorporation of the 2,5-diamino-1,4-benzoquinone group into the monomer (and eventually,

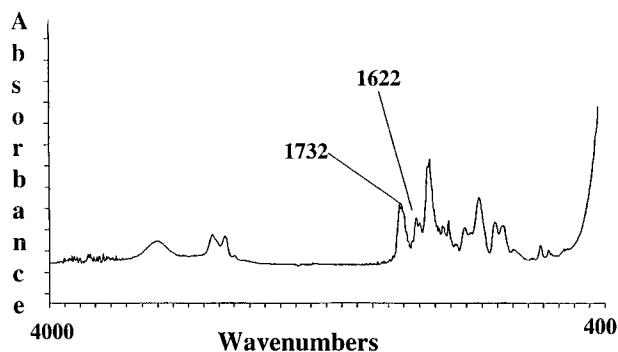


Figure 9 Infrared transmission spectrum of QAP-1B.

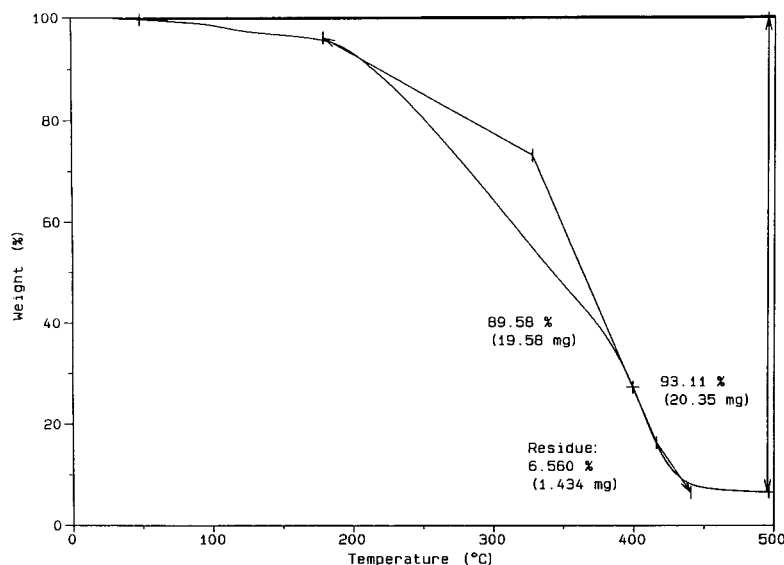


Figure 10 TGA thermogram of QAP-1B.

into the polymer). This was confirmed using several techniques:

1. A UV-visible spectral peak at 363 nm.
2. A proton-NMR singlet peak at  $\delta = 5.25$  ppm.
3. A C-13 NMR peak at  $\delta = 180.9$  ppm.
4. No OH stretches in the IR spectra.
5. A red brown color of the monomer that was not removed by repeated washing with water. A change to the hydroquinone moiety would have caused a color change.

The AQM1 is a crystalline compound with a melting point of 167°C. Elemental analysis showed that it has C = 56.70%, H = 7.19%, and N = 11.03%. These values agree very well with the calculated values of C = 56.68%, H = 7.13%, and N = 11.02%. The mass spectroscopy of the monomer yielded the value of the mass of the monomer to be 254.13, which is very close to the calculated mass of 254.29.

### Polymer Characterization

The QAPs were characterized using infrared spectroscopy, thermal analyses, mechanical testing, and gel permeation chromatography.

### Infrared Spectroscopy

The Fourier transform infrared transmission spectra of a typical QAP is shown in Figure 9. The spectra shows the typical peaks expected in a QAP. The C=C peak at 1622  $\text{cm}^{-1}$  and the C=O peak at 1732  $\text{cm}^{-1}$  are characteristic of these compounds. These peaks also confirm that the 2,3-diamino-1,4-benzoquinone group is present in the compound and that the keto-enol tautomerization to the hydroquinone moiety was not important.

### Thermal Analyses

The QAPs were analyzed using DSC and TGA. The thermogram of a typical QAP is shown in Figure 10. The QAP-1B is thermally stable up to

Table III Thermal Properties of the QAP Series

| Polymer | Hard Segment Content (%) | $T_g$ of the Soft Segment (°C) | $T_g$ of the Hard Segment (°C) |
|---------|--------------------------|--------------------------------|--------------------------------|
| QAP-1B  | 67                       | -49                            | 152                            |
| QAP-2B  | 34                       | -39                            | 34                             |
| QAP-3B  | 51                       | -45                            | 138                            |



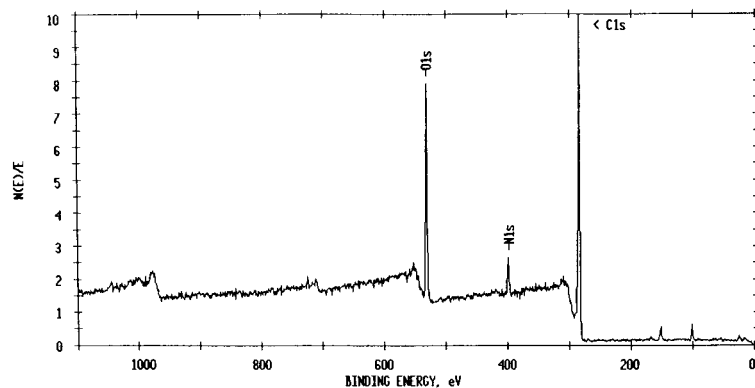


Figure 11 XPS spectrum of QAP-1B on steel.

200°C, beyond which it starts to decompose. The maximum cure temperature of the epoxy resin-curing agent system used for topcoating the coupling agent treated steel coupons is 150°C. This will be the maximum temperature the coupling agent would experience during the coating process. Since the QAP-1B is very stable to this temperature, it can safely be used as a coupling agent for the steel-epoxy system. The other QAPs showed a very similar thermal behaviour to QAP-1B. The decomposition of the QAPs typically started at 250°C and was almost complete at 400°C. Thus, these coupling agents will be suitable for conventional applications, but will not be the best suited for very high temperature applications.

Mass spectroscopy on the QAP-1B also indicated that the polymer is very stable at the conventional cure temperature of the epoxy topcoats. Traces of water and residual solvent evolved from the polymer sample, but little else until 200°C (the maximum projected use temperature).

The detailed results of thermal analysis on the QAP series is summarized in Table III. The poly-

mers in the QAP series show a wide variation in their thermal properties. These polymers show a typical block copolymer behavior, with a different  $T_g$  for the hard and soft segments. It was noted that the polymer with the higher hard segment content (QAP-1B) showed the highest value of the hard segment  $T_g$  (152°C). Also, the polymer with the lowest hard segment content (QAP-2B) showed an apparent  $T_g$  value of the hard segment close to room temperature (34°C). Hence, in this QAP series, we have some polymers that are hard and brittle at room temperature and some that are soft and flexible. The polymer with the intermediate hard segment content (QAP-3B) behaved more like QAP-1B than like QAP-2B. It was brittle at room temperature and showed a hard segment  $T_g$  of 138°C.

### Gel Permeation Chromatography

The QAPs exhibited an apparent number average molecular weight in the range of 11,000 to 20,000. This molecular weight range is very suitable for

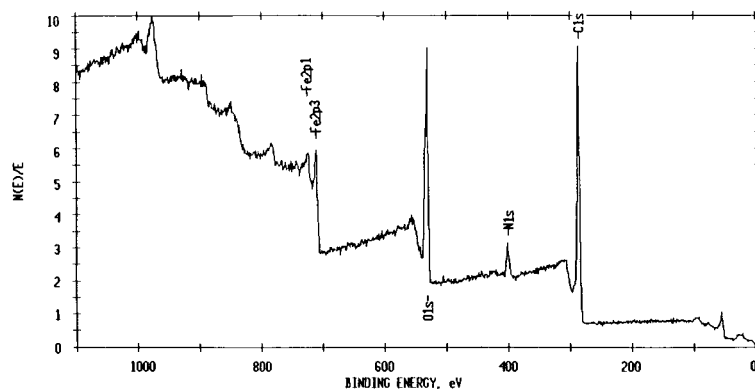
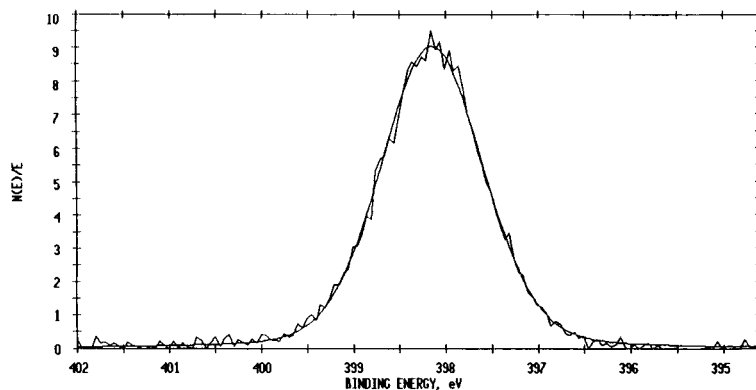


Figure 12 XPS spectrum of QAP-1B on steel—partially coated.



**Figure 13** Nitrogen region spectrum (multiplex) of QAP-1B on steel.

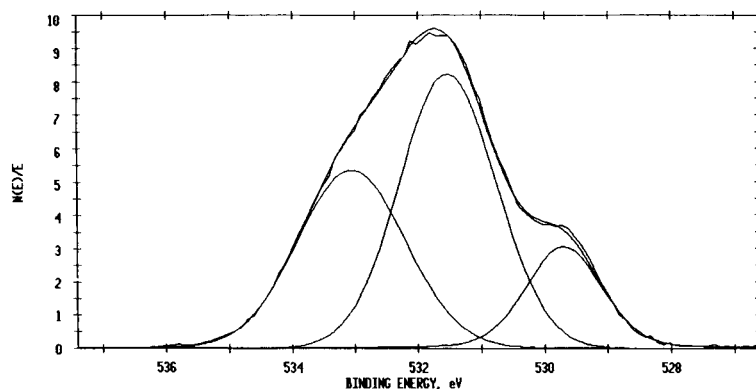
coupling agent applications. In a coupling agent, we do not want a very high molecular weight because that would retard wetting and spreading. Neither do we want a low molecular weight coupling agent because a low molecular weight moiety can result in a weak interphase between the polymer and the metal that we are trying to tether together. These values of molecular weight support the QAPs as polymeric coupling agents that can wet the metal surface completely and spread out the thermal and mechanical stresses that arise at the metal-polymer interface.

#### X-ray Photoelectron Spectroscopy

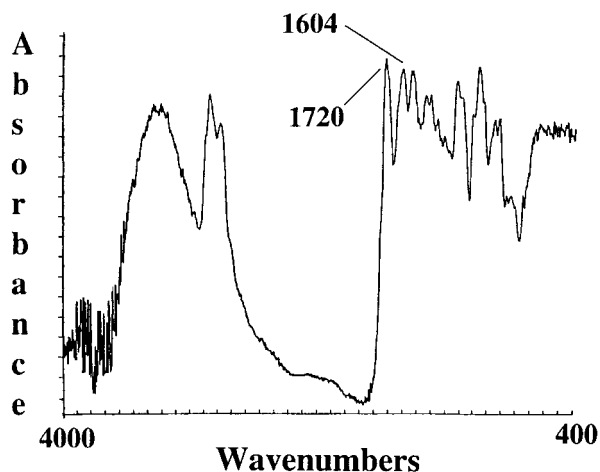
X-ray photoelectron spectra were obtained after treatment of the steel coupons with the QAP and washing off the excess coupling agent using pure solvent (tetrahydrofuran). A typical XPS survey spectra (at a take-off angle of  $62^\circ$ ) of a QAP coated on a steel surface is shown in Figure 11. The spectrum shows that the QAP-1B has not been washed from the steel surface by the solvent

treatment. This indicates a strong affinity for the QAP to the steel surface. Figure 12 shows the XPS survey spectrum of a partially coated steel coupon. We can clearly see that in the previous case (Fig. 11), the QAP-1B coated the surface of the steel coupon completely and there were no iron peaks visible, while in Figure 12, there are many iron peaks visible. Similar results were observed with soxhlet extracted coated steel coupons as well. This gives further proof for the tenacity of the QAP-1B to steel bond.

The XPS scans were also done on the QAP treated steel coupons in the multiplex mode. The multiplex spectra of the nitrogen and oxygen region in the XPS of QAP-1B on steel are shown in Figure 13 and Figure 14, respectively. The presence of oxygen and nitrogen from the coupling agent indicates that the QAP was not washed off the surface by the solvent. The spectra obtained with each QAP sample showed both iron(II) oxide and benzoquinone type as well as a third type of oxygen peak, shifted very downstream from the



**Figure 14** Oxygen region spectrum (multiplex) of QAP-1B on steel.



**Figure 15** Infrared reflection spectrum of QAP-1B on steel.

other two. These three kinds of oxygen peaks probably indicate the interaction of the oxygen from the quinone moiety with the steel surface. There was only a single nitrogen peak in all these spectra. So, the amine moiety is free to react with the epoxide ring (and the MDA curing agent) of the top coat in the system. The low molecular weight analogue AQM-model compound has also been used to confirm such binding of the amine-quinone moieties with the steel surface.

#### Infrared Reflection Spectroscopy

The surface of a QAP-treated steel coupon was analyzed (after washing it with copious quantities of solvent) spectroscopically using IR reflection

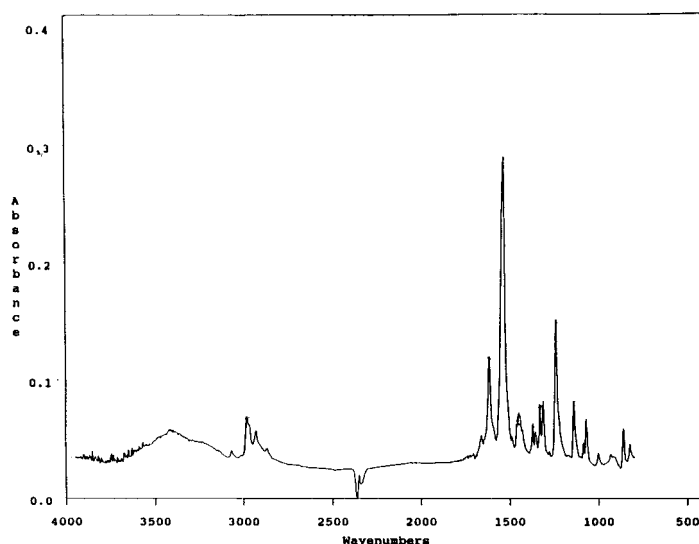
techniques. Figure 9 and Figure 15 respectively show the IR spectra of QAP-1B and QAP-1B coated on steel. It can be seen that the two C=O peaks, which are at 1622 and 1732  $\text{cm}^{-1}$  respectively in Figure 9, shift to lower wavenumbers (1604 and 1720  $\text{cm}^{-1}$  respectively) in Figure 15. Thicker coatings of QAP-1B on steel did not show this behavior. Instead, they showed spectra identical to Figure 9, the transmission spectrum of QAP-1B. This indicated that there is a chemical interaction occurring at the polymer-steel interface that can only be seen when most of the excess polymer is washed from the steel surface.

#### Reflection-Absorption Infrared Reflection Spectroscopy

The RAIR spectrum of QAP-1B on steel is shown in Figure 16. This spectrum was taken after the soxhlet extraction of the steel coupon for one day. The presence of the QAP on the steel surface after such a vigorous extraction indicates that it is strongly held on to the steel surface. The spectrum obtained using the RAIRS technique cannot be directly correlated to the IR reflection or the IR transmission spectra due to the inherent difference in the physics of the experiments. The large amount of noise seen with the RAIRS spectrum is an outcome of using large grazing angles on rough steel surfaces.

#### Mechanical Testing of Steel-Epoxy Torsional Butt Joints

The effectiveness of the compound as a coupling agent for improving the mechanical strength of



**Figure 16** RAIR spectrum of QAP-1B on steel.

**Table IV Joint Shear Strengths of QAP Coupling Agent Treated Steel Joints**

| Weight of CA in Solution (%) | Joint Shear Strength (psi) |              |              |
|------------------------------|----------------------------|--------------|--------------|
|                              | QAP-1B as CA               | QAP-2B as CA | QAP-3B as CA |
| 0                            | 8760                       | 8760         | 8760         |
| 0.1                          | 9830                       | 9855         | 9835         |
| 0.2                          | 9855                       | 9995         | 9955         |
| 0.5                          | 9950                       | 10240        | 10145        |
| 1.0                          | 10475                      | 10890        | 10745        |

the steel–epoxy system was tested using modified tubular steel butt joints, using the torsional testing method,<sup>66</sup> which measures the strength of the joint in pure shear.

The QAPs were found to be effective, even in low solution concentrations, in increasing the joint shear strengths of the steel–epoxy modified tubular butt joints. The joint failure shear stresses of the coupling agents (CAs) QAP-1B, -2B, and -3B (with tetrahydrofuran as the solvent) treated joints are shown in Table IV. The QAP-2B has a lower melting point and a higher soft segment content, and so is much more flexible and tough when compared to the QAP-3B and QAP-1B. This probably leads to much more energy dissipation by chains in the interphase and consequent improvement in joint strength.

Another point to note in these results is that the joint shear strength increases with increase in the solution concentration. This could indicate that there is a good amount of entanglement within the multilayers of the coupling agent without loss in strength or creation of a weak interphase. The scatter in the data in these dry strength values are really small ( $\pm 75$  psi per set of seven joints). This is one of the advantages of using the torsional testing method.

## CONCLUSIONS

A new series of polymeric coupling agents have been designed, developed, and tested for effectiveness in enhancing the adhesion of the steel–epoxy system. The QAPs are effective coupling agents for the steel–epoxy system, even when they are applied from very low solution concentrations. The process conditions (in such coupling agent based polymer coating processes) are very mild

and hence the process control is relatively simple. Also, this process is much more environmentally friendly when compared to the conventionally used toxic chromic acid etch process for steel.

The QAPs improve the adhesion of the steel–epoxy system through chemical interactions with the two surfaces. Solvent washing and Soxhlet extraction were found to be ineffective in removing the polymeric coupling agent from the surface of a coupling agent dip-coated (and rinsed) steel coupon. Spectroscopic investigation of the steel surface shows some evidence in support of these chemical interactions.

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