

Poly(2-allyl)phenylene Oxide Electropolymer Films as an Adhesion-Enhancing Treatment for Steel

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SYNOPSIS

The enhancement of metal-polymer adhesion via thin reactive electropolymer films of poly(2-allyl)phenylene oxide was studied using adhesive joint failure techniques. Thin (0.2–0.4 micron) films were formed on steel blocks using potentiostatic electrooxidation. Two blocks were cemented together to form adhesive joint specimens using an unsaturated polyester/styrene resin system. Adhesive joint specimens were also formed from both untreated blocks and treated blocks where the allyl functionality of the electropolymer was destroyed by heat crosslinking. Failure energies were then determined for joints with variable areas of adhesion using an impact-based technique, and the relationship of adhered area to measured failure energy was obtained for the three systems. The failure interface was examined by scanning electron microscopy. It was found that the poly(2-allyl)phenylene oxide-treated system gave the highest failure energies, followed by the untreated system. The electropolymer film system with pre-crosslinked allyl functionality produced the lowest failure energies. These results were related to the nature of the chemical interactions present at the interfaces, in accordance with the theories of adhesion proposed by Kinloch. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Commercial polyphenylene oxide (PPO) is prepared via the catalyzed chemical oxidative polymerization of 2,6-dimethyl phenol to produce a linear straight-chain aromatic polyether structure,¹ with the aromatic units linked via C—O bonds (Fig. 1). It was found by Hay et al.^{2,3} that if the phenol derivative was not 2,6-disubstituted the polymers formed were highly crosslinked, nonworkable, and of low solubility in almost all solvent systems. It was also found that if the 2,6-dimethyl functionality is replaced with larger alkyl groups then steric hindrance of the 1-oxygen atom results predominantly in the formation of low molecular weight species such as diphenoquinones. Thus, only 2,6-dimethyl phenol can be chemically polymerized to produce a commercially viable product.

A number of research groups have previously examined the electrooxidative polymerization of so-

lutions of monomeric phenol derivatives with respect to forming films or coatings on metal substrates. As no working or solvating of the polymer is required, a large number of phenol derivatives could form viable commercial products.

Dubois et al. performed a number of mechanistic experiments on the electropolymerization of dimethyl-substituted phenol derivatives on a variety of metal substrates,⁴ under alkaline conditions using sodium hydroxide as the base. It was found that the polymers formed during the electrooxidation of alcoholic phenolic solutions were of a polyphenylene oxide structure. The electrooxidative mechanism put forward for 2,6-dimethylphenol (Fig. 2) involved the initial formation of phenoxy radicals, followed by coupling of the oxygen radical mesomer with the 4-carbon mesomer to form the cyclohexa-2,5-dienone dimeric intermediate. Tautomerization and subsequent oxidation produce a radical dimer, which can then couple with a monomeric radical mesomer to give further chain extension. Repetition of this process results in the formation of the polymeric system.

Other published work on the mechanism of polymerization, and the suppression of current flow

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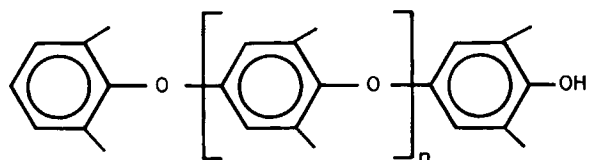


Figure 1 Structure of poly(2,6-dimethylphenylene oxide).

observed upon film formation on an electrode surface (often incorrectly described as passivation), include publications by Dijkstra and De Jonge,⁵ Gileadi et al.,⁶⁻⁸ and Marsh et al.⁹

The use of electropolymerization as a technique for producing relatively thick (> 30 microns) organic coatings on steel and other metals was examined by Musiani et al.^{10,11} Electropolymer coatings were generated based on 2-allyl phenol¹⁰ and a 2-allylphenol/phenol copolymer.¹¹ The anticorrosion performance was described as excellent. Allylamine and ammonia were used as a base, as opposed to sodium hydroxide. This, also examined in detail by Marsh,¹² leads to continuous uniform coatings on the electrode surface, whereas sodium hydroxide results in powdery discontinuous deposits. The exact mechanism of action is not as yet fully understood.

The concept of growing a thin functionalized polymer film with reactive properties was first examined in a series of articles by Dubois et al., where polymer films were formed from carboxyl-¹³ and amine¹⁴-substituted phenol derivatives. Infrared studies showed the capability of these groups to react with small organic molecules with compatible chemical reactivity.

Few studies have been undertaken with respect to the use of a thin (< 0.5 microns) reactive electropolymer film as a precoating surface treatment for metal substrates, where a thick conventional polymer coating is subsequently applied as a top coat. Preliminary studies by Marsh et al.¹⁵ found that the adhesion of an alkyd coating to a steel sub-

strate under wet (water immersion) conditions could be improved for several days of exposure if a thin poly(2-allyl) phenylene oxide film was grown on the surface of the steel prior to coating.

This work attempts to quantify the changes in the dry adhesion strength of an unsaturated polyester/styrene resin to steel when thin reactive and reduced reactivity electropolymer films are present on the surface of the steel substrate. Impact failure of adhesive joints, via techniques developed by Faidi et al.^{16,17} from work by Plati and Williams,¹⁸ and scanning electron microscopic (SEM) examination of the failure interfaces are the principal tools of investigation.

EXPERIMENTAL

Sample Preparation

The adhesive joint specimens were prepared in the following way: Blocks measuring 40 × 25 × 10 mm were cut from a rectangular cold rolled steel bar. The 10 × 25 mm face to be polished was dipped in a metallographic mounting resin to coat the sides of the specimen to a depth of 10 mm. The face was then polished to a "1200 grit" finish and degreased using ethanol. For the untreated specimens, 60 blocks were cemented together across the polished faces using a solventless unsaturated polyester/styrene resin system, with curing initiated using a peroxy-based hardener. PTFE tape was used to partly mask one of the polished steel surfaces, starting from and parallel to one of the 10 mm edges of the face. This both acted as a crack initiator and produced a variable area of adhesion. The PTFE tape was also used to generate a constant thickness profile of the polyester/styrene resin of 30–40 microns. Any excess adhesive resin beyond the dimensions of the adhesive joint was removed by filing.

A further 120 blocks were polished and degreased as above and then coated with a 0.2–0.4 micron elec-

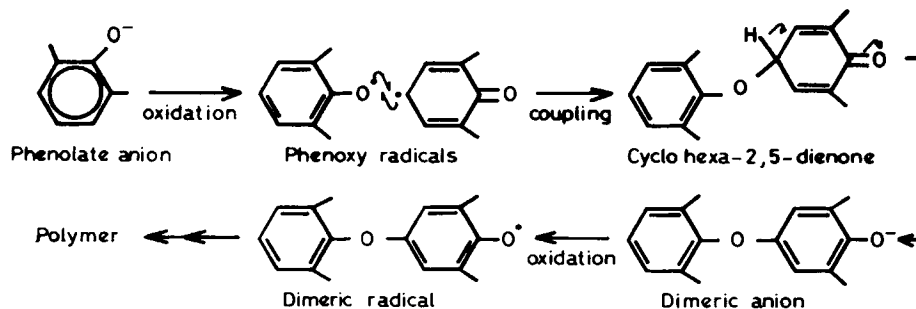


Figure 2 Radical coupling electropolymerization mechanism.

tropolymer film. The electropolymerization bath was a 0.25 M solution of 2-allylphenol in 10 : 10 : 1 water : methanol : 2-ethoxyethanol, raised to pH 10.2 by addition of allylamine. The polished steel surface was then polarized in the bath at -1000 mV (SCE) for 30 s to reduce any air-formed oxide film on the steel substrate. The sample was then polarized at $+1000$ mV (SCE) for 10 min, producing a gel-like film of poly(2-allyl)phenylene oxide at the electrode surface. The films slowly became hard and glassy upon drying, especially if heat-crosslinked. The conditions used are those found by Marsh¹² to produce thin continuous films while avoiding significant corrosion of the steel substrate during polarization. Sixty of these treated steel blocks were dried in a vacuum desiccator for 3 days to remove solvent from the films without crosslinking the allyl functionality, then formed into 30 adhesive joints as described previously. The final 60 blocks were heated in air at 90°C overnight. This heat treatment removes solvent from the electropolymer films, but also induces crosslinking of the allyl groups,^{10,11} significantly reducing their reactivity. These blocks were then also formed into adhesive joints as described previously.

Adhesive Joint Impact Failure Techniques

These experiments were performed using a bench-mounted Charpy-type impact tester, with a force transducer built into the impacting hammer (Fig. 3). The adhesive joint specimens were positioned across the support blocks with the PTFE masking to the bottom of the specimen. The hammer was then allowed to impact on the specimen with a velocity of 2.8 m/s. The corrected effective mass of the hammer, after allowing for energy absorbed by flexing of the arm of the hammer during impact, was 0.19 kg.¹⁶⁻¹⁸ The force-time transient was cap-

tured as a voltage-time signal using a "Bruel and Kjaer 2635" charge amplifier and a "Gould 4035" digital storage oscilloscope. The energy input required to bring about specimen failure was then calculated^{16,17} and plotted against the macroscopic adhered area. As failure does not simultaneously occur at the same point on both metal blocks, the area refers to one block of the adhesive joint. The gradient of the best-fit line directed through the origin gave the energy required to initiate specimen failure per unit area of adhered material. The fractured specimens were then examined using both optical and scanning electron microscopy.

RESULTS

As described in detail by Faidi et al.,^{16,17} the failure energies were calculated from the force/time transients as follows:

The time component was changed to a displacement using the formula

$$X = V_0(t_2 - t_1) - \frac{1}{Me} \int_{t_1}^{t_2} F \cdot dt \cdot dt$$

where t_1 is the time of the initial force interaction point; t_2 , the fracture completion point; V_0 , the impact velocity of the hammer; M_e , the effective mass of the hammer; and F , force.

The energy required to bring about fracture was then calculated using

$$E = \int_0^x F \cdot dx$$

where E is the energy input required to bring about fracture of the adhesive joint specimen, x , the displacement, and F , the force.

This was expressed graphically against the macroscopic adhered area and a best-fit line attributed to the data, assuming an energy value of 0 at an adhered area of 0. The graph obtained from the untreated adhesive joints is shown as Figure 4. The graphs for the reactive and heat-crosslinked electropolymer-treated adhesive joints are Figures 5 and 6, respectively. The gradient of the best-fit line is defined as the energy required for failure per cm^2 of adhered area.

Figure 7 is an SEM micrograph of a poly(2-allyl)phenylene oxide film formed on a thin polished steel substrate. The polymer film has been made visible by stressing the sample in liquid nitrogen to

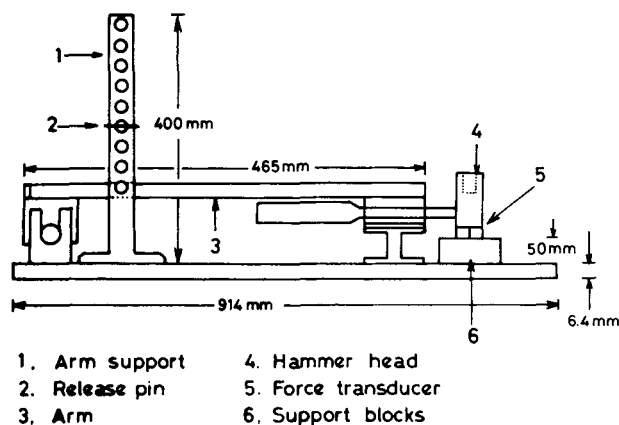


Figure 3 Charpy impact testing apparatus.

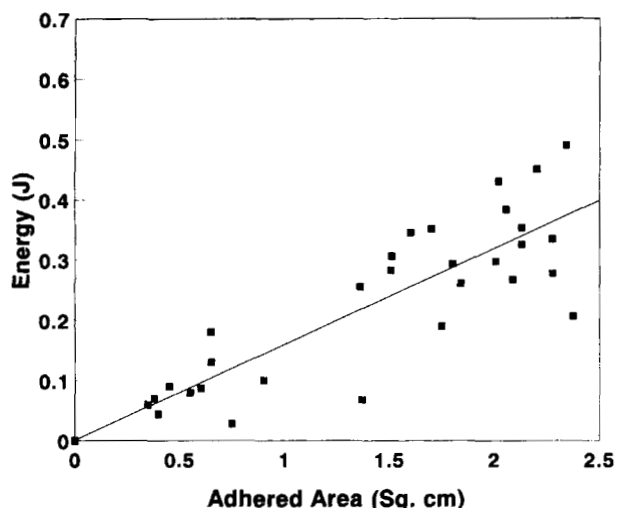


Figure 4 Energy vs. adhered area for the impact failures obtained from untreated steel blocks.

fracture and delaminate the polyphenylene oxide film.

Figures 8 and 9 are SEM micrographs of a fracture interface of a crosslinked electropolymer-treated adhesive joint. Figure 10 is similar to Figures 8 and 9, but for a reactive poly(2-allyl)phenylene oxide-treated adhesive joint.

DISCUSSION

Conceptual Basis

The fundamental reason for undertaking these experiments was to examine the importance of chem-

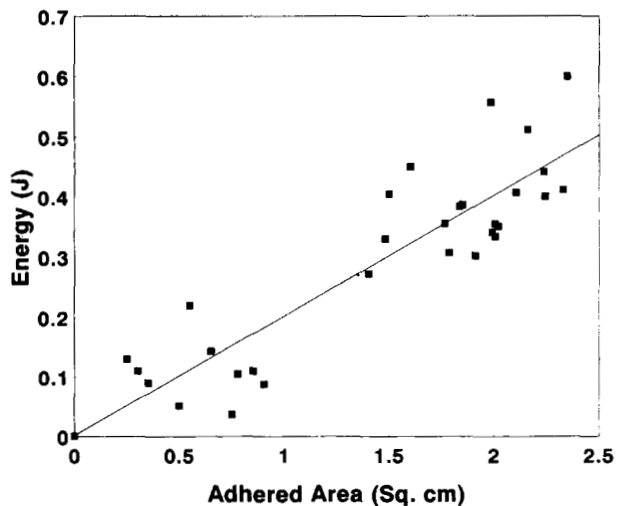


Figure 5 Energy vs. adhered area for the impact failures obtained from adhesive joints treated with poly(2-allyl)phenylene oxide electropolymer films.

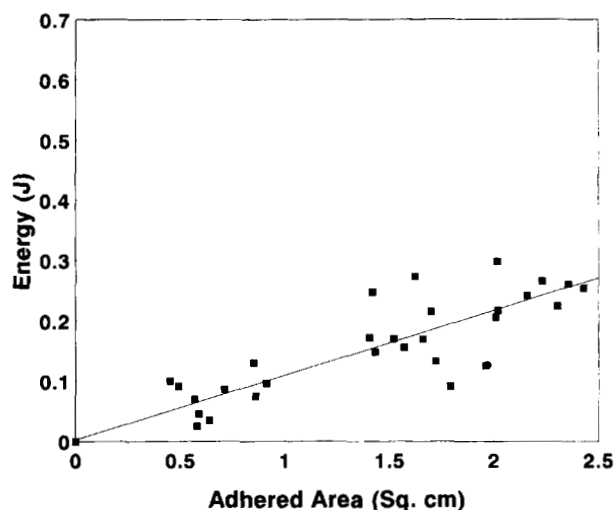


Figure 6 Energy vs. adhered area for the impact failures obtained from adhesive joints treated with heat-crosslinked electropolymer films.

ical bonding on adhesion strength in a coated steel system. Kinloch stated that four theories of adhesive interaction exist¹⁹:

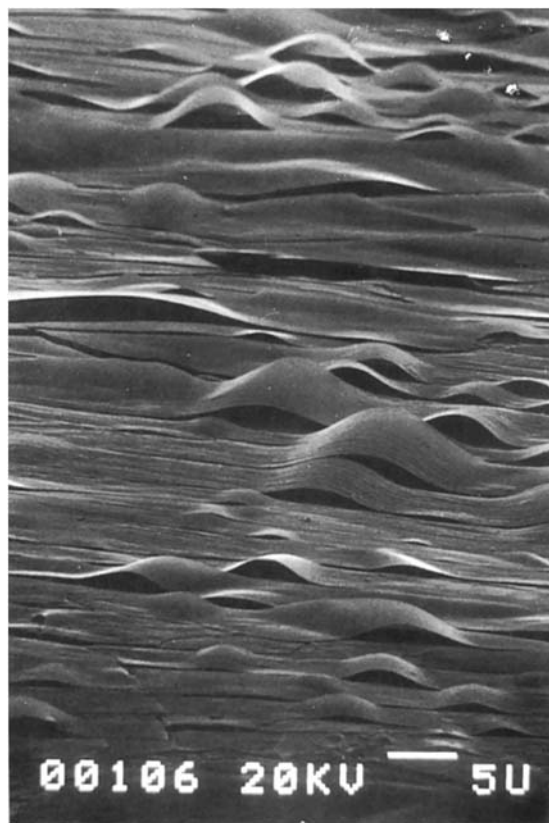


Figure 7 Microcryofractograph of a poly(2-allyl)phenylene oxide film formed on a steel substrate.



Figure 8 Fracture surface of an adhesive joint treated with a heat-crosslinked electropolymer film.

- (A) The Mechanical Keying Theory: Here, penetration of the adhesive into pores and irregularities on the substrate surface leads to cohesive rather than adhesive failure, giving an increase in the adhesion response.
- (B) The Diffusion Theory: Here, penetration of the adhesive into the substrate occurs at a molecular or atomic level.
- (C) The Electrostatic Theory: Here, the adhesion strength is dependent on electron transfer between the adhesive and the substrate. This leads to a double-layer charge separation at the interface, the attraction across which holds the adhesive and substrate together.
- (D) The Adsorption Theory: This is Kinloch's preferred theory, in which the adhesion

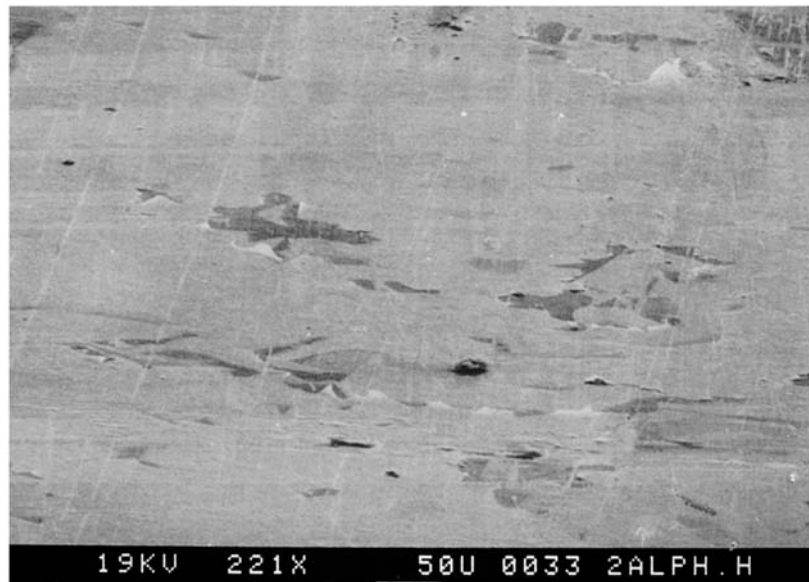


Figure 9 Fracture surface of an adhesive joint treated with a heat-crosslinked electropolymer film.

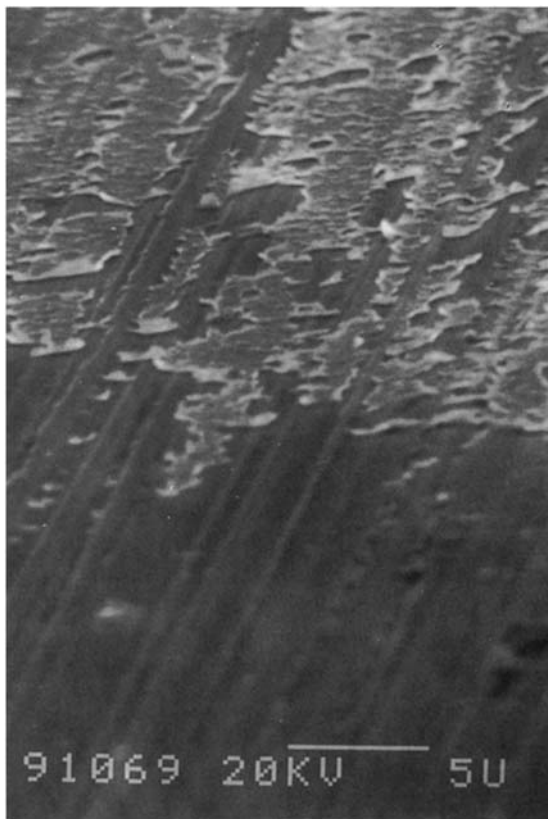


Figure 10 Fracture surface of an adhesive joint treated with a poly(2-allyl)phenylene oxide electropolymer film.

strength is determined by the sum of all the strong and weak chemical interactions across the interface.

It should be noted that only in the adsorption theory does adhesion have any dependence on chemical bonding phenomena.

2-Allylphenol was used for electropolymer film formation as it is one of the best-understood polyphenylene oxide film formers that is potentially reactive, with retention of the allylic functionality in the polymer film. This allyl functionality is also easily crosslinked, reducing the potential reactivity of the electropolymer film.^{10,11}

The use of an allyl-substituted film determined the choice of adhesive system. An unsaturated polyester/styrene resin system consists of a straight-chain unsaturated polyester dissolved in monomeric styrene.²⁰ Curing is initiated via the addition of an organic peroxide. This initiates radical polymerization of the styrene, which also crosslinks with the unsaturated functionality of the polyester to give a three-dimensionally crosslinked resin. Given that the polymerizing styrene can react with the unsat-

urated functionality of the polyester, it was hoped that it would also react with the allylic functionality of the electropolymer film. Also, if the adsorption theory is important in this system, precrosslinking the allyl functionality of the electropolymer film should lead to a drop in the measured failure energy/unit area.

The whole concept assumes that the electropolymer film has a significantly greater adhesion strength to the steel substrate than does the chosen adhesive system. However, this is a reasonable assumption as the electropolymer film should have very few, if any, interfacial faults. Interfacial faults are thought to lead to a substantial reduction in adhesion strength by acting as crack initiation sites.¹⁹

Failure Energies

A comparison of Figures 4–6 shows that the smallest value for energy per unit area is obtained from the precrosslinked electropolymer system (Fig. 6) with a mean of 0.11 J cm^{-2} . This can be compared to the mean value obtained for the reactive system (Fig. 5) of 0.20 J cm^{-2} . As described previously, these results clearly indicate that chemical bonding is an important factor in the adhesion strength and, thus, the failure energies obtained from these systems. This supports the adsorption theory of adhesion as put forward by Kinloch,¹⁹ as an increase in the theoretical bonding interactions has led to an increase in the observed energy of failure and thus the adhesion strength. Additional support can be surmised from the failure energy of the untreated control system. At 0.16 J cm^{-2} , this lies between the two electropolymer systems. From the theories described by Kinloch,¹⁹ this can be explained in terms of high- and low-energy surfaces. The crosslinked polymer surface can be described as a low-energy surface, where only van der Waals interactions will occur with the polyester/styrene adhesive system. This system should give the lowest failure energy and does. The metal-oxide film of the control system is a high-energy surface, with a greater tendency to form stronger polar and/or hydrogen bonds with the adhesive system. The adhesion of this system should thus give a higher-energy response than should the previous system, while giving a lower value than that obtained from the system treated with the poly(2-allyl)phenylene oxide film, where covalent chemical bonding with the adhesive appears to take place.

Microscopy

From the microcryofractograph of the thin steel substrate treated to form a poly(2-allyl) electropolymer film (Fig. 7), it should be noted that the visible electropolymer film is relatively uniform. The thickness of the reactive films is usually in the order of 0.2–0.4 microns. Comparative examination of a fracture surface from an adhesive joint treated with a precrosslinked electropolymer film (Figs. 8 and 9) shows that failure is mostly interfacial in nature and occurs between the adhesive and the surface treatment. Slight failure between the electropolymer film and the steel substrate also occurs. The low-energy polymer–polymer interface has formed the principal mode of failure as would be expected from the adsorption theory. When a fracture surface treated with the reactive poly(2-allyl) phenylene oxide film is examined (Fig. 10), it can be noted that a far greater proportion of the failure apparently occurs at the interface between the electropolymer film and the steel substrate. In conjunction with the increased failure energies observed for this system, this clearly indicates an increase in the strength of the interactions at the polymer–polymer interface. These observations are in accordance with those that would be expected from the adsorption theory of adhesion.

CONCLUSIONS

The electrooxidative polymerization of 2-allylphenol can be used to form a reactive thin polyphenylene oxide film on a steel substrate. This can produce an increase in adhesion strength between an unsaturated polyester/styrene resin and the steel substrate, observed from the failure energies of treated and untreated adhesive joint specimens. The failure energies and mode of specimen failure is in accordance with the adsorption theory put forward by Kinloch.¹⁹

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