Drying and property studies on protective coatings formed by spontaneous surface polymerization

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DRYING AND PROPERTY STUDIES ON PROTECTIVE COATINGS FORMED BY SPONTANEOUS SURFACE POLYMERIZATION

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Drying studies on a protective coating formed by spontaneous polymerization on aluminum are described. The polymer coating studied here was formed from styrene, n-phenyl maleimide (NPMI), bismaleimide (BMI), and 2-(methacryloyloxy) ethyl acetoacetate (MEA). The coating successfully changed into an adherent film through drying in the presence of a coalescing solvent. Drying at a high temperature (> 170°C) enhanced the performance of the coating in terms of corrosion resistance and adhesion. It was found that the drying process involved removal of surface water on the substrate followed by formation of a dense protective layer associated with thermal crosslinking of β-diketone functional groups in the coating. The reaction mechanism, glass transition temperature, adhesion strength to aluminum, and corrosion resistance of these coatings are reported. The resultant coatings show excellent adhesion strength in a torsional test and very good resistance under the ASTM B-117 accelerated salt fog test.

INTRODUCTION

In 1995, Zhang, Agarwal, and Bell developed an environmentally friendly polymeric coating process on aluminum substrates through a surface spontaneous polymerization [1–5]. This polymer coating is formed by dipping the metal specimens into certain monomer solutions, in which styrene and n-phenyl maleimide are main components.

These two monomers form an alternating copolymer on the aluminum surface. As compared with coating processes using highly viscous polymers, the coating formed by spontaneous polymerization uses monomer solutions and is directly synthesized on the metal surface. Thus a conformal, pinhole free, and uniform coating can be easily formed on an object with complex topography. The resultant polymer coating after polymerization is a soft gel-like layer containing residual monomer solution; rinsing and drying convert this coating into a solid film. This paper describes a postpolymerization treatment process for formation of a protective polymer coating on aluminum. It is revealed that crosslinking through β-diketone groups (from added MEA) by heating changes coating structure, and improves the coating properties in terms of adhesion and corrosion resistance.
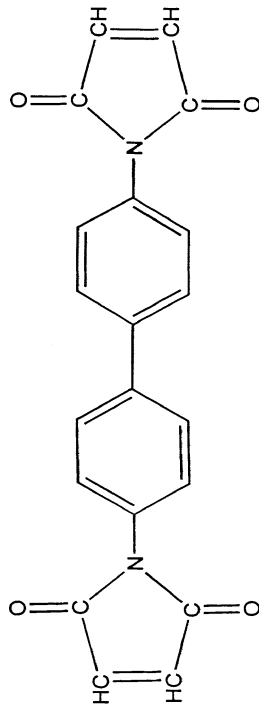
Spontaneous polymerization is conducted at room temperature in a single tank of monomer solution without any added initiator or external driving force. Besides styrene and n-phenyl maleimide, two additional monomers are incorporated into the copolymer: 2-(methacryloyloxy) ethyl acetoacetate (MEA), which is used as an adhesion promoter and internal plasticizer, and bismaleimide (BMI), which is used in a low concentration as a precrosslinking agent to arrest flow during drying of the coating. Figure 1 shows the structures of the monomers in this research, along with their roles in the coating process. In addition to the above monomers, the monomer solution is composed of a 57% N-methyl pyrrolidone/43% water (v/v) mixture. After polymerization, the coated aluminum specimens are removed from the monomer solution. At this stage, the coating is wet and soft, and contains unreacted monomers and a relatively high amount of solvent and water. In the following post-treatment process, rinsing and drying are carried out to form a strongly adherent protective film on the aluminum. Coatings as thick as 50 microns can be obtained.

The incorporation of MEA has dramatic effects on the development of the properties of the final coating. It was observed that coatings incorporating some MEA showed no cracking as compared with severe cracks for those without MEA, and had higher adhesion strength after drying [1–2]. In the present research, we found that coatings incorporating MEA went through further crosslinking through the β-diketone functional groups. As a result, this coating has a glass transition temperature above 200°C, and a degradation temperature above 400°C.

The focus of this research has been threefold: (1) to study the effects of rinsing and drying conditions on the properties of the resultant coating, (2) to develop a post-treatment process to enhance a protective coating on aluminum for corrosion protection, and (3) to investigate the crosslinking mechanism of β-diketone groups during drying. The

Bismaleimdie(BMI): Precrosslinker to prevent flow in drying
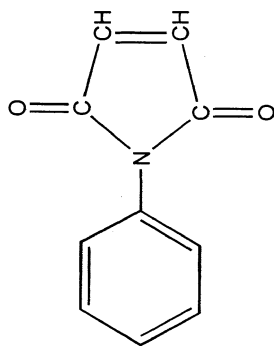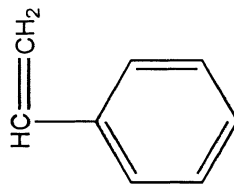
N-phenyl maleimide (NPMI):
Electron Acceptor
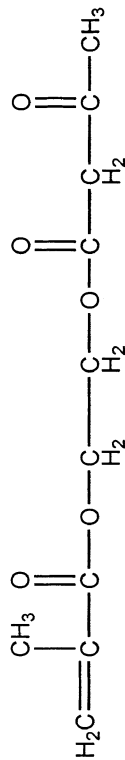
2-(methacryloyloxy) ethyl acetoacetate (MEA):
Adhesion Promoter and internal plasticizer

Styrene: Electron Donor

FIGURE 1 Monomers, structures, and their roles.

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desired properties for corrosion protection are high temperature resistance and stability, uniform thickness, and conformation to the substrate. The measurements of the above properties are reported.

EXPERIMENTAL

Materials

Reagent-grade styrene (ST) from Aldrich Chemical Co. (St. Louis, MO, USA) was vacuum distilled at $40°C$ or passed through a DTR-7 removal column from Scientific Polymer Products, Inc. (Ontario, NY, USA). N-phenyl maleimide (NPMI) and bismaleimide (BMI) were purchased from TCI America Chemical Co. (Portland, OR, USA). NPMI was sometimes purified by recrystallization in cyclohexane. BMI was generally used as received. The 2-(methacryloyloxy) ethyl acetoacetate (MEA) from Aldrich Chemical Co. was purified by passing it through a DHR-4 inhibitor removal column from Scientific Polymer Products. N-methyl pyrollidone (NMP) solvent from Lancaster Chemical (Windham, NH, USA) and BASF Chemical (Mount Olive, NJ, USA) was used as received. Distilled water was prepared using a Barnstead Model 210 Distilled Water Center (Barnstead, Dubuque, IA, USA). Aluminum alloys used in this research included Al 2024, 6061, and 7075. Al 2024 (4.5% Cu, 1.5% Mg, 0.6% Mn) has high shear strength and is commonly used as a structural material, and it is highly prone to corrosion. Al 6061 (1.0% Mg, 0.6% Si, 0.2% Cr, 0.27% Cu) is used in air and marine applications, where corrosion resistance is needed. Al 7075 (5.5% Zn, 2.5% Mg, 1.5% Cu, 0.3% Cr) has both good strength and resistance to corrosion [6]. Aluminum samples were supplied by DACCO SCI. Inc. (Baltimore, MD, USA) and United Technologies Corporation (East Hartford, CT, USA).

Aluminum Pretreatment

Aluminum alloys were pretreated by one of two methods.

1. Aluminum samples were degreased and cleaned with Micron-90® detergent (a common laboratory alkaline soap of pH 9.5) from Cole-Parmer Instrument Company (Vernon Hills, IL, USA) followed by etching in 5% aqueous hydrofluoric acid solution for 20 s. The etched samples were then washed with tap water for 60 s, followed by drying in air.
2. Aluminum samples were grit blasted at 60 PSI (0.4 MPa) by 180 mesh alumina using a lab blasting instrument, then washed with

tap water and wiped by Kimwipe® paper towels. Sometimes the grit-blasted samples were also etched as above to smooth the rough surface after blasting.

Monomer Feed Solution

NPMI, BMI, and styrene were directly dissolved into NMP. Dilute aqueous sulfuric acid (0.025 M) was added slowly to the solution with stirring until a 57/43 volume ratio of NMP/water was reached. A cold-water bath was used to dissipate the heat generated from the exothermal mixing of NMP and water. MEA was finally added to the solution. By this method, a clear yellow solution was obtained.

Polymerization

Polymerization was conducted in glass or polypropylene food-type containers, or in custom-designed $8 \text{ cm} \times 8 \text{ cm} \times 1 \text{ cm}$ polypropylene tanks. The monomer solution was first purged with nitrogen to reduce the dissolved oxygen concentration to less than 3 ppm. When the pretreated aluminum was immersed in the monomer solution, a white polymer coating started to form on the aluminum surface within seconds. The polymerization time was varied from 1 min up to 120 min in order to produce coatings of different desired thicknesses.

Rinsing

Following the polymerization, the coated samples were immersed in a gently stirred aqueous NMP solution to remove excess NMP and residual monomers. The amount of NMP used in the rinsing bath was *ca*. 10–20% by volume determined by the thickness of the coating; thicker coatings required more NMP. The NMP provided plasticization of the coating during the film formation process. The rinsing time varied from 20 min to 60 min with a gentle agitation of the rinsing bath.

Drying

After rinsing, the wet coating was then dried in a laboratory 2 ft^3 (9.3×10^{-1} cm^3) circulating air oven. The sample was first dried by air purging at temperatures ranging from $80°C$ to $150°C$ for 1 h to remove water and most of the NMP. At this stage, the coating converted from a white swollen layer into a solid transparent adherent film on aluminum. The coating was then dried at $180–230°C$ for 2 to 4 h to

crosslink the coating thermally and remove residual NMP. After drying, the sample was slowly cooled (3 to 4 h) to ambient temperature by turning off the oven.

Characterization

To evaluate the amount of residual solvent as a function of drying time, the coatings were scraped off the surface and then extracted in methanol. Next, a Hewlett Packard 5780 Gas Chromatograph (GC) (Hewlett Packard, Palo Alto, CA, USA) was used to analyze the extract for residual solvent. To characterize products generated during heating of the polymer containing MEA, a direct dynamic thermal desorption device on a Hewlett Packard GC/MS 5780 was used. The device could thermally extract compounds from the solid directly into the capillary column of the gas chromatograph [7]. The heating time for the polymer sample was chosen as 2 min. A liquid nitrogen trap at the beginning section of the column was used to freeze the compounds generated by heating. Following the heating, these compounds were carried into the capillary column for separation and characterization by a mass spectrometer. The temperature program of the GC was chosen as $10°C/min$ from $35°C$ to $250°C$, holding 2 min at the final high temperature.

A Perkin Elmer Differential Scanning Calorimeter (DSC-7) (Perkin Elmer, Shelton, CT, USA) was used to measure the glass transition temperature (T_g) of the polymer at a heating rate of $10°C/min$ in nitrogen. A midpoint method was employed to estimate the T_g of the sample.

Fourier transform infrared (FTIR) spectra for polymer samples were taken using a Nicolet Magna 560s SpectraTech FTIR (Nicolet, Madison, WI, USA) with a deuterated triglycine sulfate (DTGS) detector and a germanium/KBr beam splitter. The samples were prepared by mixing about 150 mg KBr powder with 1–2 mg polymer. The pellet of KBr was compressed by a Mode C Carver Laboratory Press (Carver, Wabash, IN, USA) under 12–13 KPa. All spectra were recorded with 64 scans at a $4 \ cm^{-1}$ resolution. To reveal the interaction of the polymer coating with the aluminum surface, a reflection adsorption infrared accessory was used to obtain the spectra from an adsorbing film on the metal surface. This technique involves reflecting infrared radiation that is polarized parallel to the plane of incidence from the surface at grazing angles ($80°C$ or more) of incidence [8, 9].

A Bruker ^1H 500MHz digital NMR spectrometer (Bruker, Billerica, MA, USA) was used to obtain the NMR spectra of the copolymer of styrene, NPMI, and MEA. $CDCL_3$ was used as the solvent for all

NMR samples. To run a test, a delay time of 1 s was used for quick scan and 10 s for quantitative analysis.

Molecular weights were measured using a Waters 550C-150 Gel Permeation Chromatography (GPC) system (Waters, Milford, MA, USA) using a universal calibration curve from polystyrene standards. Coating samples were prepared by dissolving 10 to 15 mg polymer in 5 ml solvent. All samples were passed through a 0.2 μm Teflon® filter. For the polymer formed by spontaneous polymerization, tetrahydrofuran (THF) was used as the solvent and the mobile phase in the GPC system.

The adhesion of polymer coatings to the aluminum substrate was evaluated using the torsional testing method of Lin and Bell [10]. The joint assembly that was used in shown in Figure 2. Using this test, the joints were broken in torsion, giving an almost pure shear mode with very good reproducibility. To prepare the joint assembly the copolymer coatings were first formed spontaneously on the grit-blasted aluminum joint halves (shown in Figure 2 as A) and then dried under different conditions for evaluation. The joint halves were then adhered together by applying 0.045 mg of an equal molar mixture of epoxy (Epon 828 from Shell Chemical, Houston, TX, USA) with methylene dianiline curing agent (from Eastman Chemical, Kingsport, TN, USA) uniformly on the annular ring, and cured at 100°C for 1 h and 150°C for 2 h. In this research, 5–7 joint assemblies were used to produce one data point.

A laboratory salt fog spray test, following ASTM B-117 specifications (ASTM, Philadelphia, PA, USA), was used to evaluate the
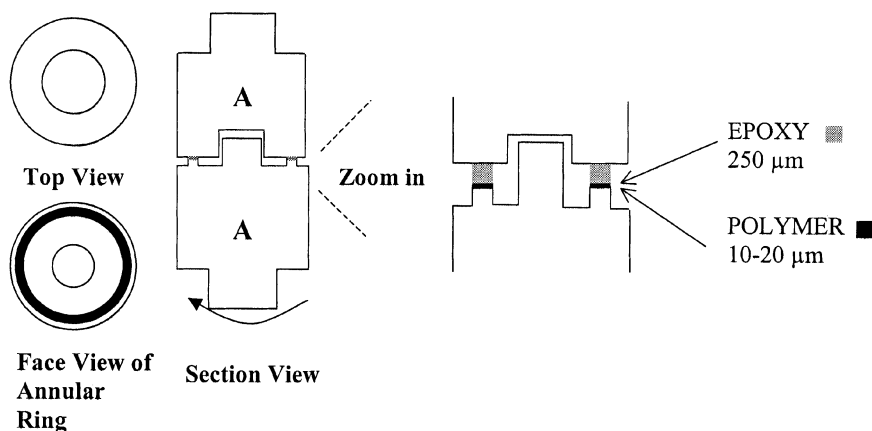
FIGURE 2 Schematic of the torsional joints (dark ring is the contact face).

relative corrosion resistance of coatings. A 5% sodium chloride solution was used as the salt solution, which was passed from an elevated container into the testing chamber. The salt solution was blown into the testing chamber as a stream of salt fog with the aid of pressurized air at 45 PSI. The salt fog chamber was maintained at 35°C. The samples were mounted in the chamber at 45° relative to the inlet of the fog.

RESULTS AND DISCUSSION

Film Formation

The wet coating after polymerization was converted into a uniform film with the aid of NMP introduced into the rinsing solution. A 10–20% NMP/water rinsing bath enabled conversion of the wet coating into a uniform film at drying temperatures ranging from 80°C to 150°C. Drying at these temperatures overall facilitated water evaporation without bubble formation. In addition, such drying temperatures enhanced the plasticization of the coating by NMP. Otherwise, cracks or even chalky spots formed during drying in this temperature range. In this first step, the chemical nature of the polymer was little changed, and the coating still contained a few percent of NMP (B.P. 204°C).

Removal of Residual Solvent

Further drying at a higher temperature efficiently removed the residual solvent. At a drying temperature of 180°C, the solvent residue in the coating became less than 0.1 wt% after 1 h. When the temperature was 230°C, the coating lost NMP more rapidly, resulting in less than 0.1 wt% solvent remaining after 20 min of drying. One explanation for this is the improved diffusion of NMP inside the coating at a temperature above the Tg of the coating. After film formation, the Tg of the coating was about 170°C; when the heating temperature was higher than the T_g, polymer chains became mobile, and NMP had more freedom to diffuse inside the coating.

Crosslinking of Coatings at High Temperatures

Incorporation of MEA into the styrene, N-phenyl maleimide copolymer resulted in crosslinking in the coating at drying temperatures above 170°C. When a copolymer formed from 0.1 M NPMI/0.1M MEA/ 0.1M styrene was heated at a temperature below 170°C, the copolymer easily dissolved in the THF and NMP at room temperature. However, when the copolymer was heated above 170°C, it became insoluble in both THF and NMP, and was only plasticized by these

solvents. This illustrates that the copolymer went through a thermal crosslinking reaction above 170°C, resulting in a crosslinked network in the copolymer. On the other hand, the copolymer of styrene and NPMI without MEA always easily dissolved in THF and NMP, even after being dried at temperatures up to 250°C.

Crosslinking Mechanism

It was observed that a free film of the copolymer formed from a monomer solution of 0.1 M styrene/0.1M NPMI/0.1M MEA became sticky and generated bubbles when the copolymer was heated at temperatures above 170°C. This suggests that the crosslinking reaction involves the evolution of low molecular weight compounds. Considering the structure of MEA, β-diketone moieties are by far the most reactive. Such a thermally induced crosslinking involving β-diketone groups in polymers has not been previously reported. The fact that the reaction was only significant above 170°C indicates that the high temperature caused reaction of the β-diketone groups, resulting in new structures within the polymer. It has been reported that β-diketone groups in simple compounds can be thermolyzed [13–15]. Binder [11] and Thomas [12] individually studied the thermolysis of acetoacetoxy compounds. They both proposed that the enol form of the β-diketone group was not chemically stable at temperatures above 160°C. The group was easily broken down through the reactive double bond and ester bond in its structure, and acetone and carbon dioxide were evolved. The presence of traces of water enhanced the thermolysis of the β-diketone group.

To understand the thermal reaction occurring during heating at temperatures above 170°C, coatings formed from a monomer solution of 0.1M styrene/0.1M NPMI/0.1M MEA/0.005M BMI were tested using thermal desorption GC/MS. GC spectra of the coatings heated at 150°C and 190°C are shown in Figures 3 and 4, respectively. It is seen that the coating heated at 150°C gave off residual NMP only. In contrast, the coating heated at 190°C gave off three other volatile compounds, *e.g.*, carbon dioxide, acetone, and acetoacetic acid. Even higher temperatures could cause the evolution of additional simple compounds from the coating.

Based on the discussion above, it is proposed that β-diketone groups in the copolymer chains are decomposed at elevated temperatures through the double bond and the next ester bond of their enol form, resulting in two kinds of free radicals and subsequent crosslinking through the combination of free radicals. Figure 5 shows the proposed crosslinking mechanism for coatings containing MEA. The generation
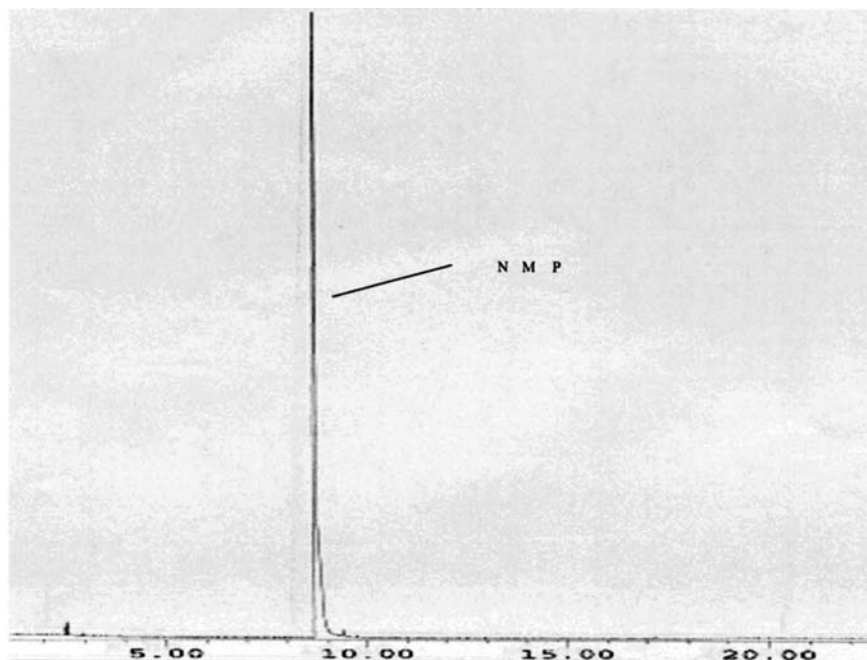
FIGURE 3 GC spectrum of the coating containing MEA, heated at 150°C (formed from 0.1M styrene/0.1M NPMI/0.1M MEA/0.005M BMI).

of the species A causes the evolution of acetoacetic acid, and the generation of the species B causes the evolution of acetone. The combination of species A and species B creates an intermolecular bond, resulting in the evolution of carbon dioxide.

Effects of Crosslinking on Coating Properties

Crosslinking had several effects on the coating's properties. Table 1 lists the apparent average molecular weights of copolymers of styrene and NPMI as well as copolymers of styrene, NPMI, and MEA, after heating at different temperatures for 1 h. It is seen that the molecular weights of the copolymers containing MEA remained stable when the heating temperature was below 170°C. When the heating temperature was higher than 170°C, the copolymer would not dissolve in the solvent (THF) used for molecular weight determination. On the other hand, the apparent molecular weights of the copolymers of styrene and NPMI were almost independent of heating at temperatures up to 220°C for 1 h.
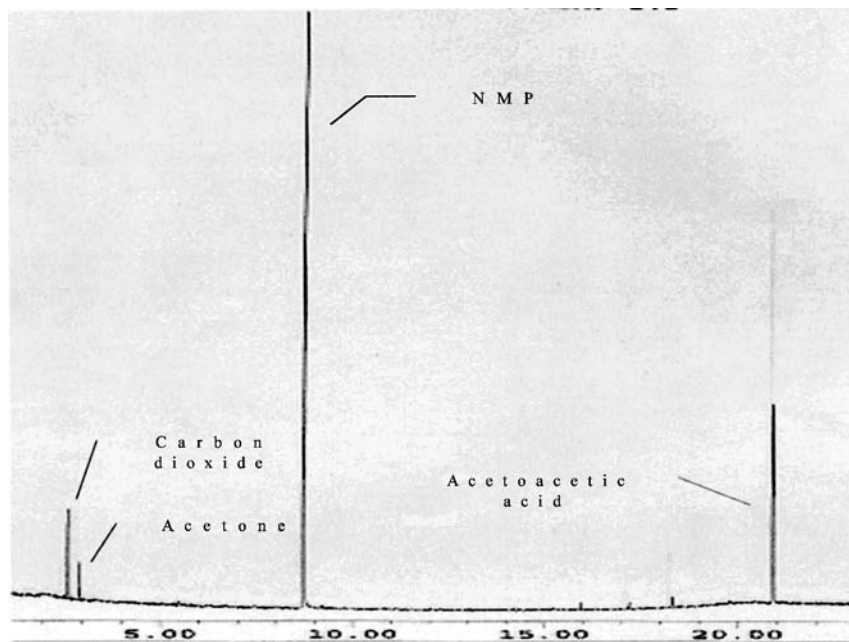
FIGURE 4 GC spectrum of the coating containing MEA, heated at 190°C (formed from 0.1M styrene/0.1M NPMI/0.1M MEA/0.005M BMI).

The extent of crosslinking of coatings containing MEA was estimated using the gel content of the coatings after immersion in tetrahydrofuran (THF) for 72 h. Figure 6 shows the gel content of coatings formed from a monomer solution of 0.2M styrene/0.1M NPMI/0.1M MEA heated at 180°C and 220°C for various times. It is clear that the heating temperature influenced the gel content of the coatings. The coating heated at 180°C for 2 h exhibited a gel content of about 15%, and longer heating increased the gel content only slightly. In contrast, the coating heated at 220°C showed a more rapid increase of gel content, resulting in a gel content over 20% in 30 min; longer heating gradually increased the gel content further. The influence of the temperature would be associated with the change of the Tg of the coating during heating. Since the crosslinking occurred at temperatures above Tg, the magnitude of $(T_{heating} - T_g)$ would affect the extent of crosslinking. Coatings formed from a monomer of 0.2 M styrene/0.1M NPMI/0.1M MEA/0.005M BMI were also tested for gel content. Figure 7 shows that the coatings reached gel contents of 98% in 30 min heating at both 180°C and 220°C. However, it was observed
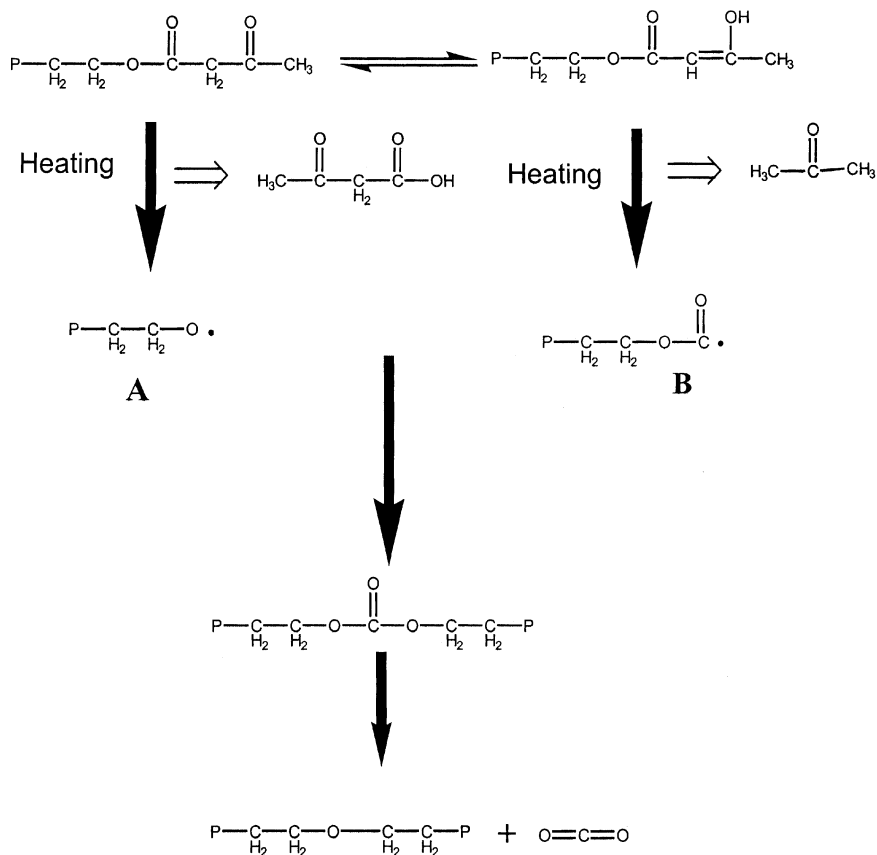
FIGURE 5 Proposed mechanism of crosslinking reaction through β-diketone groups.

TABLE 1 Apparent Average Molecular Weights of Copolymers after Being Heated at Different Temperatures for 1 Hour

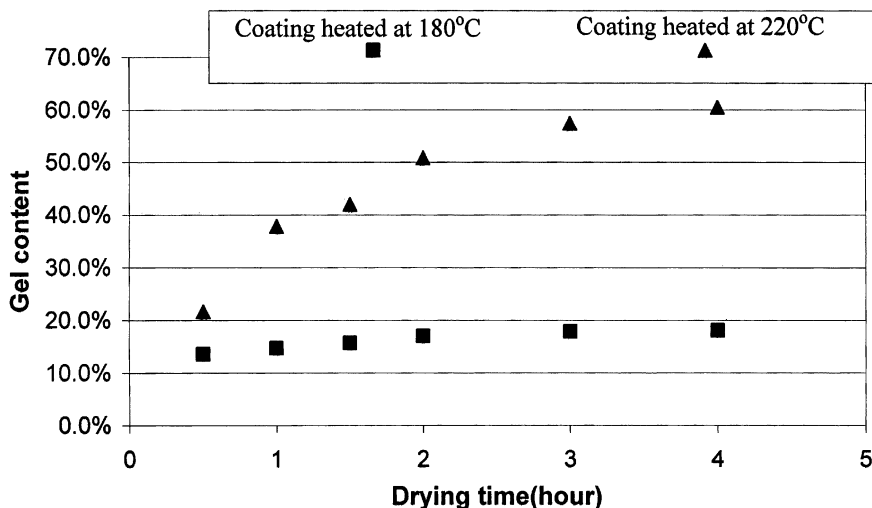| Heating temperatures (°C)	Copolymers formed from 0.1 M styrene/0.1 NPMI		Copolymers formed from 0.1 M styrene/0.1 M NPMI/0.1 M MEA	
	M_n	M_w	M_n	M_w
105	28929	80497	33459	99130
145	28987	78965	33654	105953
167	29030	79358	35252	112450
170	30107	81678	Crosslinked	Crosslinked
190	31046	83547	Crosslinked	Crosslinked
220	30905	82563	Crosslinked	Crosslinked

FIGURE 6 Gel content of coatings formed from 0.2 M ST/0.1M NPMI/0.1M MEA after heating at 180°C and 220°C for different times.

that the coatings which were not heated above 170°C delaminated from the aluminum surface when they were immersed in THF. When heated above 170°C, these coatings became very stable in the
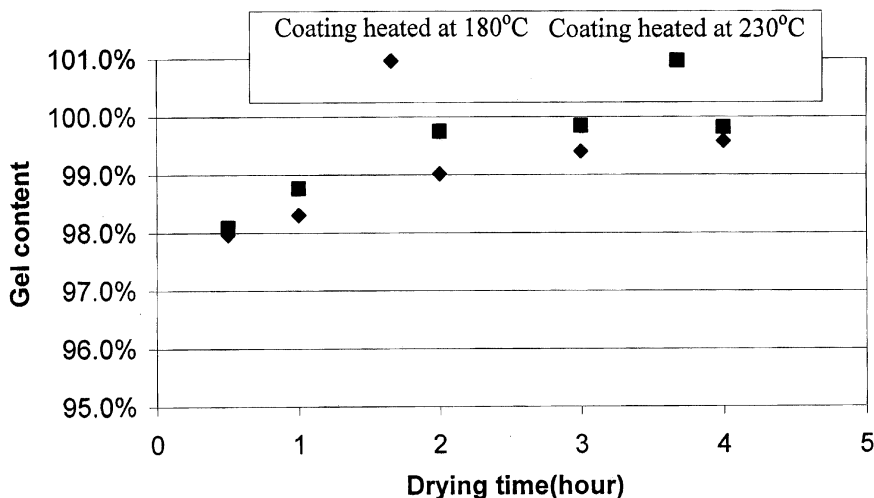

FIGURE 7 Gel content of coatings formed from 0.2 M ST/0.1M NPMI/0.1M MEA/0.005M BMI after heating at 180°C and 220°C for different times.
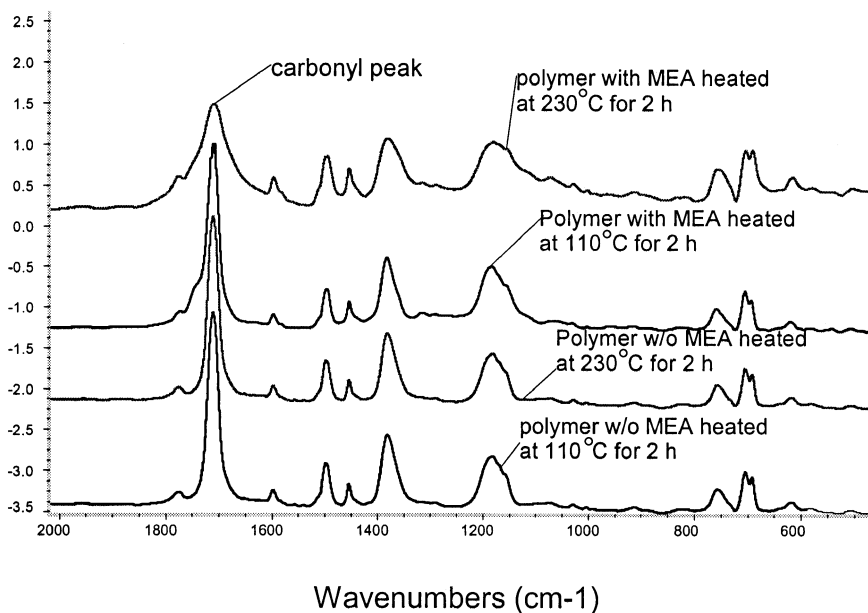
FIGURE 8 FTIR spectra of coatings with or without MEA, heated at 110°C and 230°C for 2 h.

immersion test. These results imply that the crosslinking through β-diketone further enhanced the adhesive bond strength of the coatings.

FTIR spectra of coatings before and after crosslinking are shown in Figure 8. It is seen that the spectra of coatings formed from a monomer solution of 0.1M styrene/0.1M NPMI and dried at 110°C and 230°C, respectively, were identical. However, for the coatings formed from a monomer solution of 0.1M styrene/0.1M NPMI/0.1M MEA, the coating heated at 230°C had a shorter and broader carbonyl peak at 1700 cm^{-1} relative to the spectrum from the coating heated at 110°C; the rest of the spectra were still essentially the same. The results indicated that a reaction occurred associated with the changes of β-diketone groups in the MEA units in the polymer, which contain two reactive carbonyl groups.

Shrinkage of the coating was also measured at high temperatures. Figure 9 shows the thickness of dried coatings prepared from a monomer solution of 0.2M styrene/0.1M NPMI/0.1M MEA/0.005M BMI as a function of drying temperature. The thickness of the coating dropped 20% when the heating temperature was increased from 110°C to
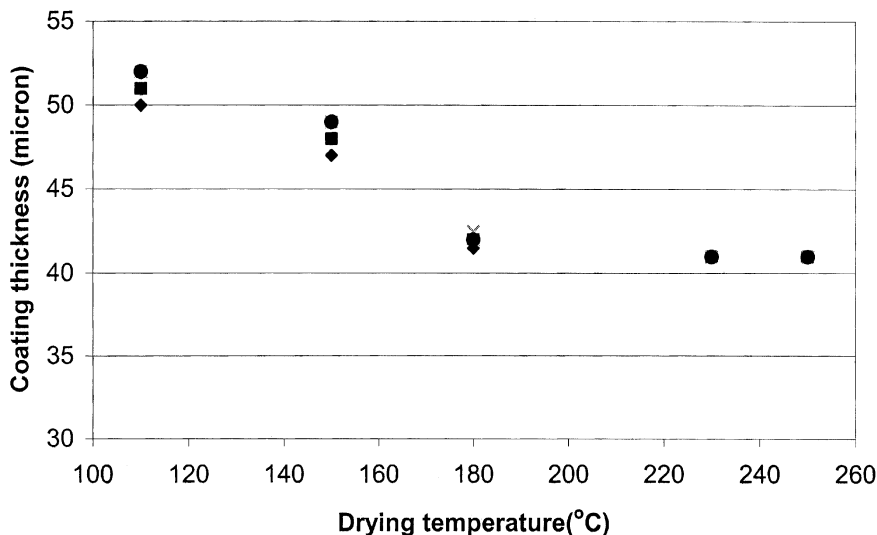
FIGURE 9 Effects of drying temperatures on the thickness of coatings formed from 0.2M styrene/0.1M NPMI/0.1M MEA/0.005M BMI.

180°C, but the thickness was almost constant above that temperature. The initial decrease of thickness was due to the reduced volume of the coating through the removal of the residual solvent and movement of the polymer chains. However, at temperatures above 180°C, the residual solvent was minor. Also, crosslinking occurring in the coating might hinder the movement of molecular chains in the coating, resulting in almost constant thickness.

Higher temperature heating also helps to eliminate crevices and ridges on the coating surface. Figures 10 and 11 show the environmental scanning electron microscopy images of the coating surfaces dried at 110°C and 185°C for 2 h, respectively. It is seen that the coating surface dried at 110°C had some crevices and ridges, as seen under 2550× magnification. The presence of these crevices seemed to be due to the evaporation of the solvent and water, and these crevices perhaps served as channels for evaporation. When the coating was heated at 185°C, the surface showed no crevices under 4000× magnification. Flow of the polymer at high drying temperature leveled the crevices on the surface. This implies that such cavities present in the coating at low drying temperatures consolidated when the heating temperature was higher than the coating's Tg.
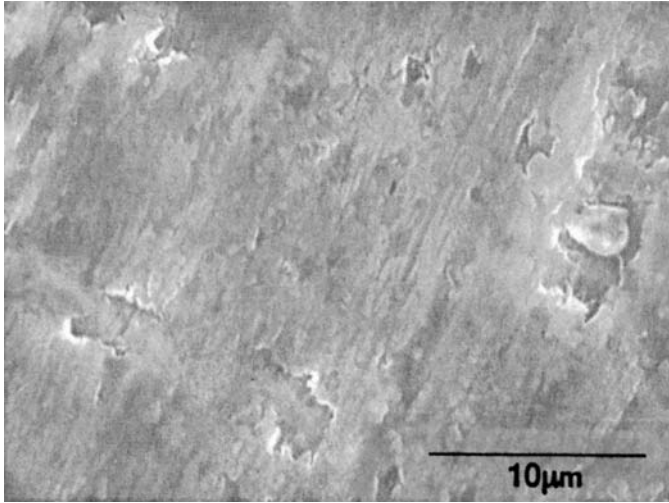
FIGURE 10 ESEM image of the coating from 0.2M ST/0.1M NPMI/0.1M MEA/0.005M BMI dried at 110°C for 2 h.
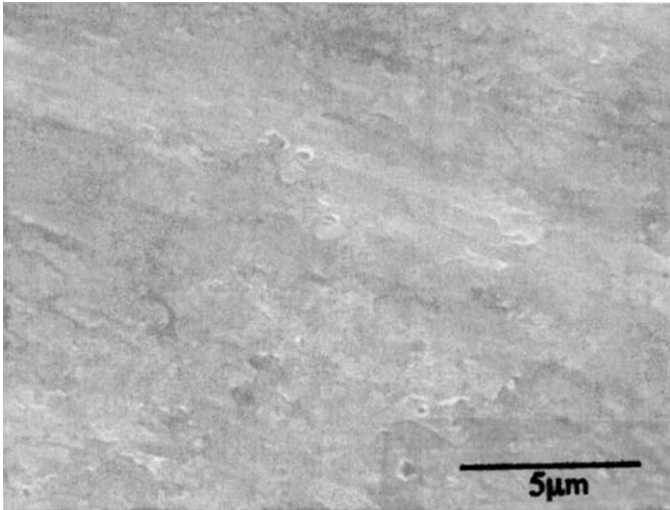

FIGURE 11 ESEM image of the coating dried at 185°C for 2 h.

Glass Transition Temperature (Tg)

The Tg of coatings containing MEA was previously studied by Agarwal [1, 2]. He concluded that the incorporation of MEA into the coating

TABLE 2 Incorporation of MEA into Coatings and their Tg

Monomer feed composition (NPMI/MEA/styrene)	Relative amount of MEA units in coatings (mol%)	Tg measured by DSC (°C)	Tg calculated by FOX equation (°C)
0.1/0/0.2	0	219.9	—
0.1/0.05/0.2	9.6	187.3	183.2
0.1/0.1/0.2	13.7	168.8	169.1
0.1/0.15/0.2	16.8	157.7	159.0
0.1/0.2/0.2	20.6	147.6	148.2

only slightly decreased the Tg. He reported that the Tg of coatings containing MEA was always higher than 200°C. His results seem to conflict with the nature of pure poly (MEA), which has a Tg of −5°C [1]. In this research, it was found that the addition of MEA lowered the Tg of the coating; however, further crosslinking induced by high temperature heating counterbalanced the MEA mobility and increased Tg.

The effect of MEA on the Tg of the coatings before thermal crosslinking is shown in Table 2, for which the amount of MEA in the coatings was measured by ^{1}H NMR. The copolymer samples were washed with ethanol and heated to only 60°C to minimize the crosslinking. It is seen that MEA was incorporated into the copolymers, resulting in decreased Tg. For the copolymer formed from 0.2M styrene/0.1M NPMI/0.2M MEA, the copolymer contained about 20.6% of MEA units, resulting in a Tg of 148°C. The data also show that the Tg from DSC measurements agrees with the Tg value calculated by the Fox equation. The decreased Tg of the coating might help to reduce internal stresses developed in the coating during drying, so that incorporation of MEA into the coating inhibited crack formation.

The coating formed from styrene, NPMI, and MEA showed an increase in glass transition temperature when heated at temperatures above 170°C. The changes of the Tg of coatings formed from a monomer solution of 0.2M styrene/01.M MEA/0.1M NPMI, and heated at 180°C and 220°C, are shown in Figures 12 and 13, respectively. The results show that a coating with an initial Tg about 168°C increased in Tg to a level near the heating temperature after heating for about 1 h. When the coating was heated at 180°C, its Tg reached 180°C in about 1 h, and further heating increased the Tg slowly; when the coating was heated at 220°C, its Tg reached 220°C in about 4 h. Heating at this higher temperature resulted in a more rapid increase of the Tg than at 180°C, and a higher final Tg of the coating. However, once the Tg became higher than the drying temperature, the rate of the

FIGURE 12 Tg of coatings after heating $180°C$ for different times (the coatings were formed from a monomer solution containing 0.2 M styrene/0.1M MEA/ 0.1M MEA/0.1M NPMI).
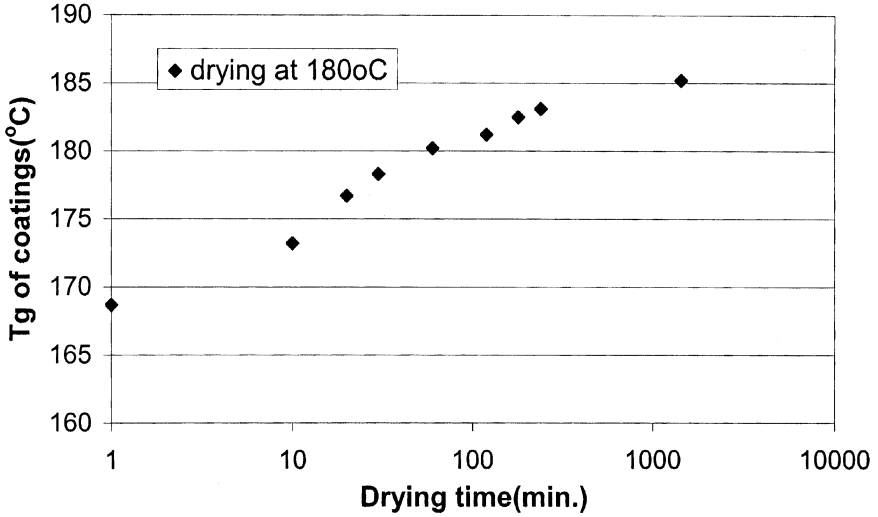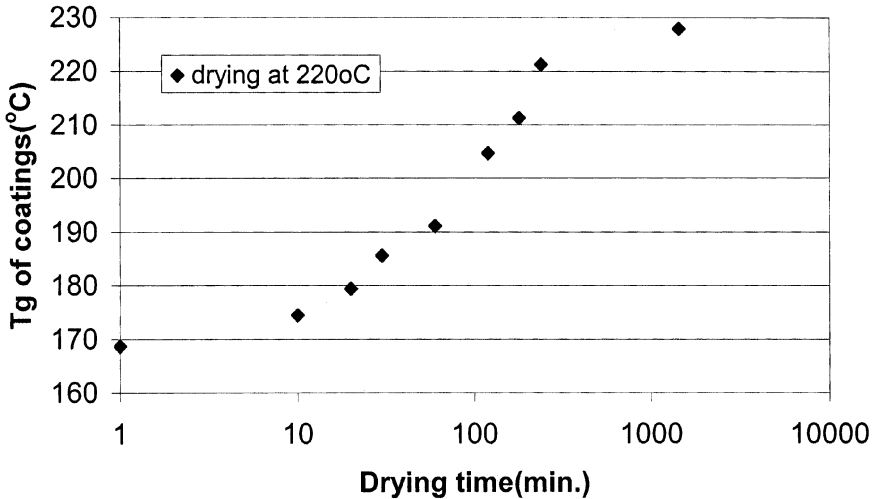

FIGURE 13 Tg of coatings after heating $220°C$ for different times (the coatings were formed from a monomer solution containing 0.2M styrene/0.1M MEA/0.1M NPMI).

increase of Tg slowed, resulting in only a few degrees increase after heating for 24 h.

The change of the Tg in Figure 13 can be attributed to the crosslinking reaction. As the coating becomes crosslinked, movement of polymer chains is more difficult, resulting in an increased Tg. This increased Tg, in turn, influences the extent of the crosslinking. When the Tg becomes higher than the heating temperature, the crosslinking is almost arrested. As the coating crosslinks, it also changes its composition associated with the β-diketone moiety, with the loss of low molecular weight compounds, *e.g.*, acetone, carbon dioxide, and acetoacetic acid. Heating at 220°C caused more evolution of volatile compounds from the coating than at 180°C, resulting in a higher final Tg. In contrast, the coating heated at 180°C was of low degree of crosslinking, and the composition of the coating did not change as much as the sample heated at 220°C.

Adhesion of Coatings

The bonding strength of the coating to the aluminum was examined by the torsional joint method of Lin and Bell (see experimental section). Failure of the joint assembly was consistently in the coating-metal interphase or in the bulk coating. As shown in Figure 14, the shear
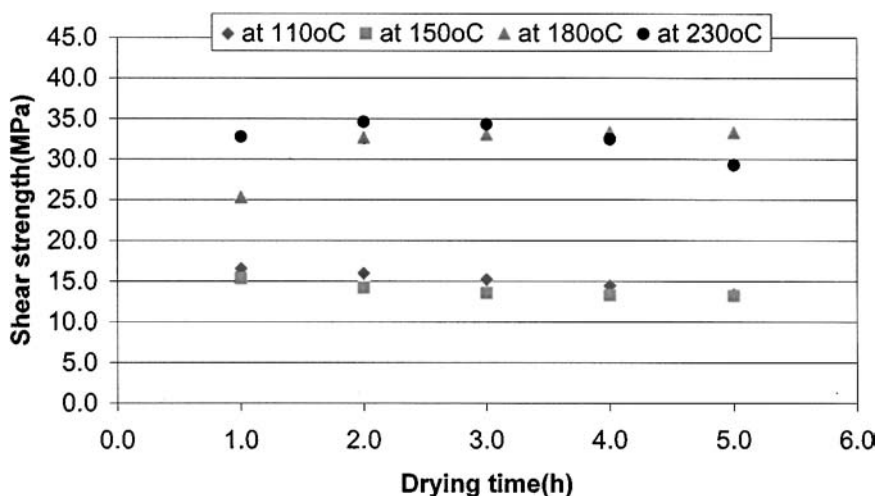

FIGURE 14 The joint shear strength of coatings heated at different temperatures for different times (coating formed from 0.2M styrene/0.1M NPMI/0.1M MEA/0.005M BMI).

strength of joint assemblies prepared from a monomer solution of 0.2M styrene/0.1M MEA/0.1M NPMI/0.005M BMI increased for 180°C or 230°C drying. When heated at 110°C and 150°C, the joint assemblies exhibited torsional shear strength of only about 15 Mpa, due to the lack of thermal crosslinking. However, after heating at 180°C and 230°C, the value of joint assembly strength jumped to over 30 Mpa after 1 h of heating. The data also show that the joint assembly strength for samples heated at 180°C was maintained to over 5 h of heating. However, the joint assembly strength of the samples heated at 230°C began to decrease after 3 h. This implies deterioration of the coating structure due to long high temperature heating.

Photographs of cross-section of broken aluminum joints heated at 110°C and 230°C are shown in Figures 15 and 16, respectively. These photographs show that the broken surface of a coating heated at 110°C was still covered with "scales" of the copolymer; in contrast, the broken surface of a coating heated at 230°C was clearer, with only scraped polymer visually present on the surface. This illustrates that the failure of the coating heated at low temperature was cohesive, and changed into adhesive when the coating was heated at higher temperature and thereby crosslinked. It is well recognized that for coatings with strong bonding on metal surfaces, there might be a weaker layer
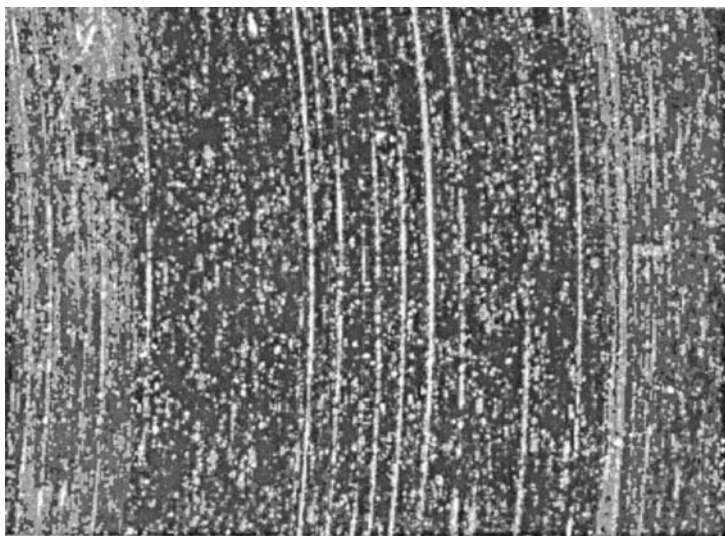

FIGURE 15 A cross-section of the surface of a broken aluminum joint heated at 110°C for 2 h (the coating formed from 0.2M styrene/0.1M MEA/0.1M NPMI/0.005M BMI).
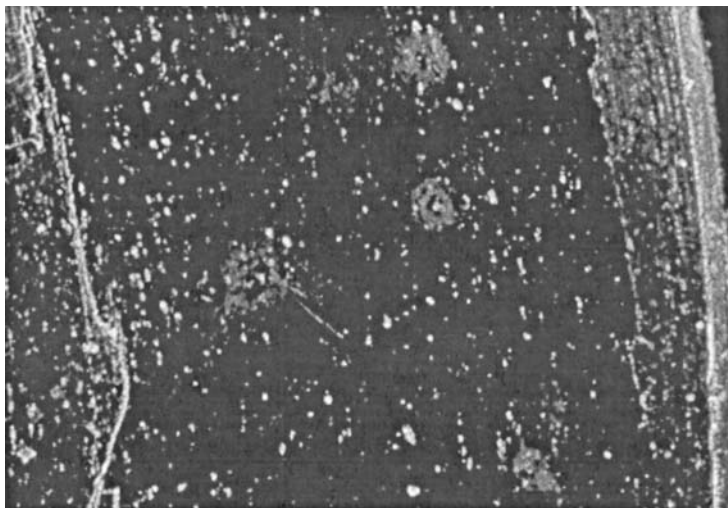
FIGURE 16 A cross-section of the surface of a broken aluminum joint heated at 230°C for 2 h (the coating formed from 0.2M styrene/0.1M MEA/0.1M NPMI/0.005M BMI).

between the adsorbed bonding layer and the rest of the coating due to the preferred segregation of polar groups on the metal surface [14, 15]. The remaining polymer on the aluminum joint suggests that, for the coatings formed by spontaneous polymerization, uncrosslinked polymer has lowered cohesive strength, resulting in cohesive failure within the coating during the torsional test. However, when the coating was crosslinked during heating, the bonding layer strongly interacted with the rest of the coating, resulting in an increased cohesive strength and higher bonding forces between the polymer and the aluminum substrate. At this stage, the polymer-aluminum bonding forces controlled the failure of the coating, resulting in a value of joint assembly strength close to that of the bulk coating.

The bonding strength between the coating and the substrate was initially attributed to the chelation of β-diketone with aluminum; a reaction can be seen from the reflection FTIR spectrum of MEA monomer on aluminum. In this research, coatings containing MEA formed by spontaneous polymerization on the aluminum surface were analyzed by reflection FTIR. The spectra of the coatings formed from 0.1M styrene/0.1M NPMI/0.1M MEA/0.005M BAM on aluminum are shown in Figure 17. The results showed a variation of the peak position of the carbonyl band based on the thickness of the coatings.
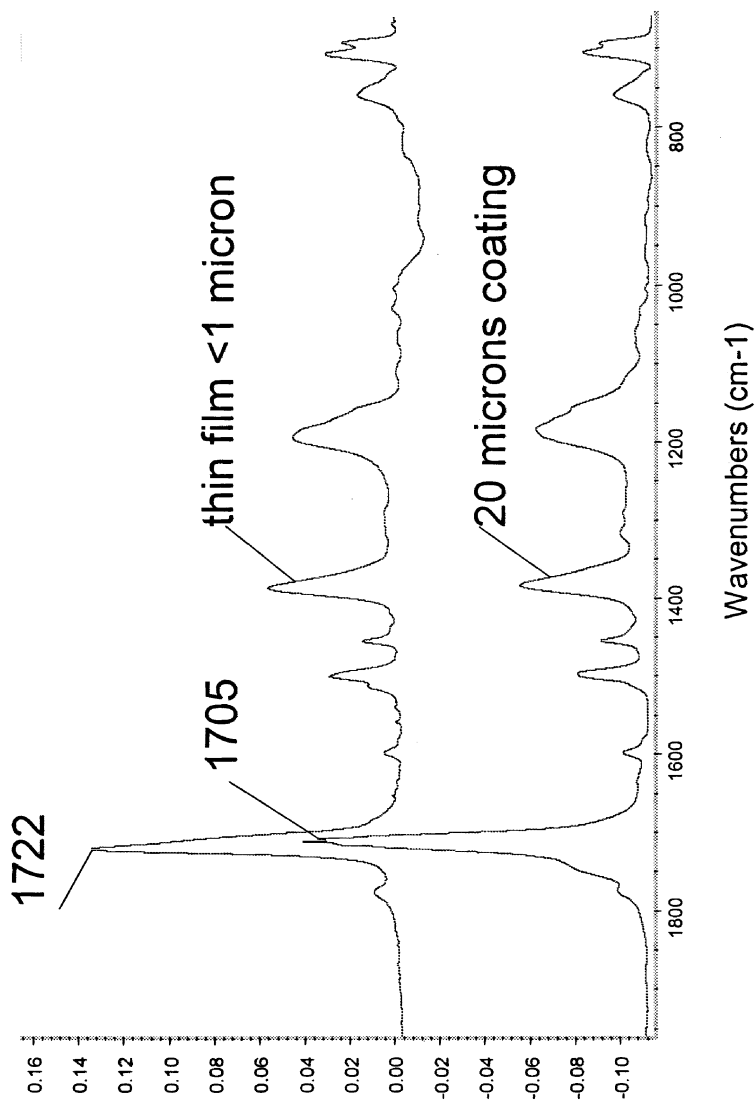
FIGURE 17 Reflection FTIR spectra of the coatings on aluminum (coatings formed from 0.1M ST/0.1M NPMI/0.1M MEA/0.005M BAM).

The spectrum of the thick coating on the substrate was similar to that of the copolymer obtained by transmission FTIR. As the thickness of the coating decreased, the frequency of carbonyl peak in the coating spectrum increased. For a thin coating of thickness less than one micron, the coating showed a carbonyl peak at 1722 cm^{-1}, which had shifted from 1705 cm^{-1} in the thick coating spectrum. The chemical shift suggested that there was some interaction between the coating and the substrate. However, there was no evidence of chelate formation, which has a unique peak around 1550 cm^{-1}. The bonding force between the coating and aluminum is proposed to be associated with physical interactions in terms of dispersion force, hydrogen bonds, and polar interactions [16, 17]. These interactions would cause the segregation of carbonyl groups at the interphase, and a higher coverage of carbonyl groups in the interphase gives rise to a higher frequency in the FTIR spectrum [18–20]. This segregation of MEA favored the interaction between the coating and the substrate, resulting in improved adhesion of the coating containing MEA compared with the coatings without MEA.

Corrosion Resistance

Aluminum is a chemically active metal and easily reacts with oxygen and water in humid environments or aqueous solutions. Once water contacts an aluminum surface, the aluminum at anodic sites will lose electrons and become Al^{3+}, and oxygen and water at cathodic sites will reduce to OH^{-1}. The resultant electrochemical cell will accelerate the corrosion. The coating formed by spontaneous polymerization is able to prevent aluminum from corrosion by blocking the aluminum surface from water and oxygen using its durable, low permeability film, which is crosslinked through its β-diketone functional groups.

A salt fog spray test following ASTM B-117 specifications was used to evaluate the relative corrosion resistance of the coatings. The test involved exposure of the coated aluminum sample in a 5% NaCl fog chamber at 35°C. This test was for relative comparison only, not for comparison with atmospheric exposure tests. Table 3 lists the results from a series of samples that had previously been heated at different temperatures. All samples were prepared from a monomer solution of 0.2M styrene/0.1M MEA/0.1 NPMI/0.005 BMI. The results show that coatings heated at 110°C for 2 h behaved poorly in terms of corrosion resistance and failed by delamination within 24 h of exposure. The corrosion resistance of coatings heated at 150°C showed improved performance. However, corrosion spots or blisters developed within

TABLE 3 Results of Salt Fog Spray Test for Coatings Dried at Different Temperature for 2 Hours (Coatings Formed from 0.2 M Styrene/0.1 M MEA/0.1 M NPMI/0.005 M BMI and 18–20 Micron Thick)

Samples	Drying at 110°C	Dried at 150°C	Dried at 180°C	Dried at 220°C
1	Delamination within 24 hours	Some corrosion spots throughout within 24 hours	Corrosion free for 127 days	Corrosion free for 131 days
2	Delamination within 24 hours	Some corrosion spots at edges and a few at middle within 24 hours	Corrosion free for 127 days	Corrosion free for 131 days
3	Delamination within 24 hours	Some corrosion and a few blisters within 24 hours	Corrosion free for 127 days	Corrosion free for 132 days
4	Delamination within 24 hours	Some corrosion spots at edges	Corrosion free for 127 days	Corrosion free for 132 days

24 h of exposure. In contrast, after crosslinking, the coatings showed much better corrosion resistance. Coatings heated at temperatures of 180°C and 230°C for 2 h were both corrosion free even after 3000 h of salt fog testing. Figure 18 shows the appearances of the coatings prepared under different conditions after salt fog exposure.

The improved corrosion resistance of coatings after heating at high temperatures is attributed to the enhanced interaction between the coating and substrate after crosslinking. As described in the previous sections, the crosslinking strengthens the interface between the coating and the substrate. In addition, the crosslinking reduces the crevices and ridges in the coating, resulting in slower diffusion of oxygen and water through the coating. Thus, the corrosion was hindered. Besides the crosslinking effect, the surface water underneath the coating is also removed during high temperature heating. In the coating process, the aluminum substrate was exposed to aqueous solutions, *e.g.*, the rinsing bath and the monomer solution, resulting in the presence of the surface water in the form of loosely held aluminum trihydroxide and its water complex. Such surface water is a weaker layer underneath the coating. Corrosion can then easily occur since this layer can not prevent the initiation of electrochemical corrosion. It has been reported that aluminum trihydroxide (Bayerite) is only stable up to 100°C, and converts into aluminum monohydrate (Boehmite) when heated at higher temperatures in air [21]. This monohydrate is a stable and densely compacted layer, and can enhance the

(a)
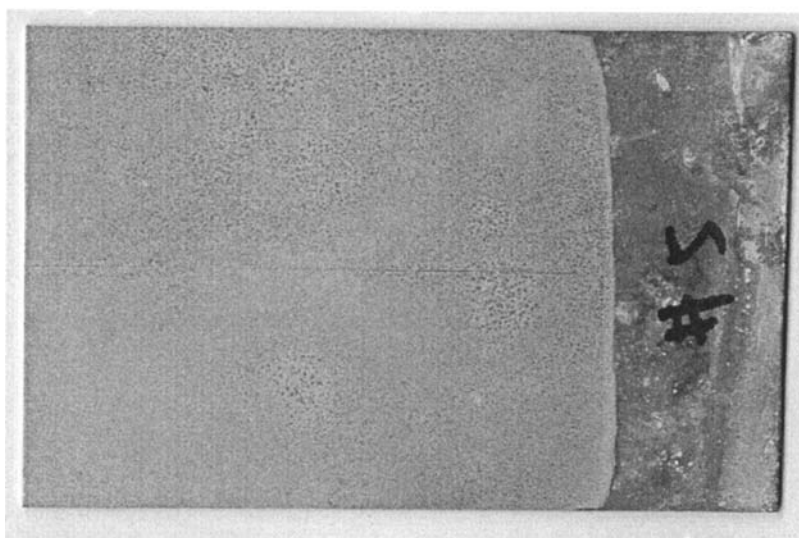
(b)

FIGURE 18 Coatings on Al 6061 after salt fog test (coatings formed from a monomer solution of 0.2M styrene/0.1M MEA/0.1M NPMI/0.005M BMI). (a) An SP coating heated at 110°C for 2 h developed corrosion in 24 h, (b) an SP coating heated at 150°C for 2 h developed corrosion in 24 h, (c) an SP coating heated at 180°C for 2 h was corrosion-free after 3000 h, and (d) an SP coating heated at 230°C for 2 h was corrosion-free after 3000 h. (*Continued*).
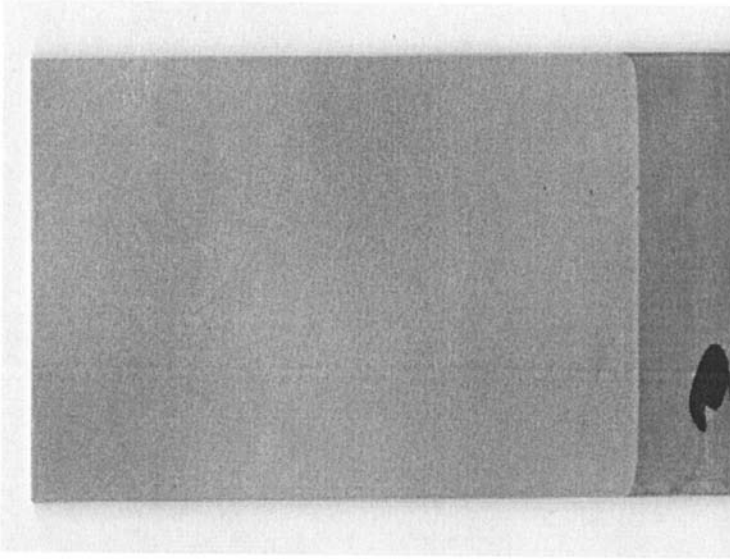
(c)
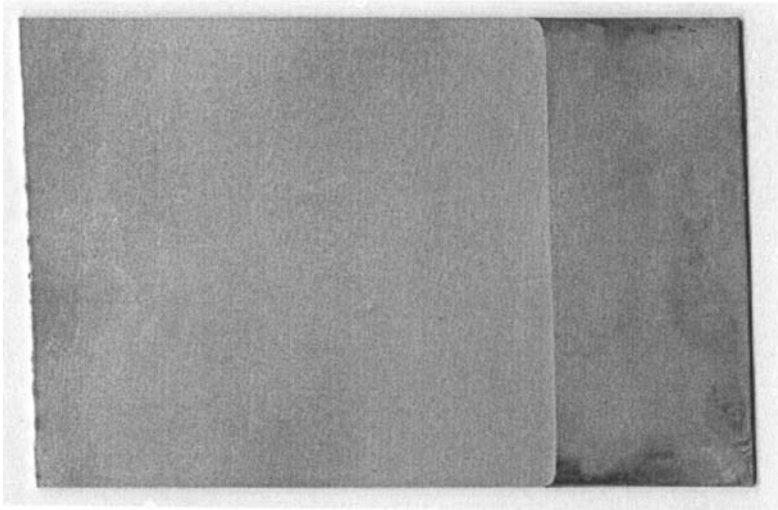
(d)

FIGURE 18 (*Continued*).

coating's corrosion protection [22]. Thus, the conversion of aluminum hydroxides at high temperatures also contributes to improved corrosion resistance of the coating.

CONCLUSIONS

The properties of coatings formed by spontaneous polymerization can be enhanced by drying, especially by heating at temperatures above 170°C. Our research has shown the following:

1. The coating after polymerization can be consolidated into a solid adherent film by initial heating at temperatures ranging from 80 to 150°C, due to the plasticization effect of NMP in the coating.
2. The residual solvent in the coating is removed by further higher temperature heating.
3. Higher temperature heating causes coating crosslinking through the β-diketone groups from MEA units in the coating. It is proposed that β-diketone groups are decomposed during heating to generate reactive species, resulting in the formation of intermolecular bonding in the polymer.
4. High temperature heating causes a change in the coating structure, evidenced by the carbonyl peak in FTIR becoming broader after heating at high temperatures.
5. High temperature heating causes carbon dioxide, acetone, and acetoacetic acid to be evolved as shown by GC-MS results.
6. Crosslinking increases the Tg of the coatings containing MEA, and higher heating temperatures result in a more rapid increase of the Tg and a higher final Tg.
7. Adhesion between the coating and aluminum substrates is improved by interaction between the coating and bonding interface due to crosslinking. Coatings heated above 180°C showed shear strength over 30 Mpa in the torsional test compared with less than 17 Mpa for coatings heated below 150°C.
8. High temperature heating improves the coating's corrosion resistance, and the resultant coating exhibits better corrosion resistance in a salt fog test (ASTM B-117). Coatings on A16061 heated at temperatures at 180 and 230°C remained corrosion free after 3000 h exposure.

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