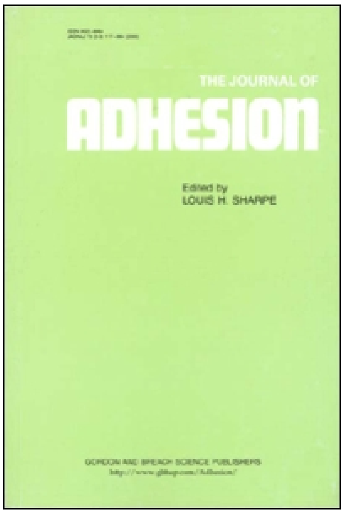

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Nesbitt, Stephanie L. , Emerson, John A. and Bell, James P.(2000) 'Evaluation of β-diketone-containing Polymeric Coupling Agents for Enhancing the Adhesion of Epoxy to Aluminum', The Journal of Adhesion, 72: 3, 245 — 268

To link to this Article: DOI: 10.1080/00218460008029285

URL: http://dx.doi.org/10.1080/00218460008029285

J. Adhesion, 2000, Vol. 72, pp. 245-268
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Evaluation of β-diketone-containing Polymeric Coupling Agents for Enhancing the Adhesion of Epoxy to Aluminum*

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(Received 5 May 1999; In final form 26 July 1999)

β-diketone-containing polymeric coupling agents (PCA) were evaluated as potential adhesion enhancers for an epoxy/aluminum bond system. Torsional shear joint measurements revealed that the β-diketone-containing PCA did not influence the joint strength and durability, positively or negatively, as compared with untreated controls. Grazing angle infrared spectroscopy revealed that despite reactivity of the β-diketone-containing monomer with aluminum substrates, no reactivity of the β-diketone was observed once the monomer was incorporated into the polymer. Deposition studies showed that the resulting PCA coating thickness following treatment and solvent rinsing was not a function of solvent solubility parameter, solution concentration, or immersion time. It was hypothesized that preferential physisorption of the phenyl and/or epoxy functionalities in the PCA inhibited reactivity of the β-diketone functionality.

Keywords: Polymeric coupling agents; β-diketones; adhesion; aluminum; epoxy

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*One of a Collection of papers honoring F. James Boerio, the recipient in February 1999 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*. Presented in part at the 21st Annual Meeting of The Adhesion Society, Inc., Savannah, Georgia, USA, February 22-25, 1998.

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1. INTRODUCTION

The strength and durability of the polymer/aluminum bond has been shown to be strongly dependent on surface pretreatment [1 – 3]. Bonding technology in the aluminum industry has evolved over the years as pretreatments have progressed from initial simple cleaning techniques. Solvent and mechanical cleaning gave way to etching and anodization processes in which the substrate was not only cleaned, but the natural oxide was etched away and an oxide of controlled composition and structure regrown. Along the way, researchers found that they were able to improve adhesion further by the application of primers and coupling agents. At the heart of coupling agent technology was the idea of improving adhesion through chemical connectivity (ionic or covalent) of the adhesive or polymer topcoat to the underlying metal substrate. As an extension of coupling agent technology, Bell and Schmidt [4] patented the use of pre-synthesized polymeric coupling agents (PCA) in 1989. Polymeric coupling agents are multifunctional polymers that have the ability to react chemically with both the polymer adhesive or topcoat and the metal substrate. The functionalities and their relative concentrations on the PCA backbone can be tailored to be system specific, while improving adhesion and corrosion resistance. In addition, the viscoelastic properties of the polymer permit dissipation of mechanical and thermal stresses that may develop within the bond due to the large mismatches in thermal expansion coefficients of the metal substrate and the polymer topcoat.

When developing a prospective polymeric coupling agent many factors must be taken into consideration. First and foremost is selecting functional groups that are reactive with both the polymer topcoat and the metal substrate. Identification of functional groups that are reactive with the polymer topcoat is not as difficult as identifying a suitable metal-reactive functional group. In the case of the epoxy/aluminum bond system the aluminum-reactive group would preferably form water-stable covalent bonds with either the aluminum ions in the oxide, the oxygen atoms in the oxide, or the surface hydroxyls.

This research has investigated the use of a β-diketone functional group as the aluminum-oxide-reactive functionality of the polymeric coupling agent. β-diketones are bidentate ligands that have been shown to form stable chelates with a wide variety of metal ions [5 – 15]. The general structure of a β-diketone is shown below in Figure 1. By the loss of a proton in the position alpha to the two carbonyls, the β-diketone has the ability to form very stable six-membered ring structures *via* hydrogen bonding. In addition to the hydrogen-bonded six-membered ring, β-diketones are also known to form very stable six-membered ring structures with a wide variety of metal ions as shown in Figure 2. The literature includes references to the formation of β-diketone-metal chelates with the following metal ions: Li(I), K(I), Zr(I), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Cr(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Cr(III), Mn(III), Fe(III), Co(III), Al(III), Ga(III), In(III), and Zr(IV) [5–15]. The stabilities of the metal complexes are related to the acid dissociation constants of the acid proton [5].

The stability of the β-diketone metal complexes is attributed to the "benzenoid resonance" of the six-membered ring, in which the ring has a partial double bond character [13]. This resonance stability was first suggested by Calvin and Wilson in 1945 [14]. Holm and Cotton supported the "benzenoid resonance" and suggested that π-bonding may be possible if the electron donation is from the oxygen to the metal atom ($O_{p\pi} - M_{p\pi,d\pi}$), against the "electrical neutrality principle" [6]. This is the theory that is generally accepted today.

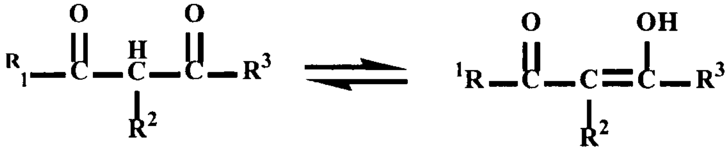

FIGURE 1 General structure of a β-diketone, keto-enol tautomerism.

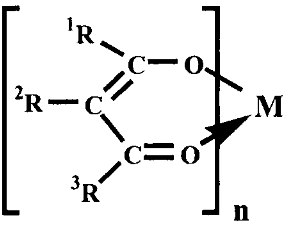

FIGURE 2 General structure of a metal β-diketonate chelate complex.

Literature over the past 25 years supported the incorporation of the β-diketone functionality into a polymeric coupling agent for an aluminum-epoxy system. The first patent evidence of the use of low molecular weight β-diketones for the purpose of increasing coating adhesion and corrosion resistance was by V. P. Wystrach and F. C. Rauch of the American Cyanamid Company, 1971 [16]. The patent describes the application of low molecular weight β-diketones by immersion in aqueous and alcoholic solutions or *via* dispersion into the coating material (paint, adhesive, *etc.*) and then application of the coating material. Enhanced adhesion and corrosion resistance was attributed to the "pseudo-chemical" bond of the diketone to the aluminum substrate and was "described as a chemisorption or chelation of the diketone by the metal" [16].

Dow Chemical Company holds a patent describing the use of β-diketone compounds for increasing the corrosion resistance of radiators and heat exchangers of internal combustion engines [17]. The patent claims that the addition of one or more low molecular weight β-diketones to aqueous glycol solutions containing common corrosion inhibitors such as: alkali metal silicates, borates, mercaptobenzotriazoles, nitrates, nitrites, and phosphates improves the overall corrosion inhibition of the coolant solution. The claims of the patent include the following metals: aluminum, copper, solder, brass, steel, and cast iron.

PPG Industries, Inc., patented two methods by which β-diketones were combined with an epoxy resin to produce coatings for ferrous metals that exhibited excellent corrosion resistance properties [18, 19]. β-diketones were selected such that they had a 40 or greater percent enol form and were, thus, epoxy reactive. The coating was described to be applied from dispersions by immersion, spraying, wiping, or electrocoating. Improved corrosion resistance was reported for treated ferrous substrates as compared with untreated controls.

DeNicola and Bell evaluated two low molecular weight β-diketone coupling agents for an epoxy-steel system [20, 21]. Dry shear strength measurements did not show any improvement over untreated controls. The β-diketones did improve the wet strength for shear joints immersed in 57°C water for 48 hours. After 48 hours, however, the untreated controls had comparable or better strength retention than the β-diketone treated samples.

β-diketone functionalized polymers were shown to enhance adhesion and corrosion resistance in epoxy/steel bond systems by

Vaideeswaran [22]. Copolymers and terpolymers comprised of 2-(methacryloyloxy)ethyl acetoacetate, glycidyl methacrylate, and styrene were applied from low concentration solutions in tetrahydrofuran to citric-acid-etched low-carbon steel substrates. Both dry strength and hot water durability showed marked improvements over untreated controls.

Agarwal has shown that incorporation of 2-(methacryloyloxy)ethyl acetoacetate into a spontaneous polymerization process increased coating adhesion to aluminum substrates [23]. Spontaneous polymerization is a process whereby coatings are formed directly on the metal surface from an aqueous monomer solution at room temperature without the addition of initiator or an external driving force. Wet joint strengths showed good strength retention.

This paper presents the evaluation of a β-diketone functionalized polymeric coupling agent on an epoxy/coupling agent/aluminum bond system. We present information regarding the polymer synthesis and characterization, interactions of the functional groups with the aluminum substrate and the epoxy topcoat system, deposition studies, and the influence of the PCA on adhesion.

2. EXPERIMENTAL

2.1. Materials

Styrene, glycidyl methacrylate, 2-(methacryloyloxy)ethyl acetoacetate, methylenedianiline, and γ-glycidoxypropyltrimethoxysilane were obtained from Aldrich Chemical Company and used as received. Aluminum nitrate nonahydrate was obtained from Johnson Matthey Chemicals Limited. Epon®828 was obtained from the Shell Chemical Company and used as received. ACS grade methanol, toluene, trichloroethylene, carbon tetrachloride, and ethylene dichloride were obtained from Fisher Scientific. Benzoyl peroxide was obtained from Acros Chemical.

2.2. Aluminum Substrates

Deposition studies were performed on evaporatively-deposited aluminum thin films on glass microscope slides. Glass microscope slides were ultrasonically cleaned for two minutes in acetone followed by two minutes in deionized water containing a few drops of Liqui-Nox® at ambient temperature. Liqui-Nox® is a precision liquid alkaline cleaner with a pH range of 8.2–9.2. It is phosphate free and manufactured by Alconox, Inc. The slides were then rinsed in running deionized water for a minimum of two minutes. Following the water rinse, the slides were immersed in a boiling solution of 15% hydrogen peroxide in deionized water for a minimum of five minutes to remove remaining organic contaminants. After removal from the hydrogen peroxide solution, the slides were rinsed thoroughly for five minutes in running deionized water and blown dry with dry, filtered nitrogen.

The clean microscope slides were then loaded into an electron beam evaporator on parallel bars normal to the evaporation source at a distance of approximately 11 inches. The chamber was evacuated to at least 5×10^{-6} torr. Aluminum was deposited at a rate of 10 Å per second. Samples were prepared in thicknesses of 2000, 4000, and 6000 Å. The samples were stored in Fluoroware® polypropylene containers between the time of preparation and use.

2.3. Substrate Pretreatment

Plasma cleaning was performed in a PLASMA-PREEN System, model 11-862, manufactured by Plasmatic Systems, Inc. The unit was manufactured from a microprocessor-controlled microwave oven. The system operated at a reduced pressure of 1–5 torr with an ambient atmosphere. The chamber was equipped with a water-cooled base. All samples were subjected to a one-minute plasma cleaning step at the high power setting.

Argon sputtering of the aluminum samples was performed in a Model 240SD Planetary Sputtering System. The parts were placed on one of the 7 inch (17.8 cm) diameter plates within the system. The sputtering chamber was precoated with aluminum to prevent cross-contamination. The initial system temperature was 33°C and the final temperature at the conclusion of sputtering was 75°C. The system was evacuated to at least 5×10^{-6} torr for all runs. The argon gas flow during the sputtering process was 97.8 sccm and the bias power was maintained at 580 W. Following sputtering, the sample chamber was back-filled with argon and opened. Immediately upon opening the parts were immersed into the noted treatment solutions.

2.4. Solution Spectroscopy

Fourier transform infrared spectroscopy (FTIR) analysis in transmission mode was performed on a Bio-RadFTS-7 spectrometer. All spectra were acquired at 4 cm^{-1} resolution and 64 scans.

^{13}C NMR spectroscopy was performed on a Bruker DRX spectrometer with a 5 mm broadband probe. Spectra were recorded at 100.6 MHz, using a 90° pulse angle, waltz16 decoupling of protons, 4096 scans and a 10-second delay time.

2.5. Polymer Synthesis and Physical and Chemical Characteristics

The β-diketone-containing polymer was synthesized *via* solution polymerization of 2-(methacryloyloxy)ethyl acetoacetate (MEA), glycidyl methacrylate (GMA), and styrene. Specifically, 2 mL MEA (9.3 mole percent), 2 mL GMA (13 mole percent), 10 mL styrene (77.6 mole percent), and 0.4 g benzoyl peroxide were heated at 67°C for 6 hours in 70 mL of toluene. Figure 3 shows a schematic of the terpolymer.

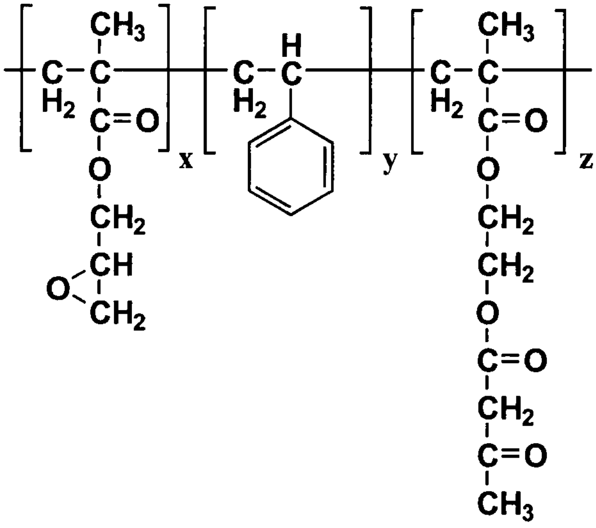

FIGURE 3 Schematic representation of the terpolymer repeat unit where $x = 2.5$, $y = 6.83$ and $z = 1$.

The infrared spectrum of the terpolymer is shown in Figure 4. ^{13}C NMR was utilized to determine the relative ratios of monomer components in the final polymer. The ratios were determined to be 6.83 : 2.5 : 1, styrene, glycidyl methacrylate, and 2-(methacryloyloxy) ethyl acetoacetate, respectively.

Molecular weight determination of the polymer was performed *via* Gel Permeation Chromatography on a Polymer Labs PL-GPC210 system equipped with two mixed bed 5 micron Polymer Labs columns, a refractive index detector and a Precision Detector PD2040 dual angle (15 and 90°) laser light-scattering detector. THF was utilized as the mobile phase with a flow rate of 1.0 mL/min. Calibration was performed using a 59,500 g/mol polystyrene standard. Apparent M_n, M_w, and the polydispersity index of the terpolymer was determined to be 51,300, 33,800, and 1.52, respectively.

The glass transition temperature of the β-diketone-containing polymer was determined to be 50°C *via* Differential Scanning Calorimetry. The T_g was found to be dependent on the thermal history and increased with subsequent heating cycles. Similar results were reported by Agarwal for other β-diketone-containing polymers [23]. Samples

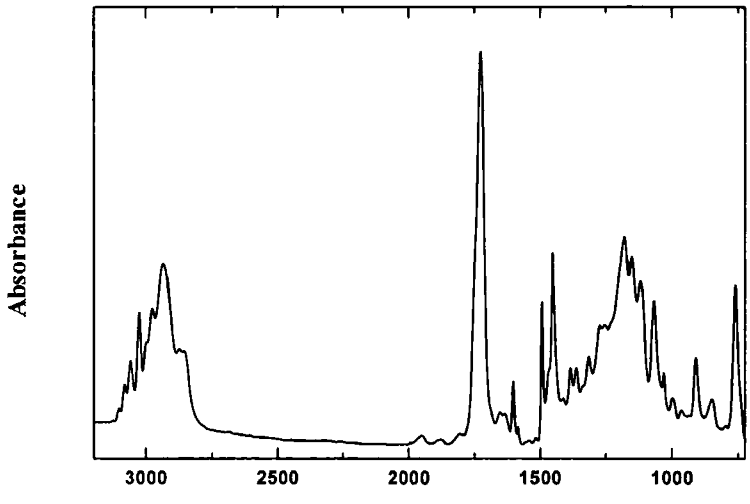

FIGURE 4 Infrared spectrum of the β-diketone-containing terpolymer.

of 2 – 10 mg were analyzed in hermetically-sealed aluminum pans. Scans were run at a rate of 10°C per minute in a nitrogen atmosphere on a Perkin-Elmer 7 System Thermal Analysis System. The mid-point method of data analysis was utilized.

The decomposition temperature of the polymer was determined to be ca. 379°C *via* Thermal Gravimetric Analysis. Scans were run at a rate of 20°C per minute in a nitrogen atmosphere on a Perkin-Elmer 7 System Thermal Analysis System. The temperature noted was the onset of decomposition as determined *via* intersection of the two slopes.

2.6. Surface Analysis

Grazing Angle Infrared Spectroscopy (GAIR) spectra were taken on a Nicolet 800 SX FTIR spectrometer complete with a MCT-A detector using p-polarized light. A "Sea-Gull" reflection attachment from Harrick Scientific was used at an angle of 85° off normal. All spectra were acquired at 4 cm^{-1} and 256 scans.

X-ray Photoelectron Spectroscopy analysis of the failure surfaces was performed on a modified Physical Electronics 3057 Spherical Capacitance Analyzer with an Omni Focus III Variable Aperture Lens. An aperture setting of 4 mm with a ± 7 degree acceptance angle and analysis area 0.8 mm × 0.8 mm was utilized for all samples. Measurements were taken at 60° off normal to the sample surface and acquired using Al Kα incident radiation (15 kV, 400 W). Survey scans were acquired in the range of 1200 to 0 eV with 0.5 eV resolution. High-resolution scans were obtained with a resolution of 0.1 eV. Data were analyzed by first smoothing with a Savitsky-Goulay 11-point algorithm followed by a standard XPS satellite subtraction in the Physical Electronics program Multipak version 5.0 [24–26]. Standard handbook sensitivity factors were applied to major elemental peak areas to determine the atomic concentrations [7].

2.7. Adhesion Measurements

Torsional shear joints were utilized to assess the adhesion enhancement imparted by the PCA [28]. The substrates were machined from 6061 aluminum. The joints were first degreased or sputtered then immediately immersed into 1% solutions of the PCA in noted solvent at room temperature if the joints were to receive a PCA treatment. Following treatment, the joints were removed from the treatment solution and rinsed with pure solvent. A stoichiometric mixture (100:28) of Epon 828 and methylenedianiline (MDA) was then applied to the raised annulus of the male joint half to a total weight of 44 ± 0.1 mg. The epoxy mixture was prepared by heating the epoxy and curing agent on a hot plate with stirring until the MDA had dissolved. The joint halves were then joined and cured vertically for one hour at 120°C and two hours at 150°C. Joint shear strength was evaluated by measuring the maximum torque at break of the joints on an MTS Tensile Testing Machine. Durability was evaluated by measuring the maximum torque at break of the joints after immersion of the joints in 57°C water for varying lengths of time (days).

Peel samples were prepared by pretreating Reynolds Wrap® Extra Heavy Duty aluminum foil. Pretreating in this regard refers to any degreasing or sputtering processes as well as PCA treatment. The piece of foil was then taped onto the back plate of the mold support with Teflon® Tape. A silicone mold was centered on the aluminum foil. Epoxy plaques were then created by pouring a stoichiometric mixture of Epon 828 and methylenedianiline into the silicone mold with the treated aluminum foil serving as the back face of the mold. The epoxy and curing agent had been previously heated on a hot plate with stirring until the methylenedianiline was fully dissolved. The epoxy was cured for one hour at 120°C and two hours at 150°C. Individual peel samples were then prepared by cutting 4 mm strips of the foil on the epoxy plaques and peeling them at 90° to the sample. Peel strengths were measured as a function of time at a peel rate of 0.51 mm per second. Forces were then divided by the average sample width to obtain the g/mm peel strength. At least 5 samples of similar preparation were measured and the resulting peel strengths averaged.

3. RESULTS

A coupling agent has been described as forming true verifiable bonds with both the polymer topcoat and the metal substrate [29]. Hence, the individual monomers were selected to provide functionalities that were reactive with the polymer topcoat system (epoxy and amine curing agent) and the aluminum substrate. The β-diketone-functionalized polymer evaluated in this research was synthesized from 2-(methacryloyloxy)ethyl acetoacetate (MEA), glycidyl methacrylate (GMA), and styrene. Commercially available, MEA has a metha- crylate group at one end such that it could be incorporated into a PCA *via* radical polymerization and a β-diketone functionality at the other end to provide the aluminum substrate reactivity. Glycidyl methacrylate (GMA) was selected for its ability to react with the epoxy curing agent, methylenedianiline. Styrene was included in the PCA to increase the polymer's solubility, thermal stability, and hydrophobicity. ^{13}C NMR determined the relative ratios of monomer units in the polymer to be 1 : 2.5 : 6.83 for 2-(methacryloyloxy)ethyl acetoacetate (MEA), glycidyl methacrylate (GMA), and styrene, respectively. The infrared spectrum of the polymer was included in the Experimental section of this paper.

3.1. Adhesion Measurements

The influence of the β-diketone-functionalized PCA on the adhesion of an epoxy/aluminum bond system was evaluated *via* torsional shear joints [29, 30]. Two sets of five joints were degreased in methanol for 30 minutes, wiped with methanol-soaked Kim-wipes® and air-dried. One set of joints was then subjected to a one-minute plasma treatment and immediately immersed into a 1% solution of the β-diketone-containing terpolymer in toluene for 30 minutes at room temperature. The synthesis of the terpolymer and its associated physical and thermal characteristics were presented in the Experimental section of this paper. Following immersion of the joints in the PCA solution the joints were rinsed thoroughly with pure toluene and air-dried. The epoxy resin system was then applied to both sets of joints, and the joint halves joined and cured. The dry joint strengths and the strengths following immersion in 57°C water for varying lengths of time (days) are shown in Figure 5. The PCA-treated joints did not show significant differences in strength or durability as compared with the untreated controls.

The geometry of the torsional shear joints did not lend itself to locus of failure analysis; therefore, peel samples were prepared using Reynolds Wrap® Extra Heavy Duty aluminum foil. The foil was prepared analogously to the torsional shear joints (degreasing, PCA treatment, and epoxy application) and epoxy plaques were molded

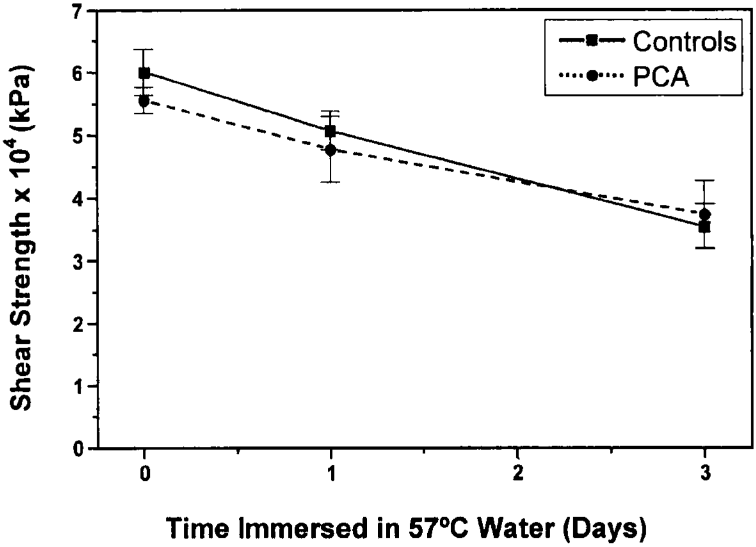

FIGURE 5 Shear strength as a function of days immersed in 57°C water for methanol-degreased controls and methanol-degreased joints that were immersed in a 1% solution of the terpolymer for 30 minutes at room temperature. The data points represent the average of at least 3 samples and the error bars represent the ($\sigma - 1$) standard deviation of the sample set.

TABLE I Atomic concentrations for the aluminum and epoxy peel sample failure surfaces of the dry methanol-degreased control and dry PCA-treated sample

Sample	*C*	*N*	*O*	*Al*
Control (Epoxy Side)	76.2	2.6	20.6	0.2
Control (Al Side)	27.1	0.4	46.6	21.5
PCA Treated (Epoxy Side)	79.4	1.4	18.5	0.3
PCA Treated (Al Side)	23.6	0.7	48.8	22.7

with the aluminum foil serving as the backing. The peel samples were pulled at 90° to the epoxy substrate in the as-prepared dry state and after immersion in 57°C deionized water for seven days. XPS analysis was performed on both the aluminum and epoxy failure surfaces at 60° off normal to the sample. The relative atomic concentrations of carbon, nitrogen, oxygen and aluminum are summarized in Tables I and II for the dry and water immersed samples, respectively.

The atomic concentrations of the dry control samples indicated a locus of failure very near the oxide/epoxy interface. The reduction in

TABLE II Atomic concentrations for the aluminum and epoxy peel sample failure surfaces of the methanol-degreased control and PCA-treated sample following immersion in 57°C water for seven days

Sample	*C*	*N*	*O*	*Al*
Control (Epoxy Side)	71.9	2.6	22.6	2.0
Control (Al Side)	24.3	0.4	52.0	22.5
PCA Treated (Epoxy Side)	75.4	1.8	20.7	1.3
PCA Treated (Al Side)	18.3	0.3	54.4	26.0

the percent nitrogen on the epoxy failure side of the terpolymer-treated samples as compared with the control suggested that the failure occurred near the PCA/oxide interface. The percent aluminum detected on both of the epoxy failure surfaces suggested that a small amount of the oxide was removed during failure which may be the result of a weak boundary layer in the native oxide [3]. The atomic concentrations of the samples following water immersion were very similar to the dry samples. The noticeable difference was an increase in the percent of aluminum on the epoxy failure surface for both the control and the PCA-treated samples. This increase suggested that the failure penetrated slightly further into the oxide, perhaps as a result of hydration of the oxide during water immersion [31].

An alternative cleaning method to degreasing, argon sputtering, was also investigated. It was hypothesized that the sputtering technique would serve a two-fold purpose: (1) provide a cleaning technique that would not leave an adsorbed organic monolayer on the surface and (2) increase the surface reactivity by removing the native oxide and, thereby, increasing the number of β-diketone-reactive aluminum sites.

The geometry of the torsional shear joints did not lend themselves to argon sputtering, thus peel samples were utilized to assess the influence of the PCA on the adhesion of the aluminum epoxy bond following sputtering. Samples were prepared from Reynolds Wrap® Extra Heavy Duty aluminum foil. The aluminum foil samples were subjected to 15 minutes of argon sputtering. Following the sputtering process, the chamber was backfilled with argon to atmospheric pressure, then opened. The samples were immediately transferred to the treatment solutions. One sample was immersed for 30 minutes in toluene, the other into a 1% solution of the terpolymer in toluene. Following immersion both samples were rinsed thoroughly with toluene. Epoxy plaque samples were prepared as described in the Experimental section. The peel samples were pulled at 90° to the epoxy substrate in the as-prepared dry state and also after immersion in 57°C deionized water for varying lengths of time (days). As a comparison, the data for silane-treated samples are also included. The silane samples were prepared by degreasing the aluminum foil for 30 minutes in methanol, then immersing the foil into a 2% solution of γ-glycidoxypropyltrimethoxysilane (GPS) in deionized water for 10 minutes, followed by a deionized water rinse. The GPS solution had hydrolyzed for 30 minutes prior to use. The peel strength data is shown in Figure 6. The β-diketone-containing PCA-treated samples showed slight improvements in strength over the untreated controls for the dry, one- and two-day water-immersed samples. After six days of water immersion, however, both samples showed comparable results. The silane-treated samples showed considerable improvements in strength and strength retention over both the untreated controls and the PCA-treated samples.

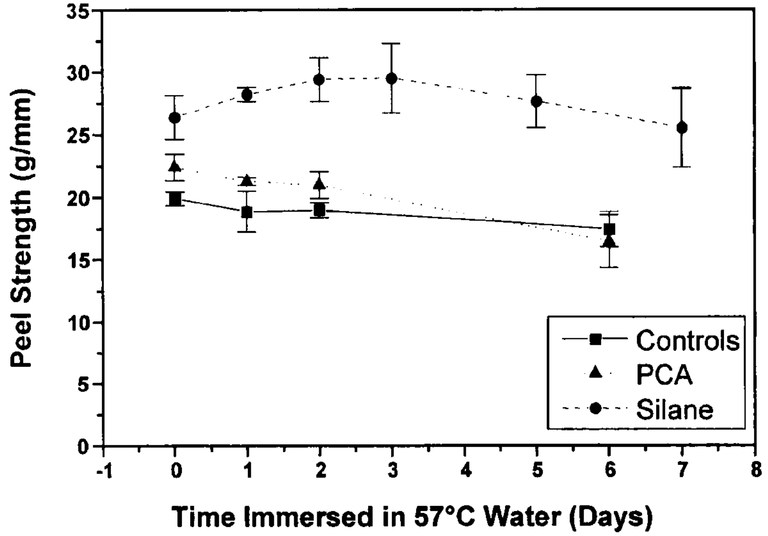

FIGURE 6 Peel strength as a function of days immersed in 57°C water for argon-sputtered controls, an argon-sputtered sample that was then immersed in a 1% solution of terpolymer for 30 minutes, and a γ-GPS-treated sample.

3.2. PCA-aluminum Reactivity

The literature includes numerous examples of the chelation reaction between β-diketones and metal ions [5 – 15]. The reactivity of MEA with aluminum ions in solution and aluminum substrates was confirmed *via* infrared spectroscopy. The transmission infrared spectrum of MEA is shown in Figure 7. A stoichiometric quantity of aluminum nitrate nonahydrate was added to a solution of MEA in toluene. An aliquot of the solution was then dried on a salt plate. The infrared spectrum is shown in Figure 8. Comparing Figures 7 and 8, there are two additional peaks in the 1650 – 1550 cm^{-1} region of Figure 8. These peaks are the result of the chelate formation of the β-diketone with the aluminum ions and are attributed to the ν(C—O) and ν(C—C) stretches of the six-membered chelate ring, Figure 2 [9]. The six-membered ring forms *via* electron density donation from the oxygen atoms of the β-diketone and through loss of the proton alpha to the diketone.

Reactivity of MEA with aluminum substrates was verified *via* GAIR. Vapor-deposited thin films of aluminum on glass slides were

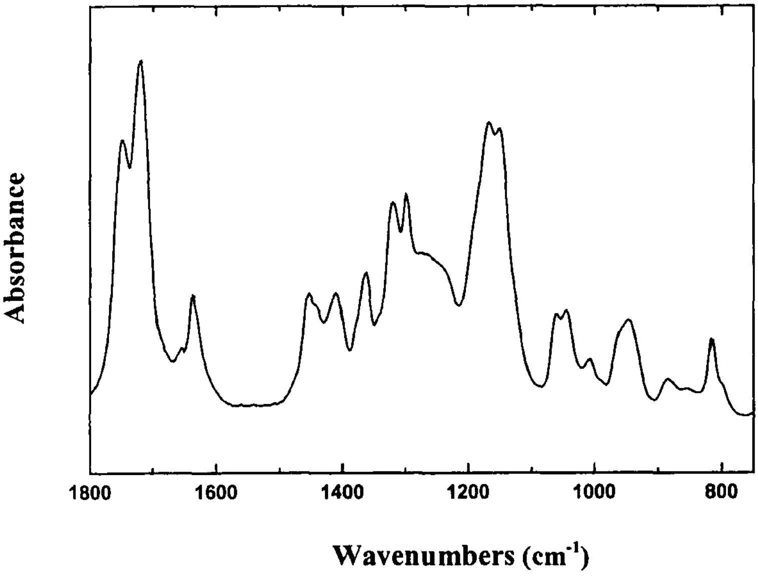

FIGURE 7 Transmission infrared spectrum of MEA deposited on a salt plate from THF.

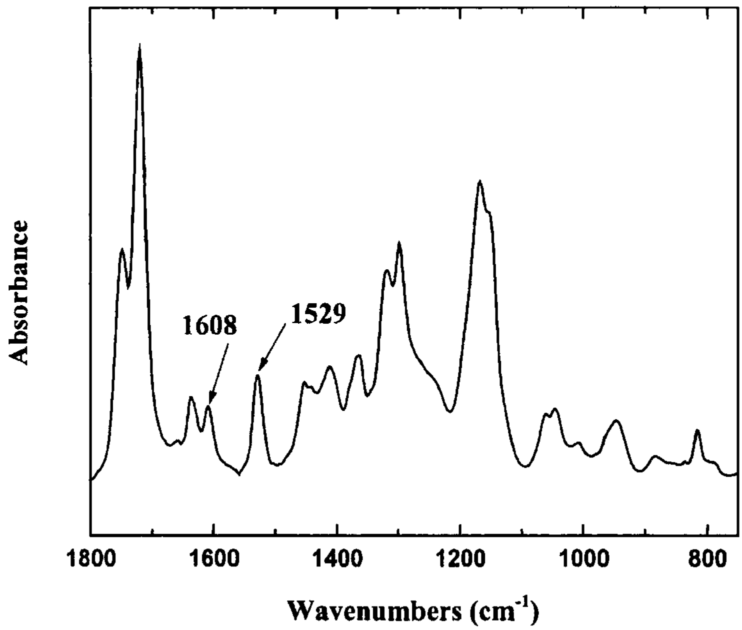

FIGURE 8 Transmission infrared spectrum of MEA following addition of aluminum nitrate nonahydrate.

cleaned for one minute in a plasma, then immersed in a 2% solution of MEA in toluene for 30 minutes. Figure 9 is the GAIR spectrum of the sample following removal from the MEA solution. As for the MEA chelation with aluminum ions in solution, a strong absorbance is observed at 1531 cm^{-1}, which corresponds to chelate formation of the β-diketone with aluminum ions in the aluminum substrate, Figure 10.

GAIR was also employed to evaluate the interaction of the β-diketone-containing PCA with aluminum substrates. Vapor-deposited aluminum thin films on glass slides were cleaned for one minute in a plasma, then immersed into a 1% solution of the terpolymer in toluene. The GAIR spectrum of the sample following immersion in the treatment solution is shown in Figure 11. Peaks at 1730, 1494, and 1452 cm^{-1}, which are characteristic of the polymer, were clearly distinguishable above the interference fringes. The vapor-deposited aluminum thin films on glass slides utilized as samples were 2000 Å in thickness. The interference fringes were the result of the infrared beam reflecting off the back of the aluminum film. The chelate peak, normally present at

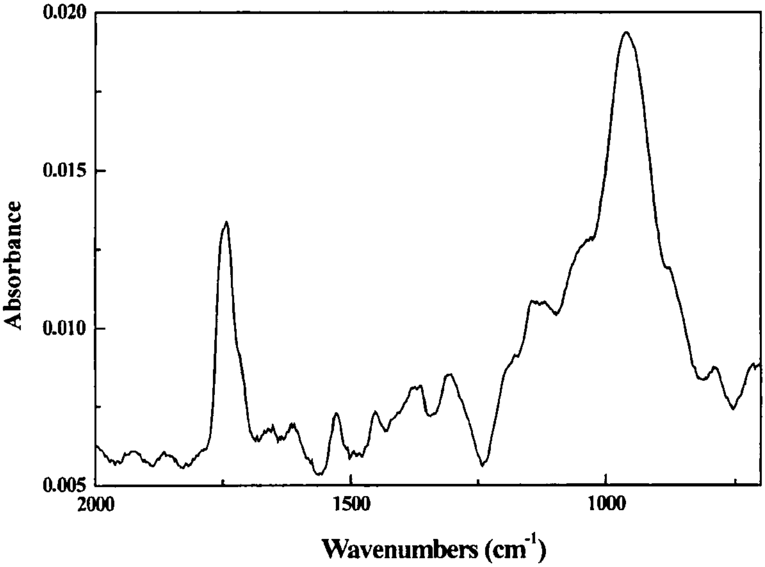

FIGURE 9 Reflection infrared spectrum of MEA on a plasma-cleaned aluminum thin film.

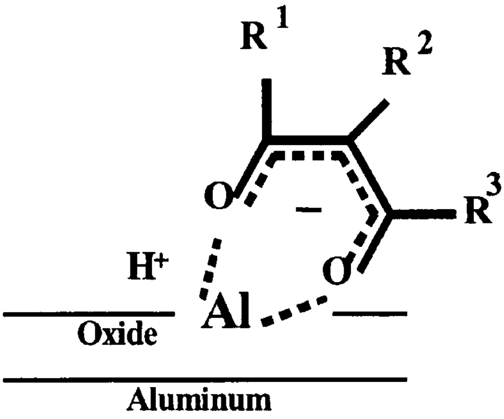

FIGURE 10 Structure of the reaction product of a β-diketone with an aluminum surface [Ref. 34].

1531 cm^{-1}, was not clearly apparent suggesting that if the chelate was formed it was not formed in significant quantities. Similar GAIR analysis of argon-sputtered samples that were treated with PCA solution did not show evidence of chelate formation.

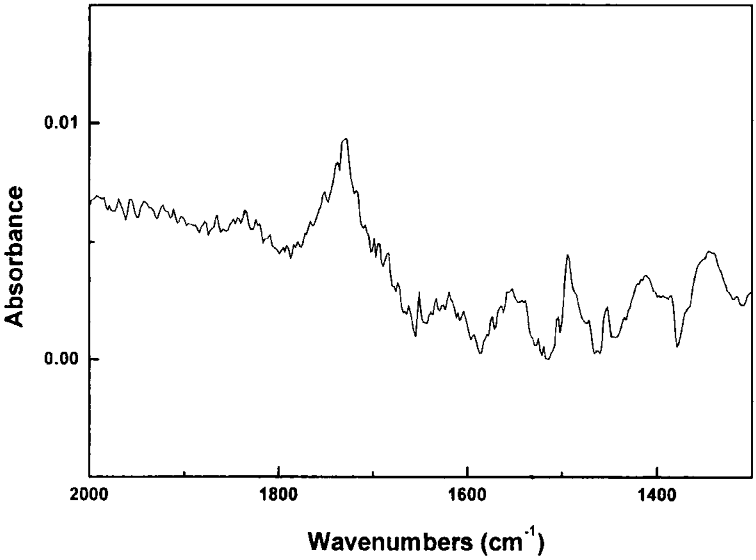

FIGURE 11 Grazing angle infrared spectrum of a plasma-cleaned aluminum thin film that was immersed in a 1% solution of the terpolymer in toluene for 30 minutes, then rinsed with toluene.

3.3. PCA Coating Deposition

The lack of influence of the β-diketone-containing PCA on the adhesion of the epoxy/aluminum bond system prompted further investigation into the as-deposited PCA coating. XPS analysis of an aluminum substrate following immersion in a 1% solution of PCA and solvent rinsing revealed strong aluminum peaks in the survey spectrum [32]. The strong aluminum peaks suggested that the coating was very thin or discontinuous such that the strong peaks were the result of exposed aluminum. Ellipsometry of a PCA coating deposited from toluene revealed a thickness on the order of 30 Å. AFM analysis showed the film to be continuous [32]. Previous work on a steel/epoxy bond system using a mercaptoester-functionalized PCA had determined that a PCA coating thickness of 140 Å optimized joint strength [33]. The influence of solvent solubility parameter, immersion time, and PCA concentration in the treatment solutions were investigated in an effort to increase coating thickness and ultimately influence coating adhesion in the epoxy/aluminum bond system.

Samples were prepared from vapor-deposited thin films of aluminum on glass slides. Each sample was cleaned for one minute in a plasma, then immediately immersed in a 1% terpolymer solution in the noted solvent. Following immersion, the samples were rinsed thoroughly in pure solvent and blown dry with nitrogen. To evaluate the influence of solvent solubility parameters on the resulting PCA coating thickness, poor hydrogen bonding solvents were selected within the solubility limits of the polymer (the polymer was insoluble in dodecane and acetonitrile with solubility parameters of 16.2 and 24.3 $(\mathrm{MPa})^{1/2}$, respectively). Poor hydrogen bonding solvents were selected to minimize solvent-substrate interactions. Solvent, solubility parameters, and resulting coating thicknesses are summarized in Table III. Over the range of solubility parameters shown, it is clear that the solubility parameter did not strongly influence the resulting coating thickness following solvent rinsing.

PCA concentration in the treatment solution and time of immersion were varied to determine their influence on the resulting PCA coating thickness. Having observed no influence of the solvent solubility parameter on the resulting coating thickness, toluene was selected for use in the remainder of this study. The concentrations, immersion times, and resulting coating thicknesses are summarized in Table IV. Neither

TABLE III The influence of solvent solubility parameter on coating thickness

Solvent	*Solubility parameter* $(MPa)^{1/2}$	*Coating thickness* (*Å*)
Carbon Tetrachloride	17.6	34
Toluene	18.2	33
Trichloroethylene	18.8	25
Ethylene Dichloride	20.1	26

TABLE IV The influence of PCA concentration and immersion time on the resulting coating thickness

Concentration (%)	*Immersion time* (*minutes*)	*Coating thickness* (*Å*)
1	5	20
1	15	20
1	30	33
1	60	31
5	30	32
10	30	31

immersion time nor concentration strongly influenced the resulting coating thickness. A maximum thickness on the order of 30 Å was again obtained.

4. DISCUSSION

The data presented in the Results section of this paper establishes that the β-diketone-containing PCA did not influence adhesion of the epoxy/aluminum bond system either positively or negatively as compared with untreated controls. The thickness of the deposited coating following solvent rinse was not influenced by the solubility parameter of the solvent, time of immersion, nor the concentration of the PCA in the treatment solution. In addition, that despite infrared evidence of MEA reactivity with aluminum substrates, GAIR spectra did not indicate reaction of the β-diketone functionality with the aluminum substrate when the MEA was incorporated into the PCA. The question then remains as to why incorporating the diketone functionality into the polymer results in a loss of reactivity toward the aluminum substrate.

Ellipsometry and GAIR both detect polymer on the aluminum surface following treatment in the PCA solution and thorough rinsing; thus, it can be assumed that the polymer is, in fact, diffusing to the surface and adsorbing. As the polymer adsorbs onto the surface it forms tails, loops and trains. The relative ratios of the three are controlled by the segmental interaction strength of the polymer's functional groups with the reactive sites on the aluminum surface. The aluminum surface has three primary types of interaction sites: hydroxyl, oxygen, and coordinately-unsaturated aluminum atoms (Lewis acid sites). Extensive evidence exists in the catalysis literature supporting the fact that defect concentration [35–38] and oxide structure [39] are direct functions of the conditions under which the oxide was prepared. Taking the monomer units into consideration, the polymer also contains three primary functional groups: phenyl, epoxy, and β-diketone. β-diketones chelate with coordinatively-unsaturated aluminum ions in the oxide. The primary mode of interaction between epoxy resins and aluminum substrates is *via* hydrogen bonding with hydroxyl functionalities in the oxide [40]. The phenyl ring has the ability to interact with the hydroxyl functionalities or the coordinatively-unsaturated aluminum atoms.

Aromatic molecules have been shown to adsorb parallel to the inorganic solid in a flat conformation *via* electron delocalization [41–43]. GAIR data did not show chelation to be occurring to any significant extent and, thus, it can be assumed that the primary mode of interaction between the β-diketone-containing polymer and the aluminum substrate was through the epoxy and/or phenyl groups as opposed to the β-diketones.

It can be envisioned that if the first monolayer of PCA were to adsorb preferentially *via* the styrene functionalities (and perhaps the epoxy groups) and then spread to attain the equilibrium conformation of an isolated chain, this process would block diketone reactive sites as well as significantly reduce chain mobility, thereby inhibiting further reactivity. The time constant of molecular motion of the adsorbed chain and desorption of the polystyrene components might then inhibit additional rearrangement and subsequent reactivity [44]. This theory explains why, despite reactivity of the β-diketone monomer, no reactivity was observed for the β-diketone-containing PCA. In addition, it also assists in elucidating why changes in PCA deposition conditions did not result in changes in the thickness of the PCA coating following solvent rinsing. Had the deposition been primarily driven by the chelation reaction, one can envision that increasing the solution concentration above the point of entanglement should have yielded thicker coatings. This is because as entangled chains adsorbed onto the surface, and the competition for adsorption sites was increased, the chains should have adsorbed and reacted in a more coiled state with the potential for higher chain density on the surface, with more loops and tails and the potential for thicker coatings following solvent rinsing and drying.

Coupling agent development, particularly polymeric coupling agents, has focused primarily on reactivity of the functional groups in the compound with the metal substrate and polymer topcoat. The results of this research clearly illustrate that in addition to reactivity, one must also consider the relative adsorptivities of any other functional groups in the compound. The β-diketone monomer showed reactivity with the aluminum substrate, whereas the β-diketone-containing polymeric coupling agent did not. The phenyl and epoxy functionalities in the PCA inhibited β-diketone reactivity. The β-diketone is still a feasible component of a polymeric coupling agent for an epoxy/aluminum bond system. Styrene and glycidyl methacrylate should, however, be replaced with monomers containing functional groups that have less affinity for the aluminum surface than the diketone.

5. CONCLUSIONS

In conclusion, joint strength and durability measurements showed that the synthesized β-diketone-containing polymeric coupling agent did not influence the adhesion, positively or negatively, of treated aluminum torsional shear joints. Grazing angle infrared spectroscopy showed evidence of chelation of the monomer with aluminum substrates. The β-diketone-containing terpolymer, however, did not show evidence of chelation. Deposition studies showed that a maximum thickness on the order of 30 Å was obtained and that the deposition thickness was not a strong function of solution concentration, solvent solubility parameter, or immersion time. It is hypothesized that adsorption of the terpolymer was primarily *via* physisorption of the epoxy and/or phenyl functional groups, thereby blocking diketone reactive sites and inhibiting chain mobility and subsequent diketone reactivity.

Acknowledgement

Portions of this work were performed at Sandia National Laboratories, which is supported by the United States Department of Energy under contract number DE-AC-04-94AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

The authors wish to thank Manuel J. Garcia at Sandia National Laboratories for the Grazing Angle Infrared Spectroscopy analysis, Roger Assink for the NMR analysis, and Tony Olhausen for the XPS analysis.

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