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Interactions of BTESPT silane and maleic anhydride grafted polypropylene with epoxy and application to improve adhesive durability between epoxy and aluminium sheet

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ABSTRACT

For improvement of adhesive strength and durability of adhesion between epoxy and aluminium sheet bis-(triethoxysilylpropyl)tetrasulfide (BTESPT) silane and maleic anhydride grafted polypropylene (PP-g-MAH) are chosen for surface pretreatment of the aluminium sheet respectively. Fourier transform infrared (FTIR) spectroscopy was used for characterization of the structure and the interactions in the systems. It is shown that BTESPT silane and the anhydride on PP-g-MAH take part in the curing reactions of the epoxy/polyamide system. The adhesive shear strength of the samples, prepared under different curing temperatures, and after immersion in boiling water and 3.5% NaCl water solution respectively, was tested. The features of the shear fractured surfaces were examined by scanning electron microscope (SEM). For the aluminium sheet pretreated by BTESPT silane, the maximum adhesive shear strength is 22.2 MPa, which is higher than that of 17.5 MPa for aluminium sheet without pretreatment by the silane. After immersion in boiling water for 80 h and in NaCl water solution at 50 °C for 180 h the adhesive shear strengths are 13.39 MPa and 18.4 MPa respectively, which are higher than these (below 6 MPa) for aluminium sheet without pretreatment by the silane. As for the aluminium sheet pretreated by PP-g-MAH, the maximum adhesive shear strength is 13.17 MPa. After immersion in boiling water for 80 h and in NaCl water solution at 50 °C for 180 h the adhesive shear strengths decline to 10.67 MPa and 8.1 MPa respectively.

1. Introduction

Owing to the favourable characteristics of excellent adhesion to metals, rapid curing, low shrinkage and high electronic and mechanical properties, epoxy resins have been widely used as protective coating for metals and as adhesive for bonding between adherends. In these applications the adhesive strength and the long-term durability of the adhesion between epoxy and the substrates under severe environmental conditions are among the top priorities [1–5].

The formation of a strong and durable adhesive bonding between polymers and metals depends on both of complex physical and chemical phenomena. One of the primary mechanisms of adhesive bonding of the epoxy resin is believed to be through interactions between the hydroxyl and the epoxy groups with the metal surface. However, when the mixture of epoxy and polyamide are applied to the aluminium sheet, polyamide will be preferentially adsorbed on surface of the aluminium oxide [6]. Hong et al. [6] reported that the curing agent was preferentially adsorbed by the substrates of electrogalvanized steel and 2024 aluminium alloy, and that a layer enriched in epoxy in the interfacial region was created between the epoxy/polyamide and the substrates. Boerio and Hong [7] reported that dicyandiamide was preferentially adsorbed onto the silver surface from the adhesive of diglycidyl ether of bisphenol-A (DGEBA) and dicyandiamide. Van Ooij et al. [8] reported that certain paint constituents of the epoxy electrocoat systems are preferentially adsorbed on galvanized steel surface. Nakamae et al. [9] reported that diaminodiphenylmethane (DDM), the curing agent of the epoxy, was preferentially absorbed on the oxidized aluminium. Therefore, under these cases the interphasial region is likely weakly cured, and consequently weak in mechanical strength. In addition this incompletely cured interphasial layer will be hydrophilic due to more polar groups in it. This implies that water can diffuse rapidly along the interphase and accumulate in it, leading to deterioration of the adhesive strength and durability.

Thus in order to promote long-term durability of the adhesion, modification of the interphase by surface pretreatment of the substrates prior to bonding is one of the important approaches. During the last 40 years, several effective methods, including chromating, phosphating, anodization, etc., have been made to modify surface

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of aluminium substrates to improve the adhesive strength and durability of aluminium–epoxy bonded interface [1–5,10]. Among these approaches chromating is an effective and extensively used approach for surface pretreatment of metal substrates. Recently the combination of the phosphoric acid anodic oxidation as pretreatment of aluminium and phosphoric acid mono alkyl ester as post-treatment has been reported to be effective for improvement of the adhesion and the durability of aluminium/epoxy bonding [10]. However, they involve environmentally hazardous materials of hexavalent chromium compounds and strong acids in surface treatment specifications [11]. In recent years there has been growing pressure from government and environmental bodies to remove such substances from manufacturing processes.

To this end considerable effort has been directed toward the application of organosilanes as a potential replacement for the pretreatment processes, especially for hexavalent chromating. Silanes have the general structure X_nSiR_{4-n}, where R is an organofunctional group like amino, epoxy, vinyl or alkyl group for reactivity or compatibility with the organic materials, X is a hydrolysable group like ethoxy group that for bonding with the substrate [12]. For epoxy resin, γ-glycidoxypropyltrimethoxysilane (GPS) is one of the most commonly used silanes. The treatment of aluminium surfaces with aqueous solution of GPS before adhesive bonding has been shown to improve bond durability [13–16]. It has been reported that pretreatment of the aluminium alloys first by immersion in boiling water and then followed by soaking in aqueous solution of GPS produced notable improvements in bond durability between aluminium and epoxy [17]. In addition, pretreatment of the aluminium by aminopropyltriethoxysilane (γ-APS) and vinyl-silane are effective for promotion of the adhesion strength between aluminium and epoxy also [18–21].

In the last decades, pretreatment of metals based on the use of several kinds of bis-silanes, aimed at replacing chromate based metal pretreatments for organic coating in corrosion protection, has attracted the attention of many researches due to its environment friendly [22–31]. Van Ooij's group investigated bis-silanes as bis-(trimethoxysilylpropyl)amine (Bis-amino), bis-1,2-(triethoxysilyl)ethane (BTSE) and bis-(triethoxysilylpropyl)tetrasulfide (BTESPT), and mixtures of two kinds of silanes as BTESPT/bis-amino and bis-amino/vinyltriacetoxy silane (VTAS), on steels, aluminium alloys, Zn and Zn coated steels, Cu and Cu alloys, etc. [22–27]. Ferreira et al., also examined silanes of BTSE and BTESPT on hot dip galvanized steel and aluminium alloys [28–31]. These published results show the potential of these chemicals to replace chromates and phosphates in metal finishing industries.

Among these silanes, bis-(triethoxysilylpropyl)tetrasulfide (BTESPT) silane is applied to pretreatment of metal substrates first by Van Ooij's group [22–27]. It is a kind of silane having been extensively used in the rubber industry for improving compatibility between the filler and the rubber compound [32]. It is insoluble in water [27,32]. Therefore in application to pretreatment of metal substrates it is hydrolysed in mixture of water and ethanol for formation of silanol groups by hydrolysation of the alkoxy groups of BTESPT silane [22–27]. This is very important for the formation of Si–O–metal bonds [12,22–25]. However, it has been confirmed that the silanols will condense with themselves to form oligomeric siloxanols [12]. This indicates that the stability time of the hydrolysed aqueous silane solution is limited by the condensation process. In the present paper BTESPT silane is in non-hydrolysed state by adding it into ethanol without water. Under this case it is stable and hence can be used for a long time.

Maleic anhydride is widely used by grafting to improve adhesion of polyolefins onto metal substrates [33–36]. Recently poly(ethylene-altmaleic anhydride) has been used as an interfacial layer to improve the adhesive durability between the epoxy coating and the aluminium substrate [37]. The anhydride groups in PP-g-MAH could chemisorb to the oxide on surface of the aluminium substrate and also react with epoxy and polyamide. The formed interfacial layer will have the properties of high chemical resistance and low water permeability as that of PP. This is beneficial to improvement of durability of the adhesion between aluminium substrate and the epoxy.

In the current work bis-(triethoxysilylpropyl)tetrasulfide (BTESPT) silane and maleic anhydride grafted polypropylene (PP-g-MAH) are chosen for improvement of the adhesive strength and the durability of adhesion between epoxy and aluminium substrate. Fourier transform infrared (FTIR) spectroscopy was used for characterization of the structures of BTESPT silane film and PP-g-MAH film formed on surface of aluminium sheets, and the interactions between BTESPT silane and PP-g-MAH with epoxy/polyamide system respectively. The adhesive shear strength of the samples prepared under different pretreatments and curing temperatures was tested. The durability of adhesion for the samples was evaluated after immersion in boiling water and 3.5% NaCl water solution at 50 °C respectively. The features of the shear fracture surfaces were examined by scanning electron microscope (SEM).

2. Experimental

2.1. Materials

The aluminium sheets used were 2 mm thick commercially 2A12 aluminium alloy (Cu 4.3 at.%, Mg 1.5 at.%, Mn 0.46 at.%, Zn 0.15 at.%, Ni 0.1 at.%, Fe 0.31 at.%, Si 0.21 at.%, Al in balance). The epoxy resin was a diglycidyl ether of bisphenol A (E-44 with epoxide value of 0.41–0.47 mol/100 g, Yuanda Chem. Co.). Polyamide resin, low molecular weight 650 by Jufeng Chem. Co., was used as the curing agent. The molecular structures of the epoxy and the low molecular weight polyamide are shown in Fig. 1.

The silane coupling agent of bis-[triethoxysilylpropyl]tetrasulfide (BTESPT), $(H_5C_2O)_3Si\text{-}(CH_2)_3\text{-}S_4\text{-}(CH_2)_3\text{-}Si(OC_2H_5)_3$, with reported purity >95% and content of $S \geq 22\%$, produced by Yingcheng Chem. Co., was used. PP-g-MAH, with the grafting degree of 1–1.2 wt% and melt flow index ≥ 40 g/10 min at 190 °C and 2.16 kg loading, was produced by Shanghai Sunny New Tech. Development Co. Ltd.

2.2. Surface pretreatment of aluminium sheets

Aluminium sheets were pre-treated in boiling water for 30 min, rinsed with distilled water, degreased with acetone at room temperature, and then ground with 600 # sandpaper, cleaned in acetone at room temperature again and washed by de-ionized water, and then blow dried in ambient air.

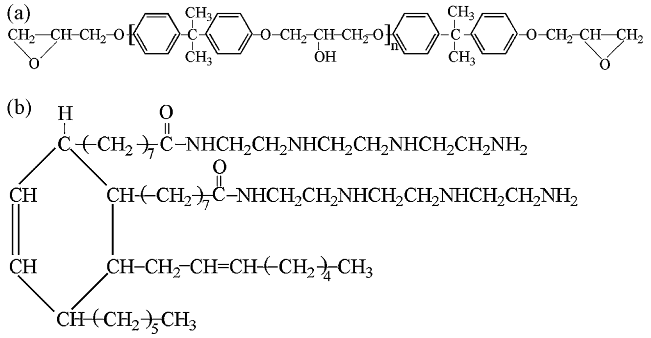

Fig. 1. Molecular structures of the epoxy and the curing agent, (a) epoxy resin based on diglycidyl ether of bisphenol A and (b) low molecular weight polyamide resin.