Surface modification of magnesium alloys using triazine dithiols

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Abstract

Polymer plating of 6-dihexylamino-1,3,5-triazine-2,4-dithiol monosodium (DHN), 6-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN), and 6-mercapto-1,3,5-triazine-2,4-dithiol (TTN) groups at 10 °C in 1 mol/dm\textsuperscript{3} NaOH aqueous solution on the magnesium alloy AZ91D yielded poly(6-dihexylamino-1,3,5-triazine-2,4-disulfide) (PDH), poly(6-diallylamino-1,3,5-triazine-2,4-disulfide) (PDA), and poly(6-mercapto-1,3,5-triazine-2,4-disulfide) (PTT), respectively. PDH-plated magnesium alloys showed excellent corrosion resistance in air containing moisture and in corrosive water because PDH films have very low critical surface tension, are composed of ordered and closely packed layer structure like the LB-films, and have high crystallinity. An increase in film thickness of the PDH films suppressed the corrosion rate of the magnesium alloys and increased the induction period to initiate the corrosion. PTT-plated magnesium alloys showed outstanding adhesion to poly(phenylene sulfide) (PPS) compounds during injection molding in 140 °C. This is because PTT films have highly active points, such as SS bonds, and show excellent strength. PTT-film thickness in the range of 20 to 80 nm provided high tensile shear strength for the direct adhesion of PPS to PTT-plated magnesium alloys. PDA-plated magnesium alloys exhibited excellent adhesion to ethylene-propylene-diene terpolymer (EPDM) in a peroxide curing system and with acrylic rubber (ACM) under a triazine thiol curing system, although the peel strength was found to depend on film thickness.

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1. Introduction

Magnesium and its alloys are considered to be important as next-generation metallic materials because they are relatively light and are recyclable \cite{1} and they can be used in large automotive components, as well as in portable electric equipment. In addition, applications of magnesium alloys have recently been extended to various industrial areas, such as automobile parts, healthiness-related equipment, home electric appliances, and building materials \cite{1-3}. Although a wide variety of applications can be envisaged for magnesium alloys, practical uses are currently limited due to various reasons, including a lack of detailed information on surface properties. To expand applications of magnesium alloys, it is necessary to improve surface characteristics, such as corrosion resistance \cite{4,5} and adhesion properties \cite{6-8}. One method for modifying and improving the surface characteristics of magnesium alloy surfaces is to use polymer coatings.

A new and effective surface finishing technology to modify metal surfaces using “polymer plating” of 6-substituted-1,3,5-triazine-2,4-dithiols (triazine dithiols) has been developed and reported previously by the Authors \cite{9,10}. Polymer plating is a method for coating various metal surfaces, such as magnesium, aluminum, iron, and copper, with triazine disulfide polymers, which are deposited by electrochemical polymerization of triazine dithiols with various functional groups on the anode surfaces. Thus, the surface properties of magnesium alloys could potentially be improved by forming various deposited polymer films.

The purpose of this study is to demonstrate that magnesium alloys can be readily polymer plated with triazine dithiols. The polymer-plated magnesium alloys were shown...
to have outstanding corrosion resistance in corrosive environments and excellent adhesion to other polymers, such as ethylene-propylene-ethylidene norborne terpolymer, acrylic rubber, and poly(phenylene sulfide) (PPS).

2. Experimental

2.1. Materials and reagents

Test specimens (1 × 10 × 50 mm) of AZ91 magnesium alloy (Al 8.1%, Zn 0.6%, Mn 0.2%, Si 0.03%, Cu 0.003%, Ni >0.001%, and Fe 0.001%) were prepared by cutting pieces from a commercial ingot of the magnesium alloy. 

Substituted groups (R)-1,3,5-triazine-2,4-dithiol monosodium salts (triazine dithiols) were prepared by the reaction of 1,3,5-triazine-2,4,6-trichloride with NaSH and amines such as dihexyle amine and diallyl amine, according to the method described in a previous paper[11]. Triazine dithiols with –N(C6H11)2 (DHN), –SH (TTN), and –N(CH2CH=CH2)2 (DAN) as the substituted groups were used for electrochemically coating magnesium alloys with polymer films. Poly(phenylene sulfide) (PPS, Mp: 280 °C, Polyplastics, Type1140A) compounds were obtained commercially containing 40 parts per hundred resin (phr) of fine glass fibers. Ethylene-propylene-ethylidene norborne (ENB) terpolymer (EPDM, JAR EP98, ENB: 4.5%) and acrylic rubber (ACM, Nippon Zeon Geon-AR72LF) were obtained from commercial sources.

2.2. Surface treatments

The electrochemical polymerization of triazine dithiols, also referred to as polymer plating, was performed using an electrochemical measurement apparatus (Hokuto Denkou HD-3000), as described previously[9,12]. The electrolytic cell was equipped with a working electrode (magnesium alloy plates), a counter electrode (stainless steel plate), and a reference electrode (saturated calomel electrode, SCE). Polymer plating was conducted with 0.5 or 1 A/m2 of current density for 0.5–15 min, at 10 °C, in 1 mol/dm3 NaOH aqueous solution of triazine dithiol (5 mmol/dm3) without agitation. The polymer-plated magnesium alloy plates were then obtained by drying under reduced pressure after washing with water.

AZ91 magnesium alloy was coated, immersing in an alkali-chromate solution composed of Na2CO3 (2 wt.%), Na2CrO4 (2 wt.%), and ion-exchange water, for 2 min at 90 °C to compare corrosion resistance with the polymer-plated magnesium alloy.

2.3. Corrosion test

Accelerated corrosion tests in moist air and salt water were carried out, exposing the magnesium alloys before and after polymer plating to saturated water vapor at 60 °C and immersing the samples in 5 wt.% NaCl aqueous solution at 30 °C, respectively. The corrosion weight was determined from weight loss before and after the removal of corrosion products, such as MgO and Mg(OH)2. The removal of the corrosion products was carried out by dipping the samples after the corrosion tests for 1 min in boiling 15% CrO3 and 1% Ag2CO3 aqueous solution.

2.4. Direct adhesion

The procedure of injection molding and the dimensions and shape of the samples obtained are described in our previous paper[8]. The magnesium alloy samples, polymer plated with triazine dithiols, were placed in molds, followed by the injection of PPS resin through a gate (1 × 30 × 5 mm). The injection molding was carried out at 30 cm3/s injection rate and 100-MPa injection pressure. The cylinder (280–340 °C) and molding temperature (80–150 °C) were in the range of those ordinarily used.

Ethylene-propylene-diene terpolymer (EPDM) or ACM rubber compounds were obtained by mixing HAF black 50 phr, ZnO 5 phr, Perhexane-25B-40 7.5 phr, and triallyl isocyanuric acid 1.5 phr to EPDM rubber, or FEF black 50 phr, N-phenyl naphtyl amine 2 phr, stearic acid 1 phr, Zisnet-F (1,3,5-triazine-2,4,6-trithiol, Sankyo Kasei) 1.5 phr, and zinc dimethyldithiocarbamate (ZnDCC) 1.5 phr with ACM rubber on a roll mill. Direct adhesion of EPDM or ACM rubber compounds to the polymer-plated magnesium alloys was carried out by compression curing the rubber compounds onto the polymer-plated magnesium alloys, for 30 min at 145 °C, in a mold.

2.5. Measurements

The thickness of the polymer films was determined using a JASCO M-150i ellipsometer (Jasco, Tokyo Japan). FT-IR spectra were measured using high-performance reflection absorption spectroscopy (high-performance RAS) using a JASCO IR-5500 instrument (Jasco). Contact angle measurements on the polymer-plated magnesium alloys were made using pure water, high alcohols, and high hydrocarbons using an Elma goniometer-type contact angle measuring apparatus (Elma-type G-1) in a clean area. These data were used to determine the critical surface tension and surface free energy of the polymer-plated magnesium alloys. XPS spectra were obtained at a base pressure of 10−8 Torr using an X-ray photoelectron spectrometer (ESCA Lab-5, VG Scientific). An Mg Kα X-ray was used as the excitation source (23,500 eV) at take off angles of 80°. The tetrahydrohuran (THF)-insoluble parts of the polymer films were calculated using the weight of treated magnesium alloy plates before and after immersion in THF; the immersion was carried out for 24 h at 23 °C. The density of the polymer films was calculated from the film thickness and weight of the polymer films. Tensile shear strength was measured at a 2 mm/min tensile rate with a tensile tester.
(Shimadzu). Autograph ABS-1000) using an installing tool to fix samples to the tensile tester was as described in the previous paper [8]. Peel strength [13] was measured using the tensile tester at room temperature, operating at a tensile rate of 5 mm/min according to ASTM 9037.

3. Results and discussion

3.1. Polymer plating of triazine dithiols

Magnesium alloys are highly susceptible to corrosion but stable in aqueous solutions with pH greater than 11.5. For this reason, for the polymer plating on magnesium alloys, an aqueous solution with high NaOH concentration was used to avoid corrosion. Fig. 1 shows the effect of plating time on film thickness for the polymer plating of three kinds of triazine dithiols in 1 mol/dm$^3$ NaOH aqueous solution at 10°C. Triazine dithiols are dissolved as dithiolate anions in the aqueous solution. The dithiolate anions transfer two electrons to the anode (magnesium alloys) to change to bisthiyl radicals [9,12]. The bisthiyl radicals cause coupling with each other to yield poly(triazine disulfide) as polymer films on the magnesium alloys. The poly(triazine disulfide) film thickness increased in proportion to the square root of the plating time, suggesting that the rate-determining step for the formation of polymer films is a diffusion process. At temperatures of more than 30°C, MgO and Mg(OH)$_2$ were found to form in large amounts from FT-IR analysis of the surfaces, but they formed in very minute quantities below 10°C. The current density had an important influence on the properties of polymer films because it has an effect on current efficiency for the formation of the polymer films. For this reason, optimal current densities for triazine dithiols were selected.

Polymer-plated magnesium alloys with the three kinds of triazine dithiol coatings had different surface properties. Polymer-plated magnesium alloys with DHN [poly(6-dihexylamino-1,3,5-triazine-2,4-disulfide) (PDH)-plated magnesium alloy] showed high contact angle (98°) and very low critical surface tension (24 mJm$^{-2}$). This suggested that the top surface of the polymer film was entirely composed of methyl groups in hexyl chains because Y-type LB films of 6-didodecylamino-1,3,5-triazine-2,4-dithiol yield a 98° contact angle [14,15]. The layer structure of the polymer film is considered to be the same as that for the Y-type LB film, indicating that the polymer film has high crystallinity and has approximately 2.23-nm layer spacing, as a peak is seen at 2θ=3.97° in X-ray measurements [12]. This polymer film may impart corrosion resistance to the magnesium alloys.

Polymer-plated magnesium alloys with TTN or DAN [poly (6-mercaptotriazine-2,4-disulfide) (PTT) or (poly(6-diallylamino-1,3,5-triazine-2,4-disulfide) (PDA)-plated magnesium alloys] could show reactivity of the surfaces to rubbers and a resin because the polymer films, PTT and PDA, contain disulfide (SS), thiol, Mg–S, and allylic groups. The presence of disulfide (164.5 eV), thiol (162.4 eV), and Mg–S (161.8 eV) groups were confirmed from the S2p$^{3/2}$ spectra in the XPS measurements of the surfaces. Allylic groups (1642 cm$^{-1}$) were observed in the FT-IR spectra measurements on the surfaces. PTT films contained disulfide, thiol, and Mg–S groups, and PDA contained disulfide, thiols, Mg–S, and allylic groups. PTT and PDA films (100%) possessed higher THF-insoluble parts than did PDH films (0%). The former had higher densities, 1.22 g/cm$^3$ for the former and 1.08 g/cm$^3$ for the latter, as well as high surface free energies of 49 mJm$^{-2}$ for the former and 26 mJm$^{-2}$ for the latter.

When magnesium alloy AZ91 plates are polymer plated in 1 mol/dm$^3$ NaOH aqueous solution of DHN (8 mmol/dm$^3$) at 10°C, the potential reached 1.8 V vs. SCE. This potential brings to the formation of the oxidation products with very slight weight, as well as polymer films on magnesium alloy; from the FT-IR spectrum measurement of polymer-plated magnesium alloy, the corrosion products were recognized. In the case of DHN, the areas rich in aluminum were hardly confirmed from the SEM observation because corrosion weight is very low, but in the case of TTN, the areas rich in aluminum were observed as a sea-island structure because corrosion weight is large.

3.2. Corrosion resistance in corrosive environments

To measure the corrosion resistance of the three samples of untreated, chromate-treated, and PDA-plated magnesium alloys in moist air, accelerated corrosion tests were carried
out in saturated water vapor at 60 °C. The relationship between mass gain and exposure time in the tests was determined from the weight gain of the samples. Fig. 2 shows the mass gain as a function of the square root of exposure time. Untreated and chromate-treated magnesium alloys were used for comparison with the DHN polymer-plated magnesium alloys. Here, mass gain indicates the weight of the magnesium oxides [MgO and Mg(OH)$_2$; [16,17]] formed by the water vapor corrosion. Mass gain ($Y$) increased in proportion to the square root of exposure period, as seen in Fig. 2, indicating that the rate-determining step in the corrosion of the magnesium alloys is the diffusion of water and oxygen. For $Y$ and $t$, the equation

$$Y = kt^{0.5} + t_0$$

applies, where $k$ is a rate constant for corrosion in saturated water vapor at 60 °C, and $t_0$ is an induction period up to the start of corrosion of the magnesium alloys. $k$ and $t_0$ indicate the rate of formation of magnesium oxides and the time when oxygen and water molecules reach the magnesium surface, diffusing through the polymer and magnesium oxide films. In other words, this period indicates the diffusion rate of oxygen and water molecules through the films. PDH-plated magnesium alloys showed a considerably low corrosion rate and had the largest induction period. Fig. 3 shows the effect of film thickness on $k$ and $t_0$ on the corrosion of the polymer-plated magnesium alloys; $k$ decreased with increasing film thickness and $t_0$ increased. That is, with increasing film thickness, the formation rate of the magnesium oxides decreased and the diffusion period of oxygen and water molecules increased. The polymer films likely work to inhibit the corrosion of magnesium, reducing the diffusion of water molecules because they have low surface tension and a tight and closely packed layer structure. These film properties are effective for inhibiting corrosion because water molecules in saturated water vapor behave as aggregates. These polymer films will not be effective for retarding the diffusion of oxygen molecules because oxygen gas behaves as individual molecules. Fig. 4 illustrates a portable MD player case made of a magnesium alloy, which is polymer plated with DHN. The surface is very shiny and homogenous, showing thin yellow interference fringes. The sample did not show any loss in brightness after exposure in a living room for a year.

Fig. 5 shows the effect of immersion time on the corrosion weight of untreated, chromate-treated, and
polymer-plated magnesium alloys in 5 wt.% NaCl aqueous solution. The corrosion weight increased in proportion to the square root of the immersion time. The corrosion rate decreased in order of untreated > chromate-treated > polymer-plated magnesium alloys, and the induction period increased in this order. The polymer films were thus demonstrated to be very effective for inhibiting the corrosion of magnesium alloys in 5 wt.% NaCl aqueous solution. The ordered and closely packed polymer films markedly retard the diffusion of water and chlorine ions.

3.3. Adhesion properties

Important factors in the direct adhesion of resin to metals during molding include the formation of strong chemical bonds at both the interface and within interfacial layers. PTT-plated magnesium alloys have reactive points such as SS groups and a high-strength, three-dimensioned film structure on the surface. When the SS groups come in contact with resins such as PPS and ABS at high temperatures, the formation of chemical bonds between the two is possible [18]. Fig. 6 shows the relationship between the tensile shear strength and film thickness for the direct adhesion of PPS to PTT-plated magnesium alloys during injection molding. Shear strength increased with increasing film thickness and reached a constant value at about 20 nm thickness, and then decreased gradually. The former increase relates to the part of the specimen on which polymer plating did not occur. During the polymer plating, the areas that were rich in aluminum atoms are formed, which are not polymer plated, and decreased with plating time up to a certain area. The latter decrease is the reason why, on the topmost surface of the polymer films, SS bond concentration and the film strength decreased markedly with plating time. For the reaction of PPS with PTT films on magnesium alloys in naphthalene chloride solution, C–S–C bonds at the interface between the two were confirmed to form using XPS analysis of reaction product surface, causing the transfer of a hydrogen atom and an electron between the benzene ring and SS bonds. Fig. 7 shows a model sample of PPS-Mg adherends. PPS resins with various shapes could be adhered on magnesium alloy plates as strong adhesion strength is obtained.

Because PDA-plated magnesium alloys have reactive groups such as SH and allylic groups, it is possible to adhere ACM and EPDM rubber compounds directly onto them during curing. Fig. 8 shows the relationship between the peel strength and film thickness on PDA-plated...
magnesium alloys for the adhesion of the rubber compounds. The allylic groups in PDA films react with EPDM compounds during peroxide curing to yield interfacial C–C bonds because they are a component of the curing agents. The SH groups in PDA films react with ACM compounds during curing to yield interfacial bonds C–S–C because they are a component of the curing agents. Peel strength increased initially with an increase in film thickness, reached a constant value at about 13-nm film thickness, and then decreased gradually. The former increases are due to an increase in the reactive area composed of SH or allylic groups, as described above. The latter decreases are also due to an increase in the reactive area composed of SH or allylic groups, as described above. The latter decreases are due also because the properties of polymer films are different from those of the curing systems, as well as the polymer plating conditions. Peroxide curing decreases the strength of PDA films during curing at 145 °C because of networks with internal stresses, which are formed by the reaction of the peroxide and allylic groups. In PDA films, the thicker the films become, the lower is the SH concentration. SH groups do not work at the interface to link ACM chains, which are spent by ZnDDC in ACM compounds. It is important to investigate curing systems sufficiently for the direct adhesion of rubbers to polymer-plated magnesium alloys during curing.

4. Conclusions

The polymer plating of 6-substituted groups-1,3,5-triazine-2,4-dithiols in NaOH aqueous solution on a magnesium alloy was carried out, and the corrosion resistance and the adhesion properties of various polymer-plated magnesium alloys were investigated. The following conclusions resulted from the study:

1. PDH films have very low critical surface tension, are composed of ordered and closely packed layered structures like the LB films are, and have high crystallinity. PDH films suppressed the corrosion rate of magnesium alloys with an increase in film thickness and increased the induction period for the start of corrosion.

2. PTT-plated magnesium alloys yielded outstanding adhesion with poly(phenylene sulfide) (PPS) compounds during injection molding in 140 °C because PTT films have a high active point, such as SS bonds, and have high strength. PTT-film thickness in the range of 20 to 80 nm provided high tensile shear strength for the direct adhesion of PPS to PTT-plated magnesium alloys.

3. PDA-plated magnesium alloys exhibited excellent adhesion to ethylene-propylene-diene terpolymer (EPDM) in a peroxide curing system and with acrylic rubber (ACM) in a triazine thiol curing system, although peel strength was found to depend on film thickness.

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References


Fig. 8. Effect of film thickness on peel strength of EPDM and ACM rubbers to polymer-plated magnesium alloys.