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Study on preparation of magnesium-rich composite coating and performance enhancement by graft modification of epoxy resin

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Abstract: Magnesium (Mg)-rich primer is considered as a substitute for high polluted chromate treatment technology to provide cathodic protection for aluminum (Al) alloy. In this paper, Mg-rich primer with comprehensive properties was prepared by modifying epoxy resin using direct mixing. Specifically, the influence factors on the dispersion of Mg powder in epoxy, the modification of epoxy resin using organic silicones and the performance of Mg-modified epoxy composite coating were studied. The results show that Mg powder with small particle size has a better dispersion in epoxy; The mechanical property such as flexibility and impact resistance decreases with the addition of Mg powder, but which was improved when using modified epoxy as the resin matrix due to introduction of Si-O-Si flexible chain; In addition, the grafting efficiency between hydroxyl terminated polydimethylsiloxane and epoxy resin was improved because of the introduced silane coupling agent like KH550 contains amino group; The electrochemical test results indicate Mg-rich primer could provide effective electrochemical protection for Al alloy by raising the corrosion potential and reducing the corrosion current density to bare substrate, respectively.

Keywords: Magnesium-rich composite coating; Grafting polymerization; Corrosion resist; Organic silicones

1 Introduction

Aluminum (Al) alloy is widely used in aircraft, automobile, machinery manufacturing, shipbuilding and other industries. Chromate treatment technology is usually used to protect Al alloy, while the high toxicity & high pollution limit its application. So, researchers did a lot of work to find the substitute treatment technologies, including functional coatings such as conducting polymer coating [1, 2], sol-gel protective film [3, 4], electrodeposition coating [5, 6] and magnesium (Mg)-rich primer [7]. Among them, Mg-rich primer is proposed as the alternative technology of chromate-free corrosion protection. In analogy to the zinc-rich primer, the Mg in Mg-rich primer provides cathodic protection for Al alloy as sacrificial anode because Mg has a lower potential than Al [8–12]. Bierwagen G P group at North Dakota State University conducted extensive researches in Mg-rich primer and developed good Mg-rich primer technology [13]. Air Force Research Laboratory (AFRL) of USA also dedicated to develop new Mg-rich primer. In addition, electrochemical studies have been carried out to understand the corrosion protection mechanism supplied by Mg-rich primers in North Dakota State University [14]. Wang et al measured electrochemical impedance spectroscopy (EIS), electrochemical noise and other electrochemical information in accelerating corrosion damage of the Mg-rich coating [15]; Allahar et al used the Transmission-Line model to analyze and explain the EIS data of Mg-rich primer [16]; Li et al studied the effect of composition on Mg-rich primer's protecting performance for Al alloy applied in aircraft using electrochemical technology such as open circuit potential (OCP), EIS and energy spectrum analysis [17].

However, the above methods to prepare Mg-rich primer were complex and costly. In this paper, Mg-rich primer was prepared by direct mixing and the key factors affecting Mg-rich coating preparation were studied. These factors include: The dispersion stability and activity holding of Mg powder in coating. Increasing compatibility of active Mg powder and modified resin to improve comprehensive performance of the composite coating. Therefore, the following contents were studied: a. The influenc-

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ing factors on the dispersing stability of Mg powder in resin; b. Analysis of the sacrificial anode activity and corrosion mechanism of Mg-rich primer through electrochemical test; c. Modification of epoxy resin using hydroxyl terminated polydimethylsiloxane (PDMS) and improvement of comprehensive performance of coating, especially the flexibility and the impact resistance. As a result, Mg-rich primer prepared by direct mixing having the advantage of low cost and could provide cathodic protection for Al alloy and was suit to protect common Al alloy applied in shiping, automobile, marine infrastructure and so on.

2 Materials and methods

2.1 Materials

Spherical Mg powder (active Mg $\geq$ 99.8%) with particle size of 60 μ m (200 mesh) 30 μ m (400 mesh) was purchased from Tangshan Weihao Magnesium Powder Co., Ltd (Hebei China); The epoxy resin (E-20, colorless, transparent solid) and reactive polyamide curing agent (Ancamide 221, yellow brown clear liquid) were purchased from Air Products (USA); The γ -(2, 3-epoxypropoxy) propyltrimethoxysilane (KH560), 3-Triethoxysilylpropylamine APTES (KH550) (content>98%) and hydroxyl terminated polydimethylsiloxane (PDMS) were purchased from Nanjing Union Silicon Chemical Co., Ltd (Nanjing China); Dibutyltin dilaurate (DBTDL) was used as catalyst, which was purchased from NanTong Advance Chemicals Co. Ltd (Nantong China); The 2024 Al alloy (CHALCO) plates were obtained from Shanghai Baoxi Industrial Co., Ltd (Shanghai China).

2.2 Preparation of Mg-rich primer and working electrode

Mg powder was pre-modified before using. First, Mg powders were immersed in enough xylene for about 6 hr and then a certain amount of KH560 was added after removing of excess xylene by infiltrating. After vibrating sufficiently, the system was placed for about 12 hr and then filtrated to remove the excess KH560. A certain amount of epoxy resin, pre-modified Mg powders and solvent were added together in a specific order. The above mixture was stirred at 3000rpm for 20-30min by high speed dispersing machine to obtain component A (the main agent). The curing agent of ancamide 221 was first diluted to 50% and then

mixed with the component A in the ratio of 6:10 (mass ratio) to obtain the Mg-rich resin.

2024 Al alloy plates were selected as substrates of Mg-rich primer. The 2024 Al alloy plates with 2 mm thickness were cut into size of 150 $\times$ 70 mm and 50 $\times$ 50 mm respectively. The cutted plates were polished by 200 mesh abrasive simply and were then cleaned by acetone. The Mg-rich primer samples were prepared by spraying Mg-rich coating on the pre-treated substrates and cured at room temperature (STP). The coatings thickness was controlled within 150 $\pm$ 10 μ m. Acting as working electrode (50 $\times$ 50 mm plates), the coating were smooth with uniform thickness and welding wire back of plate. Finally, the back & four sides of plate were sealed by epoxy resin and adhesive.

2.3 Modification of epoxy resin

The modified epoxy resin was prepared through two steps. First, 300 g of epoxy resin (70% solids), 10–20 g of KH550 and 0.6 g of DBTDL catalyst were added in a 500 ml flask equipped with an Dean-Stark and the mixture was then heated to 60 $^{\circ}$ C at 500 rpm and reacted for 2hr under purging nitrogen. Subsequently, 20-40g hydroxyl terminated PDMS and 0.8 g DBTDL catalyst were added in the above system under stirring and purging nitrogen. The resultant mixture was then heated to 155-160 $^{\circ}$ C and reacted (about 4 hr) until no ethanol produced in the Dean-Stark. Finally, the modified product was obtained by cooling the reaction system down to ambient temperature.

2.4 Characterization

Surface morphology of coating was observed by MV6000 Metallurgical microscope (Novel China). The chemical structure of corrosion products and modified resin were characterized by Nicolet380 Fourier transform infrared spectrometer (Thermo USA) using KBr pellets technique. PL-GPC50 gel permeation chromatography (Varian USA) was used to characterize the molecular weight distribution, and the glass transition temperature (T_g) of the modified resin were characterized by DSC differential scanning calorimeter (Mettler Toledo Switzerland). The aging test and the salt spray test were conducted by putting the coating samples into a Ci4000Xenon Weather-Ometer (Atlas USA) and a BGD880 salt spray test box (Guangzhou China), respectively. The chalking, blistering and other corrosion phenomena were observed at regular intervals during the whole experimental cycle.

The impact resistance of samples was tested by QCJ-50 impact tester (Shanghai China) using 500g impact force and estimated through the sustainable maximum impact height (without cracking on film surface). The flexibility of samples was tested through bending method using QTX flexibility tester (Tianjin China) and the estimated by the sustainable minimum bending diameter (without cracking on film surface).

2.5 Electrochemical test

Taking platinum electrode (20×20 mm) as auxiliary electrode and saturated calomel electrode as reference electrode, EIS and Tafel polarization curves were tested using three-electrode system through PARSTAT2273 electrochemical workstation (E&G USA) in 3.5% sodium chloride solution. For EIS, the testing frequency is in the range of 100 kHz~10 MHz with the disturbance amplitude of potential of 50 mV, and the experimental data were collected and analyzed by ZSimpWin. For Tafel polarization curve, the potential window is -600 mV~+600 mV with the scan rate of 0.5 mV/s, the experimental data were collected and analyzed by Power suit software.

3 Results and Discussion

3.1 Effect of fineness and dosage of Mg powder on Mg-rich primer's properties

Two kinds of Mg powder with particle size 60 μm (200 mesh) and 30 μm (400 mesh) were used and the dosage of Mg powder was measured using pigment volume concentration (PVC): $\text{PVC} = \text{pigment volume} / (\text{pigment volume} + \text{resin volume})$. Based on the test result of linseed oil, the oil absorption of Mg powder was 75-80 (200 mesh) & 55-60 (400 mesh). The critical pigment volume concentration (CPVC) of Mg powder was estimated by the Equation 1.

$$1/\text{CPVC} = 1 + (\text{OA} \cdot \rho / 93.5) \quad (1)$$

OA – oil absorption of pigment, ρ – density of pigment, 93.5 – density of linseed oil.

The calculate result was: 39.9%–41.7% for 200 mesh, 41.7%–45.0% for 400 mesh. According to the estimated value, five samples with PVC of Mg powder 35%, 40%, 45%, 50% and 55% were respectively prepared to furtherly definite the CPVC. Firstly, surface morphology was observed through metallographic microscope at 100X magnification as showed in Figure 1.

Figure 1: Microscope photos of the coatings with different Mg powder

Figure 1(left) shows that the distribution of 200 mesh Mg particle was inhomogeneous for the sample with 35% PVC Mg powder. However, increasing the PVC to 40–50%, the Mg particles can be closely and continuously distributed. There were part of particles accumulated with each other in coating, which indicates excessive adding of Mg powder; For the samples with 40% and 45% Mg powder, distribution of Mg particles in coating was compact and continuous with no accumulation almost; It infers that the critical pigment volume concentration (CPVC) of 200 mesh Mg powder was 40%–45%.

Figure 1(right) shows that the distribution of 400 mesh Mg particles in coating display the star morphology. For three samples with less than 45% Mg powder, distribution of Mg particles was thinning and inhomogeneous until the PVC reached 50%. For the sample with 55% Mg powder, there was yet no accumulation of Mg particles. It was deduced that the CPVC of 400 mesh Mg powder in coating was more than 50%. In addition, the comparison of the two kinds of Mg powder showed that the dispersion and compatibility of Mg powder with small particle size in the resin were better.

Further, the effects of fineness and dosage of Mg powder on coating properties were studied through salt spray test, aging test and basic performance test. Table 1 (sample 1–5) was the experimental results of the samples prepared by 200 mesh Mg powder.

It can be seen from the Table 1, the surface smoothness and glossy of the coating declined with increasing the amount of Mg powder; Flexibility and impact-resistance of the coating were negatively affected by the adding of Mg powder and became significantly worse when the dosage of Mg powder reaching 40%. After aging 1000hr, results show that different degrees of chalking occurred for all

Table 1: Performance of the coatings prepared by different Mg powder and resin

Sample		Dosage of Mg (PVC)	Surface morphology	Flexibility	Impact resistance (500g)	Salt spray (5000h)	Aging
Result							
Composite coating with 200 mesh Mg powder	1	35%	Smooth, gloss	<4mm	>50cm	A little of blistering and bloom	Slight chalking
	2	40%	Smooth	5-10mm	25-35cm	No bloom and blistering, discoloration	
	3	45%	Rough			Bloom on part of coating surface, no blistering.	Serious chalking (chalking began after 720h, more serious more amount of Mg)
	4	50%				Bloom on whole coating surface, no blistering.	
	5	55%					
Composite coating with 400 mesh Mg powder	6	35%	Smooth dense, gloss	<4mm	>50cm	no change	Loss of gloss, no chalking, discoloration
	7	40%		4-5mm	40-45cm		
	8	45%				10-15mm	
	9	50%	Bloom on part of coating surface	Slight chalking			
	10	55%	Smooth, dense				
Composite coating prepared by modified resin(different reactant ratio)	11	10:2:0.5	Smooth, gloss	40-45cm	<4mm	A little of blistering	Loss of glossy & many floating, no chalking
	12	10:1.5:0.5		>50cm		No bloom and blistering	a little of floating, no chalking
	13	10:1:0.5					No floating and chalking

Note: The time of aging for sample 1-5 was 1000hr, the time of aging for sample 6-11 was 2000hr, the time of aging for sample 12-14 was 5000hr.

coatings. Moreover, with increasing dosage of Mg powder, more serious chalking appeared with sample 3, sample 4 and sample 5. After salt spray 5000 hr, results show that there was no blistering appeared except sample 1 with the PVC of 35%. It is probably due to the lacking of Mg powder in part of coating and thus corrosion medium can easily invade into the base. In addition, there was white corrosion product like “bloom” occurred on the surface of the coatings except sample 2 (PVC was 40%) and the “bloom” rise with increasing the dosage of Mg powder. Following, the “bloom” was collected and analyzed by infrared spectroscopy as shown in Figure 2(a).

Peak distribution shown in Figure 2(a) is similar with the spectra of magnesium carbonate basic provided in standard gallery. Among them, the presence of characteristic double absorption peaks at 1425 cm^{-1} and 1483 cm^{-1} belonging to the asymmetry stretching vibration absorption of CO_3^{2-} , which emerged at $1115\sim 1235\text{ cm}^{-1}$. The multiple peaks emerging at near 801 cm^{-1} , 853 cm^{-1} and 883 cm^{-1} belonging to the bending vibration of CO_3^{2-} . In different, absorption peak emerged at 3435 cm^{-1} corresponds to the characteristic peak of crystal water. Furthermore, the wide peak emerged at around 3000 cm^{-1} and the sharp peak emerged at 3647 cm^{-1} correspond to the stretching vibration absorption of hydrogen bond in O-H and the random vibration absorption of free O-H respectively, which indicates the existing of the hydrate. So, it is deduced that the molecular formula of the “bloom” is similar to $(\text{MgCO}_3)_n\text{Mg}(\text{OH})_2\cdot m\text{H}_2\text{O}$. This material covered

Figure 2: FT-IR spectrum analysis of different substance (a) corrosion product (b) reactants and modified product

loosely on the surface of coatings and cannot provide additional shielded protection.

Table 1 (sample 6-10) was the experimental result of the samples prepared by 400 mesh Mg powder.

It can be seen from the Table 1 that the amount of 400 mesh Mg powder affect the surface smoothness and density of coating slightly. The glossiness decreases but remains smooth and compact when the amount of Mg powder reached 55% (sample 10). When the dosage of Mg powder reached 50%, the flexibility and impact-resistance property of coating were negatively affected by the addition of Mg powder. After aging for 2000hr, the result shows that there is no chalking appeared on the surface of coatings except sample 10 with slight chalking emerged, but all the coatings lose glossiness and become darker. This resulted from the discoloration of epoxy resin. After accelerated aging for 3000 hr, chalking began to emerge on the surface of sample 8 (PVC was 45%) and sample 4 (PVC was 50%). After salt spray test for 5000 hr, the result shows that there is nearly no change for the sample 6, 7, 8 with PVC of Mg powder less than 45%, and little bloom appeared on scratch or part of surface only for sample 4 and sample 5. Comparing the result in Table 1, Mg powder with small particle size is beneficial to obtaining Mg-rich primers with smooth surface and performance to resist salt spray and aging.

3.2 Electrochemical studying on protection of Mg-rich primer for Al alloy

Electrochemical testing technology is a simple, fast and effective method to study metal corrosion and anti-corrosion mechanism of coating, which includes EIS and Tafel polarization curve and so on. Among them, EIS measurement can be carried out in a wide frequency range and provide a lot of information such as development of corrosive reaction between coating and substrate metal, so it has been extensively used in researching process of coating perishing [18]. In this paper, three samples prepared by 400 mesh Mg powder with PVC 42%, 45% and 48% were analyzed by EIS and Tafel polarization curve to study the electrochemical protection of Mg for Al alloy substrate. Figure 3(a) shows the Bode plots of three samples in different immersing time obtained by EIS measurement.

Figure 3: Electrochemical test of the coatings (a) Bode plots at different immersing time (b) Tafel polarization curve after immersing 1500 hr

The equivalent circuit model is usually used to analyze EIS curve and the process of coating perishing is commonly divided into three stages: a. Immersing early stage when corrosion medium just arrived at the interface between coating and matrix; b. Immersing middle stage when multiple time constants appeared but macroscopic hole has not yet formed on surface of coating; c. Immers-

ing later stage when rust point emerged on metal matrix. The Bode plots during the immersing early stage are not characterized with diffusion in Figure 3(a). So, we chose equivalent circuit $R_s(R_cC)$ for curve fitting, as shown in Figure 4(a). In which, R_s is symbolized as solution resistance, Q_c is referred as coating capacitance and R_c is referred as coating resistance. For the Bode plots during the immersing medium stage with evident diffusion as well as three time constants but without Warburg impedance in Figure 3(a) (immersing for 48 hr, 360 hr, 1500 hr), equivalent circuit $R_s(C_{d1}R_{t1})(QR_p)(C_{d2}R_{t2})$ is chosen as the fitting circuit as shown in Figure 4(b). In which, according to penetrating process of corrosion medium from coating surface into metal matrix, three units were divided respectively representing three thin layer zones and each layer has its own capacitance and resistance [19]. The typical division of the three thin layers is: bottom zone of coating ($C_{d1}R_{t1}$), interface zone between coating bottom and matrix surface (QR_p) and surface zone of matrix ($C_{d2}R_{t2}$). Among them, the value of polarization resistance (R_p) is better for the evaluation of the protective performance of coating. The fitting values were shown in Table 2 and the change rule of EIS data was shown in Figure 5.

Figure 4: Equivalent circuits of the Bode plots (a) early stage (b) middle stage

Figure 5: Change rule of EIS data of different samples

Table 2: Fitting values of EIS plots and Tafel polarization curve

Samples	Dosage of Mg powder (PVC)	Fitting values					
		(R _c or R _p /Ω·cm ²)				E _{corr} (mV VS. SCE)	I _{corr} (A/cm ²)
		0h	48h	360h	1500h		
1	42%	7.67×10 ¹⁰	8.85×10 ⁴	6.89×10 ⁴	1.04×10 ⁴	-622.38	6.23×10 ⁻⁵
2	45%	8.41×10 ⁹	1.95×10 ⁵	1.65×10 ⁵	2.47×10 ⁴	-487.42	6.53×10 ⁻⁵
3	48%	8.61×10 ⁹	5.69×10 ⁵	4.52×10 ⁴	4.37×10 ⁴	-585.65	3.66×10 ⁻⁴
4	2024 Al alloy	-	-	-	-	-1039.59	1.18×10 ⁻⁴

As shown in Table 2 and Figure 5, the values of R_c for all samples are high at the initial immersing stage; after immersing for 48 hr, the values of R_c or R_p decreased substantially to number grade of 10^5 and multiple time constants emerge as shown in the Bode plots, indicating that the density of the coating is poor and the corrosion medium could penetrate into the bottom in a short time to cause shielding protection lost (it was generally considered as shielding protection lost when effective value of coating resistance reduced below number grade of 10^6); As increasing the immersing time, Bode plots of all the three samples show the diffusion characteristic with multiple time constants and the value of R_p decrease constantly which indicates no passivation protection provided for metal matrix.

Tafel polarization curves of the three samples and 2024 Al alloy were measured after being immersed for 1500 hr as shown in Figure 3(b) and the fitting values were shown in Table 2.

Figure 3(b) and Table 2 show that the corrosion potential rises and the corrosion current density reduces significantly for all samples in comparison with the self-corrosion potential (-1039.59 mV VS. SCE) and self-corrosion current density (1.18×10^{-4} A/cm²) of 2024 Al alloy. With reference to general principle in electrochemical of corrosion inhibitor, the corrosion is more easily to take place or get worse with lower corrosion potential and higher corrosion current density. Conversely, it exhibits better performance in corrosion-resistance. So, it is concluded that Mg-rich primer could provide efficient protection for Al alloy. Then, it was analyzed comprehensively in combination with the result of EIS (there were no barrier and passivation protection for the coating to provide after immersing for 1500 hr), this protection results from electrochemical protection.

3.3 Studying on the modification of epoxy resin and its application in Mg-rich primer [20]

Flexibility along with impact and aging resistance of coating are reduced significantly by the addition of Mg powder. Organic silicones including flexible Si-O-Si chain is commonly used as modifier for epoxy resin to improve its flexibility and impact resistance effectively [21–23]. In this paper, hydroxyl silicone oil was selected as modifier and amine silane coupling agent KH550 was added to increase the compatibility between hydroxyl terminated polydimethylsiloxane and epoxy resin to improve grafting efficiency. As an effective way, the modification process was divided into two steps.

At the first step, the main reaction occurred between KH550 and E-20 is addition reaction, and the typical equation is shown in Scheme 1.

Scheme 1: The addition reaction occurred between KH550 and E-20.

At the second step, the main reaction is the catalytic condensation occurred between hydroxyl of hydroxyl terminated polydimethylsiloxane and oxyethyl group, which is shown in Scheme 2.

Scheme 2: the condensation occurred between hydroxyl of organic silicones and oxyethyl group.

3.4 Analysis on reaction process of modification

According to the reaction equations and molecular weight (weight average Mw) of reactants (E20, Mw=1800; Hydroxyl terminated PDMS, Mw=860; KH550, Mw=221), the

theoretical mass ratio of reactants is about 10:2:1 (E-20:Hydroxyl terminated PDMS:KH550). Hydroxyl terminated PDMS and KH550 co-modified epoxy resin was prepared at this ratio according to the above two steps. After reacting for 2 hr, the intermediate product produced at the first step was extracted and characterized by IR spectroscopy. The degree of reaction can be evaluated by detecting the characteristic absorption peaks of amine group. Figure 2(b) displays the IR spectra of the intermediate product, the final product, KH550 and E-20.

In general, the characteristic absorption peaks of amine are generated from the vibrations of N–H and C–N bonds. The characteristic stretching absorption peaks of N–H bond appear at $3500\text{--}3300\text{ cm}^{-1}$. Two absorption peaks corresponding to symmetric and asymmetric stretching vibration would be observed for primary amine, and one and zero peak would be observed for secondary and tertiary amine, respectively. The stretching absorption of C–N in fatty amine would appear at $1250\text{--}1020\text{ cm}^{-1}$, which is weak and difficult to identify. Additionally, moderate bending absorption peak at $1650\text{--}1510\text{ cm}^{-1}$ would be observed for primary amine, and weak peak would be observed for secondary amine. Furthermore, the primary amine shows a wide moderate absorption peak at fingerprint region ($900\text{--}700\text{ cm}^{-1}$). From Figure 2(b), characteristic absorption peaks of primary amine cannot be observed in intermediate product, which are clearly observed in KH550, indicating the complete reaction between KH550 and E-20. Further observation indicates that the intermediate product has a similar IR spectrum with that of E-20 except some differences at the following positions. The stretching vibration absorption peak of C–O bond at $1100\text{--}1000\text{ cm}^{-1}$ shows a multiple peak due to the overlay of stretching vibration absorption peak of Si–O–C bond at around 1080 cm^{-1} . The new absorption peak appeared at 950 cm^{-1} is corresponding to the characteristic absorption of $\text{--OC}_2\text{H}_5$. The absorption peak of epoxy group at 1250 cm^{-1} and 910 cm^{-1} shows no apparent differences, indicating epoxy groups exist in the intermediate product. IR results indicate that the main reaction occurred at the first step is the addition reaction between primary amine and epoxy group, and the primary amine groups are completely consumed. According to the final modified product, strong and broad double absorption peaks are observed at $1100\text{--}1000\text{ cm}^{-1}$, which is ascribed to the superposition of stretching vibration absorption of C–O–Si, C–O–H and Si–O–Si. Double absorption peaks also emerge at $830\text{--}800\text{ cm}^{-1}$ due to the superposition of stretching vibration absorption of $\text{Si}(\text{CH}_3)_2$ group and C–C bond. Furthermore, the symmetric and asymmetric stretching vibration absorption peak of epoxy group at around 910 cm^{-1}

and 1250 cm^{-1} are still retained in the final product. Compared with the intermediate product, characteristic peak of $\text{--OC}_2\text{H}_5$ at 950 cm^{-1} become weak, indicating some of $\text{--OC}_2\text{H}_5$ groups participated in the graft reaction with Hydroxyl terminated PDMS.

3.5 Optimization of the Modification Technology

The mass ratios of reactants (E-20:Hydroxyl terminated PDMS:KH550) were set as 10:2:1, 10:1.5:1, 10:1:1, 10:2:0.5, 10:1.5:0.5 and 10:1:0.5. Molecular weight distributions of the prepared modified resins were determined by GPC, and the results are shown in Figure 6(a).

Figure 6: Chemical property characterization of different modified resins (a) GPC test (b) DSC test

From Figure 6(a), the samples are divided into two teams by the dosage of KH550. The initial peaks of samples prepared from the KH550 ratio of 1 are all detected earlier than that prepared from the KH550 ratio of 0.5, indicating a high M_w . The effect of Hydroxyl terminated PDMS on the final products is studied by fixing the ratios of E-

20 and KH550. Results indicate that hydroxyl terminated PDMS has effect on the proportion of high Mw product with i.e. product with long chain. The Mw and PDI of products were fitted according to the GPC curves and are listed in the Table embedded in Figure 6(a). The fitted results show that samples with ratio of KH550=1 have a higher Mw (17500-27000) and a bigger PDI (>10) than samples with ratio of KH550=0.5. Results indicate that too much KH550 would induce excessive growth of chain, which contributes to the formation of excessive chains of branch structure or cross-linked structure.

Glass transition temperature (T_g) of products was calculated from differential scanning calorimetry (DSC), and the result DSC curves and T_g are displayed in Figure 6(b) and Table embedded in figure. From Figure 6(b), all the modified resins show a higher T_g than E-20, which is ascribed to the enhancement of molecule stiffness resulting from the introduction of KH550. By fixing the dosage of KH550, hydroxyl terminated PDMS affected T_g slightly, which indicates the increase of T_g is originated from KH550. According to the above analyses, the suitable ratio of KH550 was selected as 0.5.

The modified products were diluted to 50% solid content and put into a 200 ml transparent beaker. The stability of the products was estimated by observing the stratification of samples at regular intervals, and the results are listed in Table 3.

Results indicate that the three samples prepared with ratio of KH550=0.5 have a better stability than those prepared with ratio of KH550=1. During the observation period, flocculation or gelling phenomenon appeared in all samples with ratio of KH550=1. However, with ratio of KH550=0.5, a certain degree of mobility is existed despite the increase in viscosity. For samples with ratio of KH550=0.5, the dosage of hydroxyl terminated PDMS affects the transparency and storage stability of the modified resins. The more hydroxyl terminated PDMS is used, the lower transparency the product has. However, the product shows a poor stability with less hydroxyl terminated PDMS. Therefore, the suitable ratio of hydroxyl terminated PDMS is 1.5.

3.6 Performance study of Mg-rich primer prepared from modified resins

According to the above analysis, three groups of modified resins with good stability (sample 1, 2, 3 in Table 3) were chosen to prepare Mg-rich primer (PVC was 45%) using 200 mesh Mg powder. The coating samples were prepared by spraying modified Mg-rich primer on pre-treated Al plates

and cured at room temperature, performances of coatings are displayed in Table 1 (sample 11, 12, 13).

Table 3: Initial state and stability of the modified products

Samples	1	2	3	4	5	6
E-20:HS:KH550	10:1:0.5	10:1.5:0.5	10:2:0.5	10:1:1	10:1.5:1	10:2:1
Color	Light yellow			Bright yellow		Earthy yellow
Transparency	Clear, transparent		translucent	Clear		Cloudy
Flow ability	Good			Bad		-
Place for 60 days	Thickening, cloudy	Good flowing, translucent			Flocculation	-
Place for 120 days	Fattening	Thickening slightly, cloudy			Gelling	-

From Table 1, the flexibility and impact resistance of Mg-rich coating prepared from the modified resin are significantly improved. After 5000 hr salt spray, no bloom was observed on all samples except a few of blistering emerged on sample 11. The proposed reason is surface migration of unreacted Hydroxyl terminated PDMS during the curing process which would make the corrosion reaction easily (cathodic reaction: $-\text{OH} + 1/4\text{O}_2 + 1/2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$, anodic reaction: $\text{Mg} + 2\text{OH}^- \rightarrow \text{Mg}(\text{OH})_2 + 2\text{e}^-$ or $\text{Mg} + 2\text{Cl}^- \rightarrow \text{MgCl}_2 + 2\text{e}^-$). After 5000 hr aging test, no chalking appeared on all samples, indicating the coating aging resistance is significantly enhanced because the introduction of Si-O-Si chain endowing the modified resin excellent aging resistance. Unfortunately, floating with wave shape appeared on sample 11 and sample 12 after aging test, which is due to the deteriorate of unreacted hydroxyl terminated PDMS which transferred to coating surface during curing process.

4 Conclusions

In this paper, results indicate Mg powder with small particle size is beneficial to obtain coatings with smooth surface and performances to resist salt spray and aging. The critical pigment volume concentration (CPVC) for 200 mesh Mg powder is 40%-45% and is about 50% for 400 mesh Mg powder. Results of EIS and Tafel polarization curves indicate Mg-rich primer can provide effective electrochemical protection for Al alloy. Additionally, the suitable ratio of reactants is 10:1.5:0.5 (E-20:Hydroxyl terminated PDMS:KH550). Flexibility and impact resistance even the spray and aging resistance of Mg-rich coating prepared from the modified resin are significantly improved.

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