Synthesis and Application of a Novel Epoxy Grafted Thermosetting Acrylic Resin

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ABSTRACT: A novel manufacturing process for high performance metallic can coating was carried out based on an epoxy-grafted acrylic resin. Firstly, the epoxy resin was reacted with acrylic amide forming a ring opened product epoxy-amide resin, and then the product obtained copolymerized with all other monomers, such as acrylic acid (AA), butyl acrylate (BA), hydroxypropyl acrylate (HPA), 2-ethylhexyl acrylate (2-EHA), methyl methacrylate (MMA), styrene (St), using free radical solvent polymerization in the presence of BPO. The resins prepared present the transparent appearance, and the target resin coating based on these resins exhibits excellent boiling resistance and chemicals resistance and can be applied as the protective coating for metallic can. The effects on the coating properties, such as amount of acrylic acid, 2-EHA wt % between 2-EHA and BA, amount of amino resin, amount of catalyst, and so forth, were investigated. In addition, the influences of polymerization time on the conversion ratio of monomers were also studied. Results show that under the optimal conditions, the target resin coating provides excellent physical and mechanical properties. The various properties tests for this coating have been performed in accordance with the standards of ASTM. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 4053–4060, 2008

Key words: graft; epoxy-amide resin; thermosetting; metallic can; high-performance polymers

INTRODUCTION

Recently, there has been a growing development in metallic-canned food, and a demand for materials for protection of metals has been increased rapidly. According to the data of experts' analysis, the corrosion losses constitute 10%–15% of all products made of ferrous metals due to the consequences of corrosion wear[1]; so the protection of metal has attracted much attention.[2–9]

The metal package can is made mainly of tinplate. Therefore, both its inner[10–15] and outer surfaces would require some materials, such as polymer coatings, to protect them from corrosion. Acrylic resin is commonly used as protection coating[16–19] for its many characteristics, such as high gloss, hardness, anticorrosion, weatherability, and solvent resistance. Because of its variety, acrylic resin, especially thermosetting acrylic resin, can satisfy different demands and has been applied more widely than alkyd-trimeric cyanamide resin used before.

Epoxy resins are commercially used in coatings and various structural applications. Through the proper selection of resin modifier and curing agent, the cured epoxy resin can be tailored to specific performance characteristics. Cured epoxy resins exhibit excellent adhesion to a variety of substrates, good chemical and corrosion resistance, excellent electrical insulation, high tensile, flexural and compressive strength and thermal stability. The largest single use is in coatings, where high chemical and corrosion resistance and adhesion are important. The exceptional adhesion performance is due to the presence of polar hydroxyl and ether groups into the backbone structure of epoxy resins.[20–22]

Up to now, many studies about can-coating-based acrylate have been reported,[23–26] but the comprehensive properties are not satisfactory. To improve the comprehensive performance and safety and reliability of the coating, we report here a novel manufacturing process for high performance metallic can coating. Firstly, the epoxy-amide resin was formed by the reaction of epoxy resin and acrylic amide, and then the product achieved copolymerized with other monomers involved. This grafted resin obtained can offer some advantages over conventional resins with respect to the application/appearance of coatings as well as the final film properties, such as a better compatibility between epoxy and other resins, a convenient selection of different monomers and an easy control of the final coating performance.

EXPERIMENTAL

Processing route

Generally, the compatibility between acrylic resin and epoxy resin by mechanical blend is poor, and because

of an insufficient cure course, the product cannot be used for the protection of metallic can, which requires better mechanical properties. Additionally, the appearance of resin from mechanical blend is not transparent, lacking applied value. In this work, we utilize the reaction of epoxy resin and acrylic amide to form an epoxy-amide resin, and then the resin obtained copolymerized with all monomers based acrylate to attain a thermosetting resin, in which the epoxy resin is grafted as one composition.

Material and instruments involved mainly

Acrylic acid (AA), Butyl acrylate (BA), hydroxypropyl acrylate (HPA), 2-ethylhexyl acrylate (2-EHA), methyl methacrylate (MMA), acrylamide(AAm), styrene (St), heavy aromatics (*S*-150), ethylene glycol monobutyl ether(BCS), epoxy resin 1001 (Shell brand), and initiating agent dibenzoyl peroxide(BPO) were all industrial grade and were used as purchased; white titanium powder and amino resins were of imports; catalyst was a derivative of sulfonic acid.

Impact resistance was carried out on a QCJ Type Painting-Film Impact Tester (the hammer weighs 1000 g and the impacting height is 500 mm, the diameter of the steel ball is 8 mm with impacting depth of 2 mm); cupping, testing the flexibility of the coating, was treated with a QBJ Type Coating Cupping Tester (punch diameter 20 mm, digital precision 0.01 mm; the journey is beyond 6 mm when the tinplate was

damaged); boiling resistance was then tested by immersing the coating (after cupping) into distilled water and boiling at 129°C for 30 min; adhesion was determined by crosshatch; pencil hardness test was carried out by taking pencils of different grades (H, 2H, 3H, 4H); fineness gauges QXD-25 was used to test the fineness of grind; Viscometer QND-4C (C, copper, material of flow cup) was employed to estimate the viscosity of the coating at 25°C. FTIR spectra of the coating prepared were recorded on a Thermo Nicolet 170SXET-IR spectrometer in the range of 4000–400 cm^{-1}, using KBr pellets.

Synthesis of epoxy-grafted acrylic resin

Epoxy resin 1001 was dissolved firstly into the solution with the solids content of 50 wt % using required amount of *S*-150 and BCS, and then reacted with AAm at 70–75°C for 1 h to form an epoxy-amide resin. This is a significant step in which the rings of epoxy resin were opened, as shown in reaction (1), and was further proved by the IR analysis shown in Figure 1. The absorption bands lying at 3426 cm^{-1} (v_{NH}), 1548 cm^{-1} (δ_{NH} and v_{C-N}), and 1084 cm^{-1} (C—O—C, ethereal bonds) were indication of the reaction between acrylamide and epoxy resin, making the rings existed within epoxy resin open in this procedure. And then this product can copolymerize with all other monomers via double bond to form an epoxy-grafted acrylic resin.

$$\tag{1}$$
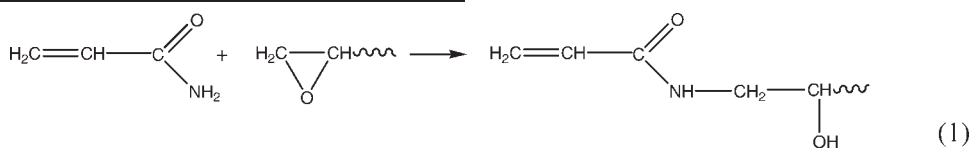
According to the formulation listed in Table I, the solvents were added to a 250-mL 3-neck flask equipped with a condenser, a stirrer, and a thermometer, and heated to 95°C while partial mixture (monomers + BPO + epoxy-amide resin) were added. When it was heated to 95°C again, the residual mixture was added dropwise for 2–2.5 h. Throughout the reaction, the temperature was maintained at 90–95°C. After 0.5 h, BPO was supplied and it was complementary again after aging for 1 h under stirring. The mixture was reacted for 2 h, and then BPO was added thirdly. The reaction was finished when the conversion ratio of monomers involved reached beyond 97%. The conversion ratio of monomers involved was calculated from the following equation:

$$\text{Conversion ratio} = \frac{s(m_1 - m_2)}{m_3}\,100$$

Where m_1, m_2 and m_3 are the weights of the total resin, the components that existed before

polymerization and cannot be volatilized after baking (180°C/15 min), and the total monomers, respectively. *s* is the solids content of prepared resin.

Preparation of coating and curing course

White enamel, prepared using epoxy-grafted acrylic resin as base and then adding some pigment-filler, curing agent amino resin and several assistant agents, was dispersed until the fineness was appropriate, then the enamel was diluted to viscosity eligible. According to definite thickness, the tinplate coated with enamel was put in an oven at 180°C for 15 min, then desired various properties were tested in terms of relational guidelines. In the course of curing, reactions might be involved between the synthesized resin and amino resins are showed in reactions of (2) to (4).

$$(2)$$

$$(3)$$

$$(4)$$
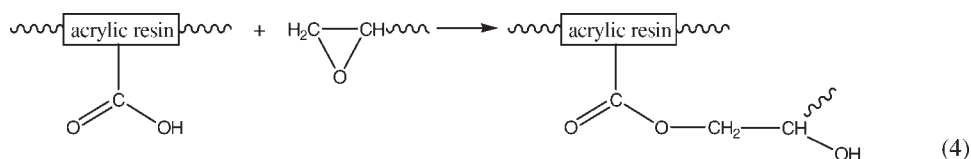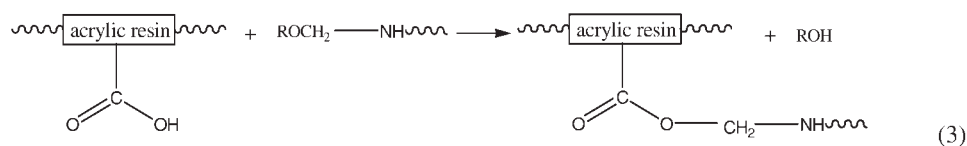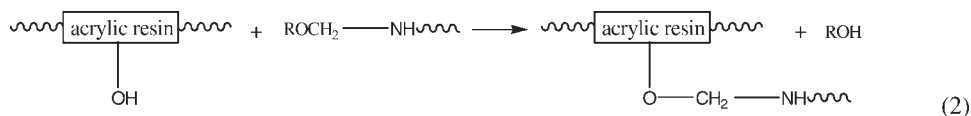
RESULTS AND DISCUSSION

The essential feature to develop a protective coating system is its good mechanical properties. The performance of an organic coating in service is related to its crosslink density and its ability to withstand mechanical strains. While developing a protective coating, a number of factors have to be taken into account including number of functionality available in the monomers, crosslinker concentration, initiator concentration, catalyst amount, and so forth.

The functionality of the monomers plays a vital role in affecting the final performances of prepared coating. The monomers involved in this work include the called soft monomers, such as BA and 2-EHA, which are used to adjust the flexibility of the final coating, and the called hard monomers, such as AA and MMA, which are applied to regulate the hardness of the final coating. In addition, the monomers contain some functional groups, such as AA, HPA and AAm, are also introduced to facilitate the cure reactions, and also to produce some useful functional groups to improve the final properties of the coating.

Comparison of mechanical blend and chemical grafted resins

Table II shows the results of comparison of mechanical blend resin and chemical grafted resin. It can be
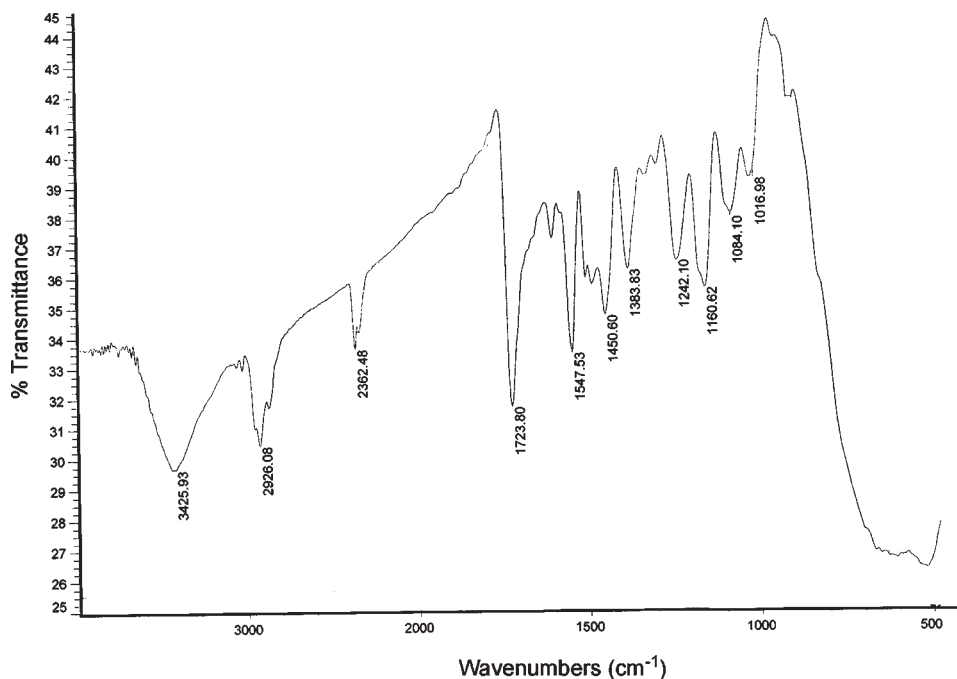
seen clearly that the coating performance prepared from mechanical blend resin is not comparable to that prepared from chemical grafted resin. Through grafting, the coating appearance and film dried are provided with excellent gloss, and the mutual solubility between this resin and amino resin can also be improved obviously. Based on these, in this work, we utilize the ring opening reaction of epoxy resin and acrylamide to form an epoxy-amide resin, and then the product copolymerized with other monomers to produce an epoxy-grafted acrylic resin. Through this ring opening reaction, primary amine existed in acrylamide would be reacted with epoxy groups, leading a decrease in activities of acrylamide, thereby extending the coating's applicability and enhancing its compatibility with epoxy resin.

FTIR analysis

The infrared spectrum of the resin prepared is shown in Figure 1. In this spectrum, the absorption bands at 3426 cm^{-1} (v_{NH}), 1548 cm^{-1} (δ_{NH} and v_{C-N}), 1084 cm^{-1} (C—O—C, ethereal bonds) were indication of the reaction between acrylamide and epoxy resin. The absorption bands at 2926 cm^{-1} (characteristic absorption of —CH$_3$ and —CH$_2$—), as well as those at 2362 cm^{-1} (O—H stretch of the carboxylic group), 1724 cm^{-1} (C=O stretch of the carboxylic group), 1625–1450 cm^{-1} (characteristic bands of benzene ring), and characteristic absorption bands of the polymer based acrylate at 1451 cm^{-1}, 1161 cm^{-1}, 1384 cm^{-1}, 1242 cm^{-1}, 1161 cm^{-1}, 910 cm^{-1} are existed in this spectrum. However, the absorption bands at 3100–3000 cm^{-1} ($v_{=CH}$), 1680–1620 cm^{-1} ($v_{C=C}$) are absent in this coating, indicating that all of monomers have participated in the polymerization reaction. It is worthy to point out that the ether groups are higher polar functional groups, and when they are introduced into back-

TABLE I
Formulation of Acrylic Resin

Compositions	wt %	Compositions	wt %
AA	2–4	AAm	1–2
2-EHA	5–7	BPO/g	1.2 + 0.2 × 2 + 0.4
BA	30–35	Solvent:	
HPA	10–16	BCS	28.6
St	35–45	S-150	71.4
MMA	0–6		

Figure 1   Infrared spectrum of the prepared resin.

bone structure of the coating will improve the adhesion between the coating and metal substrates. Thus, the adhesion performance can be enhanced remarkably.

Effect of acrylic acid

Acrylic acid amount can notably affect the resin performance. The effects of AA amount on the coating properties are shown in Figure 2. With the increase of AA amount from 2.0 to 4.0 g, the impact resistance of coating is improved. This can be ascribed to the fact that with an increase in AA amount, the active points present in the thermosetting resin and can react with epoxy resin, are more, resulting in higher crosslinking density, thus enhancing the impact resistance of the coating. However, an excessive AA amount will result in a strongly glutinous resin which can easily turn into gel. Besides, after high temperature boiling (*ca.* 129°C/30 min), the cupping part of the coating will exfoliate severely [as seen in Fig. 3(d)]. On the other

hand, with decreasing the AA amount, the boiling resistance will become excellent. But in this coating, the active points could react with epoxy resin are insufficient, inducing the impact resistance to get worse, and the appearance of this resin presents rather poor transparence. From the analysis above, AA amount in the range of 2.8–3.0 g will balance the inconsistencies in boiling resistance and impact resistance, and thus a value of 2.8 g was selected for further study.

Effect of 2-ethylhexyl acrylate

Flexibility is an important property of a coating when fabricating the coating into final shape. 2-Ethylhexyl acrylate, as one component, can observably improve the flexibility of a coating. Figure 4 shows the effects of the percent of 2-EHA between BA and 2-EHA on the properties of coating. It can be seen that with increasing the 2-EHA wt %, the impact resistance was improved, whereas the solvent resistance decreased.

TABLE II
Comparison of the Properties of the Coating for Mechanical Blend and Chemical Grafted Resins

| Comparison items	Mechanical blend resin	Chemical grafted resin
Appearance	Turbid, opacity, easily demix	Homogeneous, transparent, limpid
Dried film	Turbid	lucency
Combine with the amino resin	Bad mutual solubility	Excellent mutual solubility
Film dried	Poor gloss and mechanical properties	Excellent gloss and mechanical properties
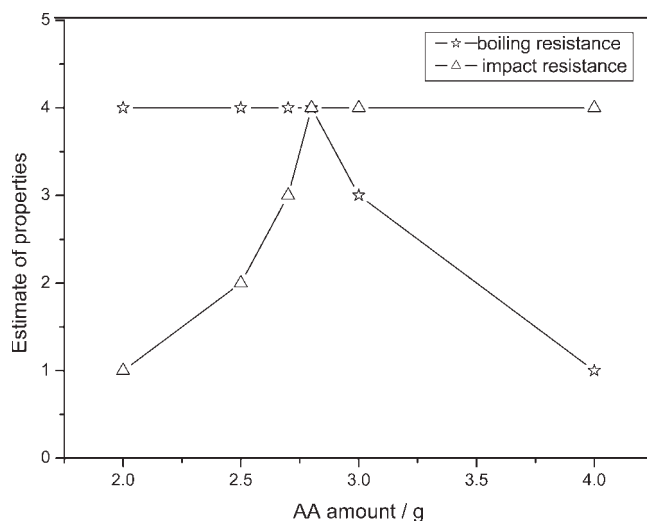
Figure 2 Effect of AA amount on the coating properties. Estimate of properties was in the order of 4 (excellent), 3 (good), 2 (fair), and 1 (poor). It is the same with these estimated criteria hereinafter.

Moreover, the resin in our experiment turns opaque gradually and the solids content decreases slightly. These phenomena can be attributed to that with an increase in 2-EHA wt % between BA and 2-EHA, the flexibility of coating gets improved, but due to the poor polarity of mixture solvents, the 2-EHA is not well compatible, therefore leading the appearances of
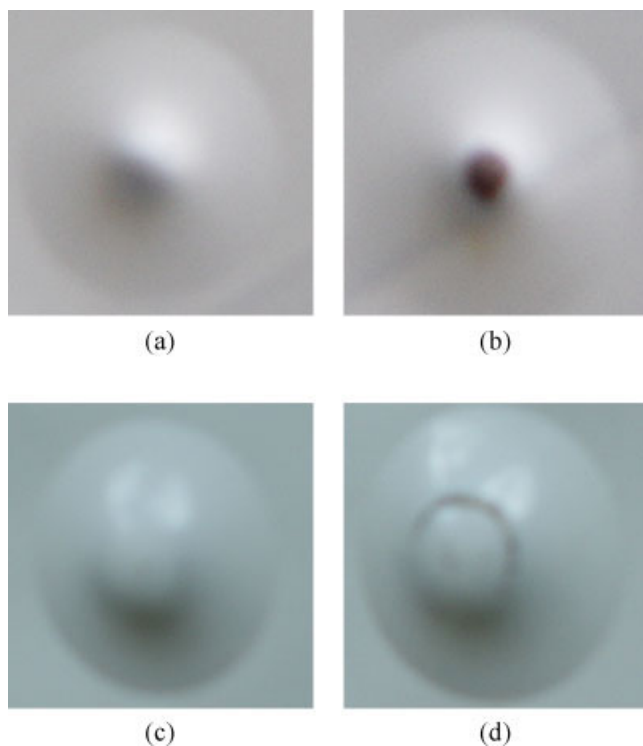
Figure 3 Snaps of impact resistance and boiling resistance after cupping. Impact resistance is excellent (a) and is poor (b, detected using CuSO$_4$ solution); after cupping, boiling resistance (ca. 129°C/30 min) is excellent (c) and is poor (d).
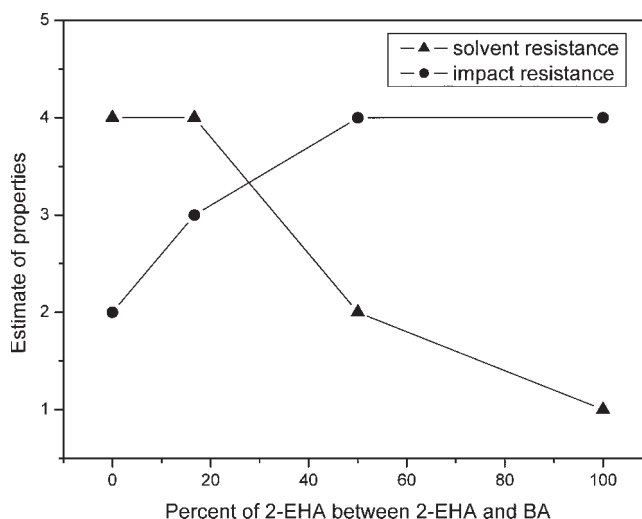

Figure 4 Effect of percent of 2-EHA between 2-EHA and BA on the coating properties.

final resin and coating opaque. To improve these properties, it is necessary to increase the amount of polar solvent BCS to improve the compatibility, and accordingly increasing the cost of the resin prepared. For further study, 16.7% was chosen as percent of 2-EHA between BA and 2-EHA.

Effect of hydroxypropyl acrylate

Hydroxypropyl acrylate was generally supplied hydroxyl into polymer to provide hardness and crosslinking degree, in addition, HPA was also used to facilitate the polymerization of monomers, reduce the polymerization time and decrease the interaction of remnant monomers. The higher the hydroxyl content is, the larger the crosslinking density of the coating is. It benefits the coating in hardness and gloss retention.
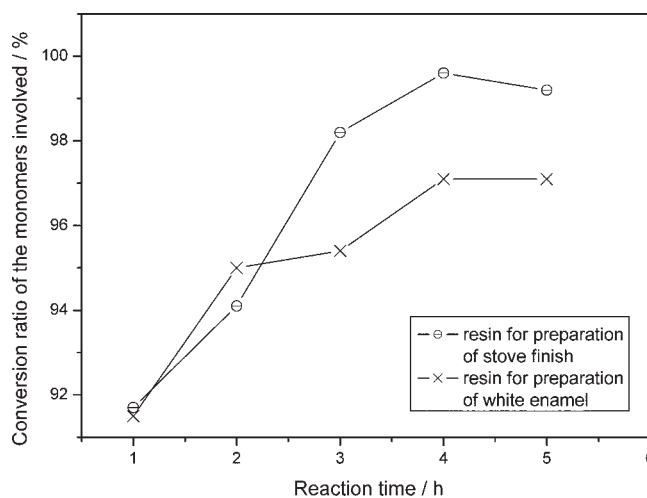
Figure 5 Effect of polymerization time on the conversion ratio of monomers involved. Reaction time on x-axis is relative to second addition of BPO.

TABLE III
Effect of Amino Resin on the Coating Properties

Samples	Solvent resistance	Adhesion	Cupping	Impact resistance I[a]	Impact resistance II[b]
1#	1	4	4	4	4
2#	2	4	3	4	3
3#	3	4	3	4	3
4#	4	4	1	4	1

[a] and [b] denote the impact resistance before and after boiling, respectively. And the samples experience an impact of 50 cm. AR-Me was used as curing agent. From 1# to 4#, the weight percent was 2%, 4%, 6% and 9%, respectively.

For Figures 2 and 4, the properties estimate was in the order of 4 [excellent, that is, the coating remained unchanged after being tested, as seen in Fig. 3(a,c), 3 (good), 2 (fair), and 1 (poor, that is, the coating was damaged or exfoliate strongly, as shown in Fig. 3(b,d)]. It is the same with these estimated criteria hereinafter.

Effect of polymerization time on the conversion ratio of monomers

Polymerization time can remarkably affect the conversion ratio of monomers and the effects are shown in Figure 5. The conversion ratio of monomers was important for resins and final performance of coating. In the presence of BPO as initiating agent, with the prolonged reaction time, the conversion ratio of monomers increased. When the BPO was added thirdly, the conversion ratio of monomers could reach to 99.6% and 97.1% for resins to prepare stove finish and white enamel, respectively. So, when the BPO was added thirdly, aging for 2 h was proper to obtain a satisfactory conversion ratio of monomers.

Effect of epoxy resin

The influences of molecular weight of epoxy resin are apparent on coating properties. Epoxy resin with a lower molecular weight shows a higher reactivity, an outstanding transparence and can be easily modified,

but the reaction with it is not steadily, it is easy to become glutinous and the coating obtained is brittle. Epoxy resin with a higher molecular weight possesses a lower reactivity and is difficult to be modified, but the impact resistance well exceeded that of the resin with a lower molecular weight. In this work, the moderate molecular weight epoxy resin Shell 1001 (epoxy value: 0.20–0.22) was selected.

To obtain the optimal coating, the effect of epoxy resin Shell 1001 on the coating properties was investigated in the range of 0–6.3 g when the acrylic resin was fixed at 20 g. The tested results revealed that with a weight ratio of acrylic resin (55 wt % of solids content) to epoxy resin 1001 (50% wt % of solids content) of 20:2.8, the excellent coating was reached. So, this weight ratio was chose in our further study.

Effect of amino resin

Amino resin, as a crosslinking cure agent in the coating, is also important. In our study, three amino resins: amino resin etherified with methanol (AR-Me), amino resin etherified with butanol (AR-Bu) and amino resin substituted with phenyl were introduced into the coating. Firstly, AR-Bu was rejected because of its self- polymerization and poor balance between hardness and flexibility after curing. And when other two amino resins were used alone, the comprehensive properties could not satisfy the demands required. So, AR-Ph with an excellent water resistance due to exis-

TABLE IV
Influence of Amount of the Catalyst on the Properties of the Coating

Amount of catalyst[a]	Solvent resistance	Adhesion	Cupping	Impact resistance I[b]	Impact resistance II[c]
0.30%	4	4	1	4	2
0.06%	4	4	3	4	4
0.04%	4	4	4	4	4
0	4	4	4	2	2

[a] The amount of the catalyst is the percent of the total weight.
[b] Represent the impact resistance before boiling; the samples experience an impact of 50 cm.
[c] Represent the impact resistance after boiling.

TABLE V
The Comprehensive Performances of the Grafted Acrylic Resin Coating

Detection items	White enamel	Stove finish	Test standards[a]
Coating appearance	White, lucency	Buff, transparent	ASTMD1729
Solid content (resin)/%	≥50	≥50	ASTMD2369
Adhesion/grade	≤1	≤1	ASTMD3359
Fineness/μm	<10	/	ASTMD1210
Viscosity/s	160–170	80	ASTMD4287
Solvent resistance	Excellent	Excellent	ASTMD5402
Blocking resistance	Excellent	Excellent	ASTMD3003
Repeating baking	Excellent	Excellent	ASTMD2454
Abrasion resistance	Good	Good	ASTMD5178
Pencil hardness	2H–3H	3H–4H	ASTMD3363
Impact resistance/cm	≥50	≥50	ASTMD2794
Cupping/mm	>6.5	>6.0	ASTME643

[a] Referenced test standards.

tence of aromatic ring, in combination with AR-Me with better weatherability, was recommended. The effects of amino resin on the coating properties were listed in Table III.

From Table III, it can be seen that with increasing amino resin, solvent resistance of the coating was improved, but boiling resistance decreased. This result may be attributed to an increase of crosslinking points, leading an increase of crosslinking density. Furthermore, with increasing of amino resin amount from 1 to 4, the pencil hardness was also improved. In our study, the weight percent of 6% amino resin was recommended.

Catalyst

The catalyst derivatived from sulfonic acid was employed in this work, which can catalyze effectively the crosslinking reaction of amino resin with acrylic resin. Owing to the side effects of the sulfonic acid derivative as a strong acid existed in the enamel, the catalyst blocked with pyridine was used. It is found from experiment that the properties of coating using the blocked catalyst overweight those blocked before. The effects of catalyst on the coating were displayed in Table IV, from which it can be seen that the influence of catalyst on properties is evident. Along with an excessive of catalyst, the crosslinking density becomes higher, thus resulting in a decrease of the flexibility of cured clearcoats, which can be also supported by the study of Schwalm et al.[27] And because of the hydrophilicity of sulfonic groups, the boiling resistance gets worse. Whereas the catalyst amount is less, the crosslinking density is inadequate, inducing a poor impact resistance. To achieve the excellent coating, the amount of catalyst is within the range of 0.04–0.06 wt %.

The total performances of the coating are listed in Table V. It is found that the comprehensive performances are satisfactory and can applied as metallic can coating.

CONCLUSIONS

A novel manufacturing process for high performance metallic can coating was carried out based on an epoxy-grafted acrylic resin. The effects of the monomers, the amounts of grafted resin, the amount of amino resin, and the amount of blocked catalyst, etc on the properties of coating were investigated. And according to the standards of ASTM, the properties demanded were tested and the high comprehensive performance for metallic can coating was obtained. Varying the monomers composition, the resin with different characteristics can be attained. The target resin coating provides excellent physical and mechanical properties, and can be promising as the metal package materials.

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