

Preparation of Epoxy Resin/CaCO₃ Nanocomposites and Performance of Resultant Powder Coatings

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ABSTRACT: Epoxy resin/CaCO₃ nanocomposites were prepared by the methods of extruding, solution blending, and *in situ* and inclusion polymerization, respectively. The contents of nanoparticles in the nanocomposites were varied from 5 wt % to 15 wt %. Powder coatings with different content of nanoparticles were made from the nanocomposites. The results showed that the cupping property and impact resistance decreased with the increase of coating film thickness. The dispersion of nanoparticles in epoxy matrix affected the impact resistance and cupping property of the

obtained coating films greatly. The coating films made from the nanocomposite prepared by *in situ* and inclusion polymerization showed that the best impact resistance and the maximum cupping property was achieved when nano-CaCO₃ content was 5 wt %. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2656–2660, 2006

Key words: epoxy resin; impact resistance; nanocomposite; coatings; CaCO₃; performance; cupping property

INTRODUCTION

Owing to their environmental and economical advantages and excellent coating properties, the application of powder coatings are not only limited to metal substrates but also extended to wood furniture, paper coatings, and coatings for plastics.¹ Epoxy powder coatings are most widely used with respect to their distinguished properties such as corrosion resistance, dielectric properties, and mechanical properties. However, they also have demerits, the most serious of which is the lack of toughness after cured because of the brittleness of cured epoxy resin matrix. The lack of tenacity of epoxy powder coatings has prevented them from applications in many fields. And the effective method to improve the toughness of the epoxy powder coating is to improve the toughness of the epoxy resin. So toughness improvement of epoxy resin for epoxy powder coatings is of great importance. Many materials such as rubber elastomer, thermoplastic resin,² liquid crystalline epoxy, and nanoparticles were introduced into epoxy matrix to improve its toughness.^{3–8} Many researches showed that the addition of rigid nanoparticles could improve not only the toughness but also the strength of the obtained nanocomposites. Zheng et al.⁴ prepared epoxy

resin/SiO₂ nanocomposites by solution blending and the resultant epoxy resin showed a remarkable increase of impact resistance. Many researches have been performed on epoxy/montmorillonite systems.^{9–12} Isik et al.¹³ prepared epoxy/montmorillonite nanocomposites and they found the resultant composites showed best tensile strength and strain at break when the dosage of montmorillonite was 1 wt %. Adam et al.⁹ found the fracture toughness of intercalated epoxy/clay nanocomposites valued of 100% over unmodified resin and it was related to the clay morphology of the system demonstrated by the fracture-surface topology of scanning electron microscopy and atomic force microscopy results. However, most of the reported epoxy nanocomposites were obtained as cured materials especially for epoxy/clay systems. Though the resultant nanocomposites showed excellent properties, reprocess could hardly be performed and the applications are greatly limited.

In this article, we prepared uncured epoxy resin/CaCO₃ nanocomposites through *in situ* and inclusion polymerization and applied them to powder coatings.¹⁴ Impact resistance and cupping properties of the resultant nanomodified powder coatings were significantly improved.

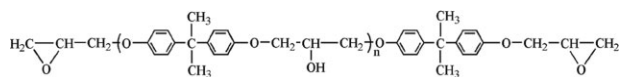
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EXPERIMENTAL

Materials

Bisphenol A was purchased from Nippon Steel Chemical (Japan). Epichlorohydrin was analytical grade and



Scheme 1 Structure of E-12 epoxy resin.

obtained from Shanghai Wulian Chemical Plant (Shanghai, China). Nano-CaCO₃ was produced by Nanomaterials Technology (Beijing, China). Hardener M68 was a salt of organic polycarboxylic acid with a cyclic amidine purchased from Huangshan Huamei Fine Chemical (Anhui, China). And E-12 epoxy resin was a diglycidyl ether of bisphenol A (the structure is shown in Scheme 1) with epoxy equivalent 775 and was produced by Huangshan Huizhou Hengyuan Chemical (Anhui, China). All the materials were used as received.

Preparation of epoxy resin/CaCO₃ nanocomposites by extruding

Nano-CaCO₃ and E-12 epoxy resin were mixed and extruded on a SY-II-40 twin screw extruder (manufactured by Xiangtan Powder Coating Machine Factory in Hunan Province, China) at 120°C.

Preparation of epoxy resin/CaCO₃ nanocomposites by solution blending

E-12 epoxy resin was dissolved in acetone, and then nano-CaCO₃ was added and dispersed by mechanical stirring and ultrasonic (with 160 w power-output) at 25°C for half an hour. Then the system was heated to 140°C gradually and vacuum was applied at 0.1 MPa to remove the solvent.

Preparation of epoxy resin/CaCO₃ nanocomposites by *in situ* and inclusion polymerization

Bisphenol A was dissolved in NaOH solution, and then nano-CaCO₃ was added in. The system was treated with mechanical stirring and ultrasonic (with 160 w power-output) for 30 min at 70°C. After the system was cooled to 47°C, epichlorohydrin was added. Then, the system was gradually heated to 90°C in 2 h. After reaction, the product was washed by hot water till no Cl⁻ could be detected in the eluate. The resultant composite was dehydrated at 150°C and 0.1 MPa. The preparation route is shown in Figure 1.

Preparation of epoxy powder coatings and coating films

The preparation process of epoxy powder coatings and the corresponding coating films were shown in Figure 2. The ratio of epoxy resin in the powder coating was 63% and the hardener was 4.5%. Certain

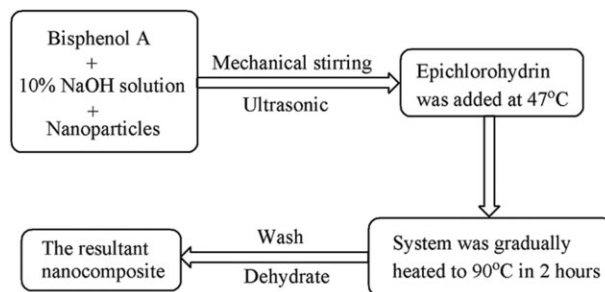


Figure 1 Preparation of epoxy resin-CaCO₃ nanocomposites.

amount of pure epoxy resin was added in to adjust the concentration of nanoparticles and the fillings was reduced according to the amount of nano-CaCO₃. Epoxy powder coating without nano-CaCO₃ was made as blank.

Measurement and characterization

The size of nanoparticles and the dispersion of nano-CaCO₃ in the resultant composites were observed on transmission electron microscopy (TEM, JEM200CX, JEOL).

Impact resistance test was performed according to ISO 6272-2:2002 on a QCJ impact tester manufactured by Zhonghuan Testing Instruments.

Cupping test was performed according to ISO 1520:1999 on a TCB Cupping Tester manufactured by Shanghai XianDai Environment Engineering Technique.

RESULTS AND DISCUSSION

Dispersion of nanoparticles in the resultant composites

Good dispersion of nanoparticles in the polymer matrix is a decisive factor in improving the properties of the corresponding nanocomposites. The nanocomposites containing 15 wt % nanoparticles prepared by extruding, solution blending, and *in situ* and inclusion polymerization were observed on TEM. The TEM photos are shown in Figure 3.

The original nano-CaCO₃ particles are small cubes with a size of 40~50 nm as Figure 3(a) shows. Figures 3(b) and 3(c) are TEM images of nanocomposites prepared by *in situ* and inclusion polymerization, solution blending, and extruding, respectively. It can be

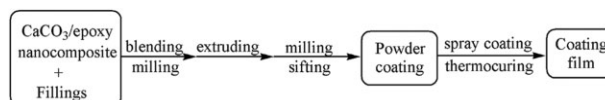


Figure 2 Preparation of powder coating and coating film.

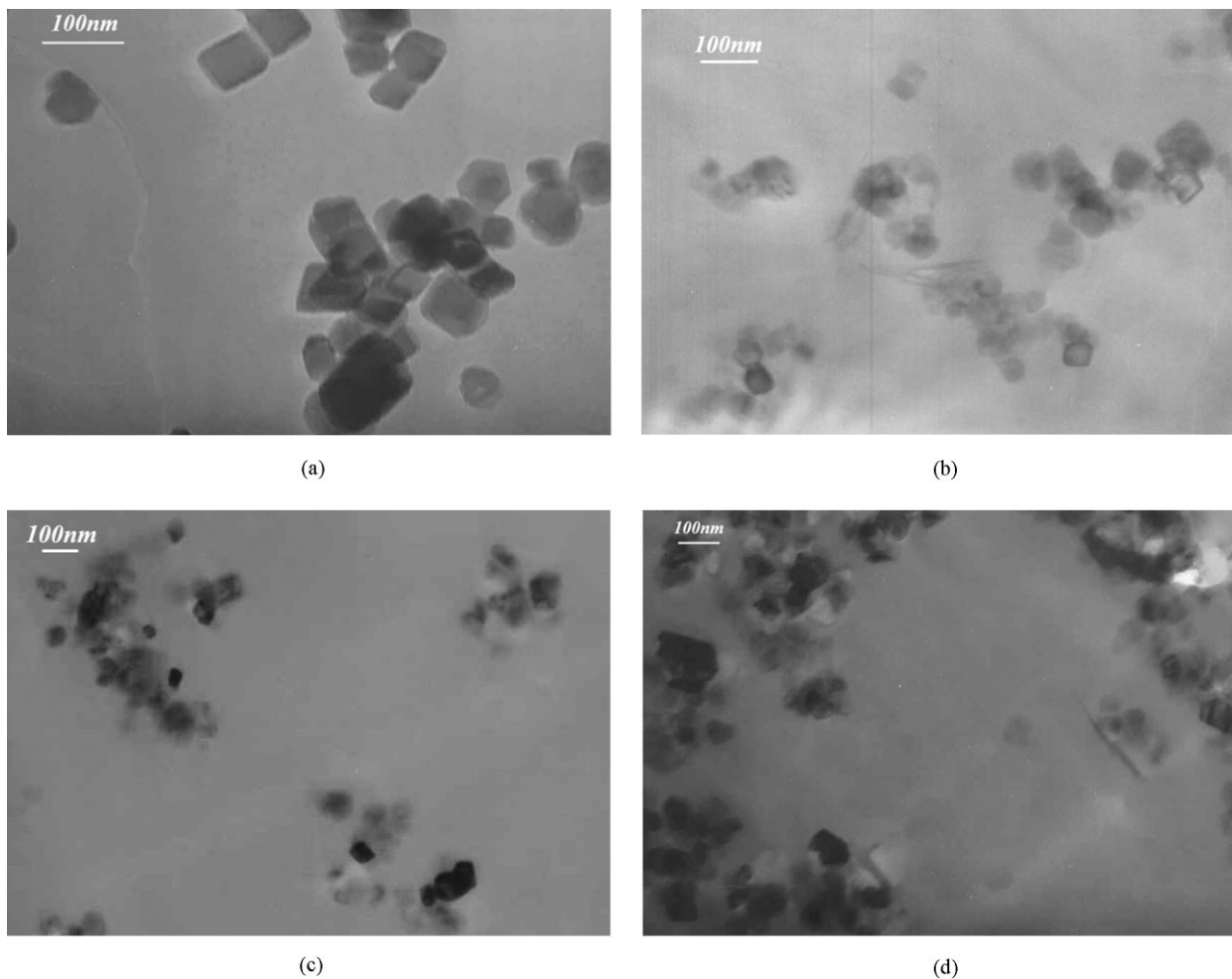


Figure 3 TEM images of (a) nano- CaCO_3 particles dispersed in $\text{CH}_3\text{CH}_2\text{OH}$, (b) composite prepared by *in situ* and encapsulating polymerization, (c) composite prepared by solution blending, and (d) composite prepared by extruding; the scale bar is 100 nm.

found that in composites prepared by extruding, most nano- CaCO_3 particles agglomerated and formed larger groups with a diameter more than 500 nm. This size is nearly the same of common fillings. Particles in composites prepared by solution blending agglomerated more slightly than in that prepared by extruding. But most of the particles still formed large groups with a size of 200~300 nm. The TEM image of nanocomposite prepared by *in situ* and inclusion polymerization shows the best dispersion of nano- CaCO_3 . Most of the nano- CaCO_3 particles dispersed in the epoxy matrix separately with a size of 40~60 nm.

Impact resistance of coating films

The thickness of coating film greatly affects the impact resistance as shown in our experiment results, so the influence of thickness to the impact resistance was studied. The results are shown in Figure 4.

We can find that the impact resistance decreased fast with the increase of film thickness in Figure 4. Because the cured epoxy coating films were lack of

toughness, the resultant films are harder to be deformed with the increase of thickness and resulted in the less impact resistance. So impact resistance of dif-

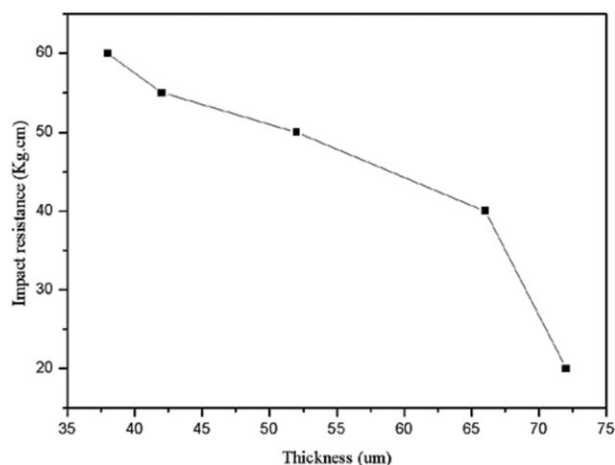


Figure 4 Relation between impact resistance and thickness of the coating film.

TABLE I
Impact Resistance of Powder Coatings Containing Different Nanocomposites

Preparation method of nanocomposite	Content of nanoparticles in powder coatings	Film thickness (μm)	Impact resistance (kg cm)
<i>In situ</i> and inclusion polymerization	3.1%	60	60
Solution blending	3.1%	56	45
Extruding	3.1%	55	30
Blank	0	56	40

ferent powder coating films can be compared only at the similar film thickness. For coating films applied to the substrate are usually ranging between 50 μm and 70 μm in real use, films with thickness about 60 μm were chosen to study the influence of different nanoparticle dispersion on the resultant film impact resistance and film without nanoparticles was used as blank. The results are shown in Table I.

It can be found from Table I that with respect to the impact resistance of the blank, approximately 50% increase in impact resistance was achieved in the powder coating with nanocomposites prepared by *in situ* and inclusion polymerization. And the impact resistance of the solution blended sample was also slightly higher than the blank. The reason is that the well-dispersed nano-CaCO₃ particles can form large amount of craze at the interface between nanoparticles and the matrix when the film was impacted, the impact energy could mostly be absorbed and the toughness of the film was improved. However, powder coating containing composite prepared by extruding had the lowest impact resistance, and it was even lower than the blank. As shown in Figure 3, nano-CaCO₃ in the composite prepared by extruding agglomerated badly and acted as stress concentrators when impacted, which resulted in the decrease of impact resistance.

Cupping property of coating films

Since the cured epoxy coating films is short of toughness as the impact resistance test showed, the thickness of film also greatly affects the cupping property. And the influence of thickness on the cupping property was studied to compare the influence of nano-CaCO₃ contents on the cupping properties. The results are shown in Figure 5.

Because the powder coating with nanocomposites prepared by *in situ* and inclusion polymerization showed the best impact resistance, we investigated the relationship between nano-CaCO₃ content and the cupping property of the resultant coating films con-

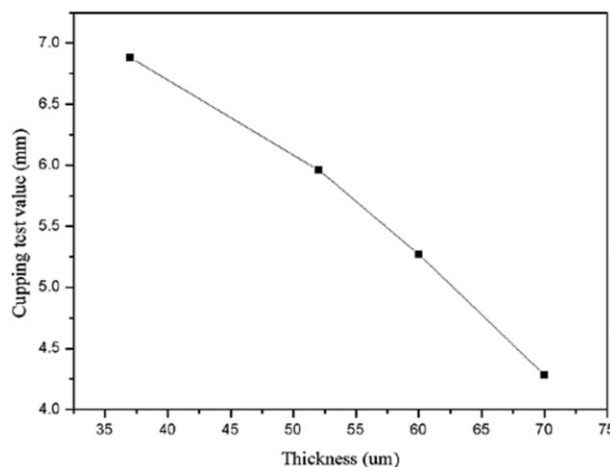


Figure 5 Relation between cupping property and thickness of the coating film.

taining this kind of nanocomposite. The results are shown in Figure 6.

From Figure 6, we can see that the cupping properties increased with the increase of nano-CaCO₃ content and reached a peak value at 5 wt %, above which it decreased gradually. The main reason for the results was also the influence of dispersion of the nano-CaCO₃ in the resin matrix. The well-dispersed nano-CaCO₃ can form craze when the film was deformed and consumed the energy; however, when nano-CaCO₃ content was above 5 wt %, some of them agglomerated and act as stress concentrators when the coating film was deformed, which resulted in the decrease of cupping property.

CONCLUSIONS

Toughness of the powder coating films were remarkably improved when nano-CaCO₃ was introduced

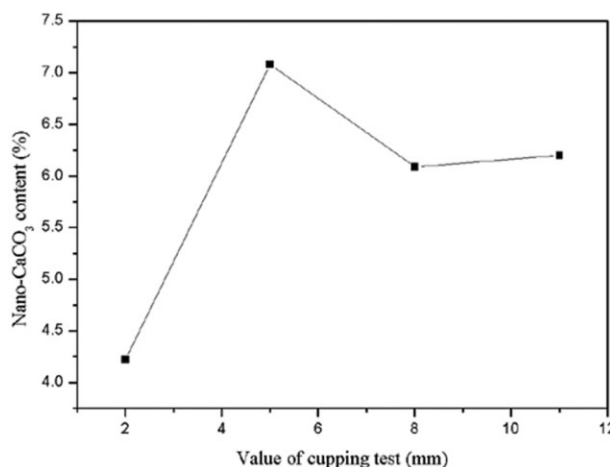


Figure 6 Cupping property of powder coating film (thickness = 40 μm) with different nano-CaCO₃ content

into the epoxy resin by *in situ* and inclusion polymerization. The results showed that the properties of nano-CaCO₃ modified powder coatings depended critically on the dispersion of nanoparticles in the resin matrix and they may even weaken the properties if were not well dispersed. Among the three nanocomposites obtained by different methods, the most satisfying properties of powder coating were achieved with the nanocomposite prepared by *in situ* and inclusion polymerization. The impact resistance of the obtained coating films containing 3.1 wt % nano-CaCO₃ was improved approximately 50%, and the cupping property also showed a distinct improvement.

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