



Article Studying the Influence of Mica Particle Size on the Properties of Epoxy Acrylate/Mica Composite Coatings through Reducing Mica Particle Size by the Ball-Milled Method

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Abstract: In this work, a series of epoxy acrylate (EA)/mica composite coatings were synthesized through introducing mica powders of different particle size into epoxy acrylate coatings and using an ultraviolet (UV) curing technique to investigate the influence of mica particle size on the coatings. Mica powders of different particle sizes were obtained by ball-milling for 4, 8, 12, 16, and 20 h with a planetary high-energy ball mill. The particle size and morphologies of ball-milled mica powders were characterized by laser particle size analyzer and scanning electron microscopy (SEM). The results indicated that planetary ball-milling reduced the particle size of mica powders effectively. Mica powders that were un-ball-milled and ball-milled were added into the epoxy acrylate matrix by a blending method to synthesize the organic-inorganic UV curable coatings. The optical photographs of the coatings showed greater stability of liquid mixtures with smaller particle size fillers. The chemical structures of EA/mica composite coatings were investigated by Fourier transform infrared spectroscopy (FTIR), and the conversion rate of C=C bonds was calculated. The results indicated that the C=C conversion of coatings with mica powders of smaller particle sizes was higher. Tests of mechanical properties and tests using electrochemical impedance spectroscopy (EIS) showed that pencil hardness, impact resistance, and coating resistance were improved due to the reduction of mica powders particle size.

Keywords: mica; ball-milled; particle size; UV curable coatings

1. Introduction

Ultraviolet (UV) curing, as a way to synthesize polymer composite coatings, has been extensively investigated owing to its advantages such as no volatile organic compound emission, low energy consumption, and ultrafast curing rate [1]. The UV curable coatings are generally composed of multifunctional monomer, reactive diluent, photoinitiator, and other auxiliaries [2–4]. In addition, inorganic particles are added to UV curable coatings to obtained composite coatings with enhanced mechanical properties. UV curable composite coatings with inorganic fillers generally show unique and versatile properties [5,6].

It is generally recognized that the sort, quantity, size, and surface features of fillers can affect the performance of composite coatings [7,8]. Much work has been done to study the effect of quantity and surface modifications on properties of UV curable epoxy acrylate (EA) coatings by Javidparvar et al. [8], Wang et al. [9], Yari et al. [10], and Ingrosso et al. [11], and to investigate the difference in homogeneity and mechanical properties of composite coatings with micrometer and nanometer ceramic particles [7]. Little attention has been given



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). to the influence of filler particle size in UV curable coating systems. Wang et al. [12] synthesized fast- curing ultraviolet light emitting diode (UV-LED) polymer materials with different particle size talcum powder, and the results showed that materials filled with smaller size talcum powder showed superior surface/mechanical performance. Yang et al. [13] prepared UV curable matting composites using different particle size micron silica matting agents. The study showed that smaller particle size related to lower gloss and stronger hydrophobicity of coatings with the same content. However, the effect of filler particle size on the curing process and properties of photocurable materials in this study is not described in sufficient detail. There should be more detailed studies about the effect of particle size on the curing process and properties of photocurable coatings.

The incorporation of layered silicate into polymer matrices has resulted in significant improvements in tensile strength, barrier protection, and thermal stability [9,14,15]. Mica is widespread in the natural environment. As an easily obtained layered silicate mineral, mica has attracted great attention because of its unique electric insulation, chemical durability, thermal stability, and lack of toxicity [16,17]. Many studies have been reported for mica applications in different polymer matrixes due to its superior performance in enhancing the properties of coatings [18–20]. Combined with polymer coatings, mica can strengthen corrosion resistance as an anticorrosive component, improve mechanical properties including compressive strength and yield strength, and enhance electrical insulation and thermal stability of composite materials [21–26]. Wang et al. [20] prepared a hydrophobic coating of mica particles and polypropylene by copolymerization and the result indicated that the composites had great quality compatibilities and mechanical properties. Xia et al. [26] synthesized low density polyethylene (LDPE)/mica composite coatings with enhanced sound insulation and improved mechanical properties compared to the conventional composites. Most of the polymer/mica composite coatings are synthesized by the heat curing method. A distinct disadvantage of heat curing is the production of volatile organic compounds. In contrast, the polymer/mica composite coatings prepared by the environmentally-friendly UV curing method can be fast cured and have no emission of volatile organic compounds. To our knowledge, there are few investigations on mica as a filler in UV curable coating systems. Gao et al. [27] prepared a series of UV curable coatings containing different content of mica, and the results showed that mica provided positive effects on the mechanical properties and thermal stability of coatings. Cheong et al. [28] synthesized and characterized the delaminated muscovite mica/UV coating and obtained coatings with advanced anticorrosive properties. However, the influence of mica as filler on coatings was not studied in detail, and the effect of mica size on coating was not considered.

In this work, a series of UV curable EA/mica composite coatings was synthesized and the effect of mica particle size on the coatings was investigated. The mica powders were ball-milled to obtain different particle size mica and the effect of ball-milling time on mica powders was investigated. The influence of mica particle size on the stability of liquid mixtures was explored. The morphologies, particle size, and structures of mica powders were characterized by scanning electron microscopy (SEM), laser particle size analysis, and X-ray diffraction (XRD). The morphologies, chemical structures, and electrochemical performance of the coatings were investigated by SEM, Fourier transform infrared spectroscopy (FTIR), and electrochemical impedance spectroscopy (EIS). The mechanical properties of the coating were measured in accordance with the corresponding standard test methods.

2. Experimental

2.1. Materials

Epoxy acrylate, as a photosensitive oligomer, was purchased from Jiang-men everray Co. Ltd. Tripropylene glycol diacrylate (TPGDA, 99.99%), as a reactive diluent, was obtained from Allnex (Shanghai, China) Co., Ltd. Triethanolamine (TEA, 78%) (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), benzophenone (BP, 99.99%) (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and 1-hydroxycyclohexyl phenyl ketone (Irgcure184, 98%) (Shanghai Aladdin Biochemical Technology Co. Ltd., Shanghai, China) were used as photoinitiators. Mica powder, as an inorganic filler, was the muscovite purchased from Hebei Jinglong mining Co. Ltd. (Shijiazhuang, China). The 3-(trimethoxysilyl)propyl methacrylate (KH-570, 98%) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2.2. Sample Preparation

2.2.1. Ball-Milling of Mica Powders

20 g mica powder and 40 mL absolute ethyl alcohol were placed into a 250 mL zirconia jar with 200 g zirconia balls (Φ 10 mm). These materials were mixed by a planetary highenergy ball mill (Pulverisette 4, Fritsch GmbH, Idar-Oberstein, Germany) at the disk speed of 300 r/min and the rotation-to-revolution speed ratio of -1.5. The slurries with balls were sifted through a 10-mesh sieve. After removing the balls, the obtained slurries were dried at 60 °C for 24 h.

2.2.2. Preparation of EA/Mica Composite Coatings

The formulations of the UV composite coatings used in this study are listed in Table 1. First, the solid BP, Irgcure184, mica powders, and KH-570 were added to the TPGDA solutions. The mixture was dispersed for 30 min by the ultrasonic cleaner. Then TEA and EA were added in sequence. A homogeneous coating was obtained after being dispersed in a high-speed homogenizer for 60 min and in an ultrasonic cleaner for 30 min. The obtained samples with un-ball-milled and ball-milled for 4, 8, 12, and 16 h mica powders were labeled as S-1, S-2, S-3, S-4, and S-5, respectively. The resulting coatings were spread onto a glass slide or a thin steel sheet with an OSP coating rod (10 μ m, OSG System Products Corporation, Shenzhen, China). Finally, the wet films were cured by the UV curing machine (RW-UVAD301-501y, Shenzhen Run-wing Co. Ltd., Shenzhen, China) with the UV radiation intensity of 20 mW/cm² and curing time of 60 s. The process of the coating preparation is illustrated in Figure 1.

Table 1. Formulation of UV curable EA/mica coatings.



Figure 1. The process illustration of the coating preparation.

3. Characterization

3.1. Laser Particle Size Analysis

Particle size distribution is a good method to show the change of particle size during ball-milling. The particle size distribution of mica powders was measured by laser size analyzer (Master sizer 3000; Malvern, Egham, Britain).

3.2. Scanning Electron Microscopy

The morphologies of mica powder particles and EA/mica composite coatings were observed by Ultra Plus scanning electron microscopy (Zeiss Electron Microscope Co., Ltd., Oberkochen, Germany). The surfaces of the samples were sprayed with gold to make them conductive before observation.

3.3. Fourier Transform Infrared Spectroscopy

The chemical structures of the composite coatings were studied by Fourier transform interferometer (Nicolet iS50, Thermo Nicolet, Waltham, MA, USA). The liquid mixtures were coated on the KBr wafer, then the uncured and cured coatings were analyzed by FTIR. The scanning range was 4000 to 400 cm⁻¹.

3.4. X-ray Diffraction Analysis

X-ray diffraction analysis adopted a computer-controlled X-ray diffractometer (X'Pert PRO, PANalytical, Almelo, Netherlands) at a speed of 8°/min from 5° to 90° at a generator voltage of 35 kV and a current of 25 mA.

3.5. Mechanical Testing

Tests of pencil hardness, adhesion, flexibility, and impact resistance were employed to investigate the mechanical properties of the coatings. The wet films ($10 \mu m$) were coated on the 0.28 mm thick sheet of tinplate to test the impact resistance, and coated on the 0.8 mm thick sheet steel to test pencil hardness, adhesion and flexibility. The mechanical properties of coatings were measured according to the corresponding standard test methods including pencil hardness (ISO 15184:1998), adhesion (ISO 2409:2020), flexibility (ISO 1519:2002), and impact resistance (Chinese Standard GB/T 1732-2020).

3.6. Electrochemical Impedance Spectroscopy

The measurement of electrochemical impedance spectroscopy was recorded by Solartron SI1260/SI1287 (Solartron Metrology). A three-electrode system was adopted. The counter electrode and the reference electrode were a platinum plate and a saturated calomel electrode, respectively. A steel plate coated with UV-curable coatings was used as the working electrode. The electrolyte solution was 3.5 wt.% NaCl solution. The sinusoidal perturbation voltage was 20 mV, and the measured frequency range was $10^5 \sim 10^{-2}$ Hz.

4. Results and Discussion

4.1. Morphologies of Mica Powders

As shown in Figure 2, the particle size of mica powders exhibited an obvious decreasing trend with the increase in the ball-milled time. As shown in Figure 2a, the original size of mica powders was about 10 μ m without ball-milling. The particle size was significantly reduced after 4 h (Figure 2b), but the particle size distribution was not uniform, with particle size ranging from ~0.5 to ~10 μ m. Figure 2c shows the morphologies of mica powders ball-milled for 8 h. The number of particles larger than 5 μ m significantly decreased and most of the particles were below 2 μ m. After being ball-milled for 12 h, the mica powder particles became significantly smaller and more uniform, and most were less than 2 μ m (Figure 2d). There was a slight agglomeration, and some small particles were adsorbed on the surface of large particles (Figure 2e) when the mica was ball-milled for 16 h. This agglomeration was more obvious when the ball-milled time was 20 h (Figure 2f). The



particle size became larger and the powders showed a flake structure. Figure 2 shows the reduction of the mica particle size during the ball-milling progress.

Figure 2. Morphologies of un-ball-milled (**a**), and ball-milled 4 h (**b**), 8 h (**c**), 12 h (**d**), 16 h (**e**) and 20 h (**f**) mica powders.

4.2. Particle Size Distribution of Mica Powders

Figure 3 shows the changes of the particle size distribution (Figure 3a) and average particle size respective to the ball-milled time; the changes of D_{10} , and D_{90} are shown in the inserts (Figure 3b). It was clearly shown that with the increase in ball-milled time, the peak of particle size distribution firstly moved to a smaller size region and then shifted back to a larger size region (Figure 3a), and D_{10} and D_{90} showed a tendency of decrease followed by an increase (Figure 3b). D_{10} , D_{90} , and average particle size decreased more steeply from un-ball-milled to ball-milled time of 4 h. Average particle size and D_{10} increased after dropping slowly from ball-milled time of 4 to 20 h. D_{90} approached a plateau from milling time of 4 to 16 h and had a great increase from 16 to 20 h. The increase of D_{10} , D_{90} , and average particle size suggested agglomeration, and it was verified as shown in Figure 2e,f. The results suggest 12 h may be the most suitable ball-milling time for obtaining the smallest and low agglomeration powders.



Figure 3. Particle size of mica (**a**) Particle size distributions, (**b**) average particle size of mica at different ball-milling times, and (**c**) the relationship of D_{10} and D_{90} with the milling time.

Due to the violent agglomeration of mica powder after ball milling for 20 h, only 0~16 h ball milling samples were chosen for the following experiments.

4.3. XRD Analysis

Figure 4 shows the XRD spectrum of un-ball-milled mica powders and powders ball-milled for different times. All diffraction peaks of mica powders corresponded to the muscovite in the JCPDS card. The intensity of mica powder's characteristic diffraction peaks gradually decreased, the peaks of ball-milled mica products broadened, and even part of the diffraction peaks disappeared. This indicated that the particle size of mica was reduced with the increase in ball-milling time, and that the amorphous mica crystal gradually appeared. Combined with Figure 2, the particle size of mica was reduced and the layered structures were destroyed during the high-energy ball-milling process. The diffraction peaks of zirconia can be seen in the mica powder products after 16 h of ball-milling. This suggested that a small amount of zirconia in the ball-milled jar and balls was doped in the mica powders ball-milled products in the process of ball-milling.



Figure 4. X- ray diffraction diagrams of mica powders with different ball-milling time.

4.4. Stability of Liquid Mixtures

The uncured composite coatings with mica powders ball-milled at different times were obtained after homogenization. Figure 5 shows the digital photographs for these liquid mixtures placed at different times. The overall colors of the samples were different due to the different milling times. The coatings with mica powders un-ball-milled had higher transparency. The transparency of the coatings decreased visibly when the fillers were ballmilled mica powders. S-1, S-2, and S-3 were layered after being placed for 30 days. After being placed for 120 days, solid-liquid separation was more obvious in S-1, S-2, and S-3 and the upper layers were more limpid. However, the delamination of S-4 and S-5 was still not obvious. It was clear that the coatings with mica powders ball-milled 12 h or 16 h were more stable. It was speculated that the compatibility between fillers and epoxy acrylate coatings was improved because of the reduction of particle size [29–31]. The particle size of the mica powders was reduced by ball-milling, and the specific surface area of the mica powder particles with smaller particle size was larger. In the composite coatings, silane coupling agent KH-570 was added to improve the compatibility and dispersion between inorganic fillers and epoxy acrylate. Particles with larger specific surfaces bonded more to the silane coupling agent and had better compatibility with organic coatings [32–34]. The composite coatings where smaller particles were located were more stable because of their smaller gravity and larger specific surface area.

4.5. FTIR Analysis

The chemical structures of the composite coatings before and after being cured were checked by FTIR spectroscopy. Figure 6 shows FTIR spectra of the uncured S-4 and cured S-4. The characteristic absorption band at 1725 cm⁻¹ was attributed to the stretching vibration of C=O bonds [35]. The absorption peak at 1635 cm⁻¹ was C=C bonds linked to =C-H bonds at 810 cm⁻¹ [36]. The bands at 1100 and 834 cm⁻¹ were attributed to the *trans*-stretching and *cis*-stretching vibration of C=O-C bonds [37]. The spectra of cured S-4 show that the C=C bonds and =C-H bond were both almost absent, suggesting that the C=C bonds were consumed during the UV curing process. As shown in the FTIR spectra, the band intensity around 1100 cm⁻¹ of the curve for cured S-4 was increased since the stretching vibration of Si–O–Si bonds located at such wave numbers coincided with the stretching vibration of the original C–O–C bonds [10,38]. These facts indicated that Si–O–Si structures were formed in the composite coatings, and the coatings polymerized under the irradiation of ultraviolet light [8,36,37].



Figure 5. Digital photographs of the mixed coatings with different ball-milling times.



Figure 6. FTIR spectra of the uncured S-4 and cured S-4.

4.6. Conversion of C=C Bonds of Coatings

Figure 7 shows the FTIR spectra of uncured S-1, S-2, S-3, S-4, S-5 and cured S-1, S-2, S-3. S-4, S-5 in the range of 1800–1600 cm⁻¹. The characteristic bands of C=O at 1725 cm⁻¹ and the absorption peak of C=C bonds at 1635 cm⁻¹ were exhibited. The absorption peaks at 1635 cm⁻¹ almost disappeared after UV irradiation, and the C=C bonds had a blueshift due to the disappearance of the conjugation effect between C=C bonds and C=O bonds [39–41]. The C=O bonds were not affected after UV irradiation since the C=O bonds did not participate in the photopolymerization reaction. Herein, the stretching vibration of C=O bonds at 1735 cm⁻¹ was a suitable candidate as an internal standard to calculate the

conversion rate of C=C bonds [36,42,43]. The conversion rate of the C=C bonds equation is as follows:

$$Conversion = 100\% \times \left(1 - \frac{A_t S_0}{A_0 S_t}\right)$$
(1)

where A_0 , S_0 are the characteristic peak areas of C=C and C=O bonds in uncured coatings, respectively; A_t , S_t are the characteristic peak areas of C=C and C=O bonds in cured coatings, respectively.



Figure 7. FTIR spectra of coatings before and after being cured.

The conversion rate of C=C bonds of the coatings after curing was calculated as shown in Figure 8. It was shown that compared with the samples containing un-ball-milled mica powders, the C=C bonds conversion rate of samples with ball-milled mica powders was increased. The C=C bonds conversion rate of coatings with ball-milled 12 h mica powders was the highest (75.85%). The conversion seemed to relate to the average particle size of the mica powders since it was increased when the particle size of mica powders was reduced. There are two possible reasons for this [13,35,39,44]: one is that the coatings with smaller particle size fillers have better fluidity, and the resistance to chain growth in the reaction was less; the other is that mica can also absorb ultraviolet light, and it can be reasonably speculated that the crystal structures of mica were destroyed in the process of particle size reduction, which weakened the ultraviolet absorption ability of mica [19] and changed the conversion rate of the C=C bond. The shielding effect of mica to ultraviolet light is mainly related to two factors, including the polarized light effect of crystal and the interlayer reflection and interference-effect. The lamellar mica has a high degree of orientation in a film and is aligned in parallel in the matrix, which made it easier to produce a total extinction phenomenon [8,18]. The photons received by the photoinitiator are reduced due to the absorption of ultraviolet light by mica. The absorption of ultraviolet radiation decreased due to the crystal structure and the lamellar structure of mica being destroyed during the high energy ball-milling process. Thus, the efficiency of UV curing was increased after mica powders were milled.



Figure 8. Conversion rate of C=C bonds of coatings.

4.7. Morphologies of Coatings

The morphologies of the coatings modified by different ball-milled mica powders are shown in Figure 9a–e. As Figure 9 shows, the organic phase and inorganic phase had good compatibility in the coatings and no obvious phase separation can be observed. There were some large bulges on the surface of the coating with un-milled mica powders (Figure 9a) because the particles of un-ball-milled mica powders were large and raised on the surface. Figure 9b–e shows that the surface of coatings with ball-milled mica powders was smooth. As seen in Figure 9b–d, the mica particles were dispersed in the organic matrix uniformly without the agglomeration phenomenon. The agglomeration of mica particles is observed in Figure 9e. As with Figure 2e, mica powders agglomerated when ball-milled for 16 h. Even though the mica particles were treated by ultrasonic and homogenization methods during coating preparation, the mica particles did not disperse and continued to exist in the coatings as aggregates.

4.8. Mechanical Properties

The mechanical properties of the UV curable coatings were evaluated by pencil hardness, adhesion, flexibility, and impact resistance test. As shown in Table 2, the coatings with mica particles exhibited excellent flexibility and good adhesion. The flexibility of samples S-1, S-2, S-3, S-4 and S-5 was <2 mm according to the mandrel bend tests. The results of adhesion tests showed that the particle size of mica fillers had little effect on adhesion. There were small differences in hardness and impact resistance of UV curable coatings modified with different particle size of mica powders. The mica particle size of sample S-4 was the smallest and sample S-4 showed the greatest hardness and impact resistance. This is mainly because that mica particles with large particle size were more difficult to disperse evenly in the coatings and large particles and uneven dispersion were more likely to produce defects. The mechanical properties of coatings are also related to the double bond conversion rate. The coatings with higher double bond conversion have better mechanical properties. As a result, coatings with smaller mica particles presented better performances in hardness and impact resistance.





Figure 9. SEM micrographs of coatings with mica powders ball-milled for different times (**a**) 0 h, (**b**) 4 h, (**c**) 8 h, (**d**) 12 h, (**e**) 16 h.

Sample	Pencil Hardness	Adhesion	Flexibility (mm)	Impact Resistance (cm)
S-1	3H	1	<2	5
S-2	3H-4H	1	<2	10
S-3	3H-4H	1	<2	10
S-4	4H	1	<2	15
S-5	4H	1	<2	10

Table 2. Pencil hardness, adhesion, flexibility, and impact resistance of coatings.

4.9. EIS Analysis

(a)

20 µm

(c)

Figure 10a shows the Nyquist plots of the coatings immersed in 3.5 wt% NaCl solution for 1 h and the equivalent circuit model. The plots showed a large capacitive loop, which corresponded to one time constant. The inserted circuit in Figure 10a was introduced to fit the experimental data in which R_s is the solution resistance; C_c and R_c are the coating capacitance and the coating resistance, respectively [45–47]. The Nyquist plots of the coatings immersed for 24 h displayed a double capacitive loop, and the experimental data were fitted by the equivalent circuit model shown in Figure 10b, in which C_c is the capacitance, and C_{dl} is the double-layer capacitance; R_s and R_t are the solution resistance and the charge transfer resistance, respectively [45–47]. With the increase in immersion time, the solution gradually penetrated into the interior of the organic coatings, and the protective effect of the coatings was significantly reduced after immersion for 24 h. When the aqueous solution passed through the organic coating and reached the interface between the coating and the metal matrix, a corrosive microcell was formed at the interface. The bonding force between the coating and the metal matrix was destroyed and the interface structure was changed.



Figure 10. Nyquist plots of different coatings in 3.5% NaCl solution for immersion time of 1 h (**a**) and 24 h (**b**).

Electrochemical parameters fitted from EIS results of coated systems at different immersion times are shown in Table 3. The resistance of the coatings with added ballmilled mica powders was higher than that with un-ball-milled powders. The resistance of the coating increased with the increase in ball-milling time of the fillers when the samples were immersed for 1 h. However, the resistance and charge transfer resistance of the coatings with ball-milled powders were almost the same when the samples were immersed for 24 h, but far greater than the coatings with un-ball-milled mica powders. The metal substrate had been corroded, and the effect of particle size on the coating resistance had been greatly weakened at this time, and all samples except S-1 had similar protective power to the metal substrate. It suggested that composite coatings with ball-milled mica powders provided better protection to the steel sheet compared with coatings with un-ball-milled mica powders.

1 h	24	h	
$R_{\rm c} (\Omega \cdot {\rm cm}^2)$	$R_{\rm c} \ (\Omega \cdot {\rm cm}^2)$	$R_{\rm t}$ ($\Omega \cdot {\rm cm}^2$)	
4106	736	463	
6167	3743	3806	
7926	3311	3409	
11,800	3442	3404	
12,000	3423	3422	
	1 h R _c (Ω·cm ²) 4106 6167 7926 11,800 12,000	$\begin{tabular}{ c c c c c }\hline & 1 \ h & 24 \\ \hline R_c (\Omega \cdot cm^2$) & R_c (\Omega \cdot cm^2$) \\ \hline 4106 & 736$ \\ 6167 & 3743$ \\ 7926 & 3311$ \\ $11,800$ & 3442$ \\ $12,000$ & 3423$ \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c }\hline \hline 1 h$ 24 h$ \\ \hline R_c (\Omega\cdotcm^2$) R_c (\Omega\cdotcm^2$) R_t (\Omega\cdotcm^2$) \\ \hline 4106 736 463 \\ 6167 3743 3806 \\ 7926 3311 3409 \\ $11,800$ 3442 3404 \\ $12,000$ 3423 3422 \\ \hline \end{tabular}$

Table 3. Fitting electrochemical parameters of different immersion times.

Figure 11 shows the optical images of these samples before and after the EIS experiment. The coatings were transparent and smooth and there were no obvious differences between the samples before the EIS test (Figure 11a). After EIS tests, the surface of sample S-1 was obviously uneven (Figure 11b). The coating surfaces of samples S-2, S-3, S-4, S-5 were still smooth except that some small rusty spots were observed between the coating and the substrate (Figure 11b). When these samples were observed under an optical microscope, it was found that the corrosion of sample S-1 was obviously more violent than for other samples. Rusty spots were seen in all samples, indicating that the solution has passed through the coating and corroded the surface of the metal matrix. These results were consistent with the EIS test results. The rust spots of sample S-1 were larger than those of other samples which indicates that the composite coating with mica powders provides better protection to the metal matrix once again.



Figure 11. (a) Optical images of samples before electrochemical impedance spectroscopy test; (b) Optical images of samples after electrochemical impedance spectroscopy test.

5. Conclusions

UV-curable organic-inorganic coatings were prepared by introducing different sized mica powders as fillers. The mica powders were put into a high-energy ball mill and ground for different times to obtain powders with different particle sizes. SEM and laser particle size analysis results showed that ball-milling effectively reduced the particle size of mica powders. The most suitable ball-milling time for obtaining the smallest and low agglomeration powders was 12 h due to the increase of average particle size and agglomeration that appeared for ball-milling times of 16 and 20 h. The crystal structures of the mica powders were destroyed by ball-milling, according to XRD analysis. Composite coatings were prepared by adding ball-milled mica powders into epoxy acrylate through a blending method. The delamination of the liquid mixtures after standing for 120 days

showed that the stability of the composite coatings was related to the size of mica powders, and the coatings with a smaller size of mica powders had better stability. The chemical structures of the coatings before and after curing were studied by FTIR. The results showed that the reduction of particle size was beneficial to the conversion of C=C bonds. Mechanical properties tests suggested that the hardness and impact resistance of coatings was improved with the reduction of mica particle size. EIS results showed that the coatings with ball-milled mica powders had better protective performance than the coating with un-ball-milled mica powders.

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