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Synthesis and Characterization of Nanocomposite Hybrid Coatings Based on 3-Glycidoxypropyl-trimethoxysilane and Bisphenol A

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ABSTRACT

Organic-inorganic hybrids were prepared using 3-glycidoxypropyl-trimethoxysilane (GPTMS) and bisphenol A (BPA) as a cross-linking agent, via the sol-gel process. The cross-linking agent was used to prevent brittleness and the formation of cracks in hybrid coatings. Attenuated total reflectance infrared (ATR-IR) spectroscopy was used to characterize the structure of the hybrids. The morphology of the hybrid coatings was examined by scanning electron microscopy and Si mapping. The hybrid systems have a uniform network structure and inorganic phases have a size of less than 100 nm. In addition, the effect of BPA/GPTMS molar ratio on cross-linking was investigated by ATR-IR and corrosion protection properties of hybrid coatings were evaluated by linear sweep voltametry (LSV) and 2000-h salt spray test methods. The results of these experiments show that the increasing of cross-linking between silica-network and BPA, would prevent the formation of cracks and decrease the brittleness. Increasing BPA content in organic-inorganic hybrid coatings or nanocomposites led to the formation of an efficient barrier to water and corrosion initiators such as chloride and oxygen.

Key Words:
nanocomposite;
hybrid coatings;
sol-gel process;
corrosion resistance;
electrochemistry.

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INTRODUCTION

Organic-inorganic hybrids as a new class of materials, have recently attracted more attention in nanomaterial science [1]. These materials can be synthesized through the synergistic combination of organic and inorganic polymers via the sol-gel process [2, 3]. These systems combine the advantages of organic polymers, such as toughness, flexibility, and ease of processing, with those of inorganic polymers, such as high heat resistance, good barrier, mechanical and optical properties [2, 4-6].

But the properties of the hybrid systems are not simply the average properties of their components. Besides, the volume fractions of these components, their size, shape and the uniformity of distribution are also important [3, 4]. The fineness of the formed inorganic particles, is usually below 100 nm and therefore, these hybrid materials are also called nanocomposites. They often yield optically transparent materials [3, 7, 8].

The sol-gel process is a well known technique for preparing organic-inorganic hybrid materials [3, 9]. As the name implies, it involves the evolution of inorganic networks through the formation of a colloidal suspension (sol). The network is formed by converting of this sol phase to a continuous gel phase. The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides are most popular because they react readily with water. The most widely used metal alkoxides are the alkoxy silanes, such as tetramethoxysilane, tetraethoxysilane, and 3-glycidoxypropyl-trimethoxysilane. In accordance with the functional group, three reactions are involved in the sol-gel process: Hydrolysis, alcohol, and water condensation.

The microstructure of the metal oxide obtained with the sol-gel process depends on those hydrolysis and condensation reactions that are generally controlled by pH of solution [3, 8]. In the acid catalyzed reaction, the hydrolysis step is faster than the condensation step, resulting in a more extended and less branched network structure. In the base catalyzed reaction, condensation is faster than hydrolysis, resulting in highly condensed species that may agglomerate into fine particles [3, 4, 12, and 13]. Furthermore, the sol-gel process includes a very complex reaction involving many variables such as pH, type and amount of solvent, water/alkoxide ratio [13, 14], concentrations of organic [4] and inorganic [15] reactants, aging [16], cross-linking agent/alkoxide ratio, and drying methods. We investigated some of these factors in previous studies [4,13-15].

GPTMS Modified ormosil is one of the organic-inorganic hybrid materials that has found uses in different applications that have been reported by various researchers. Metrok et al. [17], have studied sol-gel derived GPTMS-TEOS hybrid materials. Their results indicate that organic content and water/alkoxide ratio have a dramatic effect on the corrosion resistance of ormosil films. Their observations showed that failure of these films in corrosion resistance test (i.e., salt spray) has been through localized pit formation. It is likely to occur at hydrophilic regions such as non-condensed silanol group in the films. To solve this problem, it is necessary to produce a dense, continuous, and impermeable film against the corrosion initiators [18]. Schmidt et al. [19] have found that organic-inorganic nanocomposites prepared from epoxy-functionalized silicones act as scratch and abrasion resistant and hard coatings on glass and polymers. They found that the wettability of nanocomposites increase with epoxide ring opening reaction. Diol cross-linking leads to improving scratch resistance, corrosion resistance, and flexibility of ormosil coatings.

This study took advantage of the sol-gel process to prepare the organic-inorganic hybrid materials or nanocomposites by using the GPTMS as the precursor, bisphenol A (BPA) as the cross-linking agent and hydrochloric acid as the acidic catalyst. In this research the influence of cross-linking agent/alkoxide ratio on the protective properties of the hybrid systems has been investigated by ATR-IR and corrosion resistance evaluation test methods.

EXPERIMENTAL

Materials and Reagents

3-Glycidoxypropyl-trimethoxysilane (GPTMS) and cross-linking agent, bisphenol A (BPA) were purchased from Fluka and Merck, respectively and were used as received. Sodium chloride and hydrogen chloride were purchased from Merck and used without further purification.

Sol Preparation

The sol hybrid was prepared by admixing GPTMS precursor, and the organic cross-linking agent, bisphenol A (BPA), as follows:

GPTMS was placed in a beaker with 0.01 M HCl which H_2O/GPTMS molar ratio was 3/1 at room temperature. The resultant two-phase solution was vigorously stirred at a rate of 240 rpm for 1 h. Then BPA (BPA/GPTMS molar ratio was 1/1) was added to the solution and vigorously stirred again at a rate of 240 rpm for 4 h at room temperature. The transparent GB_1 sol solution was formed without any phase separation. Other hybrid samples were prepared through the same process with various BPA/GPTMS molar ratios (Table 1).

Substrate Preparation and Film Deposition

1050 Aluminium alloy as a substrate was used for the analysis of the sol-gel coatings. This substrate was polished by using the 400 and 800 grit sandpaper. Each substrate was initially rinsed with DI H_2O and then etched with 0.01 M NaOH solution. The substrates were rinsed with DI H_2O again and then immersed in 0.01 M HCl solution to remove excess NaOH solution from the substrate s surface. In the end, before air drying each substrate had been cleaned with hexane and methanol to remove all the dirts and greases [17, 18].

Cleaned aluminium alloy substrates were immersed into the hybrid sol for 1 min. The coating was air-dried onto the substrate and placed in a furnace to cure at temperatures ranging of 25-130 C for 90 min.

Electrochemical Analysis

Electrochemical measurements were performed under extreme environmental conditions, consisting of an aqueous, air exposed 3% sodium chloride solution.

Each sample was sealed with waterproof tape in order to prevent premature corrosion along the edges of the substrate. A 1 1cm^2 area at the center of each sample was exposed to the solution during testing. Corrosion analysis of bare and coated substrates was done using an Auto lab PGSTAT30 potentiostat system connected to a corrosion analysis of a software programme. Polarization measurements were carried out potentiostatically at room temperature using an Ag/AgCl/Cl^- (0.222 V) reference electrode and a platinum counter electrode. The potentiodynamic measurements were taken within the range of -2000 to +2000 mV versus Ag/AgCl/Cl^- at a rate of 5 mV/s. Prior to the measurements, in order to reach steady potential, the electrodes were kept in the working solutions for at least 30 min.

Corrosion Resistance Test

Corrosion resistance tests of the coated aluminium alloy substrates were done by exposing the samples to salt fog atmosphere generated from 5 wt% aqueous NaCl solution at 35±1°C for 2000 h in accordance with ASTM B117 specifications.

Table 1. The compositions of GPTMS/BPA hybrid materials.

Sol	BPA/GPTMS Molar ratio	H_2O/GPTMS Molar ratio
GB_1	1/1	3/1
GB_2	1/4	3/1
GB_3	1/8	3/1

Attenuated Total Reflectance Infrared Spectrometry (ATR-IR)

Attenuated total reflectance infrared spectrometry of the hybrid coated substrates were recorded using ATR-IR objective of a Bruker microscope, between 400 and 4000 cm^{-1}.

Morphological Properties

Scanning electron microscopy technique (SEM) was performed on the coated substrates to characterize the surface morphology with a Cambridge S360 microscope using a back-scattered or a secondary electron image detector at 20 KV and 2.85 A probe current.

Si Mapping Technique

The distribution of Si atoms in the hybrid system was obtained by SEM EDX mapping (LEO 440) that Si atoms were denoted by white points.

RESULTS AND DISCUSSION

Characterization

Figure 1 shows ATR-IR spectra of a series of hybrid films prepared with and without aromatic diol as cross-linking agent. The most resolved bands are attributed to several vibrational frequencies of the epoxy ring of organosilica-network of glycidoxypropylsiloxane structural fragment. They are including oxirane s methylene bending at 1480 cm^{-1}, epoxide ring breathing band at 1250 cm^{-1}, and antisymmetric epoxide ring deformation bands at 750 and 906 cm^{-1}. The band of the antisymmetric epoxide ring deformation at 750 and 906 cm^{-1} appears to be almost intense. It allows monitoring of chemical reaction of epoxy functional groups of organosilica-networks coupling with diol cross-linker groups. ATR-IR Spectra of the cross-linked film (Figure 1) show almost the disappearance of this band which indicates the formation of a cross-linked network [21].

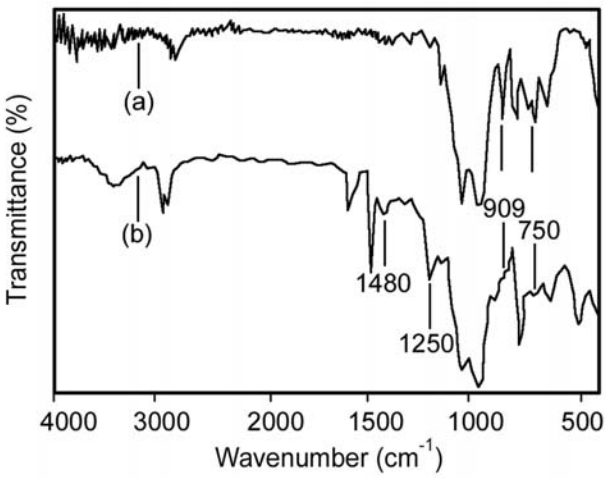

Figure 1. ATR-IR Spectra of (a) uncross-linked and (b) cross-linked organic-inorganic hybrid films with cross-linking agent (BPA).

Morphological Properties

The compatibility between the organic and the inorganic phase strongly affects the thermal, mechanical, and optical properties. The morphology of the coating surface was elucidated by SEM and a mapping technique to investigate the dispersion of inorganic phase in the hybrid matrix. Figures 2 and 3 present an SEM photograph and Si mapping of hybrid nanocomposites, respectively. According to these figures, the Si particles were uniformly dispersed throughout the polymer matrix with sizes below 100 nm.

These results revealed that these nanocomposites exhibit good miscibility between organic and inorganic phases. It is found that the Si particles are distributed uniformly in the hybrid nanocomposite.

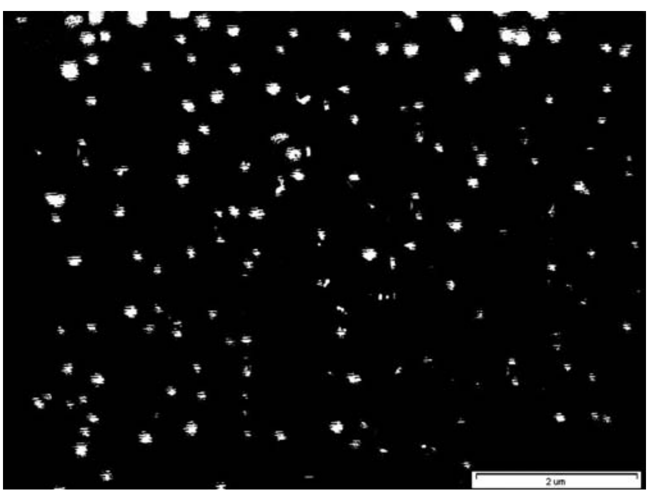

Figure 2. SEM Photograph of hybrid nanocomposite.

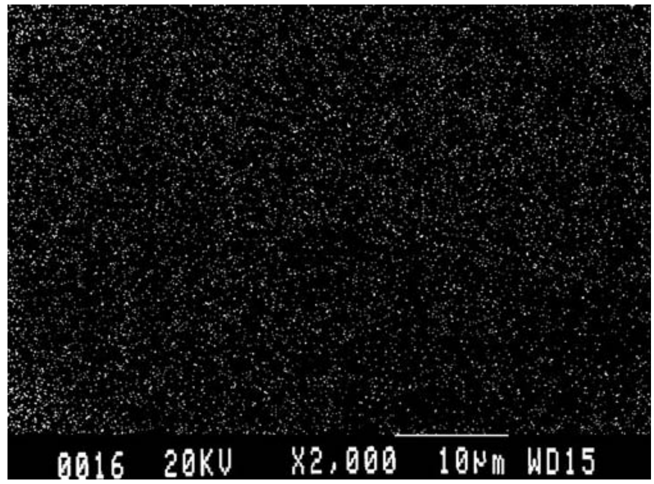

Figure 3. Si Mapping of hybrid nanocomposite.

The SEM micrograph was analyzed by Image-Pro plus Software (version 4.5, Media Cybernetic Co., USA). A particle size distribution is shown in Figure 4. From this figure, the size of the majority of particles is 45 nm. Consequently, silica networks are restrained at the molecular level in nanocomposites and the prepared nanocomposites would be transparent.

Effect of BPA/GPTMS Molar Ratio on Cross-linking and Corrosion Properties of Nanocomposite Coatings

Figure 5 shows the ATR-IR spectra of the hybrid nanocomposites with various cross-linking agent concentrations. According to this figure, the intensity of the antisymmetric epoxide ring deformation bands at 750 and 906 cm^{-1}, increased by decreasing the amounts of BPA. This observation indicates that decreasing the

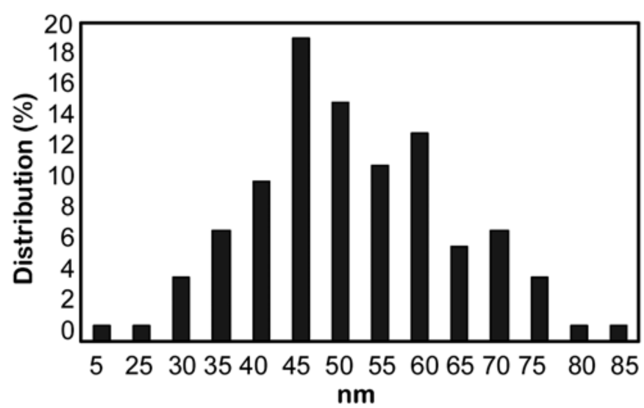

Figure 4. Distribution of particle size.

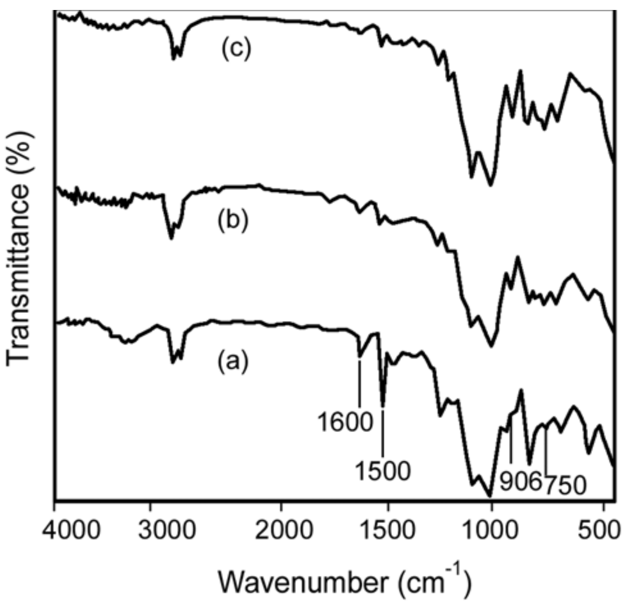

Figure 5. ATR-IR Spectra of aluminium alloy substrates coated with (a) GB_1, (b) GB_2, and (c) GB_3 sol solutions.

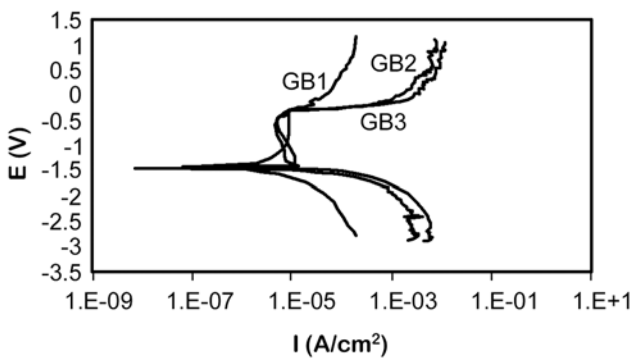

Figure 6. Polarization curves of aluminium alloy substrates coated with GB_1, GB_2, and GB_3 sol solutions.

amount of BPA would lead to the decreasing of cross-links between silica network and BPA, which resulted in the formation of crack and increasing brittleness in nanocomposite coatings [21].

The effect of BPA/GPTMS ratio on corrosion properties of nanocomposite coatings was studied by linear sweep voltametry (LSV) method to provide information about electrochemical corrosion occurring in the system. Figure 6 shows the polarization curves of aluminium alloy substrates coated with GB_1, GB_2, and GB_3 sol solutions. The sample prepared with the higher BPA content has shown better corrosion protection properties than the substrate with lower BPA content. The open circuit potential and corrosion resistance decreased from -1.298 V and 1.323 10^4 ohm to -1.483 V and 7.827 10^2 ohm, respectively. In addition, the corrosion current density and corrosion rate was increased from approximately 6.744 10^{-7} A/cm^2 and 2.207 10^{-2} mm/year to 6.107 10^{-6} A/cm^2 and 1.998 10^{-1} mm/year, respectively. These results indicate that the coating with lower BPA content is less effective in corrosion protection than the coating with higher BPA content.

Moreover salt-spray tests were conducted to confirm the results of electrochemical corrosion tests. Figure 7 shows the results of 2000-h salt spray tests for aluminium alloy substrates coated that with GB_1, GB_2, and GB_3 sol solutions. According to this figure, in substrates coated with GB_1 sol solution, no delamination or crack was observed and this sample showed good barrier properties in comparison with other samples.

All of these results demonstrate that the cross-linking agent/metal alkoxide ratio has a dramatic effect on corrosion protection properties of these nanocompos-

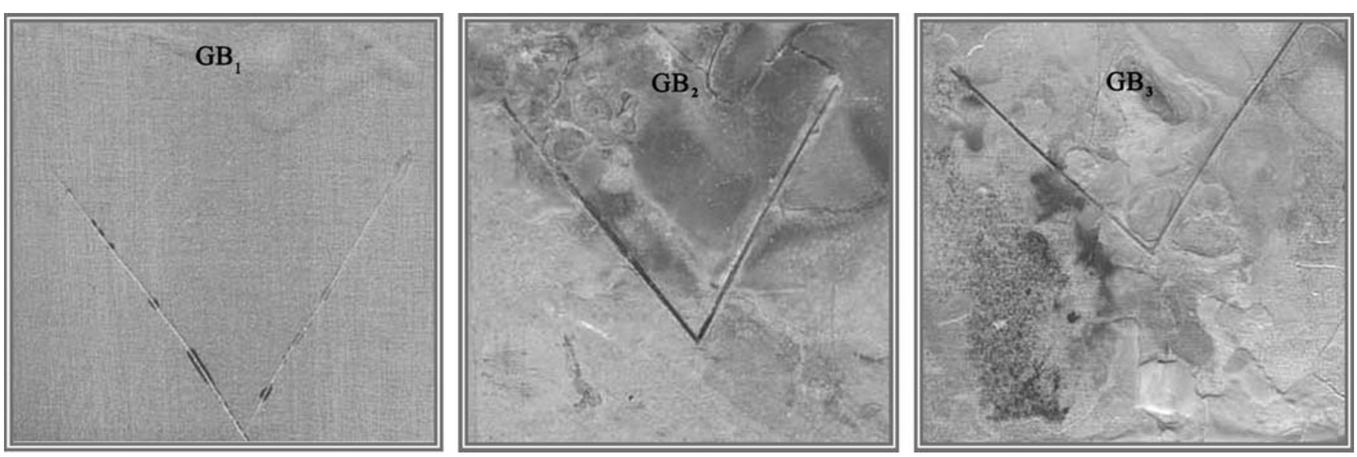

Figure 7. Results of 2000-h salt spray tests for aluminium alloy substrates coated with GB_1, GB_2, and GB_3 sol solutions.

ites. Increasing the cross-links between the silica-network and BPA, prevents the formation of crack and decreases the brittleness. On the other hand, increasing BPA content in organic-inorganic hybrid coatings or nanocomposites would lead to the formation of an efficient barrier to water and other corrosion initiators such as chloride and oxygen.

In fact, in hybrid systems organic groups that are dispersed throughout the film apparently serve to increase the hydrophobicity of the coatings, repelling water, and enhancing the corrosion protection properties.

CONCLUSION

Organic-inorganic hybrid nanocomposite coatings containing GPTMS and BPA were prepared successfully by the sol-gel process. The hybrid systems have a network structure and inorganic phases have a size of less than 100 nm. The Si mapping image confirms that the inorganic particles were distributed uniformly in hybrid nanocomposites, which results in the formation of transparent coatings.

Electrochemical and 2000-h salt spray tests demonstrated that these coatings are promising surface treaatment systems which provide improved corrosion protection for aluminium alloy by forming a crack-free and efficient barrier to water and corrosive agents (e.g., chloride and oxygen). Also it was found that the cross-linking agent/metal alkoxide ratio has a significant effect on corrosion resistance of the hybrid coatings. Electrochemical and 2000-h salt spray tests results confirm that the hybrid coatings prepared with higher BPA content show better corrosion protection properties than coatings prepared with lower BPA content.

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