

# Organic/Inorganic Composite Materials for Coating Applications

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Received 11 June 1998; accepted 25 February 1999

**ABSTRACT:** A new organic/inorganic coating material based on the modification of a conventional melamine/polyol system has been developed. Polyhydroxyethylmethacrylate functionalized with alkoxy silane group was mixed with hexamethoxymethylmelamine. Upon heating under an acid catalyzed condition, both sol-gel reaction and melamine/polyol reactions occurred simultaneously, leading to highly crosslinked hybrid composites. The synthesis and characterization of the hybrid materials are reported. The organic/inorganic material was also coated and cured on polycarbonate substrates. The coated/cured samples exhibited excellent optical property. Surface scratch and abrasion resistance of the samples was found better than those of pristine polycarbonate substrate. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1341–1346, 1999

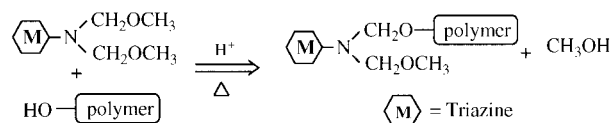
**Key words:** melamine; coating; hybrid material; organic/inorganic composite

## INTRODUCTION

The use of plastic materials has become popular in a number of applications, such as lenses, panels, and lamp covers, etc., due to their light weight, good mechanical and impact strength, as well as easy processability. In order to enhance the overall performance of the plastic parts for such applications, surface-hardening coatings are applied on the plastic substrates. These coating materials are usually based on organic compounds such as melamine, polyurethane, and acrylic-based polymers.<sup>1–5</sup> The hardening effect is a result of chemical reactions that convert molecules of the coating layer into a highly crosslinked network structure.

Melamine compounds are widely used as protective coatings due to their transparency, good

adhesion, as well as heat and chemical resistance.<sup>4,5</sup> Hexamethoxymethylmelamine (HMMM) is a fully alkylated melamine. Since active hydroxyl groups are no longer present, it has a longer shelf life than other types of melamines. HMMM has been used together with acrylic copolymers containing hydroxyl group on the side chain for coating applications.<sup>6</sup> Such a combination is often referred as a melamine/polyol system. The crosslinking reaction of this system is based on the transesterification between melamine and the pendant hydroxyl group of the copolymer under an acid catalyzed condition. The reaction scheme is shown below. The reaction kinetics and mechanism of such a reaction have been studied extensively.<sup>7–9</sup> Upon baking at an elevated temperature, a highly crosslinked polymer network is formed.



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Contract grant sponsor: Rachadapiesaksonpoch Foundation at Chulalongkorn University.

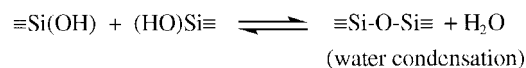
*Journal of Applied Polymer Science*, Vol. 74, 1341–1346 (1999)  
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Inorganic materials can also be used for surface coating on plastic substrates. This is usually achieved by a sol-gel reaction since the traditional melting process for glasses at high temperature is not suitable when organic polymer substrates are used. A typical sol-gel reaction scheme based on alkoxy silane functionality is shown below.<sup>10</sup> Through the hydrolysis and condensation reactions, vitrification can occur leading to glassy inorganic materials.

#### Hydrolysis

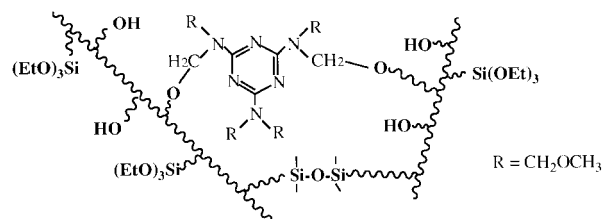


#### Condensation



There is an increasing interest in synthesizing hybrids of organic and inorganic materials.<sup>11–23</sup> Various approaches have been adopted to prepare organic/inorganic composite materials. Recent studies on organic/inorganic composite materials have been reviewed by Wilkes and co-workers.<sup>13</sup> Structure–property relationship and phase separation behavior of these hybrid materials have also been investigated.<sup>13,14</sup> The *in situ* polymerization of tetraethoxysilane in several organic polymers was studied. The properties of these materials have also been reported.<sup>15–18</sup> Low molecular weight organic polymers were functionalized with alkoxy silane groups. Through sol-gel reaction, organically modified sol-gel glasses were prepared.<sup>19–21</sup> Nanocomposites were prepared by aging of a solution that allows radical polymerization of monomers and sol-gel reaction to occur concurrently.<sup>22</sup> Schmidt et al. reported organic/inorganic hybrid coatings for metal and glass surfaces. Nanoscaled composite coating materials with very high scratch resistance have been developed.<sup>23</sup> Other related works, such as nonshrinking organic/inorganic composites,<sup>24</sup> and optical materials,<sup>25,26</sup> have also been reported. Most of these works were based on the sol-gel reaction of alkoxy silane functionalities in organic polymer matrices.

Tamami et al.<sup>27</sup> have developed an abrasion resistant transparent coating material based on melamine functionalized with the trialkoxy silane group. After processing and heating of this low



**Figure 1** Chemical structure of the organic/inorganic hybrid material prepared from HMMM and a polymer containing both hydroxyl and alkoxy silane pendant groups.

molecular weight compound, a crosslinked organic/inorganic hybrid coating layer (1–3  $\mu\text{m}$ ) was formed through a sol-gel reaction. Although the melamine moiety is not involved in crosslinking reaction in this work, it provides good adhesion to the substrate as well as rigidity of the film. The abrasion resistance of the coated polycarbonate (PC) samples was superior to that of an uncoated one. This work demonstrated that highly crosslinked materials based on sol-gel reaction of the alkoxy silane group exhibited optical transparency and good abrasion resistance.

In this work, the preparation of novel organic/inorganic composite materials based on HMMM and functionalized acrylic polymers is presented. The chemical structure of the hybrid material is shown in Figure 1.

The functionalized acrylic polymer contains both hydroxyl and alkoxy silane pendant groups. The hydroxyl group reacted with HMMM through transesterification forming an organic polymer network. Meanwhile, the reaction among alkoxy silane groups formed an inorganic network through inter- and intramolecular sol-gel reactions. Both reactions were catalyzed by a strong organic acid. As a result, a new class of organic/inorganic composite materials was prepared for the first time. The synthesis, processing, and characterization of these hybrid composites as coating materials are reported.

## EXPERIMENTAL

Hydroxy ethyl methacrylate (HEMA, >95%) was obtained from Siam Chemical Industry and was used as received. Synthesis of poly[hydroxy ethyl methacrylate] (PHEMA) was carried out by free radical polymerization using benzoyl peroxide (Merck) as an initiator and laurylmercaptan (Fluka) as a chain transfer agent. HEMA (73.0 g)

and ethanol (663.3 g) were mixed in a round bottom flask. To this solution, benzoyl peroxide (2.06 g) and laurylmercaptan (0.22 g) were added. The solution was heated to reflux and the reaction was allowed to continue for 24 h. The polymer was precipitated out by pouring the reaction solution into a mixture of benzene and hexane (1:1 v/v).<sup>28</sup> The polymer was washed several times with a benzene/hexane mixture in order to remove unreacted monomer and impurities. The polymer, PHEMA, was then dried at 60°C under vacuum.

A solution made of 1.37 g of PHEMA and 11.28 g of dried dimethylformamide (DMF, reagent grade from Carlo Erba) was prepared in a round bottom flask purging with dry nitrogen. To this solution, 2.60 g of 3-isocyanatopropyltriethoxysilane (IPSE, Fluka) was added in order to functionalize PHEMA. The reaction was carried out at 90°C and the extent of reaction was monitored using IR spectroscopy by analyzing the reaction solutions at various reaction time. The starting molar ratio of isocyanate in IPSE to hydroxyl group in PHEMA was 1 to 1. Polymers with various degrees of functionalization were obtained by controlling the reaction time. The reaction solution containing functionalized PHEMA as well as unreacted IPSE was used subsequently without further purification.

A coating solution was prepared by mixing the polymer solution with HMMM (Monsanto, Resimene® 747) and an acid catalyst. The polymer solution (1.01 g) and HMMM (0.039 g) were mixed thoroughly prior to the addition of the catalyst, *p*-toluenesulfonic acid (Fluka). The acid added into the coating mixture was in solution form (2%). When acid was added directly in solid form, the local concentration was too high, leading to instant partial gelation of the solution. The acid added was 0.3 wt % of the total solid contents in the coating mixture. The resulting homogeneous solution was applied on PC substrates using a four-sided applicator (Sheen Instruments) to form a coating layer. The side with a 90 μm gap of the applicator was chosen for the coating process. The coated PC samples were dried at 60°C under vacuum. Final curing of samples was carried out at 135°C for 12 h.

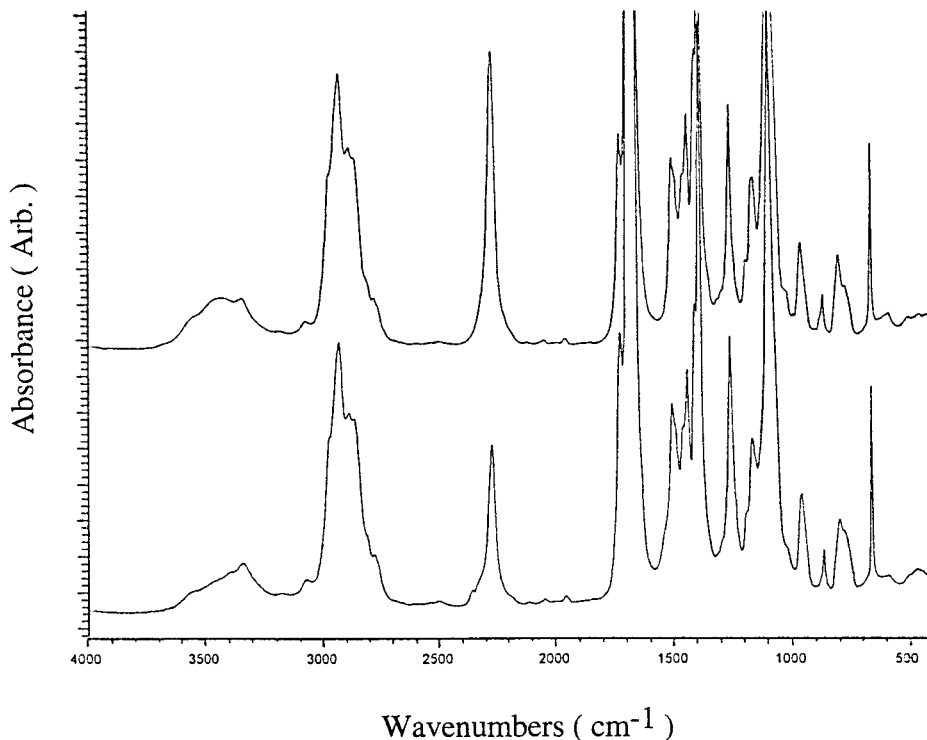
PC sheets (UV concentrated grade KU1-1241) with a thickness of 2 mm were obtained from Eastern Polymer Group. The sheets were cut into 12 × 7 cm pieces. The surface of PC substrates was cleaned by ethanol and dried before the application of coating. Visible light transmission spectra were measured using a spectrophotome-

ter (Macbeth®, Model Color-eye 7000). The abrasion resistance was performed by means of an abrasion scrub tester (Sheen Instruments). Two brushes weighing 0.45 kg each were mounted on two holders. The brushes reciprocated on the testing samples to cause wearing of surfaces. The test was carried out under dry condition without the use of detergent or any other liquids. The scratch resistance of samples was measured using a scratch test apparatus (Sheen Instruments). For the measurement, a scratch test steel needle loaded with a weight was moved on a testing sample surface. Measurements were carried out by gradually adding weights until a line on the specimen surface caused by the scratch test needle was observed. The minimum weight causing an observable scratching line was then recorded. Infrared spectra were obtained using an Fourier transform IR (Nicolet Impact 400D) spectrophotometer.

## RESULTS AND DISCUSSION

The functionalization of PHEMA was monitored by means of IR spectroscopy. Figure 2 shows the IR spectra of the polymer solution right after adding IPSE and 8 h after the addition. A decrease in isocyanate peak at 2270 cm<sup>-1</sup> and a decrease in hydroxyl peak at 3465 cm<sup>-1</sup> indicated that the reaction of isocyanate with hydroxyl group has occurred forming urethane linkages. The urethane peak signal was not identified since it overlapped with carbonyl peaks from both PHEMA (1727 cm<sup>-1</sup>) and DMF (1679 cm<sup>-1</sup>). The changes in the absorbance of the isocyanate peak were also used to calculate the degree of functionalization. When the reaction proceeded for 3, 6, and 8 h at 90°C, the percentages of hydroxyl group reacted (degree of functionalization of PHEMA) were calculated to be 10, 40, and 65 mole %, respectively. These three polymers are named and coded with degree of functionalization as Copoly-10, -40, and -65.

In a commercial melamine/polyol coating system, typical hydroxyl content in the polymer is approximately 30–40%. In our system, a similar or even higher percentage of hydroxyl group is desired as the steric hindrance effect from the bulky alkoxy silane group may obstruct the reaction between hydroxyl group and melamine. As a result from steric hindrance, some hydroxyl groups will not be able to react and will remain in the sample. Therefore, investigation was carried



**Figure 2** IR spectra of the polymer solution, Top: right after adding IPSE. Bottom: 8 h after the addition.

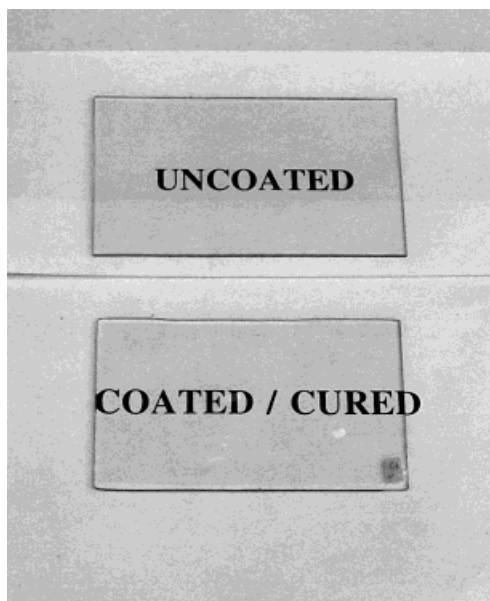
out only on polymers with hydroxyl contents of 35 % or higher. It was also found that gelation of reaction solution occurred when the reaction time was longer than 15 h. This is a result of the crosslinking process from the sol-gel reaction of the alkoxy silane group. IR spectrum of the gelled product showed a significant increase and broadening of the hydroxyl group at around  $3400\text{ cm}^{-1}$ . It suggested that the ethoxysilane (Si—O—Et) linkages were hydrolyzed to Si—OH bonds. A small amount of alkoxy silane linkages may undergo hydrolysis and even condensation when heated for a prolonged period. Cross-polymer sol-gel reactions can cause gelation of solution easily, especially when the degree of functionalization of PHEMA is high.

The coating solutions were prepared by thoroughly mixing the polymer solution with HMMM. The solid content in the coating solution is approximately 28%. No reaction was observed as both the reaction between the hydroxyl group and HMMM as well as the sol-gel reaction are very slow at room temperature when an acid catalyst is not present. The addition of acid catalyst leads to partial gelation of coating solution in approximately 10 min. The application of the coating

solution on substrates was carried out before gelation occurred. It was also found that the gelling time of Copoly-65 was the shortest. As mentioned earlier, the inter- and intramolecular sol-gel reaction is responsible for one type of crosslinking reaction while the reaction between hydroxyl group and HMMM contributes to the other type of crosslinking reaction. Copoly-65, which possessed less pendent hydroxyl group than Copoly-10 and Copoly-40, gelled faster, indicating that the initial networking process mainly arose from the sol-gel reaction. However, both types of reactions are expected to proceed simultaneously.

The drying process at  $60^\circ\text{C}$  under vacuum removed most of the solvent and volatile contents. The final curing temperature was set at  $135^\circ\text{C}$  because the glass transition temperature ( $T_g$ ) of PC is approximately  $150^\circ\text{C}$ . Curing at higher temperatures may have provided a higher extent of crosslinking reaction from the sol-gel process, but it led to the distortion of samples and, in some cases, samples became opaque probably due to crystallization of PC.

The coated/cured samples showed very good optical quality. Figure 3 shows the appearance of a pristine PC and a coated/cured sample. Al-



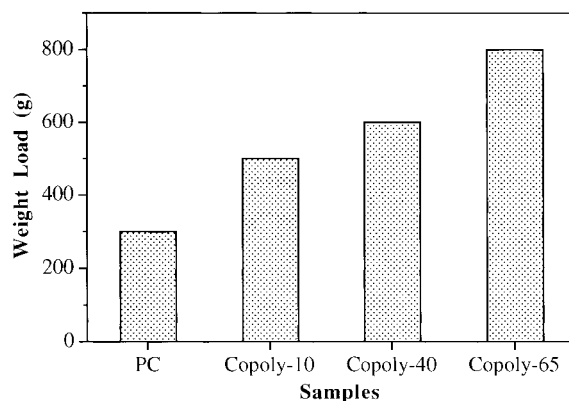
**Figure 3** A comparison of the appearance of a pristine PC and a coated/cured sample (Copoly-65 based coating).

though both melamine/polyol and sol-gel reactions generate volatile contents such as alcohol and water, all samples exhibited excellent optical clarity before and after curing. The results also indicated that there was no significant phase separation in these organic/inorganic composite materials. Inorganic components are distributed evenly in the coating layer. However, it is possible that minor phase separation can occur in the material. When the size of scattering sites due to the presence of various domains is small relative to the wavelength of visible light, severe light scattering will not happen. Therefore, the samples can still exhibit good optical clarity. IR spectrum of the cured sample on a KBr window showed broad peaks at  $1200\text{--}1000\text{ cm}^{-1}$ , suggesting the formation of a sol-gel network. A differential scanning calorimetry scan on the coating material showed no observable  $T_g$  due to a highly crosslinked structure in the organic/inorganic composites.

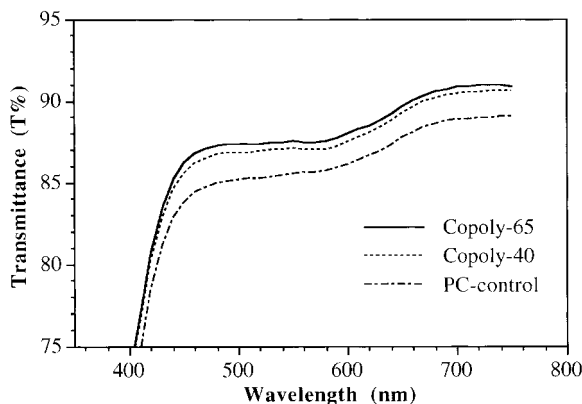
The coating materials were tested for both their scratch and abrasion resistance. Figure 4 shows the results from the scratch resistance measurement. The minimum weight required to make a visible scratching line on the sample surfaces is indicated. The performance of samples from this measurement is related to material properties, such as hardness, adhesion, lubricity, resilience, etc. For uncoated PC, a scratching line

was first observed when the load was 300 g. Coated samples showed improved scratch resistance compared to that of pristine PC. It was also found that the scratch resistance was enhanced as the degree of functionalization increased within the range studied. It is worthwhile to mention that Copoly-10 with 90% of hydroxyl groups intact allows more reactions with HMMM due to less steric hindrance. However, the results showed that Copoly-65 exhibited better scratch resistance than Copoly-10 and Copoly-35. When Copoly-65 was used, sol-gel reaction from the alkoxy silane moiety imparted more cross-polymer reaction in the organic/inorganic hybrid material. Consequently, the scratch resistance of Copoly-65 is the best among the samples investigated. Peeling tests were also carried out for coated/cured samples by using a pressure sensitive tape. All coated/cured samples showed good adhesion to the substrate and no fragment was peeled off from the substrate by the tape.

Both coated samples and pristine PC were subject to the abrasion test. As the abrasion cycles increased, the quality of the surfaces became worse for all samples. However, coated samples showed better abrasion resistance than the pristine PC sample judged by the naked eye. In addition, the transmittance of samples in the visible region of samples was measured. Figure 5 shows transmittance of pristine PC and coated/cured samples (both Copoly-65 and Copoly-40 after 500 cycles). The coated samples have better abrasion resistance and less scratches on the surface than the pristine PC after testing. As a consequence, higher transmittance of light was measured for the coated samples due to their less scattering



**Figure 4** Scratch resistance results for various samples. The minimum weight load required to make a scratch line on a sample surface is indicated.



**Figure 5** Transmittance of various samples after the abrasion test (500 cycles).

surfaces. Copoly-65 also performed better than Copoly-40 and Copoly-10 in the abrasion resistance test.

## CONCLUSIONS

A melamine/Copoly system was developed as an organic/inorganic hybrid coating material. The coated/cured samples exhibited excellent optical quality, indicating the uniform distribution of the inorganic composition. Both surface scratch and abrasion resistance of PC substrates was enhanced by the organic/inorganic coating. These properties were also affected by the degree of functionalization in the polymer.

The authors would like to acknowledge the financial support from the Rachadapesaksompoch Foundation and the Office of Academic Affairs at Chulalongkorn University. We also thank Professor R. J. Jeng at the National Chung Hsing University in Taiwan for his help and fruitful discussion. Materials provided by SCI and EPG are appreciated.

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