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Novel Organic/Inorganic Composites for Coating Applications

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Abstract

Novel organic/inorganic coating composites based on hexamethoxymelamine and functionalized acrylic polymer containing both hydroxyl and alkoxysilane pendent groups were developed. These optically clear composites were used for coating polycarbonate(PC) substrate. The evaluation of surface properties of coated polycarbonate was made with respect to abrasion and scratch resistance test. The preliminary data showed that coated PC sample performed a better resistance to abrasion and scratch test than uncoated one. The best performance was found when using functionallized acrylic polymer with an inorganic content of 65% without causing shrinkage of the coating film.

Introduction

The application of surface hardening coating onto plastic is aimed at improving surface hardness and scratch/abrasion resistance. Among these coating materials, organic compounds such as melamine, polyurethane, and acrylic-base polymers are often used (Automotive coating, 1987; and Treadway, 1981). The hardening effect is a result of chemical reactions which 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 (Blank, 1982; and Ntsihlele, *et al.* 1995). An example of these types of crosslinking agents is hexamethoxymethylmelamine (HMMM) (Figure 1). HMMM is practically used to crosslink hydroxyl group containing acrylic copolymers. Such a combination is often refered as a melamine/polyol system. The crosslinking reaction of this system involves the tranesterification between melamine methylol group and the pendent hydroxyl group of the copolymer in the presence of acid catalyst. The reaction kinetics and baking at elevated temperatures have been investigated extensively. Upon baking at elevated temperature, a highly crosslinked polymer network is formed as shown in Figure 1.

Inorganic materials can also be used for surface coating on plastic substrates. The sol-gel reaction of inorganic coating material is wholely responsible for the improvement in abrasion/scratch resistance of coated substrates. An example of inorganic coating materials such as Accuglass®

marketed by allied signal is based on oligomers of organosilane with reaction group, Si-O-R, where R can be either alkyl or phenyl. After heating and vitrification at an elevated temperature, the resulting coating layer becomes transparent and glassy-like. However, in order to achieve a sufficient degree of reaction for obtained film properties, high curing temperatures were required. In addition, the film thickness should be only in the order of angstorm to prevent film shrinking and then cracking during vitrification.

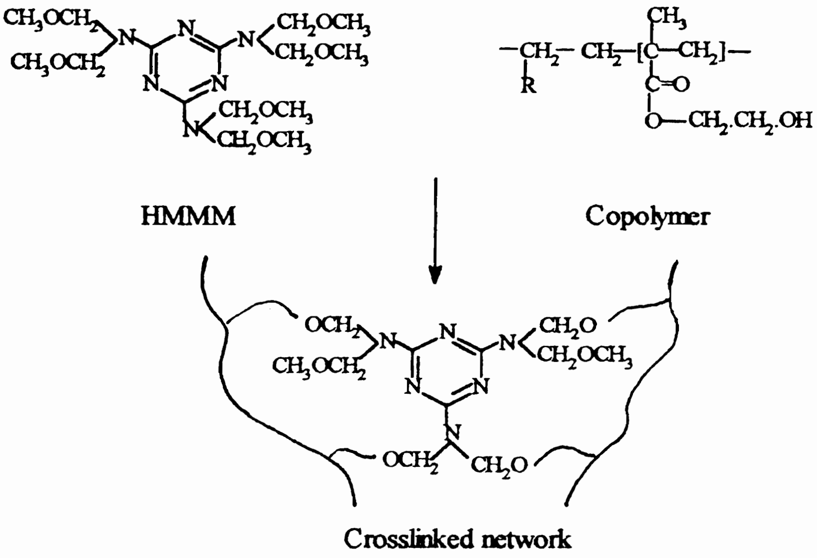

Figure 1 HMMM/polyol condensation reaction to produce crosslinked network

Recently, there is an increasing interest in searching for inorganic/organic hybrid materials. Various approaches have been adapted to prepare organic /inorganic composite materials (Landry, *et al.* 1992; Fitzgerald, *et al.* 1992; Brennan, *et al.* 1992; and Coltrain, *et al.* 1992). The in-situ polymerization of tetraethoxysilane in several organic polymers has been studies. The properties of these materials have also been studied. The properties of these materials have been reported. Low MW organic polymers were functionalized with alkoxysilane group. Through sol-gel reaction, organically modified sol-gel glasses were prepared. Nanocomposites were prepared by aging of a solution which allows radical polymerization of monomers and sol-gel reaction to occur concurrently. Other related works have been reported, such as nonshrinking organic/inorganic composites, optical materials based on polyceramers (Ellsworth and Novak, 1993), organic/ inorganic composites for nonlinear optical applications (Motakef, *et al.* 1994) etc.

In this project, the preparation of novel organic/inorganic composite materials based on HMMM and functionallized acrylic polymers is proposed. The functionlalized acrylic polymers contain both hydroxyl and alkoxysilane pendent groups. The hydroxy groups will react with HMMM through transetherification (Figure 1) forming an organic polymer network. Meanwhile, the reaction among alkoxysilane groups will form an inorganic network through inter- and intra- molecular sol-gel reactions. It is expected this coating system will give a superior surface properties with low volume shrinkage.

Experimental

MATERISLS

Polycarbonate(PC) sheets (uv concentrated grade kul-1241) were obtained from Eastern Polymer group. PC sheets with a thickness of 2 mm. were cut into 12 cm. by 7 cm. Ethanol was used to clean PC sheet's surface prior to coating. Hydroxyethylmethacrylate (HEMA) was kindly supplied by Siam Chemical Industry and was used as received. Benzoyl peroxide was obtained from Merck. Laurylmercatan was purchased from Fluka. Benzene, hexane and N, N-dimethylformamide were obtained as laboratory grade. 3-isocyanotopropyltriethoxysilane (IPSE) and p-toluenesulfonic acid were obtained from Fluka. Hexamethoxymethylmelamine (HMMM) was commercial available.

SYNTHESIS OF POLYHYDROXYETHYL METHACRYLATE (POLY-HEMA)

HEMA (73.0 g.) and ethanol (663 g.) were mixed in a round bottom flask. To this solution, Benzoylperoxide (2.06 g.) and laurylmercaptan (0.22 g.) were added. The solution was stirred and refluxed. The reaction was continued for 24 hours. The reaction mixture was then cooled to room temperature. The resulting polymer was precipitated by pouring the reaction solution into a mixture of benzene and hexane (1:1 v/v ratio). The polymer was washed several times by benzene/hexane mixture to remove unreacted monomer and impurities. The obtained polymer, poly-HEMA, was then dried at 60°C under vacuum. The characterization of the reaction product was carried out using NMR and FTIR techniques. The molecular weight of the polymer was determined by gel permeation chromatography.

THE PERPARATION OF POLY (HEMA-CO-3-ISOCYANOTOPROPYLTRIETHOXYSILANE)

A solution made of 1.37 g. of poly-HEMA and 11.28 g. of dried dimethylformamide was prepared in a round bottom flask. To this solution, 3-isocyanotopropylethoxysilane (IPSE) (2.6 g.) was adde;the mole ratio of 3-isocyanotopropylethoxysilanes to the hydroxyethyl groups was 1:1. The reaction solution was raised to 90°C and the reaction was allowed to continue at this temperature under nitrogen atmosphere. The progress of the reaction was monitored using IR spectroscopy by analyzing the reaction solutions at various reaction times.

COATING OF POLYCARBONATE SHEET

Prior to coating, PC sheets surface was cleaned with ethanol and dried. A coating solution was formulated by mixing the poly (HEMA - co - IPSE) solution (1 g.) with hexamethoxymethylmelamine (HMMM) (0.041 g). A p-toluenesulfonic acid (0.3 wt % of the total solid content in the coating mixture) was added. The resulting homogeneous solution was applied to PC substrate using four-side coating applicator (Sheen Instrument). The coating layer obtained was 90 μm thick. The coated PC sheet was dried at 60°C under vacuum before being cured at 135°C for 12 hours.

FTIR ANALYSIS OF COATED/CURED PC SHEET

FTIR spectrophotometer (Nicolet Impact 400D) was used to monitor the chemical reaction of HMMM with hydroxyl group of poly-HEMA. The sample preparation used in this experiment was press-disc technique by mixing sample in potassium bromide (KBr) and then pressing it into disk. IR spectra of the samples was recorded using parameters as follows : scan range 400-4,000 cm^{-1}, scan No. : 32.

Results and discussion

CHARACTERIZATION OF POLY-HEMA BY ^{1}H NMR ANALYSIS

^{1}H NMR spectrum of HEMA (C①H$_2$=C② (CH$_3$)COOC$_2$H$_4$OH) is illustrated in Figure 2. The figure shows the chemical shifts of HEMA ethylene protons at 5.6 and 6.3 ppm. which represent the proton signals at carbon atom position 1 and 2 respectively. Figure 3 shows the ^{1}H-NMR spectrum of poly-HEMA. The disappearance of the signals of ethylene protons at 6.3 and 5.6 ppm. are indicative of the absence of HEMA monomer in the final polymer product. The degree of conversion which quantitatively defines the percentage of HEMA monomer to poly-HEMA is 85%.

THE CHARACTERIZATION OF POLY- (EMA-CO-IPSE)

The reaction between poly-HEMA and IPSE was monitored using IR spectroscopy. Figure 4a and 4b shows the IR spectrum of polymer solution taking at the beginning of reaction and 8 hours after addition respectively. A decrease in isocyanate (-N=C=O) peak at ~2,270 cm^{-1}and a decrease in hydroxyl peak at ~3,465 cm^{-1} indicated the reaction of isocyanate with hydroxyl group of poly-HEMA gradually proceeded and urethane linkage was formed . The urethane absorption peak was not clearly indentified due to its superimposing with carbonyl peaks from both poly-HEMA (~1,727 cm^{-1}) and DMF (~1,679 cm^{-1}). By comparison with unchanging intensity, the decrease in intensity at ~2,270 cm^{-1} is an indication of the consumption of hydroxyl group in poly-HEMA by isocyanate group. The change in intensity of isocyanate absorbance compared with the unchanging intensity of methylene group at ~2,929 cm^{-1} was quantitative evaluated to obtain the degree of remaining hydroxy content.

In this experiment, three polymers whose hydroxyl contents was 10, 40 and 65% were prepared at the reaction times of 3, 6 and 8 hours, respectively. There three polymers were named and coded as copoly-10, copoly-40 and copoly-65. It was found that gelation of reaction solution occurred when the reaction time was longer than 15 hours. IR spectrum of the gelled product revealed that a significant increase in hydroxyl band intensity at ~ 3,400 $cm^{-1}$was observed. This suggested that the ethoxysilane (Si-O-R) groups were hydrolyzed forming silanol (Si-OH) bands. Silanol group subsequently underwent self-condensation reaction and thus gellation occurred.

Application of organic/inorganic coating composite onto PC sheet

The coating solutions were prepared by mixing the copolymer with HMMMand the catalyst, p-toluensulfonic acid, throughly. It was possible that at this stage the gelation would occur even at room temperature due to the acid catalyzed sol-gel reaction. Therefore, to avoid the gelation occured before application of coating, all coatings were carried out immediately. The drying process at 60°C under vacuum removed most of solvent and volatile substances. Dried coated PC sheet was cured at 135°C for 12 hours. Curing at higher temperatures is desirable but it may lead to distortion of samples and in some cases, sample become opaque probably due to crystallization of PC.

The coated/cured PC was tested for both scratch and abrasion resistance using scratch tester of Sheen Instrument Ltd. A series of standard loads were used to rub coated/cured PC sheets to assess the surface properties including hardness and adhesion. Table 1 shows the results obtained from the scratch resistance measurement. For uncoated PC, scratching line was first observed when the load was 300 g. On the other hand, coated sample was left unscratched up to 600 g. load. This indicated that coated/cured showed improved scratch resistance than the uncoated one. Two types of crosslinking reactions were expected to simultaneously occur during curing at 135°C; the sol-gel reaction of alkoxysilane groups to produce siloxane linkaged and HMMM/polyol reactions to produce ether (CH_2-O-CH_2) linkage .

Peeling tests were carried out for coated/cured samples by using a presure sensitive tape. All samples showed good adhesion of coating and no fragment was peeled off from the substrate by the tape.

Both coated samples and uncoated PC were subjected to abrasion testing. As the number of

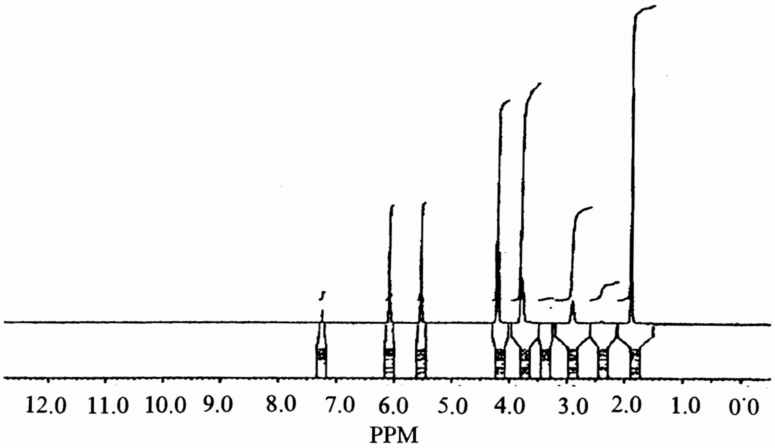

Figure 2 ^{1}H-NMR Spectrum of HEMA

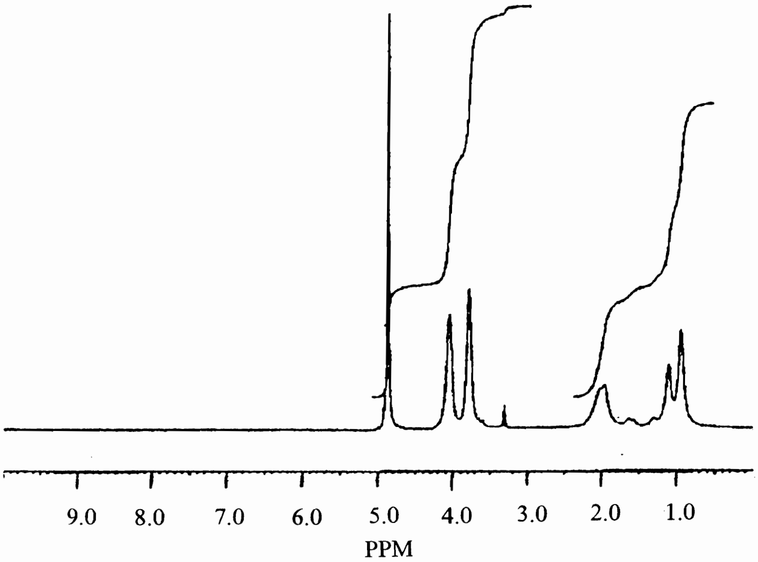

Figure 3 ^{1}H-NMR Spectrum of Poly-HEMA

brasion round increased, the quality of the surface became worse for all samples. Judging by the naked eye All coated samples showed better abrasion resistance than the uncoated PC sample. In addition, the transmission of visible light was measured. Figure 5 shows transmittance of pristine PC and coated/cured samples,copoly-65 and copoly-40 after 500 rounds. The coated sample has better abrasion resistance and less scratches on the surface after testing. As a consequence, higher transmittance of light was measured due to its less scattering surface. By comparison, the performance of abrasion resistance of copoly-65 coated sample was better than copoly-40 coated sample.

Conclusions

Inorganic/organic coating based on organosilane and methylolmelamine has been investigated. A copolymer containing pendent ethoxysilane and hydroxyethyl groups was synthesized and analyzed using spectroscopy techniques. The coating solution was prepared by mixing the obtained copolymer, HMMM and the catalyst, p-toluensulfonic acid, throughly , and then applied to PC sheets. Curing of coated sample was carried-out at 135°C for 12 hours where two types of crosslinking reactions ocured; one was sol-gel reaction and the other was HMMM/polyol reaction.

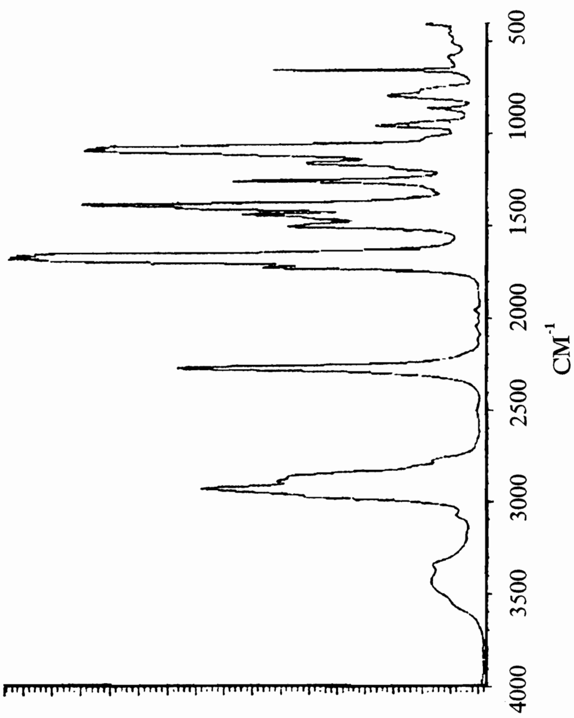

Figure 4a FTIR spectrum of polymer solution taking at the beginning of the reaction

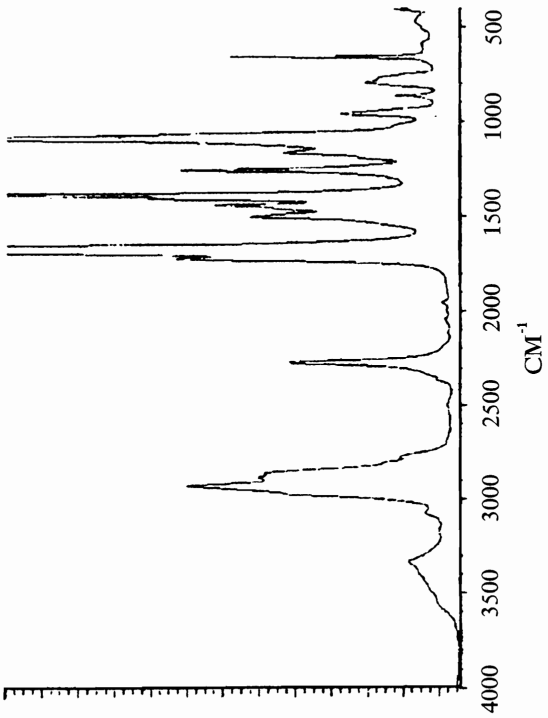

Figure 4b FTIR spectrum of polymer solution taking affter 8 hours

Table 1 Scratch test of uncoated and coated polycarbonate Sheets

Load Weight/g.	**Uncoated Polycarabonate**	**Coated and Cured Polycarbonate**
0	O	O
100	O	O
200	O	O
300	√	O
400	√	O
500	√	O
600	√	O
800	√	√
1000	√	√
1500	√	√

√ = Scratch line observed O = Intact

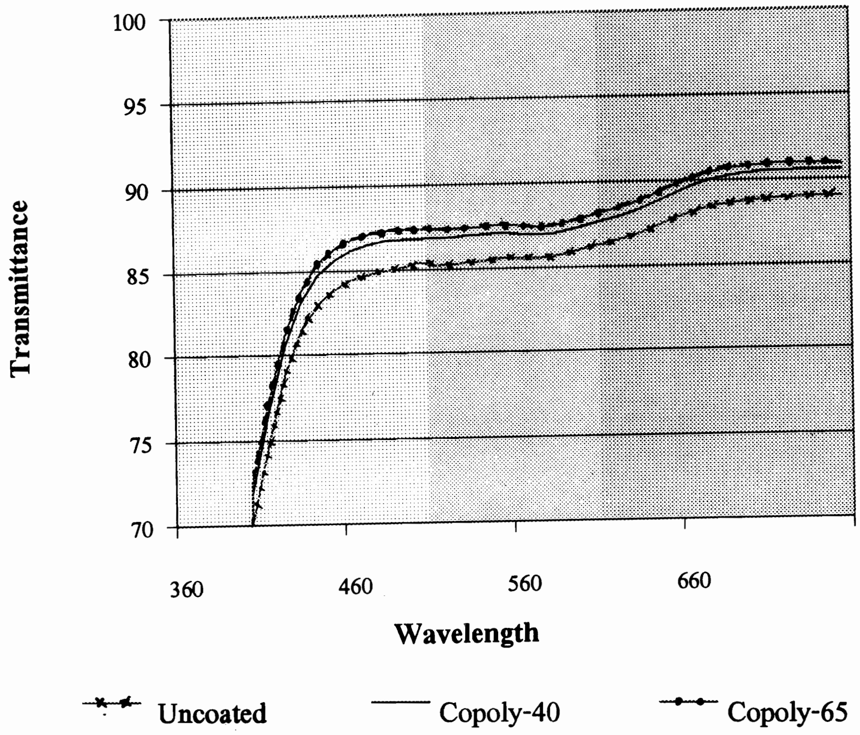

Figure 5 Comparison of transmittance between uncoated and coated samples

The results showed that the inorganic/organic coating composites developed in our laboratory was completely miscible in each other and produced transparent thin layer on PC substrate. Coated/cured PC sheets were subjected to scratch and abrasion test. It was clearly evident that coated PC sample performed a better resistance to abrasion and scratch test than uncoated one. The performance of coating thin film was found to be dependent on the inorganic/organic content ratio. The best performance was found when using functionalized acrylic polymer with 65% of inorganic content without causing the shrinkage of coating film. In the future, it would be worth recommending that further investigation of cured thin layer by spectroscopic techniques would be desirable in order to understand the relationship between inorganic/organic content ratio and then its coating performance.

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