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Transparent Coating Materials Based on Inorganic/Organic Composites

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Abstract

A siloxyl group functionalized copolymer of low molecular weight was synthesized, aiming at preparing transparent inorganic/organic coating composites. Two types of coating systems were investigated: two-component system (based on functionalized copolymer-HMMM) a three-component system (based on functionalized copolymer-HMMM-TEOS). Their properties were investigated and compared. Coating films obtained from these systems exhibited good optical clarity, which was largely dependent on the content of indicated Materials. For instance, to prevent phase separation in the 3-component system, TEOS was "effectively" linked to pendent siloxyl groups on the organic moiety Hence, coating formulations containing a high degree of pendent siloxyl groups exhibited better optical transparency. These coating systems improved abrasion/scratch resistance properties of coated/cured PC sheets Further investigation for the system properties revealed that two crosslinked networks were responsible for the coating film hardness : an organic network resulting from transetherification between copolymer hydroxyl group and HMMM methylol group, and an inorganic network resulting from a sol-gel reaction The inorganic network was the main contributer to the improved surface performance of coated PC samples.

Introduction

Transparent polymeric materials usually exhibit poor abrasion/scratch resistance which limits their applications. Surface properties of these materials can be improved by the application of hardening coatings(1-5) Among these coating materials, organic compounds such as melamine, polyurethane, and acrylic-based polymers are often used. 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 chemical resistance. An example of these types of crosslinking agents is hexamethoxymethylmelamine (HMMM). HMMM is practically used to crosslink hydroxyl group containing acrylic copolymers. Such a combination is often refered as 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.(6-8) Inorganic/organic hybrid composites were introduced, aiming at improving abrasion resistance property of coated materials. Recently, transparent inorganic/organic hybrid composites have been developed thanks to the advent of sol-gel technology.(9-15) The use of inorganic/organic hybrid composites as surface coatings has also been widely investigated. There are several approaches in preparing transparent inorganic/organic materials through sol-gel processing. Starting inorganic materials are based on silicon, aluminium, titanium or zirconium metal alkoxides. A variety of oligomers such as poly(dimethylsiloxane) (PDMS) and poly (tetramethylene oxide) (PTMO) and polymers such as polyimides, poly(ether ketone) (PEK), polyester, and polycarbonate (PC) have been employed as organic components. In order to prevent phase separation between organic and inorganic components these organic components require functional groups that are capable of forming the covalent bonds between both components. Various silanol functionalized polymers and copolymers have been synthesized. Typical preparation of inorganic/organic crosslinked film is carried out by mixing functionalized polymers with metal alkoxides such as TMOS or TEOS and then curing at suitable temperatures.

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In a previous paper a functionalized acrylic polymer containing both hydroxyl and pendant alkoxysilane groups was prepared.(16) Then this functionalized polymer was homogeneously mixed with hexamethoxymethylmelamine (HMMM) using *p*-toluenesulfonic acid as a catalyst. The prepared coating solutions were applied onto PC sheets, followed by curing the coated sample at 135°C for 14 hrs. Upon heating under acid-catalyzed condition, both the sol-gel reaction and melamine/ polyol reactions occurred simultaneously, leading to highly crosslinked hybrid materials. The coated/ cured samples were optically transparent. Surface scratch and abrasion resistance of the samples was markedly improved compared with those of pristine PC substrate. Two types of crosslinking reactions were expected, transetherification of acrylic polymer hydroxyl groups with HMMM and a sol-gel reaction. Coating films exhibited good optical transparency. However, there was a limitation in terms of increasing the clarity of the hybrid materials. In this work, further study was extended to the investigation of the addition of triethyl orthosilicate (TEOS) as an external inorganic network precursor. Surface properties such as scratch/abrasion resistance and optical clarity were evaluated and compared with those obtained from two component systems.

Experimental

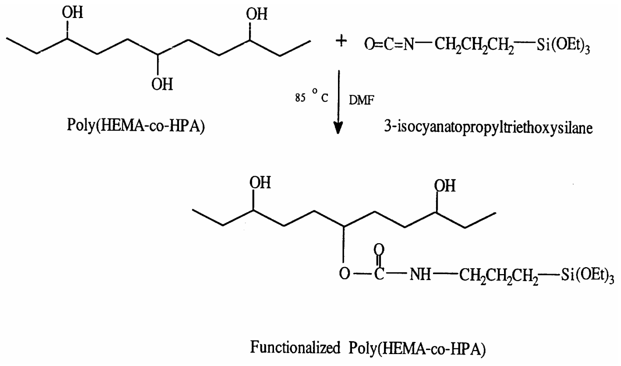
Chemicals and Materials

2-hydroxyethyl mathacrylate (HEMA) and hydroxypropyl acrylate (HPA) were donated from Siam Chemical Industry Co., Ltd. 3-isocyanatopropyl triethoxysilane (IPSE), tetraethyl orthosilicate (TEOS), laurylmercaptan and p-toluenesulfonic acid were purchased from Fluka. Hexamethoxymethylmelamine (HMMM) was obtained from Monsanto. Polycarbonate sheets (PC) were kindly supplied from Eastern Polymer Industry Co., Ltd.

Functionalization of Poly(HEMA-co-HPA) with IPSE

First, copolymerization of HEMA and HPA was carried out. Then 1.375g (0.01 mole) of poly (HEMA-co-HPA) prepared by random copolymerizetion of 50 wt% HEMA and 50 wt% HPA and 11.28 g of DMF were placed in a 25 ml round bottom flask which was purged by nitrogen. To this solution, a series of appropriate amounts of IPSE were added under continuous stirring while raising the temperature to 85°C. The reaction was carried out at this temperature for 8 hrs. In this experiment, the IPSE functionalized copolymers with the degrees of functionalization of 10%, 20%, 30%, 40%, 50%, 60%, and 70% were prepared and designated as $COIPSE_{10}$ to $COIPSE_{70}$, respectively. A solution containing IPSE functionalized poly (HEMA-co-HPA) was subsequently used without further purification.

The progress of the reaction was monitored using FT-IR spectroscopy on a Nicolet Impact 400D spectrophotometer by analyzing the reaction mixture every 4 hours until the isocyanate peak at ~2,200 cm^{-1} completely disappeared. Sample preparation was carried out by casting the solution mixture on IR grade salt plates. The FT-IR spectra of the polymer thin films coated on salt plates were recorded using the parameters as follows: scanning range: 4,000-400 cm^{-1}, scanning no: 32 cm^{-1}, and resolution: 4 cm^{-1}. The reaction involved can be schematically represented by the following equation:



Application of Inorganic/Organic Coating Composites on PC Sheets

Two-component system (COIPSE-HMMM) and three-component system (COIPSE-HMMM-TEOS) were investigated. Coating solutions of the two-component systems were prepared by mixing the functionalized copolymer solution with different amounts of HMMM, calculated based on available hydroxyl groups of the copolymer and hydrated *p*-toluenesulfonic acid (0.3 wt% of total solid content). For three-component system, additional TEOS was included into coating solutions of two component system. Specific amounts of coating components are presented in Table 1.

Table 1. Compositions of Inorganic/Organic Coating Formulations.

Sample Code	Copolymer Weight(g)	HMMM (g/percentage[a])	TEOS (g/percentage[b])	*p*-Toluenesulfonic acid (% total solid content)
COIPSE$_{30}$-HMMM	1.22	0.48/70	-	0.3
COIPSE$_{40}$-HMMM	1.20	0.41/60	-	0.3
COIPSE$_{50}$-HMMM	1.18	0.34/50	-	0.3
COIPSE$_{60}$-HMMM	1.15	0.27/40	-	0.3
COIPSE$_{70}$-HMMM	1.13	0.20/30	-	0.3
COIPSE$_{10}$-HMMM-TEOS$_{30}$	1.52	0.41	0.65/30	0.3
COIPSE$_{10}$-HMMM-TEOS$_{40}$	1.52	0.34	0.87/40	0.3
COIPSE$_{20}$-HMMM-TEOS$_{30}$	1.52	0.34	0.65/30	0.3
COIPSE$_{20}$-HMMM-TEOS$_{40}$	1.52	0.27	0.87/40	0.3
COIPSE$_{30}$-HMMM-TEOS$_{30}$	1.52	0.27	0.65/30	0.3
COIPSE$_{30}$-HMMM-TEOS$_{40}$	1.52	0.20	0.87/40	0.3

a= calculated based on the copolymer hydroxyl group available
b= calculated based on the weight of the copolymer

The coating mixture was stirred in a 20 ml beaker. The resulting homogenous solution was immediately applied onto cleaned PC substrate using a four-side applicator (Sheen Instruments). The coated PC sample was dried at 60ºC in vacuum before curing at 135°C for 14 hrs. Table 1. Compositions of Inorganic/Organic Coating Formulations.

The visible light transmittance was measured using a uv/vis spectrophotometer (Macbeth Model Color-Eye 7000). The specimen was tested before and after abrasion testing. TGA analysis of the coated/cured films was aimed at the determination of weight loss of cured films and was carried out using a Perkin-Elmer Thermal Gravimeter (Model TGA 7). Heating rate was performed at 20oC/min over the temperature range of 25-700ºC. The abrasion resistance was measured 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 testing was carried out under dry conditions without detergent or any other solvents.

Results and Discussion

FT-IR Analysis of Poly(HEMA-co-HPA) Functionalized with IPSE

The reaction of poly(HEMA-co-HPA) with IPSE was monitored by FT-IR spectroscopy. The strong absorption band of the isocyanate group of IPSE measured at the beginning of the reaction showed up clearly at 2,270 cm^{-1}. This reactive group readily underwent a chemical reaction with the poly(HEMA-co-HPA) hydroxyl group to produce urethane linkages, for which an absorption band appeared at 1,528 cm^{-1} as the reaction proceeded. However, identification of this band was difficult due to the interference of solvent bands. The gradual disappearance of the isocyanate peak at 2,270 cm^{-1} was mainly indicative of the continuing reaction of isocyanate group. Completion of the reaction could be observed when the isocyanate peak totally disappeared. The FT-IR spectra of 40 wt% IPSE functoinalized copolymer collected at the beginning and at the end of reaction, shown in Figure 1 and Figure 2, respectively confirmed the successful functionalization. Prevention of the undesired gelling due to early hydrolysis and subsequent condensation of pendant siloxyl groups was accomplished by complete removal of all traces of commonly found in the solvent prior to use.

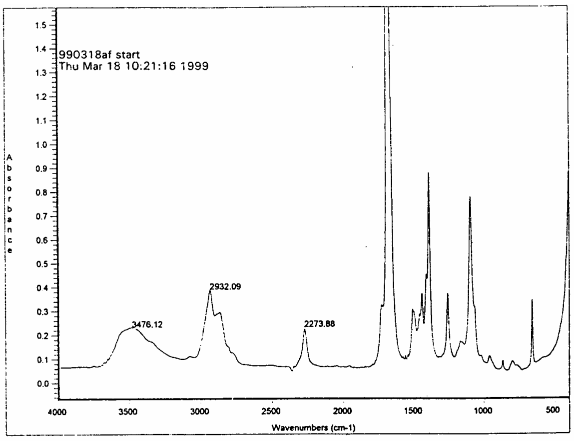


Figure 1. FT-IR spectrum of 40wt% IPSE functionalized poly(HEME-co-HPA) taken at the beginning of the reaction.

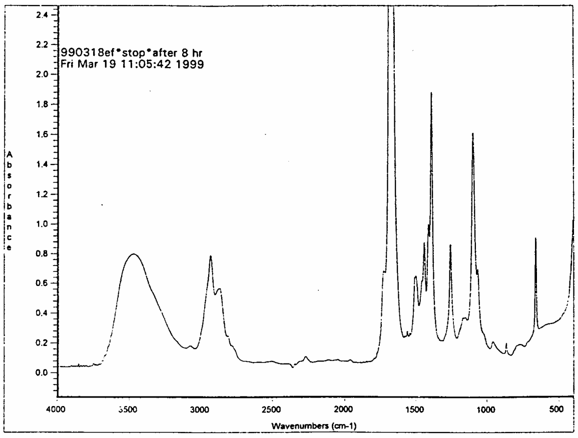


Figure 2. FT-IR spectrum of 40 wt% IPSE functionalized poly(HEME-co-HPA) taken at the end of the reaction.

Application of Inorganic/Organic Coatings onto PC Substrate

In this experiment, two coating systems (COIPSE-HMMM and COIPSE-HMMM-TEOS) were investigated. In the case of two-component system, a typical coating formulation was prepared by mixing the IPSE functionalized copolymer and HMMM in the presence of p-toluenesulfonic acid as an acid catalyst. The transparent inorganic/ organic crosslinked network was formed when curing the coating film in a vacuum oven at 135°C for 14 hrs. The produced transparent network was derived from two different crosslinking reactions.

The transetherification reaction between hydroxyl groups of poly(HEMA-co-HPA) and methylol groups of HMMM produced an organic network. The extent of crosslinking was controlled by controlling the rate of reaction at a high temperature for a long period of time. In this experiment, a curing temperature of 135ºC for 14 hrs was used to prevent the deformation of PC substrate.

An inorganic network was achieved by sol-gel reactions which involved two-step processes: hydrolysis and subsequent condensation of alkoxysilane groups to produce a siloxane (Si-o-Si) network. The distinguished advantage of the sol-gel process is that it produces an inorganic crosslinked network at a mild temperature, allowing possible combinations of inorganic materials into an organic matrix. However, the problem of gelation often arises during the preparation of coatings due to early formation of an inorganic SiO_2 network. Hence, care must be taken during mixing of the coating composition. For the COIPSE-HMMM system where two components are involved, the inorganic/organic network produced may be simplified as shown in Figure 3. Two types of inorganic crosslinks, intra- and inter-molecular siloxane bonds, were expected. The disadvantage of the COIPSE-HMMM system was that the production of hybrid composites with a high inorganic content was limited. Moreover, the extent of crosslinking to yield a high crosslink density was restricted due to the limited mobility of polymer chain by pendant siloxane bonds.

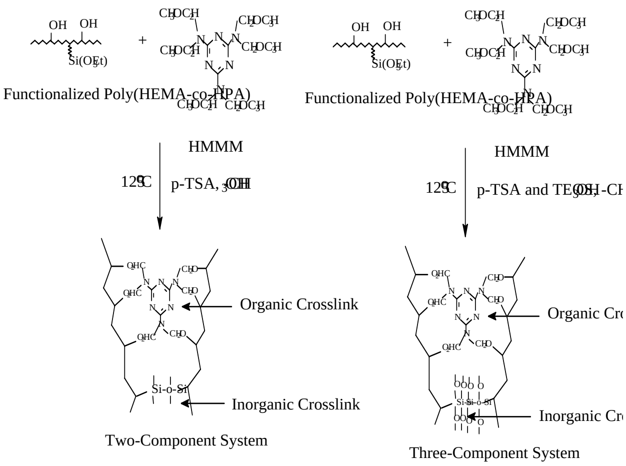


Figure 3. Inorganic/organic networks produced from OIPSE-HMMM and COIPSE-HMMM-TEOS system

The introduction of TEOS into the COIPSE-HMMM system was investigated to improve the transparency as well as surface performance of coated substrate. It was expected that TEOS, which is small in molecular weight and easily undergoes a sol-gel reaction, could form nanoparticles evenly distributed in an organic network. Therefore, an optically transparent hybrid coating without inorganic/organic phase separation could be created. For both systems, the inorganic/ organic networks produced may be simplified as shown in Figure 3. It should be noted that care must be taken during preparation of the coating formulation due to the danger of early gelation. To avoid this problem, mixing of coating components should be carried out in a dry room and solvent must be free of trace amounts of water.

TGA analysis of Cured Inorganic/Organic Composites

TGA analysis was used to determine the inorganic content (SiO_2) as well as the thermal stability of the composite. The percent weight loss of the sample plotted against temperature is shown in Figure.4 and 5-6 for the COIPSE-HMMM system and COIPSE-HMMM-TEOS system, respectively. From Figure. 4 to Figure. 6, the decomposition process involves two main steps of weight loss rates. The weight loss observed at temperatures ranging from 50°C – 500ºC could be attributed to the decomposition of part of the functionalized copolymer, where network crosslinking was incomplete. Organic crosslinking brought about increased heat resistance of the network, which could be stable up to 500ºC according to Mukhopadhay's report.(18) Hence, it can be claimed that an increase in percent weight loss above 500ºC was indicative of the extent of organic crosslinking reaction. It was unlikely that the weight loss profile in the temperature range of 500-700ºC could be attributed to the depolymerization of the functionalized copolymer chain as a result of pendant siloxyl groups undergoing intra- and inter-molecular crosslinking among adjacent chains. The reason is that the percent weight loss tended to decrease with an increase in the degree of functionalization. From Figure 4 the results showed that the percent weight loss in this region was found to be 9.5% and 8.2% for COIPSE40-HMMM and COIPSE50-HMMM, respectively. A similar trend holds true for the COIPSE-HMMM-TEOS system.

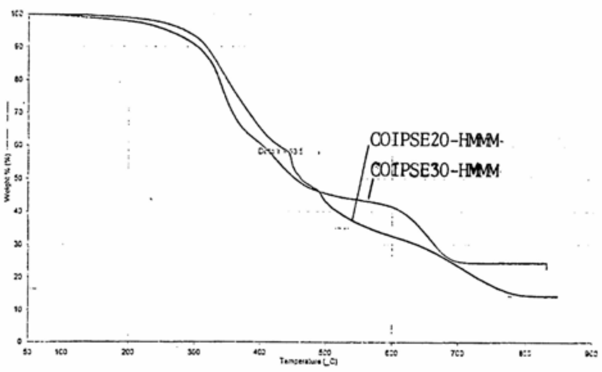


Figure 4. Typical TGA thermograms obtained from two -component system.

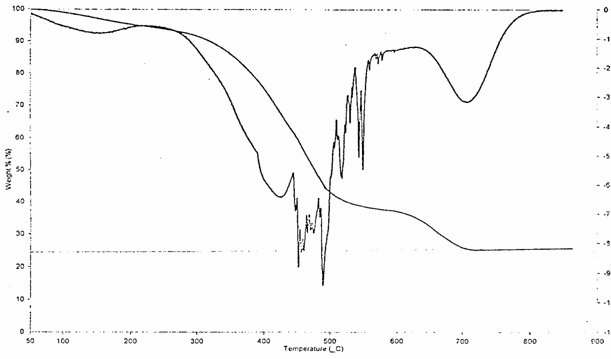


Figure 5. TGA thermogram of a coating film of the COIPSE20-HMMM-TEOS30 sample.

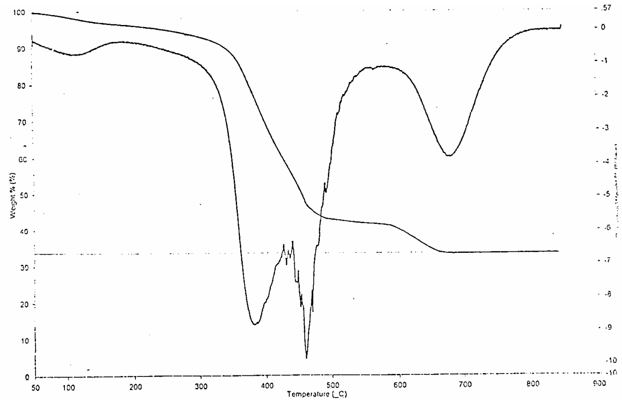


Figure 6. TGA thermogram of coating film of the COIPSE30-HMMM-TEOS40 sample.

It was probable that the extent of organically crosslinking reactions was affected by three major factors: the restricted mobility of pendant hydroxyl segments due to siloxane bonds, the inappropriate curing temperature due to a concern about the thermal stability of the substrate, and the availibility of hydroxyl groups on the copolymer. Generally, the decomposition of the organic network was complete at a temperature of about 750ºC. Upon further heating little changes in weight loss were observed in all cases.

The thermally stable residue was believed to be the inorganic SiO_2. The weight percentage of inorganic residual components in cured films varied accordingly with the amount of pendant siloxyl groups and TEOS used in each formulation. The inorganic content determined by TGA and calculated values are quite comparable for both systems (see Table 2). The presence of inorganic components in coating films played a crucial role of, not only contributing to the thermal stability but also providing optical clarity to the material. Those properties could be optimized by controlling the appropriate degree of siloxyl groups in the copolymer as well as the amount of added TEOS. Table 2. Inorganic and Organic Contents of the Inorganic/Organic Composites

Table 2. Inorganic and Organic Contents of the Inorganic/Organic Composites

Sample Code	Calculated Value		TGA Result	
	Organic Content (wt%)	Inorganic Content (wt%)	Weight Loss (wt%)	Slica Content (wt%)
COIPSE30-HMMM	88.0	12.0	88.0	12.0
COIPSE40-HMMM	84.6	15.4	85.7	14.3
COIPSE50-HMMM	81.1	18.1	83.6	16.4
COIPSE10-HMMM -TEOS30	79.6	20.3	82.5	17.5
COIPSE20-HMMM -TEOS30	72.7	27.3	76.0	24.0
COIPSE30-HMMM -TEOS30	61.1	38.4	66.7	33.3

Optical Clarity of Coated/Cured Films

Judged by the naked eye, all coated/cured samples exhibited excellent optical transparency. In addition, a uv/vis spectrophotometer was to measure the clarity of coated/cured films. The optical clarity of cured films obtained from both systems was dependant on the presence of inorganic contents. Typical comparison of transmittance curves is given in Figures 7 and 8-9 for COIPSE-HMMM and COIPSE-HMMM-TEOS systems, respectively. Compared with sample $COIPSE_{10}$-HMMM-$TEOS_{40}$, $COIPSE_{30}$-HMMM-$TEOS_{40}$ is more transparent. The difference between these two formulas is the degree of siloxyl groups in the copolymer. The poorer optical transparency of $COIPSE_{10}$-HMMM-$TEOS_{40}$ sample is believed to be due to the fact that inorganic SiO_2 nanoparticles were less capable of bonding to the copolymer. This resulted in some phase separation leading to loss in optical clarity of the coating film. These results suggest that the number of siloxyl groups in the copolymer chains played an important part in incorporating the inorganic network into the organic network. With fewer numbers of siloxyl groups ($COIPSE_{10}$), the copolymer chains might lose their ability to bond effectively to the TEOS component, hence segregating the inorganic monolithic glass from the organic matrix.

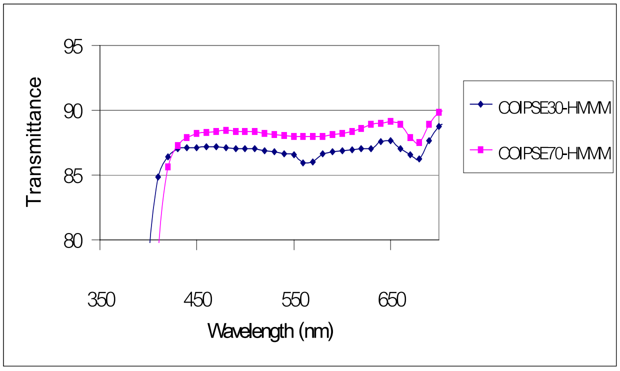


Figure 7. Compared transmittance of coating films obtained from two-component system

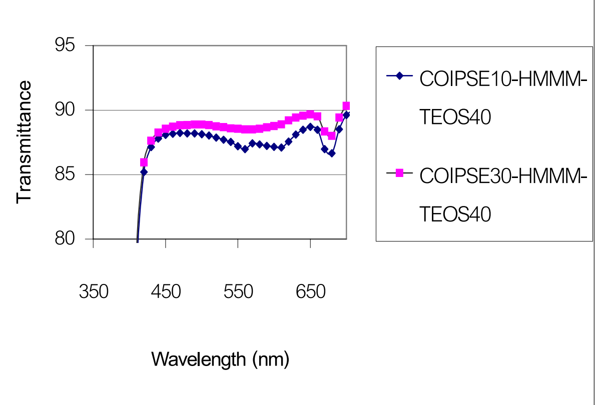


Figure 8. Compared transmittance of coating films obtained from three component system

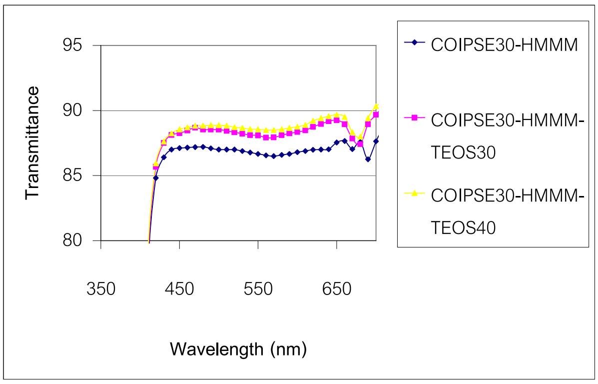


Figure 9. Transmittance comparisons of coating films between two component system and three component system

For the two-component system, there was no phase separation because inorganic SiO_2 was the part of the copolymer. However, the disadvantage of this system was that an increase in inorganic content, which is important to obtain excellent transparency, was limited. As a result of less inorganic SiO_2 content, these series show relatively lower optical clarity than three-component system.

Light Transmittance Measurement of Abraded Coated PC Sheets

Abrasion testing with 500 abrading cycles was carried out on coated/cured samples. After that, abraded samples were subjected to light transmittance measurement using a uv/vis spectrophotometer. Abrasive resistance properties of coating films were assessed by comparing the reduction in the degree of light tansmittance transmittance among different coated samples and uncoated PC.

Figure 10 compares light transmittance values obtained from the COIPSE-HMMM system and virgin PC. Typically, uncoated PC exhibits poor abrasion resistance as from the results shown PC has the lowest transmittance among test samples. It can be observed that the abrasion resistance of coated samples is dependant on the degree of siloxyl functional groups in the copolymer. To be precise, the formation of siloxane bonds, which readily occurred, played an important role in the improved surface surface performance of coated PC. This conclusion is drawn from the fact that an increase in pendant siloxyl groups led to a decrease in the copolymer hydroxyl groups, resulting in a decrease in organic network/inorganic network ratio. TGA evidence supports the above explanation in that the proportion of the organic network decreased as the degree of siloxyl groups increased. However, the presence of an organic network was preferable in order to prevent film shrinkage and provide a synergistic effect on abrasion resistance properties of the coating. Figure 11 compares light transmittance values of virgin PC and COIPS-HMMM-TEOS system after abrasion testing. It is obvious that the addition of TEOS brought about higher abrasion resistance. It is believed that the introducetion of TEOS resulted in an increased proportion of the inorganic network, providing better abrasion resistance. Finally, Figure 12 confirms the dominant influence of the inorganic network on the surface performance of inorganic/organic coatings.

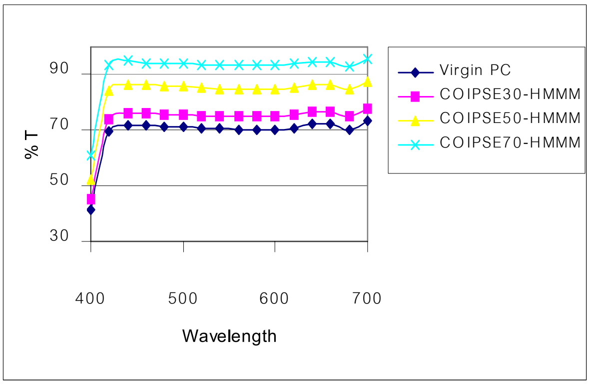


Figure 10. Compared transmittance of virgin PC and coated PC samples from COIPSE-HMMM-TEOS system after abrasion testing.C

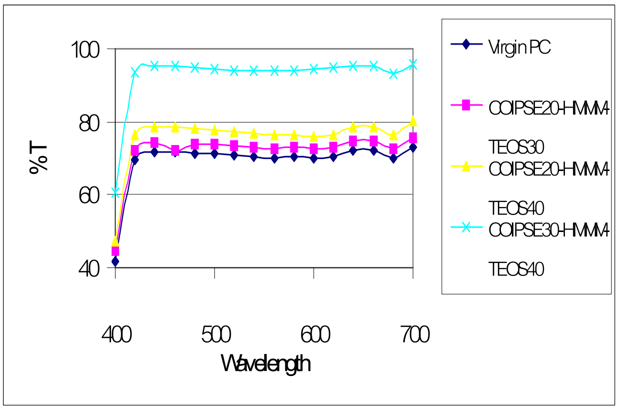


Figure 11. Compared transmittance of virgin PC and coated PC samples from COIPSE-HMMM system after abrasion testing.

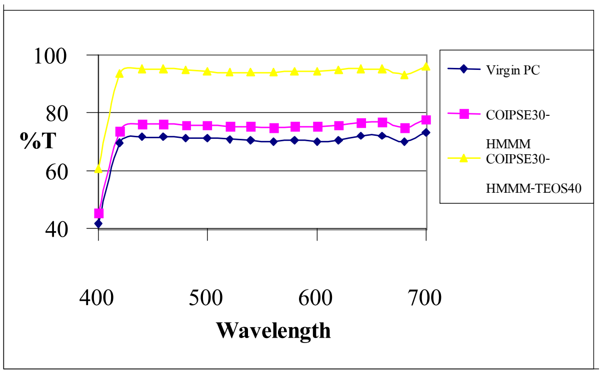


Figure 12. Comparison of abrasion resistance between two component system and three component system

Conclusions

Inorganic/organic composites based on siloxyl group functionalized copolymer/melamine/ TEOS were developed as transparent coating materials. The function of pendant siloxyl groups of the functionalized copolymer was to minimize the phase separation between two components, which have different refractive indices. As found experimentally, the coating formulation containing the functionalized copolymer with a higher degree of siloxyl group content offered optical clarity to the coating materials.

Abrasion/scratch resistance of PC substrate was enhanced by the application of inorganic/ organic coatings. The hardening effect of the coating film was attributed to two different types of crosslink networks: organic crosslink network resulting from the transetherification between the copolymer hydroxyl group and HMMM methylol group, and an inorganic network resulting from sol-gel reactions of the TEOS component and pendant siloxyl groups.

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