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Characterization of UV curable hybrid hard coating materials prepared by sol-gel method

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Abstract−Using sol-gel method, UV-curable urethane acrylate resin system was hybridized with inorganic silicate network to produce hybrid coating materials with high anti-abrasive property. In preparation of acrylate/SiO_2 hybrid materials, various acrylic reactants with multi-functional groups in addition to urethane acrylate oligomer as the main network former were employed to obtain more densified organic network structure with a high degree of cross-linking. As a silane coupling agent, 3-methacryloxypropyl-trimethoxysilane (MPTMS) was used to promote interfacial attraction between UV-cured organic acrylate resin and inorganic silicate component in the hybrid. The addition of MPTMS offered significant effect on the improvement of phase compatibility between organic and inorganic phases, which resulted in stable and homogeneous morphology with a dispersion of nano-sized fine silica particles. The results of morphological observation, glass transition behavior, and optical transparency for the hybrid gels provided an evidence for the increased interfacial attraction between two phases. From the Taber abrasion test for the hybrid coating films, it was revealed that there existed optimal ranges of inorganic silicate precursor TEOS and silane coupling agent MPTMS contents for the preparation of UV cured acrylate/SiO_2 hybrid with high abrasion resistant property.

Key words: UV-curable, Coating, Anti-abrasive, Sol-gel Method

INTRODUCTION

Polymeric materials such as polycarbonate (PC), poly(methyl methacrylate) (PMMA), and poly(ethylene terephthalate) (PET), which have many advantages of excellent transparency, toughness, and processability, have been widely used for optical lenses and goggles, head ramp covers of automobiles, display panels, soundproof walls, and so on. However, the qualities of these polymeric materials can be easily deteriorated by surface scratches or environmental stimulus of ultraviolet radiation and chemicals due to their poor abrasion resistance, hence greatly limiting their application [1,2]. Accordingly, a variety of coating materials have been developed and used to protect the surface characteristics of polymeric products [3]. In recent years, organic-inorganic hybrid materials prepared by sol-gel method have received great attention as the new class of hard coating materials, because such materials can offer remarkably improved surface abrasion resistance by incorporating nano-structured inorganic particle at molecular scale [4,5]. Curable polymer resin system or organically modified alkoxides such as glycidoxypropyltrimethoxysilane (GPTMS), 3-methacryloxypropyl-trimethoxysilane (MPTMS), vinyltriethoxysilane (VTES) have been used as the organic component in the hybrid coating materials [6-9]. In the case of hybrids based on organically modified alkoxides, the resultant organic network can be obtained by the polymerization reaction of reactive groups within the network former under specific catalyst [10]. However, these organic precursors show limitation for the practical application of hard coating materials due to their lack of adhesion to substrate and expensiveness. Alternatively, oligomeric resin systems that can be polymerized into three-dimensional solid network by thermal or UV radiation curing have been employed more extensively in comparison with organically modified alkoxysilane for the formation of organic components in the abrasion resistant hybrid coating materials. Among various organic network resins, UV-curable oligomer has most frequently been used in the coating industry related to the production of scratch and abrasion resistant hybrid coating materials, because the UV-curing process has many significant advantages over the thermal-induced cure process, such as short processing time at room temperature, low energy cost, solvent-free polymerization allowing environmental friendly process, and feasible application of temperature sensitive substrate [11].

In the present study, nano-structured hybrid coating materials with anti-abrasive property were prepared by the combination of UV-curable urethane-acrylate resin system as the organic phase and silicate network as the inorganic component via sol-gel process. In particular, in preparation of organic phase during UV-curing process, various acrylic oligomers with multi-functional groups were employed to obtain a densified network structure with high degree of cross-linking in the cured hybrids. The effect of addition of silane coupling agent, 3-methacryloxypropyl-trimethoxysilane (MPTMS), on the phase compatibility was investigated in terms of morphology and thermal property. In addition, abrasion resistance property of the coated film was also studied.

EXPERIMENTAL

1. Materials and Preparation

Tetraethoxysilane (TEOS, Acros Organics, 98%) and methacryloxypropyl-trimethoxysilane (MPTMS, Acros Organics, 98%) were

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used as the inorganic silicate precursor and silane coupling agents, respectively. As the organic component in the hybrid, the uv-curable acrylic resin system is composed of aliphatic urethane hexaacrylate (EBECRYL 1290, SK Cytec) and three different diluting acrylates with various multi functional groups: acrylated dipentaerythritol (DPHA, SK Cytec), trimethylolpropane triacrylate (TMPTA, Aldrich), 1,6-haxanediol diacrylate (HDODA, Aldrich). 1-Hydroxycyclohexyl-phenyl-ketone (IRGACURE 184, Ciba Specialty Chemicals) was used as a photoinitiator.

A mixture of TEOS, distilled water, and ethyl alcohol was stirred for 3 h at room temperature under acid catalyst of hydrochloric acid solution (2 M) to obtain partially hydrolyzed TEOS sols. The initial pH of TEOS solution was adjusted at 2. The molar ratio of TEOS : water : EtOH was kept at 1 : 3 : 3. And then, in order to prepare modified silica sol, the silane coupling agent MPTMS, of which content was adjusted as 4.0 molar ratio of TEOS to MPTMS, was added into the hydrolyzed TEOS sol, followed by stirred for 18 h. The organic UV-curable resin system was prepared by mixing four different acrylic oligomers based on composition as 40 wt% of EBECRYL 1290, 30 wt% of DPHA, 20 wt% of TMPTA, 10 wt% of HDODA, and then combining with 5 phr of photoinitiator. This acrylic resin system was mixed with TEOS sol modified with MPTMS and then the mixture was stirred vigorously for 3 hr at room temperature to produce urethane acrylate based silica hybrid coating sols with various compositions. The coating was performed by obtained hybrid coating sols on the pretreated PET substrate with a thickness of 100 μm using a bar coater (# 12, Webster). Prior to UV curing, the hybrid coated films were dried at 60 °C for 10 min in a drying oven to eliminate the volatile diluent that was used to control the flow behavior of the viscous acrylic oligomers. The dried coated films were cured in a batch type UV curing system (Unilam) equipped with a UV-lamp (MFUV-01L21) with irradiation intensity of 120 mW/cm^2. All of the cured samples were kept in a dessicator to prevent the moisture influence prior to performing the characterization. The experimental procedure for the preparation of acrylate/SiO$_2$ hybrid coated films and hybrid gels is presented in Fig. 1.

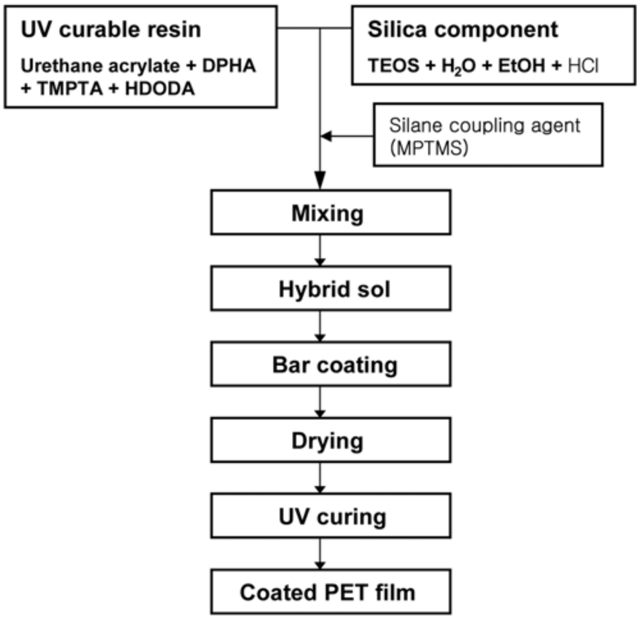

Fig. 1. Experimental procedure for the preparation of UV-cured acrylate/SiO$_2$ hybrid coated film.

2. Characterization

The morphology of fractured surfaces of the hybrid materials was observed by using field-emission scanning electron microscope (FE-SEM, JSM-6500F). The surface topologies of the hybrid materials were examined by atomic force microscope (AFM, D3100, Tecsco) in the contact mode with being focused on the micro-domain of 1 μm×1 μm. The values of root-mean-square (RMS), which may be considered as a parameter for surface roughness, were calculated from the roughness profile determined by AFM. The glass transition behavior of the hybrid material was examined by using differential scanning calorimetry (DSC 2010, TA Instrument) at a temperature range of 30-250 °C with a heating rate of 10 °C/min under nitrogen atmosphere. The optical transparency of the hybrid coating film was measured by visible spectrometer (Optizen 1412V, Mecasys Co.) in the visible-light wavelength range of 350-850 nm. The abrasion resistance of the hybrid coated film was measured according to ASTM D4060 using Taber abrasion tester (WL210T, Withlab Co.) at 250 g load with CS10F wheels. The coated films were abraded to 100 cycles in a wheel rotation speed of 60 rpm, and then the light transmittance through the wear track area was measured by visible spectrometer at a wavelength of 700 nm. The anti-abrasive property of the hybrid coated film was evaluated in terms of percentage light transmittance loss with respect to non-abraded coating film, as following equation:

$$\Delta T\ (\%)=[(T_1-T_2)/T_1]\times 100\ (\%) \tag{1}$$

where T_1 and T_2 are light transmittance of the non-abraded and abraded coated film, respectively.

RESULTS AND DISCUSSION

In the organic-inorganic hybrid materials, the phase interaction between organic polymeric resin and inorganic silica particle has been considered as the crucial factor, because it greatly influences the performance as well as phase morphology of the hybrid [12,13]. In this study, therefore, we prepared UV-curable acrylate/SiO$_2$ hybrids via sol-gel process in the presence of silane coupling agent, MPTMS, to increase the interfacial attraction between two phases. Fig. 2 shows the morphology observed by FE-SEM for the UV-cured acrylate/SiO$_2$ hybrid gels containing different TEOS content of 0.01 and 0.03 mol. Morphological variation caused by addition of MPTMS is also exhibited in this figure. In the case of hybrid samples without addition of MPTMS silane coupling agent, a microphase separation was observed to occur during gelation, which may be attributed to weak interfacial attraction between organic and inorganic phases. In particular, in the hybrid incorporated with 42.9 wt% inorganic silica, corresponding to 0.03 mol of TEOS, which was theoretically calculated under the assumption of 100% conversion from the TEOS precursor to the silica network, silica clusters with larger domain size were formed as can be seen in the micrograph as compared with the hybrids with small amount of 0.01 mol TEOS. This formation of micro-sized cluster which induces the microphase separation can be ascribed to the coalescence of primary silica particles

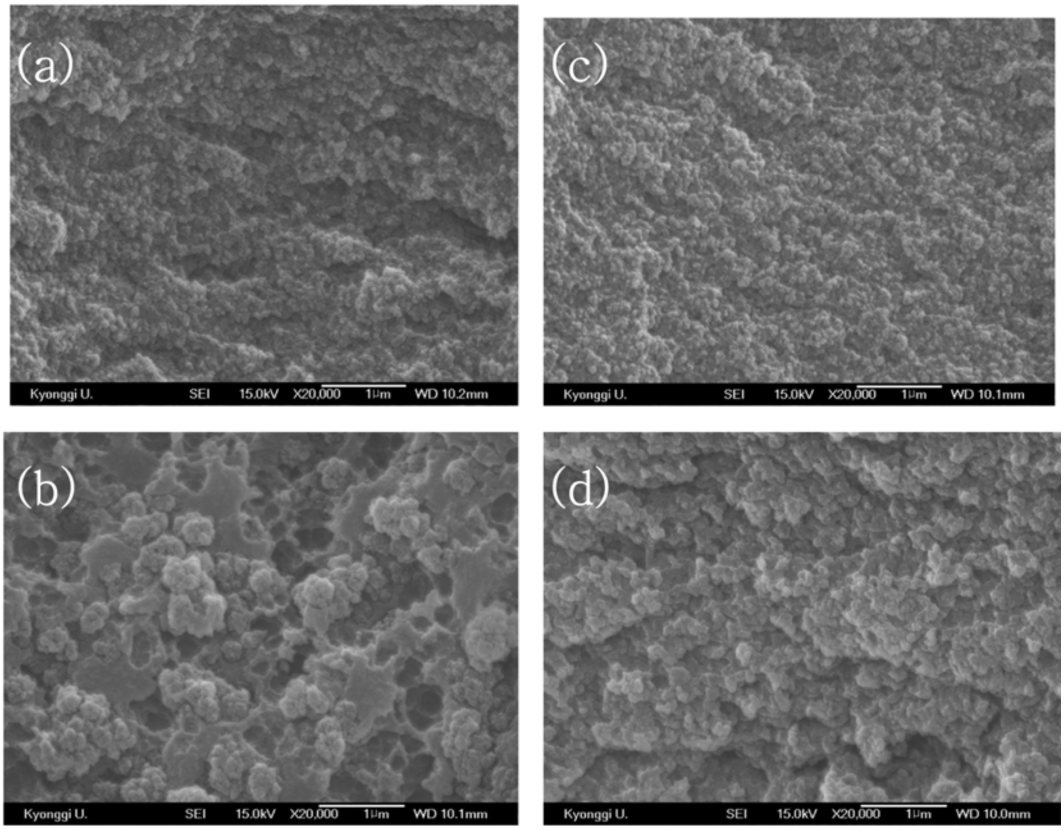

Fig. 2. SEM images of acrylate/SiO$_2$ hybrids without MPTMS; (a) TEOS=0.01 mol, (b) TEOS=0.03 mol, and hybrids with addition of MPTMS; (c) TEOS=0.01 mol, (d) TEOS=0.03 mol.

caused by a chemical condensation reaction between Si-OH groups on the silica surfaces and physical interaction among silica particles, as reported in the earlier study [13]. Whereas, addition of silane coupling agent MPTMS resulted in more stable and homogeneous morphology exhibiting finely dispersed silica particles, indicating that the tendency of agglomeration among nano-sized silica particles could be substantially suppressed due to enhanced interaction between organic and inorganic phases.

The interfacial attraction between organic polymers and inorganic dispersed silica network can also influence the glass transition behavior of the UV-cured acrylate resin consisting of the hybrids. To evaluate the phase compatibility between organic and inorganic components, we investigated the glass transition behavior of the UV-cured acrylate resin from the heating thermograms obtained by DSC experiment, which is displayed in Fig. 3. The glass transition temperature was observed to be increased from 145.5 °C for cured neat acrylate polymer to 149.3 °C for the hybrid without addition of MPTMS by temperature increment of 3.8 °C. This increase in the glass transition temperature for the hybrid without MPTMS may be attributed to more restricted chain mobility of the cured acrylate polymer by the presence of silica network [14]. Moreover, the hybrid with MPTMS showed higher glass transition temperature of 155.1 °C by temperature increment of 5.8 °C as compared with that of hybrid without MPTMS, demonstrating that interfacial adhesion between organic acrylate polymer and inorganic silica component was prominently improved by the addition of silane coupling agent MPTMS, as confirmed in the previous morphological analysis.

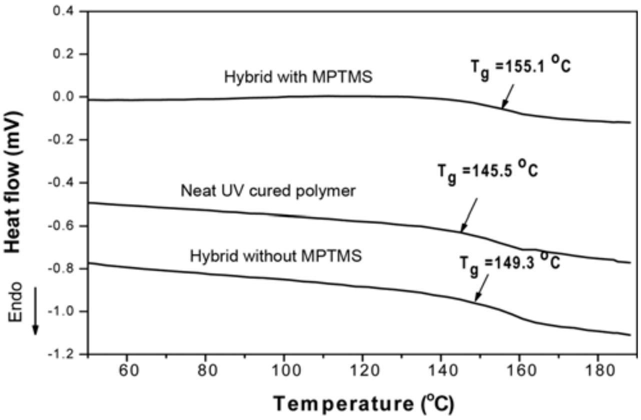

Fig. 3. DSC heating thermograms of the UV-cured resin and hybrids.

The storage time or gel time of coating sol has been recognized as the significant factor in practical use for coating application. In general, hybrid sols prepared through sol-gel process can be converted into hybrid gels via gelation and aging process undergoing continuing physical and chemical changes [15]. This hybrid gels cannot be used for the coating process due to lack of fluid flow property. To evaluate the sol stability of the hybrids, therefore, we investigated gel time for the various hybrid sols kept in the closed vial at room temperature, and the obtained results are presented in Fig. 4.

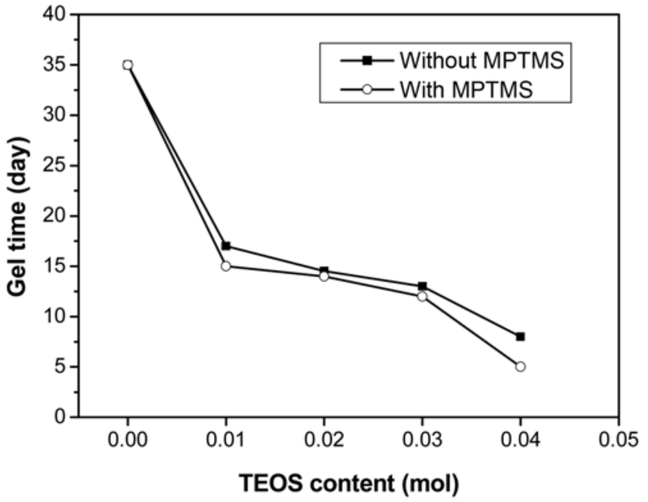

Fig. 4. The measured gel time for the hybrids without MPTMS and with MPTMS.

The gel time was reduced dramatically from 35 days for the pure UV-curable acrylate coating solution to 16 days for the MPTMS added hybrid sol with only 0.01 mol TEOS content. This remarkable reduction in the gel time by hybridization can be caused by the additional formation of 3-dimensional silica network combined with partially cross-linked organic acrylate resin, which ultimately promotes the entrapment of solvent fluid within the space bounded by the silica skeleton. However, when TEOS precursor was incorporated at more than 0.01 mol corresponding to 20 wt% silica content, the gel time of hybrid sol was observed to be very slightly decreased with increasing TEOS content. It can be also seen that the addition of silane coupling agent MPTMS gave rise to slight reduction in a gel time as compared with that of hybrid sol without addition of MPTMS, implying an insignificant effect of MPTMS on the gel time in the hybrid.

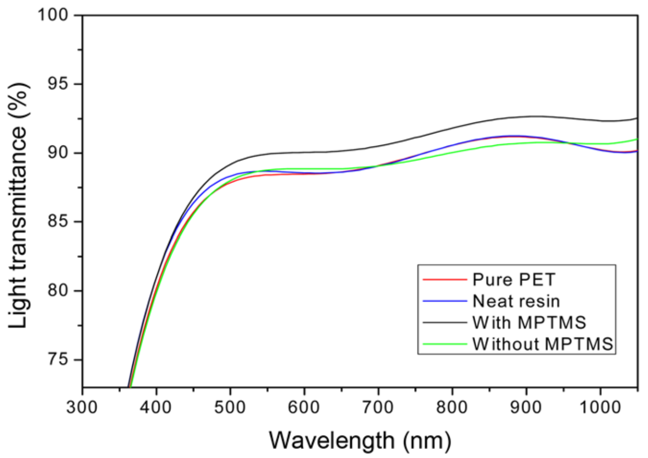

Fig. 5. Optical transmittance of the non-coated PET substrate, coated film with neat acrylate resin, and hybrids.

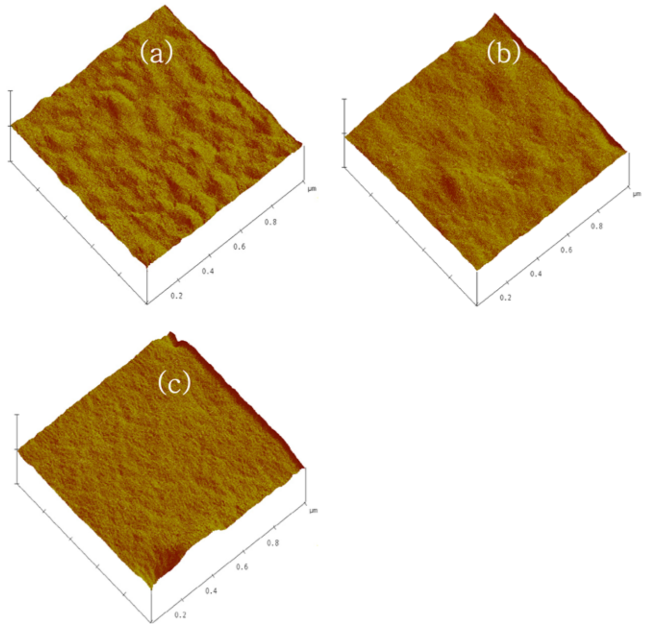

Fig. 6. AFM images of the surfaces of (a) pure PET substrate, and films coated with hybrids with MPTMS contents of (b) 0 mol and (c) 0.0075 mol.

Fig. 5 shows the optical transmittance in a range of visible light wavelength for the PET substrate, neat acrylate resin coated film, and films coated by two different hybrids containing 0 and 0.0075 mol MPTMS. The light transmittances of the films coated by neat acrylate resin and hybrid without addition of MPTMS were measured to be almost same as that of PET substrate, exhibiting 85-90% transmittance rate in the visible light range of 500-900 nm. On the other hand, MPTMS added hybrid coated film showed a remarkable enhancement in transparency with the measured light transmittance rate above 90% in the entire visible light range. This result for the optical transparency suggests that the addition of MPTMS silane coupling agent with only small amount could significantly contribute to the improvement in the optical transparency of the coated film as a result of a more homogeneous and finely dispersed nanostructured morphology, which resulted from increased interfacial attraction between organic and inorganic phases, as observed in the previous SEM images.

In general, optical transparency of the polymeric film is predominantly influenced by the surface topographic structure because the extent of visible light scattering on the film surface is determined by the surface roughness. Fig. 6 shows the AFM images of the surface for the pure PET substrate and two different hybrid (TEOS content: 0.03 mol) coated films with 0 mol and 0.0075 mol MPTMS content. From the AFM observation, the RMS (root mean square) values for the PET substrate and hybrid coated films without MPTMS and with MPTMS were determined to be 1.102 nm, 0.996 nm, and 0.821 nm, respectively. A smooth surface with low RMS value could be obtained by applying UV-curable acrylate/SiO_2 hybrids onto the PET substrate with relatively larger RMS value. Particularly, in the case of hybrid coated film with the addition of the MPTMS silane coupling agent, the surface topology was observed to be substantially improved because of homogeneous morphology with well-dispersed nano silica particles resulting from increased phase compatibility between two phases.

The anti-abrasive property of the hybrid coated film was examined in terms of light transmittance loss percentage obtained from

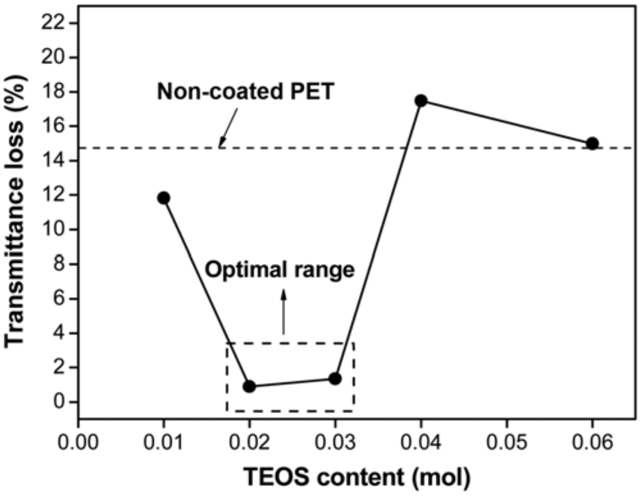

Fig. 7. Optical transmittance loss percentage for the hybrid coated film as a function of TEOS contents.

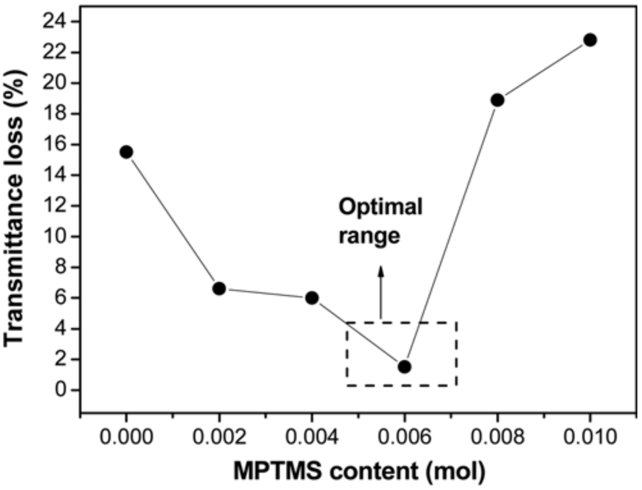

Fig. 8. Optical transmittance loss percentage for the hybrid coated film as a function of MPTMS contents.

Taber abrasion test. The measured light transmittance loss percentage as a function of TEOS and MPTMS content is displayed in Figs. 7 and 8, respectively. The abrasion resistance of the hybrid coated film was considerably improved by incorporating inorganic silica in the content range of 33.4-43.9 wt% (corresponding to 0.02-0.03 mol TEOS), exhibiting a marked reduction in the light transmittance loss percentage from 14.7% for the non-coated PET substrate to 0.9-1.3% for the hybrids. This improvement in the anti-abrasive property up to some level of silica content was ascribed to the formation of three-dimensional silicate network with superior abrasion resistance through condensation reaction, along with homogeneously developed nano-structured morphology. However, in the case of hybrids with silica content at more than 50 wt% (0.04 mol TEOS), the abrasion resistance was decreased, which may be due to poor dispersion of silica cluster with large domain size caused by coalescence of primary silica particles. Fig. 8 shows the effect of MPTMS content on the abrasion resistance of the hybrid coated film with fixed content of 0.03 mol for added inorganic precursor TEOS. In a similar trend with result shown in Fig. 7, the abrasion resistance was also steadily improved up to 0.006 mol of MPTMS content, and then reduced above 0.006 mol of MPTMS content. The reason for this reduction in the abrasion resistance at excess amount of silane coupling agent MPTMS is that the additional silicate network produced from hydrolysis and condensation reaction of the MPTMS as the secondary inorganic source can result in phase-separated morphology due to formation of silica cluster with large domain size, as the case of hybrid added with excess amount of TEOS. Consequently, it was confirmed from these results that there existed an optimum level of content in the inorganic precursor TEOS and silane coupling agent MPTMS, as represented with dotted rectangle in the figures, to obtain UV-cured acrylate/SiO_2 coated film with high anti-abrasive and scratch resistant property.

CONCLUSIONS

UV-curable urethane acrylate based hybrid materials for high abrasion resistant coating application were prepared by the incorporation of inorganic silicate network via sol-gel method. As the organic component consisting of hybrids, three different diluting acrylic oligomers with multi-functional reactive groups in addition to urethane acrylate oligomer as the main network former were employed to obtain more densified organic network structure with a high degree of cross-linking. The addition of silane coupling agent MPTMS containing functional reactive methacrylic groups was observed to give rise to the improvement in the phase compatibility between UV-cured acrylate resin and inorganic silicate component due to increased interfacial attraction between two phases, which resulted in homogeneous morphology with finely dispersed silica particles. In addition, this enhancement in the interfacial attraction was confirmed in terms of measurements of glass transition temperature and optical transparency as well as morphological observation. The amount of silane coupling agent MPTMS and the inorganic silicate precursor TEOS was found to have a significant effect on the anti-abrasive property of the hybrid coated films. It can be suggested that the TEOS and MPTMS should be used in an optimal range of content to prepare hybrid coated film with high abrasion resistant property.

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