Organic-Inorganic Hard Coating Layer Formation on Plastic Substrate by UV Curing Process

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Abstract: Efficient methods for making organic-inorganic hard coating layers on a polymethylmethacrylate substrate were developed and optimized to improve the mechanical and optical properties. Colloidal silica was coupled with methacryloxypropyltrimethoxysilane to make Si-O-Si bonds before incorporating them into the organic phase of the monomer and oligomer. A combination of photoinitiators with different absorption bands could utilize the UV light throughout the entire wavelength range to show better curing results than the case of a single photoinitiator with a limited absorption band. The effects of the photoinitiator in terms of the mixing ratio and concentration in the coating solution were examined and optimized. The UV curing reactivity was improved using a mixture of different initiators with different absorption bands, and 4:1 ratio mixture of Irgacure 184 and Irgacure 907 showed the best hard coating properties, such as hardness and impact strength. The optimum initiator content was determined to be 5 wt% in the hard coating solution. However, too much initiator resulted in excessive primary radical reactions of the monomers, and the competition of primary radicals reduced the conversion and initiator efficiency.

Keywords: organic-inorganic hybrid hard coating, UV-curing, coupling agent, photoinitiator, hardness, impact strength, optical properties.

Introduction

Applications of plastic substrates are gaining great interests in flat panel display and plastic optical industries.[1] Poly (methyl methacrylate) (PMMA), poly(ethylene terephthalate) (PET), polycarbonate (PC), and polyethersulfone (PES) can be fabricated into transparent films and replace the glass substrates of heavy weight and fragility.[2] PMMA has advantages over the other plastic materials for transparent substrates, because it shows less light loss and greater transmittance in visible wavelength range due to less absorption and scattering characteristics than the other substrates. PMMA also has the least dependence of refractive index on wavelength due to its intrinsic isotropic property. Therefore, it has been applied to various display and optical products such as cellular phone, smart phone, PDA, car navigation and DMB. However, despite the advantages above mentioned, it still has limitations to be overcome for the real application in terms of surface hardness, impact strength, abrasion resistance and long term transparency.[3,4]

Especially for the application to window of cellular phone, which is always exposed to atmosphere, abrasion damages and scratch should be minimized by coating with improved hardness. Hard coating process can be classified to two categories; thermal curing process using silicone compounds for the functionalization of the coating layer and UV-curing process using acrylic compounds for process ease. Recently organic-inorganic hybrid coating by UV-curing process has been intensively investigated.[5,6] Organic-inorganic hybrid materials are made from organic and inorganic materials by chemical bonding at molecular scale. Incorporation of organic materials into inorganic materials was attempted in its initial stage for the prevention of crack formation during the drying step of sol-gel process or for the stabilization of inorganic. However, development of sol-gel process enabled the use of organic metal alkoxide, and various functionalities can be endowed with replacement of organic group inside the organic metal alkoxide or addition of organic monomers.

Organic-inorganic hybrid materials were named in several manners such as ORMOSIL (organically modified silicate), ORMOCER (organically modified ceramic), CERAMER (ceramic polymer), and POLYCERAM (polymer ceramic).[7]

Inorganic materials can be uniformly dispersed in organic phase in hybrid system, and organic-inorganic hybrid material can cover the large area by low temperature processing. Therefore, it can overcome the heat resistance problems of organic materials in its expanding the application fields. Especially for coating on plastic film it showed improved

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compatibility with organic film to enhance the adhesion properties of the coating layer.[8-10] Organic-inorganic hybrid material coating was also utilized to improve the weatherability,[11,12] staining resistance,[13] corrosion resistance,[14] antistatic,[15] gas barrier properties[16,17] as well as the surface hardness.[18] Recently UV-curing process is commonly used because it can reduce the curing time compared with thermal curing process. However, curing system composed of both organic and inorganic materials is quite different from the conventional organic system, and selection of initiator and optimization of curing conditions are very important to make desired structure and properties.

In this work organic-inorganic hybrid materials were coated on PMMA film to make hard coating layer. Colloidal silica in nano scale was selected as inorganic material and its surface was treated with silane coupling agent for its uniform dispersion in organic phase. Polyurethane acrylate, monomer, and silane coupled silica were compounded with initiator to make coating solution. Thin layer coating was performed by spin coating method and it was UV-cured to make a hard coating layer. Selection of initiator and compounding ratio were investigated in terms of properties of hard coating layer.

Experimental

Materials. Difunctional urethane acrylate (MIRAMER PU-280, Miwon Co., Korea) was used as organic materials for UV-curing, and difunctional 1,6-hexanedioldiacrylate (HDDA, Aldrich Co.) and trifunctional trimethylol propane triacrylate (TMPTA, MIRAMER M300, Miwon Co., Korea) were used as reactive diluents to control the viscosity of coating solution. Colloidal silica of 15 nm size was selected as an inorganic material, which was supplied by Shinheung Silicate Co., Korea as a dispersed form in MeOH by 30 wt%. Methacryloxy propyl trimethoxy silane (MAPTMS, KBM-503, ShinEtsu Co.) was used as a silane coupling agent for colloidal silica, and isopropyl alcohol (IPA, DW Co. Korea) was used as solvent for coating solution.

Three kinds of photo initiators were selected such as 1-hydroxycyclohexylphenylketone (HCPK, Irgacure 184), phenyl glyoxylic acid methyl ester (PGAME, Darocur MBF), 2-methyl-1[4-(methylthio) phenyl]-2-morpholino-propan-1-one (MMMP, Irgacure 907), and they were manufactured by Ciba Specialty Chemicals and supplied by Shin Young Radchem. Co., Korea. In this work it was attempted that combination of photoinitiators with different absorption band could utilize the UV throughout the entire wavelength range to show the better curing results than the case of single photoinitiator with limited absorption band. Therefore, three photoinitiators such as Irgacure 184 (205 and 248 nm), Darocur MBF (204 and 256 nm), and Irgacure 907 (238 and 305 nm) were selected among the conventional photoinitiators. PMMA substrate of 0.64 mm of thickness was supplied by I-components Co., Korea.
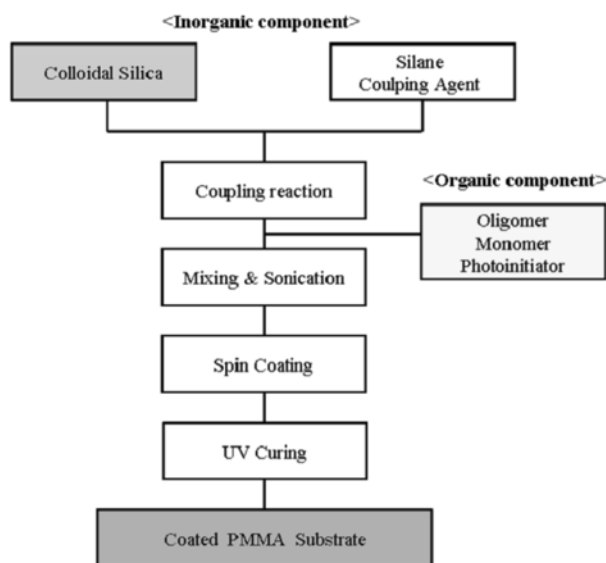

Figure 1. Schematic flow diagram of hard coating process.

Methods. Hard coating process is composed of several steps as summarized in Figure 1. Colloidal silica was treated with silane coupling agent for surface modification and was compounded with organic materials as well as the initiator to make organic-inorganic coating solution. Spin coating and UV-curing steps finally formed the organic-inorganic hard coating layer on PMMA substrate. 12.7 g of colloidal silica solution composed of 3.81 g of SiO_2 in 8.89 g of methanol was added to 77.6 g of isopropyl alcohol at room temperature and they were mixed by using a mechanical stirrer. MAPTMS, silane coupling agent, was added by dropping for an hour, and coating layer made from the mixture of colloidal silica and MAPTMS enhanced the surface hardness. In preliminary tests it was confirmed that amount of MAPTMS was optimized at 7.48 g for fixed amount of colloidal silica at 3.81 g.

Reaction temperature was raised to 70 °C and coupling reaction was performed for 3 h in a stirred reactor. In order to prevent the solidification, gelation and coagulation of particles, HDDA and TMPTA were added as diluents. Remaining solvent and unreacted MAPTMS after the coupling reaction were properly removed by vacuum distillation at 70 °C. Degree of grafting was determined by TGA analysis and it ranged from 20 to 30 wt% depending on reaction conditions. Reaction mechanism of silane coupling was illustrated in Figure 2, which was inferred from work of Mehnert et al.[18] Composition of organic materials was optimized as PU acrylate (50 wt%)/HDDA (25 wt%)/TMPTA (25 wt%) from the results of preliminary tests. Organic materials were mixed with colloidal silica and initiator at room temperature for 5 h, and mixing efficiency was enhanced by ultrasonication for 30 min. PMMA substrate (50×50×0.64 mm) was cleaned by ultrasonic cleaning process for 5 min in methanol, and it was completely dried before use. Hard coating solution was dropped
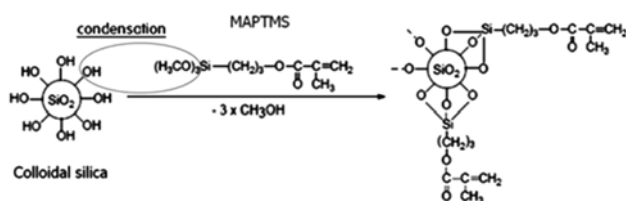
Figure 2. Silane coupling reaction mechanism.

on PMMA substrate followed by spin coating for 30 sec at 1,500 rpm. Solution coated substrate was UV-cured for 2 min at 800 W by using a high pressure mercury lamp from Oriel Co. (London, UK), which has light intensity of 40 mW/cm^2 at 365 nm. The thickness of hardcoating layer was measured about 15-20 μm using Surface profiler (Kosaka Lab., Japan).

Spectroscopic Analyses. Hard coating solution was coated on KBr plate by spin coating method and was analyzed by FTIR spectrometer (System 2000, Perkin Elmer Co.) to examine the reaction scheme of coupling process. Chemical structures of organic materials in coating layer were changed by UV curing reaction, in which crosslinking was performed by breaking C=C double bond in urethane acrylate. Total conversion of curing reaction was calculated by monitoring the change in C-H deformation peak at 811 cm^{-1} before and after UV exposure.[19]

$$\alpha(\%) = \frac{[I_{811}]_o - [I_{811}]_t}{[I_{811}]_o}$$

$\alpha(\%)$=degree of conversion
$[I_{811}]_o$=Intensity before UV irradiation
$[I_{811}]_t$=Intensity after UV irradiation

Chemical analysis at the hard coating surface was conducted by reflection method using ATR accessory (ZnSe) within the wavelength range of 4000~400 cm^{-1} with the resolution of 4 cm^{-1}. Absorption bands of photoinitiators were determined by using UV/Vis Spectrometer (Lambda, Perkin Elmer) within the range of 200~500 nm. Photoinitiator was dissolved in methanol in quartz cell.

Hardness Measurement. Pencil hardness measurement is a very useful method to measure the surface hardness in terms of simplicity, promptness, cost, and data processing. Pencils (Staedtler, Germany) with various hardness ranked as 6B~B, F, HB and 1H~9H were used. Pencil tip was ground on paper at right angle, and it was contacted with surface at 45 angle with constant load. After displacement of pencil on the surface in a determined direction, scratch formation was examined according to ASTM D3363 (Pencil Hardness Tester, CK11-112, CK Co.). Micro hardness of coating layer was determined by Nanoindentor (XP, MTS) with constant strain rate according to continuous stiffness measurement method,[20] which exclude the effects of substrate itself due to the limited affecting depth of indentor.

Impact Strength Measurement. Izod and Charpy impact

tests are good for the measurement of impact strength of isotropic metal specimen but not for polymeric materials. Ball drop method was used to measure the impact strength of plastic substrate in this work according to ASTM D3209. Metal ball was initially fixed to electromagnet at an elevated position, and electric power to electromagnet was off to release the ball to drop on the sample at bottom. Potential energy of the ball was determined to calculate the impact strength when the sample was broken by falling ball.

Optical Properties Measurement. Transmittance of hard coating layer was determined within the visible range by using UV/Vis Spectrometer (8453E, Agilent Tech.). Haze meter (NDH 5000, Denshoku) was also used to measure the haze variation by hard coating process.

$$\text{Haze (\%)} = \frac{\text{Dispersed Trasnmittance}}{\text{Total Transmittance}} \times 100$$

UV stability was examined by measuring the yellowness index (YI) change after coating using multichannel spectrophotometer (MCPD-3000, OTSUKA).

$$YI = \frac{[100(1.28X_{CIE} - 1.06Z_{CIE})]}{Y_{CIE}}$$

$$\Delta YI = YI - YI_o$$

YI_o and YI: yellowness index before and after UV exposure, respectively.

Results and Discussion

Surface Modification of Silica Particles by Silane Coupling. FTIR spectra were shown in Figure 3 for silane coupling agent and colloidal silica before and after silane coupling reaction. Colloidal silica has Si-O-Si structure in spherical shape and has numerous hydroxyl groups at the surface, and polarity of hydroxyl group caused uneven dispersion of silica in the organic phase. Therefore, hydroxyl group should be removed and be replaced by organic functional group. FTIR spectra of colloidal silica showed strong siloxane absorption peaks at 460~480 cm^{-1} and 1100 cm^{-1} and hydroxyl absorption peak at 3300~3500 cm^{-1}. MAPTMS, the silane coupling agent used in this work, has -Si-O-CH$_3$ structure, which showed the absorption peak at 760, 1000, and 1200 cm^{-1}. It also has absorption peaks at 1600, 1700, and 2950 cm^{-1} for C=C, C=O, C-H, respectively.

-Si-O-CH$_3$ in MAPTMS was changed to Si-OH by hydrolysis reaction in its initial stage of coupling reaction, and Si-OH was changed to Si-O-Si by condensation reaction at the terminating step of coupling reaction, while unreacted Si-OH group still remained at the surface. C=C peak at 1600 cm^{-1} and C=O peak at 1700 cm^{-1} remained with no change. Unreacted Si-OH could be the important factor to control the size growth of silica particle. Condensation reaction between the silica and hydrolyzed silane coupling agent resulted in the
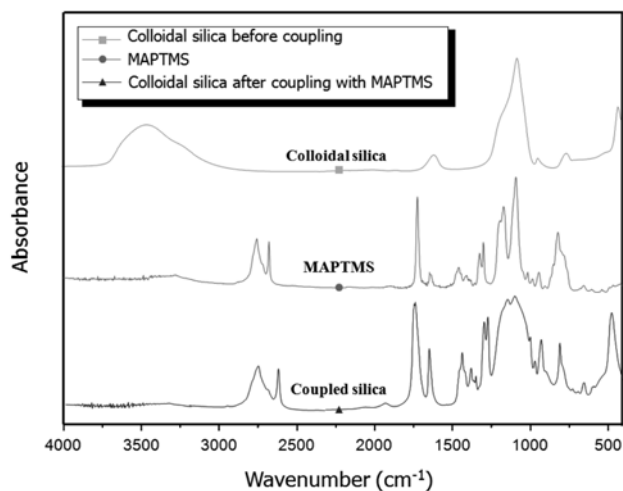
Figure 3. FTIR spectra of MAPTMS, and colloidal silica before and after the coupling reaction.

Figure 4. The absorption spectra of photoinitiators.

decrease of hydroxyl peak,[21] which confirmed the successful coupling reaction between silica particle with MAPTMS.

Absorption Wavelength of Photoinitiators. Photoinitiators were classified according to the polymerization mechanism such as free radical polymerization and cationic polymerization, and more than 90% of photoinitiators are for free radical polymerization.[22] Photoinitiator should have characteristics to produce more free radicals with high reactivity, which can be quantified as molar extinction coefficient, quantum yield. UV absorption spectrum of photoinitiator should coincide with that of UV source for more effective curing. They should have compatibility and reactivity with oligomers and monomers used.[22] They also have storage stability and should be free from toxicity and yellowness index change.

Three kinds of photoinitiators used in this work are known to cause little yellowness index change after UV exposure. Chemical structures of the photoinitiators were listed in Table I. Wavelength absorption band of initiator should coincide with that of UV source for improved photo reaction efficiency in UV curing system. Therefore, wavelength absorption band of initiator selected should be examined before UV curing. As shown in Figure 4, Irgacure 184 has absorption bands at 205 and 248 nm, Irgacure 907 has at 204, 238, and 305 nm, and Darocur MBF has at 204 and 256 nm. Irgacure 184 and Irgacure 907 have quite different absorption bands, and 1:1 mixture of both initiators could cover the both absorption bands.

Table I. Chemical Structure and Maximum Absorption Wavelength of Photoinitiators Used

	Irgacure 184	Darocur MBF	Irgacure 907
Chemical Structure			
Max. Absorption Wavelength	205, 248 nm	204, 256 nm	204, 247, 304 nm
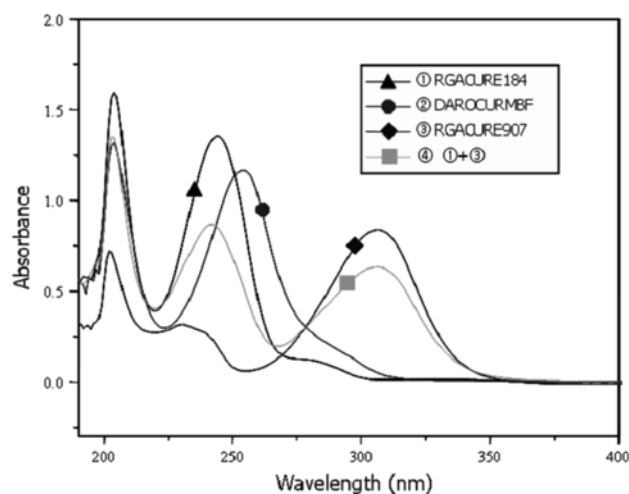
Mixing of various initiators with different absorption bands had more merits than single initiator to achieve the UV source utilization through the wavelength range. Effects of initiator mixing was examined for organic solution system composed of PU acrylate (50 wt%)/HDDA (25 wt%)/TMPTA (25 wt%) which was mixed with colloidal silica treated with coupling agent. Irgacure 184 and Irgacure 907 were used separately or as 50/50 mixture state with same total amount in every case. Final composition of coating solution was organic solution/colloidal silica/photo initiator=65/30/5wt%. Coating solution was coated on KBr plate and cured for FTIR analysis to calculate the final conversion. As shown in Table II, 50/50 mixture of Irgacure 184 and Irgacure 907 achieved the highest conversion among the various initiators used. Darocur MBF has absorption peak at 250 nm only and showed the lowest conversion, even though it had relatively good solubility. It was found that combination of photo initiators with different absorption band could utilize the UV throughout the entire wavelength range to show the better curing results than the case of single photo initiator with limited absorption band.

UV beam at short wavelength has high energy and effects at the surface, while UV beam at high wavelength has low energy and penetrates into the layer. Photoinitiator with short wavelength absorption band showed the more reactivity at the surface of the coating layer, while initiators with long wavelength have reactivity at the inner part of the coating layer. Combination of Irgacure 184 for short wavelength (250 nm) and Irgacure 907 for long wavelength (305 nm) achieved the highest conversion of curing reaction both at the surface and inner part of the coating layer (Figure 5). Pencil hardness of the hard coating layer was increased up to 4H by UV curing reaction with single photoinitiator. Combination of photoinitiators with different absorption band still enhanced the pencil hardness up to 5H, which is in good agreement with the results of conversion. Similar results were obtained for micro hardness test and falling ball impact strength test as shown in Table II.

Table II. Conversion and Mechanical Properties of the Hard Coating Layers Formed with Various Photoinitiators

Photoinitiator	Conversion (%)	Pencil Hardness	Micro Hardness (GPa)	Falling Ball Impact Strength (mJ)
PMMA Substrate	-	1H	0.78	10.4
① Irgacure 184	84.6	4H	2.43	12.5
② Darocur MBF	75.1	3H	1.85	11.8
③ Irgacure 907	82.9	4H	2.35	12.1
① + ③	85.2	5H	2.61	13.1
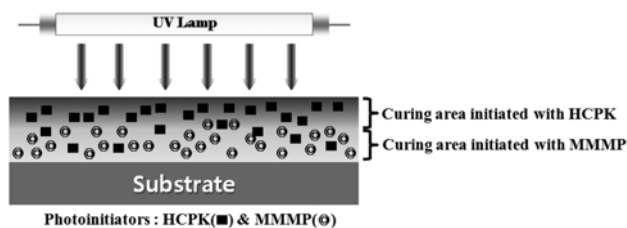
Figure 5. Curing mechanism at the surface and inner part of the coating layer by combination of Irgacure 184 and 907.

Table III. Optical Property Changes after Hard Coating with Various Photoinitiators

Photoinitiator	Light Transmittance (%)	Haze	Yellowness Index
PMMA Substrate	93.7	0.61	0.75
① Irgacure 184	92.9	0.82	1.01
② Darocur MBF	93.1	0.71	2.45
③ Irgacure 907	93.3	0.75	2.05
① + ③	93.2	0.82	1.62

Light transmittance, haze and yellowness index change were also determined for each case of photo initiator as listed in Table III. Transmittance within the visible wavelength range was very slightly decreased after hard coating and little effect was observed with photo initiator change. Haze due to the light scattering was increased after hard coating especially for Irgacure 184 and combination of Irgacure 184 and Irgacure 907. UV exposure for hard coating caused yellowness index change especially for Irgacure 907 and Darocur MBF. Yellowness index changes were caused by intrinsic initiator coloring

and by products formed from side reactions of decomposed radicals. However, overall transmittance change was not much affected by hard coating by UV curing.

Mixing Ratio of Photoinitiators. Mixing ratio of photoinitiators is one of the important factors to enhance the properties of hard coating layer, since each photoinitiator has different radical reactivity and efficiency with each other. Mixing ratio of Irgacure 184 and Irgacure 907 were controlled to be optimized for the property enhancement.

As shown in Table IV, overall conversion was maximum when the mixing ratio of Irgacure 184 and Irgacure 907 was 4:1 (wt%). Micro hardness and falling ball impact hardness showed maximum values at this ratio. Pencil hardness appeared to be unchanged with mixing ratio, since pencil hardness measurement is a rough testing method and it failed to detect the slight change. Optical property changes were little affected by the mixing ratio of photo initiators. Haze was slightly increased by hard coating and yellowness index change increased after UV exposure especially with increase of Irgacure 907 content due to its intrinsic color as shown in Table V.

Photoinitiator Concentration. Effects of photoinitiator concentration on UV curing reaction were examined in terms of reaction rate.[24,25] Polymerization rate at steady state can be expressed as below for photo initiating radical polymerization.

$$R_p = -\frac{[M]_o}{dt} = \frac{k_p}{k^{0.5}}[M_o](\phi \cdot \varepsilon \cdot I_o \cdot [A]_o)^{0.5}$$

R_p : polymerization rate
$[M]_0$: the initial concentration of monomer
k_p: the rate constant of chain propagation
k_t: the rate constant of chain termination
ε: the molar extinction coefficient
Φ: the initiation quantum yield of the photoinitiator

Table IV. Conversion and Mechanical Property Variations with Photoinitiator Ratio Change

| Photoinitiators (Irgacure 184:907)	Conversion (%)	Pencil Hardness	Micro Hardness (GPa)	Falling Ball Impact Strength (mJ)
PMMA Substrate	-	1H	0.78	10.4
1:1 wt%	85.2	5H	2.61	13.1
2:1 wt%	87.6	5H	2.73	13.6
3:1 wt%	88.0	5H	2.89	14.4
4:1 wt%	88.1	5H	2.95	14.9
5:1 wt%	87.9	5H	2.82	14.1

Table V. Optical Property Variations with Photoinitiator Ratio Change

Photoinitiators (Irgacure 184:907)	Light Transmittance (%)	Haze	Yellowness Index
PMMA Substrate	93.7	0.61	0.75
1:1 wt%	93.2	0.82	1.62
2:1 wt%	93.1	0.74	1.53
3:1 wt%	93.2	0.79	1.40
4:1 wt%	93.2	0.76	1.37
5:1 wt%	93.1	0.81	1.31

I_o: the intensity of the incident radiation
$[A]_o$: the absorbance of the photoinitiator

UV curing reaction depended on the UV intensity and concentration and efficiency of photoinitiator. Increase of photoinitiator concentration resulted in the increase of number of radicals. Photoinitiator efficiency depended on two factors; radical formation efficiency and number of primary radical reactions. Number of primary radical reaction increased with the initiator concentration, and increase of reaction reduced the relative number of primary radicals in competition. Therefore, initiator efficiency decreased with photoinitiator concentration.[23,26] Effects of initiator concentration on the hard coating layer were examined for the best mixture recipe of Irgacure 184 to Irgacure 907 as 4:1(wt%) as shown in Tables IV and V.

Effects of photoinitiator amount were examined for the 4:1 ratio mixture of Irgacure 184 to Irgacure 907, when total initiator concentration ranged from 1 to 6 wt%, while the other composition of organic and inorganic compounds was maintained as stated above. In Figure 6, overall conversion change was examined in terms of photoinitiator concentration.[27] At lower initiator concentration as 1 and 2 wt%, number of radicals to initiate the radical reaction was less than needed to cover the amount of coating solution, which showed very low conversion due to the incomplete curing reaction. Increase of initiator concentration up to 5wt% enhanced the conversion, and the results corresponded with the reaction rate equation. However, too much initiator caused decrease of conversion as shown in the case of 6 wt%. As mentioned above, increase of
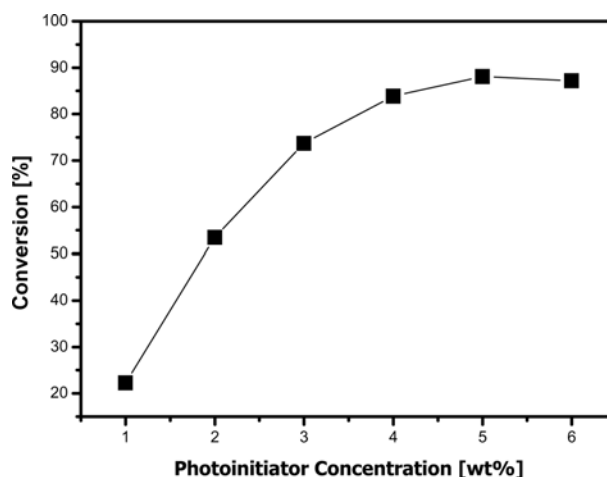
Figure 6. Conversion variation with photoinitiator concentration.

initiator concentration caused too much primary radical reactions for monomers, and competition of primary radicals reduced the conversion as well as the initiator efficiency.

As shown in Table VI surface hardness was hard to measure for the sample with incomplete curing at lower initiator concentration. Increase of initiator concentration enhanced the surface hardness, and at 5 wt% pencil hardness showed the best value of 5H. Increase of initiator amount also made contribution to crosslinking of the coating layer to bring about the enhancement of micro hardness and falling ball impact strength. Table VII showed that initiator amount had little sig-

Table VII. Optical Property Variations with Photoinitiator Concentration

Photoinitiators (Irgacure 184:907=4:1 wt%)	Light Transmittance (%)	Haze	Yellowness Index
1 wt%	93.1	0.75	1.42
2 wt%	92.9	0.77	1.48
3 wt%	93.2	0.77	1.51
4 wt%	93.4	0.79	1.49
5 wt%	93.2	0.76	1.37
6 wt%	93.1	0.75	1.39

Table VI. Conversion and Mechanical Property Variations with Photoinitiator Concentration

Photoinitiators (Irgacure 184:907=4:1 wt%)	Conversion (%)	Pencil Hardness	Micro Hardness (GPa)	Falling Ball Impact Strength (mJ)
1 wt%	22.3	-	-	-
2 wt%	53.5	-	-	-
3 wt%	73.7	3H	1.89	12.1
4 wt%	83.9	4H	2.41	13.6
5 wt%	88.1	5H	2.95	14.9
6 wt%	87.2	5H	2.82	14.5

nificant effects on optical properties, such as transmittance, haze and yellowness index change in visible wave length range. For optical application it was recommended that transmittance should be greater than 88% and haze should be less than 1.0,[28] and coating layer prepared in this work has little optical deterioration problems. Yellowness index increase was partly caused by intrinsic color of initiators and it was not so serious to cause UV degradation during its real application to products.

Conclusions

Efficient methods to make organic-inorganic hard coating layer with improved mechanical and optical properties were developed and optimized by incorporation of colloidal silica into the organic phase of monomer and oligomer. Colloidal silica was successfully coupled with MAPTMS, where Si-O-Si bond was formed by condensation reaction between the hydroxyl groups on silica surface and hydrolyzed MAPTMS. Coupling reaction helped silica be uniformly dispersed in organic phase and effectively reacted with monomer and oligomer for cross linked hard coating layer formation.

Wavelength absorption band of initiator should coincide with that of UV source for improved photo reaction efficiency in UV curing system. Combination of photo initiators with different absorption band could utilize the UV throughout the entire wavelength range to show the better curing results than the case of single photo initiator with limited absorption band. Pencil hardness, micro hardness and falling ball impact strength of the hard coating layer was much improved by combination of initiators, and UV curing did not much deteriorate the optical properties of the coating layer. Mixing ratio of photo initiators was optimized as Irgacure 184 and Irgacure 907 was 4:1 (wt%), where it showed the best mechanical and optical properties.

Effects of photo initiator concentration on were examined for the best mixing ratio recipe in terms of overall conversion. Increase of initiator concentration up to 5 wt% enhanced the conversion due to the increase of number of radicals formed. However, too much initiator caused decrease of conversion, because it also brought about too much primary radical reaction for monomers, and competition of primary radicals reduced the conversion as well as the initiator efficiency.

References

 (1) S. Wagner, S. J. Fonash, T. N. Jackson, and J. C. Sturm, *Proc. SPIE*, **4362**, 226 (2001).

 (2) M. C. Choi, Y. Kim, and C.-S. Ha, *Progr. Polym. Sci.*, **33**, 581 (2008).

 (3) D. Goutam and K. Debtosh, *J. Non-Cryst. Solids*, **288**, 221 (2001).

 (4) J. D. Mackenzie and E. Bescher, *J. Sol-Gel Sci. Technol.*, **27**, 7 (2003).

 (5) S. E. Calas, A. Duri, and P. Etienne, *J. Non-Cryst. Solids*, **344**, 65 (2004).

 (6) D. Blanc, A. Last, J. Franc, S. Pavan, and J.-L. Loubet, *Thin Solid Films*, **515**, 942 (2006).

 (7) H. Schmidt and H. Wolter, *J. Non-Cryst. Solids*, **121**, 428 (1990).

 (8) C. Sanchez, B. Julian, P. Belleville, and M. Popall, *J. Mater. Chem.*, **15**, 3559 (2005).

 (9) W. Tanglumlert, P. Prasassarakich, P. Supaphol, and S. Wongkasemjit, *Surf. Coat. Technol.*, **200**, 2784 (2004).

(10) D. Blanc, A. Last, J. Franc, S. Pavan, and J. L. Loubert, *Thin Solid Films*, **515**, 942 (2006).

(11) J. D. Cho, S. H. Kim, I. C. Chang, K. S. Kim, and J. W. Hong, *Macromol. Res.*, **15**, 560 (2007).

(12) N. B. Cho, T. H. Lim, Y. M. Jeon, and M. S. Gong, *Macromol. Res.*, **16**, 149 (2008).

(13) L. Y. L. Wu, G. H. Tan, and X. T. Zeng, *J. Sol-Gel Sci. Technol.*, **38**, 85 (2006).

(14) T. P. Chou, C. Chandrasekaran, and G. Z. Cao, *J. Sol-Gel Sci. Technol.*, **26**, 321 (2003).

(15) M. E. L. Wouters, D. P. Wolfs, M. C. V. D. Linde, J. H. P. Hovens, and A.H.A. Tinnemans, *Progr. Org. Coat.*, **51**, 312 (2004).

(16) K. Tadanaga, K. Iwashita, and T. Minami, *J. Sol-Gel Sci. Technol.*, **6**, 107 (1996).

(17) B. Singh, J. Bouchet, G. Rochat, Y. Leterrier, J.-A.E. Manson, and P. Fayet, *Surf. Coat. Technol.*, **210**, 7107 (2007).

(18) F. Bauer, H.-J. Glasel, U. Decker, H. Ernst, A. Freyer, E. Hartmann, V. Sauerland, and R. Mehnert, *Progr. Org. Coat.*, **47**, 147 (2003).

(19) S. H. Cho, H. S. Lim, B. K. Jeon, J. M. Ko, J. Y. Lee, and W. G. Kim, *Macromol. Res.*, **16**, 31 (2008).

(20) F. Mammeri, L. Rozes, and C. Sanchez, *J. Sol-Gel Sci. Technol.,* **26**, 413 (2003).

(21) Y. Y. Yu, C. Y. Chen, and W. C. Chen, *Polymer*, **44**, 593 (2003).

(22) E. Andrzejewska, *Progr. Polym. Sci.,* **26**, 605 (2001).

(23) L. Lecamp, B. Youssef, C. Bunel, and P. Lebaudy, *Polymer*, **38**, 6089 (1997).

(24) T. Scherzer and U. Decker, *Radiat. Phys. Chem.,* **55**, 615 (1999).

(25) S. W. Nam, S. H. Kang, and J. Y. Chang, *Macromol. Res.*, **15**, 74 (2007).

(26) J. H. Moon, Y. G. Shul, H. S. Han, S. Y. Hong, Y. S. Choi, and H. T. Kim, *Int. J. Adhes. Adhes.*, **25**, 301 (2005).

(27) Y. B. Kim, S. C. Park, H. K. Kim, and J. W. Hong, *Macromol. Res.*, **16**, 128 (2008).

(28) H. Y. Gil and J. Y. Bae, Korean Papent 1006752160000 (2007).