Coating Performance and Characteristics for UV-Curable Aliphatic Urethane Acrylate Coatings Containing Norrish Type I Photoinitiators

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The purpose of this study was to investigate the influence of several Norrish I (α-cleavage) type photoinitiators and UV dose on the curing behavior and coating performance of UV-curable aliphatic urethane acrylate coatings. UV-curable coatings were cured under a high-pressure mercury lamp. The curing behavior and coating performance of the UV-curable coatings that were cured using 2-hydroxy-2-methyl-1-phenyl-propan-1-one or 1-hydroxy-cyclohexyl-phenyl-ketone were superior to those of the UV-curable coatings cured using bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide or diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide, when the UV-curable coating was cured in air.

Keywords: Dynamic mechanical properties, FTIR, ATR, surface analysis, UV spectroscopy, photochemistry, photoinitiators, UV, EB, radiation cure, coatings formulation, urethane

UV-curable coatings are experiencing rapid growth in the marketplace due to both technological advances and increasing environmental pressures to reduce the emission of volatile organic compounds (VOCs). UV-curable coatings offer equivalent performance, as they have lower VOC emissions than conventional solvent-based coatings.[1] UV curing offers the advantage of low capital investment, low energy consumption, rapid curing, high productivity, and high degrees of crosslinking (giving rise to outstanding scratch, chemical, and stain resistance). In addition, heat sensitive substrates such as plastics, printed circuit boards, paper, and wood can be coated and cured with UV technology.[2,3]

UV-curable coatings usually contain four main components: oligomers, monomers, photoinitiators, and various additives. The UV curing reactions are induced by the absorption of high intensity UV light by the photoinitiator, and subsequent free radical polymerization and crosslinking of the resins. The selection of the photoinitiator is of prime importance in the design of UV-curable coatings, since the polymerization and/or crosslinking rate depends on the nature of the photoinitiator and the physical properties of the coatings.[4,5]

Photoinitiators are compounds that absorb radiation and are thereby raised to an excited state. From their radiation-excited state, the photoinitiators photolyze or degrade directly or indirectly into free radicals. These free radicals become the initiating species that cause the very rapid polymerization of photocurable formulations, based on a variety of chemistries (acrylates/methacrylates-free radical initiation, etc.). The two main types of photoinitiators are those that form an active species by a fragmentation process and those that do so by a hydrogen abstraction process. The photoinitiators that undergo Norrish Type I reactions photolyze through a homolytic fragmentation mechanism or through α-cleavage, and thereby directly form free radicals capable of initiating polymerization. The absorbed radiation causes bond breakage to take place between a carbonyl group and an adjacent carbon. Those photoinitiators that undergo the Norrish Type II reactions are activated with radiation and form free radicals by hydrogen abstraction or electron extraction from a second compound that becomes the actual initiating free radical. In addition, the Norrish Type III reactions are intramolecular, nonradical processes that involve a β-hydrogen atom. This process leads to the formation of an olefin and an aldehyde through a carbon-carbon bond scission next to a carbonyl group.[3]

The photoinitiator is an essential ingredient of UV-curable coatings and has to have sufficient absorption in the 250~400 nm range, high reactivity, and high thermal stability, as well as being nonyellowing, and nonodorous.[6] In previous studies, the intrinsic reactivity of a photoinitiator has been directly connected with (a) its molecular structure

Table 1—Characteristics of the Oligomer

Oligomer	Viscosity[b] (mPa.S)	Density (g/cm³)	Molecular Weight	Functionality	Polymer Solids (wt%)	T_g (°C)
Ebecryl® 270[a] 3000		1.10	1500	2	> 95	−32

(a) Aliphatic urethane diacrylate oligomer.
(b) Höppler viscosity at 60°C.

(which governs the intensity of the light absorbed, the absorption wavelength range, the energy or electron transfer reactions ability, etc.) and (b) the efficiency of the photophysical and photochemical processes involved in the excited states (which determines the yield of cleavage reactions, electron transfer reactions with amines, and quenching by a monomer or oxygen or other additives such as hydrogen donors, light stabilizers, interactions with the photoinitiator, etc.), as well as with the production of odors, yellowing, and photodegradation due to outdoor exposure, oxygen quenching (environmental factors), interaction with stabilizers, light intensity effects, etc.[3-7]

In particular, Norrish Type I (α-cleavage) photoinitiators are the most important photoinitiators due to their high reactivity and thermal stability. Some of the applications in which α-cleavage photoinitiators are used are clear coatings, printing inks, printing plates, and white lacquers.[4-5]

The formulation of UV-curable coatings requires considerable skill in balancing a number of competing properties such as flexibility, adhesion, toughness, abrasion resistance, resistance to discoloration, chemical and stain resistance, as well as cure rate. The class of oligomers providing the best balance of properties for this particular end use is urethane acrylates. These can either be based on aromatic isocyanates or aliphatic isocyanates. The former type offer a better balance of reactivity, toughness, and hardness, while the aliphatic type has color stability and durability, despite the double bond, but are much more expensive.[8]

The purpose of this study was to investigate the influence of the Norrish Type I (α-cleavage) photoinitiator and the UV dose on the curing behaviors and coating performance of UV-curable aliphatic urethane arcylate coatings.

EXPERIMENTAL

Materials

The UV-curable urethane acrylate system consisted of three main components: first, the aliphatic urethane diacrylate (Ebecryl® 270, UCB) oligomer (*Table* 1); second, the reactive diluent monomers; and third, the photoinitiators used to obtain the UV-curable coatings. The reactive diluent monomer was 1,6-hexanediol diacrylate (Miramer M200, Miwon, S. Korea). Four Norrish Type I photoinitiators were used: 1-hydroxy-cyclohexyl-phenyl
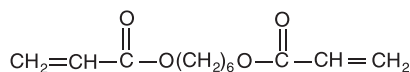
ketone (Micure CP-4, Miwon), 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Micure HP-8, Miwon), bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Irgacure® 819, Ciba Specialty Chemicals), and diphenyl (2,4,6-trimethyl-benzoyl)-phosphine oxide (Darocur® TPO, Ciba Specialty Chemicals).

The reactive diluent monomer and Norrish Type I photoinitiators are shown in *Figures* 1 and 2.

The UV-curable coatings were formulated as shown in *Table* 2. The viscosities of the prepared UV-curable coatings were measured by Programmable Viscometer Model DV-II+ at 25°C. Spindle RV 4 was used. *Table* 3 shows the viscosities of the prepared UV-curable coatings.

Methods

UV CURING PROCESS: Each UV-curable coating was coated onto a glass plate (15 cm × 6 cm × 0.3 cm) using a bar coater (No. 22) and cured in a conveyer belt type UV curing machine equipped with a high-pressure mercury lamp (100 W/cm, main wavelength: 365 nm). The surface of the glass plate was cleaned with acetone and air-dried prior to application.

For heat sensitive applications, a cold mirror was used as a reflector. Such a cold mirror is partially transparent for IR, while most of the UV and visible radiation is reflected. The UV doses used were 340, 680, 1020, 1360, 1700, and 2040 (mJ/cm²). The UV doses were measured with an IL 390C Light Bug UV radiometer (International Light Inc.). The thickness of the cured film was ca. 40 μm.

PENDULUM HARDNESS TEST: A König pendulum hardness tester (Ref. 707PK, Sheen Instruments Ltd., England) was used to monitor the surface hardness of the cured film during the process of UV curing. After exposure to UV, the
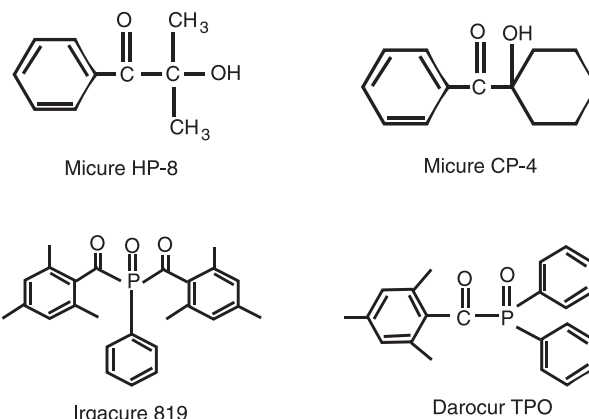

Micure HP-8

Micure CP-4

Irgacure 819

Darocur TPO

Figure 2—Norrish Type I photoinitiators.

Figure 1—Reactive diluent monomer (Miramer M200).

pendulum hardness of the UV-cured film surface was measured at 24 ± 1°C and 50 ± 2% RH.

GEL CONTENT: The cured film was carefully peeled off from the glass plate, in order to measure the gel content. A known weight of the cured film was extracted in acetone at 32°C for 24 hr. The residues were dried at 50°C to a constant weight. The gel content of the cured film was then determined by the following equation:

$$\text{Gel content (\%)} = W_t / W_0 \times 100$$

where W_t is the weight after extraction and W_0 is the weight before extraction.

PROBE TACK TEST: The probe tack test was developed in an attempt to simulate and refine the commonly used method of thumb or finger tack testing. The probe tack test was usually used in the PSA (pressure sensitive adhesives) industry, etc.[9] In general, the probe tack of the coating surface can be evaluated by bringing the smooth end of a cylindrical probe into contact with the coating surface and then plotting the curve of the force/distance produced when it is pulled away. The degree of tack is often expressed as the maximum debonding force value.[10]

As shown in *Figure* 3, a cylindrical probe was brought into contact with the coating surface to be tested under a defined contact pressure and for a well-defined contact time. During the separation of the probe from the coating surface, the tensile force was measured as a function of time (or distance).[9,11] In this study, the probe tack test was conducted using the adhesive test mode of the texture analyzer (TA-XT2i) with a polished stainless steel cylinder probe 5 mm in diameter at 24 ± 1°C and 50 ± 2% RH. Measurements were carried out at a separation rate of 0.5 mm/sec under a constant pressure of 100 gf/cm^2 and with a dwell time of 1 sec.

UV/VIS SPECTROPHOTOMETER: The absorption spectra of the Norrish Type I photoinitiators and the UV urethane acrylate curable coatings containing the Norrish Type I photoinitiators were obtained using a UV/Vis spectrophotometer (Tu-1800 PC, PGeneral, China). A quartz cell with a path length of 10 mm was used. The sample in the cell was subjected to UV/Visible light between 200 and 500 nm. The data interval of absorption was 1.0 nm.

In order to monitor the absorption of photoinitiators and the prepared UV-curable coatings, 0.01 g of photoinitiator was dissolved in 10 g of acetonitrile and 0.05 g of the prepared UV-curable coating was dissolved in 5 g of acetonitrile. In addition, after exposure to UV, the UV-cured film was carefully peeled off from the glass plate, in order to measure the UV absorption of the UV-cured film during the UV curing.

FOURIER TRANSFORMATION INFRARED SPECTROSCOPY: The IR spectra were obtained using a Nicolet Magna 550 Series II FTIR (Nicolet, WI) equipped with attenuated total reflectance (ATR). In order to obtain the IR spectra of the UV-curable coatings during their exposure to UV, each UV-curable coating was applied onto a thin aluminum foil (15 cm × 6 cm × 19 μm) using a bar coater (No. 22) and then cured under the high-pressure mercury lamp during the regular UV dose. The ATR crystal was of zinc selenide (ZnSe). The resolution of the spectrum recorded was 4

Table 2—Formulations of the UV-Curable Coatings

Components	Compositions (wt%)			
	Al-H	Al-C	Al-8	Al-T
Oligomer ....Ebecryl 270[a]	57	57	57	57
Monomer............Miramer M200[b]	38	38	38	38
Photoinitiators.....Micure HP-8[c]	5			
Micure CP-4[d]		5		
Irgacure 819[e]			5	
Darocur TPO[f]				5
Total (wt%)	100	100	100	100

(a) Ebecryl 270 (aliphatic urethane diacrylate).
(b) Miramer M200 (1,6-hexanediol diacrylate).
(c) Micure HP-8 (2-hydroxy-2-methyl-1-phenyl-propan-1-one).
(d) Micure CP-4 (1-hydroxy-cyclohexyl-phenyl-ketone).
(e) Irgacure 819 (bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide).
(f) Darocur TPO (diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide).

Table 3—Viscosities of the UV-Curable Coatings

Viscosity (cP)[a]			
Al-H	Al-C	Al-8	Al-T
480	578	636	664

(a) Measured by programmable viscometer Model DV-II + at 25°C (spindle RV 4).

cm^{-1}. The ZnSe crystal was covered with the coated thin aluminum foil. The coated thin aluminum was removed at a regular UV dose from a conveyer belt type UV curing machine to obtain the IR spectrum.

The curing behavior of the UV-curable coating was monitored by following the decrease in UV exposure of the absorption band (802~817 cm^{-1}), which is characteristic of the CH$_2$=CH– twisting motion of the acrylate group, as a function of the UV irradiation time. The conversion of the acrylate was calculated by means of the following equation, using an unaffected internal reference peak for calibration:

$$\text{Conversion (\%)} = (A_0 - A_t) / A_0 \times 100$$

where A_0 is the calibration peak area between 802 to 817 cm^{-1}, including the absorption peak at 810 cm^{-1} at UV exposure time 0, and A_t is the area at UV exposure time t.

PHOTODIFFERENTIAL SCANNING CALORIMETER: Photopolymerization was studied by using a TA differential scanning calorimeter (DSC, Q-1000 TA Instruments,
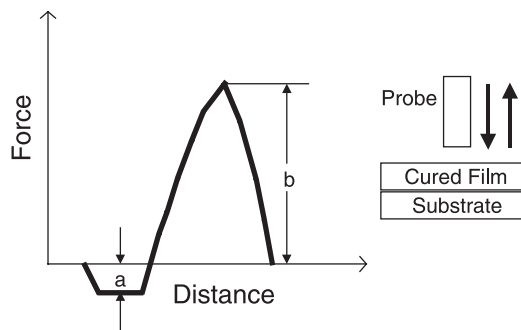
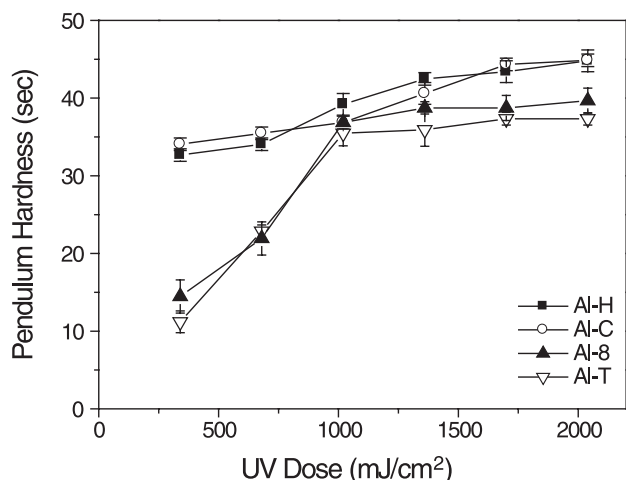Figure 3—Bonding and debonding process during a probe tack measurement.[9]

Figure 4—Influence of the Norrish Type I photoinitiator and that of UV dose on the pendulum hardness of the UV-cured films.

NICEM at Seoul National University) equipped with a photocalorimetric accessory (Novacure® 2100). Light from a 100-W high pressure mercury lamp was used. The light intensity was determined by placing an empty DSC pan on the sample cell. The light intensity was ca. 80 mW/cm² over a wavelength range of 320~500 nm. The prepared an UV-curable coating with a weight of 3 mg was placed in an uncovered aluminum DSC pan. Photopolymerization was carried out at 25°C in a nitrogen atmosphere.

RESULTS AND DISCUSSION

Pendulum Hardness

Figure 4 shows the influence of the Norrish Type I (α-cleavage) photoinitiator, and that of UV dose on the pendulum hardness of the UV-cured films. As shown in *Figure* 4, the pendulum hardness of the UV-cured films increased with increasing UV dose and depended on the type of photoinitiator used.

The pendulum hardness of Al-8 or Al-T was lower than that of the film cured using the other photoinitiators at all UV doses. The final pendulum hardness was in the following order: Al-H ≥ Al-C > Al-8 > Al-T.

The acylphosphine oxides as α-cleavage photoinitiator are derived from α-diethoxyacetophenones (DEAP) with replacing the C–H with P=O and the alkoxy groups with aryl groups. This class of photoinitiator has a relatively high susceptibility to oxygen inhibition, which may decrease acylphosphine oxide reactivity during the UV curing of the thin films.

In addition, acylphosphine oxides have absorption bands in the near UV/Visible region, which are bleached upon irradiation. Following that, there is a decrease in absorbance in the near UV/Visible range and the radiation can penetrate into deeper layers. In particular, acylphosphine oxides possess short-lived excited states and present low quenching characteristics. As shown in *Figure* 4, the bis-acylphosphine oxide was a little more effective at initiation than the mono-acylphosphine oxide, which is explained by the formation of four radicals from bis-acylphosphine oxide in contrast to the two radicals formed from mono-acylphosphine oxide.[4,5,12-14]

In general, a high extinction coefficient is associated with a high yield of radical formation and a relatively high concentration of double bonds in the case of the acrylate system.[12]

Al-8 or Al-T was less suitable for the surface curing of the UV-curable coating, unless the specific photoinitiator used has a particularly high molar extinction coefficient.[12] In this study, the surface of the film cured by using acylphosphine oxides as the photoinitiator had a tacky property after final radiation. In a previous study, it was found that a low polymerization initiating radical concentration gave rise to a reduced number of growing chains and, hence, to polymers with high molecular weights and narrow molecular weight distributions. Under conditions of high radical concentration many growing chains are generated, but the growth of these chains is also more likely to be terminated after a short period of time.
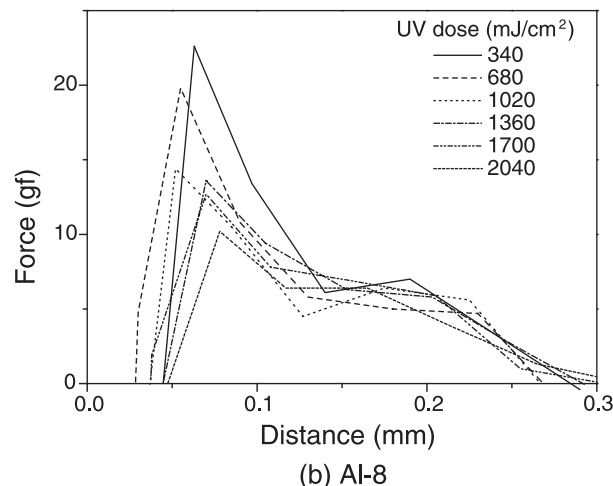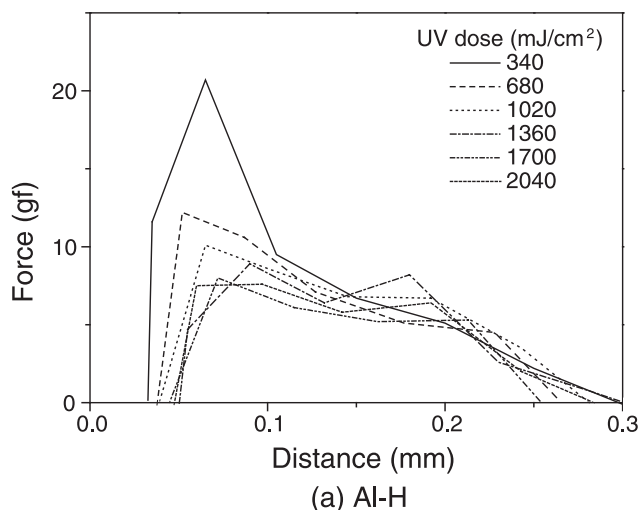

(a) Al-H

(b) Al-8

Figure 5—Probe tack of the UV-curable coatings as a function of UV dose.

Figure 6—Influence of the Norrish Type I photoinitiator and that of UV dose on the probe tack of the UV-cured films.
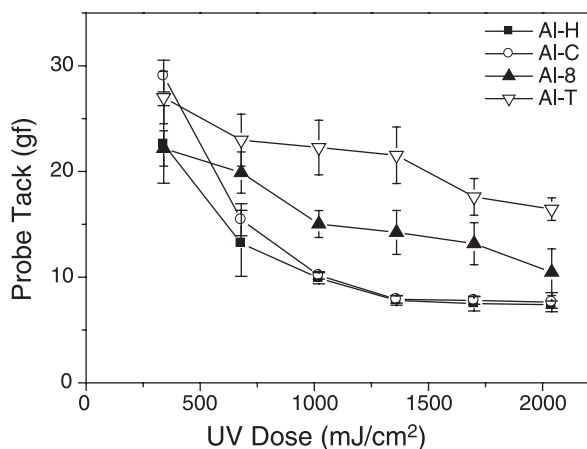

Figure 7—Influence of the Norrish Type I photoinitiator and that of UV dose on the gel content of the UV-cured films.

In UV-curable coatings, each photoinitiator should influence the polymerization reaction in a similar way.

The low radical concentration associated with 1-hydroxy-cyclohexyl-phenyl ketone or 2-hydroxy-2-methyl-1-phenyl-propan-1-one should produce hard film, due to their having a high crosslink density, while higher concentrations of these photoinitiators would be expected to produce faster curing films with lower crosslink densities and reduced hardness. Thus, lower crosslinking is related to poor surface curing.

In the case of diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide, the 2,4,6-trimethylbenzoyl radical appears to be more susceptible to atmospheric oxygen than the phosphinoyl radical. In addition, there is evidence of strong oxygen inhibition in the curing of acrylates. This high oxygen inhibition may make the acylphosphine oxides less suitable for the curing of thin films.[14]

Al-H or Al-C as the photoinitiator had better crosslinking than Al-8 or Al-T. Also, the relatively high inhibition by oxygen may have been troublesome in the curing of thin films with acylphosphine oxides, as explained previously.

Probe Tack

Figure 5 shows the force-distance curve of the surface of the UV-cured film measured by the probe tack tester. As shown in *Figures* 5 and 6, the probe tack of the surface of the UV-cured film decreased with increasing UV dose. In addition, the probe tack value depended on the type of the photoinitiator used. The probe tack of Al-H showed the lowest value during the initial stage. The probe tack of Al-8 showed the highest value of all the photoinitiators. The probe tack was in the following order: Al-T > Al-8 > Al-C > Al-H. At a given UV dose, the lower the probe tack was, the higher the surface photocrosslinking became. In this study, we did not observe any tackiness on the surface of the UV-cured film using our finger inspection under 10 gf of probe tack. However, *Figure* 6 shows that all the UV-cured films remained tacky, even after a UV dose of 2040 mJ/cm², based on the measurements made with a probe tack tester. We could obtain accurate information on the
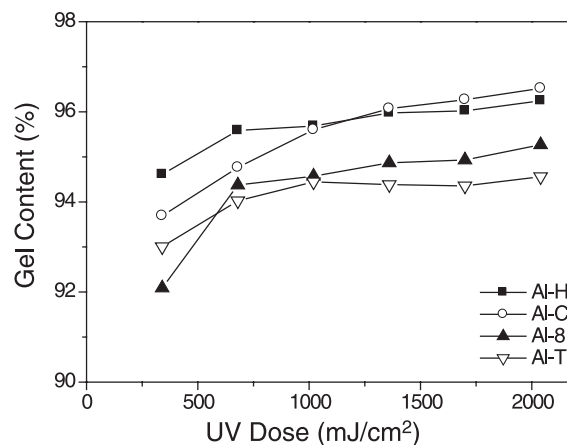
UV-cured film surface by means of the probe tack measurement.

One possible problem associated with the UV curing of acrylic formulations is that the surface of the coating layer stays tacky while the bulk is fully hard, and such a tack property of the UV-cured film surface is caused by the reaction of photoinitiator radicals and polymer radicals with dissolved and penetrating oxygen. Thus, the surface of the coating does not cure and will be sticky because the oxygen in the air inhibits the free radical mechanism.[15,16]

Gel Content

Figure 7 shows the influence of the Norrish Type I photoinitiator, and that of the UV dose on the gel content of the UV-cured films. In this study, a higher gel content value was associated with the higher photocrosslinking. The variation in the gel content of Al-T leveled off for 1020 mJ/cm² and above, while the gel content of Al-C varied only slightly as the UV dose was increased above 1360 mJ/cm². The gel content of Al-H or Al-C was the highest. This was due to the increased photocrosslinking of the UV-curable coating in the absence of air.
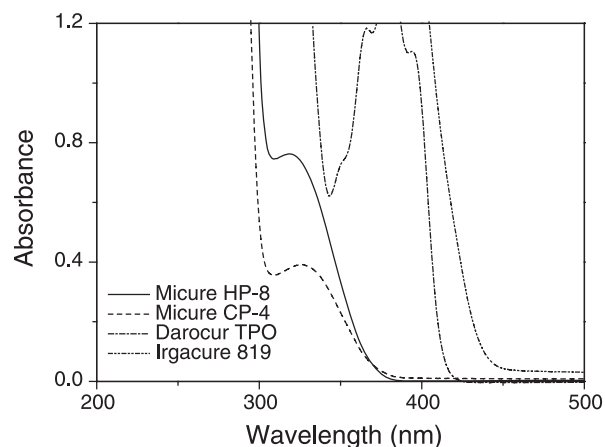

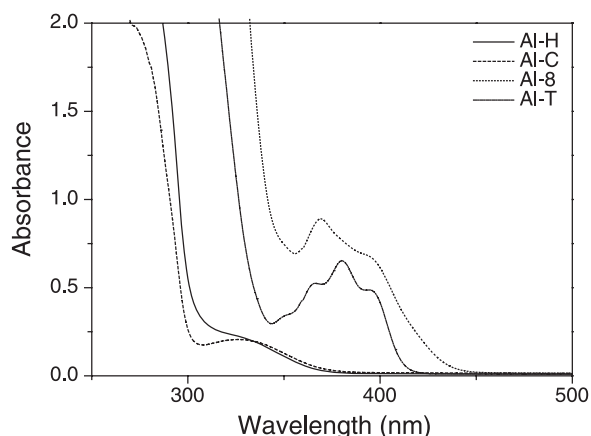Figure 8—Absorbance spectra of the photoinitiators (0.1% in acetonitrile).

Figure 9—Absorbance spectra of the UV-curable coatings containing several Norrish Type I photoinitiators (1% in acetonitrile).

The 1-hydroxy-cyclohexyl-phenyl ketone had a slightly higher reactivity than 2-hydroxy-2-methyl-1-phenyl-propan-1-one in conformity with the slightly higher radical formation associated with this photoinitiator.[5]

All the photoinitiators exhibited high gel content (>94%) at long irradiation times.

UV/Vis Spectrophotometer

Figure 8 shows the absorbance spectra of the photoinitiators. As shown in *Figure* 8, bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide absorbed below ca. 450 nm; diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide absorbed below ca. 420 nm; and 2-hydroxy-2-methyl-1-phenyl-propan-1-one or 1-hydroxy-cyclohexyl-phenyl-ketone absorbed below ca. 380 nm. The absorbance spectra depended on the type of photoinitiator used.

During UV curing, 2-hydroxy-2-methyl-1-phenyl-propan-1-one undergoes α-photocleavage to form the benzoyl radical and the dimethylhydroxymethyl radical. Upon irradiation, benzoyl radicals are formed. The benzoyl radical is the main entity responsible for the initiation of the polymerization. The α-hydroxyalkyl radical can also partic-

ipate in the initiation process. The 1-hydroxy-cyclohexyl-phenyl-ketone undergoes α-photocleavage to form the benzoyl radical and the hydroxycyclohexyl radical. Two-hydroxy-2-methyl-1-phenyl-propan-1-one and 1-hydroxy-cyclohexyl-phenyl-ketone (nonsubstituted in the phenyl ring) involve a π, π* transition between 242 and 244 nm. This type of photoinitiator includes the aromatic ketones. The absorption band at ca. 330 nm is related to the n, π* transition in aromatic ketones.[5,17]

Bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide undergoes α-photocleavage to the 2,4,6 trimethylbenzoyl radical and phenylphosphonyl radical. Diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide undergoes α-photocleavage to the 2,4,6 trimethylbenzoyl radical and the diphenylphosphonyl radical.

Acylphosphine oxide type photoinitiators have the distinct advantage of absorbing in the near UV range, which causes them to undergo fast photolysis, leading to the generation of benzoyl and phosphinoyl radicals.

Norrish Type I (α-cleavage) in the excited triplet state was the predominant primary photoreaction in this experiment.

The benzoyl and phosphinoyl free radicals proved to be very reactive and capable of initiating the polymerization of a large variety of photocuring materials, such as acrylates, etc.[5,17,18]

Previous researchers showed that UV curing is associated with either the π, π* transition or the n, π* transition (or a combination of these) that occur between 250 and 400 nm, and that the nonsubstituted benzoyl chromophore has its main absorption (π, π* transition) at around 250 nm and exhibits a low-intensity n, π* transition band at around 340 nm.[5] They explained that electronic absorption spectra arise from the absorption of radiation in the ultraviolet (UV) or visible (Vis) regions of the spectrum, which causes transitions to occur between different electronic states. For the absorption of radiation, chromophores are the most responsive, i.e., functional, groups which contain electrons originating from the π and n orbitals, such as C=C, C≡C, C=O, C=C-C=C, the benzene ring, etc.[17]
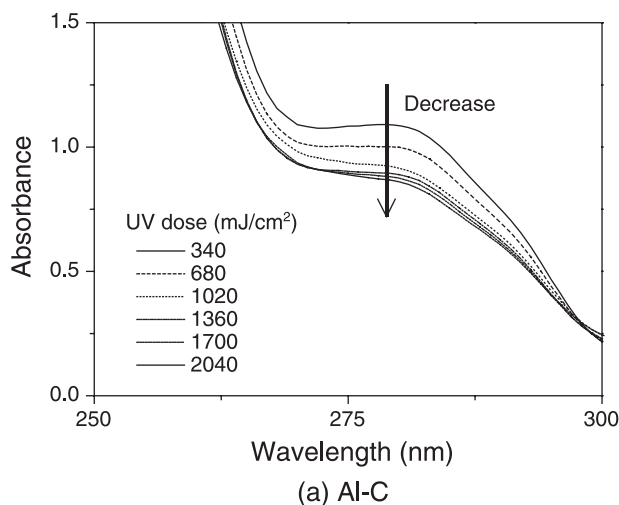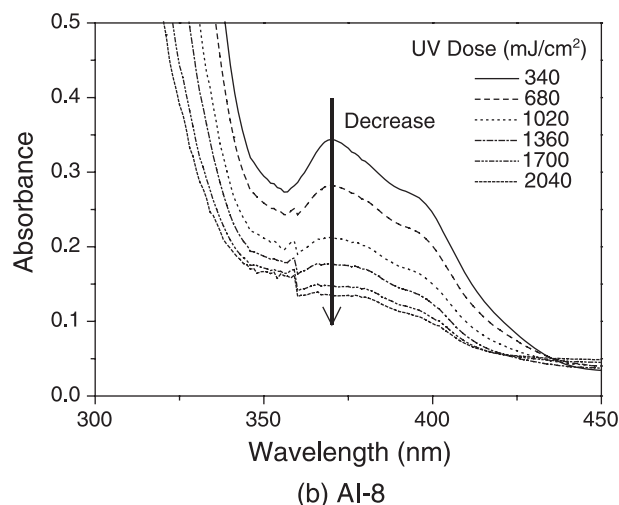

(a) AI-C

(b) AI-8

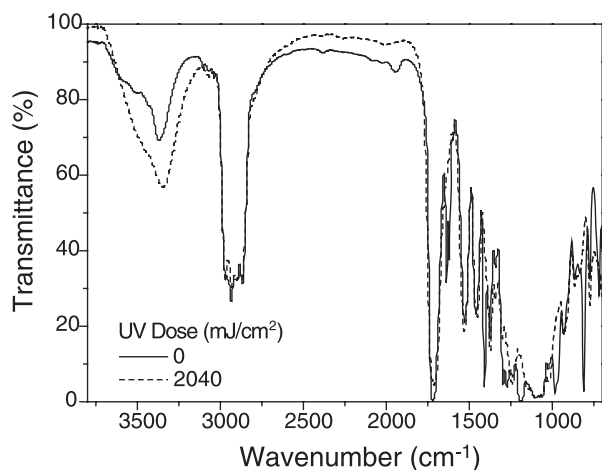Figure 10—Change of absorbance spectra of the UV-curable coatings as a function of UV dose.

Figure 11—Transmittance spectra of the UV-curable coatings cured using Micure HP-8 (Al-H) at UV doses of 0 and 2040 mJ/cm².

Figure 13—Conversion of double bonds of the UV-curable coatings as a function of the photoinitiator type and UV dose.

All of the photoinitiators absorbed UV radiation in the wavelength range of 200~300 nm due to the π, π* transition, related to an unsaturated functional group. Bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide and diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide absorbed visible light radiation in the wavelength range of 400~500 nm due to the n, π* transition, related to the unsaturated carbonyl group and their yellow color.[19] In the case of bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide and diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide, the absorption of the photoinitiator was bleached during the irradiation process, thereby allowing the incident light to penetrate to the lower layers. The long wavelength absorption of acylphosphine oxide was bleached during the irradiation process. Since the carbon-phosphorous bond was broken during the Norrish Type I photoreaction of these compounds, there was no interaction between the carbonyl and phosphonyl groups in these photoproducts. Thus, the chromophores which absorbed in the near UV/Visible were destroyed during the photochemical reaction. The resultant decreasing optical density permitted a continuously
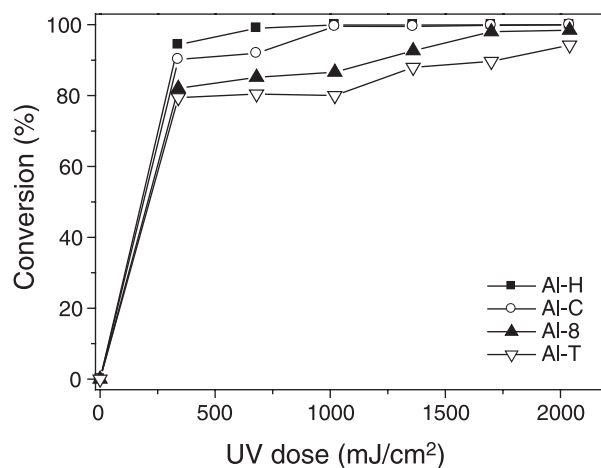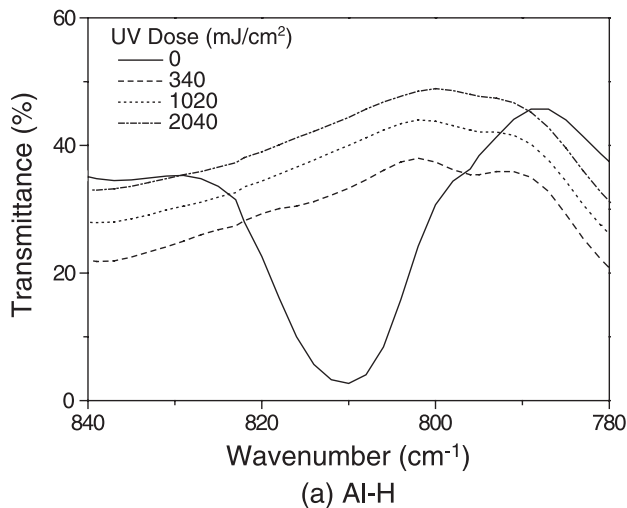
deeper penetration of the incident light and made the curing of thick layers possible.[14]

Figure 9 shows the absorbance spectra of the UV-curable coatings containing the various Norrish Type I photoinitiators. The absorption of radiation in the ultraviolet or visible regions by the UV-curable coatings depends on that of the photoinitiators.

Figure 10 shows the absorbance spectra of Al-C or Al-8 as the photoinitiator during UV curing. As shown in *Figure* 10, the absorption due to the chromophore decreased with increasing UV dose.

This decrease in the absorption of radiation in the UV or Vis regions is related to the increase in the amount of photocrosslinking and the consumption of the photoinitiator. The photoinitiator is needed for the UV-curable part of the mixture. This initiator is stimulated by UV radiation and produces reactive radicals which initiate the polymerization of resins with unsaturated double bonds, such as polyurethane acrylates, etc.

In a previous study, an examination of the UV spectrum after photopolymerization showed that little or no
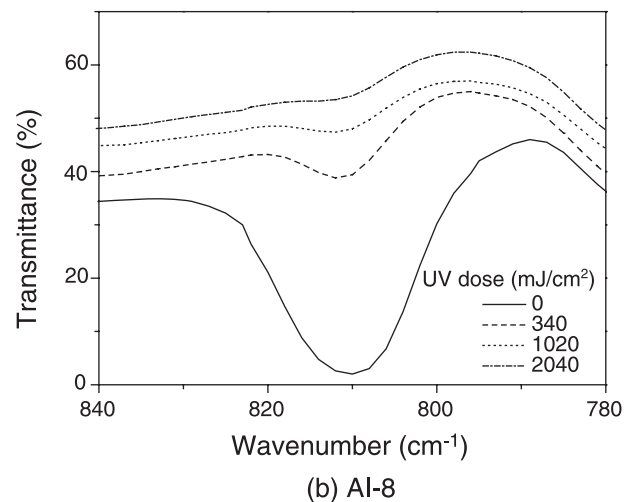

(a) Al-H

(b) Al-8

Figure 12—Changes of transmittance spectra of the UV-curable coatings as a function of UV dose at around 810 cm⁻¹.
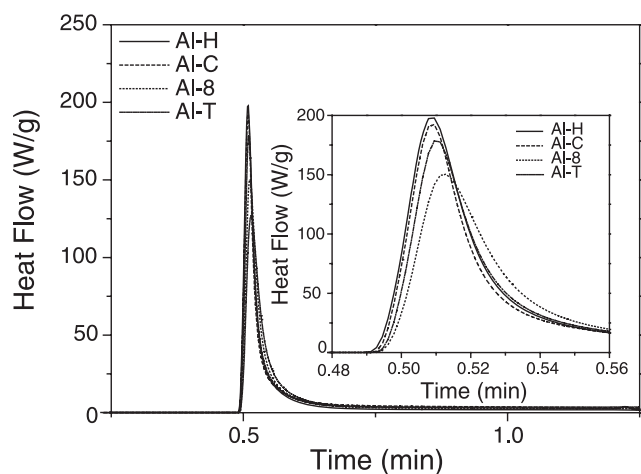
Figure 14—Photo-DSC curves of the UV-curable coatings as a function of the photoinitiator under N_2.

photo-byproducts that absorb light at any wavelength or greater were created.[20]

Particularly, 1-hydroxy-cyclohexyl-phenyl-ketone, of the Norrish Type I photoinitiator, shows better color characteristics, imparting only very slight yellowing in comparison with other commercial photoinitiators. This low degree of yellowing makes its use a necessity when clear coatings are designed.[5] With 1-hydroxy-cyclohexyl-phenyl-ketone, better results are obtained than with 2-hydroxy-2-methyl-1-phenyl-propan-1-one, which does not have a cyclic substituent at the α-position.[14]

FTIR

FTIR was used to observe the chemical structure change of the UV-cured films during UV curing. *Figure* 11 shows the IR spectra of Al-H as the photoinitiator at UV doses of 0 and 2040 mJ/cm². As shown in *Figure* 11, the intensities of the peaks at around 810 cm^{-1} and 1636 cm^{-1} decreased after UV exposure. A previous study indicated the decrease in peak area at around 810 cm^{-1} and 1636 cm^{-1}, CH$_2$=CH– twisting and CH$_2$=CH– stretching, respectively, which, for the acrylate system, exactly reflects the degree of curing of the UV-curable coating.[21,22]
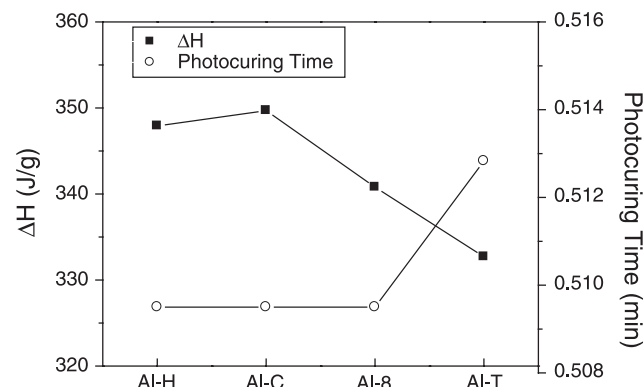

Figure 15—Enthalpy and photocuring time of the UV-curable coatings containing the various photoinitiators measured by photo-DSC.

The UV-curable acrylate-based coating system is most easily observed in terms of the decrease in the acrylate unsaturation absorbances at 810 cm^{-1} with increasing UV exposure. Thus, we used the acrylate unsaturation absorbance at 810 cm^{-1} to monitor the curing behavior of the UV-curable coating.

Figure 12 shows the change of the IR spectra of Al-H or Al-8 as the photoinitiator, at around 810 cm^{-1}, due to the acrylate group's unsaturated bond (CH$_2$=CH– twisting) in the UV-curable coating, during UV curing. As shown in *Figure* 12, the IR peak intensity at around 810 cm^{-1} decreased with increasing UV dose.

The decrease of IR peak intensity at ca. 810 cm^{-1} after UV exposure is attributable to the gradual disappearance of the acrylic double bond, due to photopolymerization.[18,22,23] Therefore, the degree of the double bond conversion is a measure of the degree of cure. To verify the degree of curing of the UV-curable coatings containing several Norrish Type I photoinitiators, we measured the conversion of the acrylic double bonds as a function of UV dose, as shown in *Figure* 13.

In the case of Al-H or Al-C as the photoinitiator, the degree of conversion of the acrylic double bonds varied only slightly as the UV dose was increased above 340 mJ/cm². In the case of Al-8 or Al-T as the photoinitiator, however, the degree of the conversion of the acrylic double bonds increased with increasing UV dose over the entire range of UV doses used in this experiment.

Photo-DSC

The results of the photo-DSC of the photopolymerization under nitrogen are shown in *Figures* 14 and 15. These figures show the enthalpy value and curing time of the UV-curable coatings containing the various Norrish Type I photoinitiators.

As shown in *Figure* 15, the enthalpy of the UV-curable coatings containing the various Norrish Type I photoinitiators was in the order: Al-C > Al-H > Al-8 > Al-T. This is associated with the trend observed for the curing time, as measured by photo-DSC: Al-T > Al-H ≅ Al-C ≅ Al-8. During the curing process, the photoinitiator only plays an active role at the beginning of the photopolymerization process.

However, since the photoinitiator is added to the formation before the curing process and the remaining photoinitiator, which is not consumed upon irradiation, as well as its photoproducts, is present during the curing process and in the cured products, there are numerous possibilities for further chemical or physical interactions. This can affect the properties of the radiation-curable system both before and after UV curing.[14]

CONCLUSIONS

The purpose of this study was to investigate the influence of the Norrish Type I (α-cleavage) photoinitiator and that of the UV dose on the curing behaviors and coating performance of the UV-curable aliphatic urethane arcylate coatings. UV-curable coatings were cured under a high-pressure mercury lamp.

In both the pendulum hardness and gel content tests, the results of the UV-curable coatings cured using 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Al-H) or 1-hydroxycyclohexylphenyl ketone (Al-C) were higher than that cured using bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Al-8) or diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide (Al-T) as the photoinitiator. Both of these higher values are due to the increased photocrosslinking of the UV-curable coating occurring in the presence of air.

In order to observe the surface curing of the UV-curable coatings during UV curing, the probe tack, which is related to the oxygen inhibition and surface photocrosslinking, was measured. The probe tack of the UV-cured film surface decreased with increasing UV dose. The probe tack of the surface of the UV-curable coating cured using 2-hydroxy-2-methyl-1-phenyl-propan-1-one as the photoinitiator was the lowest during the initial stage. The probe tack of the surface of the UV-curable coating cured using bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide was the highest over the entire range of UV doses.

The result of the FTIR and photo-DSC analyses showed that the photopolymerization of the UV-curable coating cured using 2-hydroxy-2-methyl-1-phenyl-propan-1-one or 1-hydroxycyclohexylphenyl ketone as the photoinitiator was superior to that of the UV-curable coating cured using bis (2,4,6-trimethylbenzoyl)-phenylphosphine oxide or diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide.

The results obtained by both chemical and physical measurements demonstrated that the UV-curable coating cured using 2-hydroxy-2-methyl-1-phenyl-propan-1-one or 1-hydroxycyclohexylphenyl ketone as the photoinitiator could be effectively cured at the UV dose of 1360 mJ/cm^2 in air.

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