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Crosslinking characteristics of aziridine crosslinkers in polyurethane-based clearcoats for automotive applications

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Abstract Crosslinking systems play a vital role in the coating industry by significantly improving the wear resistance, chemical resistance, and toughness of the coatings. In particular, polyfunctional aziridines, known for their distinctive nitrogen-containing three-membered ring structures, serve as versatile crosslinkers in automotive coatings and adhesives. These crosslinkers can effectively enhance both the physical and chemical properties of polyurethane coatings. This study focuses on investigating the impact of two different trifunctional aziridines on the thermal curing characteristics of 2K clearcoats containing free-isocyanate crosslinker and polyacrylic resin. The analysis confirmed the ring-opening reaction of the aziridine crosslinker with the carboxyl groups in the resin at room temperature, as evidenced by changes in the –NH stretching frequency in the Fourier transform infrared spectra. To assess the real-time curing performance of aziridines during thermal curing at 80 °C, rheological storage modulus and curing behavior of the formulated 2K clearcoats were measured using a rotational rheometer and a rigid-body pendulum tester. Additionally, nano-indentation and nano-scratch tests were conducted to quantitatively evaluate the surface hardness and scratch resistance of the cured clearcoat films. By examining the relationship between the curing dynamics and the final mechanical properties, this study offers insights into optimizing the amount of aziridines required to enhance the properties of clearcoat films.

Keywords Trifunctional aziridines, Crosslinkers, Automotive 2K clearcoat, Polyurethanes, Thermal curing

Introduction

The outer thin layer, coated over inner functional films or frames, should be properly crosslinked. This ensures that the layer has the desired target-oriented surface hardness or resistance, making it invulnerable to solvents or unexpected external loads.[1,2] Particularly, in automotive coating fields, various crosslinking or curing methods have been developed and applied to outer coating layers, which consist of electrocoats, primers, basecoats, and clearcoats, based on polymer reactive chemistry, for enhancing the crosslinked network inside layers.[3,4] Among them, the clearcoat layer on top of coating films effectively protects the inner layers or body frames of the automotive from external damages such as acid rain etching, oxidation, staining, scratching, and bird droppings.[5–7] Therefore, the demand for high-performance clearcoat materials with long durability, good mechanical properties and excellent appearance characteristics is increasing rapidly as the first defense line of automotive bodies.

To form a denser crosslinked coating layer for the original equipment manufacturer (OEM), various thermal curing methods have been developed for

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Daegeun Oh and Junyoung Park have contributed equally to this study.

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automotive coating layers with different resin types (e.g., acrylics, polyurethanes, epoxides, and polyesters).[4,8] Traditionally, thermal crosslinkers such as melamine-based urea bonding[9] and isocyanate-based urethane bonding[3,10,11] have been used extensively. However, owing to environmental concerns related to the high energy consumption during the coating cure process, the automotive coating industry has been making great efforts toward eco-friendly coating applications while continuing the development of crosslinkers with durability, solvent resistance, and mechanical strength.[12–14]

Among the many useful crosslinkers, carbodiimides[15] and aziridines[16,17] can react effectively with the carboxylic acids (R–COOH) included in various polymeric binders at room temperature (RT), even under small portion conditions.[18] They guarantee a high level of crosslinking density in aqueous and non-aqueous coatings or adhesives, greatly improving the physical and chemical resistance properties. Aziridines are trifunctional crosslinkers possessing three reactive sites within their ring structures. Studies related to aziridines have mainly focused on the specialized ring-opening reaction linked with their trifunctionality, which tunes a good balance between reliability, versatility, and reactivity.[19–22] Specifically, it is important to understand the role of aziridines under different crosslinking reaction environments[23,24] in coatings and adhesives. For example, Bückmann et al.[25] demonstrated aziridines as a new class of low-toxicity crosslinkers for crosslinking of waterborne carboxylic acid binders. The crosslinking performances of both hydrophilic and hydrophobic functionalized aziridines were analyzed to ensure good mechanical properties, chemical resistance, and adhesion. Xie et al.[26] characterized the crosslinking properties and curing kinetics of an aziridine crosslinker and an acrylate resin at room temperature. It was found that the aziridine enhanced the mechanical properties and solvent resistance of the crosslinked acrylate resin. To date, the use of aziridine crosslinkers in automotive clearcoat formulations has not become widespread, even though their application in various industrial coatings has had a significant impact on energy-savings and environmentally friendly coating processes.

In this study, the role of trifunctional aziridine crosslinkers, such as pentaerythritol tris[3-(1-aziridinyl)propionate] (PTAP) and trimethylolpropane tris(2-methyl-1-aziridinepropionate) (TTMAP), in PU-based 2K automotive clearcoats[27] was investigated to improve the crosslinking density and surface mechanical properties. First, the ring-opening reactivity of aziridines with an acrylic copolymer containing a carboxylic acid group (R–COOH) was compared using real-time curing characterization and Fourier transform infrared spectroscopy (FTIR) at room temperature to determine the formation of new amine groups (–NH). Subsequently, the crosslinking dynamics during the thermal curing of 2K clearcoats containing –OH and –COOH functionalized polyacrylic resin and a free-isocyanate crosslinker were monitored using a rotational rheometer and rigid body pendulum tester (RPT) by tuning a small portion of aziridines. The thermomechanical properties of the thermally cured clearcoat films were analyzed using dynamic mechanical analysis (DMA), a rigid-body pendulum tester (RPT) in the physical mode, and thermogravimetric analysis (TGA). The surface mechanical properties of the final thin clearcoat films were evaluated using nano-indentation (NHT) and nano-scratch tests (NST). Additionally, the car wash test with gloss retention rate, cross-cut adhesions (for both initial coatings and water resistance) and the appearance tests (wave scan and yellowness), based on commercial test methods, were performed to evaluate the impact of additional aziridine crosslinkers on the clearcoat films. The faster-curing behavior and improved mechanical properties of PU-based clearcoats containing aziridines crosslinkers were elucidated by correlating the real-time crosslinking characteristics and mechanical properties of the films.

Experimental

Materials

A polyacrylic coating solution for formulating 2K clearcoats was prepared. Acrylic resin (originally dissolved in butyl acetate with 70% non-volatile content, 6,500 g/mol, Setalux 1753 SS-70, Allnex, Germany), with hydroxyl (–OH) and carboxylic acid (–COOH) functional groups in a 9:1 molar ratio, which has an OH value of 97.02 and an acid value of 10.5, was dissolved in a mixture of solvents (xylene from GS Caltex, KOCOSOL 100 from SK Chemical, and butyl acetate from KAI Korea Alcohol Industrial, Korea) containing light stabilizers (Tinuvin 292 and Tinuvin 400, BASF, Germany), additives (BYK 306 and BYK 399, BYK, Germany), and catalyst (dibutyltin dilaurate (DBTDL), NITTO Kasei, Japan). The polyacrylic coating solution with 53.7% non-volatile contents is shown in Table 1a.

The hexamethylene diisocyanate trimer (579 g/mol, Desmodur®N-3300, Covestro, Germany, named as HDI trimer), as a thermal crosslinker, was dissolved in xylene and butyl acetate with 60% non-volatile content. Also, trifunctional aziridine crosslinkers (Fig. 1) such as pentaerythritol tris[3-(1-aziridinyl)propionate] (427.5 g/mol, Menadiona, Spain, named as PTAP) and trimethylolpropane tris(2-methyl-1-aziridinepropionate) (467.6 g/mol, Menadiona, Spain, named as TTMAP) were considered as additional crosslinkers to further activate the curing reaction.

Formulation of 2K clearcoats

To analyze the role of aziridine crosslinkers in crosslinking solventborne coating systems, 2K PU-based clearcoat samples were prepared by adding

Table 1: Formulations of (a) polyacrylic coating solution and (b) 2K PU-based clearcoat samples

(a) Polyacrylic coating solution

Acrylic resin (g)	Setal 1753	75
Solvent (g)	Xylene	9
	KOCOSOL 100	7
	Butyl acetate	7
UV stabilizers (g)	Tinuvin 292	0.5
	Tinuvin 400	0.5
Additives (g)	BYK 306 (Slip agent)	0.3
	BYK 399 (Levelling agent)	0.2
Catalyst (g)	DBTDL	0.5
Total (g)	100	
OH value (Total coating solution)	73.288	

(b) 2K PU-based clearcoat samples

Clearcoats	PU_0	PU_{P3}	PU_{P7}	PU_{T3}	PU_{T7}
Polyacrylic coating solution (g)	100	100	100	100	100
Free-isocyanate (g) (HDI trimer)	43.5	43.5	43.5	43.5	43.5
PTAP (g)	0	3	7	0	0
TTMAP (g)	0	0	0	3	7
Total (g)	143.5	146.5	150.5	146.5	150.5
[Aziridine]/[Acid]	–	1.5	3.5	1.4	3.2

Acrylic resin is dissolved in butyl acetate with 70% NV.

Polyacrylic coating solution is the mixture with 53.7% NV

NCO in HDI: –OH in polyacrylic resin = 1.05: 1

[Aziridine]/[Acid]: The equivalent ratio of aziridine and acid (MAA) functionality

aziridine crosslinkers to a mixture of polyacrylic resin and free-isocyanate HDI trimer. The HDI trimer and resin were mixed in a molar ratio of 1.05:1 between the –NCO group in HDI and the –OH group in the resin. Each aziridine crosslinker was then added up to 7 wt % based on the resin weight. The detailed formulations for clearcoat samples, along with the corresponding equivalent ratios of aziridine and methacrylic acid (MAA) functionality in acrylic resin, are presented in Table 1b. The clearcoat samples were designated as PU_0, PU_{P3}, PU_{T3}, and so on, depending on the aziridine content in each sample.

Real-time measurements of crosslinking behaviors of clearcoats

The macroscopic crosslinking evolution of the clearcoat samples containing aziridine crosslinkers (PTAP and TTMAP) was investigated in real-time using a rotational rheometer (MCR-302, Anton Paar, Graz, Austria). Under the small-amplitude oscillatory shear mode with an angular frequency of 5 Hz and a strain of 1% based on the measurement gap, the real-time storage modulus (G') was monitored to clearly substantiate the growth of a crosslinked network. A parallel plate geometry with an 8 mm diameter was used, wherein the gap between the upper and lower plates was 500 μm. The clearcoat sample was placed between the plates in a temperature-controlled chamber (CTD-450). The CTD temperature was maintained at 30 °C for 10 min to remove solvent and then cured at 80 °C for 40 min.

The crosslinking features distinguished by aziridine crosslinkers in the clearcoat samples were also analyzed using a rigid-body pendulum tester (RPT; RPT-3000W, A&D, Tokyo, Japan).[28] Unlike the previously mentioned rheological test for the thick coating film system, real-time crosslinking of a 60 μm thin film progressed through an RPT experiment. A knife-shaped edge (RBE−130) attached to an oscillating pendulum body (FRB-300) was placed on the thin coating layer, and the real-time curing behavior was quantified in terms of the oscillatory pendulum period during the thermal curing at 80 °C for 40 min.[29,30]

FTIR analysis of clearcoats during thermal curing

An attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR, Nicolet IS-10, Thermo Scientific, Waltham, MA, USA) was used to

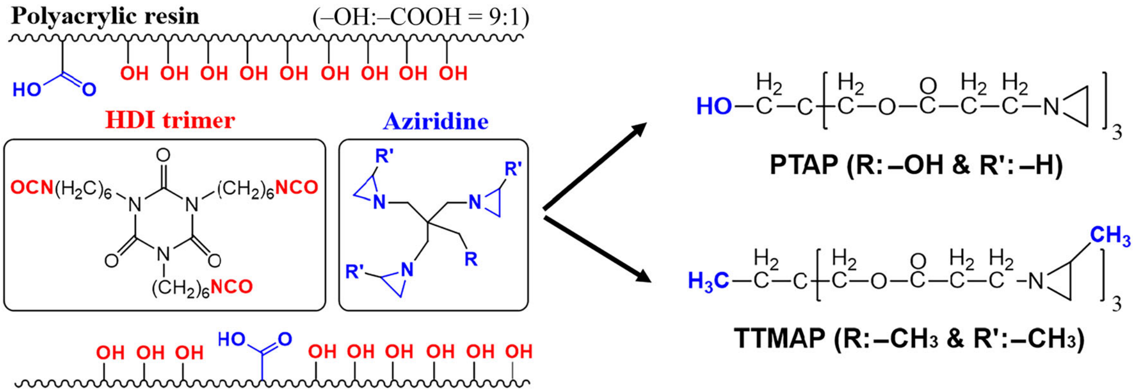

Fig. 1: Schematic of 2K clearcoat systems in this study. Two trifunctional aziridine crosslinkers (PTAP and TTMAP) are specified

characterize the reactions of the HDI and aziridines in the clearcoat samples during the thermal curing process. In this analysis, the samples were scanned 32 times under the conditions of resolution 4 cm^{-1} in the scan range 4,000~500 cm^{-1}. The rate of change of the isocyanate peaks (D_{NCO} %) during the thermally induced urethane reaction of the resin with the HDI crosslinker and the additional urea reaction between the HDI and amine group created after the ring-opening reaction of aziridine was calculated using equation (1)[31,32]:

$$D_{\mathrm{NCO}}(\%)=\frac{\left[\frac{\mathrm{Peak}_{-\mathrm{NCO}}}{\mathrm{Peak}_{-\mathrm{CH_2}}}\right]_{t=0}-\left[\frac{\mathrm{Peak}_{-\mathrm{NCO}}}{\mathrm{Peak}_{-\mathrm{CH_2}}}\right]_{t=t}}{\left[\frac{\mathrm{Peak}_{-\mathrm{NCO}}}{\mathrm{Peak}_{-\mathrm{CH_2}}}\right]_{t=0}}\times 100 \tag{1}$$

where $\mathrm{Peak}_{-\mathrm{NCO}}$ denotes the –NCO peak at 2270 cm^{-1} from the baseline between 2500 and 2000 cm^{-1} and $\mathrm{Peak}_{-\mathrm{CH_2}}$ is the –CH_2 peak at 2935 cm^{-1} from the baseline between 3900 and 2500 cm^{-1}.

Thermo-mechanical properties and thermal stability of cured clearcoat films

After thermal curing, the thermo-responsive mechanical changes in the cured clearcoat films were measured using dynamic mechanical analysis (DMA, Q800, TA Instruments, USA), including the storage modulus (G') and glass transition temperature (T_g) exerted by the polymeric networks in the films. The temperature scan was in the range of − 50 to 150 °C at a heating rate of 5 °C/min. An oscillatory strain of 0.1% at a frequency of 1 Hz was applied to the films. Based on G' data obtained from the DMA test, the average molecular weight between crosslinking sites was determined as per the following equation (2):

$$M_c=\frac{\rho RT}{G_N^0} \tag{2}$$

Here, ρ is the film density, R is the gas constant (8.3175 J/mol K), T is the absolute temperature, and G_N^0 denotes the elastic modulus in the rubbery plateau regime at a specific temperature of 100 °C, respectively. The crosslink density (X_c), that is, the reciprocal of M_c, was calculated for comparison.[33,34]

Furthermore, an RPT in physical mode[35] was employed to assess the thermo-mechanical variations of thin films cured on steel plates, similar to the DMA test. In this study, a pendulum body (FRB-200) equipped with a cylindrical edge (RBP-020) was used. The temperature was increased from 20 to 200 °C at a rate of 3 °C/min. The T_g was estimated from the variation in the logarithmic damping ratio of the cured thin coating film. The logarithmic damping ratio provides insights into viscoelastic fluctuations across a wide temperature range, offering a qualitative representation of the crosslinking and mechanical properties.

The thermal stabilities of the cured clearcoat films were investigated through thermogravimetric analysis (TGA) (TGA Q500, TA Instruments, USA) in the temperature range from 20 to 600 °C at 10 °C/min heating rate under N_2 atmosphere. Samples for DMA and TGA tests were prepared in a Teflon mold (5.6 cm × 1.1 cm × 0.1 cm) and were cured in a convection oven at 80 °C for 2 h.

Surface mechanical properties of cured clearcoat films

Scratch properties of the thermally cured thin films produced by the RPT tests were characterized using a nano-scratch test (NST, Anton Paar Tritec SA, Switzerland).[36,37] The normal load on the 2 μm

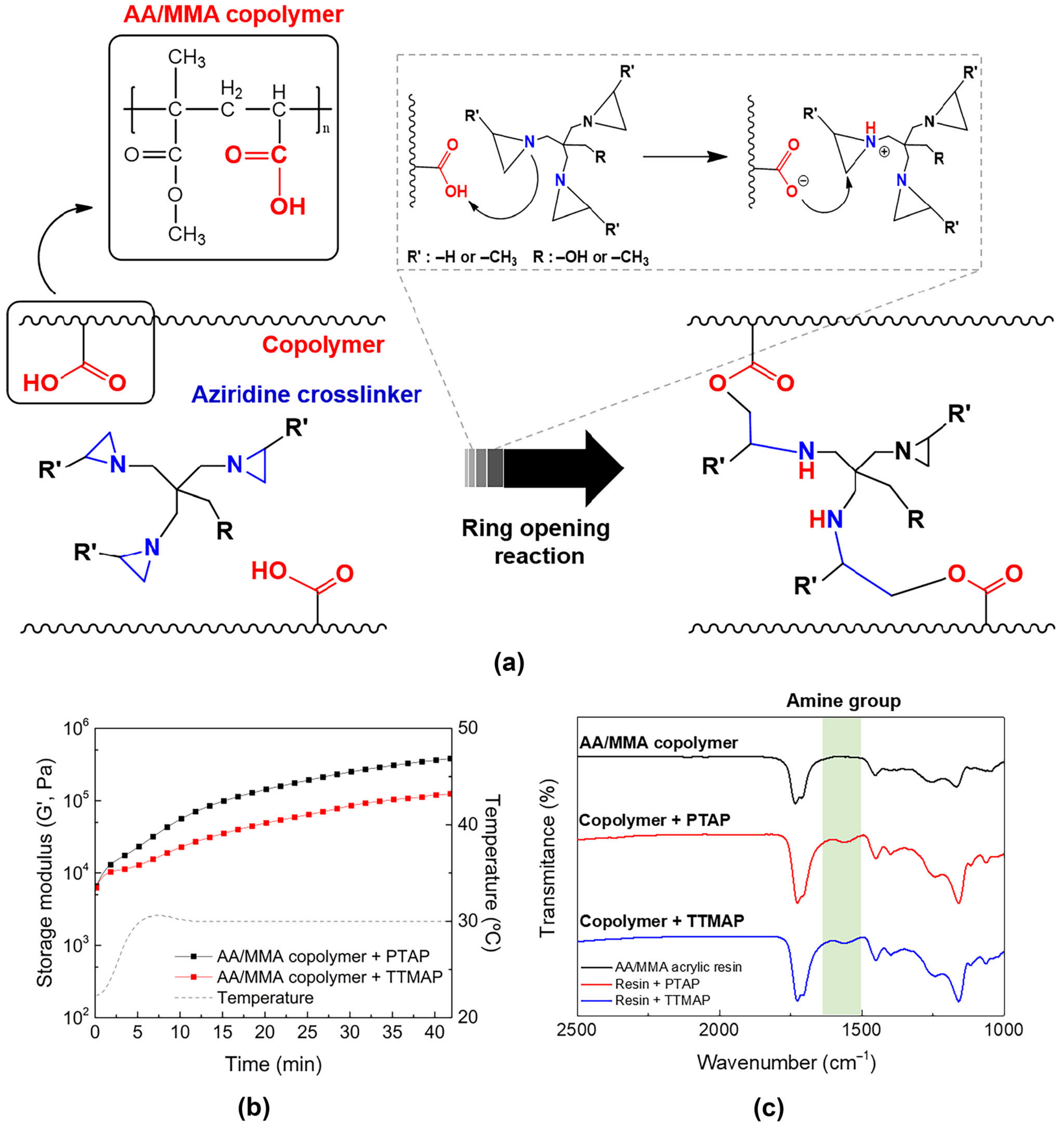

Fig. 2: (a) Schematic of the ring-opening reaction between aziridine crosslinker (PTAP or TTMAP) and AA/MMA copolymer, (b) real-time rheological behavior (*G'*), and (c) formation of FTIR transmittance peak for new amine group via the ring-opening reaction

sphere-conical diamond tip gradually increased from 0.1 mN to 30 mN at a rate of 59.8 mN/min along the total scratch length of 1 mm on the surface. The scratch resistance of the cured films was interpreted using the scratch penetration depth profile and first critical fracture load (Lc1), which represents the critical load for plastic deformation.[38]

A nanoindentation test (NHT, Anton Paar Tritec SA, Switzerland) was also performed to quantify the surface hardness of the cured thin films[39] from the indentation penetration depth versus normal force curves. During the test, the indenter recorded the vertical depth of the 2 μm sized Berkovic-type diamond tip with respect to the normal loading force applied on the film surface up to 30 mN at a load rate of 60 mN/min. A pause time of 30 s at the maximum load was assigned to eliminate possible creep behavior. The indenter was unloaded at a rate of 60 mN/min after the pause period. The surface hardness values ($H_{IT} = F/A_P$; F is the total force during loading, and A_P is the contact area) of the cured films were evaluated according to the Oliver and Pharr method.[40,41]

Various practical surface properties of the cured films were also qualitatively measured for industrial applications, including pencil hardness ranging from 2B to 3H, based on ISO 15184 application standards,[42] the cross-cut adhesions for initial coatings and water resistance, and the gloss retention rate after the car-wash test. In the cross-cut adhesion test (TQC Sheen, Netherlands) for initial coatings, the adhesion grade of the cured film coated on the PP substrate was determined. After scraping the cross-cut grid patterns on the film surface, an adhesive tape was attached and detached from the cross-cut film surface. The average adhesion grade ranging 0B to 5B was determined from five replicates, according to the ASTM D 3359 norm.[43] The cross-cut adhesion test for examining the impact of aziridine crosslinkers on the water resistance of coating films was also carried out following the procedure in ASTM D 870-15.[44] The cured films on the PP substrate were immersed in DI water at 40 °C. After 240 h of immersion, the coatings removed from the water were left at room temperature for 1 h. Subsequently, the cross-cut adhesion grade for a coating film was measured using the same method employed in the adhesion test for initial coatings.

Employing the Car-Wash Lab Apparatus (Amtec, Kistler, Germany), based on ISO/FDIS 20566,[45] to simulate a real car wash situation, the surface hardness of the cured films was evaluated.[46] To create scratches on the film surface, a water-based solution with 1.5 g/L of quartz powder was sprayed onto the surface at 2.2 L/min, which the polyester bristles (100 mm diameter, 400 mm length) rotated at 120 rpm. The film surface was exposed to a 10-cycle round trip to represent actual car wash scratch conditions using the test equipment. After the car wash test, the gloss of cured films was measured using a micro TRI gloss meter (BYK-Gardner GmbH, Germany) at a 60°. The gloss retention rate values before (B_i) and after (B_f) the car wash test were compared based on equation (3).

$$\text{Gloss retention rate}(\%) = \frac{B_f}{B_i} \times 100 \qquad (3)$$

Appearance of clearcoat films

The appearances of cured clearcoat films were compared by measuring the optical waviness of film surfaces using a wave scan dual (BYK-Gardner GmbH, Germany). Evaluation was conducted by recording the vertical appearance over a 10 mm track length. Long-term waviness (L.W.) and short-term waviness (S.W.) values were obtained through measurements using mathematical filter functions, representing variances of corresponding signal amplitudes.[47] Both longwave and shortwave values are normalized to a scale of 0 to 100, with 100 indicating the worst. The results were measured three times and are presented as average values.

For the yellowness test of clearcoat films, the L*, a*, and b* values were measured at 45° using a Spectrophotometer (MA-98, X-rite, USA).[48] The L* indicates the lightness, a* is the red/green coordinate, and b* is the yellow/blue coordinate. Also, the ΔE* values from equation (4), which represent the color difference, were compared for clearcoat films.

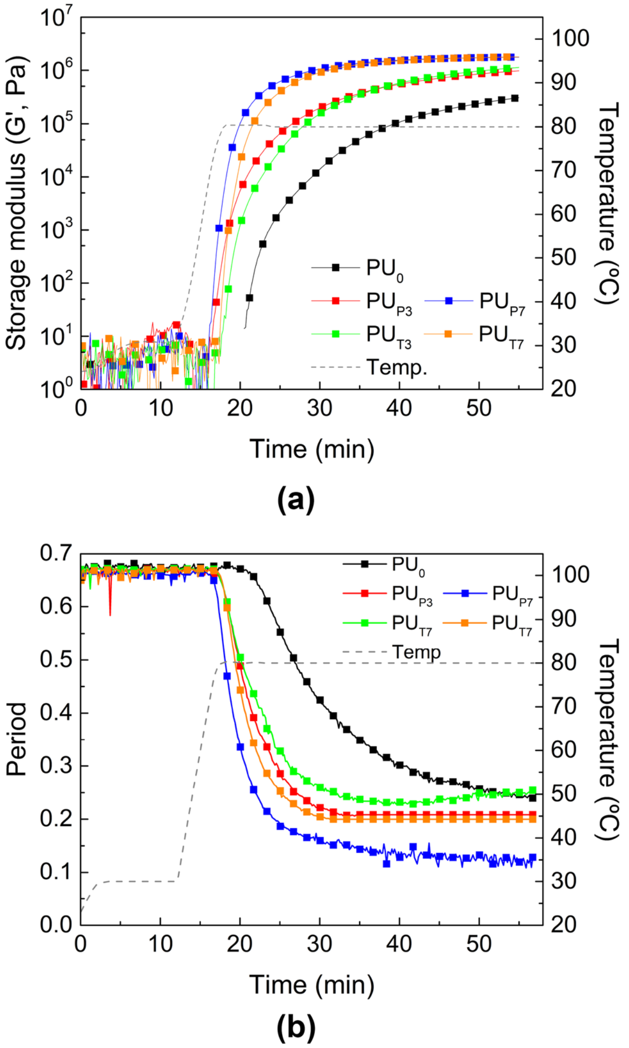

Fig. 3: Real-time thermal curing behaviors in 2K clearcoats with aziridine crosslinkers: (a) rheological properties (*G'*) using rotational rheometer in SAOS mode, and (b) pendulum period using RPT

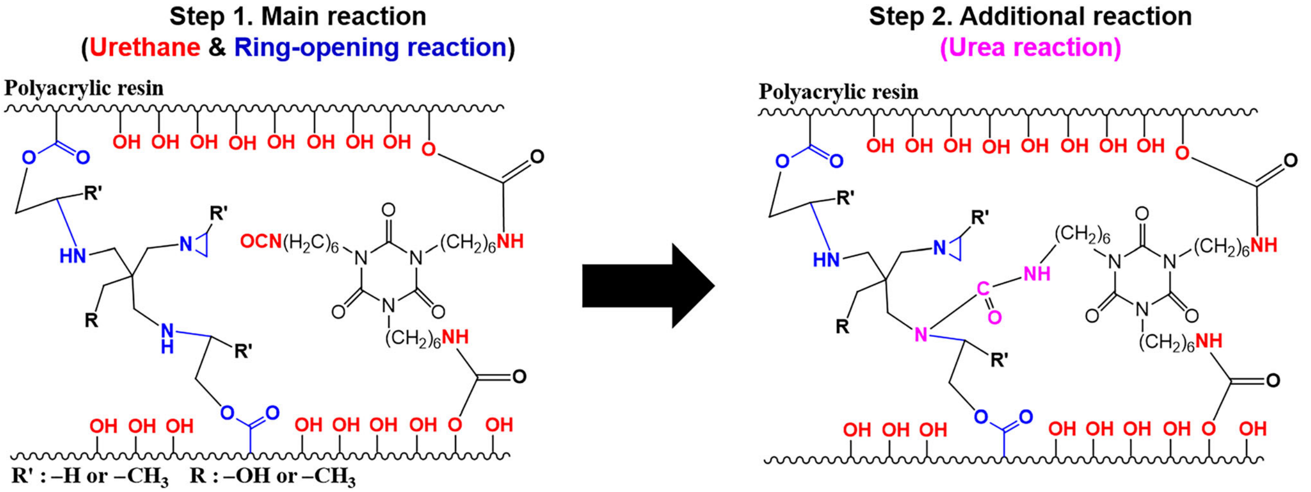

Fig. 4: Schematic reactions between polyacrylic resin with –OH and –COOH groups and crosslinkers of HDI and aziridine. Step 1: Urethane and ring-opening reactions; Step 2: Additional urea reaction between –NCO group in unreacted HDI and –NH group in ring-opened aziridine

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (4)$$

Results and discussion

Ring-opening reactivity of trifunctional aziridines

To understand the ring-opening reaction mechanism of the trifunctional aziridine crosslinkers with carboxylic acid groups,[26,49] as schematically delineated in Fig. 2a, liquid mixtures containing aziridine crosslinkers (PTAP and TTMAP) and an acrylic acid/methyl methacrylate (AA/MMA) copolymer were prepared. The AA/MMA copolymer (ACA-1416, weight ratio of AA to MMA of 4:6, Mw = 150,000 g/mol, non-volatile solids of 25 wt%) was provided by NOROO Automotive Coatings Co., Ltd. (Korea). The weight ratio of the copolymer to aziridine was fixed at 9:1. The ring-opening reaction proceeded in two steps, as shown in Fig. 2a. In the first step, the aziridine ring was instantly protonated ($NH_2{}^+$) by the carboxylic acid group in the copolymer. The deprotonated carboxylic acid (COO^-, mentioned as nucleophilic) in the second step preferentially attacks the unsubstituted carbon atom in the aziridine ring with less steric hindrance effect,[50–52] forming a secondary amine (R_2–NH) in the crosslinked network.

Rotational rheometry and Fourier transform infrared (FTIR) spectroscopy were employed to substantiate the change in the ring-opening reaction according to the aziridine structure. Figure 2b compares the real-time storage modulus data for liquid mixtures of each aziridine at RT for 40 min. Both aziridines exhibited rapid ring-opening reactivity with the carboxylic acid groups in the copolymer. Notably, PTAP showed faster and denser crosslinking behavior than TTMAP because of the lower steric hindrance effects in the aziridine ring to be opened. PTAP has no additional functional group (R' as –H) in the aziridine ring, exhibiting only unsubstituted ring structures formed in trifunctional aziridine.[16]

The ring-opening reaction was further characterized using FTIR spectroscopy. As shown in Fig. 2c, the transmittance peaks within the ranges of 1580–1650 cm^{-1} for the newly created amine group (–NH) were compared before and after the ring-opening reaction. The appearance of the amine group in the spectra indicates the actual ring-opening reaction between the aziridines and the carboxylic acid groups in the copolymer.

Crosslinking characteristics by aziridine crosslinkers in PU-based 2K clearcoat systems

After confirming the reactivity of the aziridines with the carboxylic acid groups, the effects of a small portion of the aziridines (PTAP and TTMAP) in the PU-based clearcoat systems were characterized and compared. The formation of crosslinked networks in clearcoats under thermal conditions was analyzed using various experimental methods. Note that the temperature for the thermal curing system was set to 80 °C with the aim of applying the coating process to automotive bumper parts.

Real-time rheological properties of 2K clearcoats

Figure 3 presents the real-time rheological (*G'*) crosslinking behavior of the 2K clearcoats formulated in Table 1b throughout the thermal curing process at 80 °C for 40 min. In the PU_0 case, the polyacrylic resin

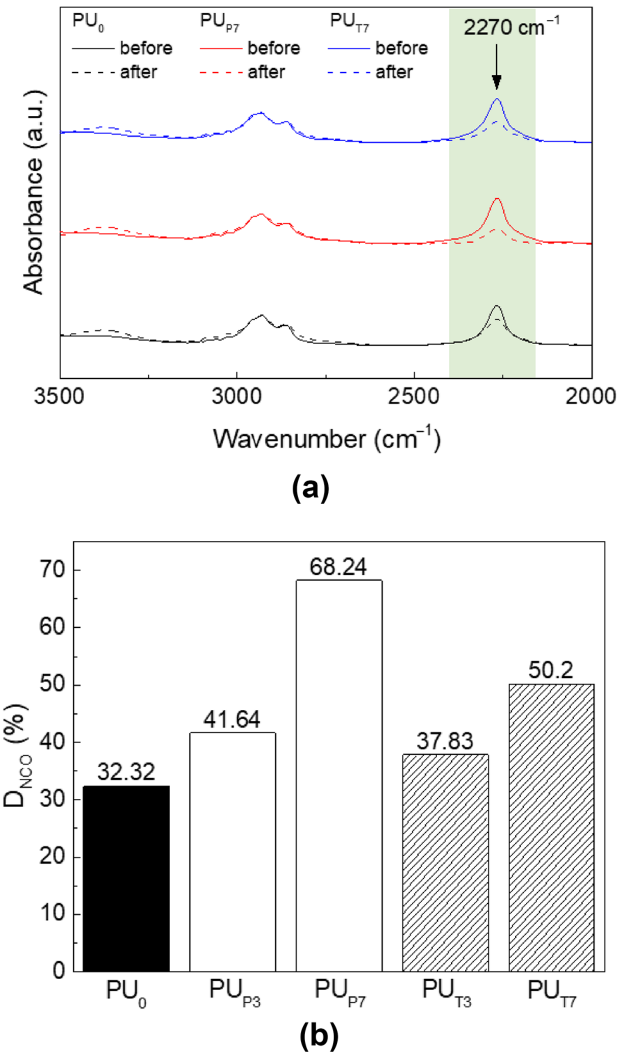

Fig. 5: (a) FTIR absorption spectra of free isocyanate at 2270 cm^{-1} peak for PU$_0$, PU$_{P7}$, and PU$_{T7}$ before and after thermal curing, and (b) the degree of the isocyanate reaction rate (D$_{NCO}$, %) of the clearcoat samples

reacted with the HDI trimer via urethane crosslinking between the –OH and –NCO groups. PU$_{P\_series}$ with PTAP and PU$_{T\_series}$ with TTMAP had faster curing rates than PU$_0$ because additional aziridines simultaneously reacted with the carboxyl group in the polyacrylic resin (Step 1 in Fig. 4). In addition, after the ring-opening reaction, an additional urea reaction between the amine (–NH) group in the aziridines and the free-isocyanate (–NCO) group in the HDI trimer forms a denser crosslinking network than PU$_0$ (Step 2 in Fig. 4). The additional urea reaction occurs only after the ring-opening of aziridine.[53] The max. *G'* value tended to increase as the aziridine content increased up to 7 wt%. In particular, the PU$_{P\_series}$ exhibited a faster crosslinking reaction than the PU$_{T\_series}$ because of the lower steric hindrance associated with PTAP.

The crosslinking dynamics of the clearcoats during thermal curing were also confirmed by RPT. Unlike the above rheological tests on rather thick wet coating films (e.g., 500 μm), RPT measures curing behavior on thin wet coating films (e.g., 60 µm), reflecting that the thermal-cured coating thickness applied in the automotive clearcoat industry ranges from 20 to 25 µm. The oscillatory pendulum periods of the coated films during thermal curing as a function of crosslinked network formation are shown in Fig. 3b. As the content of aziridine increased, there was a rapid enhancement in the curing behavior, evidenced by a shorter pendulum period and quicker initiation time, with PU$_{P7}$ exhibiting the most pronounced curing characteristics. These results agree with those of the rheological experiment for thick coating films.

Changes in isocyanate peaks depending on reactions of 2K clearcoats

The absorbance spectra of 2K clearcoat films (representatively, PU$_0$, PU$_{P7}$, and PU$_{T7}$) were analyzed to measure the change of the –NCO group at 2270 cm^{-1} from the FTIR experiment during the thermal curing at 80 °C, as shown in Fig. 5a. Based on the –CH$_2$ bond at 2935 cm^{-1}, the decrease in peak height of –NCO group was evaluated using equation (1). Based on the D$_{NCO}$ results, the samples containing aziridines had a faster rate of –NCO reduction compared to the PU$_0$ case, qualitatively supporting the occurrence of an additional urea reaction between the ring-opened aziridine and the HDI trimer upon the addition of aziridine. In particular, the PU$_{P7}$ exhibited a faster reaction rate than PU$_{T7}$ (Fig. 5b). These findings closely resemble the real-time curing properties outlined in the section, "Real-time rheological properties of 2K clearcoats."

Thermo-mechanical properties and thermal stability of cured 2K clearcoat films

The thermo-mechanical characteristics of the cured films with and without aziridine crosslinkers were evaluated using DMA and RPT in physical mode. The storage moduli (*E'*) and loss tangent (tan δ) of the cured 2K clearcoat films were measured over a temperature range of – 50 to 150 °C (Fig. 6). Across all measurements, the storage modulus of PU$_{P7}$ began to decrease at the highest temperature, followed by PU$_{T7}$, PU$_{P3}$, PU$_{T3}$, and PU$_0$ (Fig. 6a). As expected, the additional urea reaction and structural effect of PTAP resulted in a higher crosslinking density of PU$_{P7}$ cured films. In addition, peak values of tan δ were observed for the 2K clearcoat films (Fig. 6b and Table 2), indicating that crosslinked films containing the aziridine crosslinker exhibited comparatively higher T_g values than the PU$_0$ film. Linking changes in crosslinking density of clearcoat samples during thermal curing with various reactions (e.g., urethane, ring opening, and urea reactions) in Fig. 3, the PU$_{P\_series}$ and

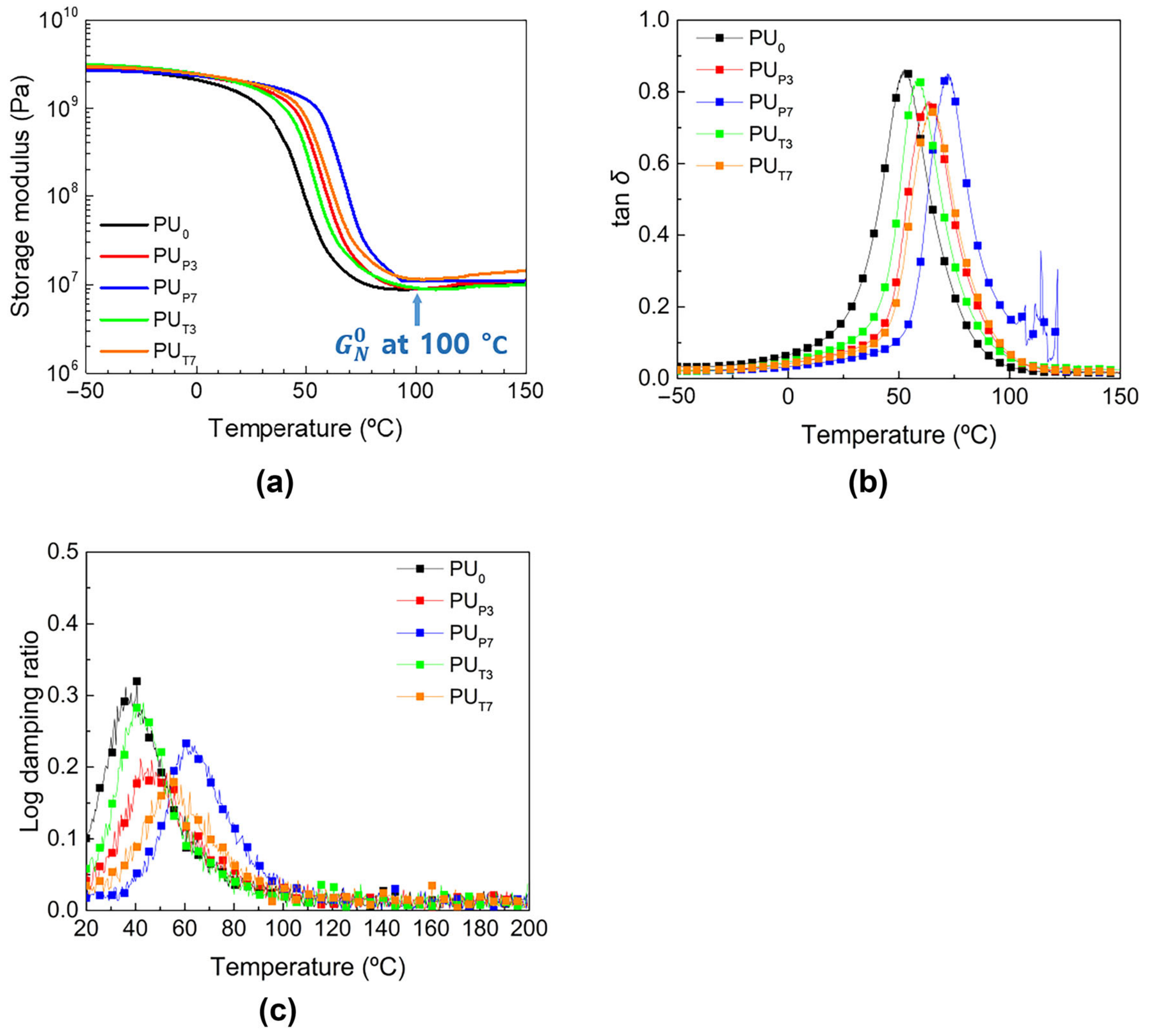

Fig. 6: Comparison of thermo-mechanical properties of 2K clearcoat films cured at 80 °C: (a) storage modulus, (b) tan *δ* from DMA tests, and (c) log damping ratio from RPT tests in the physical mode. Peaks in tan *δ* and log damping ratio denotes T_g of each clearcoat film

Table 2: Various thermo-mechanical and surface mechanical properties of cured clearcoat films

Sample	PU_0	PU_{P3}	PU_{P7}	PU_{T3}	PU_{T7}
$T_{g,DMA}$(°C)	52.59	61.11	71.86	58.13	65.04
$T_{g,RPT}$(°C)	40.5	42.0	60.0	43.1	54.0
ρ(g/cm^3)	1.17	1.05	1.07	1.09	1.15
G_N^0(MPa)	8.91	9.08	11.14	9.19	11.56
X_c(mol/g) (10^{-3})	2.45	2.78	3.36	2.71	3.25
M_c(g/mol)	408.9	360.0	298.8	369.4	307.5
Pencil hardness	HB	HB	HB	HB	HB

PU_{T_series} clearcoats containing aziridines contributed to the formation of enhanced crosslinking network.

The calculated values of the molecular weight between the crosslinking sites (M_c) and the corresponding crosslink density (X_c) for the clearcoat films based on the DMA data in Fig. 6a are listed in Table 2. For 2K clearcoats cured at 80 °C, the M_c of PU_{P7} was smaller than that of PU_{T7} or PU_0. Conversely, the X_c of PU_{P7} was higher than that of the others. As a result, the crosslinking density of the thermally cured PU_{P7} film is the highest, then followed by PU_{T7} and PU_0. As the aziridine content increased from 3 to 7 wt%, the M_c and X_c values of the PU_{T7} or PU_{P7} cured films decreased and increased, respectively, owing to the additional urea crosslinking reaction.

Furthermore, T_g of thin films, produced by RPT test and then dried for 24 h at RT, was measured over a temperature range of 20 to 200 °C in terms of the logarithmic damping ratio using the RPT equipment in physical mode (Fig. 6c and Table 2). The logarithmic damping ratio peaks of the cured films represent the thermal responses of the viscoelastic properties and crosslinking characteristics.[32,33] T_g data obtained from

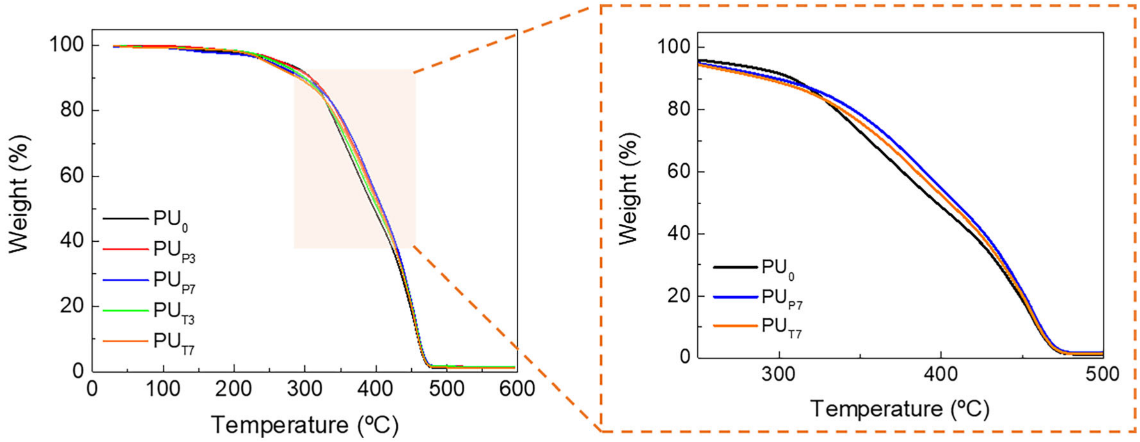

Fig. 7: Comparison of thermal stabilities of 2K clearcoat films cured at 80 °C using TGA

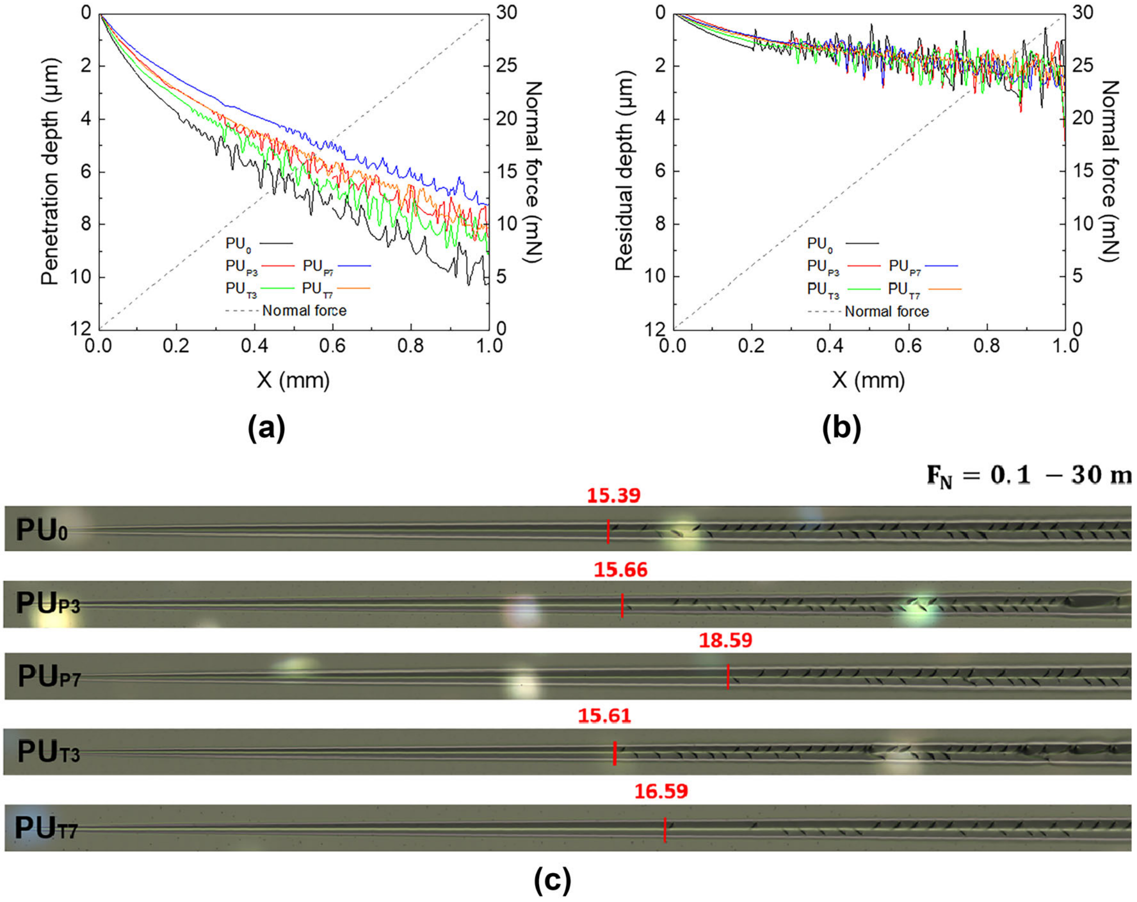

Fig. 8: Nano-scratch test results of 2K clearcoat films cured at 80 °C: (a) Scratch penetration depth profiles, (b) residual depth profiles, and (c) panoramic views with Lc1

thin cured films via RPT were compared with those from DMA. T_gs of the thinly cured 2K clearcoat samples, which fell within the range of 40 to 60 °C, were observed to be lower than those obtained through DMA testing. This difference in T_g values might be attributed to variations in sample thickness between RPT and DMA tests. As shown in Fig. 6c and Table 2, the PU_{P7} film exhibited a notably high T_g, which is in agreement with the DMA analysis. The elevated T_g can be attributed to the combined effects of the ring-opening reaction of aziridine with the carboxylic group in the resin and the additional urea reaction between the ring-opened aziridine and the HDI trimer.

The thermal stabilities of 2K clearcoat films cured at 80 °C were investigated by TGA, as shown in Fig. 7. All the samples showed similar thermal stability, showing abruptly decreasing weights over 250 °C. Especially, it was confirmed that PU_{P7} seemed to have slightly higher thermal stability compared to others, considering the mild decreasing pattern where its weight reduction started at over 250 °C. This result supports the idea that aziridine crosslinkers enhance the crosslinking network in the 2K clearcoat systems.

Surface mechanical properties of cured clearcoat films

The surface mechanical properties of the clearcoat films on a polypropylene (PP) substrate were observed using NST, NHT, pencil hardness, adhesion and gloss retention rate after the car wash tests. Note that the 2K clearcoats were targeted for automotive bumper parts. As a result of the NST, the PU_{P7} cured film exhibited the lowest penetration depth (P_d) profile with respect to the imposed load, followed by PU_{T7}, PU_{P3}, PU_{T3}, and PU_0 (Fig. 8a). The surface mechanical properties were enhanced as the amount of aziridine increased. Figure 8b provides the residual depth (R_d) profiles, which were obtained through post-scanning at a 0.1 mN load after incrementally increasing normal load from 0.1 to 30 mN. The critical load (Lc1 point), indicating the first crack on the surface of the clearcoat films, based on R_d profiles, was measured using a panoramic image captured after the scratch test (Fig. 8c). As the aziridine crosslinker content increased, Lc1 fracture appeared at a higher load level. The PU_{P7} cured clearcoat film exhibited the highest scratch resistance with a denser crosslinking network owing to the supplementary urea reaction.

Through the NHT test, which provides the relationship between the penetration depth and normal force

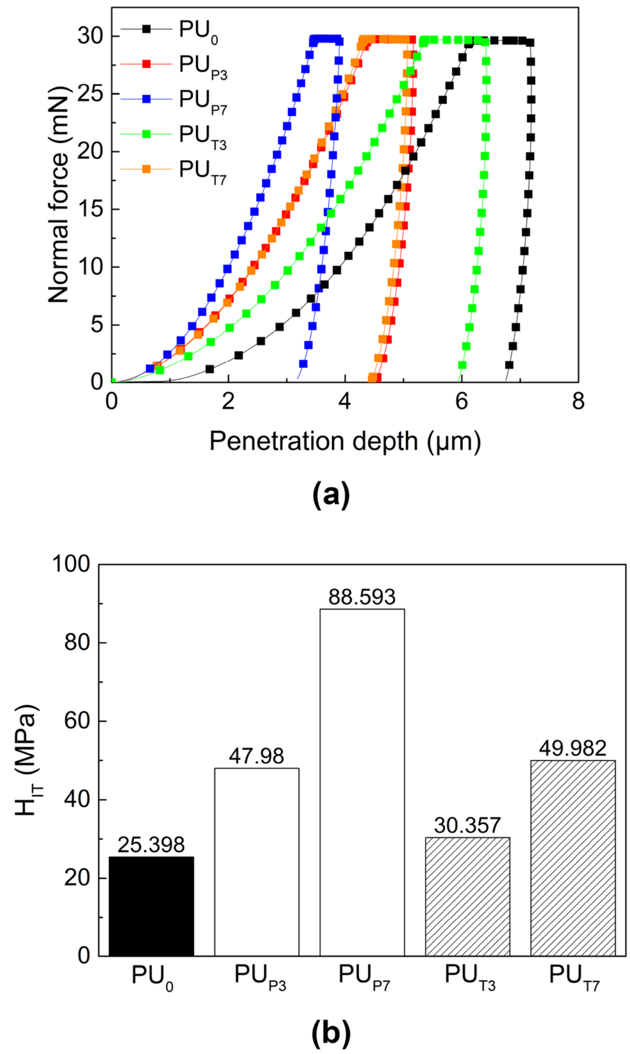

Fig. 9: Nano-indentation test results of 2K clearcoat films cured at 80 °C: (a) Indentation curves and (b) surface hardness values (H_{IT}) calculated based on the Oliver and Pharr method

Table 3: Results of adhesion test (for both initial coating and water resistance), car wash test with gloss retention rate, and appearance test (wave scan and yellowness) of cured 2K clearcoat films coated on PP substrate

Sample			PU_0	PU_{P3}	PU_{P7}	PU_{T3}	PU_{T7}
Adhesion	For initial coatings		5B	5B	5B	5B	5B
	For water resistance		5B	5B	5B	5B	5B
Car wash	Gloss retention rate (%)		86.82	89.24	90.23	85.44	87.45
Appearance	Wave scan	L.W.	9	9.30	9.60	9.10	9.80
		S.W.	15.50	15.70	15.70	16.10	16.80
	Yellowness	ΔL*	–	0.05	0.09	0.07	0.09
		Δa*	–	0.01	0.05	0.04	0.04
		Δb*	–	0.10	0.10	0.11	0.12
		ΔE*	–	0.12	0.15	0.14	0.15

Adhesion: 5B (0 % removed) > 0B (> 65 % removed) for the cured film, it can be seen that the penetration depth of the PU_{P7} clearcoat is the shallowest when the force is up to 30 mN (Fig. 9a). Compared to PU_0 system, the films with added aziridine showed a higher H_{IT} (Fig. 9b), substantiating that aziridine plays a pivotal role in improving the physical properties of the cured film. Furthermore, the PTAP aziridine exhibited superior performance within the crosslinking network by engaging in both urethane and additional urea reactions, facilitated by its ring-opened state.

In addition, various surface properties such as pencil hardness, cross-cut adhesion, gloss retention rate after car wash, and appearance of the 2K clearcoat films are briefly summarized in Table 2 and Table 3. All samples possessed a pencil hardness at the HB level (Table 2), providing strong initial adhesion up to approximately 5B onto the PP substrate (Table 3). Moreover, all coatings exhibited the water resistance adhesion levels equivalent to the initial adhesion (Table 3), suggesting that the cured films containing aziridine crosslinker, up to a slight excess amount of 7 wt%, demonstrated excellent appearance performance with no defects and good adhesion.

The actual scratch patterns created by the Amtec-Kistler car wash test were qualitatively similar to those obtained by the nano-scratch test, exhibiting improved scratch resistance when the aziridine content increased (Table 3). All the films showed over 85 % gloss retention rate values, which were closely related to Rd profiles in Fig. 8b. Note that PU_{P7} had the highest gloss retention rate due to the denser crosslinking density by PTAP aziridine crosslinker.

Appearance performance of cured clearcoat films

To determine the appearance of the given clearcoat films, the L.W. and S.W. values of coating films cured on PP substrate were measured using the wave scan test. The dried film thicknesses of all films were around 32 to 34 μ m. With increasing aziridine crosslinker content, the L.W. and S.W. values of PU_{T_series} or PU_{P_series} coating films slightly increased due to the fast reaction between aziridine and acid groups. It is noteworthy that the addition of aziridine up to 7 wt% did not significantly alter the appearance performance compared to the PU_0 case.

According to ASTM D 2244, the yellow and blue colors of thermally cured clearcoat films were assessed. The Δb^* and ΔE^* values of PU_{T_series} or PU_{P_series}, representing yellowness and the color difference, respectively, showed minimal change compared to those of PU_0. This confirms that adding aziridine crosslinkers up to 7 wt% enhances crosslinking density and surface mechanical properties without compromising appearance performance.

Conclusions

The effects of the aziridine crosslinker on various properties of the PU-based 2K clearcoat system for application on automotive bumpers were investigated, mainly focusing on crosslinking behaviors under thermal curing conditions. The results showed that adding aziridine favorably enhanced the properties of the 2K PU-based clearcoat coatings. First, it was confirmed that the aziridine crosslinkers (PTAP and TTMAP) participated in the rapid formation of a crosslinking network through a ring-opening reaction with the carboxylic acid group in the AA/MAA copolymer, resulting in the formation of a new amine group for additional urea reaction. Second, the effects of small portions of aziridines in PU-based 2K clearcoat coatings were scrutinized via chemo-rheological and mechanical tests. Compared to PU_0, which only has a urethane reaction between the polyacrylic resin and HDI trimer, PU_{P_series} and PU_{T_series} exhibited urethane and ring-opening reactions, as well as additional urea reaction between the newly formed secondary amine and HDI trimer. Among the two aziridine crosslinkers, PTAP has better performance than TTMAP because of less steric hindrance (R' as –H) effects in ring structure. Overall, PU_{P7}, containing 7 wt% PTAP aziridine along with HDI trimer, exhibited excellent crosslinking density and superior surface mechanical properties compared with the other 2K clearcoats. As automotive clearcoat systems for bumper parts continue to advance, aziridine has favorable potential to become a valuable crosslinking aid, contributing to improved crosslinking density, performance, and mechanical properties.

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