Preparation of Urethane-Acrylates by the Photo-Polymerization of Acrylate Monomers Using a Benzophenone Initiator Grafted onto a Polyurethane Copolymer

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Abstract: Photo-polymerization of the acrylate monomers, butylacrylate or 2-hydroxyethyl methacrylate, was initiated by polyurethane (PU) grafted benzophenone to prepare a series of urethane acrylate (UA) polymers. The UA polymers were characterized based on their thermal, spectroscopic, mechanical, and low temperature flexibility properties. In this system, poly(acrylate) chains grew from the grafted benzophenone by photo-polymerization and affected the molecular interactions between PU polymers. The soft segment glass transition temperature (T_g) and melting temperature (T_m) were unaffected by the grafted poly(acrylate) chains. The tensile mechanical strength and the tensile strain of the UA series increased significantly with the attachment of the poly(acrylate) chains. Furthermore, shape recovery and shape retention remained high as the test cycle was repeated. Low temperature flexibility testing demonstrated that the synthesized UA was more flexible at a lower temperature than the unmodified PU.

Keywords: urethane-acrylate, photo polymerization, benzophenone, low temperature flexibility.

Introduction

Grafting functional groups onto polymers has been researched extensively to favorably alter the various performance characteristics of the polymer.[1-3] Accordingly, functional group grafting to polyurethanes (PUs) has been reported by many researchers. For example, a PU surface was modified by graft polymerization of ionic monomers to improve blood compatibility.[4] A PU surface was modified by chemical grafting of poly(ethylene glycol) to make the PU protein resistant.[5] Functional PUs with flexibility at low temperatures[6] or electrolytic attraction in aqueous solutions[7] have been reported. PUs are known for their exceptional properties, which include excellent tensile strain, reproducible shape recovery, easy modification and functionalization, and utility for the industrial manufacturing of coatings and textiles.[8-10] Urethane acrylates (UAs), derived from PU, have been researched as hybrid polymers that combine the flexibility of PUs with poly(acrylate) cross-linking to produce materials with high mechanical strength, chemical resistance, and thermal stability. Different structural forms of UAs have been proposed for various applications in which the terminal acrylate group linked to PU is polymerized with additional acrylate monomers by either thermal or photo initiation using an appropriate initiator species. For example, UAs have been used as adhesives for low surface energy polymers such as polyethylene and polypropyl-

ene and as the adhesives for multi-chip packaging processes.[11,12] Hyperbranched UAs have also been designed to improve coating processes by reducing the viscosity compared to unmodified PU.[13,14]

For acrylate polymerization, thermal initiation is considered advantageous due to the simplicity and low cost of the initiation system as well as the homogenous polymerization achieved in the reaction mixture. Photo initiation, in contrast, requires a UV light source that is placed in close proximity to the reaction mixture, and the polymerization proceeds partially on the reaction mixture surface. However, thin layers can be rapidly polymerized, and the UV coating processes are regarded as more attractive than thermal coating processes due to the low processing temperature, duration of coating, and avoidance of thermal degradation.[15] UAs have been used for UV-cured coatings due to their excellent mechanical and chemical properties. The photo-polymerization and cross-linking of various poly(acrylate)-based polymers using either free or bonded benzophenone as a photosensitizer have been frequently and extensively researched. For example, photo-induced surface functionalization of carbon nanotubes (CNTs) using a free benzophenone was used to graft poly(acrylate) chains to CNT surfaces and improve the dispersion of CNT in solvent.[16] Photo-induced graft copolymerization of poly(acrylate) onto polyimide using a benzophenone moiety included in the polyimide was used to prepare a pervaporation membrane for the separation of gas mixtures.[17] A hyperbranched polyester pervaporation membrane was prepared for the separa-

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tion of benzene and cyclohexane mixtures by photo-polymerization using free benzophenone as a photosensitizer and initiator.[18] Photo cross-linking of a poly(ethylene terephthalate) copolymer and the effect of photo cross-linking on the gas permeability of a poly(acrylate) film were investigated by incorporating a benzophenone segment in the polymer backbones.[19,20] Photo-polymerized UAs grafted to inorganic silicate prepared by a sol-gel process using a free benzophenone initiator were investigated for improving the scratch and abrasion resistance of coated films.[21]

In this study, benzophenone was grafted to a PU using MDI (4,4'-methylene diphenyl diisocyanate) as a grafting agent. The grafted benzophenone was used to initiate the polymerization of acrylate monomers by UV irradiation to form UA, in which poly(acrylate) chains were grafted to the PU rather than terminal cross-linking with the PU, as in previous UAs. This paper investigates the followings: the grafted benzophenone initiation of acrylate polymerization, the effect of grafted poly (acrylate) chains on the physical properties (tensile strength and shape recovery) of PU, and the low temperature flexibility compared to unmodified PU.

Experimental

Materials. Poly(tetramethyleneglycol) (PTMG, M_n=2,000 g/mol, Sigma-Aldrich, St. Louis, MO, USA), 4,4′-methylenebis (phenylisocyanate) (MDI, Junsei Chemical, Tokyo, Japan), and 1,4-butanediol (BD, Junsei Chemical) were dried overnight under high vacuum (0.1 torr). 2,3,4-trihydroxybenzophenone (TBP), 2-hydroxyethyl methacrylate (HA), and *n*-butylacrylate (BA) were obtained from Sigma-Aldrich. Dimethylformamide (DMF, Duksan Chemical, Ansan, Korea)

was distilled over CaH_2 before use.

Polymer Synthesis. MDI (MDI-1, 5.00 g, 20.0 mmol) was added to PTMG (40.0 g, 20.0 mmol) in a 500 mL four-necked beaker-type flask equipped with a mechanical stirrer, condenser, temperature-controlled heating mantle, and nitrogen purge. The mixture was allowed to react for 2 h at 50 °C to prepare the pre-polymer. The chain extender BD (2.70 g, 30.0 mmol), dissolved in 10 mL of DMF, was added to the pre-polymer and the mixture was allowed to react for 1 h. MDI (MDI-2, 7.50 g, 30.0 mmol) was added to the reaction mixture. The reaction was continued for 1 h, and 10 mL of DMF was slowly added during the reaction *via* an addition funnel to prevent a sudden increase in viscosity. MDI (MDI-3, 1.25 g, 5.00 mmol) was added to the reaction mixture, and the reaction was allowed to continue for 40 min. TBP (1.15 g, 5.00 mmol) dissolved in 10 mL of DMF was then added to reaction mixture, and the reaction was allowed to continue for 2 h. After adding the acrylate, as specified in Table I, the reaction mixture was stirred and irradiated at 365 nm with a UV lamp (ZF-1, JIAPENG, Shanghai, China), placed at a distance of 5 cm, for 2 h. An increase in viscosity was observed as the irradiation was continued. After the reaction period, the UA product was precipitated in distilled water (1.5 L) to terminate polymerization. The UA product was cut into pieces and thoroughly washed with magnetic stirring in distilled water (1.5 L×3) and ethanol (1 L×2) to remove any remaining reactants. The final UA product was suction filtered and dried in an oven (60 °C) for 3 days. The control sample, shown in Table I, did not have TBP, and the L form was devoid of acrylate content. The polyurethane (PU) structure, UA synthetic steps, and the cross-linked structure are shown in Scheme I. Specimens for mechanical and shape memory testing were

Table I. Composition of the UA

Sample Code[a]	Reactant (mmol)						
	MDI-1	PTMG	MDI-2	BD	MDI-3[b]	TBP	Acrylate
L	20	20	30	30	-	-	-
Control[c]	20	20	30	30	-	-	125
BA-1	20	20	30	30	5	5	25
BA-2	20	20	30	30	5	5	50
BA-3	20	20	30	30	5	5	75
BA-4	20	20	30	30	5	5	100
BA-5	20	20	30	30	5	5	125
HA-1	20	20	30	30	5	5	25
HA-2	20	20	30	30	5	5	50
HA-3	20	20	30	30	5	5	75
HA-4	20	20	30	30	5	5	100
HA-5	20	20	30	30	5	5	125

[a]BA and HA series used butylacrylate and 2-hydroxyethylmethacrylate as the acrylate monomers, respectively. [b]MDI-3 was a connecting agent between PU and TBP. [c]Butylacrylate was used as the acrylate monomer for control.
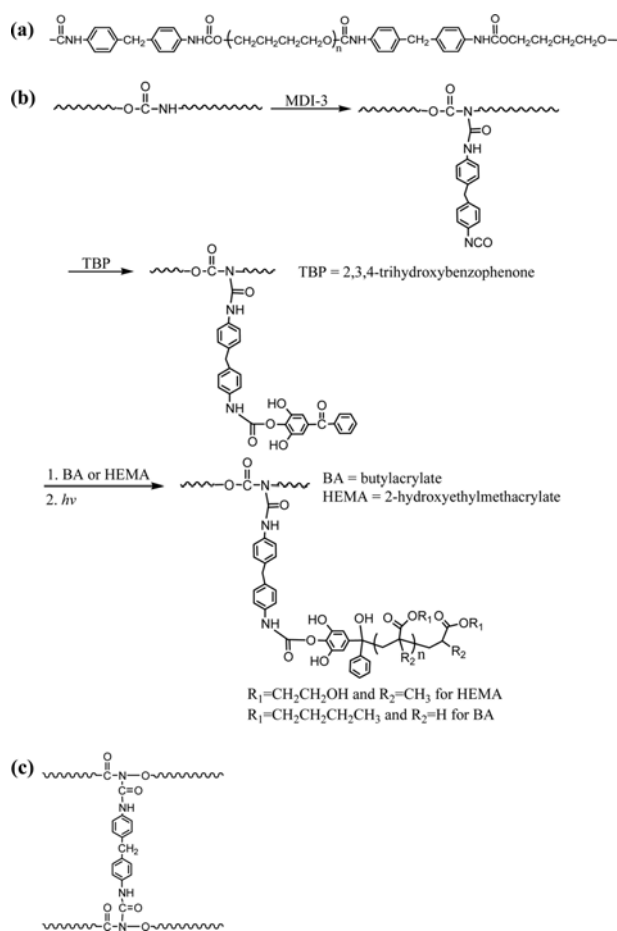
Scheme I. (a) Structure of unmodified PU, (b) preparation of UAs by photo-polymerization of BA or HA using grafted benzophenone, and (c) cross-linking by MDI.

prepared by solvent casting. Specifically, a solution of UA in DMF was slowly evaporated at 60 °C for 60 h to obtain a sheet (0.5 mm thick). The film thickness was measured using a digital caliper (Mitutoyo CD-15CPX, Tokyo, Japan), and the average thickness from five points was recorded. Specimens were prepared from the PU sheet according to ASTM D638. The UA samples were composed of two series, depending on the acrylate type (BA or HA).

Cross-Link Density. Specimens with dimensions of 20× 20×1 mm and a known weight (m_1) were swollen in 50 mL of toluene in a closed cap bottle for 24 h. The swollen weights of the specimens (m_2) were measured after quickly removing the adsorbed toluene from the polymer surfaces with a tissue. The swollen specimens were dried at room temperature for a week and then weighed to obtain their dry masses (m_3). The solvent volume (V_s) in the swollen state, averaged over five swelling experiments, was calculated using the weight difference between the swollen (m_2) and dry states (m_3) and the solvent density (0.8699 g/cm^3). The volume of the polymer (V_p) in the dry state was calculated by dividing the polymer

dry weight (m_1) by the polymer density. The volume fraction of polymer in the swollen mass (v_1) was calculated using the equation $V_p/(V_s+V_p)$. The derivation of the cross-link density is described in the results section.

Spectroscopic Analysis. A Fourier transform infrared (FTIR) spectrophotometer (JASCO 300E, Tokyo, Japan) equipped for attenuated total reflectance measurements was used to collect the infrared spectra. For each sample, 25 scans were taken at 4 cm^{-1} resolution and 2 mm/s scan speed. A UV-vis spectrophotometer (SECOMAM UVICON XS, France) was employed to collect the absorption spectra of the UA solutions (0.025 wt%) in DMF from 300-700 nm.

Thermal Analysis. A differential scanning calorimeter (DSC, TA instruments DSC-Q20, New Castle, DE, USA) was used to obtain calorimetry data for both heating and cooling scans at a rate of 10 °C/min between -50 and 250 °C. After melting at 250 °C for 5 min and cooling quickly to -50 °C, a 5 mg sample was warmed to 250 °C (at 10 °C/min) while monitoring for phase transitions. The soft segment melting temperature (T_m) and enthalpy change for the melting (ΔH) were determined by analysis with the Platinum^{TM} software included with the DSC instrument. Dynamic mechanical analysis was used to collect phase transition data at low temperatures. These measurements were made using a dynamic mechanical analyzer (DMA, Trition TTDMA, Lincolnshire, UK) to measure the storage modulus and loss modulus in a tension mode between -150 and 100 °C at 10 Hz. The low-temperature flexibility test was conducted in a temperature-controlled chamber of the UTM for a twisted sample frozen at -35 °C for 3 h and was recorded by a video camera (SONY HDR-CX 550, Tokyo, Japan) installed close to chamber window, while the temperature was increased at a 10 °C/min.

Tensile Test. Tensile mechanical properties were measured according to the ASTM D638 standard at 25 °C using 0.5 mm thick samples. Testing was performed on a universal testing machine (UTM, LR10K, West Sussex, Lloyd Materials Testing, UK) with the following parameters: 20 mm gauge length, 20 mm/min crosshead speed, and 0.5 kN load cell. A total of 7 specimens were tested for each group; the tensile properties were determined as the average of 5 specimens, excluding the high and low values.

Shape Memory Test. The same UTM equipped with a temperature-controlled chamber was employed for cyclic shape memory tests. A sample with a length L_0 was drawn 100% to $2L_0$ in a temperature-controlled chamber set at 45 °C. This test was performed over the course of 2 min, and the sample was kept at 45 °C for 5 min. The upper grip was released after the specimen in the chamber was cooled with liquid nitrogen to -25 °C for 10 min. The shrunken length (L_1) of the sample was measured once the temperature had remained at -25 °C for 10 min. Percent shape retention (%) was then calculated using eq. (1), L_0, and L_1. In the chamber, the specimen was heated to 45 °C for 10 min, and subsequently, the length (L_2) was measured. Percent shape recovery (%) was

then calculated using eq. (2), $2L_0$, and L_2. The cyclic shape memory test was repeated four times for each sample.

$$\text{Shape retention} = (L_1 - L_0) \times 100/L_0 \ (\%) \tag{1}$$
$$\text{Shape recovery} = (2L_0 - L_2) \times 100/L_0 \ (\%) \tag{2}$$

Results and Discussion

Synthesis and Structure of PU. PUs can be functionalized by covalently grafting various functional groups, and significant improvements in tensile strength can be achieved due to the light cross-linking during the grafting step.[22] However, the tensile strain remains similar or is slightly decreased after functional group grafting. In this investigation, long and flexible poly(acrylate) chains were grafted onto PU to improve both tensile stress and strain, and hydrophobic poly(butylacrylate) or comparatively hydrophilic poly(2-hydroxyethylmethacrylate) were used to produce the poly(acrylate) chains. The grafting and polymerization of acrylate monomers were conducted by UV irradiation using grafted benzophenone as a photo-initiator. The benzophenone was grafted to the PU structure that was composed of hard (MDI) and soft (PTMG) segments by using MDI-3 as the activating agent. The functionalization and modification of PU surfaces using MDI as a grafting agent has previously been reported in the literature.[23-26] The benzophenone functionalized PU and the grafted poly(acrylate) are shown in Scheme I. The 2,3,4-trihydroxybenzophenone (TBP), which contains three hydroxyl groups that can react with the MDI isocyanate group of the PU, was used as the benzophenone moiety. The benzophenyl group of TBP can sensitize the UV irradiation at 365 nm and generates radicals that can initiate the polymerization of acrylate monomers (*i.e.*, BA or HA). The viscosity of reaction mixture was observed to increase with the progress of acrylate polymerization. In Table I, the acryl monomer content increases gradually at the constant MDI, BD, PTMG, and TBP contents as the sample number increases, and the formulation devoid of TBP is used as a control. The freeze-fractured surfaces of BA-5 and HA-5 were compared with those of linear PU and the control; BA-5 and HA-5 showed corrugated sur-
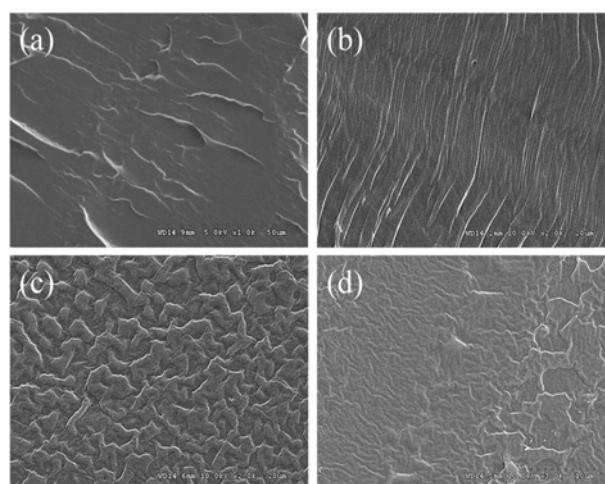

Figure 1. SEM pictures of (a) L, (b) Control, (c) BA-5, and (d) HA-5.

faces, while linear PU and the control had rugged surfaces (Figure 1). Thus, the grafted poly(acrylate) is likely responsible for the differences in surface appearance. The UV-vis spectra of the UAs dissolved in DMF were compared for the formulation L, the control, the BA, and the HA series (Figure 2). The absorbance at approximately 360 nm decreased with increasing acrylate content for both the BA and HA series, suggesting the formation of poly(acrylate). However, no absorbance at a similar wavelength was observed for the L and control groups. Thus, the grafted poly(acrylate) chains changed the UV-vis spectra of the BA and HA series compared to the L and control groups. Although acrylate monomers were used during the synthesis of the control group, the poly(acrylate) was not formed due to the lack of benzophenone initiator.

Cross-Link Density. Because MDI-3 may contribute to cross-linking as well as TBP grafting, as shown in Scheme I(c), the cross-link densities of the UAs were determined by the polymer swelling method. Importantly, the swelling of UAs is inversely related to the degree of cross-linking (Figure 3). Specifically, the interaction parameter (χ) between the solvent and UA is determined from the following expression:[27]
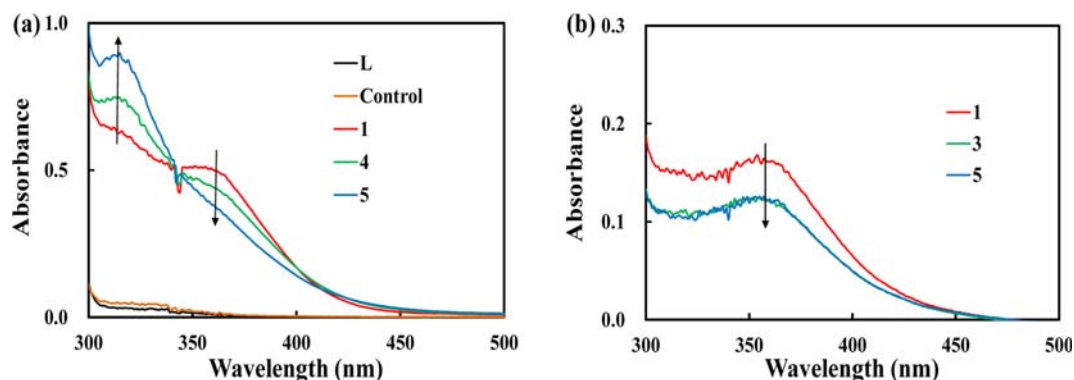

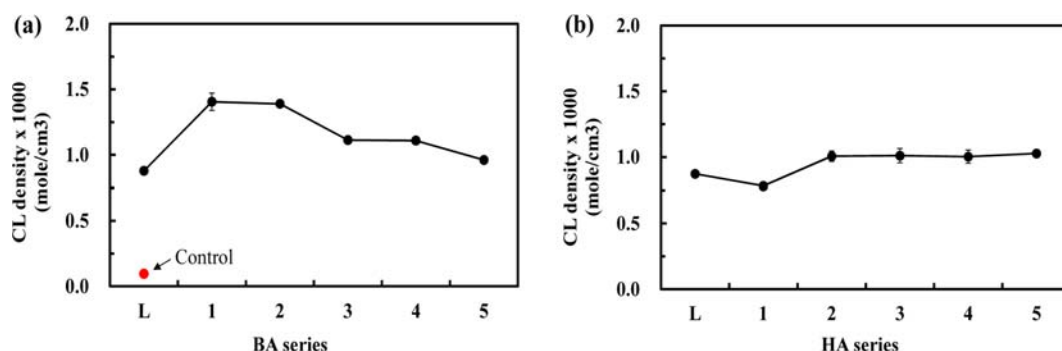**Figure 2.** UV-vis spectra of the (a) BA and (b) HA series.

Figure 3. Cross-link (CL) density profiles of the (a) BA and (b) HA series.

$$\chi = (\delta_1 - \delta_2)^2 V_1/RT \tag{3}$$

δ_1 and δ_2=solubility parameter of solvent and polymer
V_1=molar volume of solvent (106.3 cm^3/mol)
R=gas constant (8.31 MPa·cm^3·K^{-1}·mol^{-1})
T=absolute temperature (298 K)

The solubility parameters used for toluene (δ_1) and UA (δ_2) were 18.2 and 20.5 (MPa)$^{1/2}$, respectively.[28,29] The degree of cross-linking was then calculated from the Flory-Rehner eq. (4):

$$-[\ln(1-v_2)+v_2+\chi v_2^2] = V_1 n[v_2^{1/3}-1/2v_2] \tag{4}$$

v_2=volume fraction of polymer in the swollen mass
χ=interaction parameter
n=cross-link density

Compared to linear PU (L), the cross-link density of the UAs decreased slightly for the BA series and remained the same for the HA series with increasing acrylate content. This result suggests that the cross-linking by MDI-3 was minimal because the grafted poly(acrylate) chains were able to interrupt the close contact between the UA chains and inhibited the cross-linking.[22] If cross-linking by MDI-3 had occurred, the cross-link density and viscosity of the UAs would sharply increase. In addition, the cross-link density of the control UA was significantly lower than that of the BA and HA series

because the benzophenone initiation and poly(acrylate) grafting were missing for the control UA. Overall, the cross-link density results suggest that the grafted poly(acrylate) chains disturbed the cross-linking of UAs but contributed to the improvement of the tensile properties, as discussed in the following section.

The viscosity of the BA and HA polymers dissolved in DMF was investigated to determine whether poly(acrylate) grafting to PU affected the viscosity because the grafted poly(acrylate) might drag the movement of UA and, therefore, increased solution viscosity. The viscosity results showed a trend similar to the cross-link density results, as the viscosity of the BA series decreased slightly and that of the HA series remained the same with increasing acrylate content (Figure 4). Therefore, the viscosity results demonstrated that poly(acrylate) grafting did not disturb the mobility of UA chains.

IR Analysis. The free isocyanate group on PU appearing at approximately 2350 cm^{-1} can be used to monitor the progress of TBP grafting to PU. The IR spectra obtained for the reaction mixture during the TBP grafting step to PU showed that the free isocyanate disappeared almost completely in 120 min, indicating that TBP was almost completely grafted to PU by this time (Figure 5(a)). The IR spectra of the BA and HA groups presented in Figure 5(b) and (c) show peaks for C-H bending at 1527 cm^{-1}, aromatic C-C ring stretching at 1592 and 1411 cm^{-1}, O-H bending at 1362 cm^{-1}, C-N stretching at 1305 cm^{-1}, and C-O stretching at 1215 cm^{-1}. These peaks
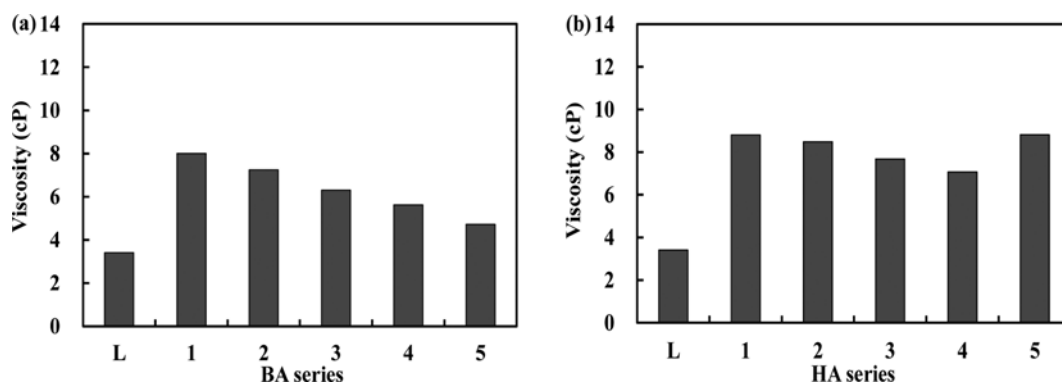

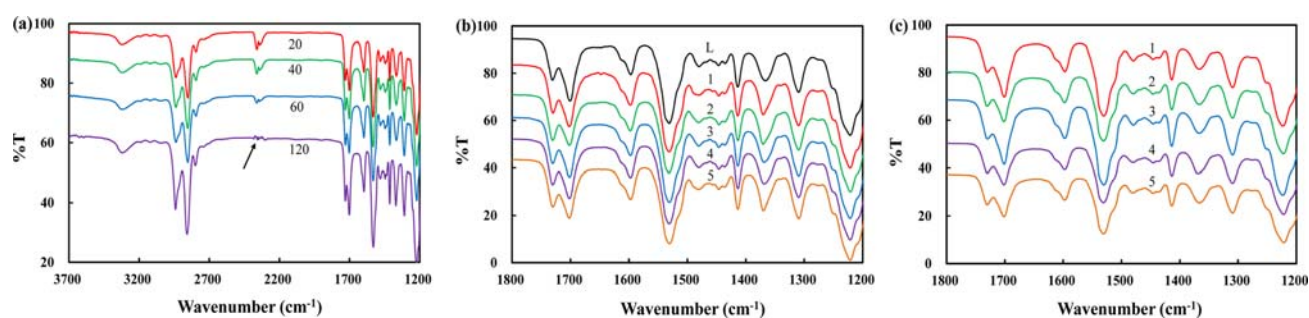**Figure 4.** Viscosity profiles of the (a) BA and (b) HA series.

Figure 5. (a) Disappearance of the free isocyanate peak after TBP addition (note: the number indicates the time in minute), and IR spectra of (b) BA and (c) HA series.

were observed for the BA and HA series, as well as the linear PU. The C=O stretching peaks at approximately 1698 and 1726 cm^{-1} were used to analyze intermolecular interactions, such as hydrogen bonding and dipole-dipole interactions between hard segments. The bonded carbonyl (1726 cm^{-1}) appears at a higher wavenumber than that of a free carbonyl group (1698 cm^{-1}).[6] Thus, the relative intensity between the bonded carbonyl stretch and the free carbonyl stretch correlates to the degree of phase separation (DPS). The DPS, which implies a change in the molecular interactions between hard segments, was calculated using the equation DPS= $A_{1726}/(A_{1726}+A_{1698})$, where A_{1726} and A_{1698} represent the absorbance at 1726 and 1698 cm^{-1}, respectively. The DPS of the BA series changed from L (40%) to BA-1 (43%), BA-3 (43%), and BA-5 (45%). The DPS of the HA series also showed a slight increase: HA-1 (37%), HA-3 (38%), and HA-5 (42%). The DPS of the HA series was less than that of BA series, presumably because the hydroxyl groups of poly(acrylate) in the HA series interrupted the hydrogen bonding between UAs. In summary, these results suggest that the molecular interactions between carbonyl groups were slightly increased by the grafted poly(acrylate) chains.

Thermal Analysis. The melting temperature (T_m) of the soft segment in the UA series was investigated using DSC. T_m was used as a reference temperature for shape memory tests, as discussed in the later section. The melting peak of

the soft segment was observed to be between 18 and 20 °C during the second heating scan (Figure 6). The T_m and enthalpy change (ΔH_m) for melting are shown in Table II. The T_m remained similar compared to L (18.5 °C) as the acrylate content increased for both the BA and HA series. For example, the T_m of BA-1, BA-3, and BA-5 were measured to be 19.8, 18.0, and 19.4 °C, respectively, and the T_m of HA-1, HA-3, and HA-5 were 19.0, 18.9, and 19.6 °C, respectively. ΔH_m was found to increase as the acrylate content increased, especially for the BA series: 20.4 J/g for L was increased to 27.4 J/g for BA-1, 37.7 J/g for BA-3, and 43.4 J/g for BA-5. For HA-1, HA-3, and HA-5, ΔH_m was 26.3, 26.9, and 25.3 J/g, respectively. The grafted poly(acrylate) chains restricted the movement of the UA chains and resulted in the higher ΔH_m with increasing acrylate content. The BA series showed higher ΔH_m than the HA series, most likely because the flexible poly(butylacrylate) chains of the BA series were better intermingled. Thus, more heat energy was required for chain movement compared to the short and relatively polar poly(2-hydroxyethymetacrylate) chains of the HA series.

The glass transition temperature (T_g) of the soft segment was investigated by DMA, which was used to monitor the storage modulus, loss modulus, and tan δ between -150 and 100 °C (Figure 7). A rapid decrease in the storage modulus and the appearance of a loss modulus peak were observed between -70 and -60 °C for both the BA and HA series, indicat-
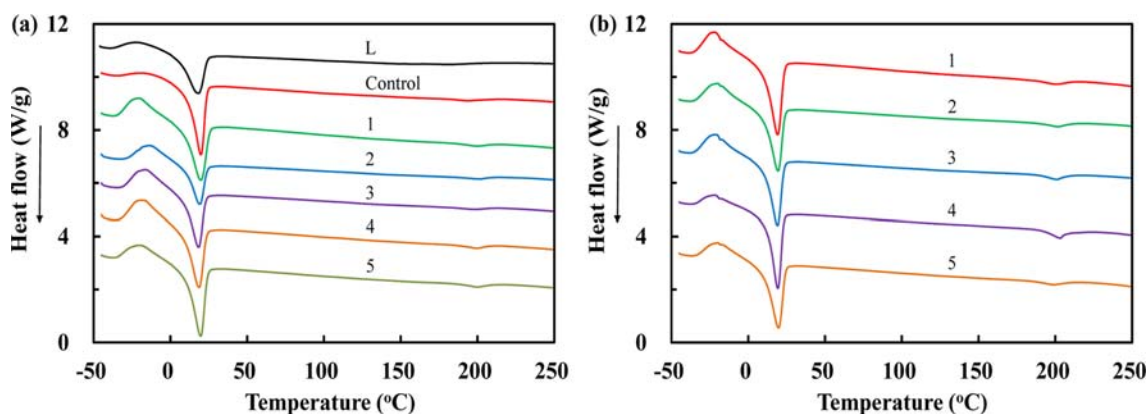

Figure 6. DSC thermograms of the (a) BA and (b) HA series.

Table II. Comparison of the Soft Segment Thermal Properties of the UA Series

Sample Code	T_m (°C)	ΔH_m (J/g)	$T_g{}^a$ (°C)
L	18.5	20.4	-67.1
Control	19.9	27.8	-63.6
BA-1	19.8	27.4	-60.4
BA-2	18.5	30.9	-61.6
BA-3	18.0	37.7	-61.4
BA-4	18.1	39.6	-61.5
BA-5	19.4	43.4	-61.0
HA-1	19.0	26.3	-62.6
HA-2	19.2	25.2	-62.3
HA-3	18.9	26.9	-61.8
HA-4	19.2	28.3	-60.9
HA-5	19.5	25.3	-61.0

$^a T_g$ was determined from the loss modulus data.

ing the glass transition of the soft segment. With increasing poly(acrylate) content, the crystallization peaks, which are indicated by an arrow, after the glass transition in the storage modulus plot were reduced compared to the L form, suggesting that crystallization of UA was interrupted by the grafted poly(acrylate) chains. T_g data for the UA series shown Table II is based on the peak observed in the loss modulus plots. T_g

was observed to slightly increase as the acrylate content increased, as the T_g values of the BA-1 (-60.4 °C), BA-5 (-61.0 °C), HA-1 (-62.6 °C), and HA-5 (-61.0 °C) groups were higher than that of the L group (-67.1 °C). The thermal results are likely due to the grafted poly(acrylate) chains restricting the rotation of the UA chains.

Tensile Mechanical Properties. The maximum tensile stress of the BA and HA series sharply increased compared to the L and control groups (Figure 8). However, the maximum tensile stress gradually decreased as the acrylate content increases. Briefly, the maximum tensile stresses were 47.8 MPa for BA-1 and 42.1 MPa for HA-1 were reduced to 22.7 MPa for BA-5 and 26.1 MPa for HA-5. In contrast, the maximum stresses were 8.1 MPa and 15.0 MPa for the L and Control groups, respectively. The initial increase in maximum stress compared to L and control was not related to the cross-linking in Scheme I(c), but rather appeared to be due to the entanglement of grafted poly(acrylate) chains. The reduced maximum stress at higher acrylate contents were most likely due to the disruption of molecular interactions between UAs by the grafted poly(acrylate) chains.

The strain at break of the BA and HA series was also increased compared to the L and Control groups with the increase in acrylate content (Figure 9). The following strains were observed: 1096% for L, 1588% for control, 1809% for BA-1, 2108% for HA-1, 1822% for BA-5, and 1752% for HA-5. The tensile strain results indicate that the strain of the BA and HA series was increased by the grafted poly(acry-
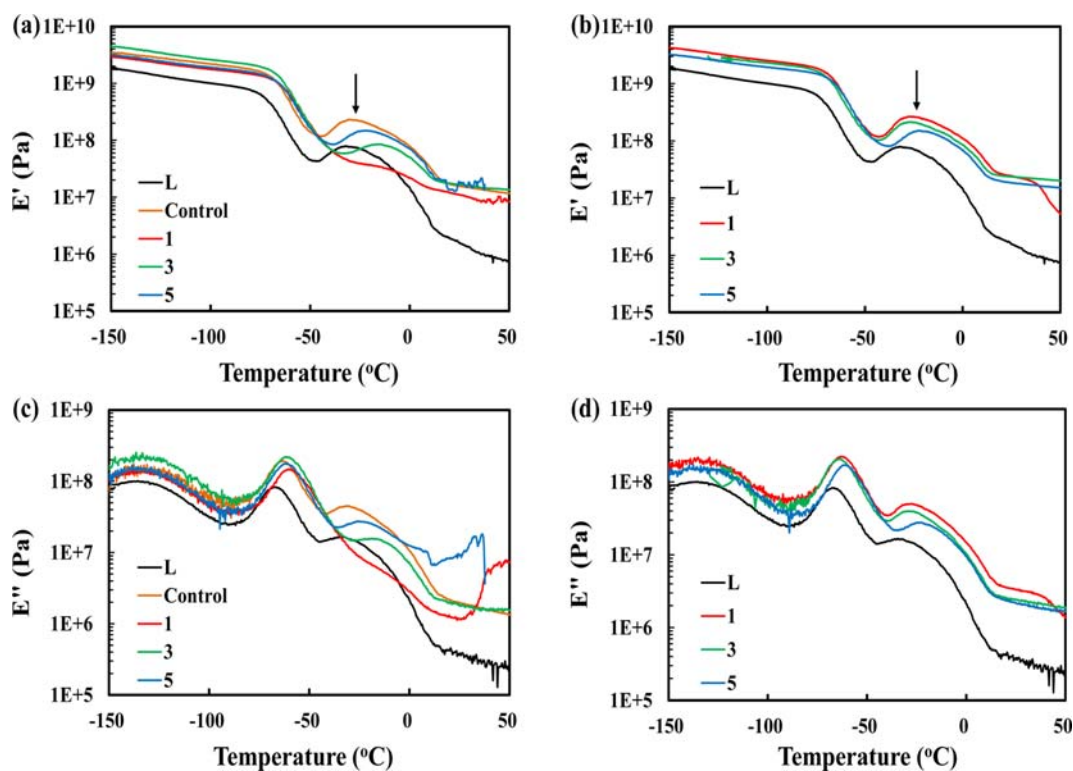

Figure 7. Storage modulus (E') profiles for the (a) BA and (b) HA series, and loss modulus (E'') profiles for the (c) BA and (d) HA series.
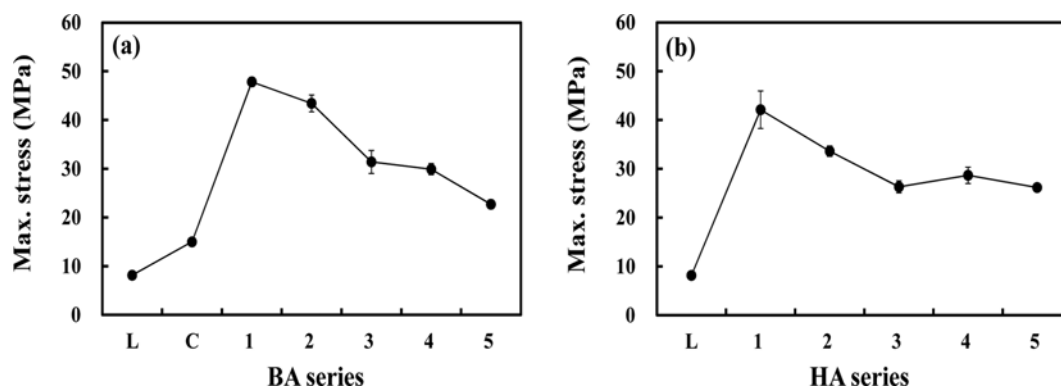
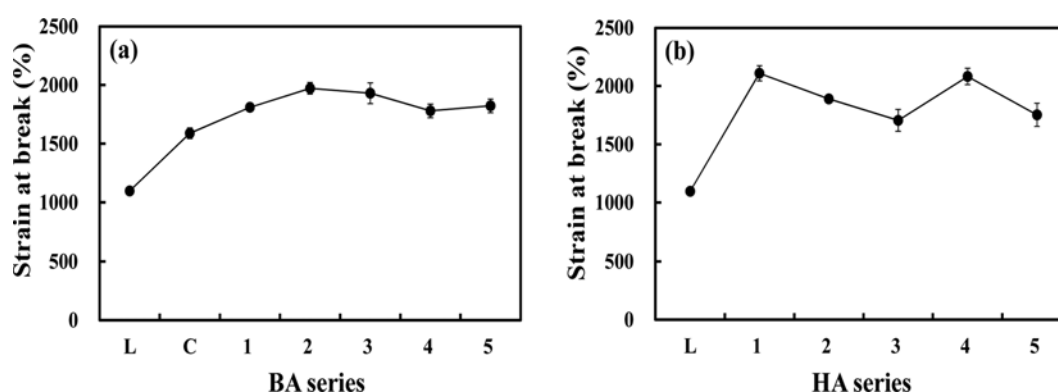**Figure 8.** Maximum stress profiles for the (a) BA and (b) HA series.

Figure 9. Strain at break profiles for the (a) BA and (b) HA series.

late) chains, possibly because they disrupted the interactions between UAs and free the UA chains for stretching. Furthermore, the tensile stress and strain results demonstrated that the tensile stress and strain of UAs could be simultaneously increased by the grafted poly(acrylate) chains.

Shape Memory Effect. Cyclic shape recovery and retention tests for the BA and HA series were conducted between -25 and 45 °C. The soft segment T_m was used as the reference temperature for the shape memory tests because shape recovery near room temperature was useful for practical applications. The shape recovery of the BA and HA series was slightly decreased compared to that of L (93%) and changed slightly as the test cycle was repeated (Table III). The shape recovery of BA-1 (93%), BA-5 (89%), HA-1 (91%), and HA-5 (86%) from the first test cycle was changed to BA-1 (91%), BA-5 (86%), HA-1 (93%), and HA-5 (86%) in the fourth test cycle. Notably, the control UA showed inferior shape recovery properties compared to the other UAs. Therefore, the BA and HA series did not lose their shape recovery and efficiency under repetitive stretching and recovery test conditions. Shape retention slightly increased as the test cycle was repeated compared to that of L (96%). The shape retention of BA-1 (96%), BA-5 (99%), HA-1 (96%), and HA-5 (98%) determined from the first test cycle was changed to BA-1 (97%), BA-5 (99%), HA-1 (87%), and HA-5 (98%)

Table III. Shape Memory Properties

Sample Code	Recovery (%)		Retention (%)	
	First[a]	Fourth[a]	First	Fourth
L	93	97	96	96
Control	86	84	95	96
BA-1	93	91	96	97
BA-2	87	85	99	99
BA-3	88	81	99	99
BA-4	89	85	99	99
BA-5	89	86	99	99
HA-1	91	93	96	87
HA-2	89	84	96	100
HA-3	92	88	96	98
HA-4	96	94	90	85
HA-5	86	86	98	98

[a]Shape memory results from the first and fourth test cycles, respectively.

in the fourth test cycle. Again, the control UA also showed inferior shape retention properties compared to the other UAs. The shape recovery and retention results did not show
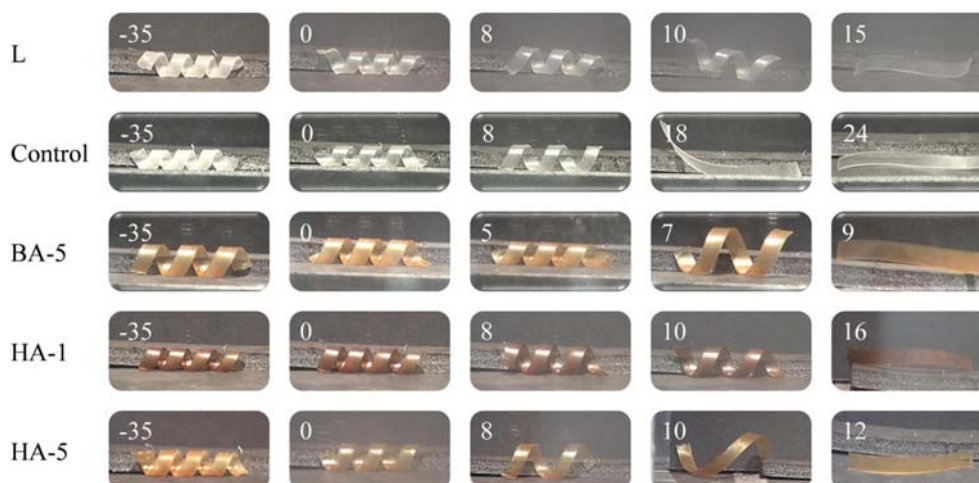
Figure 10. Low temperature flexibility testing (note: the number indicates the temperature in Celsius).

a correlation to the acrylate content. Furthermore, these results indicated that poly(acrylate) grafting to PU did not significantly change the shape memory properties.

Low Temperature Flexibility Test. Low temperature flexibility was tested for a series of spiral samples (L, Control, BA-5, HA-1, and HA-5) frozen at -35 °C (Figure 10). The spiral samples did not show a recovery to a linear shape until they were warmed to 0 °C. As the temperature was increased, BA-5 showed a slight recovery at 7 °C and a full recovery at 9 °C. HA-5 and HA-1 fully recovered at 12 and 16 °C, respectively. While the L group fully recovered at 15 °C, the control UA did not fully recover to a linear shape until 24 °C. These low temperature test demonstrated that the UA became flexible at a lower temperature than L and control PU due to the grafted flexible poly(acrylate) chains reducing molecular interactions such as hydrogen bonding and dipole-dipole interaction between PUs, as shown in Figure 11.[30,31] There-
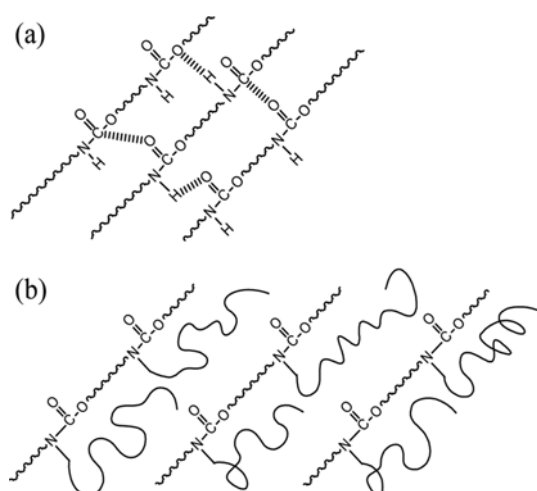
fore, poly(acrylate) grafting to PU simultaneously improved both tensile stress and strain as well as low temperature flexibility. In the previously reported UAs, PUs had been linked with the poly(acrylate) at their chain ends, whereas poly(acrylate) was grafted to PU in this investigation.[10,32,33] The poly(acrylate)-grafted UAs could be useful as UV curable coatings due to their enhanced mechanical properties and low temperature flexibility.

Conclusions

Poly(acrylate) chains were grafted to PU using an attached benzophenone initiator to form UAs by UV irradiation. The resulting polymers were characterized by spectroscopic, thermal, mechanical, shape memory, and low temperature flexibility tests. Butylacrylate and 2-hydroxyethyl methacrylate were used as the acryl monomers. The maximum stress and the strain at break of the butylacrylate and 2-hydroxyethyl methacrylate UAs were increased up to 590% and 192%, respectively, compared to that of linear PU. Notably, a simultaneous improvement in tensile stress and strain was unusual. The shape recovery for two UA series was slightly decreased compared to linear PU and remained the same after four cyclic tests. In contrast, the shape retention slightly increased compared to linear PU and remained high, especially for the HA series. Low temperature flexibility testing demonstrated an improvement for BA-5 compared to linear PU. In summary, poly(acrylate) grafting to PU reduced the molecular interactions between UAs and simultaneously improved the tensile stress and strain. The UAs introduced in this investigation were different from previously reported UAs in that poly(acrylate) chains were grafted to PU instead of being incorporated through terminal cross-linking.

Figure 11. Schematic comparison of the molecular interactions between (a) unmodified PUs and (b) UAs.

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