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Synthesis of water-soluble urethane acrylate anionomers and their ultra-violet coating properties

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Water-soluble and ultraviolet (UV)-curable urethane acrylate anionomers containing dimethylolpropionic acid (DMPA) were synthesized with varying molecular weight of soft segment and degree of neutralization. The ion group incorporated was confirmed by ^{1}H-NMR and ^{13}C-NMR spectra. In viscosity measurements, the enhancement of viscosity was achieved with increasing of ionic strength or pH of the solution. However, when the molecular weight of soft segment was high, the viscosity little changed for given parameters. This indicates that the strong hydrophobic interaction caused by the long soft segment made the anionomer chain aggregate. The UV coating properties of urethane acrylate anionomer films were depended on the molecular weight of soft segment and the degree of neutralization. For the films of high ion content and low molecular weight of soft segment, the tensile strength had a tendency toward increasing, on the contrary, for the films of low ion content and high molecular weight of soft segment, the tensile strength displayed reverse tendency. However, compared with general urethane acrylate films, overall coating properties were significantly improved. This was believed that the ionic groups acted as reinforcing filler by means of the phase separation from the crosslinked urethane acrylate network. © *1999 Kluwer Academic Publishers*

1. Introduction

Recently, waterborne coatings using ultra-violet (UV) curing technology have gained wide industrial interests, because they can decrease air pollution, reduce risks of fire, and improve aspects of occupational health and safety [1, 2]. Especially, odor, toxicity, viscosity control, and greater ease of cleaning are all reasons given for the possible use of water as a diluent in UV-curable system.

There are two types of water-based system [1, 3]; emulsion or colloidal dispersion and water-soluble or dispersible. In the former case, usually, it is common practice to add surfactants to stabilize the emulsion or dispersion once it is formed [4–6]. They may assist the ease of formation of the emulsion and be a important factor in controlling or determining the particle size of the resulting emulsion. Alternatively, however, some deterioration in performance has been observed due to the presence of these surfactants that remain in the cured film and impart sensitivity to the finished coating. In the latter case, water-soluble or dispersible resins have been achieved by the incorporation of hydrophilic sites such as nonionic and ionic groups into the molecular backbone or end without adding surfactants [7–12]. Among hydrophilic sites, the incorporation of ionic group has been more favored due mainly to the enhanced mechanical properties of the cured films. The ionic groups form an aggregate and act as a physical crosslinker, which is responsible for the marked improvement of the mechanical properties of the final films [13–17]. In our previous works [18–20], we also observed that the UV coating properties of urethane acrylate films could be enhanced by the incorporation of ionic groups into the network.

In this study, we synthesized water-soluble urethane acrylate anionomers containing α,α-dimethylol propionic acid (DMPA) as a potential ionic site and polytetramethylene glycol (PTMG) as a soft segment in a molecule. Differing from the conventional water-dispersible urethane acrylate derivatives having only one ionic site in the center or end of the molecule, the urethane acrylate anionomers prepared in this study had a peculiar molecular structure; two ionic sites in a molecule [21–23]. This was possible through stepwise reaction procedure. With the help of this large ionic content in a molecule, they easily dissolved in water. So, these urethane acrylate anionomers were believed to be many advantages in material handling and compound preparation as well as in air pollution reduction, in the field of UV curing industries.

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The goal of this study is to examine the viscosity behaviors of the water-soluble urethane acrylate anionomers in water and their UV coating properties with varying molecular weight of soft segment and degree of neutralization.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI, Junsei Chemical Co., Japan) were vacuum distilled before use. Polytetramethylene glycol (PTMG, Mw = 1.0×10^3 gmol^{-1}, 1.4×10^3 gmol^{-1}, and 2.0×10^3 gmol^{-1}, Hyosung BASF, Korea), α,α-dimethylol propionic acid (DMPA, Aldrich Chemical Co., U.S.A.), triethylamine (TEA, Kanto Chemical Co., Inc., Japan), and dibutyltindilaurate (DBTDL, Junsei Chemical Co.) were used as received. Inhibitor in 2-hydroxyethyl methacrylate (HEMA) was removed through removing column (Aldrich Chemical Co.). N,N-dimethylacetamide (DMAc) was used as a solvent of DMPA and viscosity reducer after degassing at room temperature for 48 h. Benzophenone (Janssen Chemical Co., Japan) was used as a photoinitiator.

2.2. Synthesis of urethane acrylate anionomers [21–23]

The synthesis was carried out in the 4-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and nitrogen gas inlet system. Scheme 1 is the reaction procedure and molecular structure of the urethane acrylate anionomers.

In the first step, IPDI was poured into the glass reactor after the nitrogen gas inlet for 10 min to eliminate the residual moisture. After dissolving 1 wt% of DBTDL, DMPA dissolved in DMAc was dropped into the reactor slowly at room temperature. The reaction temperature was raised to 70 °C so that 2 mole of IPDI reacted with the 1 mole of DMPA. In this stage, care must be taken to control the molar ratio of reaction, so as not to increase the molecular weight. This temperature was maintained for 4 h to retain an acceptable rate of reaction. The change of NCO value during reaction was determined using dibutylamine back titration method to find out the end point of the reaction [24].

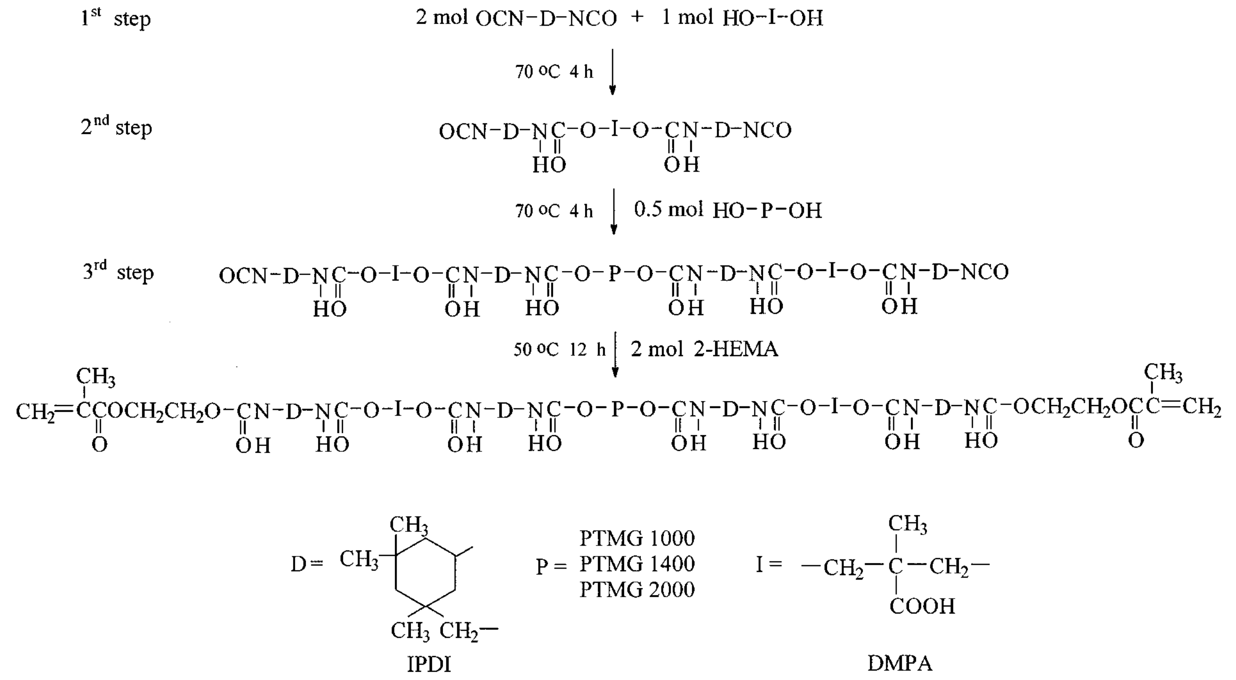
In the second step, 0.5 mole of PTMG was reacted with the same method as the first step. In the last step, HEMA was reacted to the residual NCO groups at 50 °C for 12 h, capping both molecular ends with vinyl groups. The reaction end point was determined by the disappearance of NCO stretching peak (2270 cm^{-1}) through IR spectroscopy. The ingredients for the synthesis of urethane acrylate anionomers are listed in Table I.

In order to purify DMAc, unreacted HEMA, and DMPA, the reaction mixture was precipitated from the water and filtered several times to give crude product. The crude product was dried in a vacuum oven. Carboxylic acid group in anionomers was neutralized with appropriate amount of triethylamine at room temperature for 1 h.

2.3. Preparation of urethane acrylate anionomer solution and film [19, 20]

10 g of urethane acrylate anionomer was placed in a beaker together with 3 wt% of benzophenone and stirred vigorously with a mechanical stirrer and deionized water were dropped continuously. With the amount of deionized water, the fraction of anionomers was controlled.

Solutions prepared were poured into a polyethylene mold of which inner dimension was 10 × 10 × 0.5 cm, and dried at 60 °C for 24 h *in vacuo*. The dried urethane acrylate anionomers were cured with air irradiating static UV lamp (450 watt, UV lamp from Ace Glass Co.) for 5 min and postcured at 80 °C for 5 h. The films



Scheme 1 Reaction procedure and molecular structure of the urethane acrylate anionomers.

TABLE I Ingredients used for the synthesis of urethane acrylate anionomers[a]

			PTMG ($gmol^{-1}$)[b]					
Symbol	IPDI	DMPA	1.0×10^3	1.4×10^3	2.0×10^3	HEMA	TEA	DMPA content (wt %)
ID1	50.00	15.08	56.23	—	—	14.64	11.38	10.24
ID1-75	50.00	15.08	56.23	—	—	14.64	8.54	10.24
ID1-50	50.00	15.08	56.23	—	—	14.64	5.69	10.24
ID2	50.00	15.08	—	78.75	—	14.64	11.38	8.88
ID3	50.00	15.08	—	—	112.46	14.64	11.38	7.41

[a] All units were represented in gram.

[b] Molecular weight of polytetramethylene glycol (PTMG).

Abbreviation: ID means IPDI-based urethane acrylate anionomer. ID1, 2, and 3 correspond to IDs prepared with PTMG 1.0×10^3, 1.4×10^3, and 2.0×10^3 $gmol^{-1}$, respectively. ID1-75 and -50 are ID1 neutralized with 75 and 50%, respectively.

TABLE II Molecular weights of urethane acrylate anionomers

Symbol	Mw ($gmol^{-1}$)	Mn ($gmol^{-1}$)	PDI[a]
ID1	8.25×10^3	6.25×10^3	1.32
ID2	1.06×10^4	6.13×10^3	1.73
ID3	1.36×10^4	7.10×10^3	1.92

[a] Polydispersity index (PDI).

obtained were about 0.3 mm thick and were stored in a desiccator at room temperature before testing.

2.4. Measurements

Molecular weight distributions were measured by a model 410 GPC equipped with Styragel HR 1-4 columns from Waters Associates at 25 °C. The flow rate of the carrier solvent, THF, was 0.5 ml/min. The average molecular weights were calculated on the basis of the molecular weight versus retention volume curve of monodisperse polystyrene standards. Resultant molecular weights for urethane acrylate anionomers were listed in Table II. The 200 MHz ^{1}H-NMR spectra were recorded with Varian Gemini spectrometer, and ^{13}C-NMR spectra were obtained on solution in $CDCl_3$ using a JEOL GX400 spectrometer operating at 100 MHz for carbon. Infra-red spectra were recorded using a Mahgna IR-550 of Nicolet Co. The viscosity for the solutions was measured using a Brookfield synchrolectric viscometer, Model RVRH at 30 °C. The shear rate was 0.5 s^{-1}. Tensile properties were measured with a crosshead speed of 5 mm/min at 25 °C using Hounsfield Model Instron, Serial No. R100 1231. All measurements respect the average of 5 runs. The dumbbell type specimen was 25 mm wide at two ends, 0.3 mm thick, and 6 mm wide at the neck. Dynamic mechanical properties were obtained using DMA2980 (Tainstruments) at 2 Hz. The cured films were quenched to −80 °C and heated up to 100 °C at 3 °C/min. The sample chamber was kept drying by a stream of moisture-free nitrogen. Pencil hardness, stain resistance, crosshatch adhesion, and flexibility test for the sample films were followed ASTM D 3363-92a, D 3023-87, D 3359-92a, and D 4145-83, respectively.

3. Results and discussion

3.1. Molecular structure of urethane acrylate anionomer

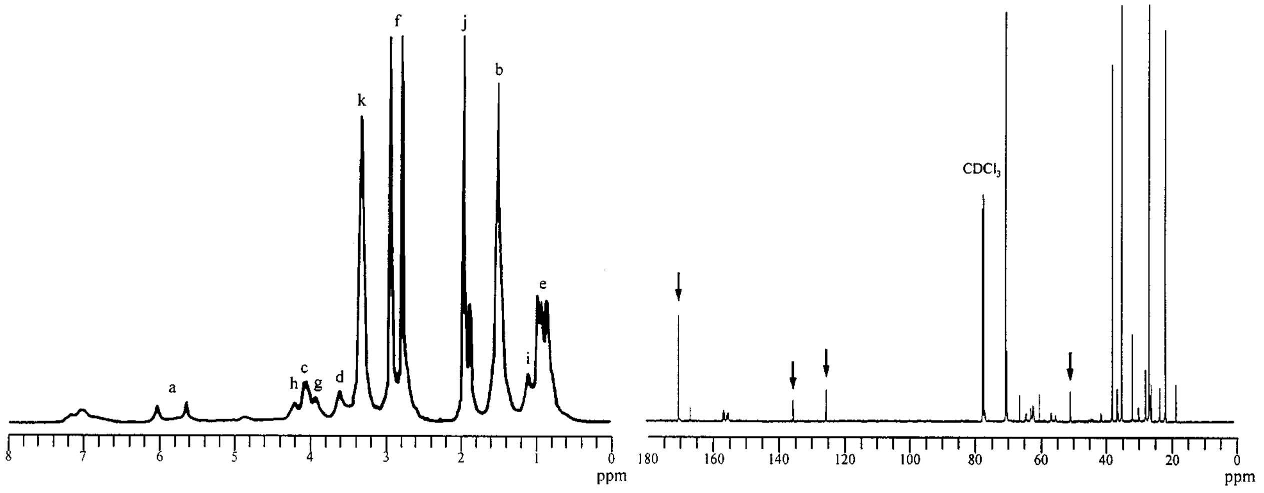
The chemical structure of the urethane acrylate anionomer synthesized was characterized using ^{1}H- and ^{13}C-NMR spectra and the result recorded shown in Fig. 1. ^{1}H-NMR signals were as follows: $\delta = 4.2$ ppm (H_f) for the methylene group of DMPA incorporated and $\delta = 1.1$ ppm (H_i) for the methyl group of DMPA. Other signals corresponded to typical protons of urethane acrylate [10]. ^{13}C-NMR signals were also as follows: $\delta = 50.05$ ppm for the *tert*-carbon of DMPA, $\delta = 125.5$ and 136.0 ppm for the carbons of vinyl group, $\delta = 171.6$ ppm for the carbon of urethane linkage. Under such results, it was reasonable to expect that the urethane acrylate molecule designed be synthesized successfully.

3.2. Viscosity behavior of urethane acrylate anionomer solutions

The viscosities of urethane acrylate anionomer (ID1, ID2, and ID3) solutions were measured with varying anionomer weight fraction, ionic strength, and pH.

In Fig. 1, the viscosity was plotted against the anionomer weight fraction where the UV coating was proper. ID1 and ID2 solutions showed shear increase of viscosity at high fraction region. However, the increase of viscosity was not observed for ID3 solution. This was resulted from the emulsion droplet formation. The emulsion droplet size of ID3 solution measured with a laser light scattering instrument (Brook Heaven Co. Ltd., BI9000AT, argon laser) was in the order of 30 nm. This means that ID1 and ID2 could be hydrated sufficiently in terms of the incorporated ionic groups. Whereas, ID3 having the longer hydrophobic soft segments than ID1 and ID2 lost their solvation sheath, and subsequently aggregated to form the aligned hydrophobic aggregates [7, 8]. In our previous work [18], we have proved the abovementioned alignment of hydrophobic soft segments in water by viscosity measurements.

Fig. 3 shows the dependence of viscosity for ID1 and ID2 solutions on the ionic strength at the fraction of 0.3 and 30 °C. The viscosity enhancement was observed with the increase of the ionic strength. This result suggests that there be a hydrophobic interaction that was caused by the hydrophobic polyether soft segments [25]. However, as the molecular weight of soft segment increased, the degree of enhancement of viscosity was rather diminished, even though the hydrophobic interaction increased. This indicates that owing to the strong hydrophobic interaction of polyether soft segments, anionomer molecules started to form or formed aggregates in water.



(a) ¹H-NMR

(b) ¹³C-NMR

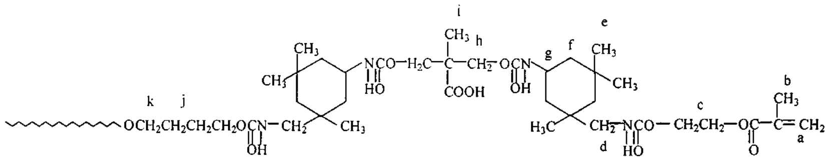


Figure 1 ^{1}H-NMR (a) and ^{13}C-NMR spectra (b) for urethane acrylate anionomer (ID1).

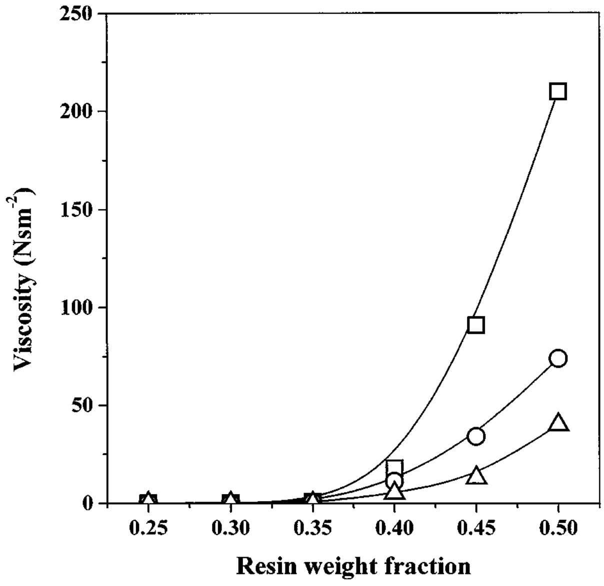


Figure 2 Viscosity change for ID1 (-□-), ID2 (-○-), and ID3 (-△-) with the resin weight fraction in water at 30 °C. Shear rate = 0.5 s^{-1}.

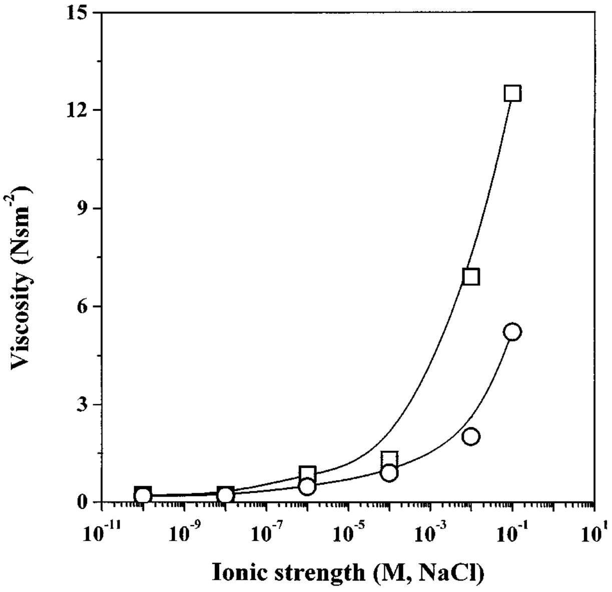


Figure 3 Viscosity change for ID1 (-□-) and ID2 (-○-) with the ionic strength (M, NaCl) at 30 °C. Anionomer weight fraction = 0.3. Shear rate = 0.5 s^{-1}.

Fig. 4 shows the dependence of viscosity for ID1 and ID2 solutions on pH at the fraction of 0.3 and 30 °C. The viscosity increased as the pH increased, leading to more extended chain structure due to the electrostatic repulsion [25, 26]. At low pH region, the precipitation was observed, since enough of carboxylates were in the acid form to render the molecules insoluble.

3.3. UV-curing procedure

IR spectra taken before (a) and after (b) 5min of UV irradiation and plotted to show the spectroscopic changes resulting from the curing process are shown in Fig. 5. The complete disappearance of the C=C band at 1633.92 cm^{-1} indicated that the vinyl polymerization reaction occurred. The conversions were determined by measuring the gel fraction of cured sample after extracting the unreacted materials in methylethyl ketone/acetone (4 : 6) mixture for 24 h. The samples were found to contain greater than 0.85 gel fraction.

3.4. UV coating properties of urethane acrylate anionomer films

Fig. 6 shows the stress-strain curves of UV-coated films having different molecular weight of soft segment (ID1 (a), ID2 (b), and ID3 (c)). The ultimate tensile strength, the elongation at break, and the initial modulus are summarized in Table III. ID1 film having low molecular

TABLE III Tensile properties of UV-cured urethane acrylate anionomer films

Symbol	Tensile strength (Nm^{-2})	Elongation at break (%)	Initial modulus (Nm^{-2})
ID1	2.78×10^7	227	1.79×10^8
ID1-75	1.82×10^7	223	1.48×10^8
ID1-50	1.33×10^7	158	1.03×10^8
ID2	1.75×10^7	351	8.48×10^7
ID3	1.43×10^7	472	3.53×10^7

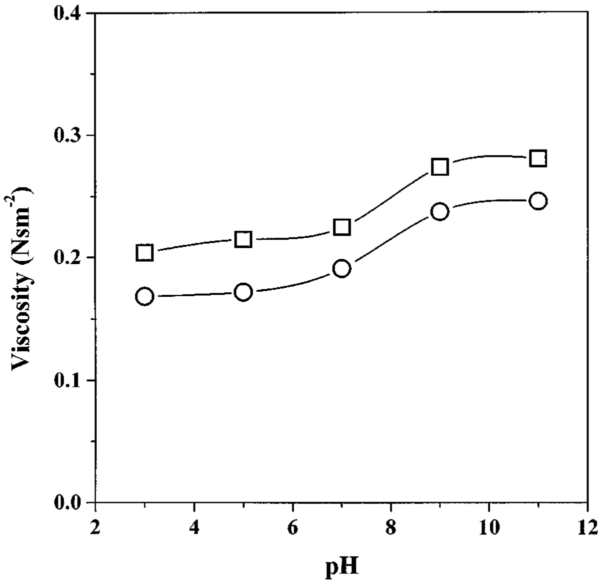


Figure 4 Viscosity change for ID1 (-□-) and ID2 (-○-) with the pH at 30 °C. Anionomer weight fraction = 0.3. Shear rate = 0.5 s^{-1}. In the preparation of pH-controlled urethane acrylate anionomer solution, ionic strength-controlled buffer solution was used.

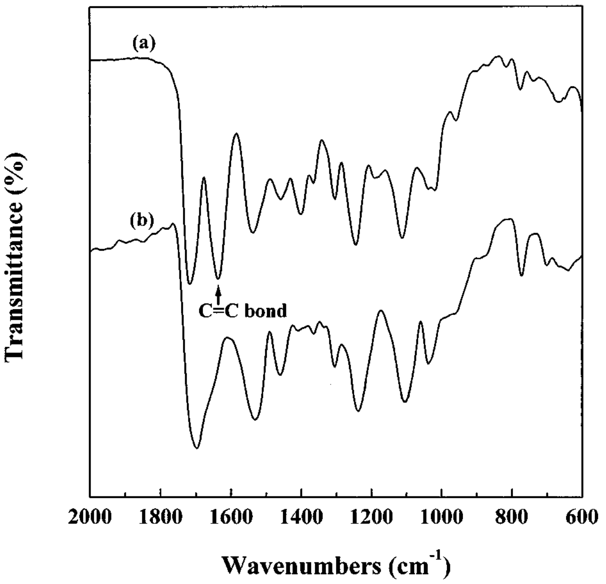


Figure 5 IR-spectra for ID1 before (a) and after (b) 5 min UV irradiation.

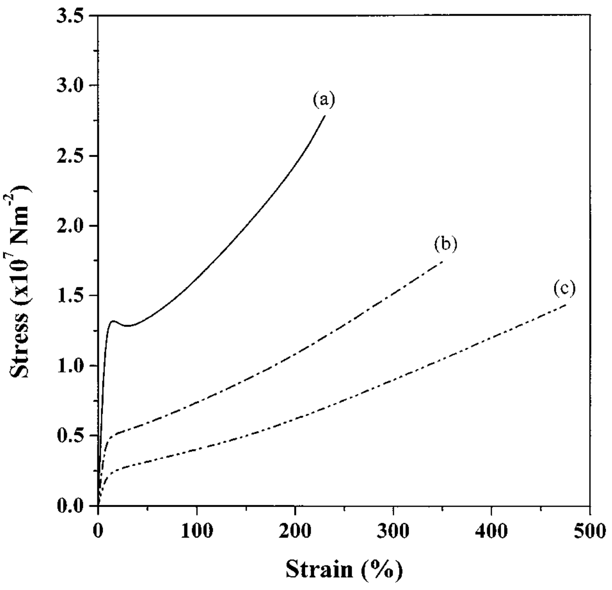


Figure 6 Stress-strain curves for ID1 (a), ID2 (b), and ID3 (c) films. All samples were neutralized with 100%.

weight of soft segment exhibited high initial modulus and tensile strength and low elongation at break. On the contrary, as the molecular weight of soft segment increased, the tensile strength and the initial modulus decreased and the elongation at break increased. This trend was in good agreement with the work of Oraby and Walsh [27]. However, for the urethane acrylate anionomer films, it is notable that the ultimate tensile strengths were much higher than those in the literatures [1, 2, 11, 12] (generally, the ultimate tensile strength of conventional urethane acrylate films prepared without using the reactive diluent was in the order of 2.0×10^6–1.0×10^7 Nm^{-2}). This suggests there be a synergistic effect in the coating property by means of the incorporation of ionic groups into the network.

From the fact that ID1 having more ionic groups exhibited high value of ultimate tensile strength, we assumed that the phase separation between ionic hard segment domain and soft segment domain improved tensile properties. This could be confirmed by dynamic mechanical analysis (DMA). The temperature dependence of storage modulus and loss modulus for ID1, ID2, and ID3 is shown in Fig. 7. Two transition peaks for ID1 film were detected around −46 and 45 °C, corresponding to the glass transition temperature of polyether soft segment domain, T_{gs}, and the glass transition temperature of ionic hard segment domain, T_{gh}, respectively. This result confirms that ID films were composed of two phases, the polyether soft segment domain and the ionic hard segment domain due to the difference in polarity between the ionic groups and the network [14, 28, 29]. Therefore, the ionic hard segment domain could act as a reinforcing filler in the urethane acrylate network, resulting in the enhancement of the ultimate tensile strength and the initial modulus, as shown in Fig. 6. However, as the molecular weight of soft segment increased, the magnitude of T_{gh} decreased. This was believed that the degree of phase separation of ionic hard segment domain from the network was reduced because of the reduction of charge density, as listed in Table I. The reduced phase separation of ID2 and ID3 films accompanied with lowering of the ultimate tensile strength and the initial modulus. Considered on the basis of literatures [13–17, 30], the incorporation of ionic group into the urethane acrylate network also made it possible to form the phase-separated urethane acrylate network and improve the mechanical properties.

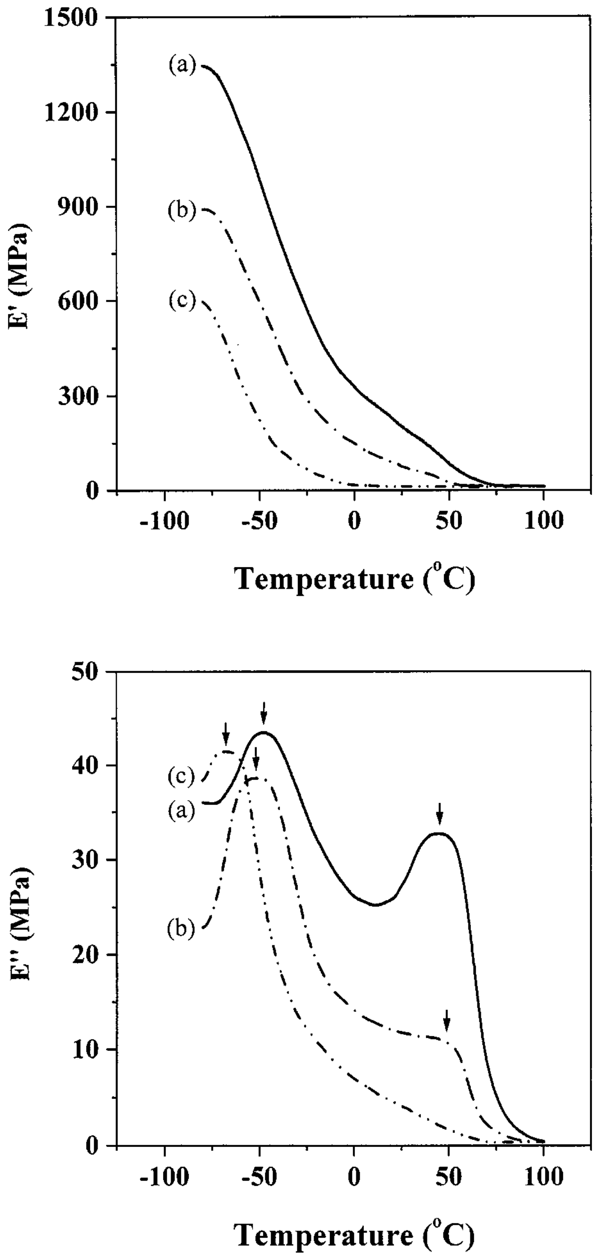


Figure 7 Dynamic mechanical properties (DMA) for ID1 (a), ID2 (b), and ID3 (c) films; temperature dependence of storage modulus (above) and temperature dependence of loss modulus (below).

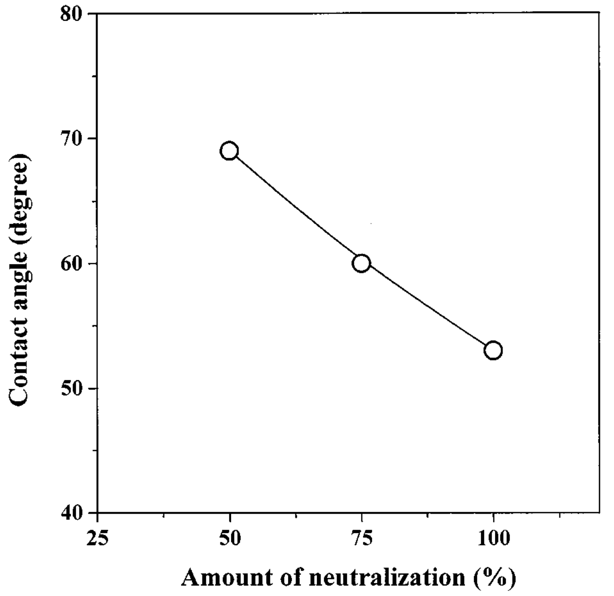


Figure 8 Contact angle for ID1 film with the degree of neutralization. 1 μl of DDI water was dropped and contact angle was read using Erma contact angle meter, model G-1.

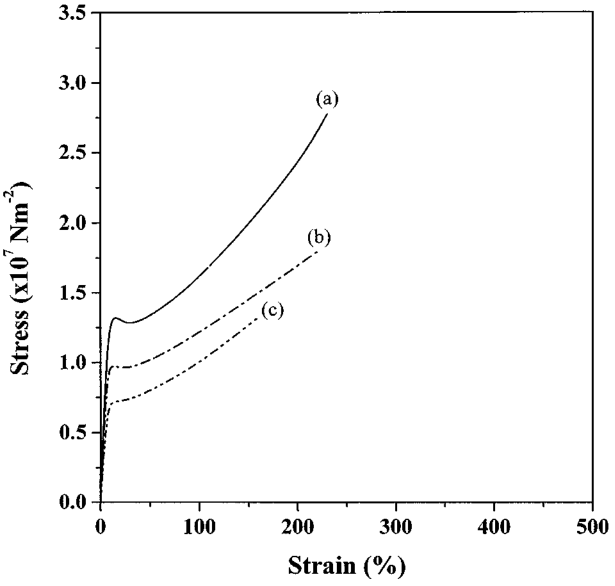


Figure 9 Stress-strain curves for ID1 film with the degree of neutralization; 100% (a), 75% (b), and 50% (c).

In Fig. 7, the shift of T_{gs} to lower temperature was observed, as the molecular weight of soft segment increased. The high phase volume of soft segment and the crosslinking density of the network accounted for the tendencies of shifts of T_{gs} to lower temperature [16, 30–32].

In order to confirm the effect of the phase separation induced by ionic group incorporation on the UV coating property in detail, ID1 film having different degree of neutralization were prepared. The degree of neutralization could be certified by the observation of contact angle, as shown in Fig. 8. The contact angle decreased gradually as the degree of neutralization increased. The stress-strain curves obtained from ID1 films are shown in Fig. 9. The tensile strength, the elongation at break, and the initial modulus increased dramatically, as the degree of neutralization increased. This result indicates that the incorporation of ionic groups into the network induced the phase separation. Therefore, the enhancement of coating properties could be achieved for the urethane acrylate anionomer films.

3.5. Other coating properties

Other coating properties of urethane acrylate anionomer films are given in Table IV. Adhesion was measured using the crosshatch adhesion method. All films

TABLE IV General UV-coating properties of urethane acrylate films

Item	ID1	ID2	ID3
Adhesion (/100)	100	100	100
Pencil hardness	6H	6H	6H
Flexibility (in.)	0	0	0
Stain resistance	Good	Good	Good

showed good adhesion. This result was due to the formation of grafting bond between PVC substrate and urethane acrylate group of the multifunctional acrylates that were initiated by photoinitiator [11, 12]. Pencil hardness showed constant good result with 6H, which is attributed to the hard network structure formed by the phase separation of ionic groups from the urethane acrylate network, as illustrated above, as well as the high crosslinking density of cured film. In the flexibility test, we could not observe any crack generation. This was interpreted by flexible network formation by incorporated polyether soft segment. In the stain resistance test, all samples showed good stain resistance because of negatively charged film surface.

4. Conclusions

Water-soluble and UV-curable urethane acrylate anionomers could be synthesized by incorporating DMPA into the urethane acrylate molecular backbone. In their viscosity behavior observation, we could find that the hydrophobic interaction caused by hydrophobic polyether soft segment resulted in sharp viscosity increase at high fraction and ionic strength. However, too strong a hydrophobic interaction gave rise to the formation of emulsion droplets. This was attributed to the alignment of hydrophobic soft segments in water by losing solvation sheath. The ultimate tensile strength of the urethane acrylate anionomer films was enhanced due to the phase separation induced by the ionic aggregate that acts as reinforcing filler in the network, which was confirmed by dynamic mechanical analysis (DMA). Pencil hardness, adhesion, flexibility, and stain resistance of urethane acrylate anionomer films were measured and showed excellent results.

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