

Water-Soluble Urethane Acrylate Ionomers: Effect of Molecular Structure on Ultraviolet Coating Properties

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ABSTRACT: Water-soluble urethane acrylate ionomers containing dimethylolpropionic acid (DMPA) were synthesized, changing the molecular components, and their ultraviolet (UV) coating properties were studied. It was found that the UV coating properties of the urethane acrylate ionomer films were very dependent on the molecular weight of the soft segment, the type of the diisocyanate, and the amount of neutralization. In general observations, the cured films displayed much improved mechanical properties, compared with conventional urethane acrylate film not containing ionic groups. The main reason for the improved film properties seemed to be attributed to the presence of ionic groups in the network. In dynamic mechanical analysis, two distinct glass transition temperatures, corresponding to the ionic hard domains and soft domains, were detected at high content of ionic groups. This suggested that the urethane acrylate network be composed of two phases. Consequently, the ionic hard domains formed by the phase separation from crosslinked network could act as a reinforcing filler, which possibly explains the improved film properties of the urethane acrylate ionomer films. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1853–1860, 2000

Key words: water-soluble; ultraviolet-curable; urethane acrylate ionomers; ionic hard domains; phase separation; reinforcing filler

INTRODUCTION

Recently, waterborne coatings using ultraviolet (UV) curing technology have gained wide industrial interest because they can decrease air pollution, reduce risks of fire, and improve aspects of occupational health and safety.^{1,2} Odor, toxicity, viscosity control, and greater ease of cleaning especially are all reasons given for the use of water as a diluent in UV-curing systems.

In usual water-based systems, emulsion or colloidal dispersions have been achieved by adding surfactants^{3–6} and/or by incorporating hydrophilic sites into the molecular backbone or end.^{7–12} The

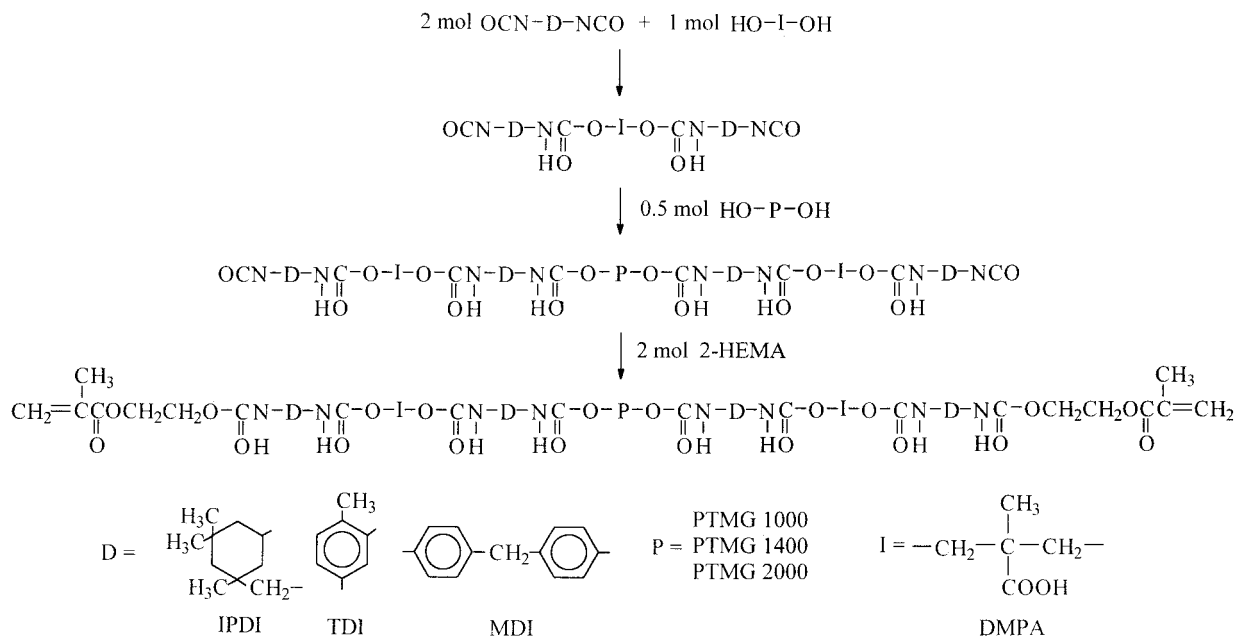
surfactants may assist the ease of formation of the emulsion and be a significant factor in controlling or determining the particle size of the resulting emulsion. However, some deterioration in performance has been observed because they still remain in the cured film and impart sensitivity to the finished coating. Therefore, the incorporation of hydrophilic sites, such as ionic and nonionic groups, into the molecule has been favored to obtain stable colloidal dispersions. Moreover, 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} Previously, we also observed that the UV coating properties of urethane acrylate films could be enhanced by the incorporation of ionic groups into the network.^{18–20}

In this study, we synthesized water-soluble urethane acrylate ionomers. Different from the

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Scheme 1 Schematic molecular structure for urethane acrylate ionomers.

conventional water-dispersible urethane acrylate derivatives having only one ionic site in the center or end of the molecule, the urethane acrylate ionomers prepared in this study had two ionic sites in a molecule.^{21–23} With the help of this large ionic content in the molecule, they easily dissolved in water. Therefore, these urethane acrylate ionomers were believed to have many advantages in material handling and compound preparation, as well as in diminishing the problem of air pollution, in the field of UV curing. Here, we observed the effect of molecular weight of soft segment, type of diisocyanate, and amount of neutralization on the UV coating properties of these urethane acrylate ionomer films.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI, Aldrich Chemicals, USA), toluene diisocyanate (TDI, 80% 2,4-isomer, Tokyo Chemical Industry Co., Ltd., Japan), and 4,4'-diphenylmethane diisocyanate (MDI, Aldrich) were vacuum distilled before use. Polytetramethylene glycol (PTMG, $M_w = 1.0 \times 10^3 \text{ g mol}^{-1}$, $1.4 \times 10^3 \text{ g mol}^{-1}$, and $2.0 \times 10^3 \text{ g mol}^{-1}$, Hyosung BASF, Korea), α,α -dimethylol propionic acid (DMPA, Aldrich), triethylamine (TEA, Kanto Chemical Co., Inc., Japan), and

dibutyltindilaurate (DBTDL, Junsei Chemical Co., Japan) were used as received. Inhibitor in 2-hydroxyethyl methacrylate (HEMA) was removed through a column (Aldrich). *N,N*-dimethylacetamide (DMAc) was used as a solvent for DMPA and viscosity reducer after degassing at room temperature for 48 h. Benzophenone (Janssen Chemical Co., Japan) was used as a photoinitiator.

Synthesis of Urethane Acrylate Ionomers^{21–23}

The schematic presentation for the reaction procedure and the molecular structure is shown in Scheme 1. ID, TD, and MD are IPDI-, TDI-, MDI-based urethane acrylate ionomers, respectively. Serial numbers 1, 2, and 3 correspond to the molecular weight of PTMG, 1.0×10^3 , 1.4×10^3 , and $2.0 \times 10^3 \text{ g mol}^{-1}$, and last number to amount of neutralization in percentage.

The synthesis was carried out in a 4-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and nitrogen gas inlet system. In the first step, diisocyanate was poured into the glass reactor after nitrogen gas was aspirated 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 80°C so that 2 mol of diisocyanate reacted with the 1 mol of DMPA. In this

stage, the reaction condition was carefully controlled, 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 mol of PTMG was reacted using the same method as the first step. In the last step, HEMA was reacted with 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.

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 ionomer was neutralized with an appropriate amount of triethylamine at room temperature for 1 h.

Preparation of Urethane Acrylate Ionomer Solution and Film^{19,20}

Ten grams of urethane acrylate ionomer was placed in a beaker together with 3 wt % of benzophenone and stirred vigorously with mechanical stirrer. Then, 30 g of deionized water were dropped continuously. In the case of solvent-cast films, methyl ethyl ketone (MEK) was used instead of the deionized water.

Each solution prepared was poured into a polyethylene mold, of which the inner dimension was 10 × 10 × 0.5 cm, and dried at 60°C for 24 h *in vacuo*. The dried urethane acrylate ionomers were cured in air with an irradiating static UV lamp (450 W, UV lamp from Ace Glass Co.) for 5 min and postcured at 80°C for 5 h. The films obtained were about 0.3 mm thick and were stored in a desiccator at room temperature before testing.

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. The molecular weights mea-

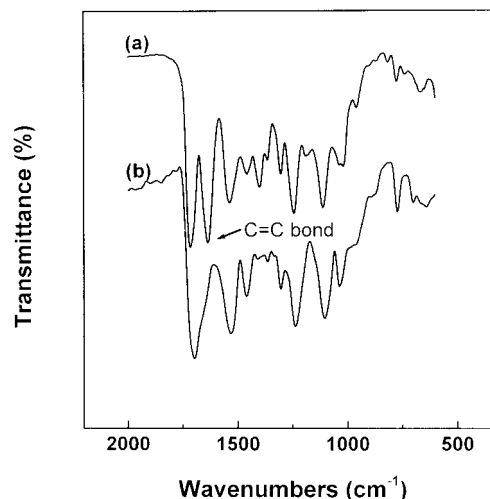


Figure 1 IR spectra for urethane acrylate ionomer (ID1) film before (a) and after (b) 5-min UV irradiation.

sured for urethane acrylate ionomers were $M_n = 1.4 \times 10^3 \text{ g mol}^{-1}$ to $7.1 \times 10^3 \text{ g mol}^{-1}$ and $M_w = 8.3 \times 10^3 \text{ g mol}^{-1}$ to $1.9 \times 10^4 \text{ g mol}^{-1}$.

Tensile properties were measured at 25°C using a Hounsfield Model Instron, Serial No. R100 1231, with a crosshead speed of 5 mm/min. All measurements quoted were the average of five 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 a DMA2980 (TA Instruments) at 2 Hz. The cured films were quenched to -80°C and heated up to 100°C at $3^\circ\text{C}/\text{min}$. The sample chamber was kept dried by a stream of moisture-free nitrogen.

RESULTS AND DISCUSSION

UV-Curing Procedure

IR spectra taken (a) before and (b) after 5 min of UV irradiation are shown in Figure 1. The complete disappearance of the C=C band at 1633.9 cm⁻¹ indicates that the vinyl polymerization reaction occurred successfully. The conversions were determined by measuring the gel fraction of the cured sample after extracting the unreacted materials in MEK/acetone (4 : 6) mixture for 24 h. The samples were found to contain greater than 0.85 gel fraction.

UV Coating Properties of Urethane Acrylate Ionomer Films

Figure 2 shows the stress–strain curves of UV-cured films, changing the type of diisocyanate and

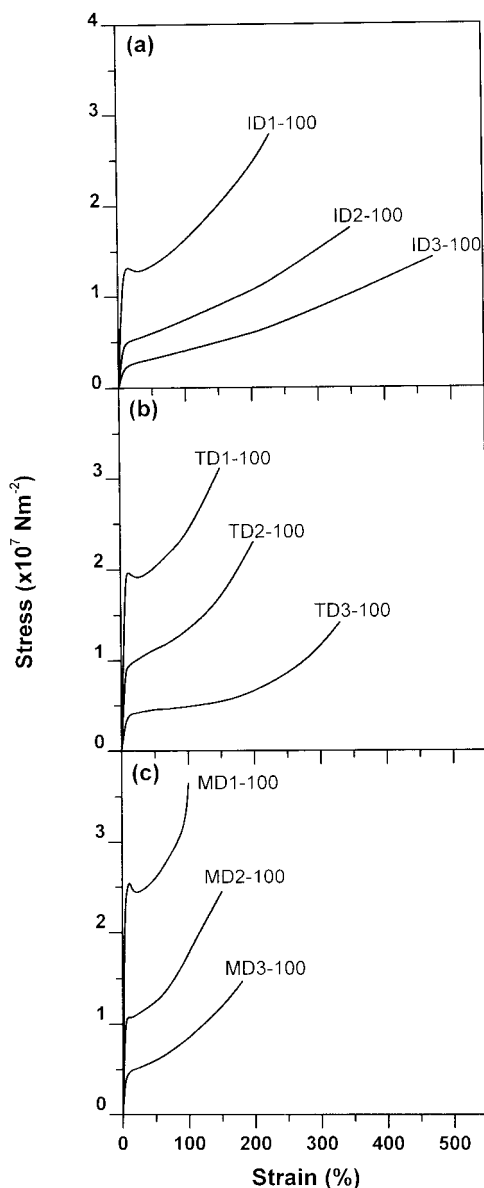


Figure 2 Stress-strain curves for urethane acrylate ionomer films having different molecular weights of PTMG: (a) ID, (b) TD, and (c) MD films.

the molecular weight of soft segment (PTMG). The ultimate tensile strength, the elongation at break, and the initial modulus obtained are summarized in Table I. The films having low molecular weight of soft segment exhibited high tensile strength and low elongation at break. On the contrary, as the molecular weight of soft segment increased, the tensile strength decreased and the elongation at break increased. This trend was in good agreement with the work of Oraby and Walsh,²⁵ meaning that the tensile strengths in

urethane acrylate films depended on the length of soft segment.

In Table I, the tensile strength and initial modulus of the films increased in the following order: IDs < TDs < MDs at the same molecular weight of PTMG. TDI- and MDI-based urethane acrylate ionomer films displayed higher tensile strength and initial modulus and lower elongation than IPDI-based ones. This was attributed to the presence of the aromatic ring which gives rise to π -electron interaction in the urethane acrylate network.²⁶ Moreover, MD films showed much higher tensile strength than TD films. MDI-based polyurethane ionomers have an ordered hard domain (i.e., are semicrystalline), because of their symmetric molecular structure, while TDI-based polyurethane ionomers have a disordered hard domain, because TDI has asymmetric 2,4-isomers.^{7,8} Consequently, MD films achieved superior tensile properties to the other films.

In stress-strain curves in Figure 2, it was interesting that, as the molecular weight of PTMG decreased, that is, as the relative ion content increased (refer to the DMPA content in Table I), yield points started to appear. This was believed to stem from the ionic groups in the network. In nonpolar medium, the ionic groups would be phase-separated by means of the difference in polarity from the hydrophobic network, which eventually form an ionic aggregate.^{14,27-29} For

Table I Tensile Properties of UV-Cured Urethane Acrylate Ionomer Films

Symbol ^a	Tensile Strength ($\times 10^7$ N/m ²)	Elongation at Break (%)	Initial Modulus ($\times 10^7$ N/m ²)	DMPA Content (wt %) ^b
ID1-100	2.78	227	17.90	10.23
ID2-100	1.75	351	8.48	8.88
ID3-100	1.43	472	3.53	7.41
TD1-100	3.11	151	34.20	11.05
TD2-100	2.30	202	21.20	10.22
TD3-100	1.42	330	9.68	7.83
MD1-100	3.64	98	49.00	9.82
MD2-100	2.45	151	27.30	9.15
MD3-100	1.47	183	14.60	7.18

^a ID, TD, and MD are IPDI-, TDI-, and MDI-based urethane acrylate ionomers, respectively. Serial numbers, 1, 2, and 3 correspond to the molecular weights of the PTMG: 1.0×10^3 , 1.4×10^3 , and 2.0×10^3 g/mol. The last number is the amount of neutralization (%).

^b The content of DMPA was calculated from the theoretical molecular weight in Scheme 1.

elastomeric or very ductile polymers, especially the presence of such an ionic aggregate produces quite different stress–strain behavior. In going to a higher content of the ionic groups, the stress–strain curve changes from that of a typical rubber to one that is similar to highly crosslinked rubber and on to a rigid material showing a yield point.^{30,31} Therefore, the increase in the content of ionic groups brought about the increase in modulus and the yield, as listed and shown in Table 1 and Figure 2, respectively.

Mechanical Properties of Urethane Acrylate Ionomer Films

From the fact that ID1, TD1, and MD1 films having more ionic groups exhibited the highest values of ultimate tensile strength and the presence of yield points, we assumed that the urethane acrylate network was composed of ionic hard segment domains (ionic aggregates) and polyether soft segment domains. This was possibly confirmed by dynamic mechanical analysis (DMA). The temperature dependence of storage modulus and loss modulus for ID1, ID2, and ID3 are shown in Figure 3. Two distinct transition peaks for ID1 film were detected around -46°C and 45°C , corresponding to the glass transition temperature of polyether soft segment domains, T_{gs} , and the glass transition temperature of ionic hard segment domains, T_{gh} , respectively. This result successfully confirms that as assumed, the films containing a large amount of ionic groups were composed of two phases, the polyether soft segment domains and the ionic hard segment domains. Actually, this ionic hard segment domain acted as reinforcing filler in the urethane acrylate network, resulting in an enhancement of the ultimate tensile strength and the initial modulus and in the presence of a yield point. However, as the molecular weight of soft segment increased, the magnitude of T_{gh} decreased. It is believed that the degree of phase separation of ionic hard segment domains from the network was reduced because of the reduction of charge density, as listed in Table I. The reduced phase separation was accompanied by lowering of the ultimate tensile strength and the initial modulus. In Figure 3, the shift of T_{gs} to lower temperature is 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 tendency of T_{gs} to shift to lower temperature.^{16,32,33}

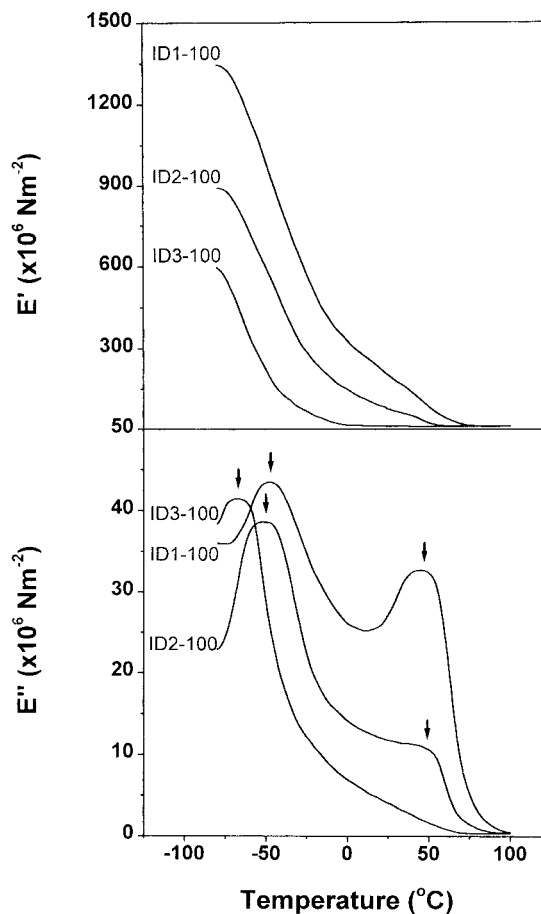


Figure 3 Dynamic mechanical properties for ID1, ID2, and ID3 films: temperature dependence of storage modulus (above) and loss modulus (below).

Effect of Amount of Neutralization

In order to confirm the effect of the phase separation induced by ionic group incorporation on the UV coating properties in detail, ID1 and ID3 films having different amounts of neutralization were prepared. The amount of neutralization could be certified by the observation of contact angle on the surface of the cured films. In Figure 4, the contact angle decreased gradually as the amount of neutralization increased. This reveals that the neutralization of the ionomers was well controlled stoichiometrically. The stress–strain curves obtained from ID1 and ID3 films are shown in Figure 5. The tensile properties are summarized in Table II. The tensile strength, the elongation at break, and the initial modulus decreased dramatically, as the amount of neutralization reduced. Moreover, the yield point was never observed, at a reduced amount of neutralization. These results

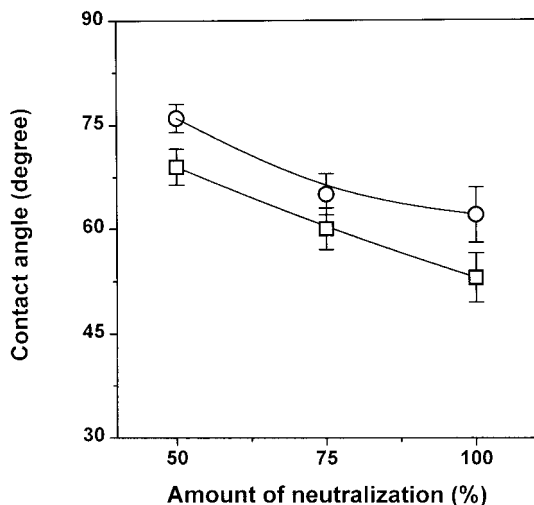


Figure 4 Contact angle for ID1 and ID3 films with the amount of neutralization. 1 μ L of DDI water was dropped and contact angle was read using an Erma contact angle meter, model G-1.

support the assumption that the incorporation of ionic groups into the network induced the phase separation. Therefore, significant enhancement

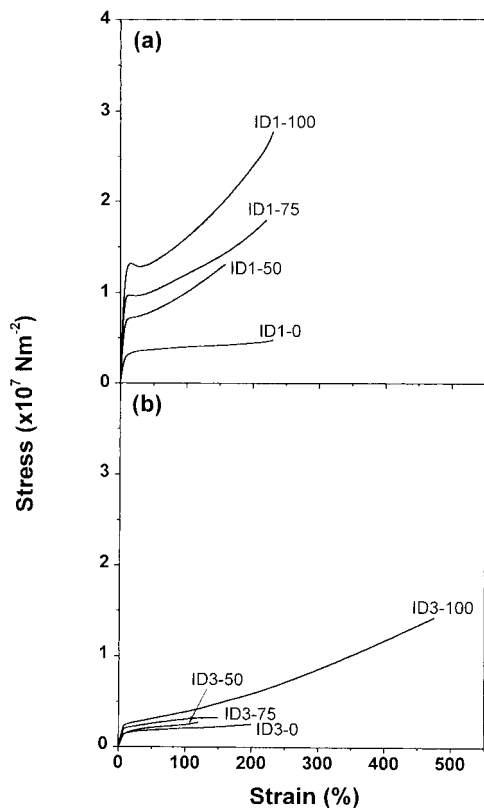


Figure 5 Stress-strain curves for urethane acrylate ionomer films having different amounts of neutralization: (a) ID1 and (b) ID3 film.

Table II Tensile Properties of UV-Cured Urethane Acrylate Ionomer Films

Symbol	Tensile Strength ($\times 10^7$ N/m ²)	Elongation at Break (%)	Initial Modulus ($\times 10^7$ N/m ²)
ID1-100	2.78	227	17.90
ID1-75	1.82	223	14.80
ID1-50	1.33	158	10.30
ID1-0	0.48	230	3.26
ID2-100	1.75	351	8.48
ID3-100	1.43	472	3.53
ID3-75	0.33	151	3.20
ID3-50	0.28	120	2.56
ID3-0	0.26	200	2.04
SID1-100 ^a	2.80	270	16.30
SID3-100	1.34	520	3.07

^a SIDs are solvent (methyl ethyl ketone) cast urethane acrylate ionomer films.

in coating properties could be achieved for the urethane acrylate ionomer films.

Effect of Solvents

The urethane acrylate ionomer films (ID1 and ID3) were formulated in water and MEK, respectively, and the effect of solvents that were used in dissolving ionomers on the coating properties was observed. Here, MEK, a common solvent in polyurethane formulations, was selected as an organic solvent. Figure 6 shows the stress-strain curves of UV-cured films cast in water and MEK. The resultant tensile properties are listed in Table II. The stress-strain behaviors were almost similar, regardless of the selection of solvents. However, it should be noted that MEK-cast films displayed lower yield stress. This lowered yield stress of MEK-cast films offers important information about the degree of phase separation of ionic hard domains. That is, when the film is cast in water, the ionic hard domains can be readily formed rather than in MEK. The phase separation degree of the ionic hard domains could be observed by the DMA analysis. Figure 7 shows the temperature dependence of storage modulus and loss modulus for ID1 films (ID1) cast in water and MEK, respectively. In both films, two glass transition temperatures, T_{gs} and T_{gh} , were detected. However, it could be found that the magnitude of T_{gh} of MEK-cast film was weaker than that of water-cast film. This indicates that the film cast in water has a more phase-separated

network structure. Previously, we observed that even in the aqueous solution state, the urethane acrylate ionomer molecules had a hydrophobic interaction due to the alignment of the hydrophobic polyether soft segments in the aqueous phase.^{34,35} In the MEK solution state, such alignment of the soft segments can not be expected, because MEK is a good solvent for the polyether soft segment. In the course of drying, the alignment of the hydrophobic soft segment would cause the ionic groups to aggregate readily. Consequently, the degree of phase separation seems to be maximal in water solvent.

CONCLUSIONS

Water-soluble and UV-curable urethane acrylate ionomers were synthesized by incorporating carboxylic groups into the urethane acrylate molecular backbone. It was found that the presence of ionic groups in the network played an important role in determining the final film properties. The ultimate tensile strength of the urethane acrylate ionomer films was enhanced by means of phase separation induced by ionic aggregates that consequently act as reinforcing filler in the network, which was confirmed by dynamic mechanical analysis. Therefore, the film properties were dependent on the content of the ionic groups. Especially, when water used as a solvent, the phase separation of the ionic groups from the urethane acrylate network was maximal.

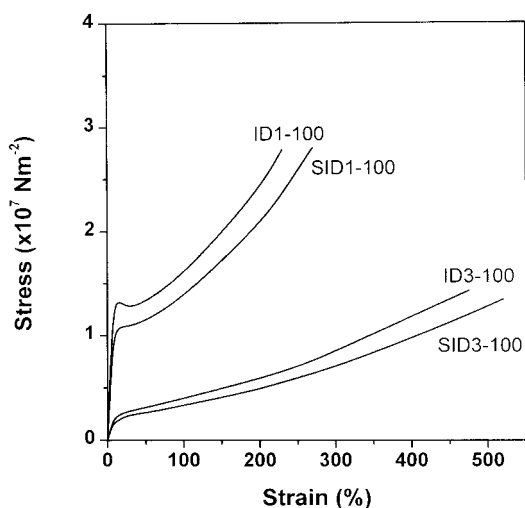


Figure 6 Stress-strain curves for urethane acrylate ionomer films (ID1 and ID3) cast in different solvents: IDs in water and SIDs in methyl ethyl ketone (MEK).

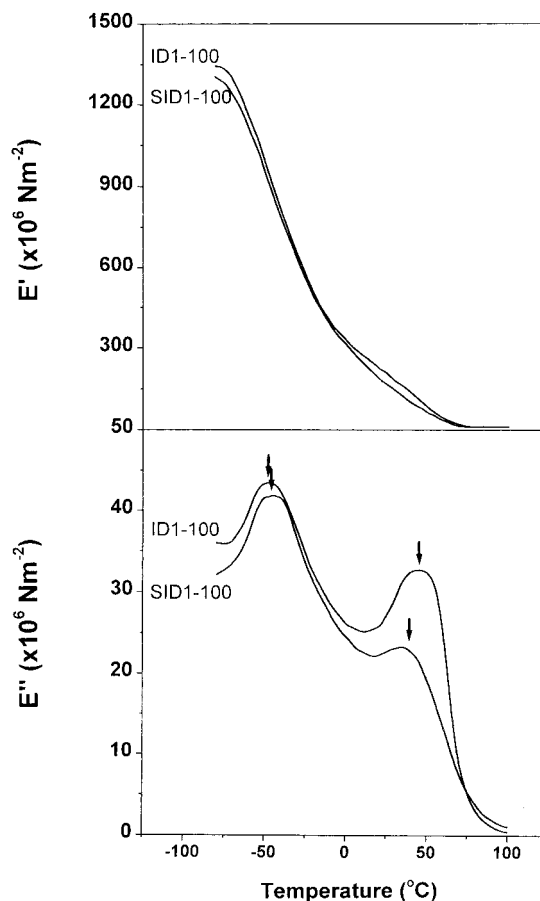


Figure 7 Dynamic mechanical properties for urethane acrylate ionomer films (ID1 and SID1): temperature dependence of storage modulus (above) and loss modulus (below).

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