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WATER-SOLUBLE URETHANE ACRYLATE IONOMERS AND THEIR ULTRAVIOLET (UV) CURING: PREVENTION OF MOISTURE ABSORPTION

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WATER-SOLUBLE URETHANE ACRYLATE IONOMERS AND THEIR ULTRAVIOLET (UV) CURING: PREVENTION OF MOISTURE ABSORPTION

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Key Words: Ultraviolet (UV)-Curable Urethane Acrylate Ionomers, Ionic Hard Domains, Moisture, Urethane Acrylate, Hydrophobic Moiety

ABSTRACT

Water-soluble and ultraviolet (UV)-curable urethane acrylate ionomers containing α,α -dimethylolpropionic acid (DMPA) were synthesized varying the molecular weight of the soft segment. In addition, their coating properties were also examined. When placed in the atmosphere for a long period, the tensile strength and the initial modulus of the UV-cured ionomer films decreased. Moreover, the disappearance of the ionic hard domains was observed by the dynamic mechanical analysis (DMA). These results indicated that the strong hydrophilicity of the ionomer network readily absorbed moisture in the atmosphere. However, by changing the stoichiometric mixing ratio of the urethane acrylate ionomer to the urethane acrylate not containing ionic groups, the moisture absorption of the ionomer network was successfully prevented. In DMA measurements, it was observed that the ionic hard domains did not disappear even in a

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comparatively long aging time (about 3 weeks). This could be achieved by the incorporation of the hydrophobic moiety in-to the hydrophilic ionomer network, which was induced by the urethane acrylate.

INTRODUCTION

In general, 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 [1-5]. Among hydrophilic sites, the incorporation of ionic groups has been more favorable due mainly to the enhanced mechanical properties of the cured films. The ionic groups form an aggregate by the Coulombic force and act as a physical crosslinker which is responsible for the marked improvement of the mechanical properties of the final films [6-10].

In our previous works [11-13], we synthesized UV-curable and water-soluble urethane acrylate ionomers containing α,α -dimethylol propionic acid (DMPA) and N-methyldiethanolamine (MDEA), respectively, for an application of UV-curing materials. The UV-cured urethane acrylate ionomer films displayed a significant improvement of the final mechanical properties. However, when stored for a long time, some deterioration of the mechanical properties of the films was observed. This seemed to be attributed to the disappearance of the ionic hard domain by means of the moisture absorption.

In this study, we synthesized water-soluble urethane acrylate ionomers containing DMPA as a potential ionic site and examined their UV-coating properties. The effect of the moisture absorption on the coating properties was studied with the hydrophobicity controlled by the stoichiometric mixing ratio of the urethane acrylate ionomer to the urethane acrylate not containing the ionic groups.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI, Junsei Chemical Co.) was vacuum distilled before use. Polytetramethylene glycol (PTMG, $M_w=1,000$ g·mol⁻¹, 1,400 g·mol⁻¹, and 2,000 g·mol⁻¹, Hyosung BASF), α,α -dimethylol propionic acid (DMPA, Aldrich Chemical Co.), triethylamine (TEA, Kanto Chemical Co.,

Inc.), and dibutyltindilaurate (DBTDL, Junsei Chemical Co.) were used as received. The inhibitor in 2-hydroxyethyl methacrylate (HEMA) was removed through a removing column (Aldrich Chemical Co.).

Synthesis of Urethane Acrylates

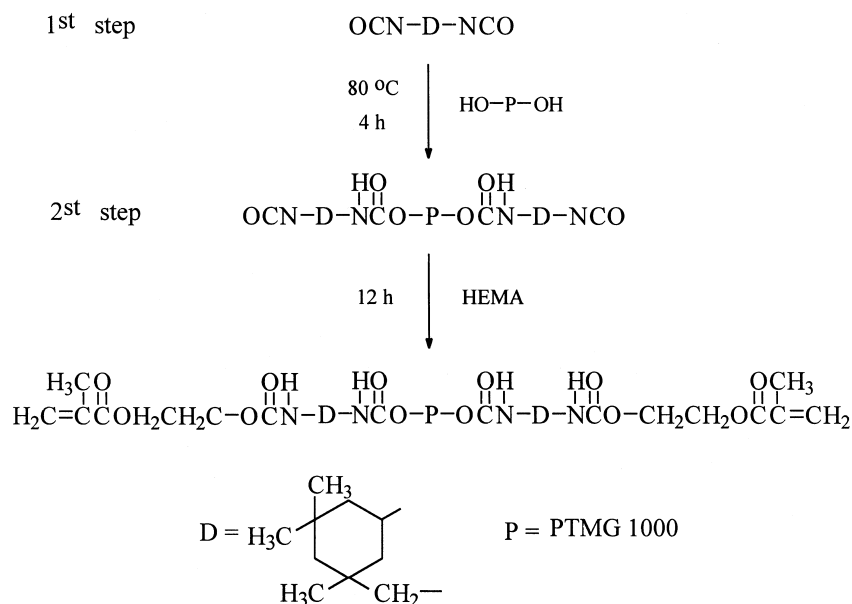
Urethane acrylate ionomers were synthesized by a stepwise reaction procedure [14-16]. In the first step, IPDI was poured into a glass reactor equipped with a stirrer, reflux condenser, thermocouples, and nitrogen gas inlet system, after nitrogen gas inlet for 10 minutes to eliminate the residual moisture. After dissolving 1 wt% of DBTDL, DMPA dissolved in dimethylacetamide (DMAc) was dropped into the reactor slowly at room temperature. The reaction temperature was raised to 80°C so that 2 mole of IPDI reacted with the 1 mole of DMPA. This temperature was maintained for 4 hours to retain an acceptable reaction rate. The NCO value change during the reaction was determined using a dibutylamine back titration method to find the reaction end point [17].

In the second step, 0.5 mole of PTMG was reacted with the same procedure as the first step. In the last step, HEMA was reacted to the residual NCO group at room temperature for 12 hours, capping both molecular ends with vinyl groups. After washing DMAc, unreacted HEMA, and DMPA with water repeatedly, carboxylic acid groups in the ionomer were neutralized with an appropriate amount of triethylamine (TEA) at room temperature for 1 hour. The reaction procedure and the molecular structure are shown in Scheme 1.

Scheme 2 shows the reaction procedure and the molecular structure of urethane acrylate (UA) [11]. UA was synthesized by the same reaction procedure as the urethane acrylate ionomer except the first step, where the DMPA was reacted. The recipe for the synthesis of the urethane acrylate ionomer and UA is listed in Table 1. Here, the ID means IPDI-based urethane acrylate ionomer and the serial numbers, 1, 2, and 3, correspond to the molecular weight of the PTMG 1,000, 1,400, and 2,000 g·mol⁻¹, respectively.

Preparation of Urethane Acrylate Ionomer Solution and Emulsion

The urethane acrylate ionomer was placed in a 20 ml beaker together with a stoichiometric amount of UA and 3 wt% of benzophenone. This mixture was stirred vigorously with a mechanical stirrer. Then, deionized water was added dropwise slowly. The solution or emulsion prepared was poured into a polyethylene mold with an inner dimension of 10 cm x 10 cm x 0.5 cm, and dried at 60°C for 24 hours *in vacuo*.



Scheme 2. The reaction procedure and the molecular structure for the urethane acrylate.

UV-Curing Procedure

The dried products were cured with an air irradiating static UV lamp (450 watt, UV lamp from Ace Glass Co.) for 5 minutes, and postcured at 80°C for 5 hours. The thickness of the cured films was about 0.3 mm. When observing the moisture effect on the coating properties, the films were placed in an isolated chamber where the temperature and relative humidity were controlled with 30±1°C and 85±5%, respectively. The cured films were also aged in the desiccator for the same period as the moisture-absorbing ones before testing in order to compare the mechanical property changes at the same condition in detail.

Measurements

Molecular weights 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 resulting molecular weights for the urethane acrylate ionomers and UA are listed in Table 1. IR spectra were recorded using a Maligna IR-550 (Nicolet Co.) The emulsion droplet size was measured with an electrophoretic light scattering particle analyzer, ELS-800 (Photal

TABLE 1. Recipes Used for the Synthesis of Urethane Acrylates^a

| Symbol | IPDI | DMPA | PTMG | | | HEMA | TEA | M _w | PDI ^{c)} |
|--------|-------|-------|--------|-------|---------------------|-------|-------|----------------|-------------------|
| | | | 1,000 | 1,400 | 2,000 ^{b)} | | | | |
| ID1 | 50.00 | 15.08 | 56.23 | - | - | 14.64 | 11.38 | 8,250 | 1.32 |
| ID2 | 50.00 | 15.08 | - | 78.75 | - | 14.64 | 11.38 | 10,570 | 1.73 |
| ID3 | 50.00 | 15.08 | - | - | 112.46 | 14.64 | 11.38 | 13,560 | 1.91 |
| UA | 50.00 | - | 112.46 | - | - | 14.64 | - | 2,500 | 1.39 |

^{a)} All units were represented in gram

^{b)} Molecular weight of polytetramethylene glycol (PTMG)

^{c)} Polydispersity index (PDI)

Abbreviation : ID means IPDI-based urethane acrylate anionomer. ID1, 2, and 3 correspond to IDs prepared with PTMG 1,000, 1,400, and 2,000 g·mol⁻¹, respectively. UA means IPDI-based urethane acrylate.

Otsuka Electronics). Tensile properties were measured at 25°C using an Instron (Model No. 4460) with a cross-head speed of 50 mm/min. All measurements represent 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 (TA-instruments) at 2Hz. The cured films were quenched to -80°C and heated up to 100°C at 2°C/min. The sample chamber was kept dried by a stream of moisture-free nitrogen.

RESULTS AND DISCUSSION

The urethane acrylate ionomer has a peculiar molecular structure, as shown in Scheme 1. It has two vinyl groups which were able to crosslink each other at both ends, two ionic groups sufficiently able to hydrate in the molecular backbone, and a long polytetramethylene glycol (PTMG) soft segment able to impart elastic properties in the middle of the molecule.

UV-Curing Procedure

IR spectra taken before (a) and after (b) 5 minutes of UV irradiation and plotted to show the spectroscopic changes resulting from the curing process are

shown in Figure 1. The disappearance of the C=C bond at 1636.83 cm^{-1} indicated that the vinyl polymerization reaction occurred completely.

Effect of Moisture Absorption on Coating Properties

The moisture in the atmosphere can have an influence on the mechanical properties of the urethane acrylate ionomer films prepared in this study. This is possible by the strong hydrophilicity of the ionomer network containing a large amount of ionic groups. In order to investigate the effect of moisture in the atmosphere on the mechanical properties in detail, the tensile properties for the ID I film were observed with the aging time and are shown in Figure 2. It can be seen that the tensile strength and initial modulus aged in the moisture atmosphere decreased sharply with the aging time, compared with those in the absence of the moisture. It was shown, as expected, that the strong hydrophilicity of the ionomer network readily absorbed the moisture from the atmosphere.

A more reasonable explanation for this result was possible through dynamic mechanical analysis (DMA). Figure 3 shows the results of DMA for the dried (a), 3 week-aged (b), and redried (c) ID1 films. For the dried ID1 film, two clear glass transition peaks of the ionic hard domains, T_{gh} , and the polyether

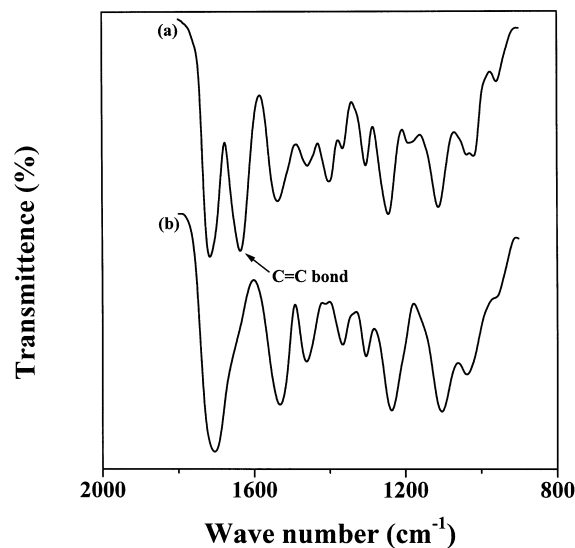


Figure 1. IR-spectra for the urethane acrylate ionomer film (ID1) containing 20 wt% of urethane acrylate (UA) before (a) and after (b) 5 minute UV irradiation.

soft domains, T_{gs} , were detected around 45°C and -40°C, respectively. Therefore, the excellent mechanical properties were displayed in the dried state [12, 13]. However, for the aged film, T_{gh} , in the high temperature region was not detected. Only single T_g was detected around -33°C. This indicates that as the time passed, the film containing a large amount of the ionic groups absorbed the moisture from the atmosphere, which eventually softened the ionic hard domains. Further evidence for the softening of the ionic hard domains by the moisture absorption is that when the 3 week-aged film (Figure 3 (b)) was redried *in vacuo* at 80°C for 5 hours, the reappearance of T_g , corresponding to the ionic hard domains was observed (Figure 3 (c)). Therefore, from the DMA measurements, the following explanation was possible: the moisture absorbed from the atmosphere made T_{gh} of the ionic hard domains move toward T_{gs} , alternatively, T_{gs} toward the T_{gh} by losing the purity of the polyether soft domains [8]. At last, coupling of the T_{gh} , and T_{gs} occurred. The resulting morphology of the aged film appeared to be one phase, resulting in the deterioration of the mechanical properties.

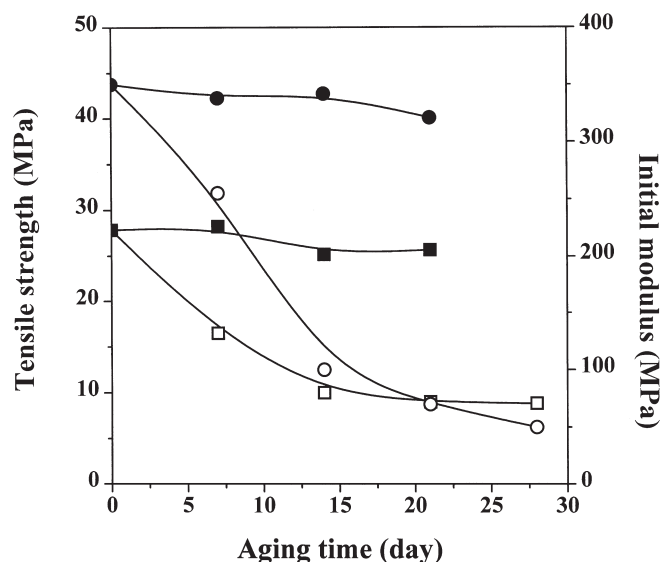


Figure 2. Influence of the moisture absorption on the tensile properties; tensile strengths with the aging time in the moisture-free desiccator (-■-) and moisture atmosphere (-□-); initial moduli in the moisture-free desiccator (-●-) and moisture atmosphere (-○-).

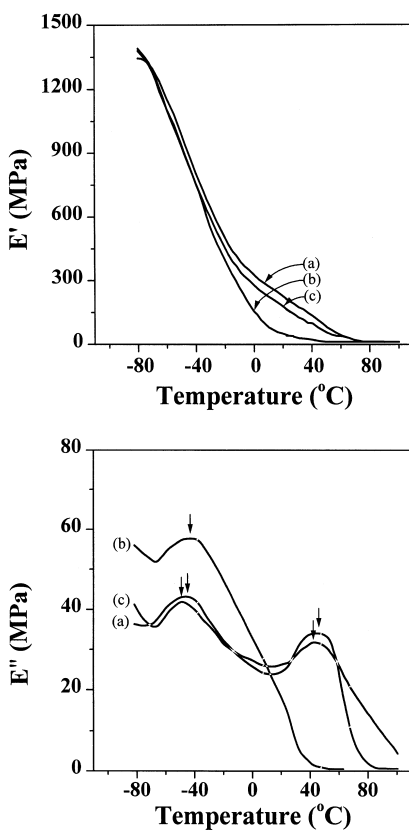


Figure 3. Dynamic mechanical properties of the dried (a), 3 week-aged (b), and redried (c) ID1 films.

Urethane Acrylate Ionomer Emulsions

The moisture absorption of the ionomer network from the atmosphere was expected to possibly be prevented by the increase of the hydrophobicity of the network. In order to increase the hydrophobicity of the urethane acrylate ionomers, the urethane acrylate (UA), not containing the ionic groups (Scheme 2), was mixed together with the ionomers, which resulted in the ionomer emulsion. The emulsion droplet size measurements results are shown in Figure 4. The droplet size of urethane acrylate ionomer emulsions was increased as the mixing ratio of UA to the ionomers increased. This suggests that the hydrophobicity was successfully controlled by mixing UA with ionomers stoichiometrically.

Mechanical Properties of Urethane Acrylate Films

Figure 5 shows the tensile strength and initial modulus of ID1 films having a different stoichiometric mixing ratio of the urethane acrylate (UA) (5 wt% UA (-□-), 10 wt% UA (-O -), 20 wt% UA (-Δ-), and 30 wt% UA (-▽-)) with the aging time. Initially, the UV-coated ID1 films, having a lower UA content, exhibited the high tensile strength and the initial modulus, compared with those of the higher UA content. However as the time passed, the tensile strength and initial modulus of the ID I films, having lower UA content, were plunged. This trend was similar to that of ID1 only in Figure 2. On the contrary, for the ID1 films having higher UA content (20 and 30 wt%), the tensile strength and initial modulus decreased slightly. This means that by the incorporation of the UA into the network, the softening of the ionic hard domains caused by the moisture absorption was prevented. This can also be verified by the measurement of DMA. Figure 6 shows the temperature dependence of the storage modulus and the loss modulus for the dried (a) and 3 week-aged (b) ID1 films containing 20 wt% of UA. Even though the glass transition peaks of T_{gh} were detected with shoulder types, the distinct T_{gh} was observed around 30°C, irrelative to the aging time. These results suggest that the incorporation of the hydrophobic moiety into

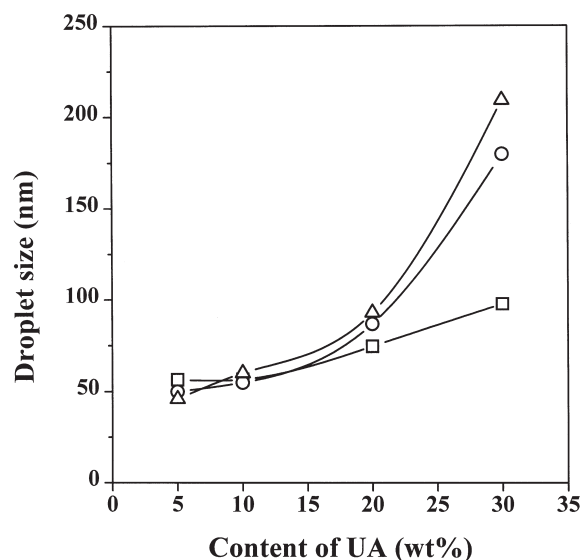


Figure 4. Droplet size change of the urethane acrylate ionomer emulsions with the content of the urethane acrylate (UA): ID1 (-□-), ID2 (-O-), and ID3 (-Δ-).

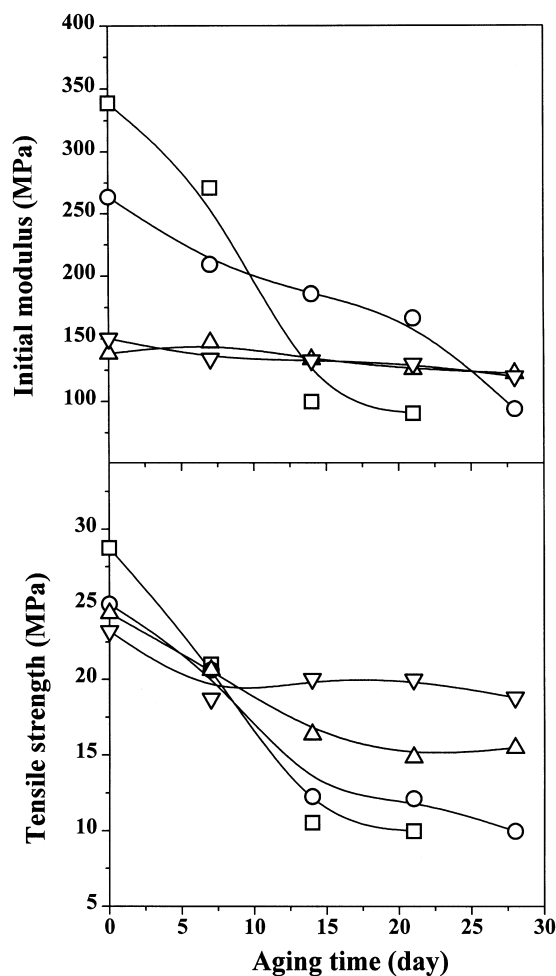


Figure 5. Tensile properties for ID1 films with the aging time: 5 wt% UA (-□-), 10 wt% UA (-O-), 20 wt% UA and 30 wt% UA (-▽-).

the urethane acrylate ionomer network effectively prevented the softening the ionic hard domains.

In order to confirm the effect of the molecular weight of the soft segment (PTNIG) on the moisture absorption, the urethane acrylate ionomer films, having the different molecular weight of PTMG, were prepared by varying the UA content. Figure 7 shows the effect of the moisture absorption on the tensile properties with the aging time (ID1 (-□-), ID2 (-O -), and ID3 (-Δ-) with UA 20 wt%). ID1 film displayed a serious drop in the tensile strength and initial modulus. However, as the molecular weight of PTMG increased, the serious drop in

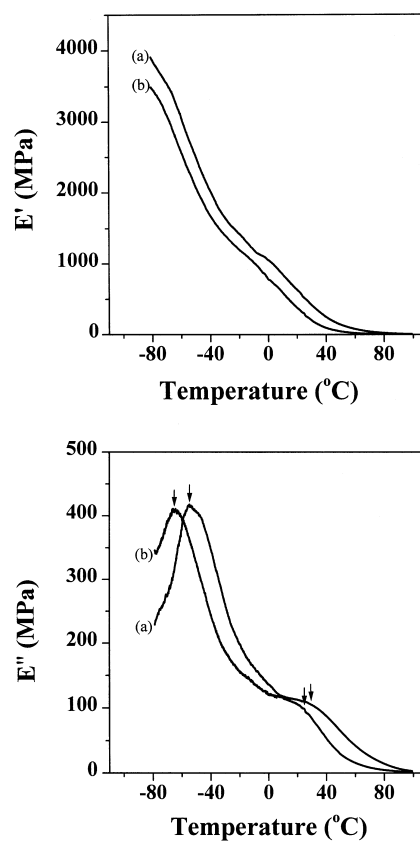


Figure 6. Dynamic mechanical properties of the dried (a) and 3 week-aged (b) ID1 film containing 20 wt% urethane acrylate (UA).

the tensile strength and initial modulus could not be observed. Notably, the ID3 film showed that the tensile strength and the initial modulus remained constant. As was observed in our previous work [12, 13], the hydrophobicity of the urethane acrylate ionomer films increases with the molecular weight of the soft segment. Therefore, the ID2 and ID3 seemed to display a good ability to prevent the moisture absorption.

CONCLUSION

UV-curable and water-soluble urethane acrylate ionomers were synthesized, and their coating properties were observed by varying the content of the urethane acrylate and molecular weight of the soft segment (PTMG). The ure-

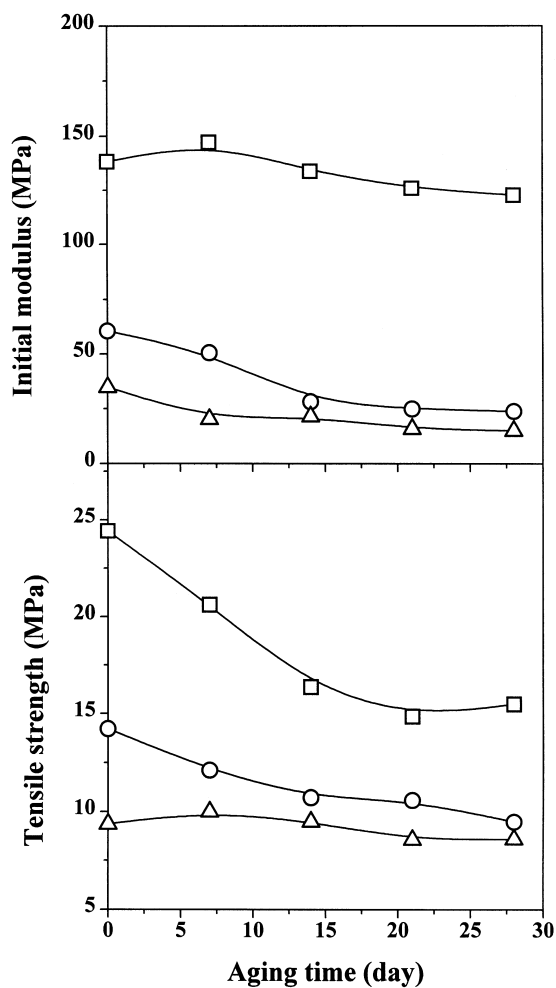


Figure 7. Tensile properties for the urethane acrylate ionomer films with the aging time: ID1 (-□-), ID2 (-O-), and ID3 (-Δ-). The content of the urethane acrylate (UA) was fixed with 20 wt%.

thane acrylate ionomer films were greatly influenced by the moisture absorption caused by the strong hydration ability of the ionomer in the network. In DMA measurements, the disappearance of the ionic hard domains was observed for the film containing a larger amount of ionic groups (ID1). This eventually lowered the mechanical properties of the ionomer films. On the contrary, the urethane acrylate ionomer films cured together with the urethane acrylate were not influenced by the moisture absorption. This could be confirmed by the measurements of the tensile strength, initial modulus, and the DMA. In particular, in the DMA

measurements, two distinct glass transition peaks, T_{gs} and T_{gh} , were detected, even in the state of 3 week-aging time. This means that by the incorporation of the hydrophobic moiety into the urethane acrylate ionomer network, the moisture absorption was successfully prevented.

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