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ORIGINAL CONTRIBUTION

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# Ultraviolet-curable epoxy acrylate dispersions: effect of urethane acrylate anionomers on stabilizing and film properties

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**Abstract** Epoxy acrylate dispersions stabilized using urethane acrylate anionomers were prepared for an application of ultraviolet (UV) curing. By observing the optical microscopy and colloidal stability for the epoxy acrylate dispersions, it was confirmed that the urethane acrylate anionomers incorporated have an interfacial activity in the interface between the epoxy acrylate oil and the water/ethanol mixture (80/20, w/w). This was possible by the structurally designed urethane acrylate anionomers, containing a hydrophobic soft segment and two hydrophilic ionic sites in their molecules. In addition, when ultraviolet (UV)-cured, the urethane acrylate anionomers agglomerated to form the rubber domains in the epoxy acrylate film, which were induced by the ionic interaction. Consequently, this agglomerated rubber domains improved the final film properties.

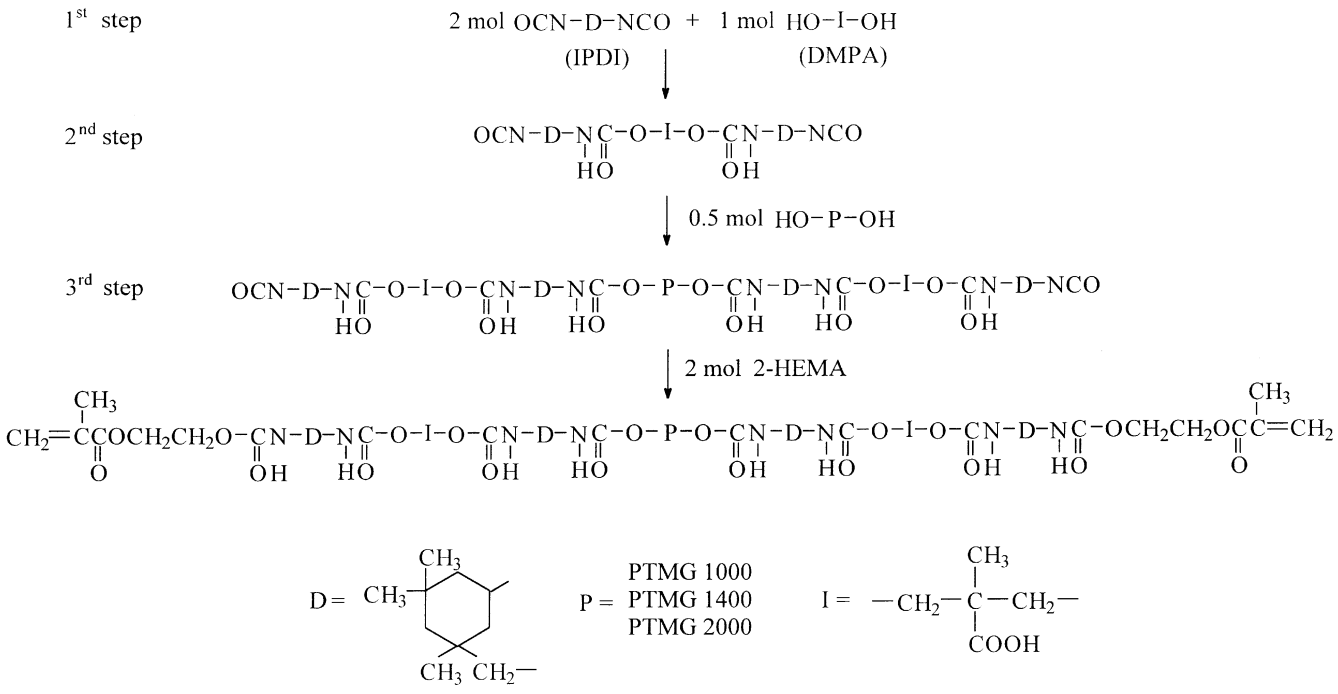
**Key words** Epoxy acrylate dispersions – urethane acrylate anionomers – two hydrophilic ionic segments – ionic interaction – final film properties

## 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 [1–5]. Especially, in the field of UV-curing industries, epoxy acrylate derivatives have been widely used as coatings, structural adhesives, and advanced composite matrices. However, in the case of the preparation of epoxy acrylate dispersions in water media [6, 7], there has been a serious difficulty through conventional procedure, because the formation of a stable epoxy acrylate droplet was prevented by the big difference in the interfacial tension between epoxy acrylate and water continuous phase. Therefore, there is a need for reducing the interfacial tension, in order to improve the stability of the epoxy acrylate dispersions.

In our previous works [8–10], we synthesized water-soluble urethane acrylate anionomers containing α,α-dimethylol propionic acid (DMPA) as potential ionic sites 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 [11–16], the urethane acrylate anionomers prepared in our study had a peculiar molecular structure; two ionic sites in a molecule. With the help of this large ionic content in a molecule, they easily dissolved in water. When these urethane acrylate anionomers were incorporated to stabilize the epoxy acrylate dispersions, the more improved stability and film properties were expected.

The goal of this study is to prepare stable epoxy acrylate dispersions and to investigate the film properties, in the case of using the urethane acrylate anionomers as a stabilizer. The effect of the concentration and molecular weight




**Scheme 1** The reaction procedure and molecular structure of the urethane acrylate anionomers

of the urethane acrylate anionomers on the epoxy acrylate dispersions and the film properties was examined.

## Experimental

### Materials

Isophorone diisocyanate (IPDI, Junsei Chemical Co.) was vacuum distilled before use. Polytetramethylene glycol (PTMG, $M_w = 1.0 \times 10^3$ g mol$^{-1}$, $1.4 \times 10^{-3}$ g mol$^{-1}$ and $2.0 \times 10^3$ g mol$^{-1}$, Hyosung BASF), $\alpha,\alpha$-dimethylol propionic acid (DMPA, Aldrich Chemical Co.), and epoxy resin ($1.2 \times 10^4$–$1.4 \times 10^4$ cps at 25 °C, $M_w = 374$ g mol$^{-1}$, Kuck-Do Chemical Co., Ltd). were used as received. Inhibitor in 2-hydroxyethyl methacrylate (HEMA) and acrylic acid (Aldrich Chemical Co.) was removed through a removing column (Aldrich Chemical Co.) Benzophenone (Janssen Chemical Co.) was used as a photoinitiator.

### Synthesis of epoxy acrylate and urethane acrylate anionomers

Epoxy acrylate was synthesized by the ring opening reaction between epoxy resin and acrylic acid at 120 °C for 4 h. The final yield was over 99.8% [6, 7].

Urethane acrylate anionomers were synthesized by the stepwise reaction procedure [8–10]. The schematic molecular structure is represented in Scheme 1. The composition for the synthesis of the urethane acrylate anionomer is listed in Table 1. In the first step, IPDI was poured into the glass reactor and nitrogen gas was introduced for 10 min to eliminate the residual moisture. After dissolving 1 wt% of dibutyltindilaurate (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 mol of IPDI reacted with the 1 mol of DMPA, resulting in the molecular structure having carboxylic acid group in the middle and isocyanates on end sides. The change of NCO value during the reaction was determined using dibutylamine back titration method to find out the end point of the reaction [17].

In the second step, 0.5 mol of PTMG was added slowly into the reactor to incorporate the soft segment into the molecular backbone with the same method of the first step. In the last step, after dissolving 1 wt% of DBTDL into the reactor, 2 mol of HEMA was reacted to the residual NCO groups at 45 °C for 12 h, which introduces the reactive vinyl groups in the molecular ends. The reaction end point was determined by the disappearance of NCO stretching peak (2270 cm$^{-1}$) through IR spectroscopy. Continuously, carboxylic acid groups were ionized with appropriate

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**Table 1** Ingredients used for the synthesis of urethane acrylate anionomers[a)]

| Symbol | IPDI | DMPA | PTMG[b)] | | | HEMA | TEA[c)] | DMPA content [wt%] |
|---|---|---|---|---|---|---|---|---|
| | | | $1.0\times10^3$ | $1.4\times10^3$ | $2.0\times10^3$ | | | |
| ID1 | 50.00 | 15.08 | 56.23 | — | — | 14.64 | 11.38 | 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).
[c)] Triethylamine (TEA) was used as a neutralization agent.
Abbreviation: ID means IPDI-based urethane acrylate anionomer. ID1, 2, and 3 correspond to IDs represented with PTMG $1.0\times10^3$, $1.4\times10^3$ and $2.0\times10^3$, respectively.

amount of triethylamine (TEA) at room temperature for 1 h. Detailed reaction procedure followed our previous reaction condition [8–10].

### Preparation of epoxy acrylate dispersions

Epoxy acrylate dispersions were prepared by varying the concentration and molecular weight of the urethane acrylate anionomers in water/ethanol mixture (80/20, w/w). The mixture of the epoxy acrylate and the urethane acrylate anionomer containing 3 wt% of benzophenone was charged into a glass container equipped with a mechanical stirrer and deionized water dropping system. The epoxy acrylate dispersions were prepared by dropping ethanol/water mixture with the speed of 0.167 g min$^{-1}$. The content was fixed at 30 wt%.

### Ultraviolet (UV) curing procedure

Epoxy acrylate dispersions prepared were poured into a polyethylene mold, and dried at 60 °C for 24 h in vacuo. The dried epoxy acrylate was cured with air 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 0.1 mm thick and stored in a disiccator 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 average molecular weights of the urethane acrylate anionomers obtained are listed in Table 2.

After centrifuging each dispersion at 8000 rpm for 10 min, the colloidal stability was measured by centrifugal method as follows [7]:

$$\text{Colloidal stability (\%)} = \frac{W_o - W_s}{W_o} \times 100 ,$$

where, $W_s$ is the weight of the precipitated oil (g) and $W_o$ the weight of oil in a epoxy acrylate dispersion (g).

Dispersions were observed by Optical microscope (OM, Nikon Microphot Fax). The fracture surface of the cured film was observed by Scanning Electron Microscope (SEM, JSM-6300, JEOL).

Tensile properties were measured by Instron (Model No. 4460) with a crosshead speed of 5 mm min$^{-1}$ at 25 °C. All measurements had an average of 5 runs. The dumbbell-type specimen was 25 mm wide at two ends, 0.1 mm thick, and 6 mm wide at the neck.

**Table 2** Molecular weights of urethane acrylate anionomers

| Symbol | $M_w$ [g mol$^{-1}$] | $M_n$ [g mol$^{-1}$] | PDI[a)] |
|---|---|---|---|
| ID1 | 8250 | 6250 | 1.32 |
| ID2 | 10 578 | 6132 | 1.73 |
| ID3 | 13 563 | 7101 | 1.91 |

[a)] Polydispersity index (PDI).

## Results and discussion

The urethane acrylate anionomer has a peculiar molecular structure, as shown in Scheme 1. It has two vinyl groups enable to crosslink each other at both ends and two ionic groups (carboxylate ions) to hydrate in the molecular backbone. In addition, it also has a long polytetramethylene glycol (PTMG) soft segment showing hydrophobicity in the middle of the molecule. By controlling the molecular weight of PTMG, the degree of the hydrophilicity or hydrophobicity of the urethane acrylate anionomer

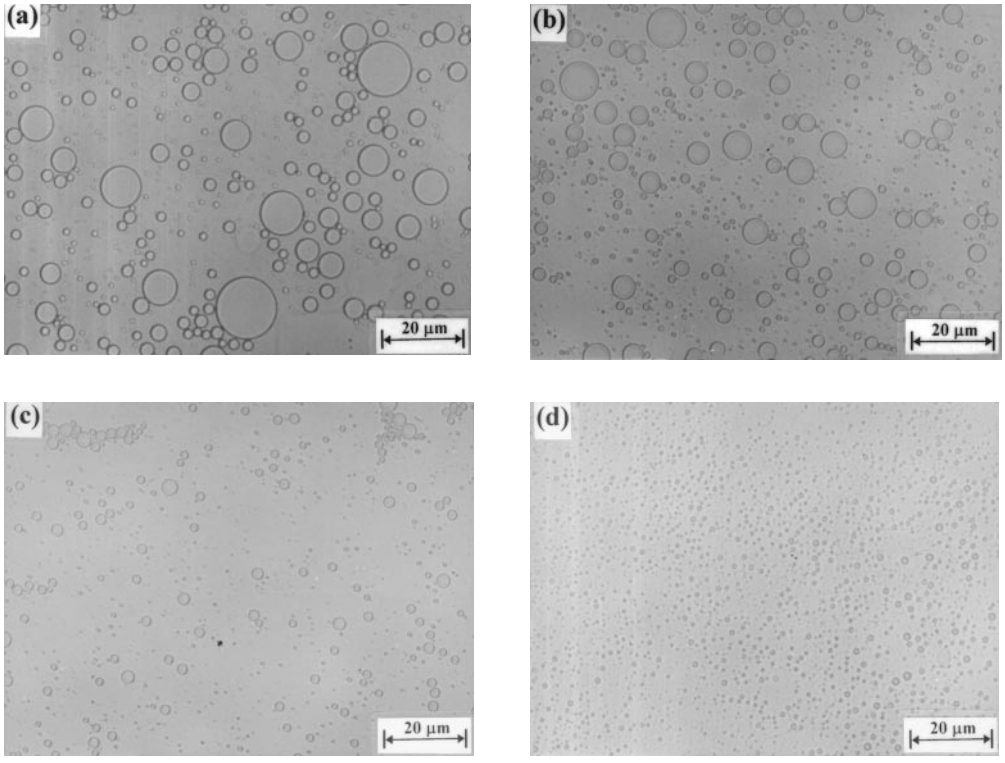


**Fig. 1** OM photographs of epoxy acrylate dispersions prepared with the concentration of the urethane acrylate aniomer (ID1): 0.0 wt% (a), 20 wt% (b), 30 wt% (c), and 40 wt% (d) (based on total resin weight)

molecules can be varied. Therefore, when this urethane acrylate anionomer is placed in the interface between the epoxy acrylate and the water solution, the reduced interfacial tension can be achieved by the amphiphilic property caused by the hydrophilic ionic groups and the hydrophobic polyether soft segments [10].

## Effect of urethane acrylate anionomers on epoxy acrylate dispersions

Figure 1 shows OM photographs of the epoxy acrylate dispersions with the concentration of the urethane acrylate anionomer (ID1); 0 wt% (a), 20 wt% (b), 30 wt% (c), 40 wt% (d). The pure epoxy acrylate dispersion in water/ethanol mixture (80/20, w/w) shows polydisperse droplet size distribution together with large size (Fig. 1a). However, upon adding the urethane acrylate anionomers, the average droplet sizes of the epoxy acrylate dispersions were significantly decreased and became considerably monodisperse. This means that, as expected, the urethane acrylate anionomers are placed in the interface between the oil phase and the continuous phase, resulting in decreasing the interfacial tension in terms of their amphiphilic properties.

In order to examine the effect of the hydrophilicity of the urethane acrylate anionomers on the interfacial activity, OM photographs of the epoxy acrylate dispersions were taken with the molecular weight of the soft segment (PTMG) and shown in Fig. 2a and b (ID2 and ID3). As shown, the increase of the average droplet size of the epoxy acrylate dispersions was observed, as the molecular weight of PTMG increased. This indicates that when the molecular weight of PTMG is high, the interfacial activity of the urethane acrylate anionomers is reduced, which is attributed to the enhanced hydrophobicity of the urethane acrylate anionomers [10].

To confirm the droplet stability of epoxy acrylate dispersions, the colloidal stability was measured with the concentration of the urethane acrylate anionomers. The results obtained are shown in Fig. 3. The colloidal stability was increased, as the concentration of the urethane acrylate anionomers increased. This suggests that the interfacial activity between the oil phase and continuous phase is improved by adding the urethane acrylate anionomers into the epoxy acrylate dispersions,

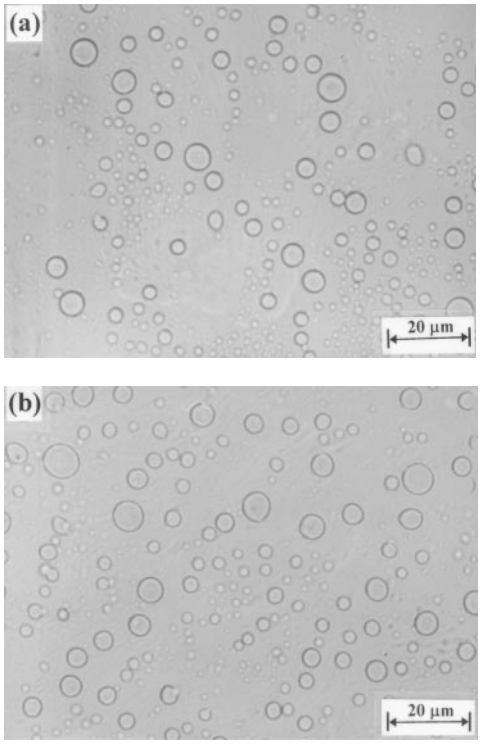


**Fig. 2** OM photographs of epoxy acrylate dispersions prepared with the molecular weight of the soft segment (PTMG) in the urethane acrylate anionomers: ID2: (a) and ID3 (b). The concentration of the urethane acrylate anionomers was 30 wt%, based on total resin weight

showing a good agreement with the results of OM photographs.

## Ultraviolet (UV)-curing of epoxy acrylates

Figure 4 shows IR spectra taken before (a) and after (b) 5 min of UV irradiation for the epoxy acrylate containing 30 wt% of the urethane acrylate anionomer (ID1). The complete disappearance of the C=C band at 1627.5 $cm^{-1}$ indicates 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 94.13 gel fraction.

## Fracture surface observation by scanning electron microscope (SEM)

Figure 5 shows the SEM photographs for UV-cured epoxy acrylate films with varying the concentration of the

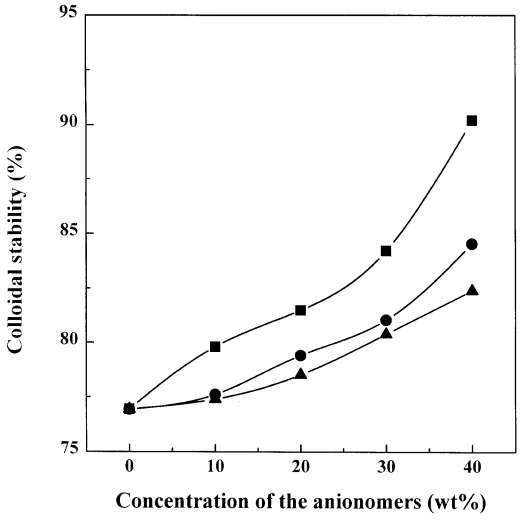


**Fig. 3** Centrifugal stability of the epoxy acrylate dispersions with the concentration of the urethane acrylate anionomers: ID1 (—■—), ID2 (—●—), and ID3 (—▲—)

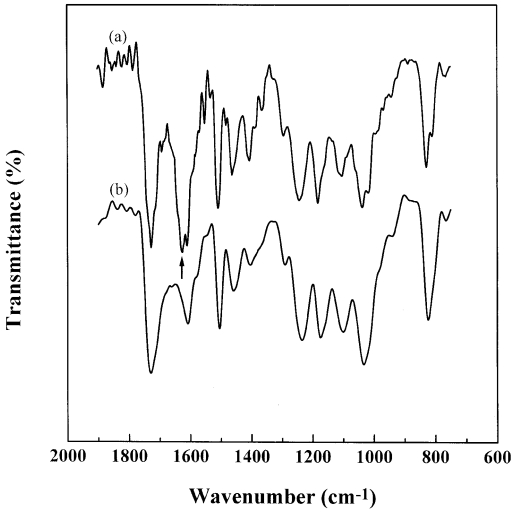


**Fig. 4** IR-spectra of the epoxy acrylate containing 30 wt% of the urethane acrylate anionomer (ID1) before (a) and after (b) 5 min UV irradiation

urethane acrylate anionomer (ID1); 0 wt% (a), 20 wt% (b), 30 wt% (c), and 40 wt% (d). In Fig. 5, below 30 wt% of the urethane acrylate anionomers in the epoxy acrylate film, only clear fractured surfaces were observed. However, above 40 wt%, agglomerates in the epoxy acrylate matrix were observed. This was considered to be the rubber domains of the urethane acrylate anionomers, which were induced by the ionic interaction. Related to this rubber domain formation, we postulated following procedure,

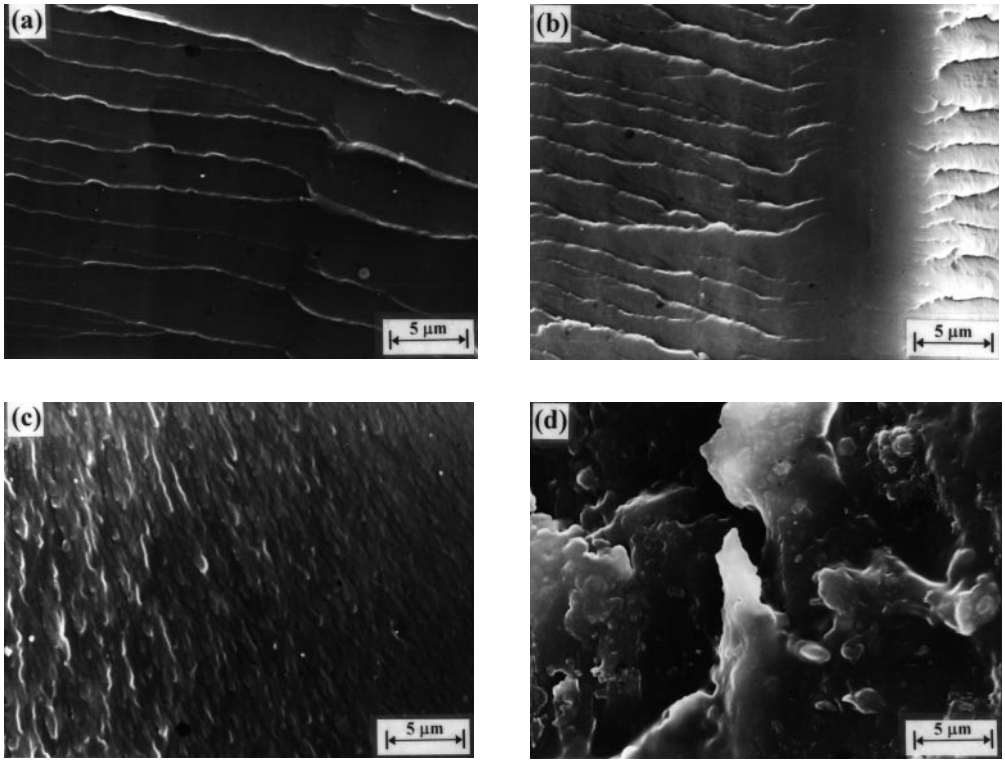


**Fig. 5** SEM photographs of UV-cured epoxy acrylate films prepared with the concentration of the urethane acrylate anionomer (ID1): 0.0 wt% (a), 20 wt% (b), 30 wt% (c), and 40 wt% (b) (based on total resin weight)

based on our previous works [10, 18]; in the dispersion state, the epoxy acrylates stabilized by the urethane acrylate anionomers form a oil phase and the water/ethanol mixture forms a continuous phase. However, in the course of drying, the phase inversion takes place. Then, gradually, the hydrated ionic groups aggregate while the hydrophobic epoxy acrylates form a continuous phase. In the dried state, finally these ionic aggregates possibly lead to the aggregation of the entire urethane acrylate anionomer molecules in the continuous phase of the epoxy acrylates. Therefore, when UV-cured, they can form the rubber domains, just as the SEM photograph.

In order to observe the effect of the molecular weight of the soft segment (PTMG) on the degree of the rubber domain formation. UV-cured epoxy acrylate films containing 30 wt% of the urethane acrylate anionomers were prepared by varying their molecular weights of PTMG. Figure 6 shows SEM photographs of UV-cured epoxy acrylate films prepared with the molecular weight of PTMG; ID2 (a) and ID3 (b). The epoxy acrylate film cured with ID1 displayed only slight rubber-separated fractured surface (Fig. 5c). However, as shown in Fig. 6, the rubber domain formation was favored with the increase of the molecular weight of PTMG. Especially, for the epoxy acrylate film cured with ID3, the rubber domains highly separated from epoxy acrylate matrix could be observed. This seems to be caused by the larger phase volume of the soft segment. These rubber domains were expected to have an influence on the final properties of the epoxy acrylate films.

## Film properties of ultraviolet (UV)-cured epoxy acrylates

Figure 7 shows the strain–stress curves of the epoxy acrylate films with the concentration of the urethane acrylate anionomer (ID1). The tensile properties obtained for the UV-cured epoxy acrylate films are summarized in Table 3. The pure epoxy acrylate acrylate film showed a brittle trend. On the contrary, the epoxy acrylate films above 30 wt% of the concentration of the urethane acrylate anionomers showed the significantly reduced initial moduli and increased percent strains. Additionally, it should be noted that the final tensile strengths were not seriously decreased, compared with that of the pure epoxy acrylate. These tensile properties propose that the rubber domains

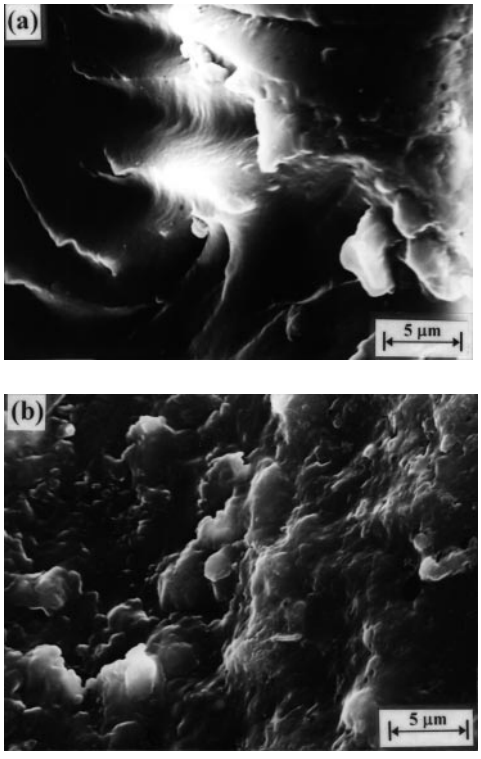


**Fig. 6** SEM photographs of UV-cured epoxy acrylate films prepared with the molecular weight of the soft segment in the urethane acrylate anionomers: ID2 (a) and ID3 (b). The concentration of the urethane acrylate anionomers was 30 wt%, based on total resin weight

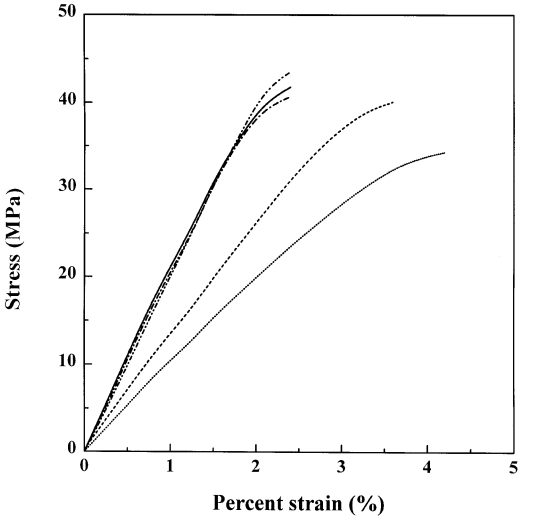


**Fig. 7** Stress–strain curves of UV-cured epoxy acrylate films prepared with the concentration of the urethane acrylate anionomer (ID1) (based on total resin weight; Pure EA (———), EA-ID1-10 (– – – – – –), EA-ID1-20 (– – – – – –), EA-ID1-30 (– – – – –), and EA-ID1-40 (- - - - - - -)

play an important role in toughening the brittle epoxy acrylate film, as observed in Fig. 5. Figure 8 shows the effect of the molecular weight of the soft segment (PTMG). The increased molecular weight of PTMG also displayed the reduced initial modulus and increased percent without serious drop of the tensile strength. Especially, the epoxy acrylate film prepared with ID3 displayed very low initial modulus and high percent strain (in Table 3). This also can be explained by the highly generated rubber domains in the epoxy acrylate matrix (Fig. 6b).

## Conclusion

Stable epoxy acrylate dispersions were prepared by adding the urethane acrylate anionomers which show a excellent interfacial activity between the epoxy acrylate oil phase and the water-based continuous phase. This was possible by the peculiar molecular structure of the urethane acrylate anionomer, structurally designed with the hydrophilic ionic sites and the hydrophobic soft segment. In the SEM photographs, the rubber agglomerates of the urethane

**Table 3** The tensile properties of UV-cured epoxy acrylate films

| Sample | Tensile strength [MPa] | Percent strain [%] | Initial modulus [MPa] |
|---|---|---|---|
| Pure EA[a)] | 41.8 | 2.4 | 2104 |
| EA-ID1-10[b)] | 40.7 | 2.2 | 2091 |
| EA-ID1-20 | 44.8 | 2.3 | 1850 |
| EA-ID1-30 | 40.1 | 3.6 | 1365 |
| EA-ID1-40 | 34.3 | 4.1 | 996 |
| EA-ID2-30 | 39.0 | 7.1 | 843 |
| EA-ID3-30 | 35.5 | 9.8 | 687 |

[a)] EA: The abbreviation of epoxy acrylate.
[b)] EA-ID$\alpha$-$\beta$ means the epoxy acrylate film cured with $\beta$ wt% of ID. The serial number of $\alpha$ corresponds to the molecular weight of PTMG $1.0 \times 10^3$, $1.4 \times 10^3$, $2.0 \times 10^3$ g mol$^{-1}$.

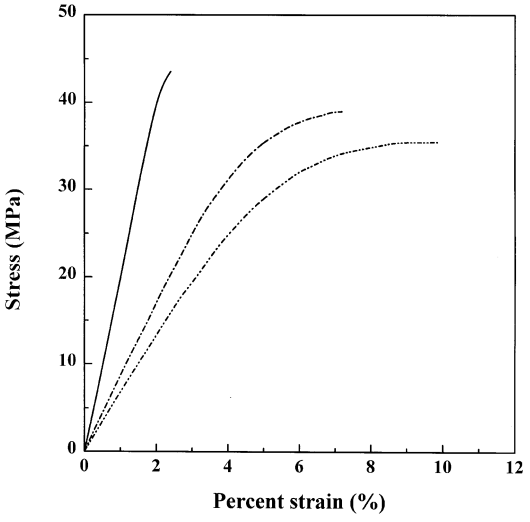


**Fig. 8** Stress–strain curves of UV-cured epoxy acrylate films with the molecular weight of the soft segment in the urethane acrylate anionomers. EA-ID1-30 (———), EA-ID2-30 (– – – – – –), an EA-ID3-30 (– – – – – –). The concentration of the urethane acrylate anionomers was 30 wt%, based on total resin weight

acrylate anionomers in the epoxy acrylate matrix could be observed above 40 wt% concentration and at high molecular weight of the soft segment (PTMG). It was found that these rubber domains in the epoxy acrylate matrix had an effect on the toughening of the final UV-coated films.

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