

Preparation of UV-Curable Emulsions Using PEG-Modified Urethane Acrylates: The Effect of Nonionic and Anionic Groups

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SYNOPSIS

To prepare self-emulsifiable urethane acrylate resin, PEG-modified urethane acrylates (PMUA), containing polyoxyethylene chains as a terminal hydrophilic group and urethane acrylate anionomers (UAA) incorporated dimethylolpropionic acid (DMPA) as a pendant hydrophilic one were synthesized. For PMUA emulsions, the reaction molar ratio of PEG to 2-hydroxyethyl methacrylate (2-HEMA) significantly influenced the viscosity and droplet size of the emulsion and tensile strength of cured films. These emulsions were stable to pH change and the addition of electrolyte, but coagulated around 60°C. In the case of UAA, emulsions, however, were very stable to elevated temperatures and coagulated in adding even a little bit of electrolyte. For soap-free emulsions of the mixture of PMUA and UAA, emulsion stabilities of these mixtures against temperature, pH change, the addition of electrolyte, and the rate of shear and freeze-thaw increased synergetically. Additionally, the tensile strength of cured films was also improved. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Waterborne coatings have been widely utilized recently in industrial coatings, which has made it possible to control pollution, to reduce risk of fire, and to improve aspects of occupational health and safety. The use of soluble, dilutable UV or EB curable formulations may appear especially contradictory from an energy saving viewpoint, because it is necessary to remove the water before irradiating the formulations. However, the application viscosity of water-based inks and coatings is greatly reduced by using water without volatile organic compounds (VOC), so these materials find widespread usage and are becoming more desirable with ever increasing environmental pressures.¹⁻²

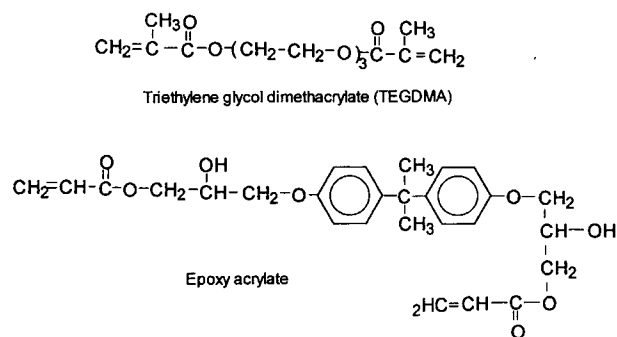
For the preparation of a water dispersible resin, in order to improve water-dispersibility, a special treatment or structural modification for polymers has been generally done by incorporating hydrophilic groups into the molecular backbone as a pendant group.³⁻⁵ However, for ionic water-dispersible resin,

a neutralization agent must be used to neutralize acid functional groups of polymers, which are very toxic and might release potentially harmful organic amines. In the case where a nonionic hydrophilic group as a pendant group is incorporated to begin with, the synthesis of prepolymer having isocyanate end groups and polyoxyethylene pendant groups at the same molecule has to be carried out through complicated reaction processes.⁶

PEG-modified urethane acrylate (PMUA) used in this study was synthesized by the reaction of polyoxyethylene glycol (PEG) with a residual isocyanate group of urethane acrylate. These molecules could be prepared by a relatively simple process and contained nonionic hydrophilic polyoxyethylene groups not as a pendant group and but as a terminal group, so PMUA was able to act as a polymeric surfactant and emulsified without an external surfactant.

The ultimate goal of this study was the preparation of UV-curable emulsion using PMUA. Thus, the effect of the reaction molar ratio of PEG on the emulsion droplet size, centrifugal stability, viscosity, coating, and mechanical properties of cured films was investigated. Additionally, to obtain the synergistic effect on emulsion stabilities against tem-

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Scheme 1 The structure of crosslinking agent and epoxy acrylate.

perature, pH change, the addition of electrolyte, and the rate of shear and freeze-thaw, urethane acrylate anionomer (UAA) was mixed with PMUA.

EXPERIMENTAL

Materials

In the synthesis of PMUA and UAA, poly(tetramethylene glycol) (PTMG, $M_w = 1,000$, Hyosung BASF), 2,4-toluene diisocyanate (TDI, Junsei Chemical Co.), 2-hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co.), poly(ethylene glycol) (PEG, $M_w = 600$, Junsei Chemical Co.), and dimethylolpropionic acid (DMPA, Shinyo Chemicals) were used.

N-Methyl-2-pyrrolidone (NMP, Junsei Chemical Co.) as the dissolution agent of DMPA and the agent of reducing the viscosity of synthesized resin was used. For neutralizing of carboxyl group of introduced DMPA, triethylamine (TEA, Waco Pure Chemical Co.) was used. (1-Hydroxycyclohexyl)phenylmethanone (Irgacure 184, Ciba-Geigy Chemical Co.) was used as a photoinitiator and *tert*-butyl benzoate (Junsei Chemical Co.) was used as a thermal initiator in order to postcure. Triethylene glycol dimethacrylate (TEGDMA, Aldrich Chemical Co.) was used as a crosslinking agent (CA) which was

used to improve physical properties rather than to reduce the viscosity of the formulation.

Epoxy acrylate (EA) was prepared by the reaction of epoxy resin (Kuk-Do Chemical Co., bisphenol A type, 11,500–13,500 cps at 25°C) with acrylic acid (Junsei Chemicals Co.); then, this resin was blended with PMUA to incorporate hardy characteristics into the UV-curable formulation. The molecular structure of CA and EA are illustrated in Scheme 1.

Synthesis of PMUA and UA

The unmodified urethane acrylate (UA) and PMUA were synthesized by two- or three-step processes. The molar ratio of reactants is summarized in Table I. These reactions were carried out in a four-neck glass reactor equipped with stirrer, thermometer, reflux condenser, and inlet system for N_2 gas. A detailed reaction procedure was reported in our previous article.^{7,8}

UAA was also prepared by four-step processes using DMPA, PTMG 1000, TDI, and 2-HEMA. The reaction molar ratio of these reagents is summarized at Table I.

The average molecular weight of PMUA and confirmation of these reactions through 1H -NMR and GPC were reported in our previous article.⁷ PMUA is composed of A- and B-type molecules and UA is an A-type molecule, which is illustrated in Scheme 2.

Preparation of UV-curable Formulations

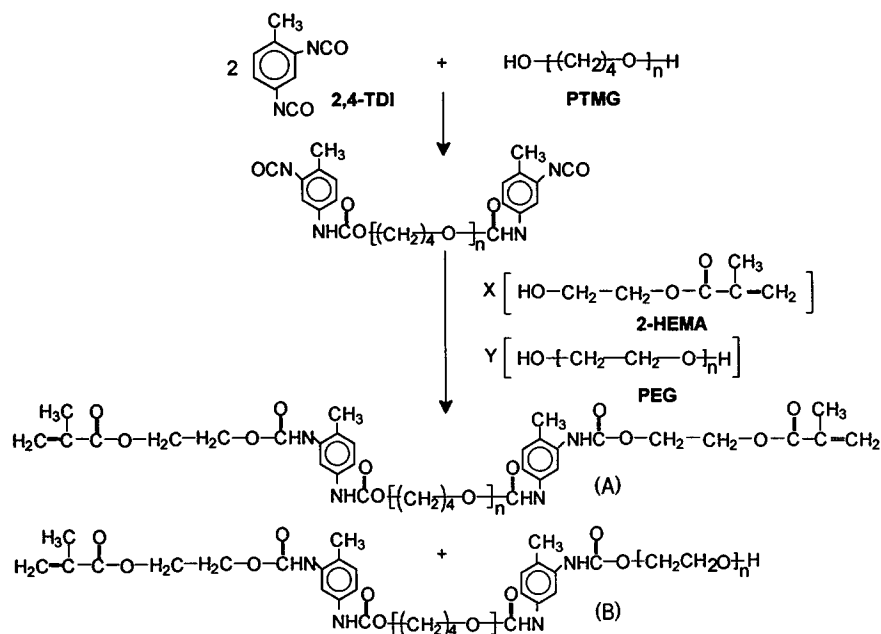
An oil solution (10 g) containing additives was placed in a 100 mL beaker and heated to 45°C to melt, then cooled to 35°C while vigorously stirring. Distilled deionized (DDI) water initially was added very slowly until a gel formed; then, the last remaining water was added gradually to reduce viscosity. The formulation used in the preparation of UV-curable emulsions is summarized in Table II.

Table I The Synthesis Composition of PMUA, UA, and UAA

Symbols	Reagents	Stoichiometry
UA ^a	PTMG 1000/TDI/2-HEMA	1/2/2
PMUA1	PTMG 1000/TDI/2-HEMA/PEG600	1/2/1.85/0.15
PMUA2	PTMG 1000/TDI/2-HEMA/PEG600	1/2/1.70/0.30
PMUA3	PTMG 1000/TDI/2-HEMA/PEG600	1/2/1.50/0.50
PMUA4	PTMG 1000/TDI/2-HEMA/PEG600	1/2/1.20/0.80
UAA ^b	PTMG 1000/DMPA/TDI/2-HEMA	0.6/0.4/1.5/1.5

^a UA: unmodified urethane acrylate.

^b UAA: urethane acrylate anionomer.



Scheme 2 The structure of PMUA (A: unmodified urethane acrylate, B: PEG-modified urethane acrylate).

For the soap-free emulsion of the mixture of PMUA and UAA, these resins were mixed prior to emulsification. The UV-curing formulation prepared using these mixtures was the same as that of the PMUA emulsion.

Measurement

The droplet sizes of emulsions were measured using Brookhaven laser light scattering instrument (BI 9000AT, 2MI98631, PM-tube, Ar—Ne laser). The viscosity changes of PMUA with water concentration were measured by a Brookfield synchroelectric viscometer with a spindle LVT No. 1-4.

To investigate the adsorption isotherm of PMUA at the water/benzene interface, PMUA and UA were dissolved in benzene; then, this solution was brought into contact with water to form the interface. The interfacial tension of water/benzene was measured using the Du Nouy ring method (Fisher Scientific Co., surface tensiometer-21).

The centrifugal stability of the UA emulsion was determined by the ratio of the weight of the precipitated oil to the one of the extracted emulsion sample, after being centrifuged at 15,000 rpm for 10 min. The centrifugal stability of the emulsion is represented by the following equation⁹⁻¹¹:

$$\text{Oil separated percent (\%)} = \frac{W_o}{W_s} \times 100 \quad (1)$$

where W_o is the weight of precipitated oil (g), and W_s , the weight of emulsion sample (g).

Emulsions were stored for 6 h in a refrigerator at -10°C and thawed and then the droplet size change was measured. The stability of the freeze-thaw was determined by the ratio of the droplet size of the emulsion before and after the freeze-thaw.¹²

The mechanical stability of emulsions was determined by the change of their viscosity after being sheared at 25°C with a homogenizer (Kleinschmitt

Table II Recipe for the Preparation of UV-curable PMUA Emulsions

PMUA (g)	10	10	10	10	10	10	10	10	10
CA (g)	—	0.3	0.5	0.7	1.0	—	—	—	—
EA (g)	—	—	—	—	—	0.2	0.3	0.4	0.5
DDI water (g)	21	21.6	22	22.4	23	21.6	22	22.4	23
PI (g)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
TI (g)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

PI: photoinitiator, Irgacure 184; TI: thermal initiator; *tert*-butyl benzoate; CA: crosslinking agent; TEGDMA; EA: epoxy acrylate.

Table III Droplet Size of PMUA Emulsions and UA Emulsion

Symbols	Molar Ratio of PEG to HEMA	Droplet Size (nm)
UA ^a	—	3240
PMUA1	0.15/1.85	79
PMUA2	0.30/1.70	54
PMUA3	0.50/1.50	48
PMUA4	0.80/1.20	29

^a UA emulsion was prepared using the mixture of TWEEN 60 and SPAN 60.

Co.) on the condition of various rpm.¹³ Mechanical properties were measured with a Hounsfield Model Instron at room temperature using a crosshead speed of 5 mm/min and load cell capacity of 50 kgf. Samples were cut from cured films using an ASTM D1708 die. All measurements respect the average of three runs. The engineering stress was calculated based on the initial area of the sample.

Characterization of Coating Properties

The formulations were drawn on a PVC plate and a glass plate and then water was evaporated at 60°C *in vacuo*. These formulations were cured in an air-irradiating static UV lamp (450 watt UV lamp from

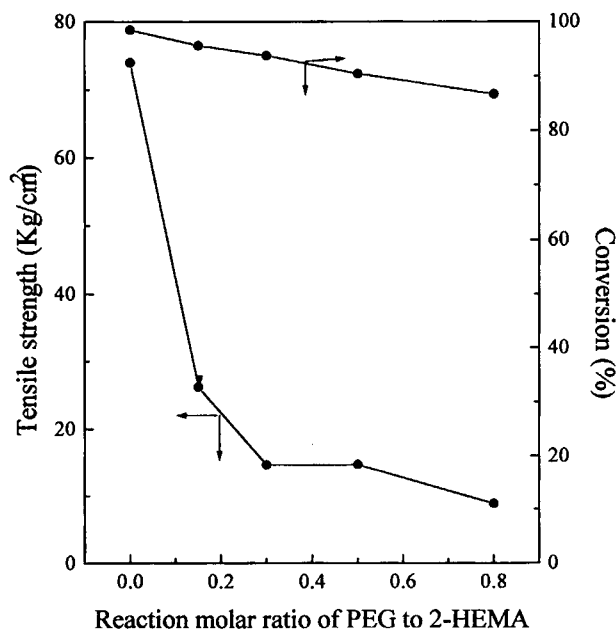


Figure 1 Tensile strength and conversion change of cured films as a function of reaction molar ratio of PEG to HEMA (—▲—: conversion change, —●—: tensile strength of PTMG type PMUA).

Ace Glass Co.) for 5 min, which were then postcured at 60°C for 2 h at reduced pressure.

The pencil hardness of the cured film was determined using the ASTM "Standard Method for Film Hardness by Pencil Test," method D3364-74. Coatings with a thickness of about 0.5 mm were used for pencil hardness and crosshatch adhesion.^{14,15} Strain resistance was determined by applying an oil ink to the cured film and by whether the stain remains or whether it can be removed by cleaning.¹⁶ Flexibility was measured by bending the coating on a PVC panel 180° around a standard cylinder with 1, $\frac{3}{4}$, $\frac{1}{2}$, $\frac{3}{8}$, $\frac{1}{4}$, and $\frac{1}{8}$ in. diameters and by observing cracking on the surface of the coating where films were coated with a thickness of about 60 μm .¹⁷

The conversion (gel fraction) was determined by peeling cured films from the substrate and weighing the dried film. Each film was then placed in a scintillation vial and extracted with 2-butanone for 30 min on a wrist-action shaker. Films were removed intact from the solvent and dried to constant weight at 60°C *in vacuo*, then reweighed. The conversion was calculated by the following equation:

$$\text{Conversion (\%)} = \frac{W_r}{W_c} \times 100 \quad (2)$$

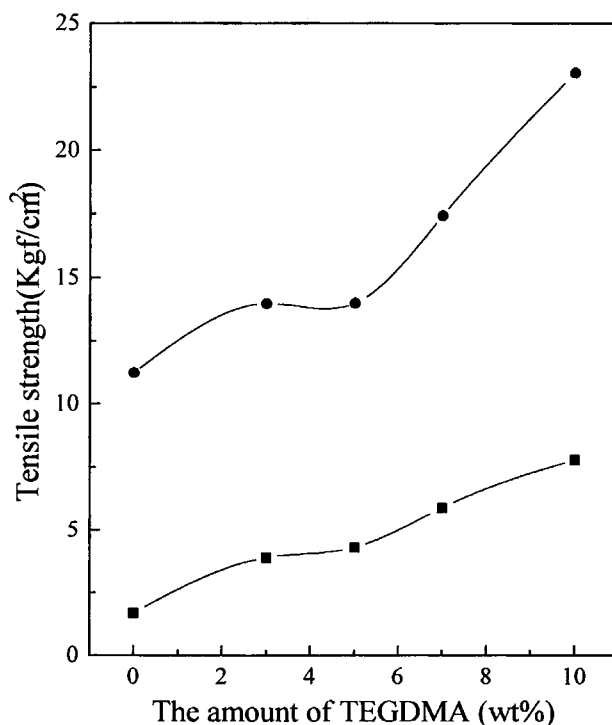


Figure 2 Tensile strength of cured films which were prepared using UA emulsion containing surfactants and soap-free PMUA emulsions (—●—: PMUA4, —■—: UA).

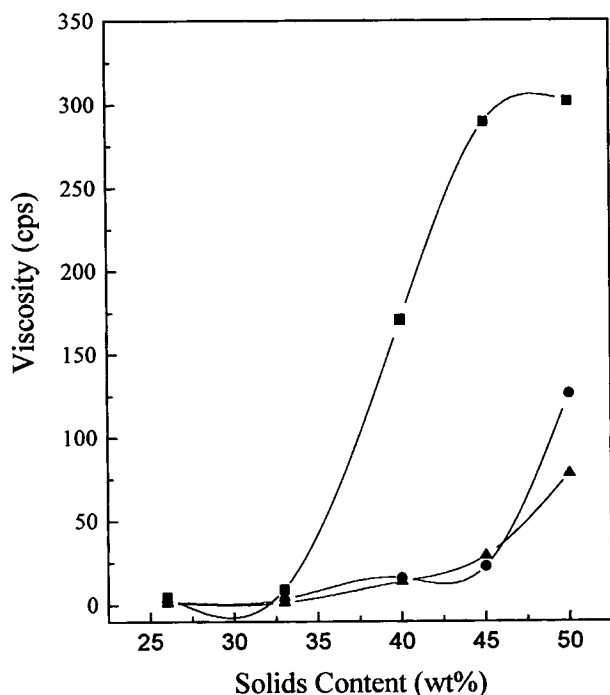


Figure 3 Viscosity change of PMUA emulsions with water contents (—■—: PMUA1, —●—: PMUA2, —▲—: PMUA4).

where W_r is the weight of sample after curing, and W_c , the weight of sample before curing (g).

RESULTS AND DISCUSSION

According to our previous experiments,¹⁸ in the case of UA emulsions, the order of centrifugal stability was TWEEN 60-SPAN 60 > TWEEN 60-SPAN 20 > TWEEN 20-SPAN 60. Therefore, the relatively stable emulsion was formed at HLB 12 of TWEEN 60-SPAN 60. However, the centrifugal stability and droplet size of these emulsions prepared using external surfactants were unsatisfactory compared with commercially available emulsions. The conversion and the tensile strength of cured films prepared using UA emulsions were much lower than that of films cured at the site of the bulk resin. These results were attributed to the fact that the surfactant arranged at the water/oil interface exerted a blocking effect on UV radiation and interfered with the crosslinking.

To prepare a soap-free emulsion to exclude the bad effect of the surfactant, PMUA was emulsified without external surfactants. The results of the emulsion droplet size measurements are illustrated in Table III. The droplet size of PMUA emulsions decreased as the reaction molar ratio of PEG in-

creased. PMUA molecules containing polyoxyethylene groups can act as a polymeric surfactant and the number of these groups increase with increase of the PEG reaction molar ratio, so finer droplet emulsion could be formed. The interfacial activity of PMUA molecules was confirmed by the adsorp-

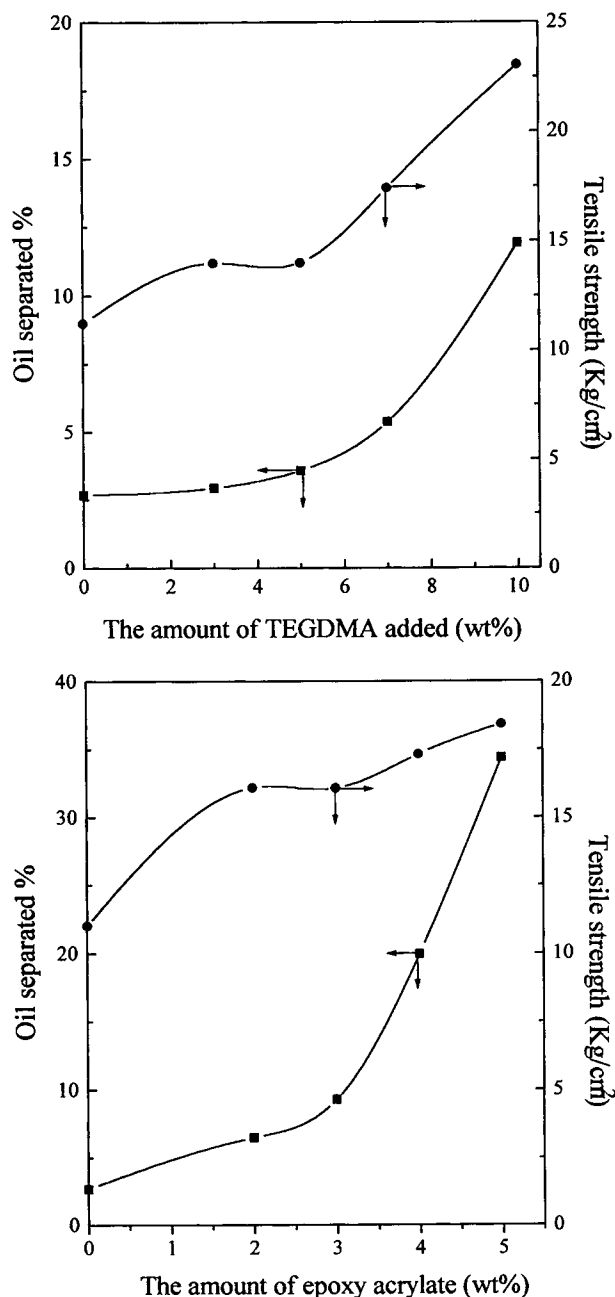


Figure 4 (a) Oil separated % of emulsion and tensile strength of its cured film as a function of the amount of crosslinking agent (—■—: oil separated %, —●—: tensile strength of cured film); (b) Oil separated % of emulsion and tensile strength of its cured film as a function of the amount of epoxy acrylate (—■—: oil separated %, —●—: tensile strength of cured film).

Table IV Coating Properties of PMUA at Different Added Amounts of CA and EA

	EA (Wt %)				
	0	3	5	7	10
Pencil hardness	6H	6H	6H	6H	6H
Stain resistance	Good	Good	Good	Good	Good
Adhesion (/100)	83	95	98	98	98
Flexibility (in.)	0	0	0	0	1/8
	CA (Wt %)				
	0	3	5	7	10
Pencil hardness	6H	6H	6H	6H	6H
Stain resistance	Good	Good	Good	Good	Good
Adhesion (/100)	83	93	96	96	96
Flexibility (in.)	0	0	0	0	0

tion behavior at the water/benzene interface in our previous experiments.^{7,8}

Figure 1 shows the tensile strength and conversion change of cured PMUA films with the reaction molar ratio of PEG. Tensile strength and conversion decreased with increase of the reaction molar ratio of PEG. These results were due to the decrease in the number of vinyl groups participating in cross-linking.

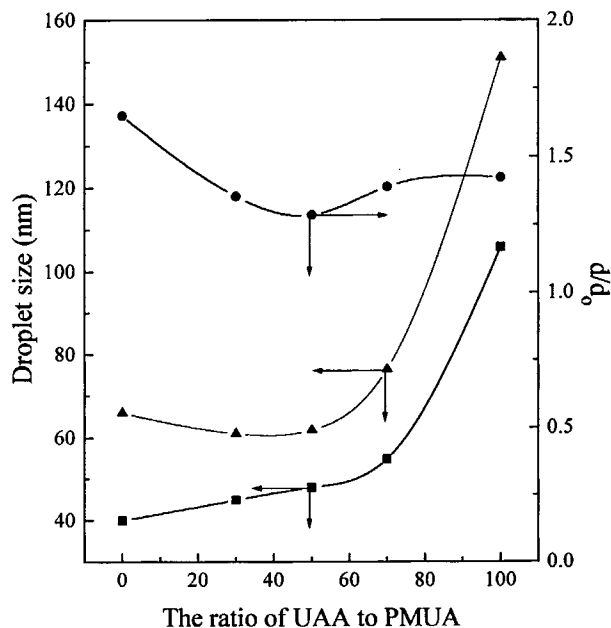


Figure 5 The droplet size of emulsions and the stability of freeze-thaw (—■—: d_0 , droplet size of emulsions before freeze-thaw, —▲—: d , droplet size of emulsions after freeze-thaw, —●—: d/d_0).

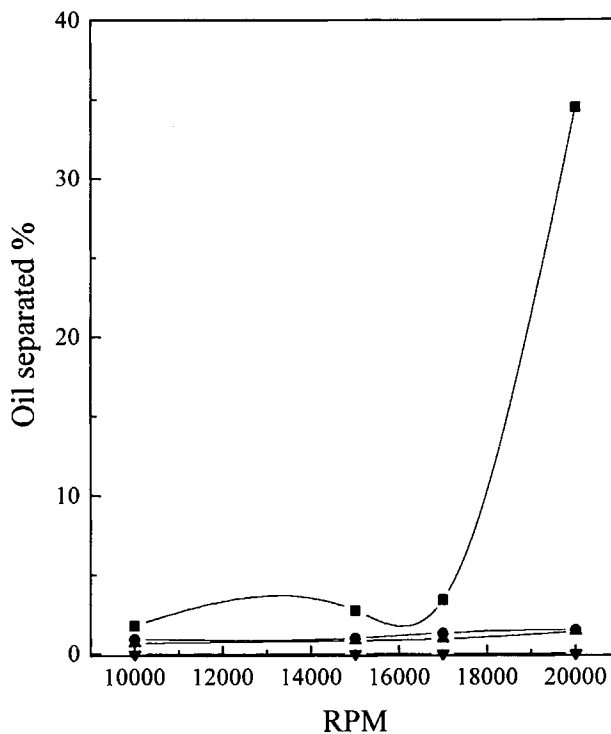


Figure 6 Centrifugal stability of emulsions (composition ratio of PMUA to UAA: —■— 10:0 (PMUA), —●— 7:3, —▲— 5:5, —▼— 0:10 (UAA)).

Tensile strengths of cured films prepared using UA emulsion and PMUA emulsions are represented at Figure 2. For PMUA films, even though with a less crosslinked network, the tensile strength of these cured films was higher than that of UA films.

It is important to measure the viscosity of emulsions in a certain amount of solids content. For emulsion-type UV-curable resins, water must be evaporated in the formulation before UV radiation; so, the higher solids content in the same viscosity is beneficial in an energy efficiency respect. Figure 3 shows the viscosity changes of PMUA emulsions with water content. As the reaction molar ratio of PEG to 2-HEMA increased, the viscosity of PMUA emulsions decreased at a constant solid content, because the decrease of emulsion droplet size caused the interaction between particles to decrease.

The Effect of Crosslinking Agent (CA) and Epoxy Acrylate (EA)

The centrifugal stability change of PMUA emulsions and tensile strength change of those films with the amount of CA and EA are represented in Figure 4(a) and (b), respectively. Droplet sizes of these emulsions were about 55–70 nm.

As the amount of added CA and EA increased, the centrifugal stability of the emulsions was re-

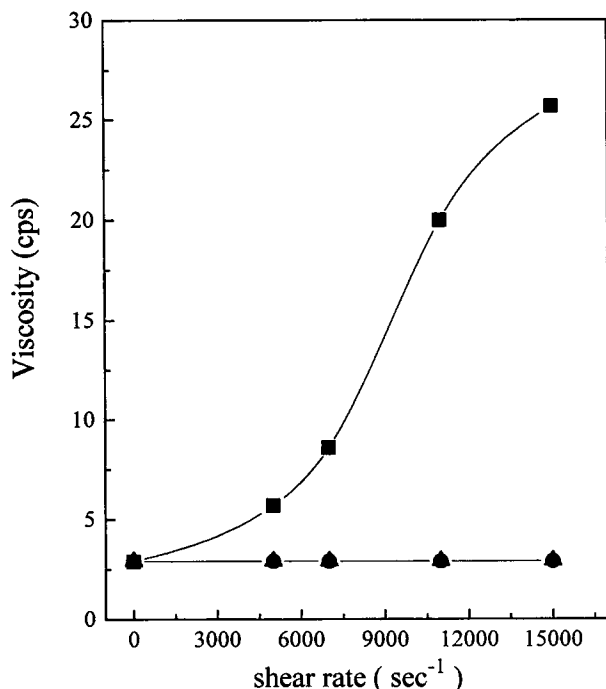


Figure 7 Mechanical stability of emulsions (composition ratio of PMUA to UAA: -■- 10 : 0 (PMUA), -●- 5 : 5, -▲- 0 : 10 (UAA)).

duced; however, the tensile strength of the cured films improved. The coating property change with the amount of CA and EA added are illustrated at Table IV.

As the weight percent of added CA and EA increased, the pencil hardness showed good results (6H) owing to the increase in crosslinking density of the cured film. As the weight percent of added CA increased, the cured film showed good adhesion. These results were due to the formation of the grafting bond between the PVC substrate and the vinyl group of multi-functional acrylate which was initiated by the photoinitiator.¹⁸ As the weight percent of added EA increased, the adhesion of the film also increased, which was attributed to the addition of EA's good adhesive properties.^{19,21} The UV-cured films of PMUA were very flexible and the flexibility of these UV-cured films could be maintained as the addition amount of CA and EA increased. The cracks did not appear, although the concentration of CA and EA increased. However, when 10 wt % CA was added, very small cracks were found.

The Effect of Urethane Acrylate (UA) Anionomer

Figure 5 shows the freeze-thaw stability of emulsions prepared with PMUA, UAA, and the mixture of both resins, which is illustrated as the ratio of the

droplet size before and after freeze-thaw. The freeze-thaw stability of the PMUA emulsion was higher than that of the UAA emulsion. When the mixing ratio of PMUA to UAA was 5 : 5, the freeze-thaw stability was higher than in any other emulsion.

Figures 6 and 7 illustrate the centrifugal and mechanical stability, respectively. At low rpm or shear rate, all the emulsions showed good stability. At a higher shear rate, the emulsion stability of PMUA decreased; however, that of UAA was not changed. When PMUA and UAA were mixed in the weight ratio of 5 : 5, the centrifugal and mechanical stability of this emulsion were similar to those of the UAA emulsion.

The viscosity change of emulsions with temperature is illustrated at Figure 8. When the temperature was increased to 60°C, the viscosity of the PMUA emulsion increased significantly owing to droplet coalescence while the UAA emulsion was invariant. These results were attributed to the fact that the solubility of ionic groups of UAA was not affected by temperature, whereas nonionic hydrophilic groups of PMUA lost their hydrophilicity at elevated temperature. Additionally, for the mixture of PMUA and UAA (5 : 5), the viscosity of this emulsion was not changed with increase of temperature, indicating that the thermal stability of PMUA was able to be improved by mixing both resins.

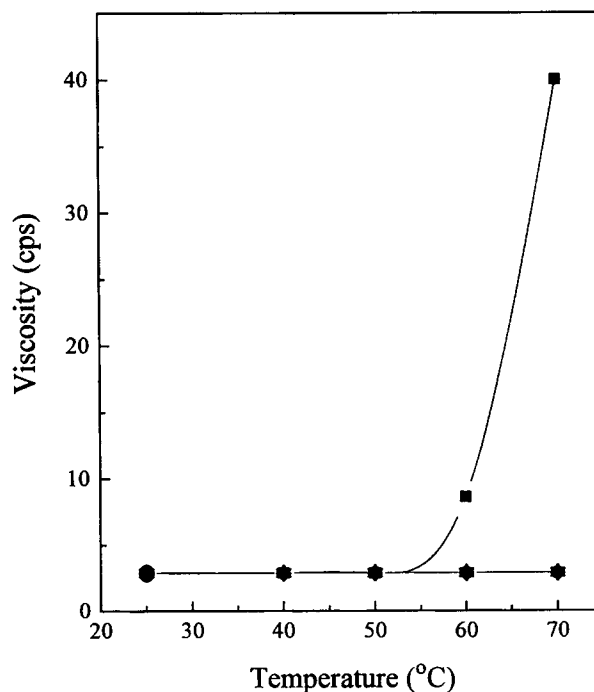


Figure 8 Viscosity of emulsions change as a function of temperature (composition ratio of PMUA to UAA: -■- 10 : 0 (PMUA), -▼- 5 : 5, -◆- 0 : 10 (UAA)).

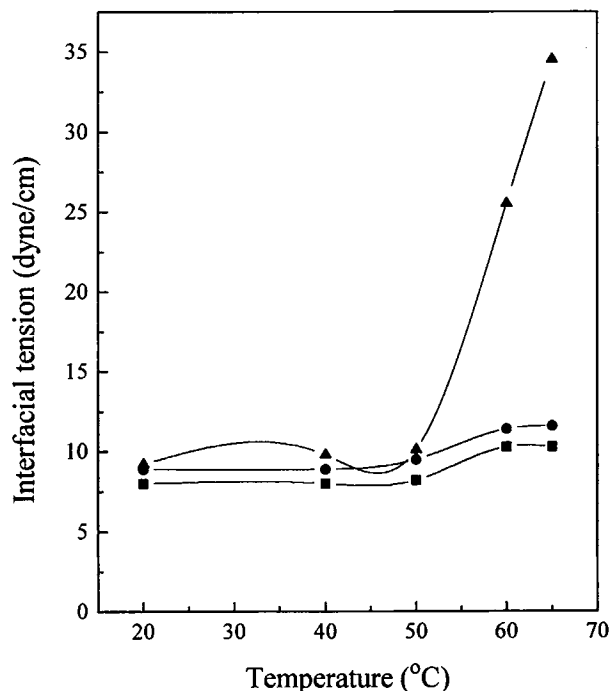


Figure 9 Adsorption change with temperature (composition ratio of UAA to PMUA: -■- 10 : 0 (UAA), -●- 5 : 5, -▲- 0 : 10 (PMUA)).

To confirm the decreases of hydrophilicity of polyoxyethylene groups, the adsorption change with temperature at the water/benzene interface was measured and is illustrated in Figure 9. As expected, for PMUA, the interfacial tension increased abruptly around 60°C, while in the case of UAA and the mixture of PMUA and UAA, interfacial tension was unchanged with increasing temperature.

CONCLUSION

PMUA, containing polyoxyethylene groups as a terminal group, was synthesized by the reaction of PEG with the residual isocyanate groups of UA, which could be soap-free emulsified, so the bad effect of surfactants was able to be removed. The droplet sizes and viscosity of PMUA emulsions could be controlled by the reaction mol ratio of PEG to 2-HEMA.

The tensile strength and conversion of UV-cured film were decreased with increase of the PEG reaction mol ratio; however, these properties could be improved by using a CA and EA, which made the centrifugal stability of the emulsion decrease

slightly. Additionally, according to the results of pencil hardness and flexibility measurements, cured films prepared using our formulations showed a hard surface (6H) and were very flexible.

The thermal stability of PMUA emulsion was able to be improved by mixing PMUA with UAA. The mixture of PMUA and UAA showed a synergistic effect on the droplet size and on the centrifugal and mechanical stability of the emulsions.

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