Preparation of UV Curable Emulsions Using PEG-Modified Urethane Acrylates and Their Coating Properties

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To prepare self-emulsifiable urethane acrylate, PEG-modified urethane acrylates (PMUA) containing polyoxyethylene groups as a terminal group were synthesized by the reaction of PEG [poly(ethylene glycol)] with residual isocyanate groups of a urethane acrylate. As the reaction molar ratio of PEG to HEMA increased, droplet sizes and viscosity of PMUA emulsions decreased, however, the tensile strength and conversion of UV-cured PMUA film decreased. The molecular weight and type polyol had a significant influence on emulsion droplet size and stability. The coating properties and mechanical properties of the UV-cured film were improved by using crosslinking agent and epoxy acrylate. However, centrifugal stability was decreased by the addition of these additives.

INTRODUCTION

Recently waterborne coatings have been widely utilized in industrial coatings. This has made it possible to decrease air pollution, to reduce risks of fire, and to improve aspects of occupational health and safety. Initially, the use of water-soluble, dispersible or dilutible UV or EB curable formulations may appear contradictory from an energy saving viewpoint, because it is necessary to remove the water before irradiating the film. Nevertheless, marked improvements in application viscosity can be achieved by using water without the use of volatile organic solvents. Water-based inks and coatings find widespread usage and are becoming increasingly desirable with the ever increasing environmental pressures.[1-2]

To prepare a water-dispersible resin, a special treatment or structural modification for polymer or oligomer to improve water dispersibility has been generally done by incorporating hydrophilic groups into the molecular backbone.[3-5] These hydrophilic groups always existed as a pendant group. However, for ionic dispersions a neutralization agent is needed to neutralize acid-functional oligomers, which are very toxic and might release potentially harmful organic amines during a curing process. In case of incorporating nonionic, hydrophilic groups as a pendant group, it was necessary to synthesize a prepolymer with isocyanate end groups and polyoxyethylene pendant groups at the same molecule through complicate reaction processes.[6]

In this paper, PEG-modified urethane acrylates (PMUA) were synthesized by the reaction of poly(ethylene glycol) (PEG), with residual isocyanate groups of a urethane acrylate. These molecules could be prepared by a relatively simple process, and they contained nonionic hydrophilic polyoxyethylene groups not as pendant groups, but rather as terminal groups. In this position, the PEG groups on paint could act as a polymeric surfactant and be emulsified without additional external surfactant.

The ultimate goal of this study was preparation of UV curable emulsions using PMUA. Thus, the effect of the reaction molar ratio of PEG on the emulsion droplet size, centrifugal stability, viscosity, coating properties, and mechanical properties of cured films were investigated. Additionally, to enhance the coating properties of PMUA, the change of mechanical properties with addition of crosslinking agents and epoxy acrylate was studied.

EXPERIMENTAL

Materials

In the synthesis of PMUA and UA, poly (tetramethylene glycol) (PTMG, Mw = 1000, 2000, Hyosung BASF), poly(proplyene glycol) (PPG, Mw = 1000 and 3000, Korea Polyol), 2,4-toluene diisocyanate (TDI, Junsei Chemical Co.), 2-hydroxyethylmethacrylate (2-HEMA, Aldrich

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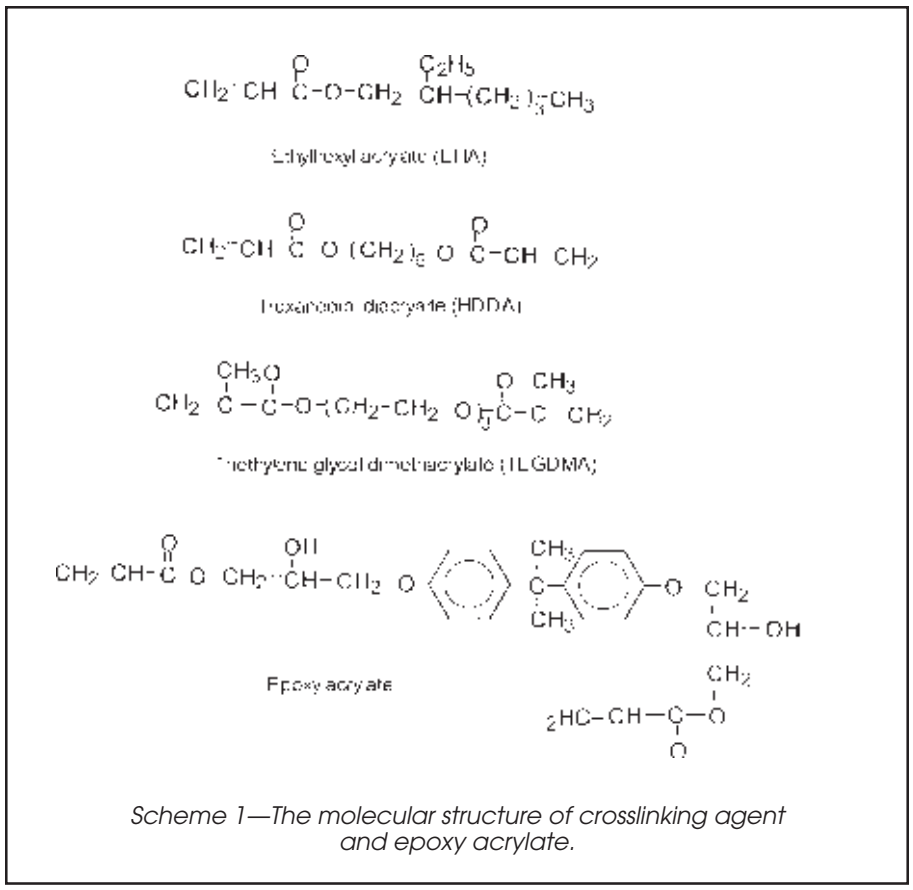


Scheme 1—The molecular structure of crosslinking agent and epoxy acrylate.

Chemical Co.) poly(ethylene glycol) (PEG, Mw = 600, Junsei Chemical Co.) were used. Tween™ 60, 20 and SPAN™ 20, 60 (Shinyo Pure Chemicals Co.) were employed in the preparation of UA emulsions.

Ethylhexyl acrylate (2-EHA), 1,6-hexanediol diacrylate (HDDA), and triethylene glycol dimethacrylate (TEGDMA) were used as crosslinking agents (CA), to improve physical properties rather than to reduce the viscosity of formulation. All of these chemicals were purchased from Aldrich Chemical Co.

To give formulation hardness characteristics, epoxy acrylate was blended with urethane acrylate. Epoxy acrylate (EA) was synthesized by reaction of epoxy resin (Kuk-Do Chemical Co., bisphenol A type, 11,500-13,500 cps. at 25°C) with acrylic acid (Junsei Chemical Co.). CA and epoxy acrylate(EA) structures are shown in *Scheme* 1. (1-Hydroxycyclohexyl)-phenylmethanone (Ciba-Geigy Chemical Co., Irgacure 184) was used as a photoinitator and tert-butyl benzoate (Junsei Co.) was used as a thermal initiator for post-curing.

Synthesis of PMUA and UA

The UA and PMUA were synthesized by two- or three-step processes. The molar ratio of reactants was summarized in *Table* 1. These reactions were carried out in a four-neck glass reactor equipped with stirrer, thermometer, reflux condenser, and inlet system for N_2 gas.

In the first step, TDI was poured into a nitrogen inerted four-neck glass reactor. Then PTMG was added dropwise while mixing at 45°C. Then the reaction temperature was raised to 55°C so that the isocyanate group of TDI reacted with the hydroxy group of PTMG. This temperature was maintained for seven hours to sustain an acceptable reaction rate. The disappearance of the NCO value during the reaction was determined using the dibutyl-amine back titration method to find the reaction end point.[7]

In the second step, 2-HEMA was slowly added to react with residual isocyanate groups at 45°C for four hours. This introduced reactive acrylate groups onto the chain end. The reaction temperature was then increased to 75°C to eliminate unreacted isocyanates. For PMUA, the reaction end point for this step was attained when the NCO value was constant with time. However, for UA, the reaction end point was determined by the disappearance of 2270 cm^{-1} infrared band which corresponds to NCO stretching.

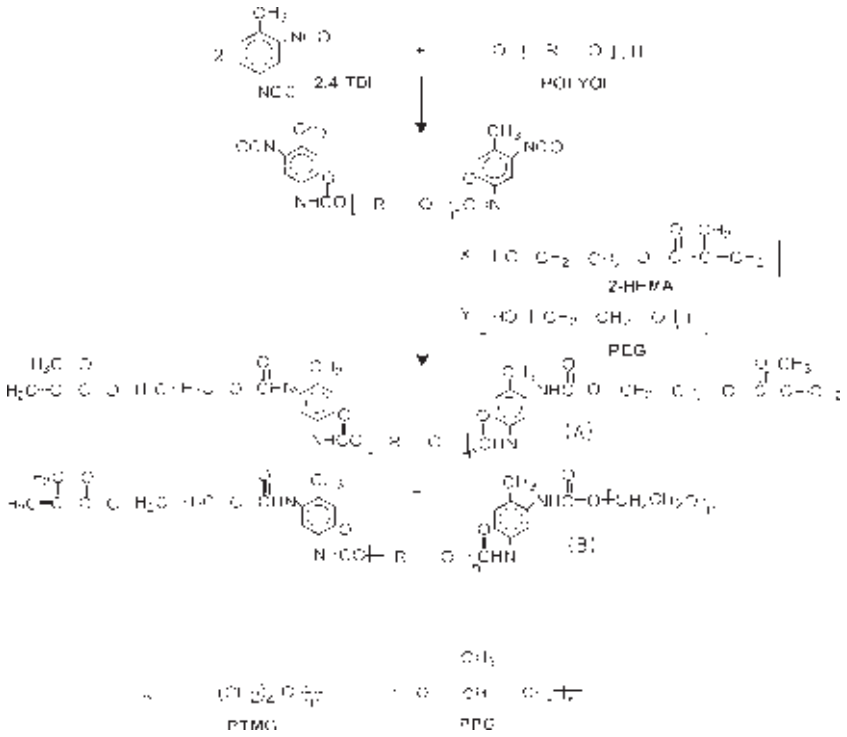
UA was prepared by a two-step reaction, however, PMUA was synthesized by three consecutive reaction processes. The first and second steps were the same process as the synthesis process of UA. In the third step, PEG was poured into the kettle to react with the last residual isocyanate. This process made it possible to introduce polyoxyethylene groups onto the molecular chain ends. Thus, both hydrophilic groups and reactive acrylate groups existed on one molecule. The reaction end point of this step was determined by the disappearance of 2270^{-1} infrared band.

Table 1—The Synthesis Composition of PMUA and UA

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
PMUA5	PTMG 2000/TDI/2-HEMA/PEG600	1/2/1.70/0.30
PMUA6	PTMG 2000/TDI/2-HEMA/PEG600	1/2/1.20/0.80
PMUA7	PPG 1000/TDI/2-HEMA/PEG600	1/2/1.85/0.15
PMUA8	PPG 1000/TDI/2-HEMA/PEG600	1/2/1.70/0.30
PMUA9	PPG 1000/TDI/2-HEMA/PEG600	1/2/1.50/0.50
PMUA10	PPG 1000/TDI/2-HEMA/PEG600	1/2/1.20/0.80
PMUA11	PPG 2000/TDI/2-HEMA/PEG600	1/2/1.50/0.50
PMUA12	PPG 1000, triol/TDI/2-HEMA/PEG600	1/2/2.0/1.0
PMUA13	PPG 3000, triol/TDI/2-HEMA/PEG600	1/2/2.0/1.0

(a) UA: unmodified urethane acrylate.

The average molecular weight of PMUA and confirmation of these reactions through ^{1}H NMR and GPC were reported in our previous papers.[8-9] *Scheme* 2 shows the molecular structure of PMUA (the mixture of (A) and (B) type molecules) and UA ((A) type molecule).



Scheme 2—The molecular structure of PMUA and UA.

Preparation of UV-Curable Formulations

An oil solution (10 g) containing additives was placed in a 100ml 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 *Tables* 2 and 3.

Measurement

Emulsion droplet size was measured with an Ostuka electronic laser particle analyzer, LPA-3000/3100 (droplet size < 1 μm) and Elzone 620 PC (droplet size > 1 μm).

The centrifugal stability of the urethane acrylate emulsions was determined by the ratio of weight of precipitated oil to that of extracted emulsion sample, after centrifugation at 15,000 rpm for 10 min. The centrifugal stability of the emulsion was represented by the following equation.[10-13]

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

W_o = the weight of precipitated oil (g)
W_s = the weight of emulsion sample (g)

The viscosity of PMUA emulsions was measured using a Brookfield Rheoset. Shear rate was raised by sec^{-1} at intervals of 20 sec. Mechanical properties were measured with Hounsfield model Instron at room temperature using a crosshead speed of 5 mm/min and load cell capacity of 50 kgf. All measurements, using samples cut from cured films,[14] 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 down on PVC plate and glass plate and then water was evaporated at 60°C in vacuo. These formulations were cured in air using a static UV lamp (450 watt UV lamp from Ace Glass Co.) for five minutes as the radiation source postcuring at 60°C for two hours at reduced pressure.

Coatings with thickness of about 0.5 mm were used for pencil hardness measurements and for crosshatch adhesion.[15-16] Stain resistance was determined by applying an oil ink to a cured film and determining whether the stain was permanent or if it can be removed by cleaning.[17] Flexibility was measured by bending coated PVC panels 180° around standard cylinders with 1, 3/4, 1/2, 3/8, 1/4, and 1/8 in. diameters and observing cracking on the surface of coating where films were coated with thickness of about 60 μm.[18]

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.[19] The conversion was calculated from:

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

Table 2—Formulation for Preparation of UV Curable UA Emulsions

UA	10 g
DDI water	50 g
PI	0.3 g
TI	0.2 g
CA	0-1 g
Surfactants	3 g
Span 20	0.4285-1.856g
Span 60	0.2650-1.147g
Tween 20	0.3306-1.424 g
Tween 60	1.147-2.734 g

PI: photoinitiator, Irgacure™ 184; TI: thermal initiator, tert-butyl benzoate; CA: crosslinking agent which was the mixture of 2-EHA, HDDA, and TEGDMA with the mixing ratio of 1:1:1; EA: epoxy acrylate.

Table 3—Formulations for 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 which was the mixture of 2-EHA, HDDA, and TEGDMA with the mixing ratio of 1:1:1; EA: epoxy acrylate.

Table 4—Centrifugal Stability and Droplet Size of PMUA Emulsions and Tensile Strength of Their Cured Films

	PMUA3	PMUA9	PMUA11	PMUA12	PMUA13
Tensile strength (Kg/cm^2)	8.883	7.157	5.7	15.693	7.12
Oil separated %	0[a]	2.687	—[b]	30.609	—[b]
Droplet size (nm)	54.11	94.27	—[b]	327.3	—[b]

(a) Means that emulsion was not broken by centrifugation.
(b) Means that emulsion could be formed.

W_r = the weight of sample after curing (g)
W_c = the weight of sample before curing (g)

RESULTS AND DISCUSSION

UA Emulsions Prepared Using Mixed Surfactants

Figure 1 shows the centrifugal stability of oil/water emulsions of UA without hydrophilic groups on the molecular backbone. The order of centrifugal stability was Tween 60-Span 60 > Tween 60-Span 20 > Tween 20-Span 60. Therefore, the most relatively stable emulsion was formed at HLB 12 with TweenN 60-Span 60.

The conversion and the tensile strength of cured films prepared using bulk resin and emulsions of UA are illustrated in *Figure*s 2 and 3, respectively.

When the properties of cured film as a bulk resin were compared with those of films prepared using UA emulsions, the emulsion type films showed lower tensile strength and conversion than bulk cured films. Additionally, properties of those resins did not improve even though the amount of crosslinking agent increased.

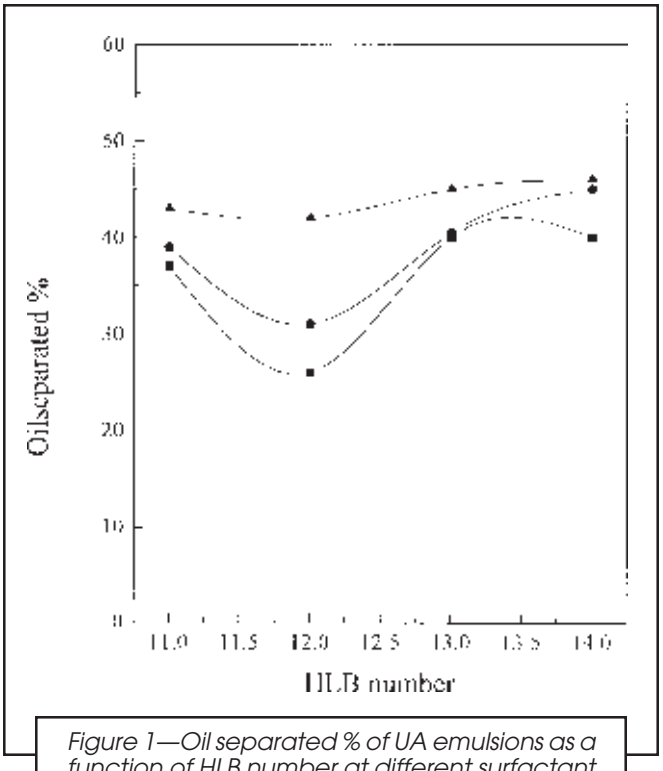


Figure 1—Oil separated % of UA emulsions as a function of HLB number at different surfactant composition. (–■– Tween 60/Span 60, –●– Tween 60/Span 20, –▲– Tween 20/Span 60).

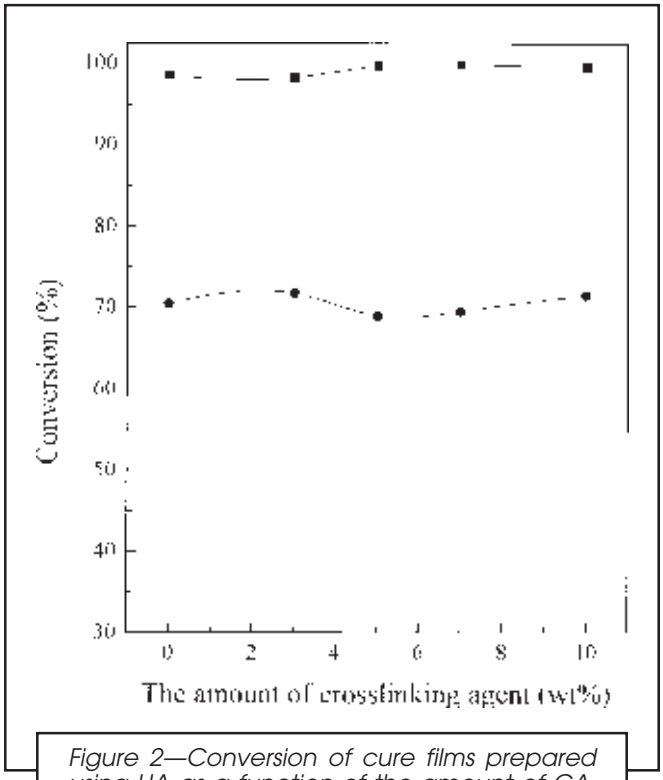


Figure 2—Conversion of cure films prepared using UA as a function of the amount of CA. (–■– bulk UA resin; –●– UA emulsion).

These results were due to the fact that surfactant was arranged in the water/oil interface and exerted a blocking effect on UV radiation and interfered with crosslinking.

Soap-Free Emulsion of PMUA

To prepare soap-free emulsions and exclude the deleterious effect of surfactant, PMUA were emulsified without external surfactants. The results of emulsion droplet size measurements are illustrated in *Figure* 4. The droplet sizes of both types of PMUA (PTMG and PPG Type PMUA) emulsions decreased as the reaction molar ratio of PEG increased. These results indicated that urethane acrylate molecules containing polyoxyethylene groups act as a polymeric surfactant and the number of these groups increase with the increase of PEG reaction molar ratio, so finer droplet emulsions could be formed.

In our previous experiments, the interfacial activity of PMUA molecules was confirmed by the adsorption behavior at water/benzene interface. As the reaction molar ratio of PEG to HEMA increased, the number of molecules acting as a polymeric surfactant increased so that interfacial tension of water/benzene decreased. In other words, the PMUA having the smallest emulsion droplet size showed the lowest interfacial tension.[8-9]

It is important to measure the viscosity of emulsions with a certain solids content, because in the case of emulsion type UV-curable resins, water must be evaporated in formulation before UV radiation. Thus, a higher solids content at the same viscosity is beneficial in terms of energy efficiency. *Figure* 5 shows the viscosity change of PMUA emulsions as a function of water content. At a constant solid content, the viscosity of PMUA emulsions decreased with the increase in the reaction molar ratio of PEG. It was thought that finer emulsion particles were formed with an increase in the reaction molar ratio of PEG owing to the decrease of the interaction between particles.

Figure 6 shows the tensile strength and conversion change of cured films with the reaction molar ratio of PEG. Tensile strength decreased with the increase in the reaction molar ratio of PEG. These results were due to reduction of the number of acrylate groups that participated in curing. *Figure* 7 illustrates the conversion change of PMUA with reaction molar ratio of PEG. As expected, the conversion of cured films decreased with the increase of reaction molar ratio of PEG.

To investigate the deleterious effect of surfactants, the tensile strength of UV cured films prepared using UA emulsions containing a large amount of surfactants were compared with that of films prepared using soap-free PMUA emulsions. Tensile strengths of both film types are illustrated in *Figure* 8. The UV cured films of PMUA, containing less crosslinked network, show higher tensile strength than the films prepared from UA emulsions.

Table 4 shows the centrifugal stability and droplet sizes for four types of PMUA emulsions, and tensile strength of their UV-cured films. PMUA3 prepared using PTMG 1000 showed smaller droplet size and higher tensile strength than PMUA9 prepared using PPG 1000.

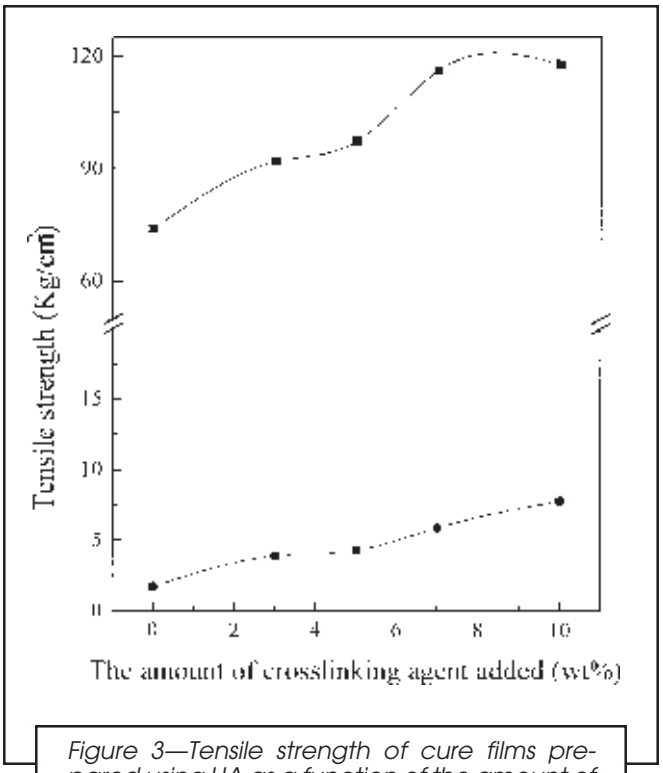


Figure 3—Tensile strength of cure films prepared using UA as a function of the amount of CA. (–■– bulk UA resin; –●– UA emulsion).

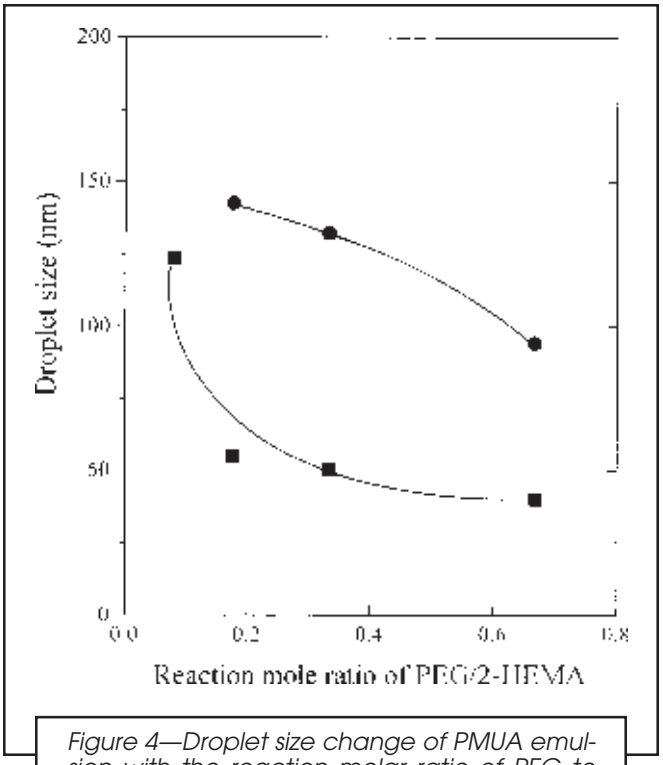


Figure 4—Droplet size change of PMUA emulsion with the reaction molar ratio of PEG to HEMA. (–■– PTMG type PMUA; –●– PPG type PMUA).

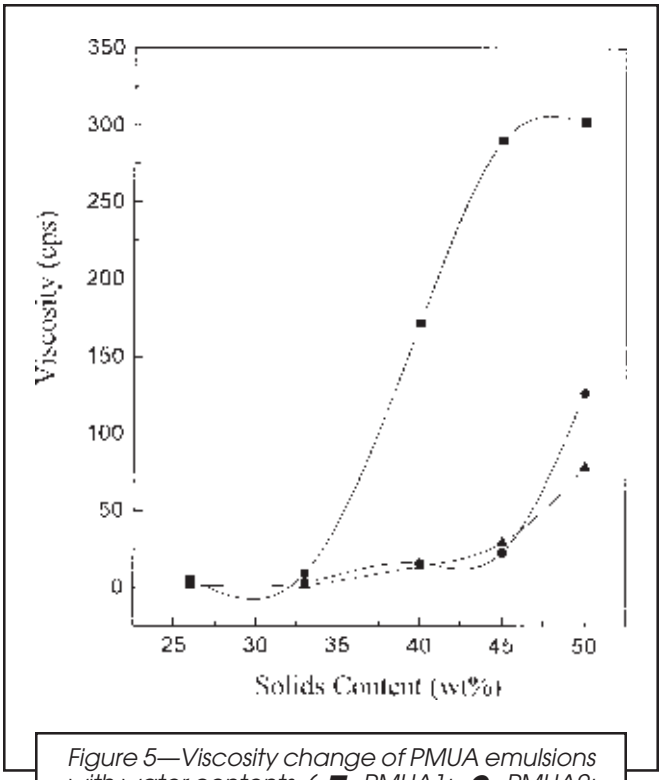


Figure 5—Viscosity change of PMUA emulsions with water contents. (–■– PMUA1; –●– PMUA2; –▲– PMUA4).

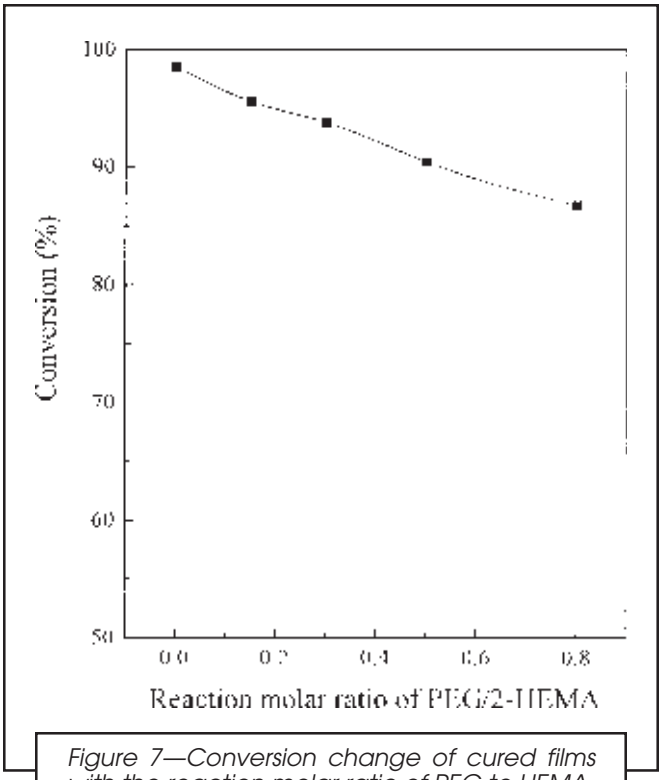


Figure 7—Conversion change of cured films with the reaction molar ratio of PEG to HEMA.

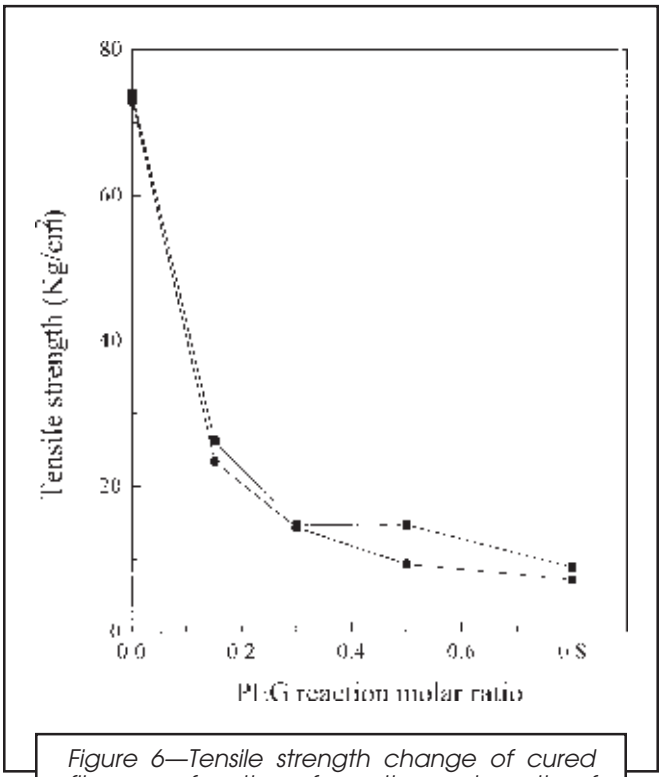


Figure 6—Tensile strength change of cured films as a function of reaction molar ratio of PEG to HEMA –■– PTMG type PMUA.(–●– PPG type PMUA

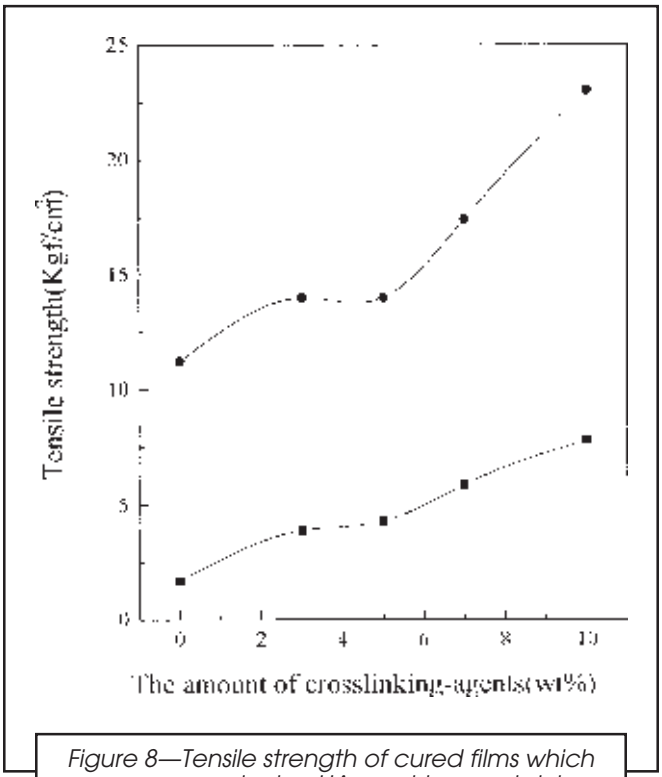


Figure 8—Tensile strength of cured films which were prepared using UA emulsion containing surfactants and soap-free PMUA emulsions. (–●–PMUA4; –■– UA).

Table 5—Coating Properties of PMUA at Different Added Amount of CA and EA

CA (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
EA (wt%)	**0**	**3**	**5**	**7**	**10**
Pencil hardness	6H	6H	6H	6H	6H
Stain resistance	Good	Good	Good	Good	Good
Adhesion (/100)	83	80	80	78	78
Flexibility (in.)	0	0	0	0	0

UV-cured film of PMUA12 had higher tensile strength than PMUA9 and PMUA13. However, centrifugal stability and droplet size of those emulsions showed opposite order.

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 were shown in *Figures* 9-a and b, respectively. Droplet sizes of these emulsions were about 55-70 nm. As the amount of added CA and epoxy acrylate increased, the centrifugal stability of emulsions reduced, however, tensile strength of cured films improved. The conversion change with the weight percent of CA and EA added is presented in *Figure* 10.

As the weight percent of CA and EA increased, the conversion of cured films increased, because crosslinking density of cured films increased owing to the reaction of pendant double bond of multifunctional monomer, and the plasticization effect of unreacted monomer was diminshed.

Coating property changes with the amount of CA and EA added are given in *Table* 5. As the weight percent of added CA and EA increased, pencil hardness showed constant good results (6H) owing to the increase in crosslinking density of cured film.[20] Adhesion was measured using crosshatch adhesion method. As the weight percent of added CA increased, the cured film showed good adhesion. These results were due to formation of grafting bond between PVC substrate and acrylate group of the multifunctional acrylates which were initiated by photoinitiator.[21] As the weight percent of added EA in-

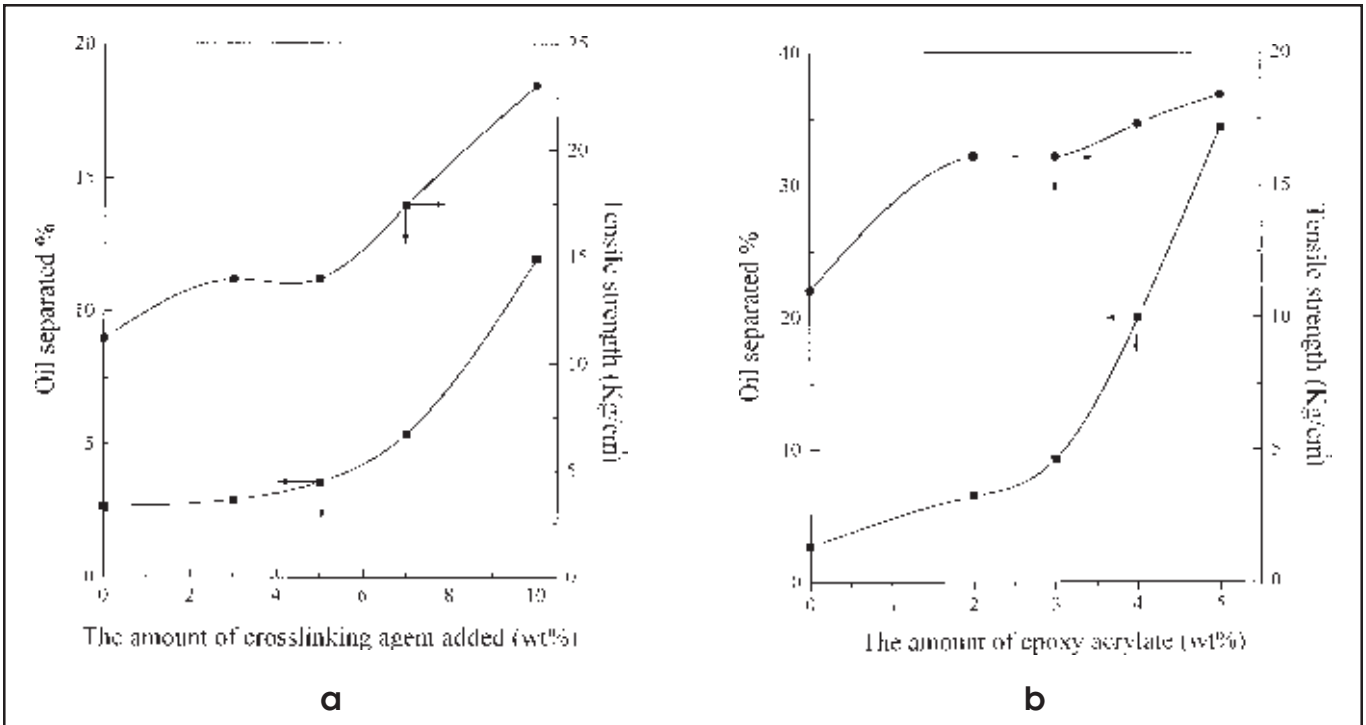


Figure 9—(a) Oil separated % of emulsion and tensile strength of its cured film as a function of the amount of crosslinking agent: –■– oil separated %; –●– tensile strength of cured film. (b) Oil separated % of emulsion and tensile strength of its cured film as a function of the amount of epoxy acrylate: –■– oil separated %; –●– tensile strength of cured film.

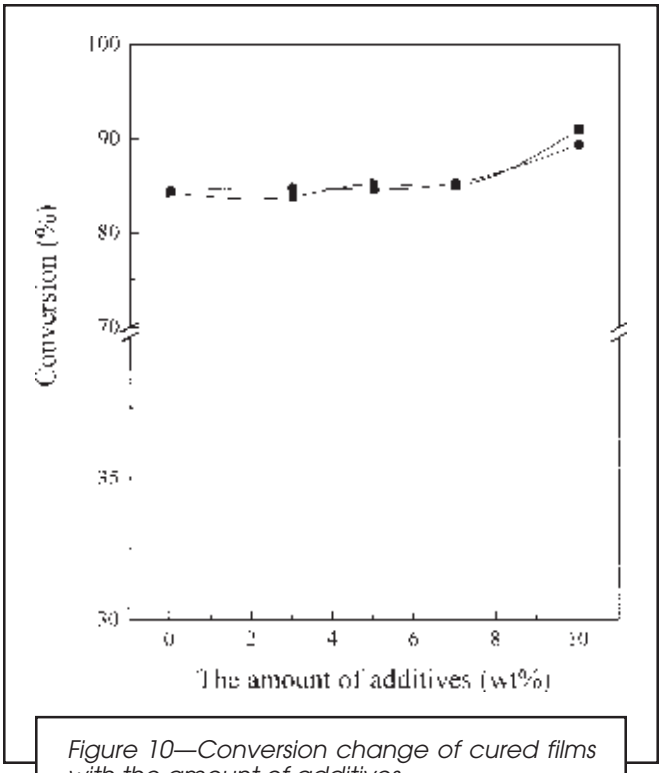


Figure 10—Conversion change of cured films with the amount of additives.

creased, the film adhesion also was good which was attributed to the addition of epoxy acrylate, a compound that has good adhesive properties, to the highly crosslinked network structure, and to excellent thermal stability.[22-23] The UV-cured films of PMUA were very flexible and it could be maintained as the amount of CA and EA increased. Cracks did not appear as the concentration of CA and EA was increased. However, in the case of 10% CA, very small cracks were found.

CONCLUSION

PMUA, containing polyoxyethylene groups as terminal groups, were synthesized by the reaction of PEG with the residual isocyanate groups of UA, which could be soap-free emulsified, so the deleterious effect of surfactants would be absent. Droplet sizes and viscosity of PMUA emulsions could be controlled by the reaction mole ratio of PEG to 2-HEMA.

PMUA12 prepared using PPG triol 1000 showed higher tensile strength than PMUA3 and PMUA9, however, the emulsion of PMUA12 represented larger droplet size and lower centrifugal stability than these PMUA emulsions.

The tensile strength and conversion of the UV cured films were decreased with the increase of PEG reaction mole ratio, however, these properties could be improved by using crosslinking agent and epoxy acrylate, which made emulsion centrifugal stability slightly decreased. Additionally, according to results of pencil hardness and flexibility measurements, cured films prepared using our formulations had a hard surface (6H) and were very flexible.

ACKNOWLEDGMENT

This work was supported by the Research Institute of Industrial Science and Science Art Promotion Division of Hanyang University.

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(23) Ellis, B., *Epoxy Resin Chemistry and Technology*, Marcel Dekker, 2nd Ed., New York, 1988.