Preparation of UV-Curable PEG-Modified Urethane Acrylate Emulsions and Their Coating Properties. II. Effect of Chain Length of Polyoxyethylene

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ABSTRACT: To prepare self-emulsifiable urethane acrylate, poly(ethylene glycol)-modified urethane acrylates (PMUA), containing polyoxyethylene chains as a terminal group were synthesized by the reaction of a residual isocyanate group with poly(ethylene glycol) (PEG). Five types of PMUA were synthesized using five types of PEG having different molecular weight. As the chain length of polyoxyethylene of PMUA increased, the thermal stability of their emulsions improved and the tensile strength of their UV-cured films were also increased. For PMUA600 prepared using PEG600, the thermal stability of the emulsion and tensile strength of UV-cured film were relatively low. However, the emulsions of PMUAs which were synthesized using PEG2000, PEG4000, and PEG6000 were stable with increasing temperature and the tensile strength of their cured films was greater than that of PMUA 600. When PMUA600 was mixed with PMUA2000, PMUA4000, and PMUA6000, the thermal stability of the emulsions and mechanical properties of their UV-cured films were improved greatly. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2657–2664, 1997

Key words: PMUA; thermal stability; mechanical stability; polyoxyethylene; UV cure

INTRODUCTION

Waterborne coatings have been widely utilized recently in industrial coatings, which has made it possible to control pollution, to reduce risks of fire, and to improve aspects of occupational health and safely.[1–6] For ionic water-dispersible resin, a neutralization agent has to 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 the prepolymer having isocyanate end groups and a polyoxyethy-

lene pendant group at same molecule has to be carried out through complicated reaction processes.[6]

In our previous article,[7] poly(ethylene glycol)-modified urethane acrylates (PMUA) were synthesized by the reaction of poly(ethylene 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 but as a terminal group, so PMUA could act as a polymeric surfactant and it emulsified without the use of an external surfactant. In addition, also investigated was the effect of the molar ratio of 2-hydroxyethyl methacrylate (2-HEMA) to PEG on the size of droplets of PMUA emulsion and the mechanical properties of their UV-cured films. When the molar ratio of 2-HEMA

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to PEG was 1.2 : 0.8, the most stable emulsion could be obtained, and PMUA showed good coating properties. However, the thermal stability of PMUA emulsion and the mechanical properties of UV-cured film were relatively low. In other words, the hydrophilic groups of PMUA are nonionic polyoxyethylene groups which lose their hydrophilicity at higher temperature,[8,9] so the water dispersibility of PMUA and the emulsion stability of PMUA decreased significantly with increased temperature and polyoxyethylene also decreased with increased temperature. The thermal stability of emulsions having nonionic hydrophilic groups could be improved by the addition of ionic water-dispersible resin or the use of an ionic surfactant.[7,10]

Therefore, in this article, PMUA using different chain lengths of PEG were synthesized and the thermal stability of PMUA emulsions was evaluated by measurement of the change of interfacial tension, viscosity, and droplet size. The mechanical properties of UV-cured films were also investigated by measuring the tensile strength and elongation at break. Generally, in the case of nonionic dispersions, the mixture of nonionic oligomer and anionomer was used to improve the thermal stability of nonionic dispersions. However, in this study, to obtain synergistic effects on the thermal stability of the PMUA emulsion and the mechanical properties of UV-cured films, PMUA600 was mixed with other PMUA having different chain lengths of polyoxyethylene. The thermal stability of emulsions and the mechanical properties of UV-cured films were also investigated.

EXPERIMENTAL

Materials

In the synthesis of PMUA, poly(tetramethylene glycol) (PTMG, M_w = 1000, Hyosung BASF) was dried and degassed at 60°C under a vacuum. 2,4-Toluene diisocyanate (TDI, Junsei Chemical Co.) was purified by filtration. 2-Hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co.) and poly(ethylene glycol) (PEG, M_w = 600, 1000, 2000, 4000, and 6000 Junsei Chemical Co.) were used without further purification. Benzophenone (Janssen) as a photoinitiator, triethylamine (TEA, Junsei Chemical Co.), and t-butyl hydroperoxide (Junsei Chemical Co.) were used.

Table I   The Molar Ratio of PMUA Synthesis

	TDI	2-HEMA	PTMG	PEG
PMUA600	0.2	0.12	0.1	0.08
PMUA1000	0.2	0.12	0.1	0.08
PMUA2000	0.2	0.12	0.1	0.08
PMUA4000	0.2	0.12	0.1	0.08
PMUA6000	0.2	0.12	0.1	0.08

Synthesis of PMUA[11]

The PEG-modified urethane acrylates (PMUA) were synthesized by three-step processes. The molar ratio of the reactants is summarized in Table I. These reactions were carried out in the four-necked glass reactor equipped with a stirrer, a reflux condenser, thermometer, and nitrogen inlet system.

In the first step, TDI was poured into the four-necked glass reactor in a N_2 atmosphere. Then, PTMG was dropped into the reactor at 35°C and the reaction temperature was increased to 45°C so that the isocyanate group of TDI reacted with the hydroxy groups of PTMG. This temperature was maintained for 7 h to retain an acceptable rate of reaction and then the temperature was lowered slowly to reduce isocyanate levels. The change of the NCO value during the reaction was determined using the dibutylamine back-titration method to determine the end point of the reaction.

In the second step, 2-HEMA was added slowly into the reactor to react with the residual isocyanate group at 45°C for 4 h, which introduced a reactive vinyl group into the molecular end. The temperature was increased to 75°C to eliminate unreacted isocyanates.

In the third step, PEG was poured slowly into the reactor to react the hydroxy group of PEG with the residual isocyanate, which made it possible to introduce polyoxyethylene chains into the molecular end as hydrophilic groups. The reaction end point was determined by the disappearance of NCO stretching peak (2270 cm^{-1}) through IR spectroscopy. In our previous study,[11] the molecular structure of PMUA was analyzed, and when the molecular weight of PEG was 600, PMUA showed the best emulsification effects. The schematic presentation of molecular structure of PMUA was illustrated in our previous article in detail.[9,11]

Preparation of PMUA Emulsions

All PMUA emulsions were prepared by a phase-inversion emulsification process.[12] First, PMUA
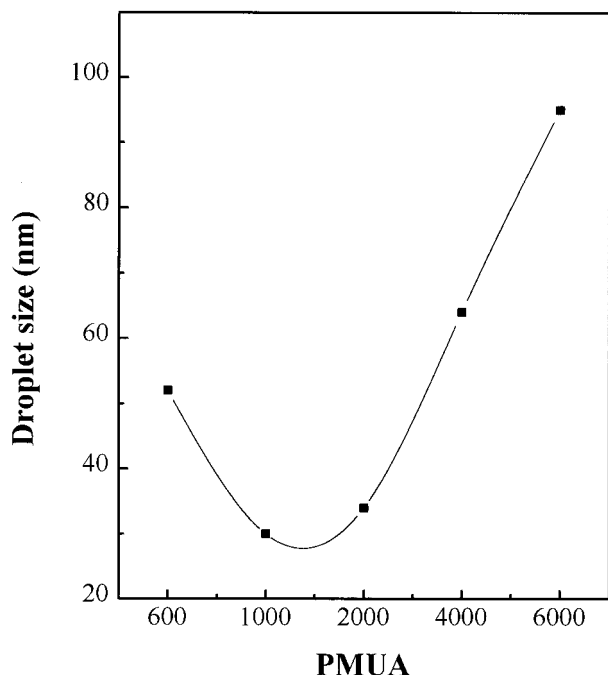
Figure 1   The sizes of droplets of PMUA emulsions.

was put into a 100 mL beaker and stirred slowly until the PMUA resin was melted. Then, distilled deionized water (DDI water) was dropped slowly while stirring 380 rpm. To protect the water evaporation, a silicone rubber plate was used for the packing beaker.

To exclude the effects of the surfactant on physical aggravation, all emulsions were prepared without using a surfactant. The solid content of emulsions was fixed at 33.3%.

UV-curing Formulation and Process[7]

Benzophenone, 3 wt %, as the photoinitiator and *t*-butyl hydroperoxide, 2 wt %, which was used for the postthermal cure, were added in a PMUA resin and mixed. Benzophenone was the bimolecular initiator, so a small amount of TEA was added as a sensitizer for benzophenone. This mixture was emulsified by soap-free emulsification and coated thinly on the glass frame. Water was evaporated at 70°C for 1 day. Then, a UV-ray was irradiated using a UV-lamp (450 W, Ace Glass Co.) for 5 min. This time was determined by ATR spectroscopy. A twisting vibrational peak of the vinyl group appeared at 820 cm^{-1}. So, the end point of polymerization could be determined by the disappearance of this peak. The postcure was executed for 2 h. In this way, UV-cured films hav-

ing 0.5 mm thickness were obtained and used in the measurement of coating and mechanical properties.

Measurements

The size of the droplet emulsions was measured using a Brookhaven laser light-scattering instrument (BI9000AT, 2MI98631 PM tube, Ar — Ne laser). The change of viscosity of the emulsions with temperature was measured using a Brookfield synchrolectric viscometer with a spindle LVT no. 1–4. To investigate the interfacial activity of PMUA resins, the interfacial tension of the water/benzene interface was measured by the Du Nouy ring method (Fisher Scientific Co. Surface Tentiomat 21).[9]

Characterization of Coating Properties and Mechanical Properties[7]

Pencil hardness, stain resistance, and contact angle were measured as coating properties. The pencil hardness of the cured film was determined by the ASTM "Standard method for film hardness
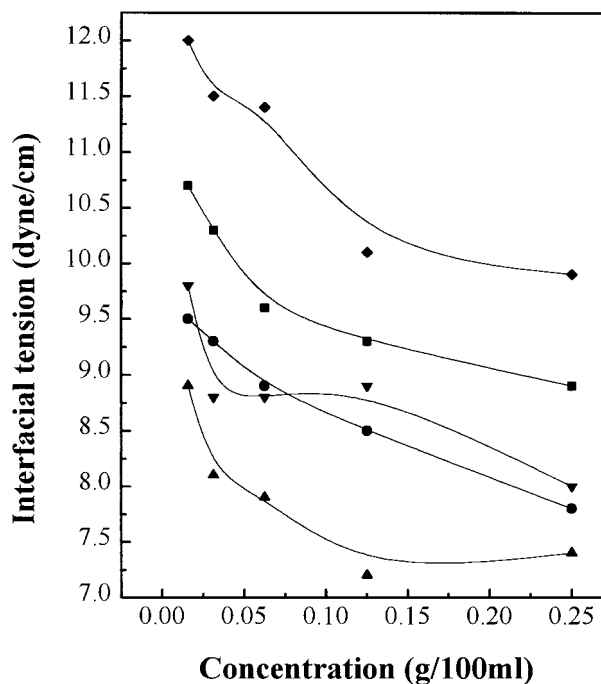
Figure 2   The change of adsorption of PMUA at the water/benzene interface as a function of concentration: (—■—) PMUA600; (—●—) PMUA1000; (—▲—) PMUA2000; (—▼—) PMUA4000; (—◆—) PMUA6000.
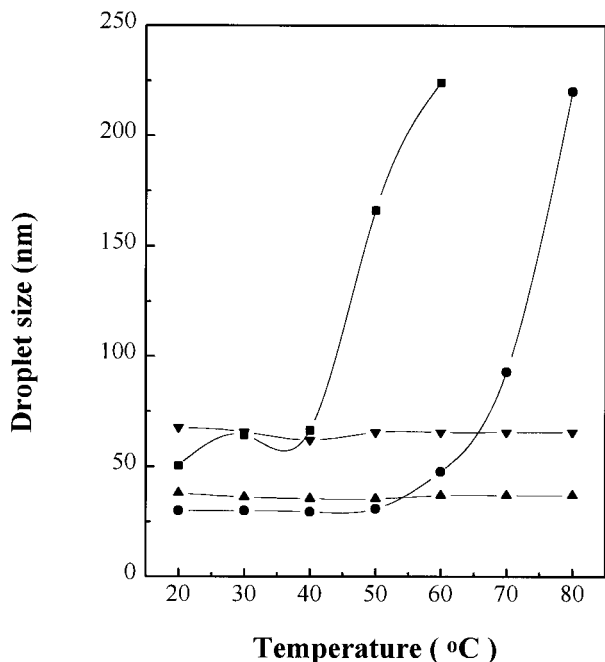
Figure 3 The change of the size of droplet of PMUA emulsions with temperature: (— ■ —) PMUA600; (— ● —) PMUA1000; (— ▲ —) PMUA2000; (— ▼ —) PMUA4000; (— ◆ —) PMUA6000.

by pencil test" method D 3364-74, which was decided on by the existence of a scar when we drew a line on the surface of film with various hardness pencils. According to ASTM D 3023-87, the stain resistance was determined by applying oil ink to the cured film and seeing if the stain remains or if it can be removed by cleansing with ethanol after 5 min. The contact angle was measured as an indirect method for the examination of adhesion (Erma contact angle meter, Model G-1). Mechanical properties were measured three times with a Hounsfield; this measurement was taken with a load cell capacity of 50 kgf and a crosshead speed of 5 mm/min.

RESULTS AND DISCUSSION

In our previous article,[7] soap-free emulsion of PMUA600 showed high centrifugal, mechanical, and pH stabilities; however, the thermal stability of the PMUA600 emulsion and mechanical properties of its UV-cured films were relatively low. Therefore, to obtain a high thermal stability of the emulsions and improved mechanical properties of UV-cured films, a series of PMUA were prepared using five types of PEG having different molecular

weights. The droplet sizes of PMUA emulsions are illustrated in Figure 1.

The size of the droplets of PMUA emulsions is varied with the molecular weight of the PEG used in the synthesis of PMUAs. PMUA1000 and PMUA2000 show the smallest droplet size of emulsion. These results are due to the differences of interfacial activity between five types of PMUAs containing different chain lengths of polyoxyethylene. It can be thought that the interfacial activity of PMUA600 is inferior to that of PMUA1000 and PMUA2000, because PMUA600 has the smallest polyoxyethylene chain-stabilizing emulsion droplet.[13] For PMUA4000 and PMUA6000 having a longer chain length than that of PMUA1000 and PMUA2000, droplet sizes of their emulsions are larger than those of the PMUA1000 and PMUA2000 emulsions, which are due to the mobility of polyoxyethylene chains. In the case of PMUA4000 and PMUA6000, the mobility of polyoxyethylene chains decreases owing to the higher molecular weight of polyoxyethylene, causing the degree of orientation of these chains into the water phase to decrease. The chain mobility of polyoxyethylene groups will be confirmed below.

To investigate the adsorption isotherm of
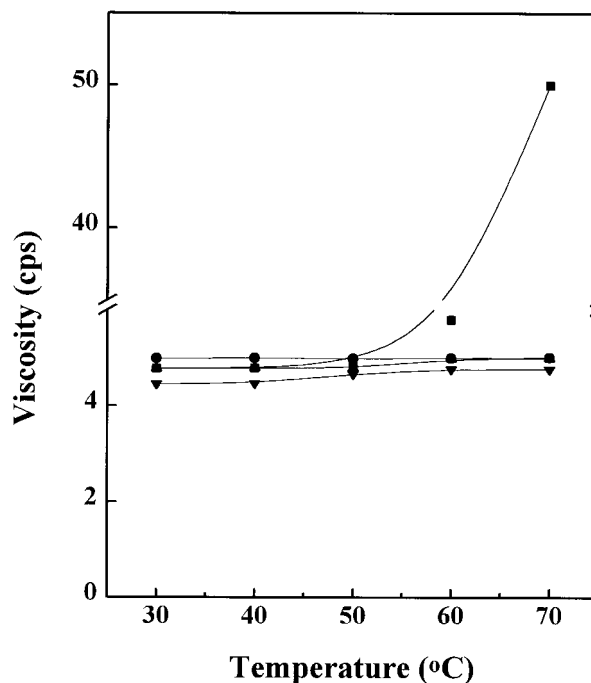
Figure 4 The change of viscosity of PMUA emulsions as a function of temperature: (— ■ —) PMUA600; (— ● —) PMUA1000; (— ▲ —) PMUA2000; (— ▼ —) PMUA4000; (— ◆ —) PMUA6000.
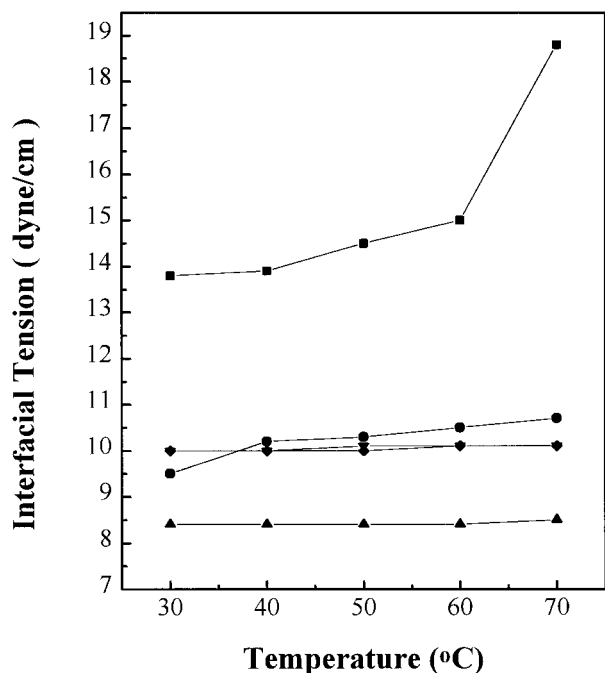
Figure 5 The change of adsorption of PMUA at the water/benzene interface as a function of temperature: (—■—) PMUA600; (—●—) PMUA1000; (—▲—) PMUA2000; (—▼—) PMUA4000; (—◆—) PMUA6000.

PMUA at the water/benzene interface, PMUA was dissolved in benzene; then, this solution was brought into contact with water to form an interface. The hydrophilic parts of PMUA are oriented toward the water phase and the hydrophobic parts are dissolved in benzene. Therefore, as interfacial activity increases, the degree of the polyoxyethylene chain on the interface is increased and interfacial tension decreases.

Figure 2 shows the adsorption behavior of five types of PMUA at the water/benzene interface. As expected, PMUA1000 and PMUA2000 show the lowest interfacial tension. The tendency of the droplet size was similar to that of the interfacial activity. It can be concluded that the interfacial activity of PMUA is greatly influenced by the chain length of polyoxyethylene, which is confirmed by measuring the adsorption behavior of PMUA.

The Thermal Stability of PMUA Emulsions

The thermal stability of PMUA emulsions was measured using a light-scattering measurement. The change of the size of droplets of PMUA emulsions with increasing temperature between 20 and 80°C was measured and is illustrated in Figure 3.

The size of the droplets of PMUA600 and PMUA1000 emulsions increased abruptly at 40 and 60°C, respectively. These results indicate that as temperature is increased the PMUA600 and PMUA1000 emulsions were coagulated to each other. In the case of PMUA2000, PMUA4000, and PMUA6000, however, the size of the droplet of emulsions remained unchanged with the increase of temperature, indicating that these emulsions are stable irrespective of temperature. These results are due mainly to the difference of hydrophilicity between five kinds of PMUA.

When the droplets of the emulsion are aggregated owing to the droplet coalescence, the viscosity of the emulsion increases. Therefore, the stability of the emulsion at higher temperature could be determined by the measurement of the viscosity change of the emulsion as a function of temperature. Figure 4 shows the viscosity changes of PMUA emulsions as a function of temperature. In the case of PMUA600 and PMUA1000, the viscosity of the emulsions increased with increasing temperature; however, the viscosity of PMUA2000, PMUA4000, and PMUA6000 remain unchanged with temperature, indicating that emulsions of PMUA2000, PMUA4000, and PMUA6000 are stable at higher temperature.

Coagulation of droplets is due mainly to the decrease in interfacial activity of PMUA. In other words, the hydrophilicities of the polyoxyethylene chain of five kinds of PMUA are different at higher temperature, so these PMUA resins have a different interfacial activity at higher temperature. Therefore, to verify the decrease of the interfacial activity of PMUA at higher temperature, the change of adsorption behavior of PMUA was measured as function of temperature and is illustrated in Figure 5.

Table II   Coating Properties of UV-cured PMUA Films

	PMUA600	PMUA1000	PMUA2000	PMUA4000	PMUA6000
Pencil hardness	6H	6H	6H	6H	6H
Stain resistance	Good	Good	Good	Good	Good
Contact angle	28.3	40	41.3	70.2	74.8
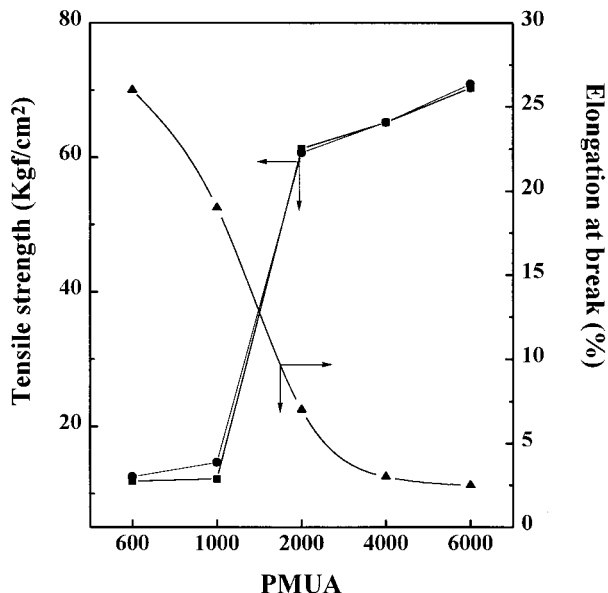
Figure 6 Tensile strength and elongation at break of PMUA series: (— ■ —) tensile strength (emulsion type); (— ● —) PMUA1000, tensile strength (bulk type); (— ▲ —) elongation at break (emulsion type).

Figure 7 The sizes of droplet of mixed-type PMUA emulsions: (—■—) PMUA2000; (—●—) PMUA4000; (—▲—) PMUA6000.
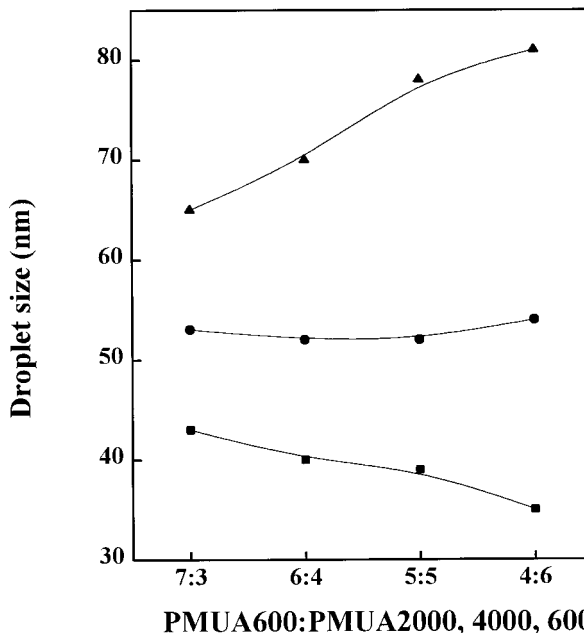
The interfacial tension of PMUA600 and PMUA1000 was increased at 40 and 70°C, respectively. For PMUA2000, PMUA4000, and PMUA6000, however, the interfacial tension was not changed with temperature, indicating that the interfacial activity was not changed with increasing temperature.

Therefore, it can be concluded that the emulsions prepared using PMUA600 and PMUA1000 are relatively unstable at higher temperature. In the case of the PMUA2000, PMUA4000, and PMUA6000 emulsions, however, they show a higher thermal stability, indicating that the thermal stability of the emulsion is improved with increase in the chain length of polyoxyethylene.

## Coating and Mechanical Properties of UV-cured Films

Table II shows the pencil hardness and stain resistance of UV-cured films of PMUA. The pencil hardness and stain resistance of UV-cured films are good irrespective of the chain length of polyoxyethylene.

Hydroxy groups of the cured film influence the adhesion of films on the substrate, because hydroxy groups form hydrogen bonding with oxygen on the substrate surface. Therefore, the contact angle is generally used as an indirect method of
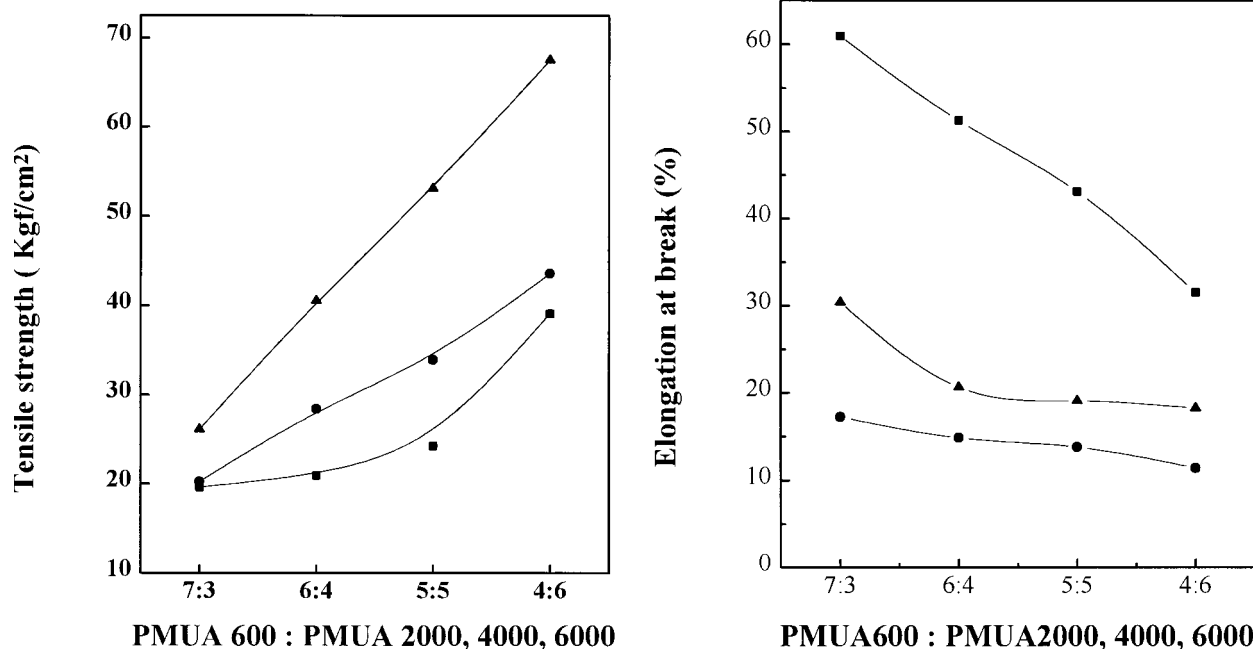
adhesion measuring.[14,15] In other words, as the number of hydroxy groups on the surface increase, the contact angle of the films to water decreases, so the adhesive ability of the film is increased.
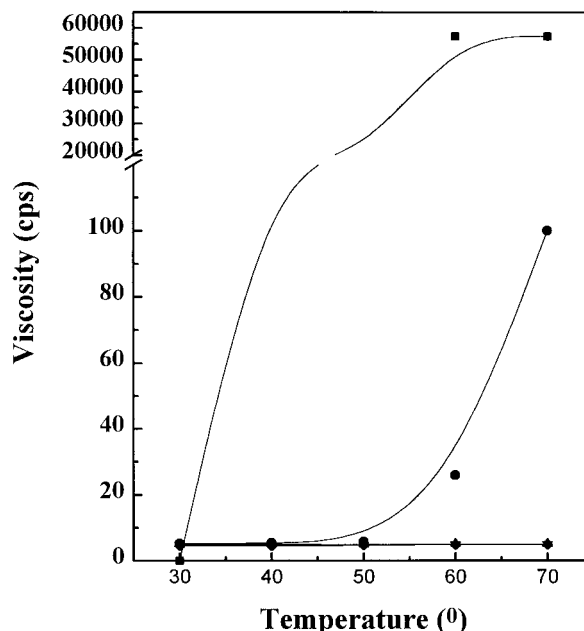
Figure 8 Viscosity of mixed-type PMUA2000 emulsions: (— ■ —) 7 : 3; (— ● —) 6 : 4; (— ▲ —) 5 : 5; (— ▼ —) 4 : 6.

Figure 9 (a) Tensile strength of mixed-type PMUA: (— ■ —) PMUA2000; (— ● —) PMUA4000; (— ▲ —) PMUA6000. (b) Elongation at break of mixed-type PMUA: (— ■ —) PMUA2000; (— ● —) PMUA4000; (— ▲ —) PMUA6000.

The contact angle of the UV-cured films of PMUA is also summarized in Table II. As the chain length of polyoxyethylene increases, the contact angle also increases, indicating that the adhesive ability is decreased with increase of the chain length of polyoxyethylene.

The mechanical properties of UV-cured films of PMUA was investigated by tensile strength and elongation at break and are represented in Figure 6. As the chain length of polyoxyethylene increases, the tensile strength increases but elongation at break decreases. PMUA6000 shows the highest tensile strength. The tensile strength of the UV-cured film is increased abruptly at PMUA2000. UV-cured films of PMUA4000 and PMUA6000 having a relatively high tensile strength, however, show a very low elongation at break.

The Thermal Stability and Mechanical Properties of Mixed-type PMUAs

For PMUA600, its emulsion showed a low thermal stability and its UV-cured films have relatively low mechanical properties. PMUA2000, PMUA4000, and PMUA6000 have good thermal stability and relatively high tensile strength; however, they were very brittle. Therefore, to obtain UV-cured films having good mechanical proper-

ties and good thermal stability of emulsions, PMUA600 and the other PMUAs were mixed at the weight ratio of 7 : 3, 6 : 4, 5 : 5, and 4 : 6. The size of the droplets of mixed PMUA emulsions are illustrated in Figure 7. Emulsions prepared using the mixture of PMUA600 and PMUA2000 show the smallest droplet size, because PMUA2000 has the highest interfacial activity. To investigate the change of thermal stability of mixed-type PMUA emulsions, the thermal stability of the emulsion was measured by the viscosity method and is illustrated in Figure 8.

In the case where the weight ratio of PMUA600 to PMUA2000 is 7 : 3, the viscosity increases at 70°C; however, viscosities of other mixtures including the mixtures of PMUA600, PMUA4000, and PMUA6000 remain unchanged with increase of temperature, indicating that most of the mixed-type PMUA emulsions have good thermal stability. In other words, the thermal stability of the PMUA600 emulsion improved by mixing it with PMUA2000, PMUA4000, and PMUA6000.

The mechanical properties of mixed-type PMUA are illustrated in Figure 9. The tensile strength and elongation at break of mixed-type PMUAs are improved in comparison with PMUA600. Especially, for the mixture of PMUA600 and PMUA2000, the most favorable properties in the aspects of thermal stabil-

ity and mechanical properties can be obtained. Additionally, the brittleness of PMUA4000 and PMUA6000 can be improved by mixing them with PMUA600.

CONCLUSIONS

The thermal stability of nonionic PMUA emulsions and their mechanical properties were improved with increase of the chain length of polyoxyethylene. PMUA2000, PMUA4000, and PMUA6000 showed relatively high tensile strength, and their emulsion is thermally stable at higher temperature; however, their UV-cured films were brittle. To improve the thermal stability and mechanical properties of PMUA600 and the brittleness of PMUA2000, PMUA4000, and PMUA6000 films, three types of PMUA which have a relatively long chain length of polyoxyethylene were mixed with PMUA600. Finally, PMUA having a good thermal stability of nonionic emulsions and improved mechanical properties could be obtained.

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