Polymer Bulletin 38, 287–294 (1997)

Polymer Bulletin

Preparation of UV curable emulsions using PEG-modified urethane acrylates and their coating properties
III: Effects of epoxy acrylate

Kyung-Do Suh[1], **Yong Seok Chon**[1], **Ju Young Kim**[2,*]

[1] Department of Industrial Chemistry, College of Engineering, Hanyang University,
Seoul 133-791, Korea
[2] School of Chemical Engineering, Olin Hall, Cornell University,
Ithaca, NY 14853-5201, USA

Received: 13 September 1996/Revised version: 27 November 1996/Accepted: 2 December 1996

Abstract

Water-dispersible UV-curable urethane acrylate emulsions were prepared with polyethylene glycol (PEG) - modified urethane acrylates (PMUA), containing terminal hydrophilic polyoxyethylene chains. To improve physical properties of PMUA, epoxy acrylate (EA) having high thermal stability and hardness, was mixed with five kinds of PMUA containing different chain lengths of polyoxyethylene (POE). For PMUA/EA mixtures, the composition ratio of EA to PMUA and the chain length of POE greatly influenced the size of droplets of emulsions and the physical properties of their cured films. At higher EA to PMUA ratio, the physical properties decreased, which was due to phase separation between EA and PMUA. Phase separation was confirmed by scanning electron microscopy.

INTRODUCTION

Waterborne coatings have been widely utilized recently in industrial coatings, because this kind of coating make it possible to control pollution, to reduce fire risks, and to improve aspects of occupational health and safety. The use of water soluble or dilutible UV or EB curable formulations may appear contradictory from an energy saving view point, because it is necessary to remove the water before irradiating the formulations. However, the application viscosity of water-based inks and coatings is much reduced by water without the volatile organic compounds (VOC), so these materials find widespread use 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 of polymer has been generally done by incorporating pendant hydrophilic groups into the backbone[3-5]. However, for ionic water dispersible resins, a neutralizing agent has to be used to neutralize acid groups of polymers, which might release potentially harmful organic amines. In the case where a nonionic pendant hydrophilic group is incorporated, the synthesis of prepolymer having isocyanate end groups and POE pendant groups in the same molecule must be carried out by complicated reactions[6].

In our previous papers[7-9], PMUA was simply synthesized by the reaction of PEG with

---

[*] Corresponding author

residual isocyanate groups of urethane acrylate. These molecules contained terminal nonionic hydrophilic POE groups, so PMUA could act as a polymeric surfactant and be emulsified without the use of an external surfactant. Emulsions and cured films of PMUAs showed low thermal stability and tensile strength, because the hydrophilicity of POE groups of PMUA decreased at higher temperature and urethane acrylate had inherently low physical properties. When PMUA was mixed with urethane anionomer, the thermal stability of the emulsion was improved, however, the physical properties did not much improve[10].

The goal of this study is the preparation of UV curable emulsions using PMUA and EA mixtures to improve the physical property of UV cured PMUA films. Thus, to determine the effect of the EA/PMUA composition on the droplet size of emulsions, viscosity, coating and mechanical properties of cured films will be investigated.

Experimental

Materials

In the synthesis of PMUA and EA, poly(tetramethylene glycol) (PTMG, Mw=1,000, Hyosung BASF), 2,4-toluene diisocyanate(TDI, Junsei Chemical Co.), 2-hydroxy ethyl methacrylate (2-HEMA, Aldrich Chemical Co.), polyethylene glycol (PEG, Mw = 600, 1000, 2000, and 4000, Junsei Chemical Co.), epoxy resin (Kuk-Do Chemical Co, bisphenol A type, 11,500-13,5000 cps at 25°C) and acrylic acid (Junsei Chemicals Co.) were used. (1-hydroxycyclohexyl) phenylmethanone (Irgacure 184, Ciba-Geigy Chemical Co.) and tert-butyl benzoate (Junsei Chemical Co.) were also used as photoinitiator and thermal initiator, respectively.

Synthesis of PMUA and EA

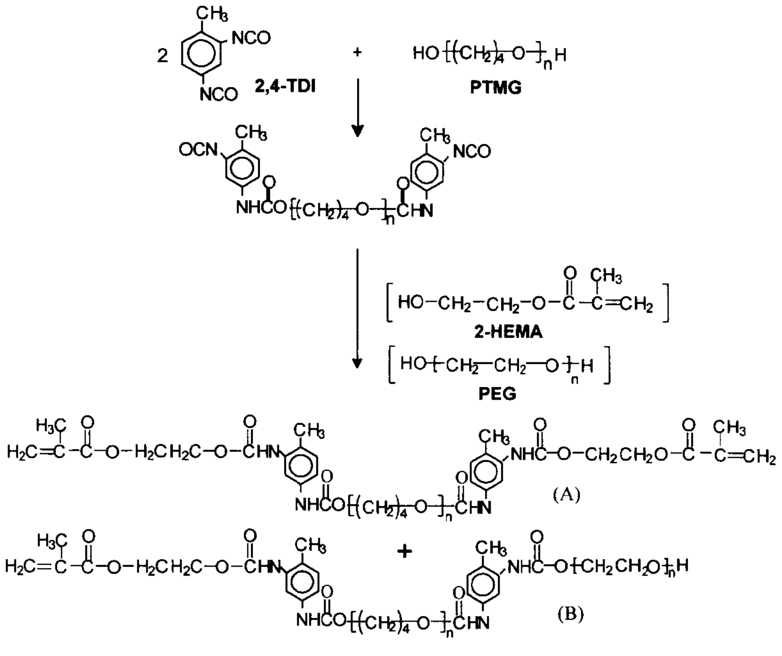
Four types of PMUAs were synthesized by three step processes. The molar ratio of reactants is summarized in Table 1. The reactions were carried out in a 4-necked glass reactor equipped with stirrer, thermometer, reflux condenser and N_2 gas inlet. Detailed procedures was reported in our previous paper[7-8]. The average molecular weight of PMUA and confirmation of these reactions by ^1H NMR and GPC were also reported[7].

EA was synthesized by the reaction of epoxy resin with acrylic acid[11]. This resin was blended with PMUA to incorporate suitable characteristics for UV curable formulation. Scheme 1 shows the molecular structures of EA and PMUA

Preparation of UV curable formulations and UV-curing

An oil solution (10g) 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 was added very slowly until a gel-like phase formed, then remaining water was added gradually to reduce viscosity (Phase inversion emulsification)[12]. The formulation used in the preparation of UV curable emulsions is summarized in Table 2.

In case soap-free emulsions of PMUA/EA mixture were prepared, these resins were mixed prior to emulsification. The UV curing formulation of these mixtures was the same composition as with that of PMUA emulsion.



PMUA

$CH_2{=}CH\overset{O}{C}OCH_2\overset{OH}{C}HR\overset{OH}{C}HCH_2O\overset{O}{C}CH{=}CH_2$

EA

Table 1. The molar ratio of reagents in the synthesis of PMUA using different PEG

Symbols	Reagents	Molar ratio
PMUA600	PTMG/TDI/2-HEMA/PEG 600	1 / 2 / 1.50 / 0.50
PMUA1000	PTMG/TDI/2-HEMA/PEG 1000	1 / 2 / 1.50 / 0.50
PMUA2000	PTMG/TDI/2-HEMA/PEG 2000	1 / 2 / 1.50 / 0.50
PMUA4000	PTMG/TDI/2-HEMA/PEG 4000	1 / 2 / 1.50 / 0.50
PMUA6000	PTMG/TDI/2-HEMA/PEG 6000	1 / 2 / 1.50 / 0.50

The formulations were drawn on a glass plate and then the water was evaporated at 60°C in vacuo. The formulations were cured in air by irradiating with a static UV lamp (450 watt UV lamp, Ace Glass Co.) for 5 mins and postcured at 60°C for 2hrs at reduced pressure[10].

Measurement

The droplet sizes of emulsions were measured using a 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 Synchrolectric Viscometer with spindle LVT No. 1-4.

To investigate the adsorption behavior of PMUA at water/benzene interface, PMUA was dissolved in benzene, then this solution was brought into contact with water to form an interface. The water/benzene interfacial tension was measured by the Du Nouy ring method (Fisher Scientific Co. Surface tensiomat-21)[7-8].

Table 2. Recipe for the preparation of UV Curable emulsions

Symbol	PMUA	EA	DDI water	Benzophenone	t-butyl hydroperoxide	Triethyl amine	PE
PMUA600/EA	4 - 10 g	0 - 6 g	30 g	0.3 g	0.2 g	0.1 g	PE600
PMUA1000/EA	4 - 10 g	0 - 6 g	30 g	0.3 g	0.2 g	0.1 g	PE1000
PMUA2000/EA	4 - 10 g	0 - 6 g	30 g	0.3 g	0.2 g	0.1 g	PE2000
PMUA4000/EA	4 - 10 g	0 - 6 g	30 g	0.3 g	0.2 g	0.1 g	PE4000

Tensile strength of UA cured films were measured with a HOUNSFIELD model Instron at room temperature using a crosshead speed of 5mm/min and load cell capacity of 50kgf. Samples were cut from cured films using an ASTM D1708 die[13]. All measurements are averages of five runs. The engineering stress was calculated based on the initial area of the sample.

Cross-section of PMUA gels were analyzed with scanning electron microscopy (Philips C. XL-30). The conventional secondary electron imaging technique was used. Samples were coated with a thin layer of gold-palladium to reduce any change build-up on the fracture surface.

RESULTS AND DISCUSSION

Fig. 1 illustrates the change of droplet sizes of emulsions prepared with PMUA/EA mixtures as a function of composition ratio. As the composition ratio of EA to PMUA increases, droplet sizes of emulsions prepared by PMUA1000, 2000, and 4000 remain unchanged. However, in the case of the emulsion prepared with PMUA600, the droplet size increases significantly. Additionally, at higher EA/PMUA composition ratio, PMUA600/ EA and PMUA2000/EA show largest and smallest size of droplets, respectively. These results are due to the difference of interfacial activity between four types of PMUAs. In other words, PMUA 2000 and 600 synthesized with PEG 2000 and 600, has the highest and lowest interfacial activity among the four types of PMUA, respectively. Thus, to confirm the difference of interfacial activity between the four types of PMUAs, the adsorption behavior of PMUA at water/benzene interface was evaluated and illustrated in Fig. 2. If PMUA containing POE chains could be located and adsorbed at the O/W interface, the interfacial tension of water/benzene would be decreased and changed with the degree of location at O/W interface.

As expected, PMUA600 shows the highest interfacial tension, indicating that PMUA600 has the lowest interfacial activity because it has the shortest POE chains. The interfacial tension of PMUA4000 is higher than that of PMUA2000, even though these resins have longer POE groups than PMUA2000. These results are due to the decrease of orientation of

POE chains, because the mobility of POE chains of PMUA 4000 decreases with the increase of chain length of POE.

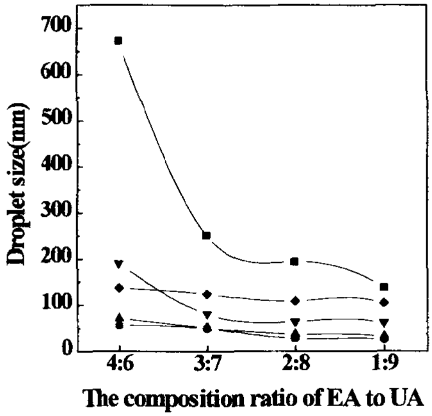


Fig. 1. The change of size of droplets of PE emulsions as a function of composition ratio of EA to PMUA (-■- PE600, -●- PE 1000, -▲- PE2000, -▼- PE 4000 -◆- PE6000)

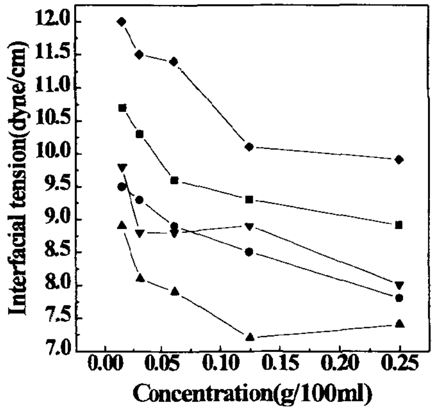


Fig. 2. Adsorption behavior of PMUA at water/benzene interface at different concentrations (-■- PMUA 600, -●- PMUA1000, -▲- PMUA 2000, -▼- PMUA 4000 -◆- PMUA 6000

Fig. 3 shows the viscosity change of PMUA/EA emulsions (PE emulsions) with temperature. When the stability of emulsion decreases with the increase of temperature, droplets of emulsions aggregate, so their viscosity increases[14]. In the case of PE 600 and PE 1000 emulsions, the viscosity increases with increasing temperature. For PE 2000 and 4000 emulsions, however, the viscosity remains unchanged with the increase of temperature, indicating that these emulsions are stable at higher temperatures. These results are mainly attributed to the change of interfacial activity of PMUA. In other words, the hydration of POE chains of PMUA by water decreases with the increase of temperature, so the hydrophilicity of these groups decreases and the interfacial activity of PMUA decreases[7, 15]. Therefore, to confirm the change of hydrophilicity of PMUA with temperature, the adsorption behavior of PMUA at water/benzene interface at different temperatures was investigated and illustrated in Fig 4. The interfacial tension of PMUA 600 and 1000 increase at 40°C and 70°C, respectively, because the hydrophilicity of POE chains decreases with an increase of temperature. For PMUA 2000 and 4000, the interfacial tension remains unchanged with temperature. These results indicate that the hydrophilicity of PMUA 2000 and 4000 can be maintained at higher temperature owing to the longer POE chains.

Fig. 5 illustrates the tensile strength of UV-cured films prepared with PMUA/EA mixtures. For PE 600 and 1000, the tensile strength of cured films increases with the increase of composition ratio of EA. In the case of PE 2000 and 4000, when the composition ratio of EA to PMUA is 2:8 and 1:9, respectively, the tensile strength of the films is maximum.

However, the tensile strength decreases with the increase of EA composition ratio. These results are due to phase separation between EA and PMUA having longer POE chains.

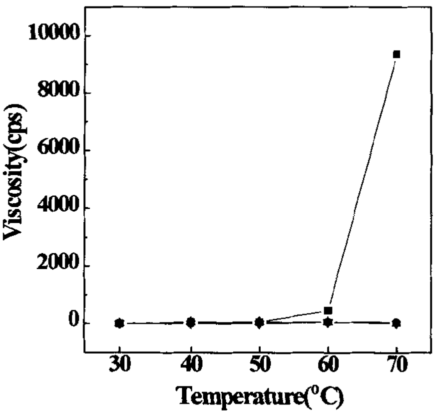


Fig. 3. Viscosity change of PE emulsions as a function of temperature (-■- PE600, -●- PE1000, -▲- PE2000, -▼- PE 4000)

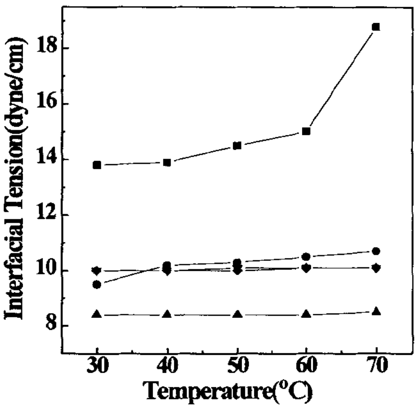


Fig. 4. Adsorption change of PMUA at water /benzene interface as a function of temperatures (-■- PMUA 600, -●- PMUA1000, -▲- PMUA 2000, -▼- PMUA4000)

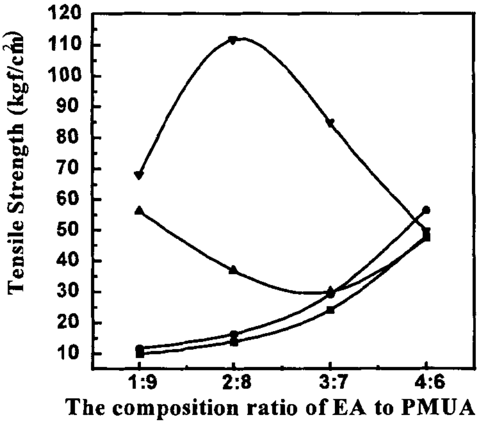
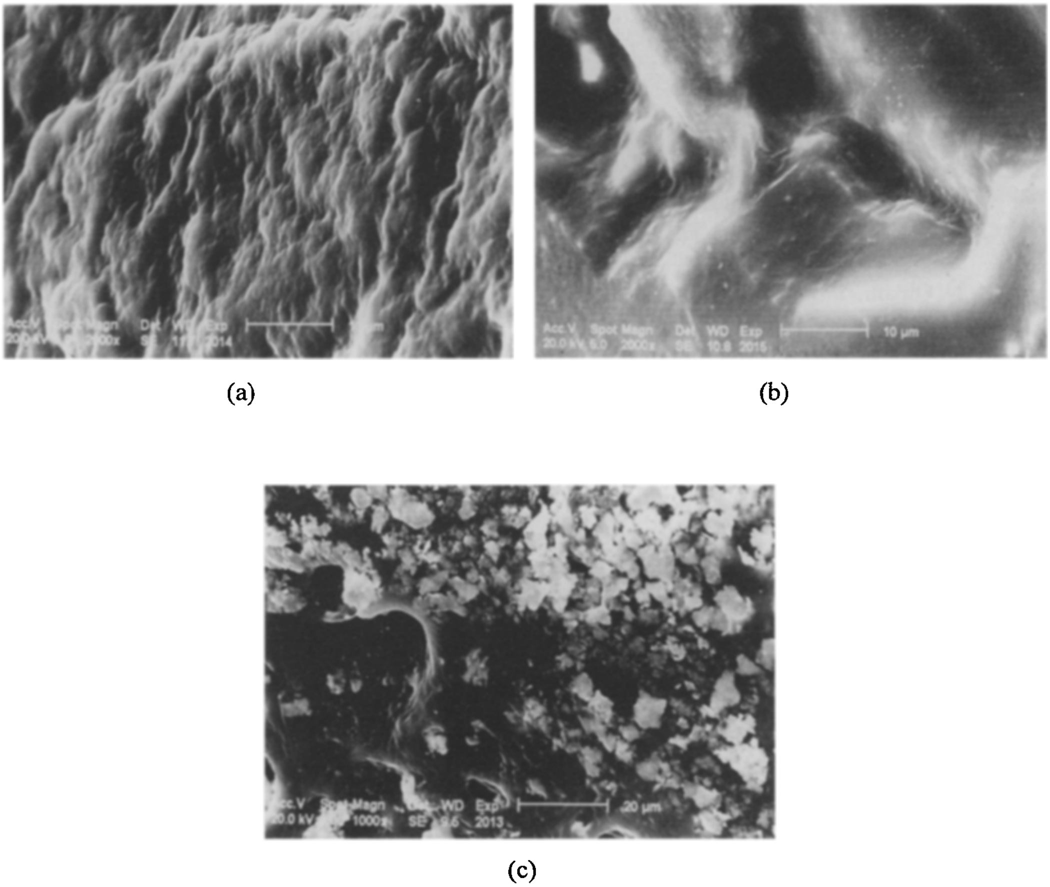


Fig. 5 Tensile strength of UV-cured films of PE emulsions as a function of EA to PMUA composition ratio (-■- PMUA 600, -●- PMUA1000, -▲- PMUA 2000, -▼- PMUA4000)

These results indicate that PMUA 600 and 1000 can be mixed with EA without phase separation. However, for PMUA 2000 and 4000 prepared with higher molecular weight PEG compared with PMUA 600 and 1000, the miscibility with EA decreases with the increase of chain POE length.

Thus, to confirm phase separation between EA and PMUA, cross sections of their cured films were analyzed by scanning electron microscopy as illustrated in Fig. 6. For PMUA 1000 and 4000, when the composition ratio of EA to PMUA is 4:6 and 1:9, the cross-section shows homogeneous morphology. However, in case PMUA4000 is mixed with EA at a composition ratio of 4:6 EA:PMUA, phase-separated EA domains appear in the PMUA matrix.



(a)

(b)

(c)

Fig. 6 Cross-section of UV-cured films prepared by using PE emulsions ((a) PE 1000 EA/PMUA 1000 = 4:6, (b) PE4000 EA/PMUA 4000 = 1:9, (c) PE 4000 EA/PMUA 4000 = 4:6)

CONCLUSION

The POE chain length of PMUA influences greatly the size of droplet and stability of emulsion prepared with PMUA/EA mixtures.

The tensile strength of UV cured films of PMUA could be improved by mixing with EA.

However, in the case of PMUA 2000 and 4000, the tensile strength of the mixture of EA and PMUA decreased because of the incompatibility of PMUA with EA. Therefore, when the composition ratios of PMUA2000/EA and PMUA4000/EA were 6:4 and 2:8, respectively, the smallest droplet size of emulsion and the highest tensile strength could be obtained.

ACKNOWLEDGMENT

This paper was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation, 1996.

REFERENCES

1. S. Kojima, Polym. Eng. Sci (1993), 33(5), 253
2. J. M. Loutz, W. Demarteau, and P. Y. Herze, "Water-Based UV Coating System", Radcure Europe 87 Conference
3. S. L. Hsu, H. X. Xiao, H. H. Szmant, and K.C. Frisch (1984). *J. Appl. Polym. Sci.*, *29*, 2467.
4. N. Ohtani, Y. Inone, H. Mizuoka and K. Itaoh (1994). *J. Appl. Polym. Sci.*, *32*, 2589.
5. S. A. Chen and J. S. Hsu (1993), *Polymer, 34*, 2776.
6. Klaus Noll, U.S. Patent (1974) 3,905,929.
7. J. Y. Kim and K. D. Suh (1996), *Colloid & Polym Sci.*, in press.
8. J. Y. Kim and K. D. Suh (1996), *Macromolecular. Chem & Phys.*, in press
9. M. E. Song, J. Y. Kim and K. D. Suh (1996), J. Coating. Technol., in press
10. J. W. Kim, J. Y. Kim and K. D. Suh (1996), Polymer Bull., 36, 141.
11. M. E. Song, J. Y. Kim and K. D. Suh (1996), *J. Appl. Polym. Sci.*, accepted for publication.
12. Hiromichi and Sagitani (1981), *JAOCS*, **53**, 738
13. ASTM D1708-84 (1991), "Standard Test Method for Tensile properties of Plastics By Use of Microtensile specimens".
14. Vold. R. D., and Mittal. K.L (1972). *J. Colloid & Interface Sci.*, *38*, 451.
15. Scick. M. J (1987) In Schick. M. J, Fowkes. F. M (eds) Nonionic Surfactants, Marcel Dekker, New York and Barsel, pp 525-527.