Preparation of epoxy acrylate emulsion using mixed surfactants and its polymerization

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SUMMARY

A series of epoxy acrylate emulsions were prepared with several surfactants ranging from HLB 12 to 14 at 40°C. For epoxy acrylate emulsion, additives and conditions were established among factors: HLB value of emulsion, agitation speed, water dropping speed, and dropping amount of the deionized water. For emulsion polymereization with water soluble initiator KPS, emulsion was broken during polymerization, because interfacial complex formed by association of surfactant with co-surfactants stabilizing emulsion was weakened by interpenetration of radicals formed at aqueous. Accordingly, the polymerization of epoxy acrylate emulsion was carried out by using oil soluble initiator, AIBN, and the conversion changes with initiator concentration and HLB values were investigated.

INTRODUCTION

Epoxy resins are currently used as coatings, structural adhesives, and advanced composite matrices in many applications involving both the aerospace and electronics industries. However, their applications were limited because of their inherent brittleness. In order to improve this weak point, several methods were proposed: the addition of second polymeric component that phase-separates on curing to the system(1-2), and the addition of functionalized rubbers such as the widely known carboxyl-terminated butadiene-acronitrile copolymers(3).

Ultimate purpose of this paper is synthesis of poly(butyl acrylate) / epoxy acrylate core-shell composite particles to be used as a impact modifier of epoxy resin, instead of blending rubbery or thermoplastic polymers with epoxies. Core-shell composite particles are always prepared by consecutive two stage emulsion polymerization and shell polymer is formed at the first or final stage polymerization(4-6). However, epoxy acrylate generally used in industries has its viscosity from 10,000 to 25,000 cps at 25°C and is insoluble in water. Moreover, the viscosity of epoxy resin used in our experiment was about 11,500~13,500 cps. Therefore, it is impossible to prepare these particles with general consecutive emulsion polymerization. It was attempted to apply the inverted core-shell emulsion polymerization process that epoxy acrylate shell was synthesized by emulsion polymerization prior to prepared poly(butylacrylate) core, and then butyl acrylate monomer was added.

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Thus, to begin with, a stable and fine epoxy acrylate emulsion should be obtained. It was, however, difficult to prepare stable and fine droplet emulsion of epoxy acrylate through the physical emulsion process. Thus, the mixed surfactants and co-surfactants system and surface chemical methods, such as phase inversion emulsification(7), D phase emulsification(8-9) and PIT(phase inversion temperature) emulsification(10-11), should be applied to form epoxy acrylate emulsion. In case of using mixed surfactants system, composed of mixed nonionic surfactants and co-surfactants, such as long chain alcohols(LCA), the droplet size and stability of emulsion are dependent on various factors, such as the mixing ratio of nonionic surfactant, agitation speed, water addition speed, and emulsification temperature. Thus, these emulsification conditions should be investigated to prepare a stable and fine droplet of epoxy acrylate emulsion. The polymerization of epoxy acrylate emulsion, prepared by abovementioned process, was carried out to obtain a high molecular weight epoxy acrylate latex. The effects of variation of initiator concentration, HLB values, and the added inhibitor or kinetics will be investigated in epoxy acrylate emulsion polymerization.

EXPERIMENTAL

Materials
Epoxy resin(the commercial grade of YD-128, 11,500~13,500 cps at 25°C, M_w : 374, Kuck-Do Chemical Co., Ltd.) was diglycidyl ether of bisphenol A. Sorbitan monolaurate(Span 20), sorbitan monopalmitate(Span 40), sorbitan monooleate(Span 60) and PEO(20) sorbitan monooleate(Tween 60) were used in emulsification of epoxy acrylate. All were from Junsei Chemical Co.,Lid. Cetyl alcohol(Hatashi Pure Industries Lid.) and stearyl alcohol(Shinyo Pure Chemicals Co., Ltd.) were used as co-surfactants. 2,2'-azobisiso- butyronitrile(AIBN), recrystallized by absolute methanol, was used as an oil-soluble initiator after drying at 30°C in decompressed condition for 3days. Potassium persulfate(KPS) of Kanto Chemical Co. was used without further purification.

Preparation of epoxy acrylate emulsion
Epoxy acrylate synthesized by ring opening between epoxy resin and acrylic acid had its yield over 99.8%. All ingredients composed of nonionic surfactants, long chain alcohol, and epoxy acrylate were charged in a kettle and maintained the temperature at 40°C. The reaction kettle was equipped with a mechanical stirrer, thermocouples and deionized water dropping system. The agitation speed was 400rpm and dropping speed 0.167g/min. The composition of epoxy acrylate emulsion is listed in Table 1.

Table 1. The composition of the surfactant for the epoxy acrylate emulsion.

HLB value	Epoxy acrylate (g)	water (g)	Nonionic surfactant(g)				Co-surfactant(g)	
			Span 20	Span 40	Span 60	Tween 60	Cetyl alcohol	Stearyl alcohol
12	10	60	0.920			1.080	0.667	0.333
13	10	60	0.604			1.396	0.667	0.333
14	10	60	0.286			1.714	0.667	0.333
12	10	60		0.708		1.292	0.667	0.333
13	10	60		0.464		1.536	0.667	0.333
14	10	60		0.220		0.780	0.667	0.333
12	10	60			0.548	1.452	0.667	0.333
13	10	60			0.358	1.642	0.667	0.333
14	10	60			0.170	1.830	0.667	0.333

Epoxy acrylate emulsion polymerization

Each reaction kettle was equipped with a mechanical stirrer, a reflux condenser, thermocouples and N_2 inlet system. Epoxy acrylate emulsion, prepared by above process ,was placed in the polymerization kettle, and then polymerization temperature was fixed to the initiation temperature of each initiators, AIBN or KPS, within ±0.5°C. Agitation speed was 100rpm. The concentrations of initiators were varied from 1.0wt% to 2.5wt% respectively. For emulsion polymerization with AIBN, the initiator was dissolved in epoxy acrylate containing surfactants, prior to emulsification, then deionized water was added slowly with stirring. On the other hand, KPS was just added in aqueous phase of emulsion.

Measurement of emulsion polymerization conversion

When polymerized latexes were dissolved in absolute methanol, each remained oligomers would be dissolved in methanol. If filtered and dried on decompressed condition, only polymerized fine latex particles only could be obtained. Following equation shows the conversion.

$$Conversion(\%) = \frac{W_d}{W_s \times TCS} \times 100$$

where, W_d : the weight of dried sample(g)
W_s : the weight of extracted sample(g)
TCS:theorethical solid content value

HLB value calculation

The mixing ratio, HLB value of nonionic surfactants, was calculated by the following equation. With this equation, HLB value for each surfactant system could be calculated.

$$H_{WS} = \frac{H_R - H_T}{H_S - H_T} \quad , \quad H_{WT} = 1 - H_{WS}$$

where, H_{WS} : the weight of Span series per 1g
H_{WT} : the weight of Tween series per 1g
H_R : the required HLB value
H_T : the HLB value of Tween series
H_S : the HLB value of Span series

The centrifugal stability of emulsion

The centrifugal stability(12-15) of epoxy acrylate emulsion was determined relatively by the weight ratio of precipitated oil to the one of emulsion sample, after centrifuged on the condition of 15,000rpm for 10min. The centrifugal stability was calculated by next equation

$$Precipitation(\%) = \frac{W_O}{W_E} \times 100$$

where, W_O : the weight of precipitated oil(g)
W_E : The weight of emulsion sample(g)

RESULTS AND DISCUSSION

Emulsification of epoxy acrylate
According to our previous research, oligomers just like epoxy acrylate and urethane acrylate couldn't be emulsified easily with monomeric surfactants(16). Thus, mixed nonionic surfactants and co-surfactants system, and surface chemical method such as inversion emulsification were employed to produce stable emulsion and fine droplets. Co-surfactants, long chain alcohols were used to elevate the efficiency of interfacial activity of surfactants. Because of their less hydrophilic group(the hydroxyl group) and the smaller size of head group: they shows a efficient adsorption on the oil surface and a reducing surface tension by the association with the mixed surfactants(17).

When mixed surfactants and co-surfactants were at a weight ratio of 2 : 1 and cetyl and strearyl alcohol also 2 : 1, stable epoxy acrylate emulsion could be prepared, which indicated that good orientation and packing of mixed surfactants and co-surfactants were formed on the interface at that ratio.

It has been known that one of the decisive factor influencing on emulsion stability containing blend of Span and Tween series is the mixing rate, HLB value. Every emulsions has its own region of maximal stability at characteristic HLB value. Fig.1 shows the influence of HLB to the various Span and Tween pairs: Span 20-Tween 60, Span 40-Tween 60, and Span 60-Tween 60. It could be found that as the HLB of surfactants is increasing, so to speak, the hydrophilicity of surfactant is increasing, the stability of emulsion was relatively increased.
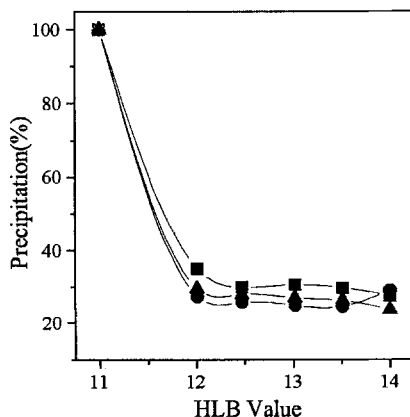

Fig.1 Emulsion stability with the variation of HLB value. Each surfactants composition was Span 20 + Tween 60 +LCA(-■-), Span 40 + Tween 60 + LCA(-▲-), and Span 60 + Tween 60 + LCA(-●-)

Emulsion polymerization using water-soluble initiator, KPS
In case of using KPS, two kinds of initiation mechanism are possible. One is that initiator radicals in water phase initiate emulsion polymerization by penetrating monomer droplets. The other is that oligomer radicals produced by the reaction of oligomers with initiators formed in water phase interpenetrate into droplets from the water phase to initiate polymerization(18-19). When the emulsion polymerization of epoxy acrylate was carried

by using water soluble initiator, KPS, epoxy acrylate was broken during polymerization. This result is attributed to the weakening of interfacial complex of epoxy acrylate emulsion: For emulsion polymerization with water soluble initiator, the initiator radicals formed at aqueous phase adsorb and interpenetrate oil droplets to initiate polymerization. Thus, in this process of initiator penetration, the interfacial complex stabilizing epoxy acrylate emulsion was weakened or destroyed.

In order to certify the weakening of intermolecular complex formed on the oil/water interface, the changes of oil precipitated percentage with the placing time at 55°C were measured(Fig.2).
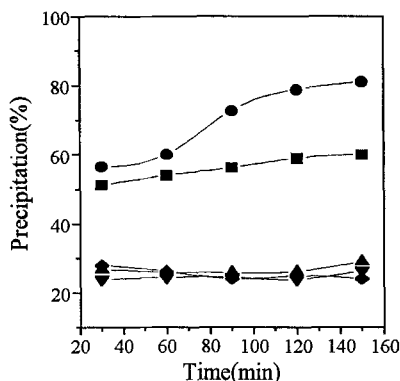
Fig.2   Thermal stability with the placing time for epoxy acrylate emulsion containing additives. Curve A(-●-) contained KPS in aqueous phase, curce B(-■-) AIBN in oil droplets, curve C(-◆-) KPS and HQ in aqueous phase, curve D(-▼-) nothing, curve E(-▲-) AIBN and HQ in oil droplets. HQ concentration was 1wt%

Curve D not having any additives shows a slight increase of oil precipitation due to the melting of long chain alcohols on the intermolecular complex. However, curve A containing KPS in aqueous phase shows a shear linear increment of oil precipitation, due to the phase separation between epoxy acrylate and water. On the other hand, curve B containing oil-soluble initiator, AIBN, shows a better stability than that of KPS. From this results, it could be guessed that AIBN radicals generated in the oil droplet have a less intermolecular destruction effect in comparison with those of KPS generating in the aqueous phase, as KPS radicals might attack the intermolecular complex. This is the reason why emulsion using KPS was destroyed around the initiation temperature of KPS.

In order to verify the intermolecular destruction effect, KPS radicals in the aqueous phase was seized by hydroquinone(HQ). As shown in Fig.2, there wasn't any special change of oil precipitation compared with curve D. Similar result could be obtained in case of curve E containing HQ in oil droplet. Accordingly, the destruction of intermolecular complex on the oil/water interface was originated in the adsorption and interpenetration of initiator radicals formed by water-soluble initiator, KPS.

In case of curve A, it was hard to get a precise conversion value, for the destruction of intermolecular complex by KPS radicals resulted in phase separation after 40min later. However, the precipitation of emulsion using AIBN(Curve B) increased slightly until the conversion reached about 83% (Curve A in Fig.5). This indicated that the stability of droplets nearly unchanged with increment of conversion. Therefore, we neglected the

conversion effect in our system, which is necessary in the comparison of the stability of droplets, and just focused on the precipitation of droplets after centrifuging for the stability comparison.

Emulsion polymerization using oil-soluble initiator, AIBN

In emulsion polymerization using AIBN, it might be said that there were not any adsorption and interpenetration of radicals or oligomeric free radicals from the water phase to the oil/water interface. Therefore, AIBN radicals and oligomeric free radicals generated in oil droplets and polymerized in oil droplets. Fig.3 shows the effect of AIBN concentration in emulsion polymerization of epoxy acrylate at 55°C.
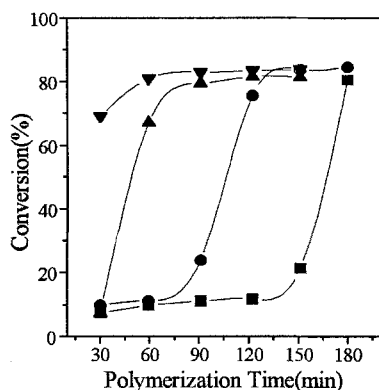

Fig.3 Effect of AIBN concentration in emulsion polymerization.1.0wt% AIBN(-■-), 1.5wt% AIBN(-●-), 2.0wt% AIBN(-▲-), 2.5wt% AIBN(-▼-) were used. Span 40, Tween 60 and LCA were used as surfactants.
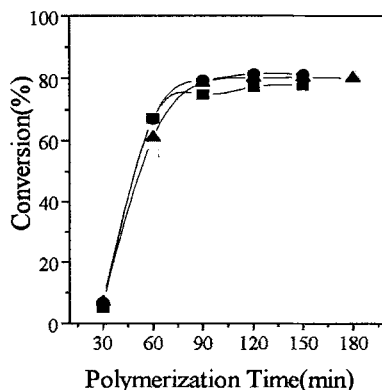

Fig.4 The effect of HLB value to conversion change in emulsion polymerization. Span 40, Tween 60 and LCA were used as surfactants. HLB 12(-■-), HLB 13(-▲-), HLB 14(-●-)

The concentrations were varied from 1wt% to 2.5wt%(based on oil). The polymerization rate was increased with the increase of initiator concentration. The overall conversion rate increased with the amount of initiator. Fig.4 shows the effect of HLB of surfactants in emulsion polymerization at 55°C. As mentioned above in Fig.2, Stable HLB region had the relatively same tendency in polymerization conversions.

In order to verify that AIBN radicals generated in oil droplet and epoxy acrylate polymerized *in situ*, polymerization inhibitor, HQ was located in oil droplets and aqueous phase, respectively.
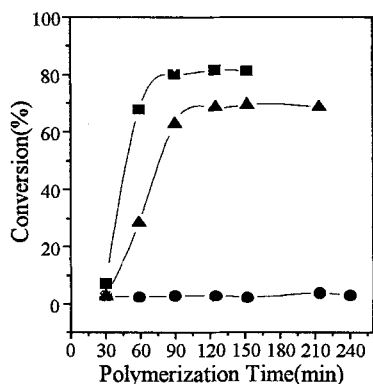

Fig.5 Effect of initiator(AIBN) and polymerization inhibitor(HQ) in emulsion polymerization. Curve A(-■-) is the conversion of emulsion containing AIBN, curve B (-▲-) the conversion of emulsion containing HQ in aqueous phase and AIBN in oil droplets, curve C(-●-) the conversion of emulsion containing HQ and AIBN in oil droplets. HQ concentration was 1wt%, and AIBN 2wt%. The surfactants composition used was the same as Fig.4

Fig.5 shows the polymerization rate in each case. If HQ is located in oil droplets, epoxy acrylate emulsion could not be polymerized due to HQ's radicals seizing. However, emulsion having HQ in water phase(curve B) shows similar polymerization rate to that having AIBN in oil droplets(curve A). These results indicated that AIBN radicals generated in oil droplets, however, the difference of polymerization rate between curve A and curve B could be explained by the fact that very small amount of AIBN radicals desorpted from oil droplets were captured by HQ in aqueous phase.

In this research, all emulsion droplets and the polymerized particle size were about 1μm. Following table shows the emulsion droplet sizes and the polymerized particle sizes with the HLB values.

Table 2. Emulsion droplet and the polymerized particle sizes.

HLB value	emulsion droplet size(nm)	polymerized particle size(nm)
12	1085	1094
13	1374	1129
14	1348	1066

CONCLUSION

When the ratio of the mixed surfactants and co-surfactants were 2 : 1 and cetyl and stearyl alcohol also 2 : 1, stable epoxy acrylate emulsion could be prepared. The centrifugal stability was good in the HLB region 13~14.

In conventional emulsion polymerization, polymerization starts by attacking of radicals generated from water phase and shows fine particle size. In our experiment, however, oil soluble initiator, AIBN, was available for a initiator of epoxy acrylate emulsion polymerization, but KPS was not, because initiator radicals and oligomeric free radicals produced by KPS attacked the intermolecular complex from the water phase to the oil/water interface, which makes the intermolecular complex weakened and broken. However, AIBN hadn't any destruction of intermolecular complex, because of its existence in oil droplets. Therefore, AIBN radicals generated and polymerized in oil droplets.

For the epoxy acrylate emulsion polymerization using AIBN as a initiator, the polymerization rate was incraesed with the increase of initiator concentration, and the stable HLB regions of epoxy acrylate emulsions had the relatively same tendency in polymerization conversion. Though the expression of "emulsion polymerization" was used in our experiment, it could be said on the base of above initiation mechanism that our polymerization system was rather close to the microsuspension polymerization.

ACKNOWLEDGMENT

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