Preparation of Epoxy Modified Polysiloxane Microemulsions

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A B S T R A C T

Microemulsion samples of epoxy modified polysiloxane were prepared by hydrolytic polycondensation of active centres instead of free radical polymerization. The reactions and mechanisms of the preparation of microemulsions were elucidated and the microemulsions were characterized by Fourier transform infrared spectroscopy (FTIR), photon correlation spectroscopy (PCS), transmission electron microscopy (TEM) and UV-visible spectrophotometry techniques. The effects of the amount of catalyzer and epoxy modifier were systematically studied. The results of FTIR spectroscopy indicated that the epoxy group successfully grafted onto the polysiloxane molecules. The microemulsions showed stability when the amounts of catalyzer and epoxy modifier were low. The particle size decreased and the size distribution widened with the increase of the catalyzer concentration. A slight variation of the particle size occurred when the amount of modifier varied under 1.0 wt%, although the particle size rose rapidly from about 40 nm to 180 nm when the content of modifier was beyond 1.0 wt%. The increasing amount of epoxy modifier gave narrower molecular size distribution and the appearance of microemulsions changed from a transparent or a semi-transparent state to an opaque state.

Key Words:

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INTRODUCTION

Coatings are widely used in industrial as well as civil fields. Becoming stricter with the environmental criteria, more and more drastic regulations aim to reduce the emissions of VOC (volatile organic contents) into the atmosphere. Thus, water-based solvent paintings and waterborne coating have been gaining importance in modern coating industry. Epoxy functional polymers are one of the most important classes of materials in coating industry because of their interesting properties, such as chemical resistance and high adhesion strength [1-3]. Epoxy polymers are commonly used in many fields and it is interesting to prepare their waterborne dispersions [4].

In recent years, many studies concerning the preparation of microemulsions have been reported because of their small droplet size and complex structure [5-7].

A prominent way to prepare microemulsion is by free radical polymerization method [8-13] and medium or short chain alcohols (propanol to octanol) are commonly added as co-emulsifiers to decrease the rigidity of interfacial membranes and prevent the formation of liquid crystal phases and metastable gel or macroemulsion phases [14,15]. Organosilicon microemulsions play an important role among these microemulsion materials in industry because of their good aging resistance and absence of toxicity. They are thermodynamically stable, isotropic, microstructured solutions with particles less than 150 nm, commonly consisted of water, oil, and surfactants [16].

In this work, we describe a pathway to epoxy functional organosilicon microemulsion, which are formed by epoxy group grafting on the polysiloxane prepolymer. The polysiloxane prepolymers were prepared by the ring-opening of D_4 (octamethylcyclotetrasiloxane) and an epoxy modifier referred to a silane coupling agent with trifunctional (trimethoxyl or triethoxyl) groups. These epoxy modified microemulsions are formed by hydrolytic polycondensation instead of the free radical polymerization. A catalyzer, $C_{12}H_{25}SO_3H$ (DBSA), a surfactant-like species was employed and none of co-emulsifier was added into the microemulsion. All the reactions such as the ring-opening and hydrolytic polycondensation were run in the acid environment.

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, D_4, was obtained from Xinghuo Organosilicone Plant, China, and it was distilled before using, melting point: 16-19ºC, boiling point: 175ºC/760 mmHg, $n_D^{20} = 1.3960$, $d_4^{20} = 0.955$. A nonionic surfactant, OP-10, $C_8H_{17}C_6H_4O(CH_2CH_2O)10H$, was used without any further purification had a purity above 95%, pH value: 5.0-7.0. Dodecyl benzenesulphonic acid, $C_{12}H_{25}C_6H_4SO_3$ (DBSA), was purchased from Xingya Washing Products Co., China, acts as catalyst, industrial material, pH value: 0.4, melting point: 16.3ºC, boiling point: 286ºC/760 mmHg. Water was distilled and deionized before using, pH value: 5.0-7.0, electrical conductivity ≤ 0.5 µs/cm (25ºC),

Table 1. Polymerization recipe of the microemulsions.

Materials	Materials concentration (wt%)
Catalyst	1.0, 2.0, 3.0, 4.0
Non-ionic emulsifier	2.0
D_4	10
Epoxy silane coupling agent	0.5, 0.8, 1.0, 1.3, 1.5

specific resistivity ≥ 2 MΩ. Epoxy silane coupling agent, $C_9H_{20}O_4Si$, which acted as modifier was purchased from the Diamond Advanced Material of Chemical Inc., Hubei, China, and it was used without any further purification with a density: 1.060-1.080 (25ºC), purity $\geq 98\%$, index of refraction: 1.420-1.430 (25ºC).

Preparation of Epoxy Modified Polysiloxane Microemulsion

Catalyst, non-ionic emulsifier and distilled water were placed in a four-neck round bottom flask, which was equipped with a mechanical stirrer, reflux condenser, thermometer, and nitrogen gas inlet. D_4 monomer was added drop by drop into the flask for about 30 min. When the mixed emulsion appeared blue, buffer solution was added and the acidity of the compound was lowered to a weak acid. Then, the epoxy silane coupling agent was dropped into the flask and the polymerization was continued for about 2.5 h. All reactions were run at about 80ºC and the flask was all along purged with nitrogen. The polymerization recipe of the microemulsions is listed as shown in Table 1.

Identification and Characterization Methods

FTIR spectra were recorded on an M-80 SPECORD spectrophotometer using KBr tablets. The particle size and size distribution were characterized by PCS (Loc-FC-963, Malvern Co., UK). The particle configuration was exhibited by TEM (TEM-100SX, Japan). UV-visible spectrophotometer, (Spectrum-1, Perkin-Elmer, USA) showed the luminousness of microemulsions. The acidity of the reaction mixture was exhibited by acidometer (PHS-4, China).

Mechanical stability, heat stability, and chemical stability of the final latexes were studied. Mechanical
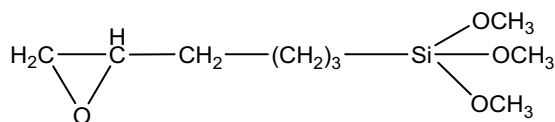
Scheme I. Structure of epoxy silane coupling agent.

stability was determined at room temperature with a high speed (3000 rpm) stirrer. Chemical and heat stabilities were determined at the conditions of acidic, alkaline, Ca^{2+} solutions and 60ºC for 48 h, respectively. The stabilities of microemulsions were assessed with visual observations of creaming and turbidity.

RESULTS AND DISCUSSION

Mechanism of Preparation of Epoxy Modified Polysiloxane Microemulsion

The influential factor of the preparation of epoxy modified microemulsions refers to epoxy silane coupling agent with trifunctional (trimethoxyl or triethoxyl) group, as presented in Scheme I. The

hydrolytic polycondensation of alkoxysilanes which are well-known for their use in preparing organosilicon materials [17-19] is a multistep and complicated process. A two-step process in which the occurrence of the trifunctional silane coupling agent hydrolyzes to active centres (SiOH) is carried out firstly in the presence of water and then the active centres undergo polycondensation with other active centres [20-22]. Polycondensation involving silanol groups is one of the most important reactions in the synthesis of siloxane polymers and is commonly involved in the manufacturing of many functional products [23].

The preparation of the epoxy modified polysiloxane microemulsion was carried out in the following steps according to Scheme II. The first step involved the ring opening of D_4 monomer in the presence of acid catalyst, which generated the polysiloxane prepolymer with active groups (-OH). After the addition of epoxy silane coupling agent, the hydrolysis takes place as shown on the second step, resulting in the formation of active centres. Under the reaction conditions, the active centres, which were generated from
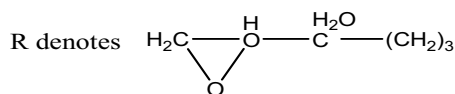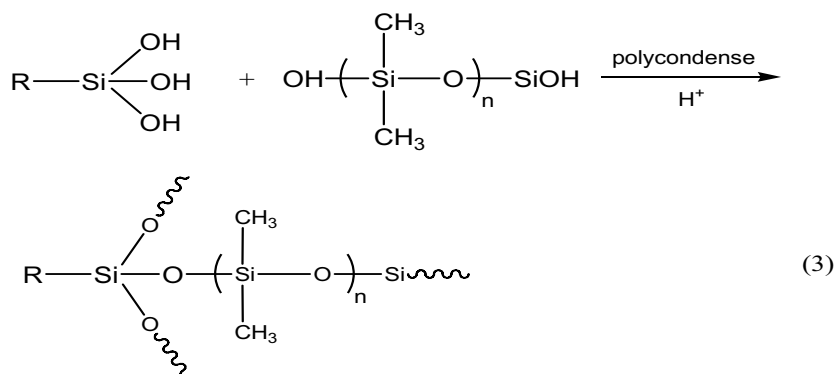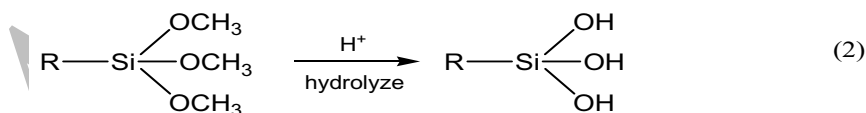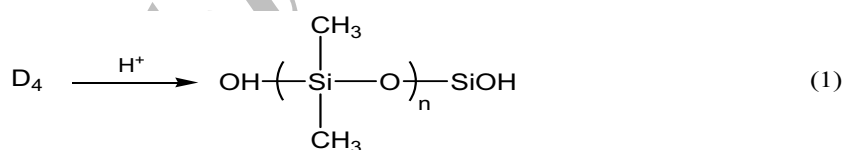
Scheme II. Preparation of epoxy modified silicone microemulsion.
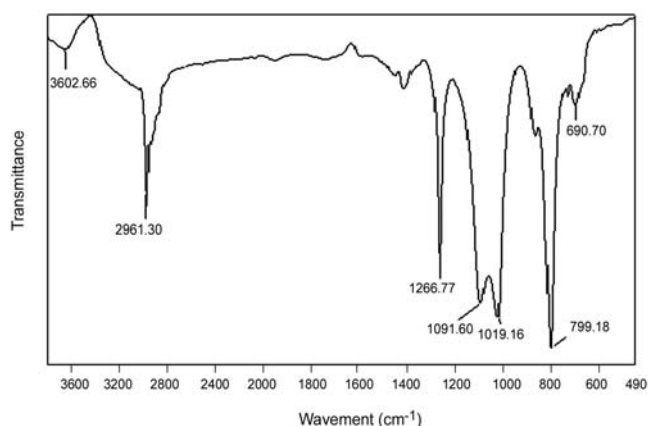
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Figure 1. FTIR spectrum of epoxy modified polysiloxane microemulsion.

the hydrolysis effect of the modifier, underwent polycondensation with the reaction product of ring opening of D_4 in the acidic condition as shown on the third step in Scheme II, and the epoxy group grafted on the polysiloxane molecule.

FTIR Analysis of Sample
FTIR spectra of pure sample were recorded using KBr tablets. The results of infrared transmittance were shown in Figure 1. The band at 1081.98 cm^{-1} is assumed to correspond to Si-O species. The band at 3602.66 cm^{-1} is only associated with Si-OH species. The band at 2961.30 cm^{-1} is associated with CH_3 species. A weak band centering at 1091.6 cm^{-1} was detected clearly which indicated that the epoxy group was successfully introduced into the polysiloxane prepolymer.

Effect of the Amount of Catalyzer on the Microemulsion
A series of epoxy modified polysiloxane microem ulsion samples were prepared with different amounts

of catalyzer (1.0, 2.0, 3.0, and 4.0 wt %) and 1.0 wt% of modifier. The stabilities of microemulsions were determined in acidic, alkaline, and Ca^{2+} solutions and heated in the oven at 60ºC for 48 h, respectively. The results in Table 2 show that the microemulsions maintain stable properties when the amount of catalyzer is below 4.0 wt%. However, above 4.0 wt%, the microemulsions exhibit instability in alkaline and Ca^{2+} solutions. It is presumably explained by the acidity effect of the microemulsions. Increasing the amount of the catalyzer can raise the acidity of microemulsions, which causes some coagulations and lowering the stability of microemulsions, even leading to microemulsions break up.

The hydrolysis and polycondensation rates are pH-dependent [24]. Increasing the amount of catalyzer would increase the acidity and the reaction rate as well. Moreover, the increase in the acidity of microemulsions increases the active centres concentration. Meanwhile, the probability of the reactions among the active centres increases, which makes particle size distribution widen, as presented in Table 3.

As shown in Scheme III, the catalyzer (DBSA) molecule which contains hydrophilic functional group (-SO_3H) and hydrophobic functional group ($C_{12}H_{25}^-$) plays the role of emulsifier as well. The increase in the amount of the DBSA enhances the emulsification effect of the microemulsions. In this case the particle size is decreased from 46.75 nm to 31.45 nm and the luminousness of microemulsions is well increased, as shown in Figure 2 and Table 3.

$$C_nH_m \diagdown\!\!\!\diagdown SO_3H$$

Hydrophobic group   Hydrophilic group
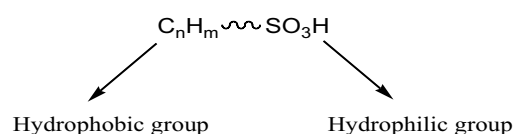
Scheme III. Molecular formula of DBSA.

Table 2. The effects of catalyst concentration on the stability of microemulsions.

| DBSA (wt%)	Acidic resistance	Alkaline resistance	Ca^{2+} resistance	Heat resistance
1	stable	stable	stable	stable
2	stable	stable	stable	stable
3	stable	stable	stable	stable
4	stable	layered	layered	stable

Table 3. The effects of catalyst concentration on the microemulsions.

| DBSA (wt%)	Particle size (nm)	Size distribution
1.0	46.75	0.076
2.0	41.38	0.098
3.0	36.93	0.132
4.0	31.45	0.161

TEM images of the microemulsions are presented in Figures 3a and 3b. An average particle size of 40 nm was obtained and no agglomeration was observed in the microemulsion with lower amount of catalyzer, as shown in Figure 3a. However, the particles agglomerated heavily when the microemulsion was prepared with higher amount of catalyzer, as shown in Figure 3b. This is in excellent agreement with the discussions of stability of the microemulsions, as shown in Table 1.

Effect of Modifier Concentration on the Microemulsions

The microemulsions were prepared with the amount of 1.0 wt% of modifier and 0.5, 0.8, 1.3, 1.5, and 3.0 wt% of DBSA. The effect of modifier on the particle size and size distribution of microemulsions are shown in Table 4. The results obtained from photon correlation spectroscopy (PCS) show that a slight variation in the particle size occurs when the amount of catalyzer increases from 0.5 wt% to 1.0 wt%.
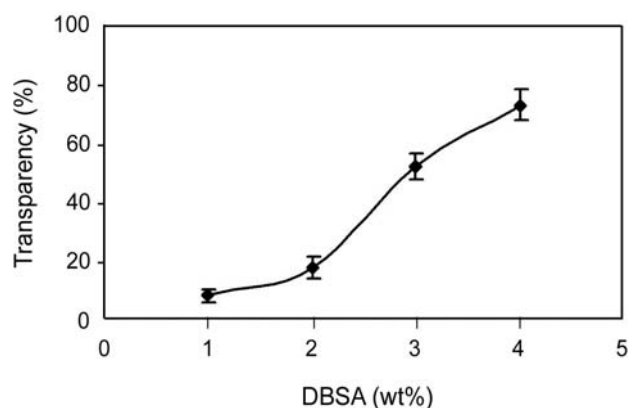
Figure 2. The effects of catalyst concentration on the transparency of microemulsions.
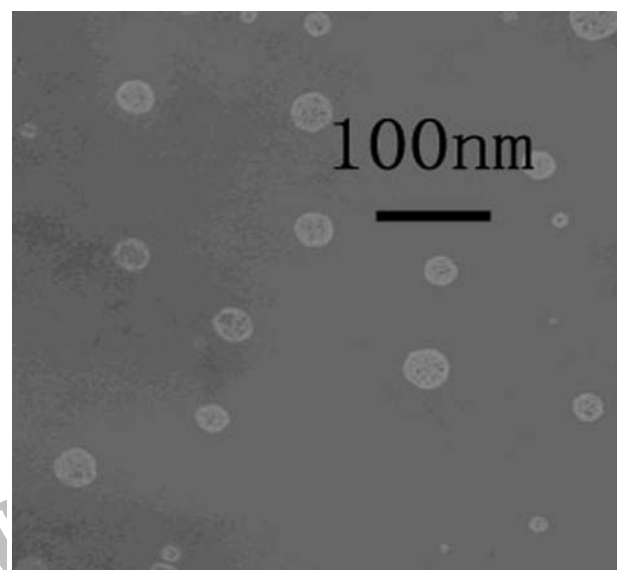
(a)
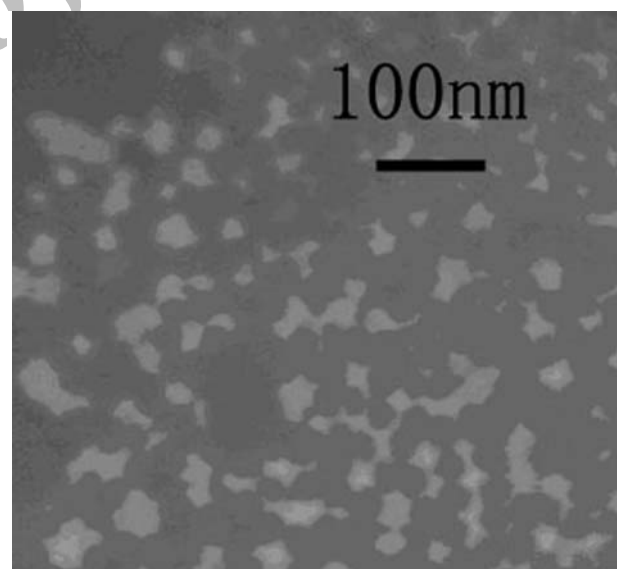
(b)

Figure 3. TEM images of microemulsions with different amounts of catalyst: (a) 1 wt % DBSA; (b) 4 wt% DBSA.

When the amount of modifier is above 1.3 wt%, the particle size rapidly rises from around 40 nm to 180 nm. This may be likely explained by the equilibrium of the emulsification. With increase in modifier content, more particles are produced. As it is an acceptable argument, small particles are stabilized by surfactants. When more modifiers are added, the number of microemulsion particles is supposed to increase and the surface coverage ratio of surfactant decreases which results in the formation of agglom-
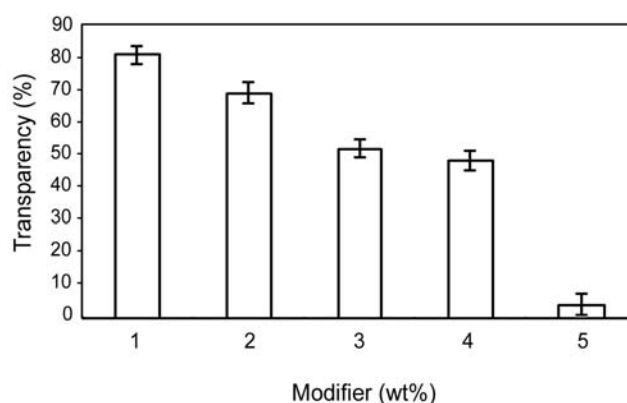
Table 4. The effects of modifier concentration on the microemulsions.

Modifier (wt%)	Particle size (nm)	Size distribution index
0.5	38.65	0.227
0.8	36.61	0.183
1.0	36.93	0.132
1.3	114.8	0.088
1.5	188.8	0.075

Figure 4. The effects of modifier concentration on the transparency of microemulsions.

erates. Thus, it may be deduced that the microemulsion retains equilibrium when the amount of modifier is below 1.3 wt% and the equilibrium is lost when the amount of modifier continues to increase (>1.3 wt%).

Moreover, one can see that the size distribution index of the microemulsions decreases with the increase in modifier concentration. This is explained by the fact that particles themselves undergo polycondensation reactions. There exist mainly two possible reactions in the microemulsion: homofunctional polycondensation of coupling agent and heterofunctional polycondensation reactions between coupling agent and active polysiloxane. As the amount of modifier increases, modifiers are inclined to be the homofunctional polycondensation reaction because of their good hydrolysable property. The probability of homofunctional polycondensation rises with the increasing in modifier concentration which results in the narrower size distribution, as shown in Table 4.

The stabilities of the microemulsions are also discussed with different chemical and physical treatments, as shown in Table 5. As can be deduced from these results, the stabilities of the microemulsions decreased with the higher amount of epoxy modifier.

This might be ascribed by the fact that the increase in modifier content gives rise to higher number of SiOH groups. Subsequent SiOH groups' polycondensation among polymer particles would link them together, resulting in larger polymer particles size. Thus, the microemulsions become increasingly turbid and flocculent because of the increase in particles size. Above all, it can be concluded from the results in Table 5 that the properties of microemulsions are stable when the amount of the modifier is below 1.3 wt%.

The transparency of the microemulsions with different amounts of epoxy modifier is depicted in Figure 4. As can be seen, the transparency of the microemulsions linearly decreases from 80.0% to 0.32% with the increasing amount of the modifier. This may be confirmed by the appearance of microemulsions, listed in Table 5, which might be explained by the above stated reasons: When more modifiers were added, the agglomerates were formed. Such agglomerates persisted in the composite and scattered visible light, leading to turbidity. Therefore,

Table 5. The effects of modifier concentration on the stability of microemulsions.

Modifier (wt%)	Appearance of microemulsions	Acidic resistance	Alkaline resistance	Ca^{2+} resistance	Heat resistance
0.5	Blue and transparent	stable	stable	stable	stable
0.8	Blue and transparent	stable	stable	stable	stable
1.0	Blue and transparent	stable	stable	stable	stable
1.3	Blue and semi-transparent	stable	stable	stable	stable
1.5	Milky white and opaque	stable	layered	layered	stable

the microemulsions turn from a transparent state with transmittance of 80.0% to a turbid system of 0.32% transmittance by increase in modifier concentration.

CONCLUSION

Translucent epoxy modified microemulsions, based on the reaction of hydrolytic condensation, were synthesized by the polycondensation of epoxy silane coupling agent and polysiloxane water medium. The following conclusions can be drawn from this study:

- The microemulsions retain stability when the amount of catalyzer and epoxy modifier are lower than 4.0 wt% and 1.3 wt%, respectively.

- The particle size decreases and the size distribution widens with the increase in catalyzer concentration.

- When the amount of modifier is below 1.0 wt%, the particle size is around 40 nm. Above 1.0 wt%, however, the particle size rises rapidly from about 40 nm to 180 nm.

- The increasing amount of epoxy modifier gives narrower size distribution and transforms the appearance of microemulsions from a transparent to an opaque state.

- Above all, one can deduce that stable epoxy modified polysiloxane microlatexes can be prepared from microemulsions containing catalyst content of 3.0 wt% and modifier contents of 1.3 wt%.

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