Vinyl Functional Polysiloxane Microemulsion: Preparation and Characterization

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A B S T R A C T

A vinyl functional microemulsion was successfully prepared via polycondensation between polysiloxane prepolymer and a modifier (vinyl silane coupling agent with alkoxy groups). The polysiloxane prepolymer was prepared by ring-opening of D_4 (octamethylcyclotetrasiloxane). The structure and properties of vinyl functional microemulsion were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR), photon correlation spectroscopy (PCS). FTIR Spectroscopy result showed that vinyl groups were successfully introduced into the polysiloxane molecules. The variation in pH, amount of vinyl coupling agent and catalyst were studied in relation to the properties of the final microemulsion. The results indicated that under strong acidic more coagulum and higher percentage of conversion occurred in the microemulsion. TEM results also revealed that particles are densely packed in strong acidic condition but become sparsely distributed in weak acidic condition. An increase in the vinyl coupling agent content leads to an increase in formation of coagulum and in particle size, but it lowers the particle size distribution. The smaller ratio of the average surface coverage of surfactant leads to higher amount of coagulation which is in linear dependence to the increased amount of vinyl coupling agent modifier. Photon correlation spectroscopy results show that increasing the amount of vinyl coupling agent modifier increases the particles size, while reduces the particles size distribution. It can be concluded that the coagulum weight fraction increases linearly with higher amount of catalyst. An increase in the vinyl coupling agent modifier leads to an increase in the coagulum. The microemulsion shows stability when the amount of catalyst is about 3.0-4.0 wt%.

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INTRODUCTION

Emulsion polymerization is an important process which has been widely used in the production of a large number of polymers. Among its many advantages, it attains both high molecular weights and reaction rates. In recent years, many studies have been reported concerning the preparation of microemulsions owing to their small droplet size and complex structure [1-4].

A prominent way to prepare microemulsion is by free radical polymerization method [5-7]. Usually medium to short chain alcohols (propanol to octanol) are added as co-emulsifier to decrease the rigidity of the interfacial membranes and prevent the formation of liquid crystal phases and metastable gel or macroemulsion

phases [8,9].

It is well known that certain physical and mechanical properties of materials considerably change as their grain size is reduced. Nano-latexes in microemulsions find numerous specific applications for example in drug delivery, microencapsulation, and biomedical diagnosis [10-14]. Most of these applications require highly functionalized polymer particles which can be achieved by introducing the functional groups into polymers. The functional polymers have attracted considerable attention over past years.

Vinyl polysiloxanes are one of the important functional polymers in microemulsion because of the functional vinyl groups which can react with other active monomers to produce the composite materials with excellent properties. Vinyl polysiloxanes microemulsions are thermodynamically stable, isotropic, microstructured solutions with particle size below 150 nm, commonly comprised of water, oil, and surfactants.

In previous reports on microemulsion, most studies referred to the addition of co-surfactants to help stabilize the microemulsion [15-17] and employing free radical polymerization method to functionalize the system [18-20]. However, these methods are often either less sensitive or have their intrinsic disadvantages, e.g., technical complications, time consuming processes or demanding that restricted available reagents. Thus, the development of new routes on preparation of microemulsions is considered to be one of the most challenging fields.

In this study, we describe a pathway to functional organosilicon microemulsions, which are formed via polycondensation between polysiloxane prepolymer and a modifier. The polysiloxane prepolymer was prepared by ring-opening of D_4 (octamethylcyclotetrasiloxane) and using a modifier referred to as vinyl silane coupling agent carrying alkoxy groups. These vinyl modified polysiloxane microemulsions were formed by hydrolytic polycondensation instead of free radical polymerization. Compared to those microemulsions composed of water, oil, surfactant, and co-emulsifier, the microemulsion prepared in this work was prepared in the presence of water, monomer, a surfactant and without co-emulsifier. A catalyst, $C_{12}H_{25}SO_3H$, (DBSA), as surfactant-like

species was employed without further treatment. All the reactions including ring-opening and hydrolytic polycondensation were run in acidic environment.

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane was purchased from Xinghuo Organicsilicone Plant, China, distilled before being used (mp: 16-19°C; bp: 175°C/760 mmHg; n_D^{20} = 1.3960; d_4^{20} = 0.955). A non-ionic surfactant (OP-10) was used without any further purification, > 95%; pH 5.0-7.0. Dodecyl benzenesulphonic acid, ($C_{12}H_{25}C_6H_4SO_3$), DBSA, as an industrial material acting as catalyst, was purchased from Henan, China, and used without treatment (pH 0.4; mp: 16.3°C; bp: 286°C/760 mmHg). Water was distilled and de-ionized before using, pH value: 5.0-7.0, electrical conductivity ≤ 0.5 μS/cm (at 25°C), specific resistivity ≥ 2 MΩ. Vinyl silane coupling agent, $C_8H_{18}O_3Si$ (TEVS) was used as a modifier which was obtained from Diamond Advanced Material of Chemical Inc., China, and it was used without any further purification with a density: 0.898-0.953 (at 25°C), purity ≥ 98%, index of refraction: 1.393-1.403 (at 25°C).

Vinyl Modified Silicone Microemulsion

The polymerization runs were all performed in similar fashion. A four-neck round bottom flask equipped with a gas inlet, mechanical stirrer, a cold water condenser and a thermometer, was placed in a constant temperature water bath. A mixture of composition consisting of catalyst, surfactant, de-ionized water was charged into the reactor flask. The process of emulsification was carried out under the condition of mechanical stirrer and heat. The monomer, octamethylcyclotetrasiloxane (D_4) was charged at a constant rate into a pressure tight flask and heated to 80°C. The ring opening of this compound was carried out under nitrogen atmosphere. When the emulsion emerged as a blue colour, the vinyl coupling agent was added dropwise in a period of 30 min and the onset of reaction time was recorded. The polymerization was continued thereafter in batch system for 4 h. As a result of the reaction taking place, a

Table 1. Recipe for vinyl modifier microemulsion.

Materials [*]	Amounts of materials (wt%)				
Catalyst	1.0	2.0	3.0	4.0	5.0
Modifier	1.0	3.0	5.0	7.0	9.0
Non-ionic emulsifier	2.0				

[*] All contents were on the gross weight of microemulsion

modified microemulsion was obtained in the reaction vessel. Detail recipes of vinyl functional polysiloxane microemulsion are shown in Table 1.

Measurements

FTIR Spectra were recorded on an M-80 SPECORD (China) spectrophotometer using KBr tablets. The particle size and size distribution of microemulsions were characterized by photon correlation spectroscopy (PCS) (Malvern Co., UK). The particle configuration was exhibited by transmission electron microscope (TEM), (MSX-100, Japan) and TEM measurements were conducted using a Tecnai G22oS-Twin electron microscope (Japan) at an acceleration voltage of 200 kV.

In a typical experiment, one highly diluted drop of the colloidal dispersion, containing approximately 0.01 wt% of solid was put on a carbon film supported by a copper grid. Negative staining was performed by adding one drop of an aqueous solution of 1.0 wt% uranyl acetate on the copper grid, and allowed to air dry before observation. The acidity of the reaction mixture was exhibited by acidometer (PHS-4, China).

In order to assess the amount of coagulum in the microemulsions, the microemulsions were filtered through a copper net filter to remove the coagulum which was then dried in oven. The amount of coagulum was determined by gravimetric measurements, expressed as follows:

$$\sigma(\%) = (W_1 / W_2) \times 100$$

where, σ is the percentage of gelatin, W_1 and W_2 are the amounts of coagulum and comonomers (monomer and vinyl modifier), respectively.

In the polymerization process, the samples were taken out at regular intervals and heated in the oven in order to assess the percentage of conversion. At first, the micro-dispersed solution was neutralized with aqueous $NH_3.H_2O$ (10%) and the solvent was removed under vacuum at room temperature. The obtained sample was washed with de-ionized water and then with acetone in order to wash out the remaining surfactants. The acetone was separated by distillation. Subsequently, the sample was allowed to dry for 48 h in a stationary dryer at 105°C. The percentage of conversion (C_P) was calculated without taking into account the coagulum formation, using the following equation.

$$C_P(\%) = (W_P / W_M) \times 100$$

where, W_M is the weight of monomers including the weights of D_4 and modifier and W_P is the weight of polymer formed.

The mechanical, chemical, and storage stabilities of the final latexes were studied. Mechanical and storage stabilities were determined at room temperature with a high speed (3000 rpm) stirrer. Chemical stability was determined under alkaline conditions and in Ca^{2+} solutions for 48 h. The stability of microemulsion was characterized by "+", and its instability by "-".

RESULTS AND DISCUSSION

Mechanism

The synthesis of vinyl modified silicone microemulsion was carried out in three steps according to Scheme I. The first step involved the ring opening of D_4 in the presence of acidic catalyst and a polysiloxane prepolymer as hydroxyl-terminated polysiloxane was obtained. The second step was the
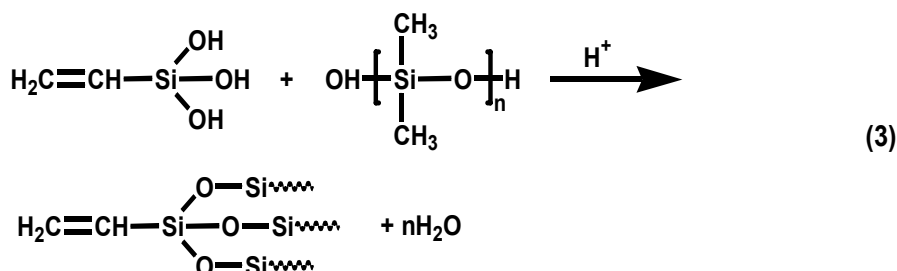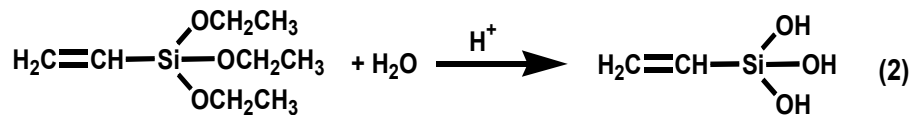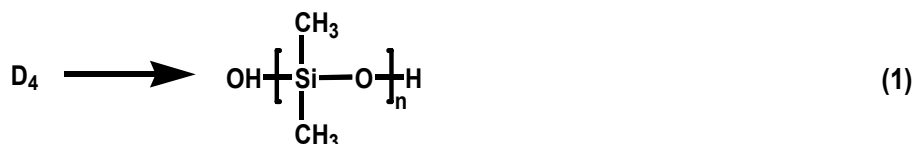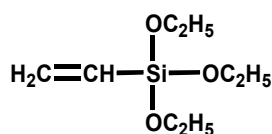
Scheme I. Preparation mechanism of vinyl modified polysiloxane.

critical stage of the preparation of vinyl modified microemulsions which refers to vinyl silane coupling agent with active groups, as presented in Scheme II. Silane coupling agent molecules have multifunctional groups with a general chemical formula of $R-SiX_3$, where X stands for hydrolyzable groups (alkoxy groups) bonded to Si and R which is a resin-compatible group [21].

The hydrolytic polycondensation of alkoxysilanes well-known for their use in preparing organosilicon materials [22] is a multistep and complicated process. A two-step process in which the trifunctional silane coupling agent hydrolyzes into active centres (Si-OH) which is carried out first in the presence of water and then the active centres undergo polycondensation with other active centres. After the addition of silane coupling agent, hydrolytic condensation of modifier with alkoxy groups is carried out as shown on the second step in Scheme I, resulting in the formation of trifunctional active hydrolysate.

Under the reaction condition, the vinyl silane coupling agent with trifunctional active hydrolyzate

undergoes polycondensation with the reaction product of ring opening of D_4 as shown in the third step depicted in Scheme I, and the grafting of C=C functional groups on the polymer segment was performed.

FTIR Analysis

FTIR spectrum of pure vinyl modified polysiloxane was recorded using its KBr tablet. The spectrum of infrared transmittance of multi-polymer is shown in Figure 1. The band at 1085.9 cm^{-1} is believed to correspond to Si-O species and the band at 3032.1 cm^{-1} is only associated with the Si-OH species. A weak band centered at 1600.94 cm^{-1} is
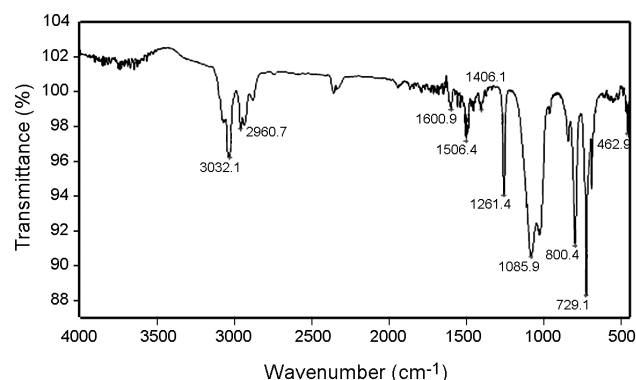

Figure 1. FTIR Spectrum of vinyl modified polysiloxane polymer.

Scheme II. Structure of the modifier.

clearly detected which is an indication of successfully introduced vinyl group onto poly-siloxane.

Effect of pH Variation on the Microemulsions

Under the acidic condition, the silane coupling agent hydrolysis occurs in water to produce the corresponding silanols which ultimately form siloxane bonds through condensation reactions. The pH value plays an important role in the hydrolysis and condensation of silane coupling agent and reaction rates are strongly dependent on pH of the medium [23]. In this study, the effect of pH on the microemulsion was assayed in the pH range 0.4-5.0, and the relationship between the percent conversion and pH is discussed. The pH values were changed by the buffer solutions before addition of the modifier.

Figure 2 shows the effect of pH on the percent conversion of the monomer. One can see that the percent conversion reaches as high as 90% when the pH is 0.4, while in weak acidic conditions, the conversion percentage of monomer almost remains at lower values (percent conversion of 10-20%). It can be explained that in acidic solution, H^+ ion plays the role of a catalyst to initiate hydrolytic polycondensation of modifier with alkoxy goups. The changes in pH affect the reaction rate and the rates of hydrolysis and condensation.

In strong acidic condition, the ring-opening of D_4, hydrolysis and condensation were catalyzed completely and the reaction rate was improved which
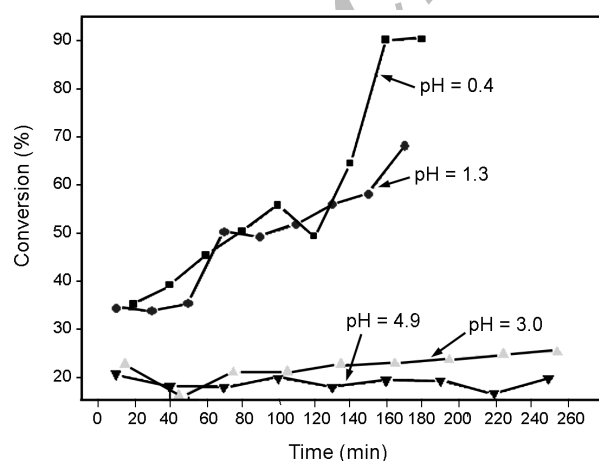
resulted in higher percent conversion of monomers in 4 h. In contrast, the reaction rate was slower and the conversion percentage of monomers was obtained at lower values under the weak acidic condition in 4 h.

As it may be observed in Figure 2, at pH value of 1.3, in the first hour, slow monomer consumption is observed. After 1 h, the conversion rises dramatically and increases almost linearly thereafter. The reaction system requires an adsorption process after the addition of monomer and it takes time to make the monomers collide with the acidic sites to initiate polymerization because of the lower concentration of active centers.

After a period of time and under continuous stirring and diffusion, the monomers started to have contact with acidic sites and subsequently the propagation started after 1 h as shown in Figure 2. At
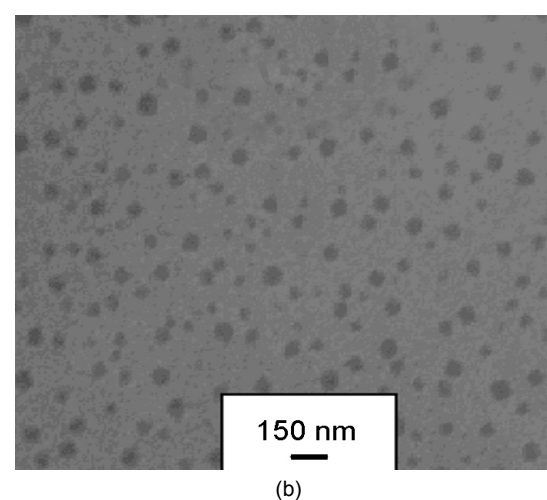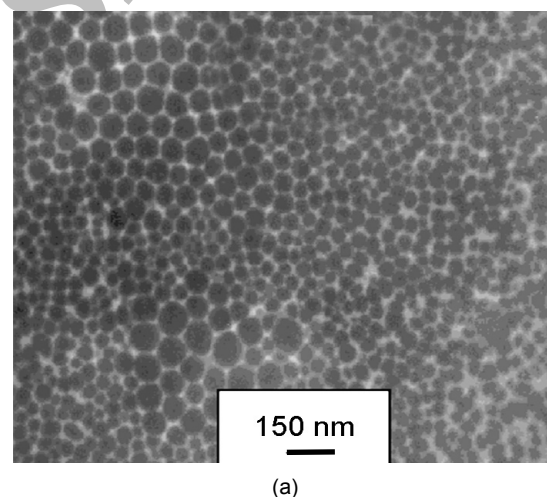

150 nm

(a)

150 nm

(b)

Figure 3. TEM Images of particles configuration at different acidic conditions (a) pH 0.4 and (b) pH 4.9.

Figure 2. Effect of pH on percent conversion of microemulsion.

Table 2. Effect of amount of catalyst on gelatin weight fraction.

Catalyst (wt%)	1	2	3	4	5
Coagulum (wt%)	0.284	0.332	0.389	0.481	0.527

pH 0.4, the higher concentration of active centres makes the initiation and propagation steps take place quickly compared to those in weak acidic condition.

TEM images clearly show the particle configuration in different acidity conditions with the same magnification scale in Figure 3. Particle configuration of microemulsions with pH value of 0.4 and 4.9 are shown in Figures 3a and 3b, respectively. The particles show dense configuration in strong acidic condition but they are sparse in weak acidic condition. This is due to the dependence of percent conversion on the acidity of the medium.

In strong acidic medium, the conversion ratio of monomers is higher which makes a larger number of particles grow and closely packed as shown in Figure 3a. However, the weak acidic medium causes the lower conversion ratio and makes the particles grow sparsely as shown in Figure 3 b. This is in good agreement with the discussion on relationship between the reaction rate and acidity.

Effect of Catalyst on the Microemulsion
The catalyst, DBSA, is a surfactant-like species which contains hydrophilic ($-SO_3H$) and hydrophobic ($C_{12}H_{25}-$) functional groups. It naturally absorbs at the interface of oil/water with the hydrophilic head-groups protruding towards the aqueous phase whereas the hydrophobic tail-groups remain in the oil phase. Because of the amphiphilic property, DBSA plays the role of emulsifier to stabilize the polymer particles. The catalyst, DBSA which determines the acidity of the polymerization and the stability of the microemulsion is the most important factor in microemulsion process. In this study, a series of modified polysiloxane microemulsion samples were prepared with different amounts of catalyst (1.0, 2.0, 3.0, 4.0 and 5.0 wt%) and 10.0 wt% of modifier.

The dependence of coagulum weight fraction on the amount of catalyst is presented in Table 2. It may be observed that the coagulum weight fraction increases linearly with the increased amount of the catalyst. In the process of polymerization, an extensive hydrolysis and condensation occur and the active latex particles are formed, followed by condensation reactions between the adjacent latex particles because of non-protective environment, leading to coagulation (bridging flocculation) [24] as shown in Scheme III. With increase in the amount of
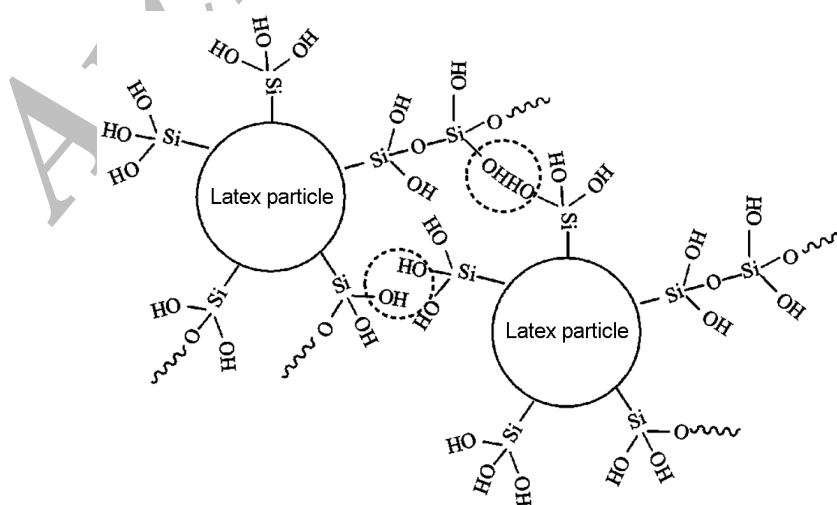

Scheme III. Condensation reactions of adjacent particles.

Table 3. Effect of catalyst content on stability of the microemulsion.

| Catalyst (wt%)	1	2	3	4	5
Stability of microemulsion	-	-	+	+	-

catalyst, the acidity strengthens. Under strong acidic condition, the rates of hydrolysis and condensation increase and the reactions among the particles become vicious leading to more coagulation.

The stability of the microemulsion is studied with different chemical and physical treatments. Table 3 shows the effect of catalyst concentration on the stability of microemulsions. As it is evident, the microemulsions show instability when the amount of catalyst is below 3.0 wt%. With increase in catalyst content to 3.0-4.0 wt%, the microemulsions show stable condition. However, when the amount of catalyst is above 4.0 wt%, the microemulsions show signs of instability again. A likely explanation is related to the function of catalyst (DBSA) in the microemulsion. As mentioned above, DBSA plays dual roles in the microemulsion, i.e., catalyst and emulsifier.

At DBSA content below 3.0 wt%, due to weak emulsification caused by smaller amount of emulsifier, the microemulsions show signs of instability. As the amount of catalyst increases to 3.0-4.0 wt% the surfactant effect of DBSA increases the average surfactant coverage of particles and the emulsification process is strengthened. Meanwhile,

the catalysis and emulsification attain equilibrium which stabilizes the microemulsion system. Further increase in the catalyst results in greater instability of microemulsions. This may be presumably explained by the acidity effect of the microemulsions. Increasing the content of DBSA, makes the acidity of the microemulsion strengthened which upsets the equilibrium and results in the instability of microemulsions, even leading to microemulsions dissolution.

This is further confirmed by TEM images shown in Figure 4. The particle morphologies of micro-emulsions with 1.0 wt% and 5.0 wt% catalyst contents are shown in Figures 4a and 4b, respective-ly. It is shown in Figure 4a, that with lower amount of catalyst, the particles are more sparse and an average particle size of 40 nm is obtained without any agglomeration observed. However, at higher particle contents, the system is conglomerated when the microemulsion is prepared as it is depicted in Figure 4b. This is in excellent agreement with the discus-sions on stability of the microemulsions, as shown in Table 3. Thus, it can be concluded that the microemulsions show stable properties when the amount of catalyst is 3.0-4.0 wt%.

(a)

(b)
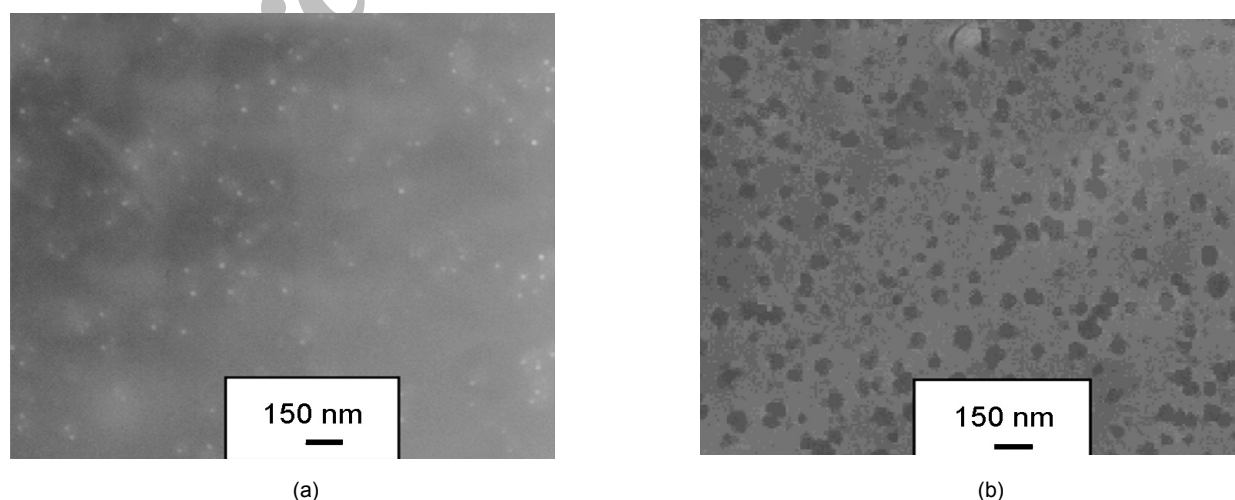
Figure 4. TEM Images of microemulsions at different amounts of catalyst: (a) 1.0 wt% and (b) 5.0 wt%.
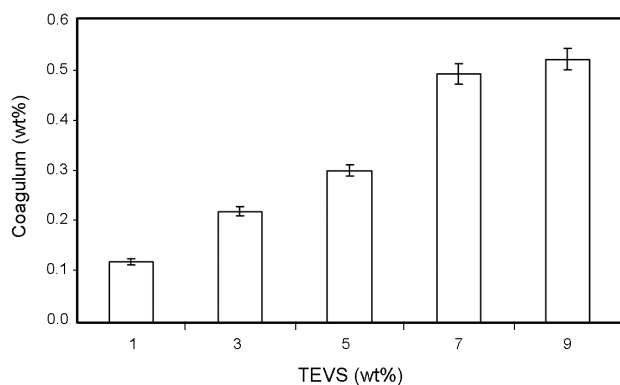
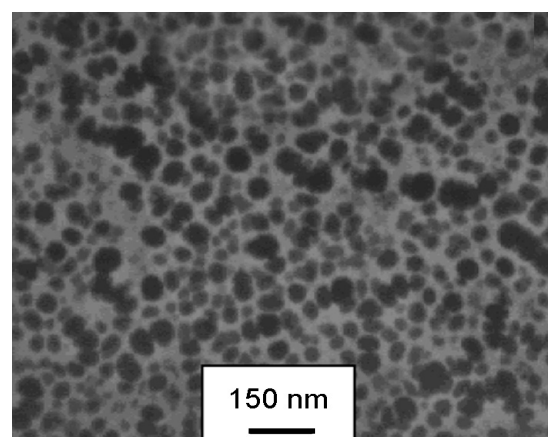**Figure 5.** Effect of modifier content on coagulum in microemulsion.

Effect of Modifier on the Microemulsion

The microemulsions were prepared with different amounts of a modifier (1.0, 3.0, 5.0, 7.0, and 9.0 wt %) and 3.0 wt% of DBSA. It was observed that the coagulum content increases linearly with greater amount of the modifier (TEVS). As it is shown in Figure 5, the coagulum of the microemulsion increases from 0.12 wt% to 0.5 wt% when the TEVS content increases. The aggregation of particles has already been observed during the synthetic process. This might be ascribed by the increase in modifier content that more -SiOH would be formed by hydrolysis of Si-OR, which settles on the surface of the particles. Subsequently -SiOH is condensed between the polymer particles, linking the polymer particles together and creating larger size polymer particles which reduces the average ratio of surface coverage of the surfactant. Thus, the microemulsions become increasingly turbid and flocculent. The excess silane coupling agent made latex over cross-linked which led to more coagulation.

Table 4 shows the effect of modifier on the particles size and its distribution. The results obtained from photon correlation spectroscopy (PCS) show that with increasing the amount of TEVS the particle size is increased while the particles size distribution is

decreased. This is due to the density of cross-linking junctions of microemulsion. The greater the amount of modifier, the greater would be the density of cross-linking junctions which finally leads to larger particles.

Moreover, it becomes evident that the size distribution index of the microemulsions drops with higher amount of modifier. This can be explained by interparticles' polycondensation reactions. There are mainly two possible reactions in a microemulsion process, i.e., homofunctional polycondensation of

150 nm

(a)

150 nm
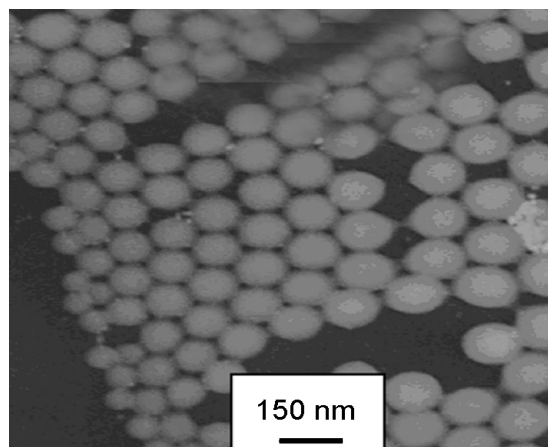
(b)

Figure 6. TEM Images of microemulsions at different amounts of modifier: (a) 1.0 wt% and (b) 9.0 wt%.

Table 4. Effect of modifier content on particle size and its distribution.

TEVS (wt%)	1.0	3.0	5.0	7.0	9.0
Particle size (nm)	37.80	40.10	52.50	68.30	137.20
Particle size distribution index	0.861	0.781	0.182	0.07	0.066

coupling agents and heterofunctional polycondensation reactions between silane coupling agents and active polysiloxanes. As the amount of modifier increases, the reactions tend to be inclined to homofunctional polycondensation type of reactions. The probability of homofunctional polycondensation rises with higher amount of the modifier which results in narrower size distribution as shown in Table 4.

TEM images of microemulsions with different amounts of modifier are shown in Figure 6. It is observed that the particles of microemulsions with a lower amount of modifier (1.0 wt %) are produced in different sizes which range between 40-50 nm as shown in Figure 6a. Opposite to that, the particles of microemulsion with higher amount of modifier (9.0 wt %) show strikingly regular honeycomb shapes and are dispersed particles with a narrow particle size distribution with larger particles size, as shown in Figure 6b. This is in a good agreement with the results shown in Table 4.

CONCLUSION

A translucent vinyl modified microemulsion, based on hydrolytic condensation reaction was synthesized by polycondensation of vinyl silane coupling agent and polysiloxane water medium.

- The percent conversion reached higher values in strong acidic condition compared to that of weak acidic condition.

- The particles are packed together in strong acidic condition and tend to disperse in weak acidic condition.

- The coagulum weight fraction increases linearly with higher amount of catalyst and the microemulsions are stable at catalyst content of 3.0-4.0 wt%.

- The coagulation of particles increases linearly with the increased amount of modifier which makes the particles size to increase, while the particles size distribution is reduced.

ACKONWLEDGEMENT

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