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Studies on Acrylic Emulsion Polymerization Containing Hydrophilic Hydroxyl Monomer in the Presence of Nano-SiO₂ Particles

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Emulsion polymerization with nano-scale SiO₂ particles as seeds composed of methyl methacrylate (MMA), butyl acrylate (BA), hydroxyethyl methacrylate (HEMA), and acrylic acid (AA) was studied from varying reaction temperatures, level of SiO₂ particle, HEMA, and emulsifier. The morphology of the emulsion particle was examined with a transmission electron microscope (TEM). The results showed that the addition of nano-SiO₂ particles decreased the coagulum greatly when its level was lower than 7%. The coagulum also decreased with the increasing of temperature from 65°C to 75°C. The level of HEMA and emulsifier had little influence on the coagulum in the presence of nano-SiO₂. The particle size of the emulsion increased with the increase of level of nano-SiO₂ and HEMA. Part of the emulsion particles connected together due to the existence of HEMA, and yet some of the nano-SiO₂ particles were not covered with polymer.

Keywords: nano-SiO₂; acrylic; emulsion polymerization; hydroxyl monomer; coagulum

1 Introduction

Polymer and inorganic nano-scale composite materials have attracted the great interest of researchers. In these composites, the polymer provides a carrier environment for nano-scale materials, which improve the dispersibility and stability of nano-scale inorganic materials. On the other hand, nano-scale inorganic materials can improve the thermal, mechanical, and flame-retardant properties of polymers. The composite can be prepared by directly mixing nano-particles with polymer, mixing with monomer, or by mixing a nano-particles precursor with monomer. Many polymers have been used to prepare polymer nano-scale composites, such as acrylic emulsion (1), poly(methyl methacrylate) (2), polystyrene (PS) (3), polypropylene (PP) (4), acrylic-based polyurethane (5) and poly(HEMA) (6). SiO₂, TiO₂, ZnO and CaCO₃ are commonly used nano-scale materials.

Emulsion polymerization is an effective method for obtaining composite particles with inorganic particle core and a

polymer shell, which is an environment friendly and easily-made method. In this method, the monomer is mixed directly with inorganic nano-scale particles, and the polymer is grafted to the surface of the inorganic particle, which may form a harder polymer film for coating, and also aggregation of the silica particles may be alleviated (7). The acrylic emulsion with hydroxyl groups has been used in a two-component polyurethane coating, as the replacement of traditional solvent-based acrylic resin (8). The study of a nano-composite emulsion made of acrylic emulsion and nano-SiO₂ is of significance in the coating industry. Styrene-acrylic/SiO₂ nano-particles composite emulsion was prepared by using SiO₂ nanoparticles as seeds (9), which showed that the level of nano-SiO₂ and reaction temperature had a great influence on the monomer conversion ratio, particle size, coagulum content and viscosity of the emulsion. The acrylic emulsion containing hydroxyl groups was also prepared with normal structure and core-shell structure in the absence of nano-SiO₂. The best emulsifier type, level, and reaction temperature were discussed in details (10, 11). This paper deals with the acrylic emulsion containing high hydroxyl content in the presence of nano-SiO₂; the influence of temperature, level of nano-SiO₂, hydroxyl monomer and emulsifier on the polymerization is investigated.

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2 Experimental

2.1 Materials

Methyl methacrylate (MMA) and butyl acrylate (BA) were distilled under reduced pressure before use. All other materials were used as received. Hydroxyethyl methacrylate (HEMA) and acrylic acid (AA) were used as copolymerization monomers to supply OH and COOH groups, respectively. Ammonium persulfate (APS), sodium hydrogen carbonate (NaHCO₃) and ammonia were used as initiator, buffer, and neutralization agent, respectively. The surfactants used were sodium lauryl sulfate (SLS), and p-octyl polyethylene glycol phenyl ether (OP). Deionized water was used in all the experiments.

The nanometer scale SiO₂ colloid (nano-SiO₂) used was Klebosol 30R12 from Clariant Co., with a 30% SiO₂ content, 12 nm particle size, 200 m² g⁻¹ specific surface area, 1.2 g/cm³ (20°C) density, and pH = 10 (20°C).

2.2 Emulsion Preparation

Polymerizations were carried out in a 250 ml glass flask fitted with a reflux condenser, stainless-steel stirrer, nitrogen gas inlet, thermometer and funnels. The recipes are given in Table 1. The weight solid content of the emulsion was designed as 45% with 0.5% initiator (APS), based on total weight amount of monomers. The effects of polymerization temperature, monomers ingredient, the levels of nano-SiO₂ colloid and emulsifier on the emulsion polymerization were investigated, respectively.

Water, buffer, composite surfactants and nanometer scale SiO₂ colloid were first filled into the reactor. The flask was heated to reaction temperature after ultrasonically treated for 5 min. A solution of initiator and the mixture of monomers were added in two streams, respectively. The entire system was degassed with nitrogen gas for 20 min when heated to 75°C (otherwise indicated), then the initiator

solution was added dropwise and 5% weight of the monomers mixture was added. The rest of the monomers mixture was added dropwise in 2 h when the system had an even bluish color and finished about the same time with the initiator solution. Finally, the mixture was neutralized with NH₃ · H₂O to pH = 7~8 at 50°C after the emulsion was kept at reaction temperature for another 2 h, filtered with a filter of 100 mesh.

2.3 Characterization

The monomer conversion ratio was determined gravimetrically. The coagulum was obtained by collecting all deposits on the flask walls, agitator, and thermometer. The dry weight of the coagulum related to the total monomers and dry weight of SiO₂ was defined as the coagulum percentage.

The particle size of the emulsion was measured by a light scattered method as described in the literature (11). Viscosity was measured with a NDJ-8S digital viscometer (Shanghai Balance Factory, China), using a rotating velocity of 60 rpm with a No. 2 rotor at 25°C.

The morphology of the emulsion particle was examined with a transmission electron microscope (TEM, JEM-1000, Hitachi Co.). The emulsion was thinned to the appropriate concentration. A drop of the emulsion was added on a copper TEM grid, dried, and examined with the TEM instrument.

3 Results and Discussion

3.1 Effect of Reaction Temperature on Polymerization

Figure 1 is the effect of polymerization temperature on coagulum and viscosity of the emulsions (No. 1~4 experiments in Table 1). The polymerization cannot be carried out below 65°C, and the emulsion system may form coagulum completely (viscosity of the emulsion cannot be

Table 1. Recipes used for the emulsion polymerization (Unit: g)

No.	Water	NaHCO ₃	SLS	OP	Nano-SiO ₂	APS	BA	MMA	HEMA	AA	Temperature °C
1	96	0.2	0.32	0.48	4.0	0.4	33.2	25.8	18.5	2.5	65
2	96	0.2	0.32	0.48	4.0	0.4	33.2	25.8	18.5	2.5	70
3	96	0.2	0.32	0.48	4.0	0.4	33.2	25.8	18.5	2.5	75
4	96	0.2	0.32	0.48	4.0	0.4	33.2	25.8	18.5	2.5	80
5	96	0.2	0	0	4.0	0.4	33.2	25.8	18.5	2.5	75
6	96	0.2	0.16	0.24	4.0	0.4	33.2	25.8	18.5	2.5	75
7	96	0.2	0.48	0.72	4.0	0.4	33.2	25.8	18.5	2.5	75
8	96	0.2	0.32	0.48	0	0.4	33.2	25.8	18.5	2.5	75
9	96	0.2	0.32	0.48	1.6	0.4	33.2	25.8	18.5	2.5	75
10	96	0.2	0.32	0.48	5.6	0.4	33.2	25.8	18.5	2.5	75
11	96	0.2	0.32	0.48	6.4	0.4	33.2	25.8	18.5	2.5	75
12	96	0.2	0.32	0.48	4.0	0.4	34.7	33.5	9.3	2.5	75
13	96	0.2	0.32	0.48	4.0	0.4	34	29.6	13.9	2.5	75
14	96	0.2	0.32	0.48	4.0	0.4	32	22.4	23.2	2.5	75

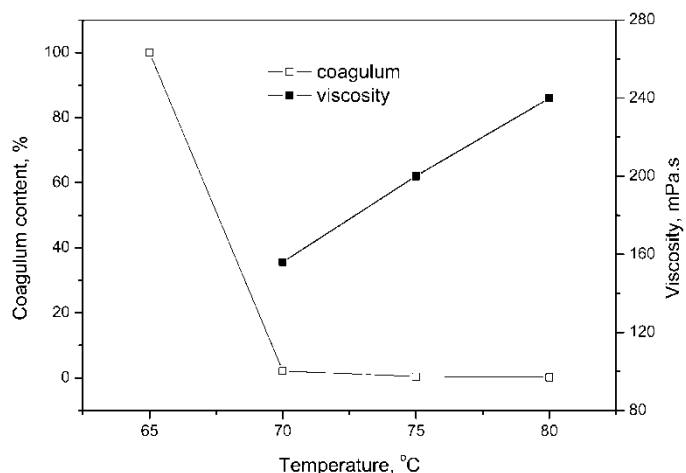


Fig. 1. Effects of polymerization temperature on coagulum and viscosity of the emulsion ([E] = 1%, nano-SiO₂ = 5%).

measured). However, the coagulum formed decreases greatly when the temperature rises to 70°C. In addition, the viscosity of the resultant emulsion increases with the increase of reaction temperature.

The polymerization rate is very slow due to the slow decomposition rate of the initiator below 65°C. In addition, the monomer is dropped continuously into the system, as it is in excess without polymerization. When such circumstance reaches a critical point, the monomer polymerizes abruptly and large bulk coagulum forms. The initiator decomposes quickly when the reaction temperature rises, the monomer polymerizes at once, it is then added dropwise to the system, keeping the system in starvation with monomer, and the coagulum decreases greatly without monomer accumulation. The coagulum is lower than 0.5% at 75°C and 80°C. The increase of viscosity may be due to the increase of particle size. When the temperature rises, the emulsion particle moves fast, the particles connect together to form a larger particle because of the existence of hydrogen bonds among hydroxyl groups and carboxyl groups as they tend to situate at the surface of the particle in emulsion polymerization.

3.2 The Level of Emulsifier on Polymerization

The influence of level of emulsifier on emulsion polymerization was summarized in Figure 2 (No 5, 6, 3 and 7 experiments in Table 1) in the presence of nano-SiO₂. It shows that the coagulum produced is about the same with that without emulsifier, and it has little increase only when the level of emulsifier is 1.5%, which is greatly reduced compared with that without nano-SiO₂. This proves that the nano-SiO₂ acts as an emulsifier function and the level of emulsifier may be reduced when the nano-SiO₂ is used. Figure 2 also shows that we might prepare the emulsion with a larger particle size without emulsifier.

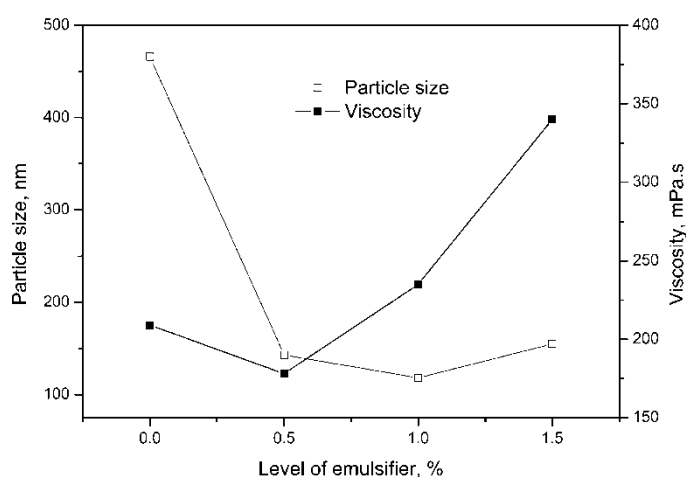
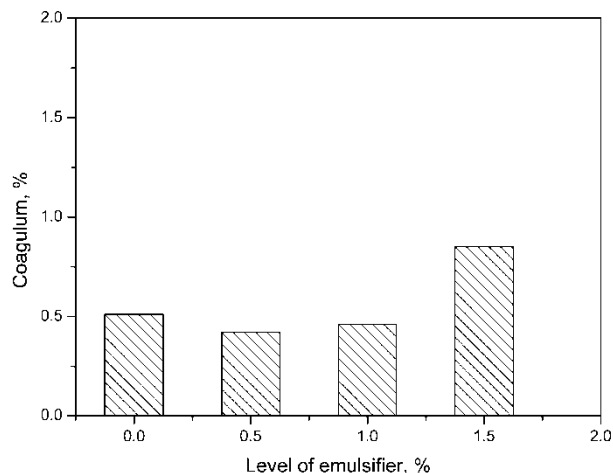


Fig. 2. Effect of level of emulsifier on the emulsion polymerization.

The particle size thus formed is decreased with the increase of the amount of emulsifier, especially from 0% to 0.5%, but a little increase from 1% to 1.5%, which is due to the difference of the nucleating mechanism. As no emulsifier is used, the water-soluble monomer HEMA and AA dissolve in water, and initiation takes place in water. The growing chains precipitate out to form a preliminary particle when they grow to a critical chain length, which is homogeneous nucleating mechanism. The less number of oligomer molecules produced fewer particles which lead to larger particle size. The introduction of a small amount of emulsifier may produce more micelles in the water phase and more active center, which leads to a larger number of particles and small particle size. Introducing a large amount of emulsifier (for example, 1.5% for this system) does not produce more micelle in water as the existence of hydrophilic monomer HEMA and AA. This is a micelle nucleating mechanism. In this system, the two nucleating mechanisms coexist. The viscosity of the emulsion decreases first from without an emulsifier to a 0.5% level of emulsifier used, and then increases with

the increase of level of emulsifier, this is about correspondence to the change of the viscosity.

3.3 Effect of Level of Nano-SiO₂ on Polymerization

Figure 3 shows the effect of the level of nano-SiO₂ on polymerization (No 8, 9, 3, 10, and 11 experiments in Table 1). It is obvious that the level of nano-SiO₂ has little influence on the coagulum produced, viscosity, and the particle size of the emulsion increases gradually when the level of nano-SiO₂ is below 7% based on the weight of total monomers, but the coagulum increases greatly when the level of nano-SiO₂ is above 7%. Furthermore, when it reaches 10%, the viscosity of the emulsion become so high that it is impossible to filter the emulsion and obtain stable emulsion. In all circumstances, the monomer conversion ratio reaches nearly 100%.

Because a small amount of nano-SiO₂ particles has not much influence on monomer polymerization in such an emulsion polymerization system with hydrophilic monomers, the coagulum produced does not increase with

the increase of the number of nano-SiO₂ particles. On the contrary, the contact between monomer molecules is severely hindered by a large amount of nano-SiO₂ and monomer molecules could not polymerize normally. Polymerization reaction might take place suddenly as more and more monomer molecules accumulate resulting in more coagulum production. The critical nano-SiO₂ level is 7% based on the total monomers.

Compare the emulsion with that without a HEMA monomer (9), the coagulum produced has decreased greatly, this may be explained that the hydrophilic monomers act as an emulsifier in this emulsion polymerization. Oligomers with a hydrophilic part (hydroxyl group and carboxyl group) and a hydrophobic part formed when the hydrophilic monomer copolymerized with other monomers at first stage, which are much alike as an emulsifier. The oligomers and emulsifier SDS/OP operated together, more active center produced, and all monomers converted to polymer.

The presence of nano-SiO₂ increases the viscosity and particle size of the emulsion. This fact indicates that the emulsion polymerization takes place on the surface of nano-SiO₂. In this case, the core is a nano-SiO₂ particle (12 nm diameter) and the shell is a polymer (about 110 nm), which accounts for the larger emulsion particle produced. When more than 6% of the nano-SiO₂ particle is used, additional larger emulsion particles form as two or more nanometer particles connect together. The larger particle size hinders the movement of the particle and leads to higher viscosity.

3.4 Effect of Level of Hydroxyl Monomer on Polymerization

Figure 4 shows the effect of level of hydroxyl monomer on polymerization (No 12, 13, 3 and 14 experiments in Table 1). It indicates that the coagulum increases gently with the increase of the level of hydroxyl monomer when the hydroxyl value of acrylic emulsion surpasses 50 mgKOH/g. However, all the coagulum in the experiment is lower than 1%, which is less than that without nano-SiO₂ (10). The reason is that all the hydrophilic monomer HEMA and AA are dissolved in water (81 wt% in water for HEMA (12)) and polymerize in a water phase forming primary radical (oligomer), when the concentration of the oligometric emulsifier exceeds critical chain length, it precipitates and forms emulsion particles. The combination of oligometric emulsifier and mixture of 1% emulsifiers SDS/OP make the emulsion system stable. More hydrophilic monomer leads to more oligomer produced, which is insoluble in water, therefore some of them formed coagulum. The less coagulum in the presence of nano-SiO₂ indicates that nano-SiO₂ particles act as an emulsifier function, the critical micelle concentration (CMC) may be lower in such a small level of emulsifier system.

Figure 4 also shows that the mean particle size of the emulsion increases with the increase of level of hydroxyl monomer. This is due to the increasing hydrophilicity at the emulsion particle surface, as the particles are swollen in

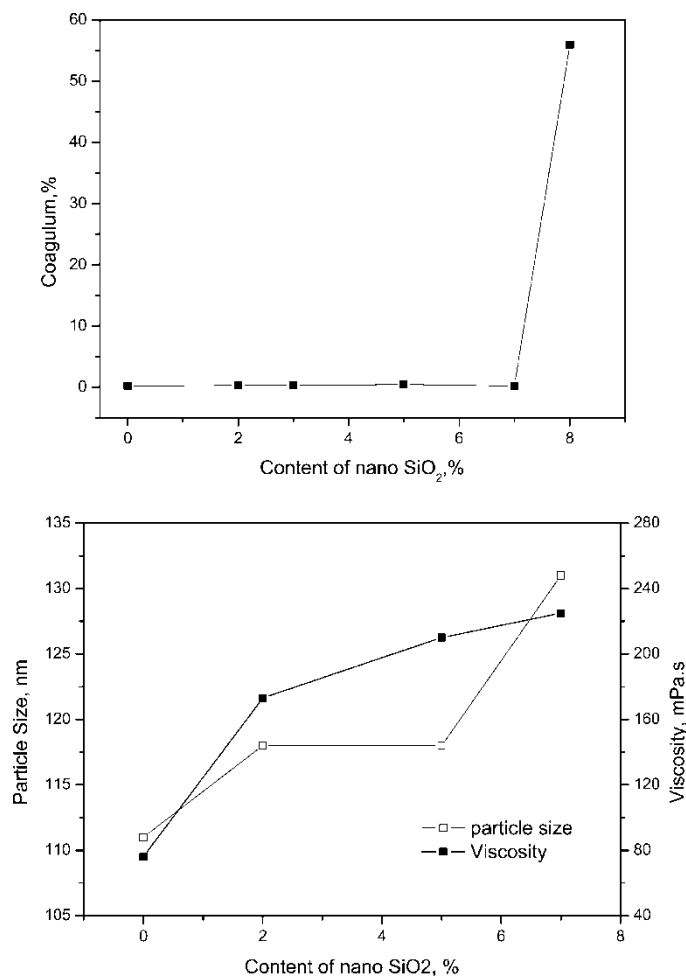


Fig. 3. Effects of content of nano-SiO₂ on coagulum, particle size, and viscosity of the emulsion (Reaction temperature 75°C, [E] = 1%).

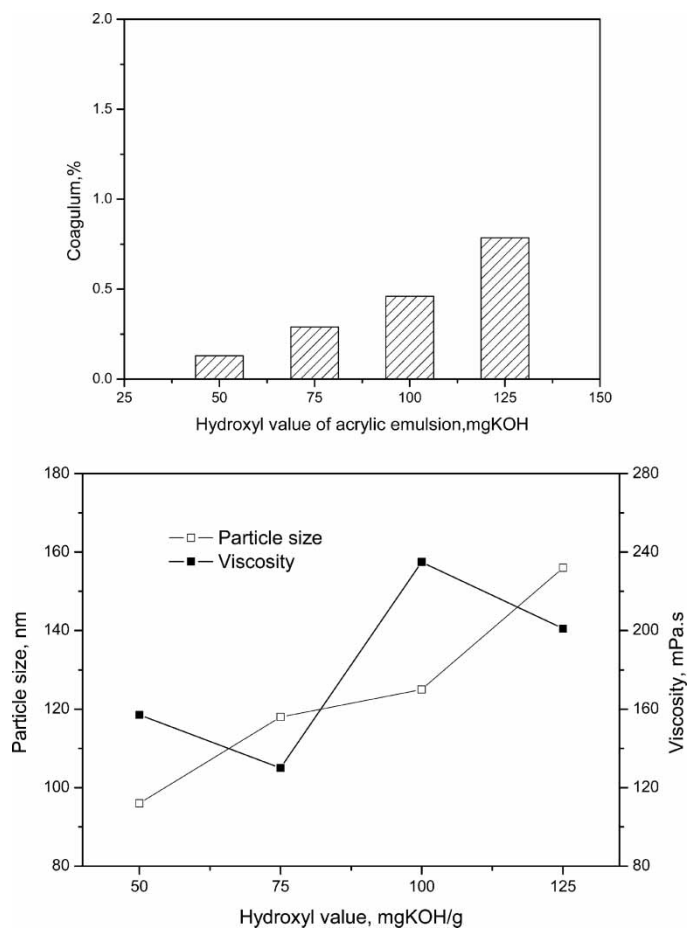
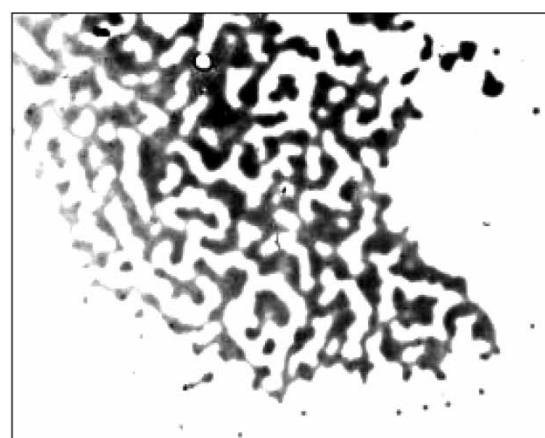


Fig. 4. Effects of hydroxyl value of the emulsion on coagulum and particle size of the emulsion ([E] = 1%, nano-SiO₂ = 5%, 75°C).

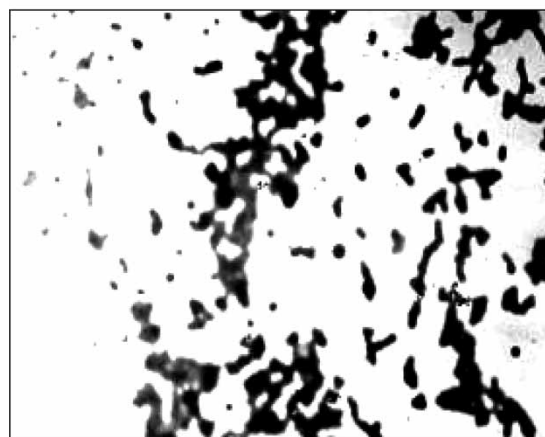
water and the hydrophilic hydroxyl monomer is intended to situate at the surface of the emulsion particle. The more hydrophilic monomer used, the more particles swollen in water, which leads to the thickening of the particle size. The viscosity of the emulsion is not strictly in proportion to the increase of the hydroxyl value of the polymer, but has some tendency to increase, the larger particle size of the emulsion and less water in a continuous phase may account for this.

3.5 Particle Morphology of Emulsion with Nano-SiO₂

Figure 5a and b show that a large amount of emulsion particles stick together and form small blocks of anomalous particles, and very few particles exist in mono-particle form. Furthermore, they also show that some of the nano-SiO₂ particles are wrapped in these blocks of emulsion particles, and still some of them are dissociated which are a sign that these nano-SiO₂ are unwrapped. The existence of the hydroxyl groups and carboxyl groups on the surface of the particle accounts for the connection of these particles, because these groups are easy to form the hydrogen bond. The surface energy is very high as a result of a large amount of hydroxyl



a



b

Fig. 5. TEM photos of the emulsion particle, magnified 1.2×10^4 multiple; 5% nano-SiO₂; Hydroxyl value (mgKOH/g): a: 50, b: 100; [E] = 1%.

groups on the surface of nano-SiO₂, it is difficult for the monomers to polymerize at the surface of nano-SiO₂ particles, when more levels of hydrophilic monomer HEMA are used, therefore, some of the nano-SiO₂ is not wrapped.

4 Conclusions

Emulsion polymerization may be used to prepare nanocomposite materials by mixing monomer and nano-scale inorganic particles directly, which is a very easy way compared with other methods, but it also has some disadvantages such as lower inorganic particles content, post-treated needed and also complicated influence factors. Monomer ingredients and reaction conditions may influence this process. The reaction temperature, level of nano-SiO₂, hydroxyl monomer and emulsifier have different influences on the acrylic emulsion polymerization containing a high concentration of hydroxyl group in the presence of a nano-SiO₂ particle.

The emulsion polymerization cannot take place under 65°C, when the level of nano-SiO₂ is 5% and the increasing of the reaction temperature decreases the coagulum. The level of emulsifier and hydroxyl monomer has little influence on the coagulum in this emulsion polymerization, nano-SiO₂ acts as the function of emulsifier. The increase of hydroxyl monomer hinders the monomer polymerization on the surface of nano-SiO₂.

The level of nano-SiO₂ does not influence the coagulum much when its level is lower than 7% based on the total monomers, but it increases the coagulum greatly and stable emulsion could not be made when its level reaches 10%. However, the coagulum decreases greatly compared with that emulsion with the same composite without nano-SiO₂ particles.

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