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Preparation of Nanometer Silica-Acrylate Composite Emulsion through Mini-Emulsion Polymerization

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ABSTRACT

In this work, the nanometre silica-acrylate composite emulsion was successfully prepared by the method of mini-emulsion polymerization. The effect on particle size by the amount of emulsifier and silica was investigated, and the property of the prepared silica-acrylate composite mini-emulsion was characterized by the stress strain. Results showed that the introduction of silica had no evident effect on the molecular weight and molecular weight distribution. With the increase of SDS concentration, the average particle size of the mini-emulsion decreased. The stress-strain curve showed that the tensile stress elongation and modulus of the polymer increased significantly when the silica was introduced, demonstrating the inorganic nanomaterial effect on the acrylate material.

INTRODUCTION

Polyacrylate is a kind of widely used polymer materials with low hardness and poor mechanical properties. When modified with inorganic materials, it is difficult to work because of the phase separation of inorganic materials. Due to the nanometer size effect of nanometer SiO_2, the powder particles have a huge surface area and high surface activity, and nanometer SiO_2 itself is easy to agglomerate, so it is greatly difficult in occurring emulsion polymerization under the circumstance of nano powder [1]. On the one hand, the nano powders lead to coagulation demulsification under the emulsion polymerization process; on the other hand, there is physical instability in the emulsion resulting in delamination of the emulsion system and it is difficult to give full play to its excellent properties. Mini-emulsion polymerization is an effective way to combine the two materials. The plexiglass substrates were doped with inorganic nano materials, or the functional organic molecules or polymers doped into the inorganic polymer network, which could be synthesized with special properties of inorganic-organic hybrid composite materials. The surface of nano silica nanoparticles modified by the reactive coupling agent was initiated polymerization with acrylate to prepare nano silica-acrylate composite materials. These composite materials had a uniform structure and could be made into glass hybrid materials according to the setting properties. Modified organic glass is made up of inorganic and organic compounds at the atomic or molecular scale. The inorganic network had excellent antiwear properties; therefore, this composite material could have a wide application prospect and excellent properties [2].

MATERIALS AND METHODS

Methyl methacrylate (MMA), Butyl acrylate (BA), Ammonium Persulfate (APS), *n*-hexadecane (HD), Dodecyl sulfonic acid sodium salt (SLS), and water-solubility nano silica (20 nm) were of industrial grade and purchased from Eastern Petrochemical Company. Distilled water was used in this experiment.

Preparation Process of Silica-Acrylate Composite Mini-Emulsion

The nano silica-acrylate composite mini-emulsion was prepared with water-solubility Nano silica and polyacrylate through the method of miniemulsion polymerization as shown in **Figure 1**. SDS was dissolved in 140 g deionized water, then adding a

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certain amount of 25% of the silica gel solution and APS. An amount of HD was dissolved in MMA, and BA monomers, and then the monomer solution was added to the emulsifier solution, stirring 30 min (1000 r/min) forming a monomer pre- emulsion [3]. The pre- emulsion was ultra-sounded in 98-3 D scientz ultrasonic cell grinder for 300 s (ice bath cooling apparatus, an output power of 50%). The ultrasounded monomer mini-emulsion were added into an equipped with a condenser and a thermometer 500 mL four reactor, passing with nitrogen for 15 min, and then heated up to a predetermined polymerization temperature. During polymerization, samples were sampled at a predetermined time of 5 g each time [4].

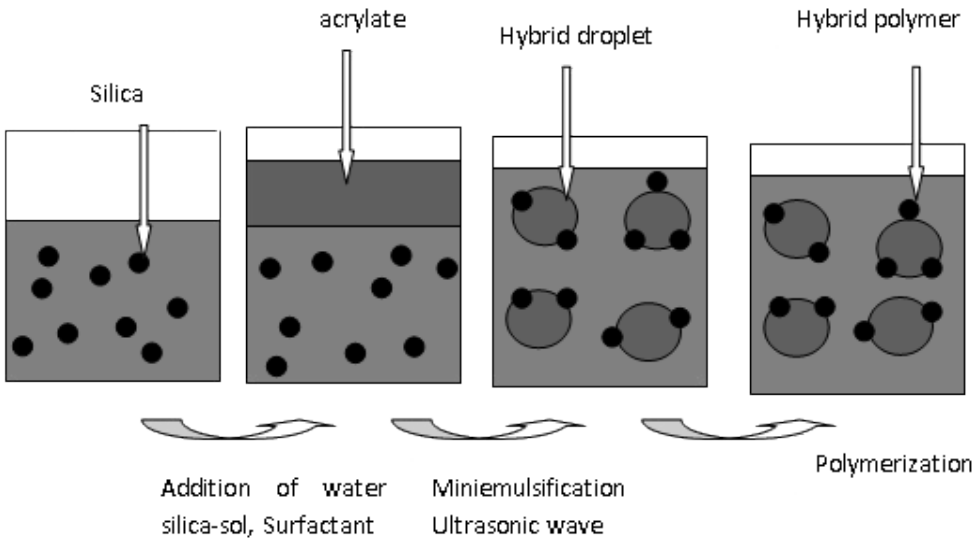

Figure 1. Principle of silica-sol-acrylate composite mini-emulsion polymerization.

The experimental conditions and reagents of the silica-acrylate composite mini-emulsion were shown in **Table 1**.

Table 1. Recipe and reaction condition for silica-sol-acrylate mini-emulsion polymerization.

Ingredients (g)									Temperature (°C)
No	Monomer (MMA/BA)	BPO	AIBN	APS	SDS	Silica-sol	H_2O	HD	
HE-0	20/20	0.1	0.4	0.2.	0.4	0	140	1.2	80
HE-10	20/20	0.1	0.4	0.2	0.6	10	140	1.2	80
HE-20	20/20	0.1	0.4	0.2	0.8	20	140	1.2	80
HE-30	20/20	0.1	0.4	0.2	1.0	30	140	1.2	80
HE-40	20/20	0.1	0.4	0.2	1.2	40	140	1.2	80

Characterization

Determination of particle size

The size of a single drop or polymer particle was measured by dynamic light scattering. The testing instrument was Malvern 2000 particle size tester with a test temperature of 25˚C, and the sample was diluted with deionized water before each test to be measured at the proper concentration. The average particle size was automatically generated by software calculations [5].

Mechanical property test of composite polymer film

The prepared emulsion is dried at a temperature higher than its Tg until the residual monomers and the moisture were completely volatilized, thereby forming a composite film. The film was made into a standard size of 20 mm × 3 mm, and the sides were left 15 mm and the tension test was carried out with the set concentration of 1 kN and tensile speed of 20 mm/min [6-8].

RESULTS AND DISCUSSION

The curve of the initial monomer droplet sizes as a function of the concentration of SDS for silica-acrylate mini-emulsion with various BA: MMA weight ratio as shown in **Figure 2**. As could be seen under the same condition of time, ultrasonic and ultrasonic intensity, when the emulsifier SDS concentration increased, the smaller monomer droplets got much more stable. Because there were more SDS molecules to stabilize the monomer droplets, the larger surface of monomer droplets could be covered. Therefore, with the increase of SDS concentration, the average particle size decreased.

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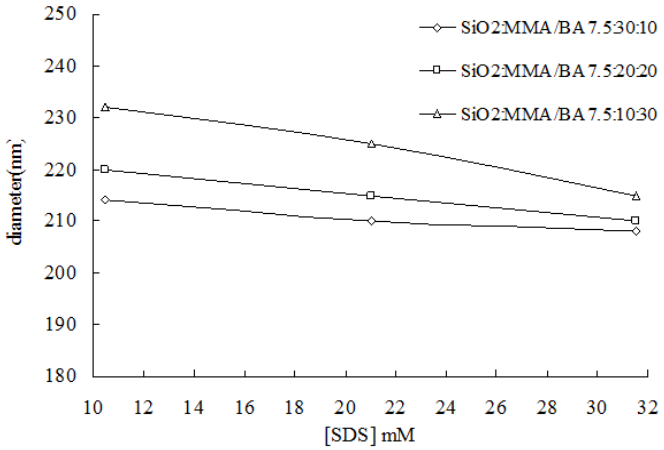

Figure 2. Initial monomer droplet sizes as a function of the concentration of SDS for silica-acrylate miniemulsion with various BA: MMA weight ratio.

Stress strain is an important means of characterizing mechanical properties of materials. **Figure 3** showed the stress-strain curves of different silica-acrylate composite mini-emulsion films. HE-0 represented silica with a dosage of 0%, and HE-10 stood for silica accounting for 10% of the total. It could be found that the tensile strength, fracture elongation and modulus of the polymers increased greatly with the increase of the amount of silica, which fully showed the effect of nano inorganic particles on the modification of acrylate materials. Because the system was silica nano materials, due to its advantages of large surface area and strong adhesion, and it had strong intermolecular force with acrylate, reflecting a synergy between the two components, thus showing an increase of stress and strain.

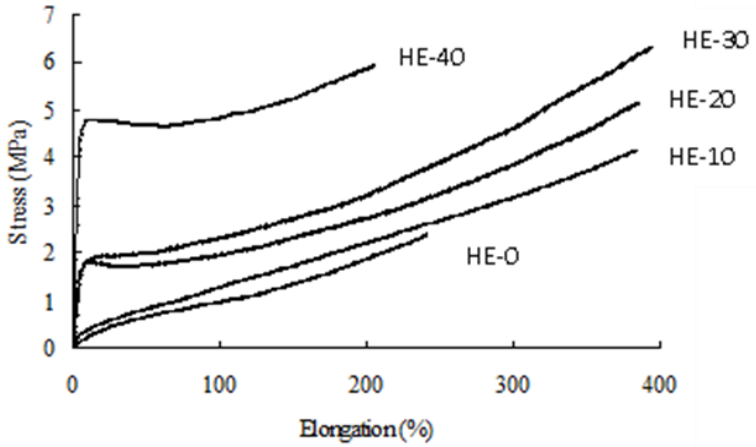

Figure 3. Strain-stress curves for silica-acrylate hybrid polymer with different amount of silica.

The number average molecular weight and molecular weight ratio were listed in **Table 2**. As could be seen from the diagram, the change of the amount of silicon dioxide had little influence on the change of molecular weight, and the free radical did not transfer to the surface of silicon dioxide.

Table 2. The molecule weight of silica-acrylate composite miniemulsion.

Specimen	HE-0	HE-10	HE-20	HE-30	HE-40
M_w	22.50×10^4	25.63×10^4	26.06×10^4	25.53×10^4	25.01×10^4
M_n	10.05×10^4	13.44×10^4	14.18×10^4	10.92×10^4	13.68×10^4
D	2.25	1.91	1.84	2.34	1.83

CONCLUSION

In this work, nano silica was dispersed into acrylate monomer by ultrasonic dispersion technique, and then stabilized nano silica-acrylate composite mini-emulsion was successfully prepared by the way of miniemulsion polymerization. The size of the composite emulsion could be adjusted by choosing different emulsifier dosage and different silica dosage. The increasing of

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reaction temperature or SDS concentration could improve the reaction rate and decreasing particle size. Using water-soluble initiator in the polymerization process enabled the increase of homogeneous nucleation probability, so that the particle size of the emulsion polymerization process reduced. The tensile strength and elongation at break of silica-acrylate composite mini-emulsion were obviously better than that of pure acrylate emulsion. What's more, in the process of miniemulsion polymerization, the introduction of silica has no obvious influence on the polymerization, and the molecular weight and distribution of the composite miniemulsion are close to the molecular weight of the pure acrylate miniemulsion.

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