

PARTICLE MORPHOLOGY OF POLY(VINYL CHLORIDE) RESIN PREPARED BY SUSPENDED EMULSION POLYMERIZATION*

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Abstract Suspended emulsion polymerization was used to prepare poly(vinyl chloride) (PVC) resin. Fine PVC particles were formed at low polymerization conversions. The amount of fine particles decreases as conversion increases and disappears at conversions greater than 30%. Scanning electron micrographs show that PVC grains are composed of loosely coalesced primary particles, especially for PVC resins prepared in the presence of poly(vinyl alcohol) dispersant. The size of primary particles increases and porosity decreases with the increase of conversion. In view of the particle features of PVC resin, a particle formation mechanism including the formation of primary particles and grains is proposed. The formation process of primary particles includes the formation of particle nuclei, coalescence of particle nuclei to form primary particles, and growth of primary particles. PVC grains are formed by the coagulation of primary particles. The loose coalescence of primary particles is caused by the colloidal stability of primary particles and the low swelling degree of vinyl chloride in the primary particles.

Keywords Suspended emulsion polymerization, Vinyl chloride, Particle size distribution, Morphology, Particle formation mechanism

INTRODUCTION

Suspension polymerization has been widely used in the production of commercial poly(vinyl chloride) (PVC) resin. In this process, vinyl chloride (VCM) is suspended, as liquid droplets, in a continuous water phase by vigorous agitation in the presence of dispersant(s). Because PVC is practically insoluble in its own monomer, it tends to precipitate from the monomer phase at very low conversion ($< 0.1\%$ conversion) forming a separate phase inside the droplets. The precipitating PVC chains aggregate to form microdomains, domains and primary particles as polymerization proceeds. At the later stage of polymerization (monomer phase disappears), further polymerization leads to the fusion of primary particles and the formation of agglomerates. As a direct consequence of the above process, and of the density difference between PVC and VCM, PVC grains with unique morphology and porosity would be formed^[1–4]. The morphology and porosity of suspension PVC resins influence the content of residual monomer and the processing properties of PVC resin.

Attempts have been made to decrease the concentration of residual VCM in PVC resin since the 1970s. This has been brought about by a number of factors, one of the most important concerns being the toxicity of VCM. Several technologies have been advanced to meet the requirement of decreasing the concentration of residual VCM, such as using composite dispersants and addition of oil-soluble surfactant in the VCM suspension process, to produce higher porosity resin from which it is easier to strip the unreacted VCM^[5, 6]. New VCM polymerization processes have also been developed to meet this requirement. Bao *et al.*^[7, 8] developed a new VCM heterogeneous polymerization process, using *n*-butane as the reaction medium, to prepare porous PVC resin with loosely coalesced primary particles. Nogues *et al.*^[9] developed the suspended emulsion polymerization

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process to prepare PVC resin with looser coalescence of primary particles and high porosity, and investigated the influences of polymerization conditions on the morphology of PVC resin. But studies on VCM suspended emulsion polymerization, especially on the aspect of mechanism of particle formation and the kinetics of polymerization, are rarely reported in the literature to date.

In this paper, a series of VCM suspended emulsion polymerizations were carried out to prepared PVC resins with different conversions. The particle features of the resulting resins were investigated and a mechanism of particle formation was proposed.

EXPERIMENTAL

Materials

Polymerization grade VCM was supplied by Hangzhou Electric-Chemical Corporation. Potassium persulphate of analytically pure grade was used as initiator. Poly(vinyl alcohol) (PVA) employed as the dispersant was available from Japan Synthesis Chemical with the trade name of LW300. A commercial suspension PVC resin (WS-1000, with DP = 1,000) was supplied by Shanghai Chloro-alkali Corporation.

Polymerization

VCM polymerizations were carried out in a 5-liter autoclave fitted with a water jacket. The agitator system of the reactor was composed of a two-blade, 45° inclined stirrer and a two-blade anchor stirrer. In a typical polymerization run, the autoclave was first charged with a certain amount of water containing the initiator (sometime the dispersant was also added). Then the autoclave was closed and evacuated repeatedly and swept with N₂ to remove the oxygen in the reactor. The reactor was charged with VCM and the reaction content was agitated at room temperature for 30 min. Finally, the reactor was heated to the required temperature to initiate the polymerization. Once the desired polymerization time was reached, the polymerization was terminated by quickly cooling down. PVC resin was obtained after venting, filtrating, washing and drying. The final conversion of VCM was calculated from the difference of weights of polymer formed and initially charged monomer.

Characterization of PVC Resin

The particle size distribution of PVC resin was characterized using a Model LS-230 Coulter Laser Particle Size Analyser. Several PVC grains were sectioned under a microscopy directly and gold-coated in vacuum. The particle morphology of PVC resin was observed using a Philips Model XL30 scanning electron microscope (SEM).

VCM desorption behavior of PVC resin was determined using an inverse gas chromatographic (GC) method. A U-shape copper tube filled with PVC resin was connected with the GC in the column position. PVC resin was allowed to achieve saturation absorption of VCM by feeding N₂/VCM mixed gas. Then, N₂ was passed through PVC resin continuously and the concentration of VCM in the mixed gas was determined by using the GC method. The desorption temperature was set at 90°C.

RESULTS AND DISCUSSION

Particle Size Distribution of PVC Resin

A low water/monomer ratio (0.1–0.6) is usually used in the suspended emulsion polymerization. Water is suspended, as droplets, in the continuous VC phase under stirring. The polymerization is started in the water droplets as monomer dissolved in the water phase initiated by the water-soluble initiator. In our study, VCM suspended emulsion polymerizations were carried out at 65°C and water/monomer ratio of 0.3. Polymerizations were carried out without dispersant or with the addition of PVA dispersant, respectively. The particle size distribution of PVC resins with different conversions is shown in Fig. 1.

It can be seen that PVC resins at low conversions contain a certain volume fraction of fine particles (with particle size smaller than 1.0 µm) and the particle size distributions are wide. As polymerization conversion increases, the volume fraction of fine particles decreases and the average particle size of resins increases. Fine particles are not found in PVC resins when conversions exceed 30%. Since polymerization was initiated in water

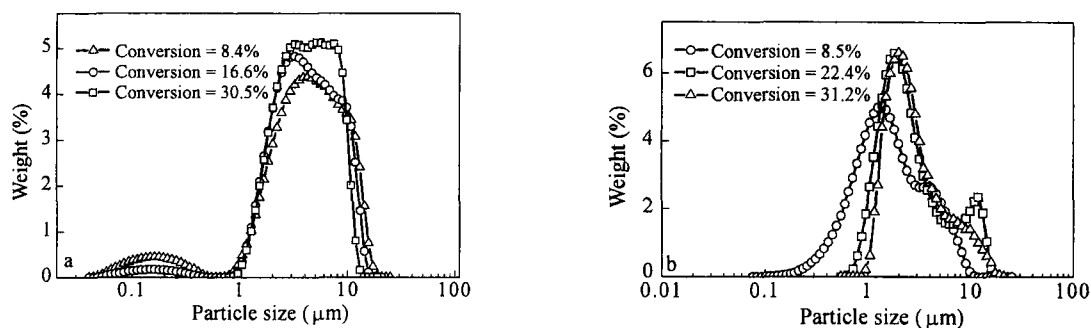


Fig. 1 Particle size distribution of PVC resins with different conversion prepared with suspended emulsion polymerization
a) No dispersant; b) With addition of PVA

droplets, PVC chains would precipitate out from the aqueous phase when they reach a critical polymerization degree. The precipitating PVC chains would aggregate to form primary particle nuclei and primary particles. The grains are formed by coagulation of primary particle. At a low conversion stage, a part of the primary particles can not coagulate to form grains and some coagulated primary particles would separate from grains under shear during the post-treatment process and the particle size measurement since the coagulation strength of primary particles is weak. The coagulation degree and strength of primary particles increase with the increase of conversion; therefore, the amount of fine particles is decreased and fine particles disappear in PVC resins at relatively higher conversions. The viscosity of the water phase and the interfacial tension of water/monomer are changed by adding PVA. The average size of water droplets and colloidal protection imposed on primary particles and grains are consequently also changed. Thus, the particle size distribution is different from that of PVC resins prepared with no addition of surfactant and with addition of PVA, as shown in Fig. 1.

Morphology of PVC Resin

SEM micrographs of sectioned PVC grains with different conversions and prepared without dispersant and with the addition of PVA are shown in Figs. 2 and 3, respectively.

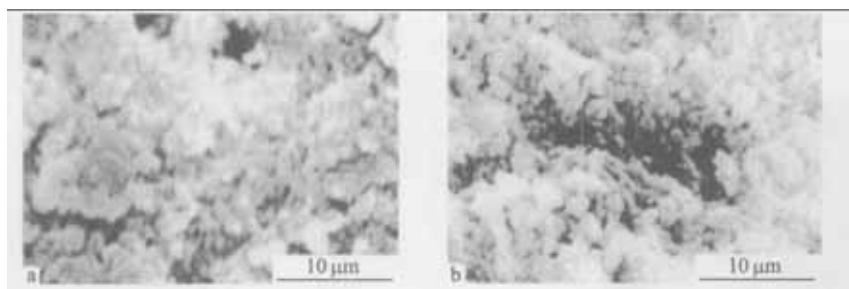


Fig. 2 SEM micrographs of sectioned PVC grains prepared without dispersant
a) Conversion = 10.3%; b) Conversion = 28.3%

It can be seen from Fig. 2 that PVC grains are composed of a great number of primary particles and pores. The size of primary particles ranges from 0.5 to 1.0 μm , but some primary particles are coalesced together. From Fig. 3, it can be seen that PVC grains are also composed of numerous primary particles. For PVC resin with conversion of 4.6%, primary particles are clearly visible, but their size is quite small ($< 0.5 \mu\text{m}$). The average size of primary particles increases and the size distribution of particles becomes more homogeneous as conversion increases. It can also be seen that primary particles usually exist in an aggregated form, but not in a coalesced or “fused” form. From the SEM micrograph of the surface layer of a PVC grain (Fig. 3d), it can be seen that the

surface of grains is also composed of primary particles, but their average size is smaller than that of the primary particles in the center of grains. The population density of primary particles in the surface is higher than that of primary particles in the center of grains and the porosity is smaller.

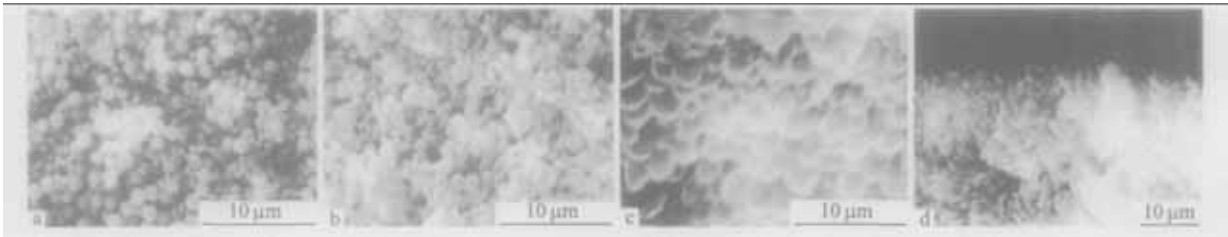


Fig. 3 SEM micrographs of surface layer of grain sectioned PVC grains prepared with the addition of PVA
a) Conversion = 4.6%; b) Conversion = 42.8%; c) Conversion = 73.9%; d) Conversion = 42.8%

In order to compare the morphology of suspension PVC resin and that of PVC resin prepared by suspended emulsion polymerization, a typical SEM micrograph of sectioned suspension PVC resin (WS-1000) is shown in Fig. 4. It can be seen that the suspension PVC grain is composed of coalesced or “fused” primary particles and a continuous “network” is formed throughout the grain. Comparing Figs. 3 with Fig.4, it can be concluded that the morphology of PVC resin prepared by the suspended emulsion polymerization process is quite different from that of suspension PVC resin. The new PVC resin features looser coalescence of primary particles, which would be favorable for VCM desorption and processing. The VCM desorption behavior of WS-1000 PVC and two PVC resins prepared by suspended emulsion polymerization process was determined by the inverse GC method. The variations of the ratio of the concentration of VCM in the resin at the time t and that at the initial time (C_t/C_0) with desorption time were obtained and are shown in Fig. 5 for different PVC resins. In Fig. 5, the PVC resins prepared by suspended emulsion polymerization exhibit higher VCM desorption rates and lower VCM concentrations than those of suspension PVC resin under the same desorption conditions. The resistance to VCM diffusion from PVC resin mainly results from the primary particles and their agglomerates. Since primary particles are loosely coalesced in PVC resins prepared by the suspended emulsion polymerization process, the VCM diffusion resistance will decrease and desorption rate will increase. As a result, PVC resins with less residual VCM are obtained.

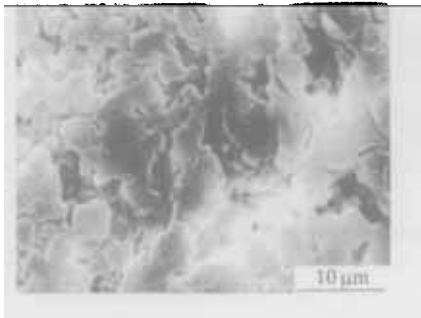


Fig. 4 Typical SEM micrograph of sectioned suspension PVC grain

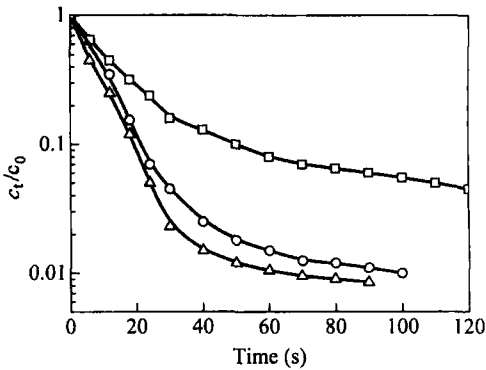


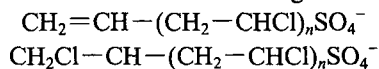
Fig. 5 Comparison on the desorption behavior of suspension PVC (□) and suspended emulsion polymerization PVC resins (○) Conversion = 83.6% (△) Conversion = 73.9%

Mechanism of Particle Formation

In view of the particle feature of suspended emulsion polymerized PVC resin, a mechanism of particle formation in such polymerization is proposed. The particle formation process includes the formation of primary particles

and grains.

The formation process of primary particles includes the formation of particle nuclei via homogeneous nucleation in water, the formation of primary particles via coalescence of particle nuclei, and the growth of primary particles. Due to the low water/oil ratio in the reaction system, the water phase is dispersed as water droplets and suspended in the continuous monomer phase under stirring. Because the initiator is water-soluble and VCM is slightly water-soluble (solubility of VCM in water is about 10 mg/1 g H₂O^[10]), the polymerization starts in the aqueous phase as free-radicals react with dissolved VCM. The reaction in the water phase tends to form oligomers as a result of disproportionation termination having the following idealized structure:



Nucleation of these water-borne oligomers may take place as the degree of oligomerization (n) reaches a value which is so high that the chains are no longer soluble in water in a very low conversion stage. This nucleation process is similar to the homogeneous nucleation process in emulsion polymerization. The nucleation process is followed by the formation of stable primary particles via limited flocculation among the unstable particle nuclei. From SEM results, it can be concluded that with the addition of PVA, the formation of primary particles is completed before 5% conversion. As polymerization proceeds, primary particles are growing through the polymerization of swollen monomer. The monomer diffuses from the continuous VCM phase into the water droplets, and then begins to swell into primary particles and polymerize within them, continuously.

PVC chains are lipophilic when they reach a certain length while persulfate residues are hydrophilic. So PVC chains and primary particles tend to stay at the boundary of water droplets. At the same time, a small amount of polymer is formed in the monomer phase as lipophilic free-radicals diffuse into the VCM continuous phase, and tends to locate at the boundary of water droplets and to coagulate with PVC grains. As conversion increases, more primary particles would aggregate at the boundary of water droplet and form a protection layer for internal primary particles. Thus, each water droplet would convert into a PVC grain and the particle size distribution of resin would change no more. From the measurement of particle size distribution of PVC resins, it can be concluded that the formation of PVC particles is completed before 30% conversion.

When PVA dispersant is not added into the polymerization system, the colloidal protection imposed on primary particles is weak and the electronic repulsive force caused by the remains of the initiator's sulfate ions in the PVC chain is not strong enough to prevent the coalescence of primary particles. Thus, PVC grains composed of looser coalesced primary particles are formed. When PVA dispersant is used in the polymerization, the colloidal protection of PVA imposed on primary particles increases the stability of primary particles. Thus, PVC grains composed of uncoalesced primary particles are formed. The low coalescence degree of primary particles in the suspended emulsion polymerized PVC resin is also related with the low swelling degree of VCM in primary particles. The concentration of VCM in the primary particles is low since the solubility of VCM in water is limited. Thus, primary particles are not sticky enough to coalesce together. For VCM suspension polymerization, the primary particles are well swollen by VCM and the glass transition temperature of swollen PVC is lower than the polymerization temperature. The primary particles are sticky for coalescence and a continuous network of primary particle aggregates is formed.

CONCLUSIONS

The particle size distribution and morphology of PVC resins prepared by the suspended emulsion polymerization process were measured and observed. It was found that PVC resins at low conversions contained a certain amount of fine particles. The amount of fine particles decreases with increasing conversion and disappears at conversion greater than 30%. SEM micrographs show that PVC particles are composed of loosely coalesced primary particles, especially for PVC resins prepared in the presence of PVA dispersant. The size of primary particles increases with increasing conversion and the porosity decreases. A particle formation mechanism is proposed based on the particle features of PVC resins. PVC chains precipitate from the water phase and coil up to form particle nuclei, which further coalesce to form primary particles at a low conversion (*i.e.* < 5% in the

presence of PVA dispersant). The primary particle grows larger as monomer diffuses into it and polymerizes within it. The grains are formed by the coagulation of primary particles. Because of the stability of colloidal primary particles and of the low swelling degree of VCM in the primary particles, PVC resins with low coalescence degree of primary particles could be prepared.

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