

# Influences of Individual and Composed Poly(vinyl alcohol) Suspending Agents on Particle Morphology of Suspension Poly(vinyl chloride) Resin

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**ABSTRACT:** Effects of individual and composed poly(vinyl alcohol) (PVA) suspending agents on the particle morphology of poly(vinyl chloride) (PVC) resins were investigated and discussed in the view of PVA absorption at the oil/water interface and interfacial behavior. It was shown that the percentage and surface coverage of PVA at the oil/water interface decreased with the increase of the degree of hydrolysis (DH) of PVA in the DH range of 70–98 mol %, while the interfacial tension of VC/PVA aqueous solution increased linearly with the increase of DH of PVA. PVC resin with more regular particle shape, increased agglomeration and fusion of primary particles, lower porosity and higher bulk density, was prepared by using PVA with a higher DH as a suspending agent. This was caused by the occurrence of drop coalescence at the very early stage of VC polymerization, the increase of particle shrinkage, and the

lower colloidal protection to primary particles. It was also shown that the interfacial tension of VC/water in the presence of composed PVA suspending agents varied linearly with the weight composition of the composed PVA suspending agents. The particle properties of PVC resin prepared by using the composed PVC suspending agents were usually situated in between the properties of PVC resins prepared by using the corresponding individual PVA suspending agent. The particle morphology and properties of PVC resin could be controlled by the suitable choice of the composed PVA suspending agents. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3848–3855, 2004

**Key words:** poly(vinyl chloride); suspension polymerization; poly(vinyl alcohol); suspending agent; morphology

## INTRODUCTION

Suspension polymerization is commercially used in the manufacture of poly(vinyl chloride) (PVC) resin. In this process, vinyl chloride monomer (VC) is suspended, as liquid drops, in a continuous water phase by a combination of vigorous agitation and the presence of suspending agent(s). The choice of the suspending agent(s) is of utmost importance for VC suspension polymerization. The suspending agent molecules would be absorbed at the VC/water interface at the early stage of polymerization, which would lead to the decrease of the VC/water interfacial tension and the increase of VC dispersion in water. The absorption of suspending agent would also give the colloid protection to drops and primary particles in the drops. Therefore, the suspending agent(s) would affect the liquid–liquid dispersion, drop coalescence, and aggregation of primary particles in VC suspension polymerization, and further affect the particle properties of the

resulting PVC resin, such as particle size and its distribution, particle morphology, and porosity.<sup>1,2</sup>

The suspending agent of VC suspension polymerization is usually based on poly(vinyl alcohol) (PVA), substituted cellulose, or a mixture of the two. The influences of suspending agent(s) on the polymerization process and particle properties of PVC resin have been investigated by several researchers. Nilsson et al.<sup>3–5</sup> reported the influences of PVA (GH20, Rhodoviol 5/270), hydroxypropyl methylcellulose (F50), and their combination with surfactant, on the VC/water interfacial tension, drop size distribution, and resin porosity. Wolf et al.<sup>6</sup> concluded that the plasticizer absorption of the resulting PVC was related to the surface activity of the suspending agent regardless of type. Cheng et al.<sup>7,8</sup> studied the VC suspension polymerization using hydroxypropyl methylcellulose (HPMC) as suspending agent and analyzed the influence of molecular weight and chemical structure of the cellulose on the particle morphology of the resulting PVC. Cebollada et al.<sup>9</sup> studied the influences of HPMC structure and concentration on the particle properties of PVC. Sarkar<sup>10</sup> reported about the mean particle size of PVC resin using cellulose ethers as the suspending agent. Ormonroyd<sup>11</sup> and Lerner et al.<sup>12</sup> investigated the effects of Alcotex series PVAs on the particle size, cold plasticizer absorption, and bulk density of PVC

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TABLE I  
Specifications and Producers of PVA Suspending Agents

Sample 1	Degree of hydrolysis (mol %)	Viscosity of water solution, cp (20°C, 4 wt %)	Producer
PVA1	98.0	26.5	Kuraray, Osaka, Japan
PVA2	93.0–95.0	90–120	Kuraray, Osaka, Japan
PVA3	86.5–89.0	48–56	Synthetic Chem., Osaka, Japan
PVA4	78.5–81.5	44–52	Synthetic Chem., Osaka, Japan
PVA5	76.5–79.0	5.5–7.0	Kuraray, Osaka, Japan
PVA6	72.0–75.0	4.8–5.8	Harco, Harlow, UK
PVA7	69.5–72.5	6.0–6.5	Kuraray, Osaka, Japan
PVA8	53.0–60.0	500–2000 (40 wt %)	Synthetic Chem, Osaka, Japan

resin produced, but no morphology information was reported. Zerfa et al.<sup>13–17</sup> investigated the dispersion of VC in aqueous solution of PVA, PVA absorption at the VC/water interface, and drop coalescence in VC suspension polymerization, using two PVAs with the degree of hydrolysis of 72.5 and 80%, respectively.

In this article, PVA suspending agents with a wide range of the degree of hydrolysis (DH) will be used in the individual and composed forms, to investigate the influences of PVA structure and composition on the absorption behavior of PVA, the interfacial tension of VC/PVA(s) aqueous solution, and the particle morphology of the resulting PVC resins.

## EXPERIMENTAL

### Materials

VC of polymerization grade was supplied by Hangzhou Electrochemical Corporation, Hangzhou, China. Di-(2-ethylhexyl) peroxydicarbonate used as the initiator was supplied by Tianjin Akzo Noble Chemical Corporation, Tianjin, China, in the emulsion form with concentration of 50%. 1,2-Dichloroethane and ethylbenzene were analytical pure. The specifications and producers of PVA suspending agents are shown in Table I.

### Absorption of PVA

A 1-L capacity glass jacketed vessel was used for the liquid–liquid dispersion. The agitator consisted of two layers of two flat-blade impellers. The liquid–liquid system consisted of a mixture of 30% (volume fraction) 1,2-dichloroethane and 70% ethylbenzene as the dispersed phase, while the continuous phase consisted of distilled water and PVA suspending agent.

The mixture of 1,2-dichloroethane and ethylbenzene was used as the model compound of VC since the solubility parameter and density of the mixture were very close to that of VC. Samples were taken from the circular region beyond the agitator by using a two-valve sampler. Concentrations of PVA in the aqueous

phase were measured using a spectroscopic method reported by Finley.<sup>18</sup> Samples stabilized with higher concentration suspending agent solution were observed by using a microscope and taken pictures.

### Interfacial tension of VC/PVA aqueous solution

Interfacial tension of VC/PVA aqueous solution was measured by the capillary method. Due to the volatility and high vapor pressure of VC, a special measurement system was designed and is shown in Figure 1. It consisted of a glass vessel, a square glass water bath connected with a thermostat, a height reader, and a camera. The glass vessel was fitted with a capillary fixing part, a pressure gauge, and a thermometer.

In a typical measurement, a glass capillary with a certain diameter was fixed in the vessel. Then the vessel was closed, and repeated evacuation and N<sub>2</sub> sweep was used to reduce the concentration of residual oxygen in it. The vessel was charged with VC and placed motionlessly for several minutes. PVA aqueous solution with a certain concentration was fed to the vessel using a high-pressure pump. After that, the vessel was placed in the water bath. The distance between the liquid surface in the capillary and the VC/water interface was measured by the height

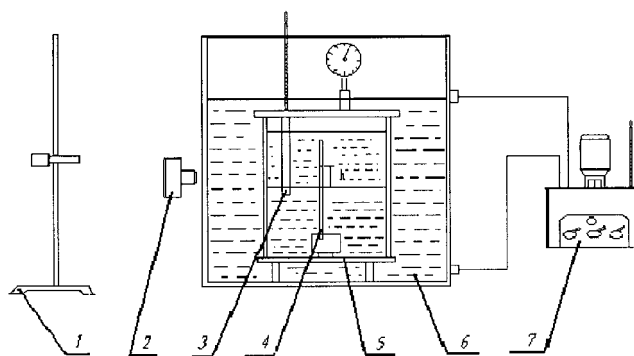


Figure 1 Experimental layout of the VC/water interfacial tension measurement system.

reader after an equilibrium state was achieved. The contact angle of VC–water–glass interface was recorded by using the camera. The interfacial tension of VC/PVA aqueous solution ( $\sigma$ , in units of N/m) was calculated as follows:

$$\sigma = \frac{\Delta \rho g h d}{4 \cos \theta} \quad (1)$$

where  $h$  is the distance between the liquid surface in the capillary and VC/water interface (in units of m),  $d$  the internal diameter of the capillary (m),  $g$  the weight force constant ( $\text{m/s}^2$ ),  $\Delta \rho$  density difference between VC and water ( $\text{kg/m}^3$ ), and  $\theta$  the contact angle between VC, PVA aqueous solution, and glass ( $^\circ$ ).

### Polymerization

VC suspension polymerizations were carried out in a 5.0-L stainless steel jacketed autoclave fitted with an agitator consisting of a two-flat-blade impeller and a two- $45^\circ$  inclined blade impeller. The autoclave was first charged with distilled water, the initiator emulsion, and PVA aqueous solution(s). Then the autoclave was closed, and repeated evacuation and  $\text{N}_2$  sweep was used to reduce the concentration of residual oxygen in the reactor. VC was then charged and the mixture was agitated for about 30 min at ambient temperature. The reactor was heated up to the polymerization temperature to start the polymerization. The polymerization was terminated at a certain pressure drop of the reaction system and the residual monomer was vented. The resin was recovered by filtration and dried at  $60^\circ\text{C}$  for about 24 h. The detailed reaction conditions are shown as follows:

Mass of distilled water:2000 g  
 Mass of VC:1000 $\pm$ 20 g  
 Mass of PVA suspending agent(s):0.8 g  
 Mass of the initiator emulsion:1.3–1.6 g  
 Reaction temperature:57 $\pm$ 0.2 $^\circ\text{C}$   
 Agitation speed:700 rpm  
 Pressure drop:2.5 kg/cm<sup>2</sup>  
 Final conversion:80–85%

### Characterization of PVC resin

The particle size of PVC resin was measured by using a Coulter Laser Particle Size Analyser. The bulk density (BD) was measured by the Chinese Standard GB3402-82 method. The principle of the method is similar to that of ASTM D1895, but the shape of the funnel is different. The porosity of PVC resin was characterized by cold plasticizer absorption (CPA). A weighed amount of PVC resin was placed in a sand-core tube and allowed to absorb dioctyl phthalate

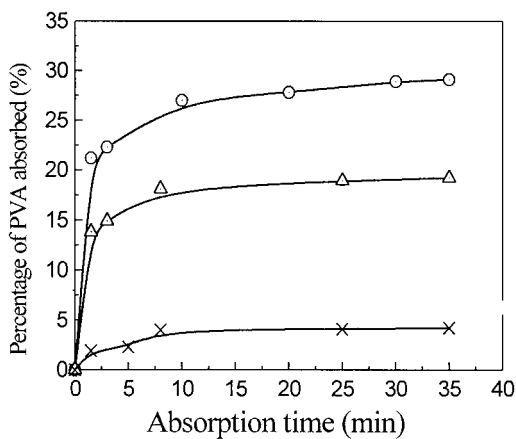
(DOP) plasticizer at room temperature ( $20\pm 2^\circ\text{C}$ ) for 30 min. The unabsorbed DOP was removed by centrifugal separation (3000 rpm, 60 min). PVC grains (sectioned or unsectioned) were gold-coated in vacuum. The morphology of PVC grain was observed using a Philips XL30 Model Scanning Electron Microscopy (SEM).

## RESULTS AND DISCUSSION

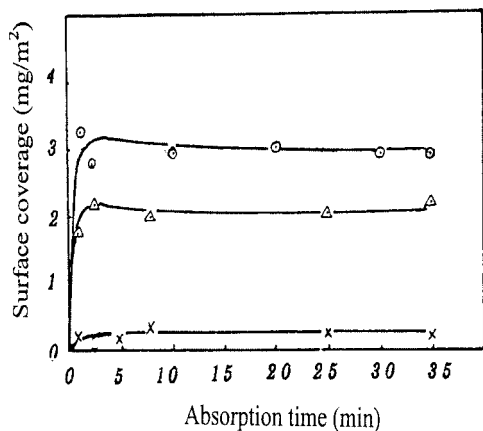
### Influences of PVA structure on absorption behavior

In the PVA absorption study, samples of the continuous phase were taken stepwise after the addition of organic mixture. The concentration of PVA in the water phase was determined after the separation of the organic phase and water phase by using a high-speed centrifuge. Knowing the initial PVA concentration, it is possible to determine the quantity and the percentage of PVA absorbed by the organic phase. The average drop size and surface area were calculated by counting the diameters of 400–800 drops. The amount of PVA absorbed per surface area (surface coverage) could be obtained from the quantity of PVA absorbed and the total surface area of drops. The variations of the percentage of PVA absorbed and the surface coverage with absorption time are shown in Figure 2 for different PVA suspending agents.

Figure 2 shows a relatively high absorption rate at the initial stage, and then a plateau indicating either an equilibrium percentage of PVA absorbed or a saturation surface coverage. The equilibrium percentage of PVA absorbed and the saturation surface coverage obtained in this work were comparable to that obtained by Zerfa et al.<sup>19</sup> The equilibrium percentage of PVA absorbed was relatively lower, while in the real VC suspension polymerization system, more and more PVA molecules would migrate to the organic phase as polymerization proceeded and PVA/VC graft polymer formed. Figure 2 also shows that the equilibrium percentage of PVA4 absorbed and surface coverage of PVA4 is greater than that of PVA3, and the equilibrium percentage of PVA3 absorbed and surface coverage of PVA3 greater than that of PVA1. This is mainly caused by the variation of DH of PVAs. PVA with a higher DH exhibits higher hydrophilicity and would diffuse slowly to the interface. The absorbed PVA molecules would form a configuration as follows: poly(vinyl acetate)-enriched segments (lipophilic segments) penetrate into the organic phase, whereas poly(vinyl alcohol)-enriched segments (hydrophilic segments) extend to the water phase. PVA molecules with a higher DH would occupy more surface area and achieve the saturation absorption at the lower quantity. Due to the high initial absorption of PVA molecules at the interface and the delayed rear-



a



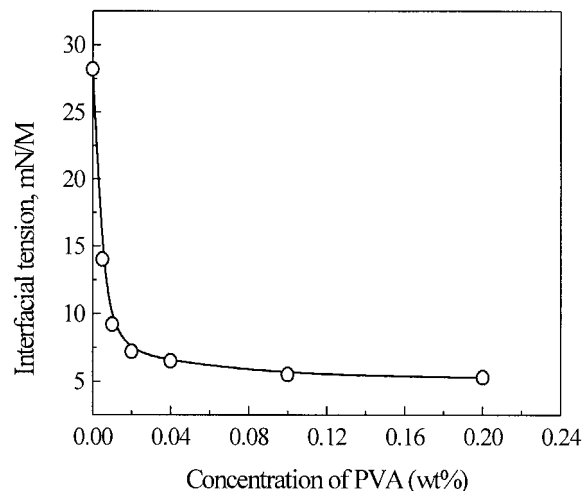
b

**Figure 2** Variations of the percentage of PVA absorbed (a) and surface coverage (b) with absorption time for different PVAs (25°C, agitation rate 350 rpm, phase ratio 0.25, initial PVA concentration 0.1% to water), (x) PVA1, (Δ) PVA3, and (○) PVA4.

rangement of PVA molecules, the overabsorption of PVA molecules appeared for PVA3 and PVA 4.

**Influences of PVA structure and combination on interfacial tension**

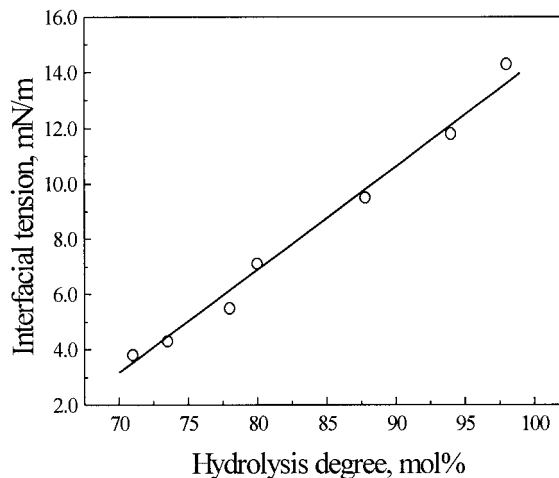
In order to verify the accuracy of interfacial tension measured by the capillary method, the interfacial tensions of tetrachloromethane/water and VC/pure water were measured at first. The measured interfacial tension of tetrachloromethane/water was 45.3 mN/m at 20°C, which was very close to the result of Girifalco et al. (45.0 mN/m).<sup>20</sup> The measured interfacial tension of VC/pure water was 32.2 mN/m at 25°C, which was close to the value (33.3±0.9 mN/m) determined by



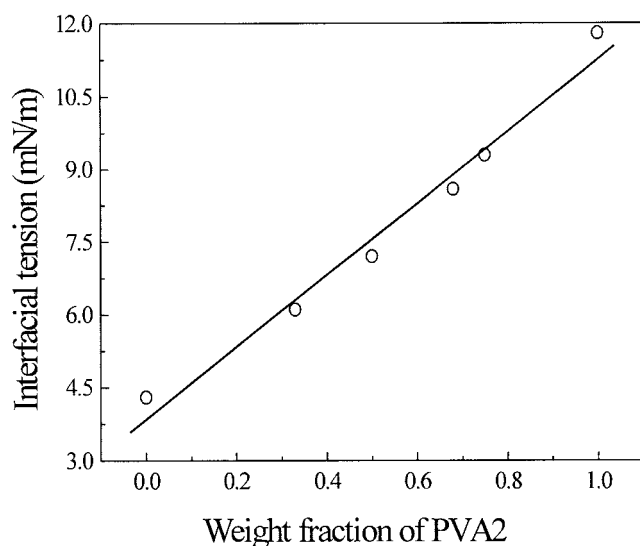
**Figure 3** Influence of PVA5 concentration on the interfacial tension of VC/PVA aqueous solution (50°C).

Nilsson et al. using the drop volume method.<sup>3</sup> The interfacial tension of VC/water decreased as PVA suspending agent added. The influences of PVA (PVA5) concentration (wt % to water) and the DH of PVA on the interfacial tension of VC/PVA aqueous solution are shown in Figure 3 and Figure 4, respectively.

From Figure 3, it can be seen that the interfacial tension of VC/PVA aqueous solution decreased rapidly when the concentration of PVA5 was less than 0.04 wt %, and decreased slowly as the concentration of PVA5 increased again. Padovan et al.<sup>21</sup> working on the *n*-butyl chloride/water, found that the interfacial tension decreased from 31 mN/m to less than 5 mN/m when the concentration of PVA (with DH of 72%) was greater than 60 ppm. Nilsson et al.,<sup>3</sup> working with VC/water at 50°C and with PVA 71.5% hydro-



**Figure 4** Influence of DH of PVA on the interfacial tension of VC/PVA aqueous solution (50°C, PVA concentration: 0.1 wt % to water).



**Figure 5** Influence of the composition of PVA2/PVA6 composite on the interfacial tension of VC/water (50°C, PVAs concentration: 0.1 wt % to water).

lyzed, found that for 100 ppm the interfacial tension was about 4 mN/m.

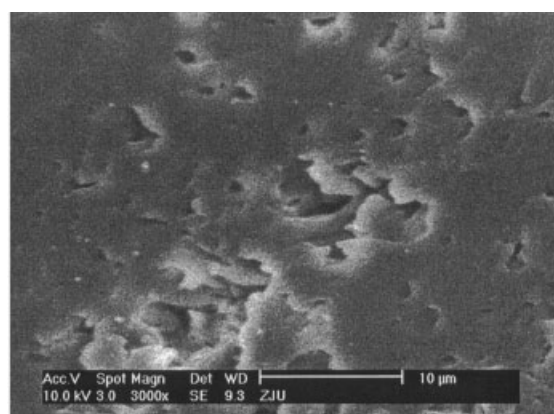
From Figure 4, it can be seen that the DH and interfacial tension have a good linear relationship in the studied DH range. The interfacial layer between VC and water phase would form as PVA molecules absorbed at the oil/water interface. The interfacial tension was raised by the nonbalance of hydrophilic action and lipophilic action of PVA molecules in the interfacial layer. The increase of interfacial tension was caused by the increased PVA hydrophilicity as its DH increased.

The interfacial tension of VC/water in the presence of PVA2/PVA6 composite was measured and related with the composition of the composite in Figure 5. It can be seen that the interfacial tension increased linearly with the increase of weight fraction of PVA2. This means that there is no obvious interaction between PVA components in affecting the interfacial properties.

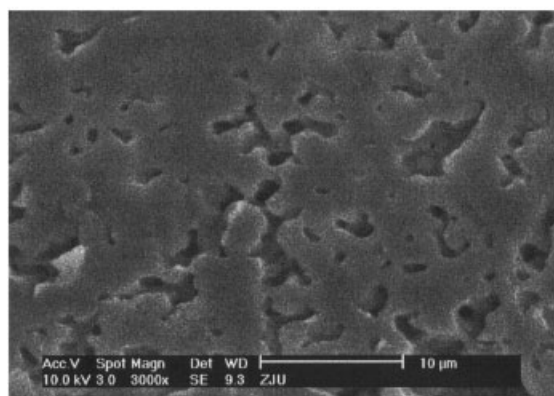
#### Influences of PVA structure on the particle morphology of PVC resin

PVA suspending agents with different structure were first used in VC suspension polymerization in an individual form. SEM micrographs of sectioned PVC grains prepared by using individual PVA2, PVA4, and PVA7 are shown in Figure 6. It can be seen that PVC primary particles exist in the agglomerated and "fused" forms, but the degree of agglomeration and fusion is different from PVC samples prepared by using different PVAs. For PVC resin prepared by using PVA with a high DH (PVA2), the primary particles

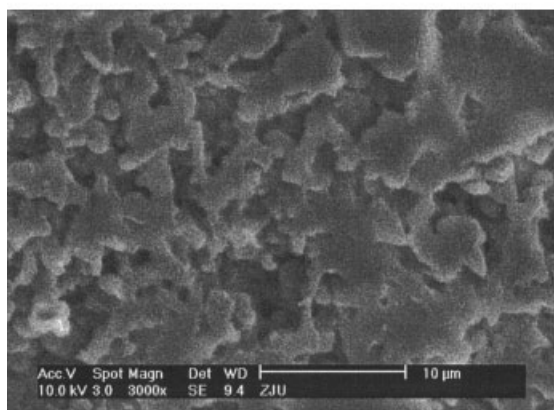
are seriously agglomerated and fused, and the porosity of particle is very low. For PVC resin prepared by using PVA with a medium DH (PVA4), although the primary particle still exist in the agglomerated and "fused" forms, the degree of agglomeration and fusion is lower than that of PVC resin prepared by using PVA2, and more porous structure can be found in the



a

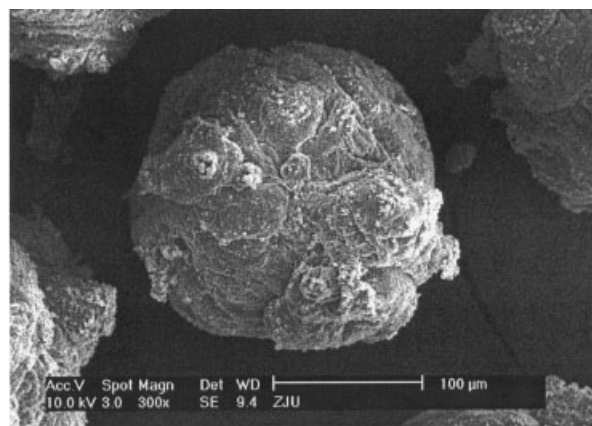


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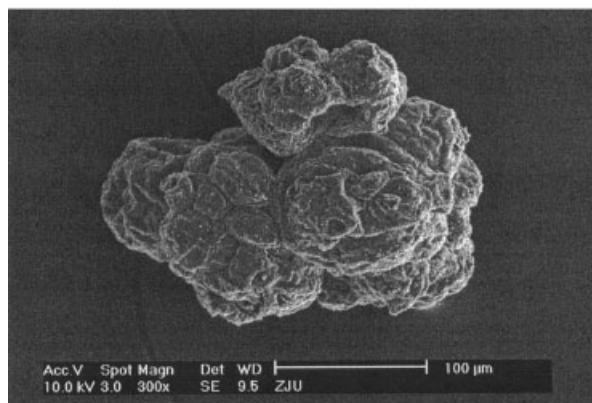


c

**Figure 6** SEM micrographs of sectioned PVC grains prepared by using PVA2 (a), PVA4 (b), and PVA7 (c) as suspending agent.



a



b

**Figure 7** SEM micrographs of PVC grains prepared by using PVA2 (a) and PVA7 (b) as suspending agent respectively.

internal of particle. For PVC resin prepared by using PVA with a low DH(PVA7), the degree of agglomeration and fusion decrease again, and some small aggregates of primary particles and more porous structure can be found. The variations of PVC morphology are caused by the variation of the structure of PVAs. The content of lipophilic poly(vinyl acetate)-enriched segments decreases as the DH of PVA increases, which would lead to the decrease of the colloidal protection to primary particles and the increase of

agglomeration and fusion of primary particles. On the other hand, the absorption rate of PVA at the VC/water interface decreases as the DH of PVA increases. The drop shrinkage (caused by the density difference between VC and PVC) would be increased since the grafting degree of VC on PVA would decrease and the weaker membrane would be formed at the interface. As a result, the porosity and CPA decrease, and BD increases as the DH of PVA increases.

PVA suspending agent also affects the external particle morphology of the resulting PVC resin. For PVC resin prepared by using PVA2 as the suspending agent, one may find many particles like that shown in Figure 7(a), which is approximately spherical and composed of few subgrains. For PVC resin prepared by using PVA7 as the suspending agent, one may find many particles like that shown in Figure 7(b), which possesses irregular particle shape and composed of more subgrains. The external morphology of PVC particles is mainly determined by the drop coalescence and shrinkage processes, which happen at the early stage of polymerization ( $\leq 15\text{--}20\%$  conversion). The absorption rate of PVA2 is lower than that of PVA7, so the drop coalescence would happen at even early stage of polymerization. The viscosity of drops is lower at that time and the coalesced drops are easy to deform. On the other hand, the degree of particle shrinking would increase since few PVA/VC graft copolymers would be formed due to lower absorption of PVA2. Thus, the more regular PVC particles would be formed through the particle shrinking. The regularity of PVC particles would also lead to the increase of bulk density (BD) of PVC resin.

The BD, CPA, and the volume average particle size ( $D_v$ ) of the resulting PVC resins prepared by using different PVAs are shown in Table II. It can be seen that BD of the resulting PVC resin decreases and CPA increases as the DH of PVA decreases. This is caused by the above variations of PVC particle morphology with PVA structure. The particle size of PVC resin increases with the increase of DH of PVA. Since the interfacial tension of VC/water increased when a PVA with a higher DH was used, the mean size of initial drops increased in the polymerization process. Adding the increased drop coalescence, the particle size of PVC resin increased finally.

**TABLE III**  
BD, CPA, and  $D_v$  of PVC Resins Prepared by Using Different PVA Composites

Run	Combination type	Weight ratio	BD (g/mL)	CPA (g/100 g PVC)	$D_v$ ( $\mu\text{m}$ )
6	PVA2/PVA4	1/1	0.54	15.0	212.5
7	PVA2/PVA7	3/1	0.58	11.0	195.4
8	PVA2/PVA7	1/1	0.52	20.9	192.7
9	PVA2/PVA7	1/3	0.46	21.3	160.8
10	PVA2/PVA4/PVA8	1/1/0.5	0.44	24.0	194.6

**TABLE II**  
**BD, CPA, and  $D_v$  of PVC Resins Prepared by Using**  
**Different PVAs**

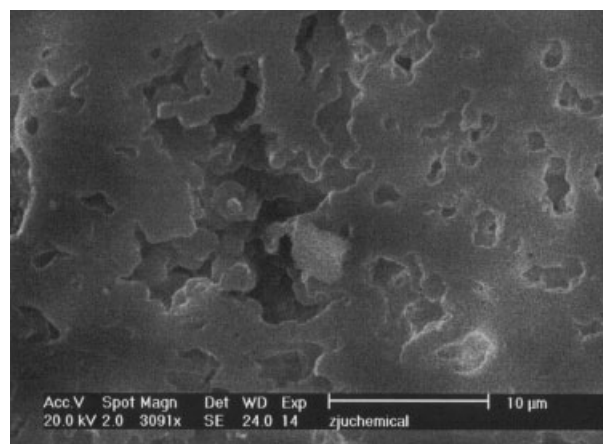
Run	Type of PVA	BD (g/ml)	CPA (g/100g PVC)	$D_v$ ( $\mu\text{m}$ )
1	PVA2	0.64	8.0	227
2	PVA3	0.57	10.2	195
3	PVA4	0.49	18.1	185
4	PVA6	0.44	25.3	162
5	PVA7	0.43	25.9	168

### Effects of the composed PVA on the particle morphology of PVC resin

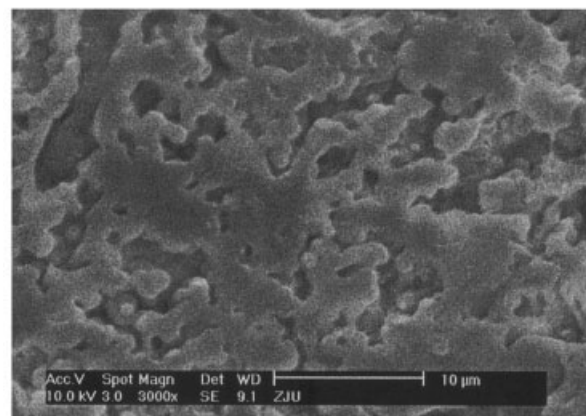
In this part, the composed PVA suspending agents were used in the VC polymerization. The influences of the composition type, ratio between PVA components on BD, CPA, and  $D_v$  of the resulting PVC resins are shown in Table III.

On comparison with runs 1 and 3 in Table II and run 6 in Table III, it can be seen that the BD, CPA, and  $D_v$  of PVC resin prepared by using the PVA2/PVA4 composite are usually located in between the corresponding values of PVC resins prepared by using PVA2 and PVA4 individually. One may also find this law in the cases of using individual PVA2, PVA6, and PVA2/PVA6 composite as the suspending agent(s). It also shows that PVC resin prepared by using the composite of high HD PVA/medium HD PVA (PVA2/PVA4) exhibits higher BD and lower CPA than that prepared by using the composite of high HD PVA/low HD PVA (PVA2/PVA7). On comparison with runs 7–9, it can be found that BD and  $D_v$  decrease, and CPA increases as the weight fraction of lower DH PVA (PVA7) increases. All these results show that the PVA components in the composite had no obvious interaction in affecting the VC suspension polymerization process and the particle properties of the resulting PVC resin. In run 10, a low HD PVA with high oil affinity (although it is still water soluble) was added based on the PVA2/PVA4 composite. It can be found that CPA increases, and BD and  $D_v$  decrease, as expected. SEM micrographs of sectioned PVC resins obtained from run 6, run 8, and run 10 are shown in Figure 8.

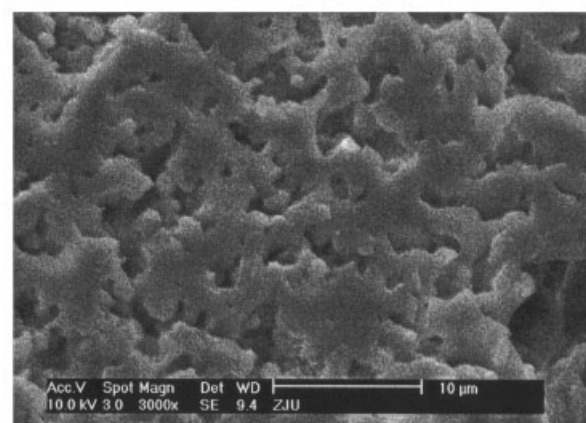
On comparison with Figure 6(a) and Figure 8(a), and Figure 6(a) and Figure 8(b), one may find that the degree of agglomeration and fusion of primary particles decreases and the porosity resin increases when part of PVA2 is replaced by PVA4 or PVA7. PVA7 is more effective in decreasing the degree of agglomeration and fusion and in increasing of the porosity due to its lower HD. On comparison with Figure 8(a) and Figure 8(c), it can be seen that the addition of a small amount of PVA8 can effectively decrease the agglomeration and fusion of primary particles and



a



b



c

**Figure 8** SEM micrographs of sectioned PVC grains obtained from run 6, run 8, and run 10 polymerizations

increase the porosity of PVC resin. This is caused by the strong colloidal protection of PVA8 molecules to primary particles due to their high oil affinity. According to the above results, one may conclude that the particle morphology of PVC resin can be adjusted by

the suitable choice of PVAs composite. The combination of PVA suspending agents also allows one to produce PVC resin with a higher bulk density and a suitable porosity.

### CONCLUSIONS

The structure and the combination of PVA suspending agent(s) had significant influences on the VC suspension polymerization process and particle morphology of the resulting PVC resins. The surface coverage of PVA at the oil/water interface decreased, and the interfacial tension of VC/water increased linearly, with the increase of the DH of PVA added in the DH range of 70–98 mol %. It would lead to the early occurrence of drop coalescence, the increased degree of particle shrinking, and the lower colloidal protection to primary particles, when PVA with a higher DH was used in the polymerization. The resulting PVC resin would exhibit more regular particle shape, higher degree of agglomeration, and fusion of primary particles, lower porosity, and higher bulk density. The interfacial tension of VC/water in the presence of the PVA-composed suspending agents varied linearly with the weight composition of PVAs composite. The particle properties of PVC resin prepared by using of PVC composites were usually situated in between the properties of PVC resins prepared by using the corresponding individual PVA. This illustrated that PVA components in the composed suspending agents had no obvious interaction. The particle morphology and

properties of PVC resin could be controlled by the suitable choice of PVA type and combination of PVAs in the VC suspension polymerization.

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