

# Dispersion of Nanoparticles in Poly(vinyl chloride) Grains During *In Situ* Polymerization

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**ABSTRACT:** Inorganic nanoparticles such as calcium carbonate, silica, or hydrotalcite were dispersed in vinyl chloride prior to suspension polymerization. That led to the production of poly(vinyl chloride) (PVC) composite grains with higher porosity and different internal morphology from those of commercial PVC. The PVC/composite grain sizes and their distribution were also influenced by the presence of nanofillers. The distribution of filler nanoparticles (either calcium carbonate or silica)

was not uniform throughout the PVC grains. Regions of high and low filler concentration were observed. Regions of pure polymer were also observed. Reasons for that are suggested. Hydrotalcite did not remain in the PVC grains. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1824–1830, 2012

**Key words:** vinyl chloride; suspension polymerization; nanoparticles; calcium carbonate; morphology

## INTRODUCTION

Nanoparticulate fillers, or ultra fine particulate fillers, have attracted interest because they could be more effective than conventional microdimensional fillers in enhancing the mechanical properties of polymers.<sup>1–3</sup> For poly(vinyl chloride) (PVC), the use of nanoparticulate fillers could also increase grain porosity.<sup>4</sup> The benefits of using ultra-fine fillers are unlikely to be obtained unless the primary particles are well dispersed in the polymer. Dispersion is not always easy because the nanoparticles exhibit a strong tendency to aggregate. The agglomerates can contain trapped gas, which inhibits the adhesion of the polymer to the particles and form crack initiation points. Better dispersion may be achieved if nanofillers are dispersed in the monomer prior to suspension polymerization. Previous work<sup>5</sup> showed that, when ultra fine particulates were dispersed in vinyl chloride before polymerization, the time required for the drop size distribution of monomer drops to reach a dynamic steady state increased. The average drop size also increased and the formation of very small PVC particles was avoided. The presence of fine particles can also affect the shape of PVC grains.<sup>6</sup>

It has been generally accepted that, when nanofillers are dispersed in the monomer prior to polymerization, better filler dispersion is achieved. In previous work, the quality of dispersion was shown by melting the polymer grains and performing Transmission Electron Microscopy (TEM) studies. The TEM studies showed improved dispersion in the molten PVC state and hence it was concluded, by extrapolation, that the dispersion of the fillers in the PVC grain was uniform and that the particles were well dispersed to single unit level.<sup>1,4,7–10</sup> However, the internal structure and morphology of the PVC/CaCO<sub>3</sub> grains have not been examined, so far, to verify the assumption of the uniform nanofiller dispersion within the grain. In this study, nanoparticles were added into vinyl chloride monomer (VCM) and the internal morphology and structure of PVC/CaCO<sub>3</sub> grains, which were produced by suspension polymerization, are examined. The grains were sectioned and the dispersion of the nanofillers within the grain was examined.

## EXPERIMENTAL

### Materials

VCM was supplied by Ineos ChlorVinyls. Commercial PVC was supplied by Ineos Vinyls (Evipol SH6030 with weight average molecular weight of about 64,000). Hydrolyzed poly(vinyl acetate) (PVA) was supplied by Synthomer (Alcotex 72.5; 72.5% hydrolyzed). Bis(4-*tert*-butylcyclohexyl) peroxydicarbonate (Perkadox 16) was supplied by Akzo Nobel.

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Particulate calcium carbonate, coated with stearic acid, was supplied by Solvay (mean particle diameter 55 nm and specific surface area  $23.6 \text{ m}^2 \text{ g}^{-1}$ ).<sup>11</sup> Sidistar amorphous silica (average particle diameter 0.15  $\mu\text{m}$ ) was supplied by Elkem Materials. Two types of silica were used, a silica aqueous slurry, and a powder. Hydrotalcite (Alcamizer P93 with mean particle diameter 0.7  $\mu\text{m}$ ) was provided by Kisuma Chemicals.

### Experimental procedure

The suspension polymerization experiments were run using a 1-L jacketed stainless steel reactor equipped with three equidistant baffles and a four flat bladed stirrer. The nanoparticles and the initiator (Perkadox 16) were initially charged in the reactor, which was then sealed and purged with nitrogen (to remove oxygen). The monomer was then charged to the reactor and the mixture was stirred for 30 min at ambient temperature to dissolve the initiator and disperse the particles. The suspending agent (PVA) solution and deionized water were then purged with nitrogen (to remove oxygen) and added to the reactor. The amount of the PVA was 0.3 wt % of the organic phase and the volume fraction of monomer was 0.3. The dispersion was then stirred for 30–40 min, to allow PVA to stabilize the monomer drops, and the temperature was then raised to 328 K. The polymerization was stopped after the pressure in the reactor dropped by 3 bar; by then,  $\sim 80\%$  of the monomer was converted. After polymerization, unreacted monomer was removed from the PVC grains, which were then dried.

The grain size distributions of the PVC were measured by using a Coulter LS 230 Laser diffraction particle sizer. PVC morphology was examined by using a Carl Zeiss (Leo) 1530 VP scanning electron microscope (SEM). The porosity was measured by Nitrogen absorption using a Micromeritics Tristar 3000 porosimetry analyzer and by Mercury absorption using a Micromeritics 9310 Pore Sizer.

To examine their internal morphology grains were sectioned by using a microtome—diamond knife to produce sections of 10 and 20 microns thick. With conventional sectioning techniques, polymer grains are embedded in resin, which may interfere with the polymer. That risk was avoided by using a new technique in which the grains were embedded in ice and the ice/grain composite was sectioned. Water from the melted ice was then removed by drying to obtain uncontaminated grain sections. The sections were then examined via SEM.

Contact angles were obtained at room temperature by using Dataphysics OCA-20 contact angle equipment. Water and diiodomethane were used as two testing liquids.

## RESULTS AND DISCUSSION

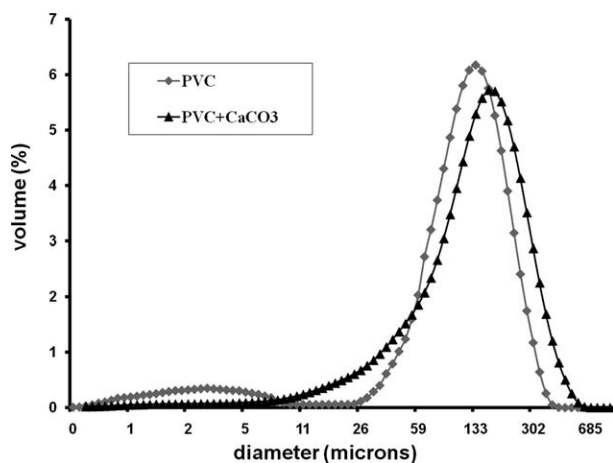
### Filler surfaces

When determining contact angles from experimental data it is usually assumed that the solid surface is flat and smooth. In this case, these contact angles are measured for compacted particles, not for a perfectly smooth surface. Therefore, the relationship of Lim et al.<sup>12</sup> was used to obtain corrected values of contact angles from the measured values. After the corrections, which were relatively small, the contact angles for calcium carbonate were  $92 \pm 1^\circ$  against water and  $68 \pm 1^\circ$  against diiodomethane; for hydrotalcite, the contact angles were  $100 \pm 2^\circ$  against water and  $74 \pm 1^\circ$  against diiodomethane. A contact angle could not be measured for the silica particles because water was absorbed by silica quickly. That indicated that the silica was not coated (as expected for SidiStar). However, contact angles for water on the other filler surfaces were greater than  $90^\circ$  indicating that those fillers were hydrophobic. Uncoated calcium carbonate and hydrotalcite would absorb water easily, but their hydrophobic nature arose from the stearic acid coating on the particle surfaces. That conclusion was confirmed by attempts to disperse the fillers in water. It was found that only silica was completely dispersed in water but the other fillers floated on the water.

A surface coating is expected to improve adhesion between the filler particles and the PVC. However, the total surface free energy also depends on the interfacial surface area and on subsequent processing conditions. Therefore, comparison of surface-coating effects should be made with particles, which have similar sizes.

### Effect of filler particles on grain sizes

The presence of filler particles during suspension polymerization was found to influence the final PVC grain sizes and distributions. Figure 1 shows particle size distributions (PSDs) of unfilled PVC and filled PVC/ $\text{CaCO}_3$  grains. It can be seen that the PSD of the unfilled polymer is bimodal as there are two peaks, a small and wide secondary peak corresponding to a fraction of PVC grains with diameters smaller than 10 microns, and the main peak corresponding to diameters around 150 microns. In the case of the filled polymer, the presence of 5% calcium carbonate seems to eliminate the formation of fine grains and hence the secondary peak disappears and the PSD becomes single/mono-modal. It also shifts towards larger sizes with average size of about 200 microns. Therefore, the presence of  $\text{CaCO}_3$  leads to the production of larger grains. The changes in the grain sizes and their distribution could arise because the calcium carbonate particles increase the



**Figure 1** Effect of calcium carbonate particles on grain size distribution of PVC.

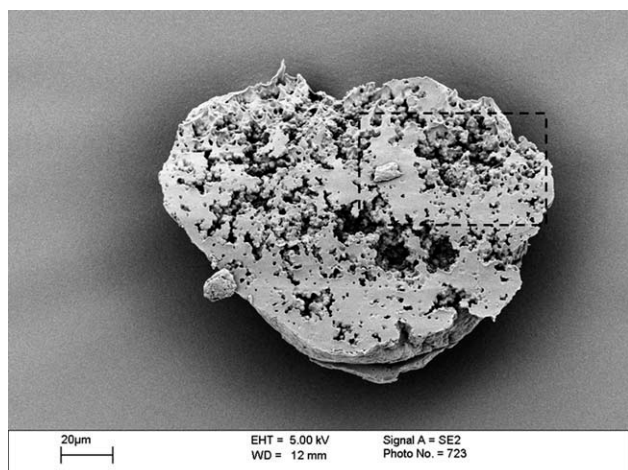
viscosity of the organic phase at the early stages of polymerization.<sup>13</sup> Such an increase would give larger monomer drops (which become polymer grains) and make the drops less susceptible to erosive breakage (so that very small drops, and very small polymer grains are eliminated).

#### Morphology of PVC grains and PVC/nanoparticle composite grains

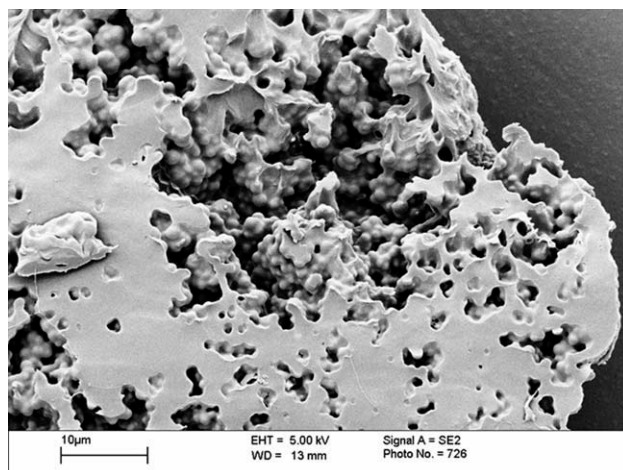
The presence of nanoparticulate fillers influences the internal morphology of the PVC composite grains.

#### Poly(vinyl chloride) (PVC)

Figures 2 and 3 show SEM images of sections through a grain of commercial PVC. In Figure 3, the area that is marked with a rectangle in Figure 2 is shown at higher magnification. That shows primary PVC particles, which are, to an extent, fused together. The internal morphology of a PVC grain can



**Figure 2** Commercial PVC.

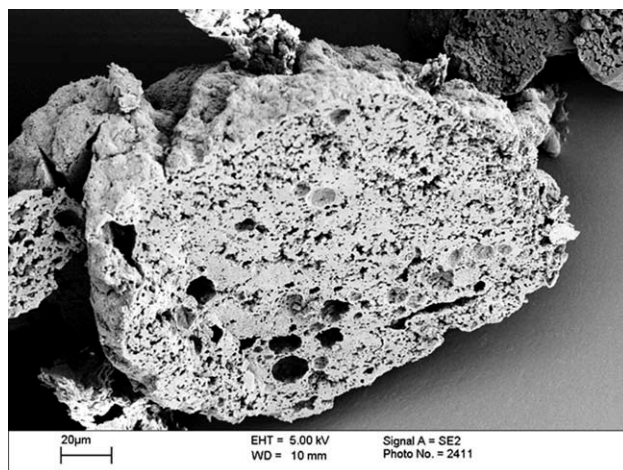


**Figure 3** Enlarged section of Figure 2 for Commercial PVC.

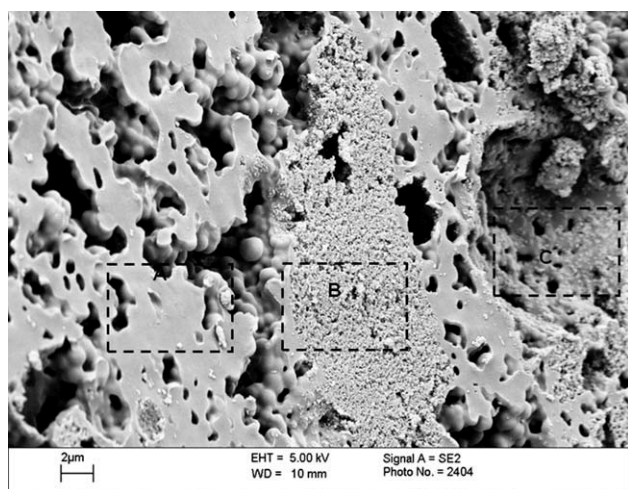
be characterized by areas of high porosity and areas of fusion. The distribution of the pores is not uniform throughout the grain. There are regions of high porosity and regions where there is little or no porosity, and where the primary particles are fused together.

#### PVC/CaCO<sub>3</sub>

Figures 4–7 show the internal structure of PVC/CaCO<sub>3</sub> composite grains. Figure 4 shows the porous structure of a PVC grain containing 5 wt % of calcium carbonate. It can be seen that the pore sizes in the composite particle are smaller than those of plain PVC grains and they are also more uniformly distributed throughout the bulk of the grain. Figure 5 shows that, within the grain, there are some regions where the filler particles are relatively concentrated and other regions where the particles are dispersed more evenly. Clearly, the distribution of the nanoparticles is not uniform. Three distinct areas

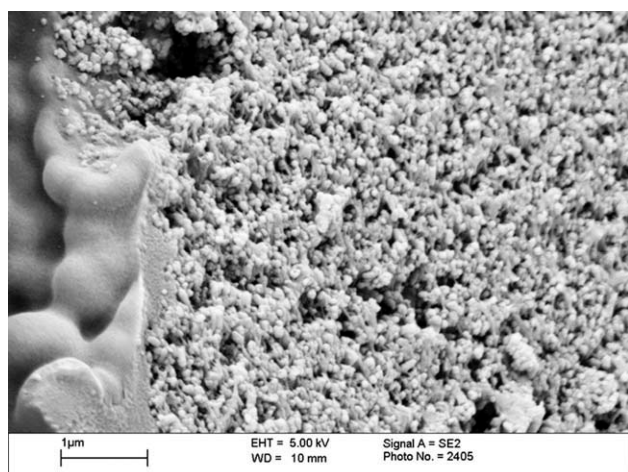


**Figure 4** PVC containing 5% calcium carbonate.

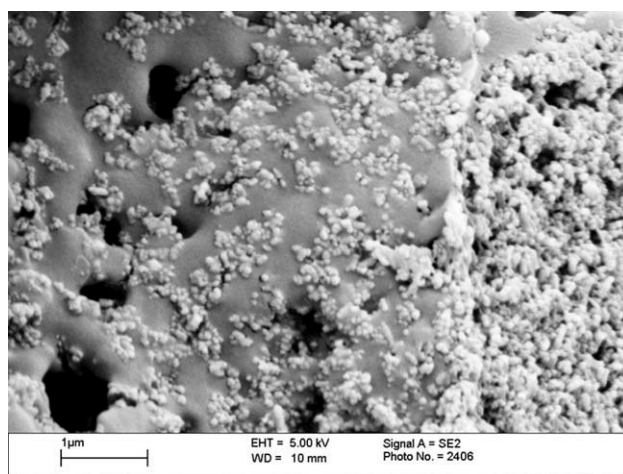


**Figure 5** PVC containing 5% calcium carbonate at higher magnification.

can be distinguished. In area A, there are very few or no calcium carbonate particles, in area B the concentration of nanoparticles is very high (as shown in Fig. 6) and in area C the calcium carbonate particles are embedded in the polymer matrix and distributed more evenly (as shown in Fig. 7). The clear outlines of individual carbonate particles indicate that they are not coated with polymer and that adhesion between the polymer matrix and the particles may be weak. That could happen if the coating of the particles was partially dissolved in the monomer so that particle-polymer affinity was reduced. During polymerization, partially coated particles would coagulate in monomer rich regions and eventually become trapped together to form areas such as that shown in Figure 6. Areas such as those shown in Figure 7 could arise because some calcium carbonate particles are embedded in the matrix at the interfa-



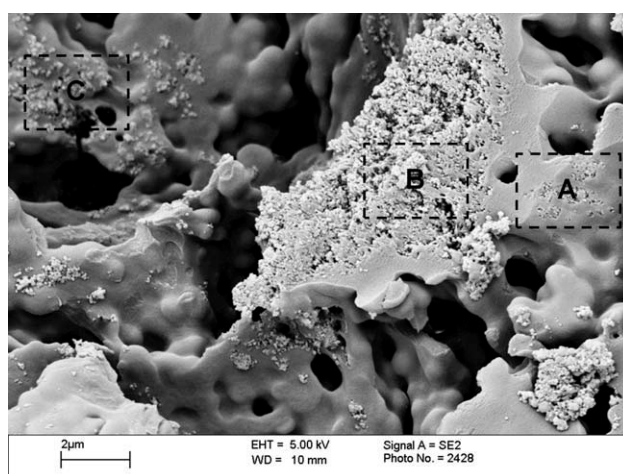
**Figure 6** PVC containing 5% calcium carbonate at higher magnification, showing an area of high concentration of filler particles (area B in Fig. 5).



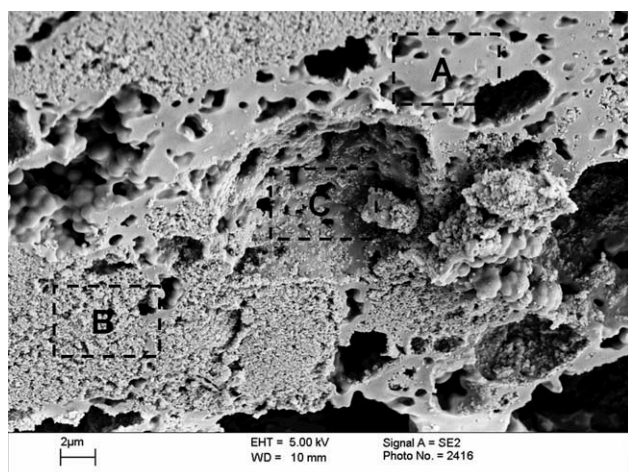
**Figure 7** PVC containing 5% calcium carbonate at higher magnification corresponding to area C in Fig. 5).

ces between polymer rich and monomer rich areas. The same types of areas were observed for calcium carbonate loadings of 2.5 or 8 wt %. Figures 8 and 9 show the internal structure of PVC/CaCO<sub>3</sub> composite grains produced with 2.5 and 8 wt % CaCO<sub>3</sub>, respectively. Areas of type A with very few or no CaCO<sub>3</sub> particles, areas of type B with very high concentration of CaCO<sub>3</sub> particles and areas of type C where the CaCO<sub>3</sub> particles are embedded in the polymer matrix are clearly identified in both cases as shown in the SEM micrographs, although the percentage of the areas seems to change for different CaCO<sub>3</sub> loadings.

The percentage of areas of type A decreases with increasing CaCO<sub>3</sub> concentration while the percentage of areas of type C increases with increasing concentration. It could not be clearly determined from the micrographs though, how the percentage of type B



**Figure 8** PVC with 2.5% calcium carbonate.

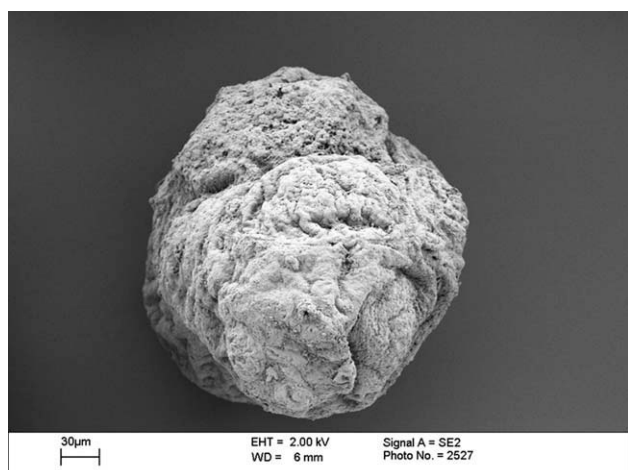


**Figure 9** PVC containing 8% calcium carbonate.

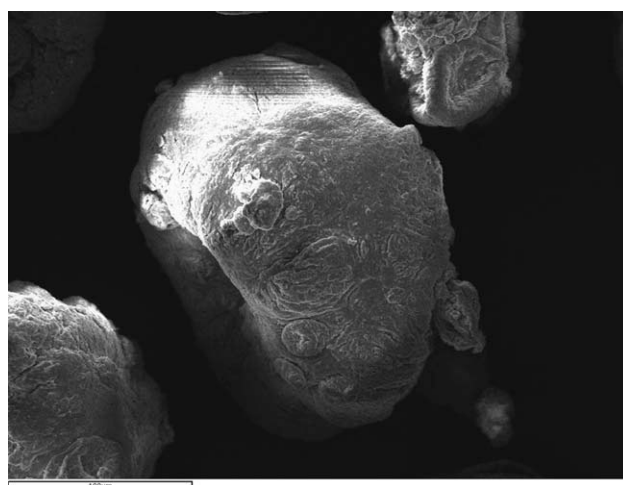
areas changes with increasing nanofiller concentration.

#### PVC/silica

Two types of silica were used, an aqueous slurry and a dry powder. In the slurry, the silica particles were already in dispersion; therefore, dispersion in the monomer could be facilitated compared to the dry powder. The two silica types behaved in different ways when they were added to monomer in the polymerization reactor. When silica slurry was added in the reactor, pure PVC grains were produced and there were no silica nanoparticles incorporated in the PVC grains. This led to the conclusion that the silica nanoparticles did not mix with the monomer but they remained in the aqueous phase, and that they never migrated to the monomer phase. This could probably be attributed to the nature of the silica surface, which is hydrophilic and exhibits



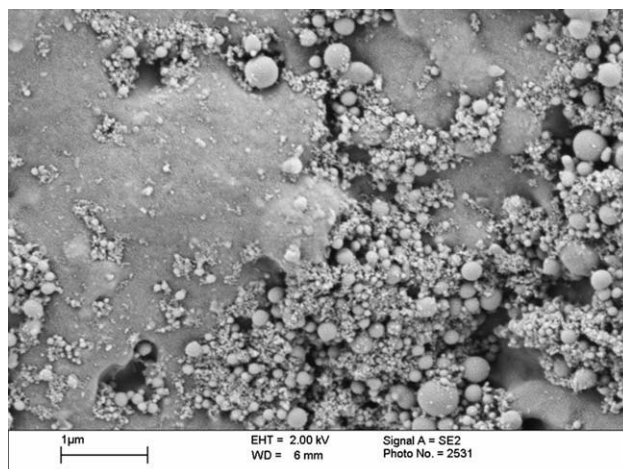
**Figure 10** External morphology of a PVC grain containing 5% silica powder.



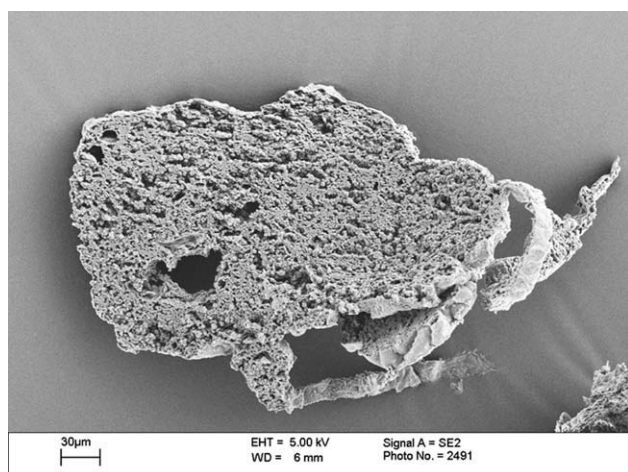
**Figure 11** External morphology of a conventional PVC grain.

stronger affinity for the water phase than for the polymer phase.

When silica powder was added in the monomer, the polymerization produced PVC grains with silica particles clustered on the surface of the PVC or clustered within the PVC grains. More specifically, Figure 10 shows that, when powder silica is dispersed in VCM, the polymerization produces PVC grains with external morphology similar to that of conventional PVC grains (Fig. 11) but with the silica particles clustered on the external surface of the grain (Fig. 12). Although the external morphology of the grain was similar, sections of those PVC grains showed that the internal morphology was significantly different from that of the typical PVC grain. Figure 13 shows a section of a PVC/silica powder grain where it can be seen that the distribution and the sizes of the pores are affected to a significant



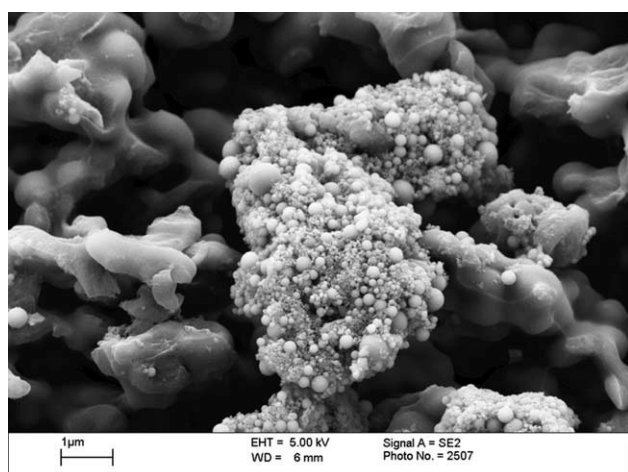
**Figure 12** External surface of PVC grain with 5% silica powder. Silica particles are clustered on the surface of the grain.



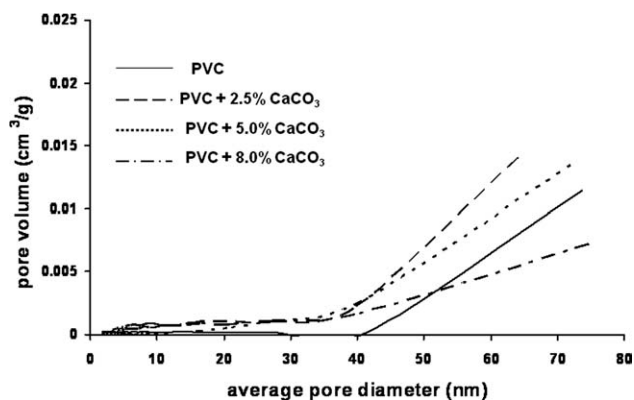
**Figure 13** Internal surface (section) of PVC grain containing 5% silica.

extent by the presence of the silica particles. The pore sizes are smaller than those in the commercial PVC and they are more uniformly distributed throughout the grain (compare Fig. 13 with Fig. 2). Figure 14 shows distinct clustering of silica particles in the grain. That may arise because the silica nanoparticles were uncoated and particle-polymer interaction was weak. It is possible that the silica migrated to the aqueous phase and that particle clusters were subsequently occluded within the grains without the dispersion of individual silica particles.

When PVC was produced in the presence of hydrotalcite, photomicrographs of PVC grain sections showed that no hydrotalcite could be detected within the grains. The hydrotalcite migrated to the water and some fouling of the reactor always occurred. The hydrotalcite may have adsorbed much of the PVA so that there was insufficient PVA to stabilize the VCM drops.



**Figure 14** PVC containing 5% silica at higher magnification.



**Figure 15** Pore size distribution of PVC containing calcium carbonate nanofibers.

### Polymer porosity

Figure 15 shows how the pore size distribution of PVC is affected by the presence of calcium carbonate particles (which were incorporated at the polymerization stage) and Table I shows how the overall porosity is affected. It can be seen that the carbonate increases the contribution of smaller pores and can give a small increase in overall porosity. When the filler loading reached 8 wt %, the porosity began to decline. The presence of calcium carbonate also leads to a small increase in bulk density. This increase in porosity could be probably attributed to the physical presence of the nanoparticulate fillers. The presence of the nanoparticles may interfere and physically hinder the fusion of the primary particles together causing the extent of fusion to decrease. This decrease in fusion could lead to/cause the formation of more pores. Furthermore, the decrease in fusion allows more uniform distribution of pores throughout the volume of the grain. The presence of silica particles affected the porosity to a smaller extent, causing only a very slight increase, probably due to the very limited dispersion of the silica particles in the polymer grain.

### CONCLUSIONS

The addition of inorganic nanoparticles to vinyl chloride, before suspension polymerization, leads to the formation of PVC grains with increased porosity and to the elimination of very small polymer grains.

**TABLE I**  
Effect of Nanoparticles on Porosity of PVC

% CaCO <sub>3</sub> in the PVC	Bulk density (g cm <sup>-3</sup> )	Porosity (cm <sup>3</sup> g <sup>-1</sup> )
0	0.612	0.258
2.5	0.634	0.291
5	0.629	0.273
8	0.632	0.237
% Silica in PVC		
5	0.628	0.262

The distribution of calcium carbonate particles throughout the grains is not uniform. Distinct types of areas are formed with varying concentrations of nanoparticles; these are areas with high concentration of particles, areas with particles embedded in the polymer matrix and areas with very few or no particles present. The porosity of the grains is affected by the presence of the nanoparticles, which seems to lead to a decrease in fusion of the primary particles within the grain. Some silica becomes incorporated in the PVC but the silica particles are not dispersed. Hydro-talcite particles did not appear in the PVC grains.

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