Influences of Some Polymerization Conditions on Particle Properties of Suspension Poly(vinyl chloride) Resin

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ABSTRACT: Effects of polymerization temperature, conversions, and nonionic surfactant on the particle properties of suspension poly(vinyl chloride) (PVC) resins were investigated. It was shown that polymerization temperature has no significant influences on the mean particle size of PVC resin, and that the cold plasticiser absorption (CPA) of resin decreases linearly with the increase of polymerization temperature. Agglomeration of VCM droplets finishes before 20% conversion, and the mean particle size keeps almost constant at later stages of the polymerization process, but the CPA continues decreasing with the increase of conversion. Scanning Electron Microscopy (SEM) micrographs show that the degree of agglomeration of primary particles increases with polymerization temperature and conversion. Addition of nonionic surfactant to the VCM suspension system, as a secondary suspending agent, has a great influence on the particle properties of PVC resin. The particle size and CPA increase as the concentration of nonionic surfactant increases. The nonionic surfactant with a greater HLB value is more effective in raising the mean particle size, but is less effective in raising the CPA. It is considered that the added nonionic surfactant would be absorbed faster on the VCM/water interface than the poly(vinyl alcohol) (PVA), which was used as the primary suspending agent. Because the colloid protection ability of the nonionic surfactant is less than that of PVA, droplets become less resistant to coalescence, and the mean particle size of the final PVC resin increases consequently. The increase of porosity is caused by the combined effects of increased coalescence of VCM droplets and the nonionic surfactant's steric effect inside the droplets. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1544–1552, 2002

Key words: poly(vinyl chloride); surfactants; particle; porosity; suspension polymerization

INTRODUCTION

Suspension polymerization is a commercially used process in the manufacture of poly(vinyl chloride) (PVC). In this process, vinyl chloride monomer (VCM) is suspended, as liquid droplets, in a continuous water phase by a combination of vigorous agitation and the presence of suspending agent(s). Because of the insolubility of the polymer in its own monomer, VCM suspension polymerization is a heterogeneous process. PVC chains start to precipitate from the monomer phase at a very low conversion ($<0.1\%$ conversion) forming a separate phase inside the drop-

lets. The precipitating chains aggregate to form very small particles which, with increasing conversion, will also aggregate to form bigger particles. Further aggregation steps occur throughout the polymerization. The overall mechanism and the nomenclature of the particles formed in each step (microdomains, domains, primary particles, agglomerates, fused agglomerates, grain) have been suggested by Allsopp et al.[1–4]

As a direct consequence of the above process, PVC grains have a complicated and unique morphology and a high degree of porosity. Both the particle size and its distribution, the morphological characteristics, and the degree of porosity of PVC grains depend on polymerization conditions, including the agitation in the reactor, the type, and concentration of suspending agent(s), secondary suspending agents (SSAs), polymerization temperature, conversion, and ratio of VCM to water. Effects of agitation on the mean particle size of PVC resins have been studied by many researchers using different reactor capacities, and many correlations have been developed.[5–9] Effects of agitation on the porosity were also studied by several researchers.[6,10] The choice of the suspending agent system is of utmost importance, as it not only contributes to controlling the particle size distribution of the PVC produced but also has a major effect on the substructure and porosity of the particle. The primary suspending agent system is usually based on poly(vinyl alcohol) (PVA), substituted cellulose, or a mixture of the two. Wolf and Schuessler[11] concluded that the plasticizer absorption (i.e., porosity) of the resulting PVC was related to the surface activity of the suspending agent regardless of type. Ormonroyd[12] investigated the effect of structure of PVA on the particle size, cold plasticiser absorption, and bulk density of the PVC produced. Cheng[13] and Cheng and Langsam[14] studied the VCM suspension polymerization using hydroxypropyl methylcellulose (HPMC) as the 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.[15] studied the influences of HPMC structure and concentration on the particle properties of PVC. Sarkar and Archer[16] reported about the mean particle size of PVC resin using cellulose ethers as a suspending agent. SSAs are regularly used in the production of suspension PVC, specifically to allow for the more complete removal of VCM at the end of polymerization, and to impart higher porosity to the PVC grains. PVA, with low degree of hydrolysis and nonionic surfactants, such as sorbitan monolaurate, were employed commercially.[2] The mechanism by which such SSAs work is open to some debate.[10,17–19]

Recently, influences of some polymerization conditions, such as agitation, type and concentration of suspending agent, the method of addition of initiator, etc., on the dispersion, drop behavior, and coalescence in suspension polymerization of VCM were investigated experimentally by using an on-line sample withdrawal technique during reaction.[20–24] In the present article, effects of polymerization temperature, conversion, and nonionic surfactant on the particle properties of suspension PVC resin will be studied.

EXPERIMENTAL

Materials

VCM was supplied by EVC, UK Ltd. Bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, used as initiator, was supplied by Akzo Nobel Co. with the trade name Perkadox 16S (95% purity). Poly(vinyl alcohol), used in the suspension polymerization as a suspending agent, was supplied by Harlow Chem. Co. Ltd., with the trade name Alcotex 72.5. Nonionic surfactants, such as sorbitan monostearate (Span60), sorbitan monolaurate (Span20), and sorbitan trioleate (Span85), were used as the second suspending agents and supplied by Sigma Chemical Co., Aldrich, Koch-Light Laboratories Ltd., UK, respectively.

Polymerization

The polymerizations were carried out in a 1.0-L glass autoclave (Buchi AG, Switzerland) fitted with a water jacket to control its temperature. The autoclave was fitted with four equally spaced baffles and an agitator consisting of a six flat-blade turbine. The autoclave was first charged with deionized water, the initiator, and the suspending agent(s). The autoclave was closed, and purged with high-pressure nitrogen to check for leaks in the reactor and to reduce the concentration of oxygen in the reactor. Finally, a weighed amount of VCM was added and the mixture was agitated for about 30 min at room temperature to dissolve the initiator and create a dispersion. After that, the reactor was heated to the required temperature to initiate the polymerization. The polymerization temperature was then well controlled. At the end of polymerization, the reactor

Table I   Polymerization Conditions and Properties of the Temperature Series PVC

| Polymn. Temp. (°C) | Conversion (%) | MW and MWD | | | Mean Particle size D_{50} (μm) | CPA (g DOP/100 g PVC) |
		$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n		
36	78.5	17.5	8.31	2.1	127	38.9
40	74.7	15.7	7.86	2.0	121	37.8
45	76.7	13.1	5.37	2.4	124	35.8
50	74.0	11.8	5.12	2.3	118	34.3
54	77.8	9.93	4.51	2.2	131	32.3
57	77.0	8.03	3.38	2.4	145	31.3

PVA concentration = 0.10% based on H_2O, H_2O/VCM = 2.06.

was cooled-down quickly by cold water. The unreacted VCM was vented at room temperature initially, and then the reactor was heated up to about 60°C to remove VCM completely. The resulting PVC resin was filtered and dried. The conversion was determined by the weighing method. Three series of PVC resins were prepared in this work. The first series was synthesized at different polymerization temperatures (referred to as the temperature series). The second series was obtained with different conversions (referred to as the conversion series) by stopping polymerization at different polymerization times. The third series was obtained by VCM suspension polymerization in the presence of nonionic surfactant (referred to as the surfactant series).

Sample Characterization

The mean particle size (D_{50}) of PVC resins was measured on a MALVERN Mastersizer equipment, using a 1000-μm channel.

The internal structure of PVC particles was studied by sectioning particles previously embedded in epoxy resin and observed using a Scanning Electron Microscopy (SEM). The porosity of PVC resin was characterized by cold plasticiser absorption (CPA). A weighed amount of PVC resin was placed in a sand-core tube and allowed to absorb dioctyl phthalate (DOP) plasticiser at room temperature (20 ± 2°C) for 30 min. The unabsorbed DOP was removed by centrifugal separation (3000 rpm, 60 min).

The molecular weight (MW) and molecular weight distribution (MWD) of PVC samples were obtained by gel permeation chromatography (GPC) analysis by using tetrahydrofuran solutions of PVC at 25°C. Polystyrene samples, with narrow molecular weight distributions, were used as relative standards.

RESULTS AND DISCUSSION

Effects of Polymerization Temperature

A summary of the polymerization conditions and properties of the temperature series PVC samples are given in Table I. To separate the interaction of other process variables, this series PVC were prepared using the same recipe (only initiator concentrations changed for polymerizations carried out at 36 and 57°C) and the same agitation speed, and the conversions of different PVC samples are close.

Table I shows that the molecular weight of PVC decreases gradually on raising the polymerization temperature, which can be connected with the increasing importance of the chain transfer reaction of macromolecular free-radicals to monomer. It also shows that the influence of polymerization temperature on the mean particle size of PVC resin is not significant within the range of studying temperature. The CPA shown in Table I is relatively high (usually, CPA is less than 30 g DOP/100 g PVC for commercial products[25]), and the CPA of PVC resin decreases with the increase of polymerization temperature. A linear relationship between the porosity and polymerization temperature is obtained and shown in Figure 1.

SEM micrographs of PVC resins prepared at different temperatures are shown in Figure 2. The agglomerated and "fused" structures of PVC primary particles can be seen from the micrographs, but the level of agglomeration and fusion is different for PVC samples prepared at different temperatures. For the sample prepared at 36°C, the degree of agglomeration and fusion of primary particles is lower, and some primary particles still exist in the individual form. As polymerization temperature increased, the degree of agglomeration and fusion of primary particles increased.
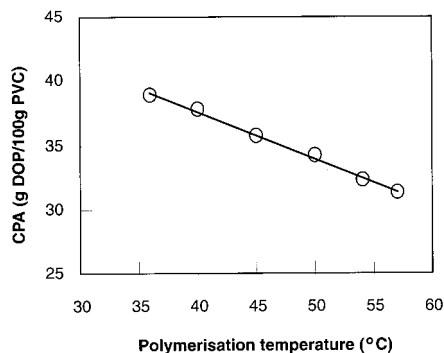
Figure 1 Effect of polymerization temperature on the cold plasticizer absorption of the resulting PVC resin.

Smallwood[10] also found the primary particle diameter increased with temperature at a given conversion, and considered that the increasing of polymerization temperature could reduce the colloidal stability of the domains and primary particles thus reducing their number and increasing their size. It also can be seen that the number of primary particles per area in the SEM micrographs of this work is lower than that of Smallwood's result, and the fraction of core area is relatively higher. This could be caused by the lower polymerization temperature and higher agitation intensity applied in this work.

Effects of Polymerization Conversion

A summary of polymerization conditions and properties of the conversion series PVC resins are shown in Table II.
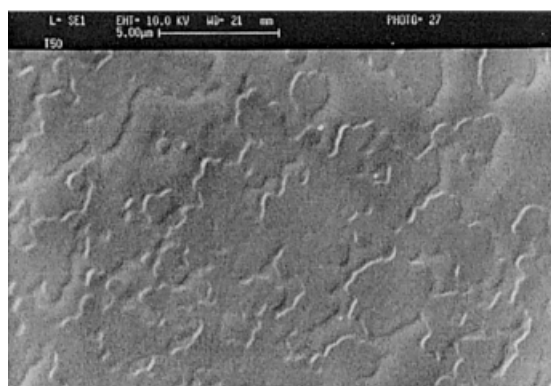
It can be seen that the molecular weight of PVC increases gradually with the increase of conversion, and almost levels off at the higher con-
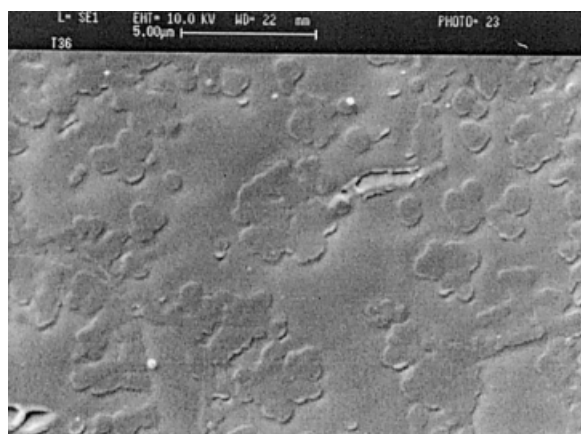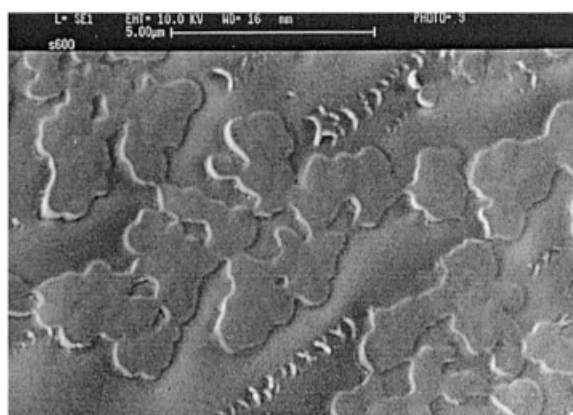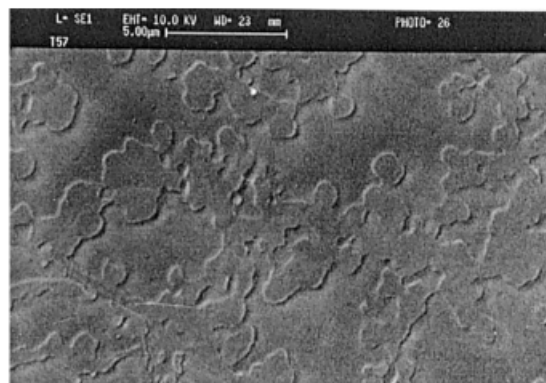

Figure 2 SEM micrographs of PVC sections prepared at different polymerization temperatures (a) 36°C, (b) 45°C, (c) 50°C, (d) 57°C.

Table II Polymerization Conditions and Properties of the Conversion Series PVC

Conversion (%)	Mw and MWD			Mean Particle Size D_{50} (μm)	CPA (g DOP/100 g PVC)
	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n		
14.1	12.4	4.60	2.7	115	89.5
26.1	12.6	4.79	2.6	154	83.2
34.5	12.8	4.93	2.6	106	69.7
50.9	12.8	4.90	2.6	101	55.7
62.7	13.2	5.38	2.5	133	40.5
76.7	13.1	5.37	2.4	124	35.8
81.7	13.4	5.58	2.4	119	32.9

Polymerization temperature = 45°C, PVA concentration = 0.10% based on H_2O, H_2O/VCM = 2.06.

version stage. The mean particle sizes of most PVC resins are quite similar. The eventual value of the mean particle size is established at low conversion (14.1%). This means that coalesence of VCM/PVC droplets finish the agglomeration at the early stage of polymerization (<20% conversion). Meanwhile, the formation of a continuous network of primaries throughout the VCM/PVC droplets resulted from the aggregation of primaries and gave resistance to the droplets shrinkage. With increased conversion from monomer to polymer, the CPA tends to decrease. A further linear relationship between the conversion and the CPA is shown in Figure 3.
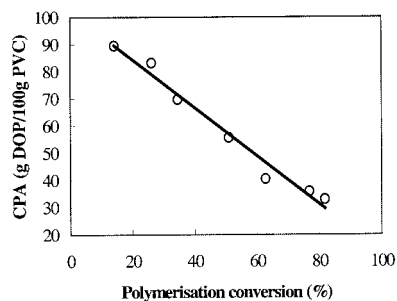
SEM micrographs of PVC sections with different conversions are shown in Figure 4. For the PVC sample with conversion of 14.1%, it can be seen that primary particles exist in separate or lightly agglomerated forms, which means a network of primary particles starts to form. The average diameter of primary particles is less than 1.0 μm, and the porous structures occupy a high percentage of the area shown. For the sample obtained at the beginning of the pressure drop during polymerization (conversion = 62.7%),

most of the primary particles exist in the aggregated form. For the sample obtained after the disappearance of pure monomer phase (conversion = 81.7%), primary particles were almost fused together. As a result, the porosity of PVC decreases with the increase of conversion.

Effect of Nonionic Surfactant

Nonionic surfactants, such as Span85, Span60, and Span20, were used as SSAs in the preparation of the surfactant series PVC samples. The type and concentration of surfactant were varied in the polymerization, while keeping other polymerization conditions (polymerization temperature and time, concentrations of PVA and initiator, water/H_2O ratio) constant. The conversions were controlled to be near to 78%. Effects of type and concentration of nonionic surfactant on the mean particle size and on the CPA of PVC resins are shown in Figures 5 and 6.

Figure 5 shows that the mean particle size of PVC resins increases quickly as the concentration of nonionic surfactant increases, and the nonionic surfactant with a greater HLB value is more effective in raising the mean particle size of PVC (HLB value of Span85, Span60, and Span20 are 1.8, 4.7, and 8.6, respectively). Addition of the surfactant would decrease the VCM/water interfacial tension and affect the mean size of initial VCM droplets. So, the increase of the mean particle size of the final PVC resin would only be caused by increased coalescence of VCM/PVC droplets during the polymerization process. It is well accepted that most of the suspending agent(s) molecules would be absorbed by VCM droplets and located at the VCM/water interface to form high viscosity layers during the VCM suspension polymerization process, which would give colloid protection and coalescence resistance


Figure 3 Effect of polymerization conversion on the cold plasticiser absorption of the resulting PVC resin.

(a)

(b)

(c)
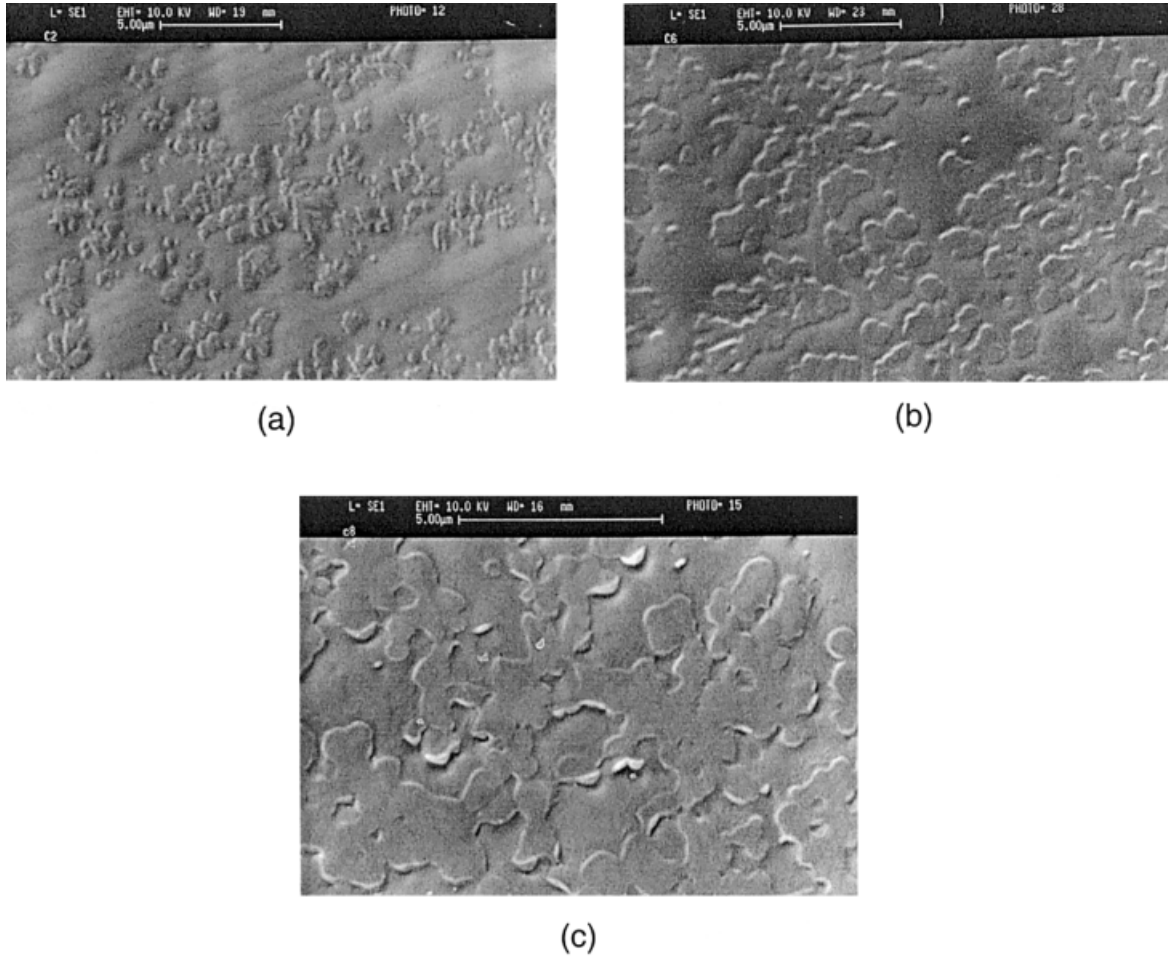
Figure 4   SEM micrographs of PVC sections with different conversions (a) 14.1%, (b) 62.7%, (c) 81.7%.

to droplets. The absorption rate, configuration of the molecules of suspending agent(s) at the VCM/ water interface, the viscosity and colloid protec-

tion ability of the viscous layer, and the coalescence resistance of droplets are related to the structure of suspending agent(s). Usually, a suspending agent with a higher oil affinity would have a higher rate of absorption. The absorbed
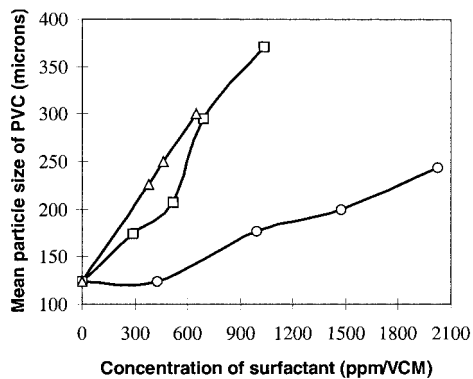
Figure 5   Effect of surfactant type and concentration on the mean particle size of the resulting PVC resin (○) Span 85, (□) Span 60, (△) Span 20.
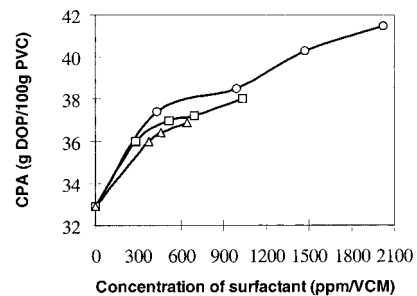
Figure 6   Effect of surfactant type and concentration on the cold plasticiser absorption of the resulting PVC resin. (○) Span 85, (□) Span 60, (△) Span 20.

molecules of suspending agent would form a configuration as follows: the lipophilic segments (poly(vinyl acetate) enriched segments for PVA) penetrate into the VCM phase, whereas other segments of suspending agent are in the outer part of the interface. Because nonionic surfactants like Span20, Span60, and Span85 have more affinity with VCM than the PVA, they would be absorbed faster on the VCM/water interface than PVA, and a part of interface originally occupied by PVA molecules would become occupied by nonionic surfactant molecules. Thus, the colloid protective ability of the composite suspending agent would decrease because the nonionic surfactants used here are low molecular weight substances and their colloid protective ability is less than that of PVA. This is the first reason for the increasing of coalescence of droplets as nonionic surfactant use added in the VCM suspension polymerization system. The second reason is that the addition of nonionic surfactant would decrease the mean size of initial VCM droplets and increase the surface area of VCM, and the surface coverage of PVA would decrease consequently. This would also lead to the decrease of colloid protection and coalescence resistance of VCM/PVC droplets. The nonionic surfactant with a greater HLB value, such as Span20, would partition predominantly in the monomer phase, and the low HLB value nonionic surfactant, such as Span85, would probably partition entirely in the monomer phase. So, Span20 is more effective in changing of interfacial properties of VCM/water and in increasing the coalescence of VCM droplets and particle size of the final PVC resin. As the concentration of nonionic surfactant continued to increase, the enhanced coalescence of VCM/PVC droplets would lead to the blockage of the polymer and failure in polymerization in the early stage of polymerization. This phenomenon was observed when the concentration of Span60 exceeded 1060 ppm/VCM.

Figure 6 shows that the CPA of PVC resins increase as the concentration of nonionic surfactant increases. This increase depends on the combination effect of two factors. First, VCM droplets undergo enhanced coalescence as the nonionic surfactant is added. The primary particles inside the droplets will be subjected to greater shear and form a network earlier and the final product will have a higher porosity.[10] Increased coalescence of droplets would also result in an increase in porosity because some porous structures would form at the sites where droplets are not well contacted.

Second, a great part of the molecular chain of the nonionic surfactant would penetrate into the VCM droplet due to their higher affinity with VCM. Therefore, the surfactant would influence the way in which the different agglomeration steps take place by steric effects and increase the porosity. The contributions of the two factors to the increase of porosity depend on the HLB value of the nonionic surfactant. The increase of porosity would be caused mainly by the increased coalescence effect for the nonionic surfactant with a greater HLB value and by the steric effects inside the droplets for the nonionic surfactant with a lower HLB value. From Figure 6, it can be seen that the nonionic surfactant with a lower HLB value (hence, with a higher affinity for VCM and a higher solubility in VCM) is more effective in raising the CPA. SEM micrographs of PVC sections prepared in the presence of nonionic surfactant are shown in Figure 7. From a comparison between the micrograph of PVC prepared without surfactant and that of PVC prepared with surfactant, it can be seen that the surface of primary particle aggregates became coarser as surfactant was added. This is due to the altering interfacial tension between PVC-rich phase and the monomer, which might be expected to decrease the contact deformation of the primary particles and filling of pores by unreacted monomer.

CONCLUSIONS

PVC resins have been prepared at different polymerization temperatures and at different polymerization (conversions), in the presence of nonionic surfactants. It was found that changes in polymerization temperature and conversion ($>14\%$) had no significant influences on the particle size of the PVC resin, whereas the cold plasticiser absorption of resin decreased linearly with an increase of polymerization temperature and or with an increase in conversion. SEM micrographs show that the degree of agglomeration of primary particles increases with polymerization temperature and conversion. Addition of nonionic surfactant has significant effects on the particle size, cold plasticiser absorption, and internal structure of PVC resin. The particle size increases as the concentration of nonionic surfactant increases, and a nonionic surfactant with a greater HLB value is more effective in raising the particle size. It is considered that the coalescence resistance of VCM/PVC droplets decreases as the surface cov-
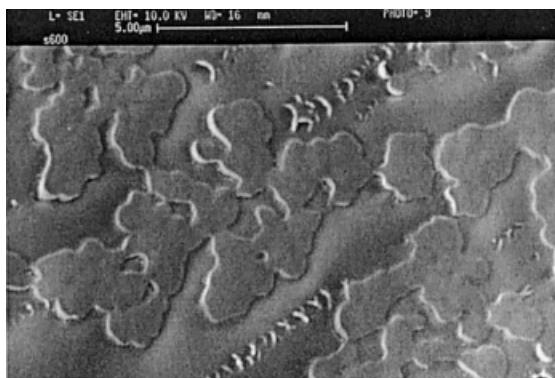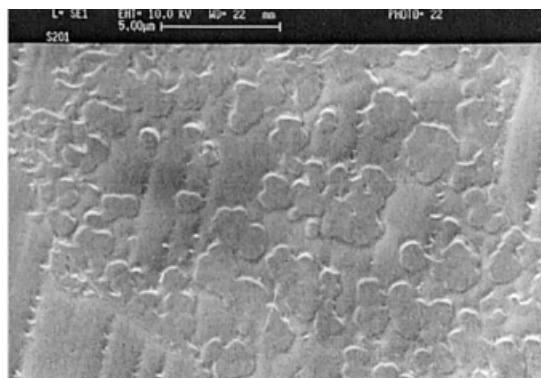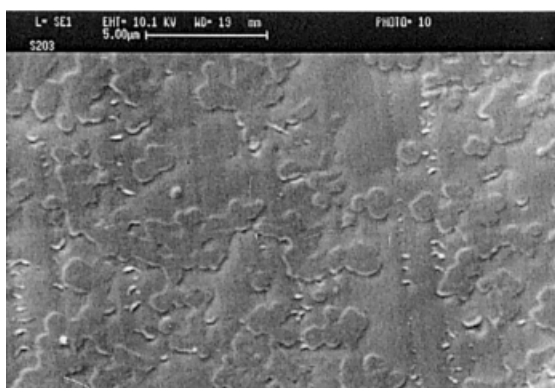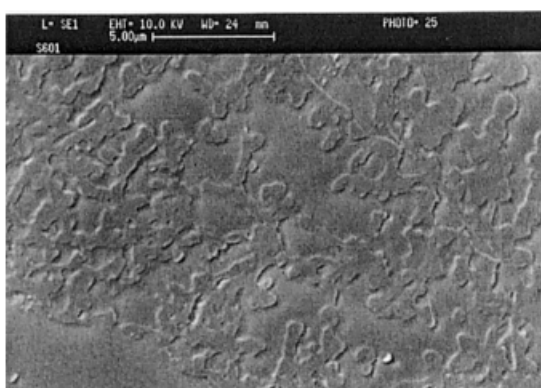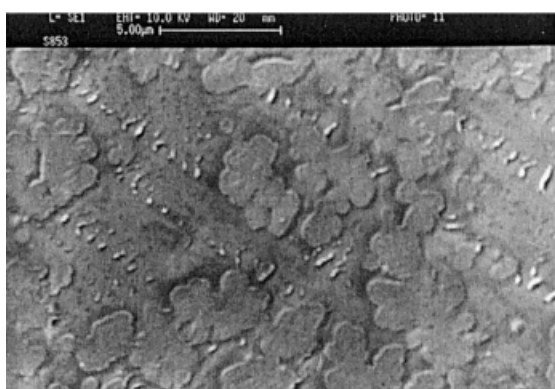
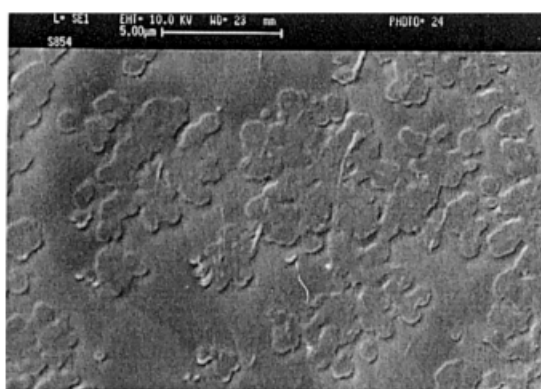**Figure 7** SEM micrographs of PVC sections prepared in the presence of nonionic surfactant. (a) no surfactant, (b) 377 ppm Span 20/VCM, (c) 644 ppm Span 20/VCM, (d) 286 ppm Span 60/VCM, (e) 1472 ppm Span 85/VCM, (f) 2023 ppm Span 85/VCM.

erage of the droplets by PVA decreases as a result of substitution of PVA by nonionic surfactant and by the increase of VCM surface area as nonionic

surfactant added. The cold plasticiser absorption, and thus the porosity of PVC resin, increases as the concentration of nonionic surfactant in-

creases. A surfactant with a lower HLB value is more effective in raising the porosity. The increase of porosity is caused by the combination of increased coalescence of VCM/PVC droplets and the nonionic surfactant's steric effect inside the droplets when nonionic surfactant added. The contribution of each factor to the increase of porosity is connected with the HLB value of nonionic surfactant.

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