Effect of Cellulose Suspension Agent Structure on the Particle Morphology of PVC. Part II. Interfacial Properties

John T. Cheng[a]; Michael Langsam[a]

[a] Air Products and Chemicals, Inc., Allentown, Pennsylvania

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JOHN T. CHENG and MICHAEL LANGSAM

Air Products and Chemicals, Inc.
Allentown, Pennsylvania 18105

ABSTRACT

The particle structure of polyvinyl chloride is controlled by the shear field imposed on the monomer droplet and the interfacial behavior of the vinyl chloride/water phases during polymerization. The interfacial tension in the presence of hydroxypropyl methylcellulose (HPMC) was measured as a function of concentration and temperature. The molecular weight distribution of HPMC was determined by coupled GPC-LALLS (low angel laser light scattering) technique. By monitoring the concentration of HPMC in the aqueous phase during polymerization, the coverage powers of HPMC were calculated and compared with the theoretical value based on Langmuir layer consideration. The effects of agitation on resin porosity were also examined. These results are discussed with respect to the particle structure.

INTRODUCTION

The particle structure of polyvinyl chloride (PVC) is one of the major factors determining the plasticization process and the end-use application of the resin. A fundamental understanding of the relationship between particle morphology and the structure of the suspending

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agent is very important in the synthesis of the PVC resin. In recent
work we have identified the effects of structure/composition of HPMC
on particle properties [1]. The effects of polymeric materials used
as additives on the formation and size of primary particles have been
reported by Tornell and Quy [2, 3]. Their work is concerned with the
agglomeration of primary particles within the droplet boundary which
determines resin porosity/morphology. The presence of additives af-
fects the agglomeration among primary particles by altering the inter-
facial characteristics. In continuing our study we have investigated
the following factors: 1) the effect of HPMC on interfacial tension of
vinyl chloride/water phases, 2) the coverage power of HPMC, and 3)
the effect of shear rate on particle properties.

EXPERIMENTAL

Raw Materials

Water. Tap water was passed through a deionization column and
then double-distilled under a nitrogen purge.
Suspension Agent. Hydroxypropyl methylcellulose (HPMC) Type 1,
Type 2, and XD series from Dow Chemical were used as received.
These are detailed in Table 1.
Monomer. CP-grade vinyl chloride obtained from B. F. Goodrich
was used as received.
Initiator. Experox 33M (75% t-butyl perneodecanonate in mineral
spirit) supplied by U. S. Peroxygen was used as received.
Other Chemical. Sodium bicarbonate (reagent grade) supplied by
J. T. Baker Chemical Company.

Polymerization Procedure

The following procedures were used.
Reactor Equipment. Chemco MDX-CJ, 1.5 L, manufactured by
Chemical Equipment Corp. of Tulsa, Oklahoma, temperature control
to ±0.5°C.
Recipe:

1.	Water	700 g
2.	Suspension agent (Table 1)	0.26 g
3.	Sodium bicarbonate	0.16 g
4.	Vinyl chloride	400 g
5.	Experox 33M	0.36 mL

Charge Procedures. Components 2 and 3 were added to Component
1 and then charged to the reactor under nitrogen purge. The suspend-
ing agent was predissolved in 1.0% aqueous solution. Components 4

and 5 were added rapidly. Reactor contents were quickly heated to 60°C under constant agitation of 500 rpm. Polymerizations were carried to about 85% conversion. At the end of the polymerization, the reactor contents were quickly cooled to ambient, vented to atmospheric pressure, filtered, dried, and tested.

Test Procedures. IPTU (ASTM D-3367), a measure of porosity in grams of DOP plasticizer per 100 g polymer; HPMC concentration (Air Products analytical method, based on procedures supplied by Dow Chemical); particle size, screen analysis (ASTM A1921-75) mercury porosimetry (ASTM D-2873).

GPC-LALLS 150 C Model (Water Associates) with PW Toyo Soda Columns.

DISCUSSION

HPMC Characteristics

HPMC are cellulose ethers made by reacting cellulose with propylene oxide and methyl chloride in an alkaline medium. The characteristics of HPMC used in this investigation are summarized in Table 1.

Interfacial Tension Measurements

The effects of suspending agent on interfacial tension were investigated in VCM/aqueous system using the spinning drop method. The

TABLE 1. Characteristics of HPMC

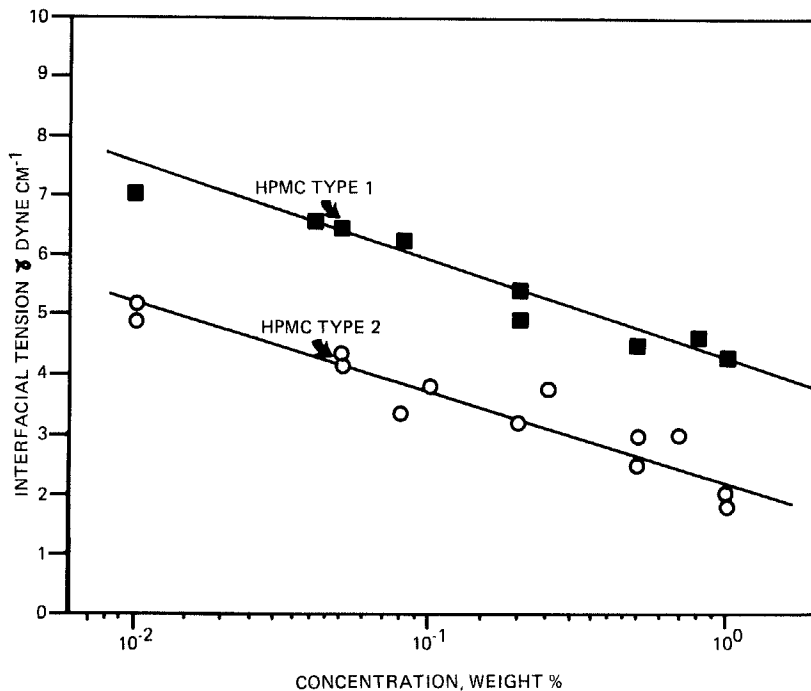| Grade	Viscosity (cP)[a]	Methoxyl (%)[b]	Hydroxypropoxyl (%)[b]	Salt (%)
XD-1	38.9	23.0	11.1	0.73
XD-3	108.0	23.9	8.4	0.95
XD-4	81.0	23.5	10.1	0.78
XD-5	28.7	22.8	9.5	1.49
XD-7	31.0	23.1	9.5	1.65
Type 1	31.2	21.0	8.4	5.0
Type 2	42.9	28.1	8.5	0.35

[a]2% at 20°C.
[b]ASTM D-2363.

FIG. 1. Effect of concentration on interfacial tension at 25°C.

principle and application of this method are described by Wade et al.
[4]. The experimental results were taken at a spinning time of 20 min
after the two phases were brought into contact. In Fig. 1 the interfacial
tensions for two different HPMC structures are plotted as a function of
its concentration. The differences in interfacial tension values are
significant not only in terms of their effect on initial monomer droplet
size but on the degree of agglomeration in forming the final particles.
Both of these factors may contribute to the different morphologies ob-
served. In contrast to the partitioning behavior, the temperature effect
on interfacial tension was found to be small. This is shown in Table 2
where a number of XD series are also included.

Concentration of HPMC as Affected by Conversion

The partition coefficient is a static measurement and may not be
applicable to the polymerization system where the interfacial areas
are dramatically increased as a result of droplet formation. A cor-
rection factor is needed which can be obtained by monitoring the con-

TABLE 2. Effect of Temperature on Interfacial Tension

HPMC	Interfacial tension,[a] (dyne/cm)			
	20°C	30°C	40°C	50°C
Type 1	6.4	6.0	5.7	5.4
Type 2	3.8	3.7	3.3	4.0
XD-1	7.2	6.6	5.8	6.2
XD-3	6.8	6.3	5.9	6.5
XD-4	7.1	6.6	6.2	6.2
XD-5	6.4	5.9	5.7	6.2
XD-7	6.9	6.0	5.8	6.2

[a]Concentration, 0.10%.

centration change as a function of conversion. The concentrations of HPMC in aqueous phase for both Type 1 and Type 2 were found to have decreased linearly up to 15-30% conversion and then leveled off. This is seen in Fig. 2. Such behavior, which has also been observed by Allsopp [5], appears to have the following implications: mechanistically the polymerization procedes in, at least, two distinctive stages. At low conversion ($< 30\%$) the nucleation and particle growth are in an unsteady state involving the transport of HPMC molecules in various phases. The driving force is the concentration gradient induced by the precipitation of HPMC associated with primary particles. After 30% conversion, the total number of droplet/surface areas has reached a pseudoequilibrium state, and the packing mode of primary particles is affected only by the suspending agent solubilized in the monomer droplet. By extrapolating to zero conversion, the concentration of HPMC at the interface can be estimated with other known parameters—about $45 \pm 10\%$ of total HPMC is distributed at the interface. Due to experimental error, we could not quantify if there are any differences between Type 1 and Type 2 systems as far as their concentration at the interface is concerned. Nevertheless, we are reasonably sure that the correction factor for partitioning is relatively small for these two types of HPMC.

The partition coefficient (Pc) has a fundamental significance in terms of such basic thermodynamic properties as free energy, enthalpy, and entropy. Some of these relationships have been derived by Cratin [6]. The free energy change for the transfer of the hydrophilic segment from the organic to the aqueous phase and vice versa can be calculated provided the logarithm of the partition coefficient is a linear function of the number of hydrophilic segments. This cal-
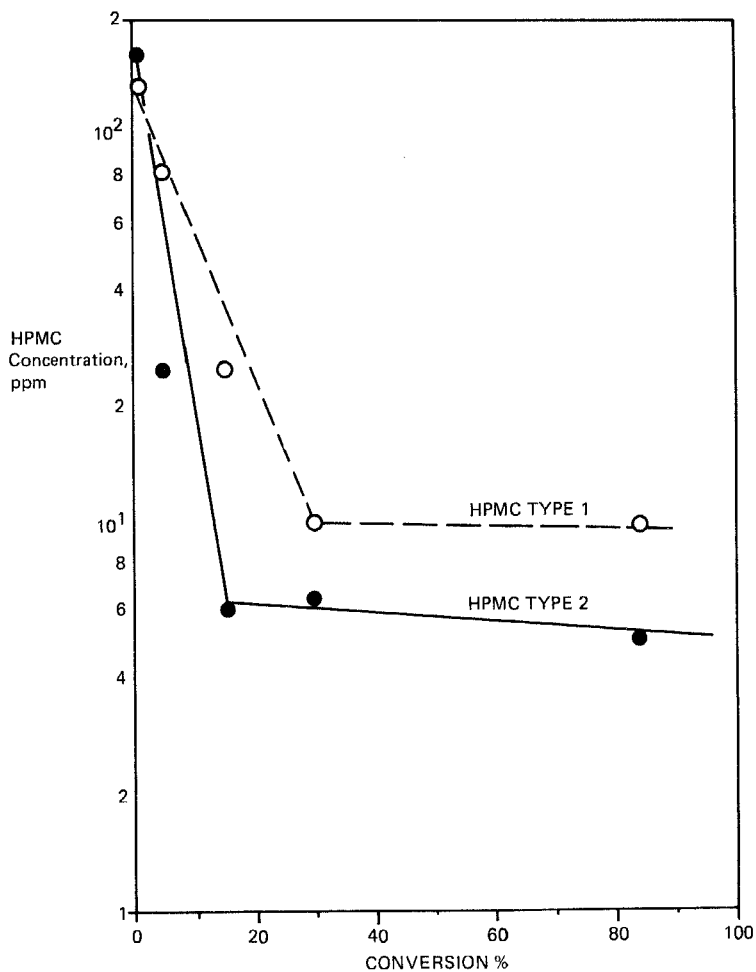
FIG. 2. HPMC concentration in aqueous phase vs percent conversion.

culation could not be completed due to an insufficient data base. Since
the partitioning behavior of a molecule depends upon the hydrophile-
lipophile balance (HLB), the HLB values can be calculated if Pc is de-
termined. The simplist form of equation was given by Davies [7].

$$HLB = 0.36 \ln \frac{C_a}{C_m}$$

where C_a and C_m refer to the equilibrium molar concentration of the suspending agent in the aqueous and monomer phases, respectively. A simple calculation indicates that the HLB for Type 1 HPMC is 7.1 and for Type 2 HPMC, 6.5, both of which are consistent with the experimental value of 11 vs 9.

Based on a separate study, the mean droplet size before polymerizing for HPMC of the Type 1 and Type 2 systems was determined to be 130 and 80 μm, respectively [8]. The coverage power HPMC was calculated to be 2.2×10^5 for Type 1 and 3.5×10^5 cm^2/g for Type 2 in comparison with 4×10^6 cm^2/g from theoretical calculation assuming a Langmuir layer [9]. The formation of a multilayer is difficult because of the repulsion forces in a random coil and the distance between layers [10].

Molecular Weight Distribution of HPMC

The molecular weight effect of HPMC on particle structure was discussed in a previous paper. It was uncertain at that time whether the molecular weight distribution (MWD) of HPMC had contributed to the variation in particle morphology. In particular, the presence of a low molecular weight tail might have adverse effect on particle structure. Using GPC coupled with low angle laser light scattering, the MWD of HPMC has been determined. This is detailed in Table 3 and Figs. 3-5. Within the MWD range of 1.72 to 3.02 the experimental results show no apparent correlation with particle structure, porosity, and median particle size.

TABLE 3. Effect of MWD on Particle Properties of PVC

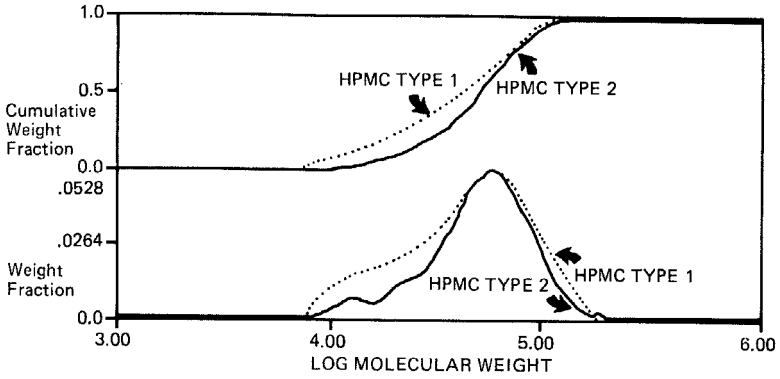| HPMC	$M_N \times 10^{-4}$	$M_W \times 10^{-5}$	M_W/M_N	PVC	
				IPTU	MPSμ
Type 1	3.74	0.644	1.72	18.1	180
Type 2	5.14	0.699	1.36	24.4	160
XD-1	3.64	1.00	2.75	20.8	180
XD-3	7.65	1.38	1.80	15.6	180
XD-4	6.26	1.27	2.02	16.4	180
XD-5	3.51	0.919	2.63	18.0	180
XD-7	3.25	0.981	3.02	15.6	180

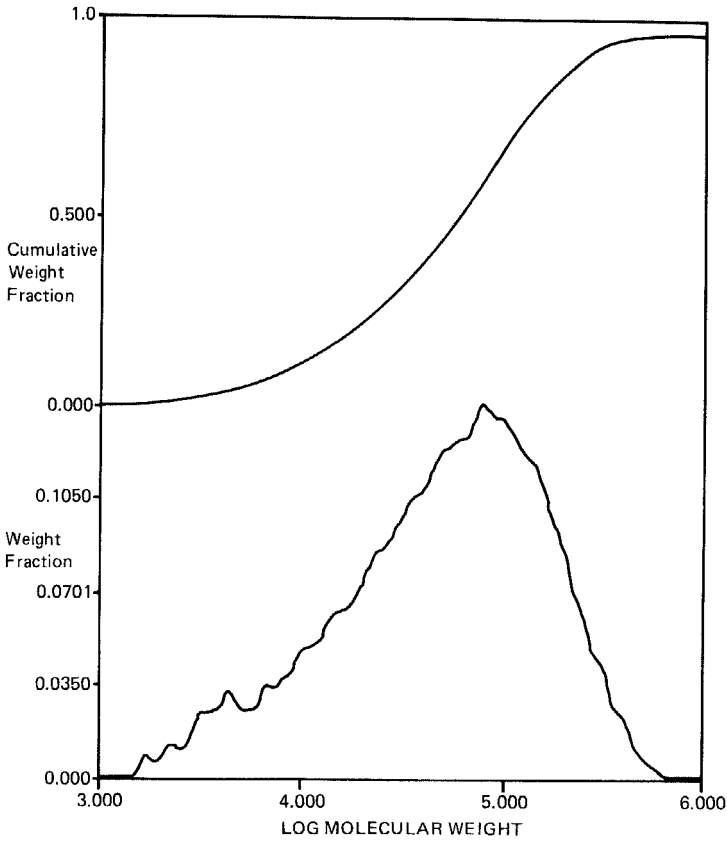FIG. 3. Molecular weight distribution of HPMC (Types 1 and 2).

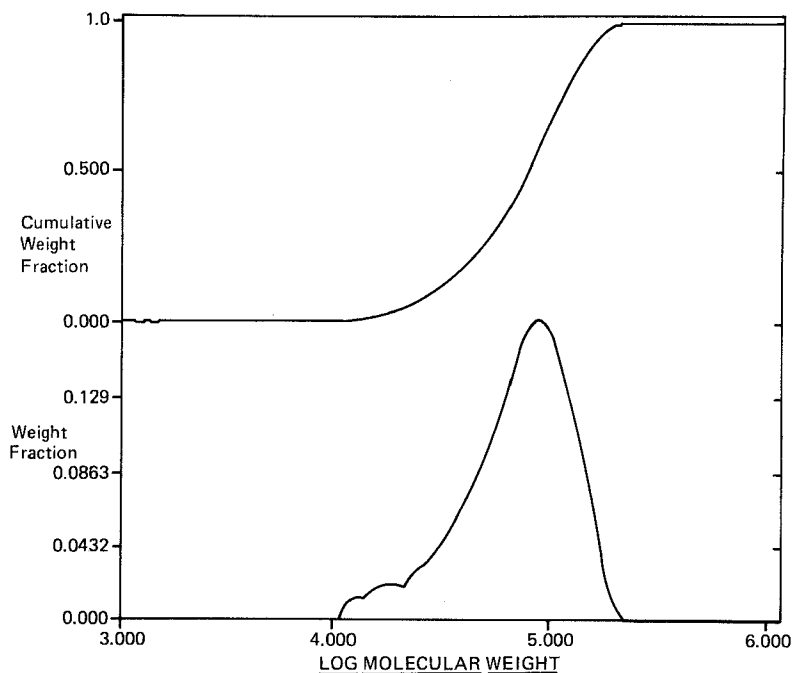FIG. 4. Molecular weight distribution of HPMC (XD-7).

FIG. 5. Molecular weight distribution of HPMC (XD-3).

    In suspension polymerization, stabilization is achieved by adsorp-
tion or grafting of HPMC onto the polymer particles. This has been
determined by extraction studies. A protective layer is formed which
covers the droplets, shielding them from direct contact, and therefore
reducing the potential for agglomeration. The protective layer owes
its effectiveness to a net repulsion force which originates from an
entropy effect due to protruding segments of HPMC molecules. The
degree of stabilization depends upon two major factors: 1) the thick-
ness of the adsorbed layer and 2) the extent of which the grafted/
adsorbed polymer segments protrudes into the aqueous media. Both
factors are governed by the affinity between polymer particles and
the suspending agent and the MW/MWD of the latter. The thickness
of the protective layer was reported to range from 100 to 5000 Å [11,
12]. The results from our study indicate the layer thickness is
1000 Å. Apparently the effectiveness of the protective action–both
the thickness of the layer and the extruding volume by segments–has
not been significantly altered within the MWD range investigated.

Effect of Shear Field

Agitation has a major effect on resin properties in suspension polymerization. Preliminary evidence indicates that the agglomeration proceeding both inside and outside of the droplet is strongly shear dependent while the nucleation is less shear sensitive. Correlation studies have been reported between agitator design and drop/ particle size [13-15]. Most of these studies are empirical, being applied only to specific conditions. We are interested in the shear effect on particle structure, and we determined whether the improved porosity from Type 2 HPMC can prevail under different shear conditions. Independent of the HPMC system, we observed that the resin porosity, based on IPTU measurement, was found to have increased with increasing shear from 200 to 650 rpm. Five to eight IPTU units were consistently maintained between Type 1 and Type 2 suspension, as shown in Table 4. As expected, the median particle size showed a typical U-shaped curve when plotted as MPS against rpm. Initial results indicate that the increase in porosity by shear is largely attributed to the increase in interparticle porosity as a result of alteration of the packing mode of primary particles. When the two types of HPMC were scaled-up to pilot plant and production reactors, a similar effect on porosity was consistently observed, suggesting the dominating influence exerted by the composition/structure of HPMC.

Morphology

The packing mode of primary particles based on Type 1 and Type 2 suspension was examined by SEM as exemplified in Figs. 6-8. The particle was fractured at low temperature and embedded in epoxy resin. Some morphological differences were observed:

TABLE 4. Effect of Shear Field on MPS

| Shear (rpm) | MPSµ | | ΔIPTU |
	Type 1 HPMC	Type 2 HPMC	
200	460	400	5.2
350	290	210	6.4
500	180	160	6.4
650	330	180	7.6
800	560	780	0

30KV X510   100U 101 02271 APC
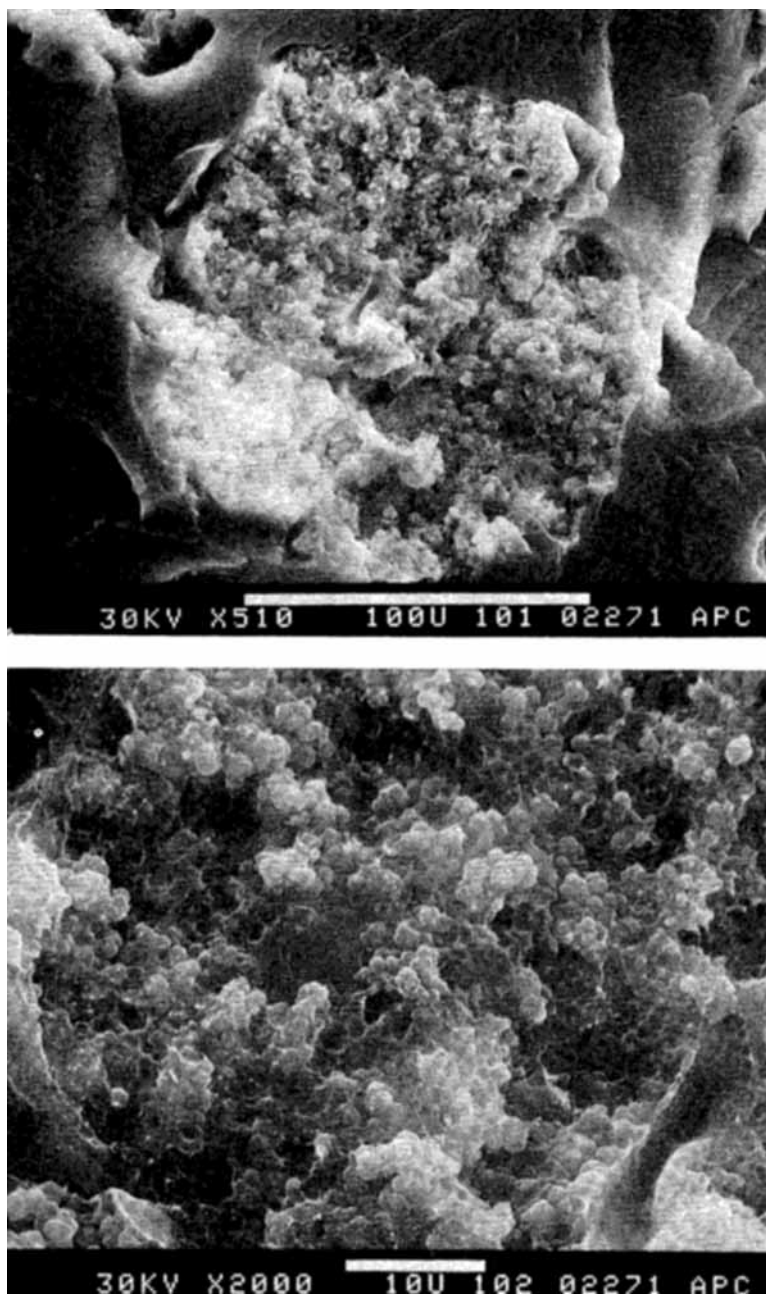
30KV X2000   10U 102 02271 APC

FIG. 6. Scanning electromicrograph of primary particles in a PVC
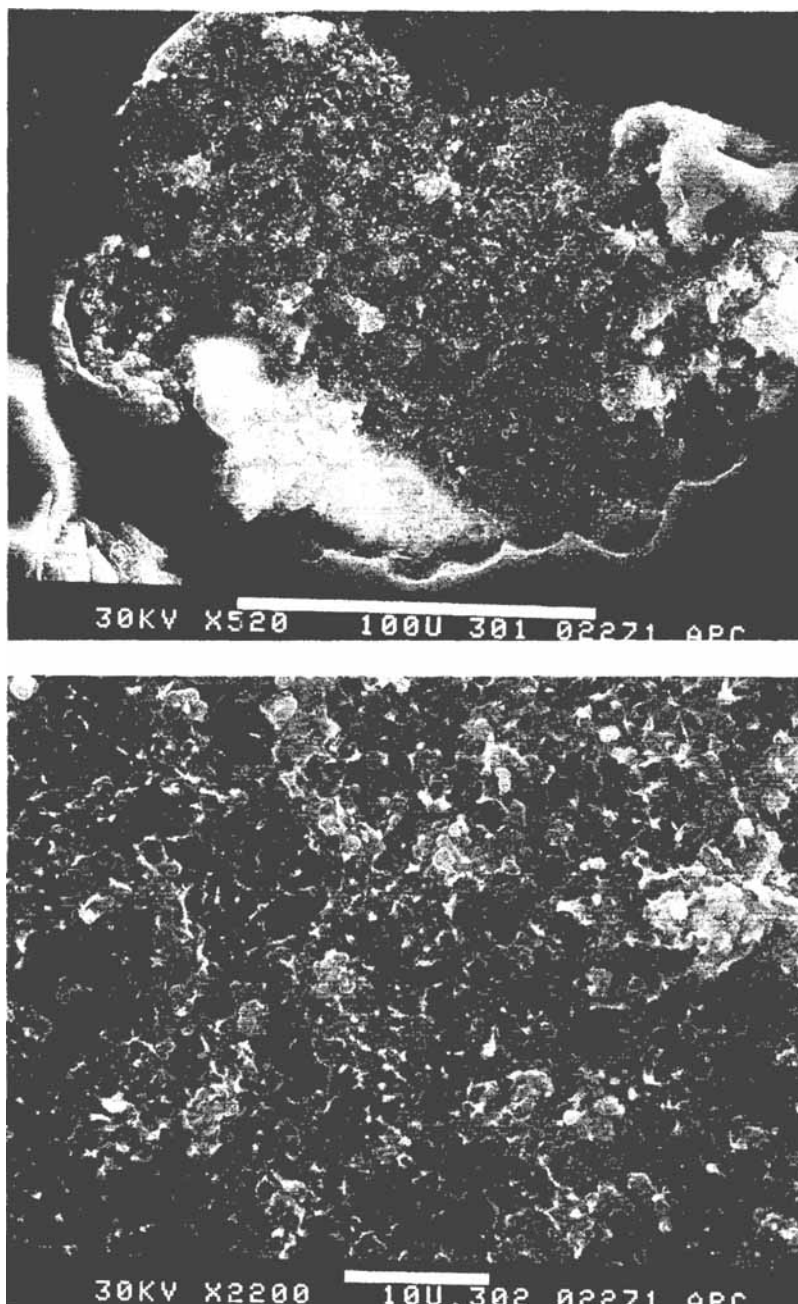particle (HPMC Type 1, IPTU = 18.1).

FIG. 7. Scanning electromicrograph of primary particles in a PVC particle (HPMC Type 2, IPTU = 24.4).
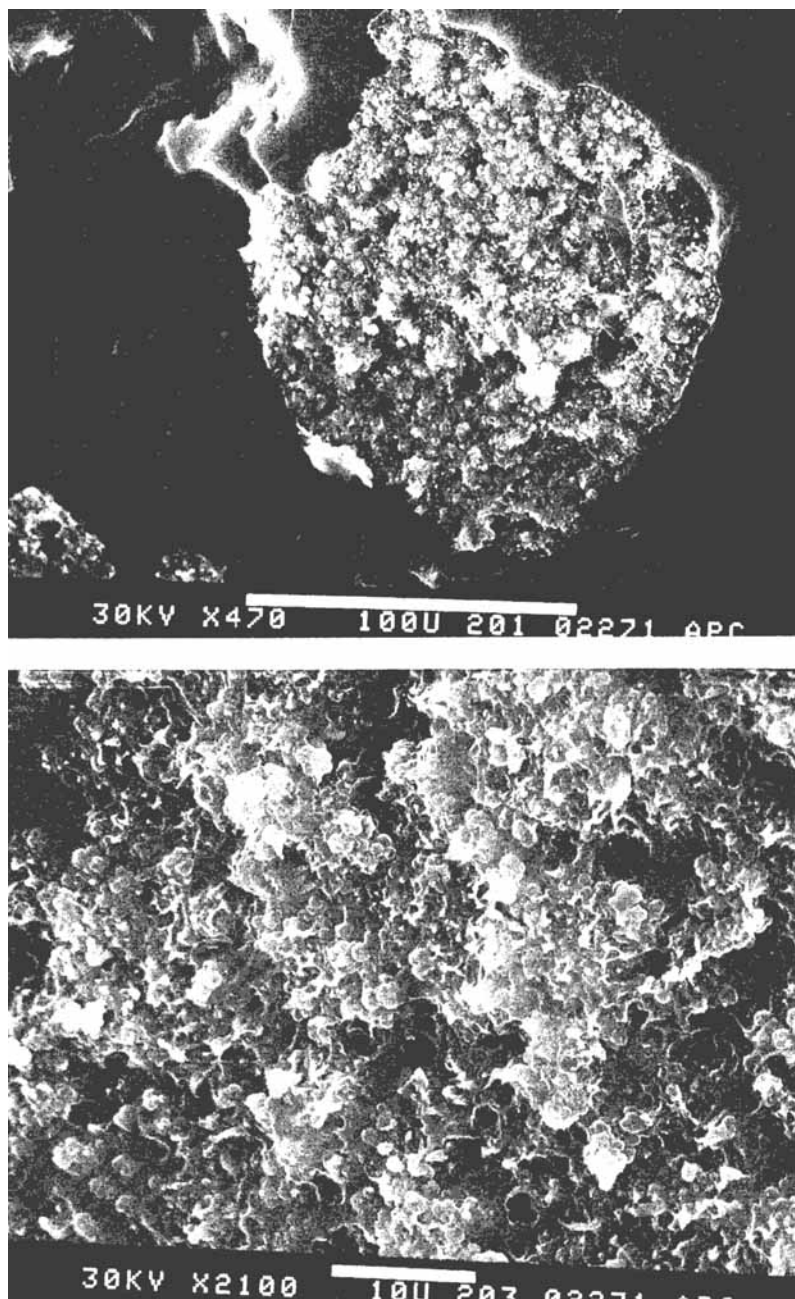
FIG. 8. Scanning electromicrograph of primary particles in a PVC
particle (HPMC Type 2, IPTU 31.4 prepared in a 500-gal reactor).

The mean size of agglomerated primary particle for Type 2 suspension appears to be smaller than that of the Type 1 system by 2-4 µm.

There is no detectable difference for the mean size of single primary particles between these HPMC. The size was found to be 1-2 µm.

The size and size distribution of primary particles are uniform and narrow for both HPMC systems. The agglomeration process has definitely broadened the distribution.

The above observations, which are based on a large number of micrographs, are consistent with the results of other investigators [5, 16, 17]. It is conceivable, among the huge number of primary particles, that different porosities require very little variation in packing mode, and these differences can be rationalized by the partitioning behavior of the suspending agent.

CONCLUSIONS

1. The particle structure of PVC is controlled by the substitution and molecular weight of hydroxypropyl methylcellulose while the molecular weight distribution shows no apparent effect.

2. Criteria in defining particle porosity are proposed based on the partition coefficient, Pc, which is expressed as the weight fraction of the suspending agent in the organic phase. Pc >0.80 for a resin with high porosity (IPTU > 30; pore volume > 0.30 cm^3/g). Pc <0.20 for a resin with low porosity (IPTU)< 15; pore volume < 0.15 cm^3/g). Resins with intermediate porosity are obtained when the Pc value for the suspending agent falls between these two limits. Preliminary studies indicate that the above criteria are also valid for a number of PVOH-stabilized suspension systems.

3. The resin porosity increases with increasing shear rate. However, the degree of substitution and molecular weight of HPMC have an overriding effect on PVC particle structure.

4. There is no simple correlation between median particle size and interfacial tension because of the complexity of the polymerization system. In particular, the lack of well-defined parameters that can be employed for characterizing the agglomeration process both for primary and for final particles. The viscosity of the reaction media and the gel strength of the suspending agent may also have an effect on particle agglomeration.

ACKNOWLEDGMENTS

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