

Particle Structure of PVC Based on Cellulosic Suspension System. III. Effect of Monomer Refluxing

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Synopsis

The effects of monomer refluxing on both resin properties and reactor fouling of suspension PVC have been studied in a laboratory-scale 14-L reactor. Process control equations were developed which related the particle properties to the reflux condenser operation by controlling the parameters of (1) the time at which refluxing is begun and (2) the rate profile of heat removal from the condenser. An operating envelope has been developed for laboratory scale operations which optimizes the cycle time of polymerization while minimizing the adverse effects on particle properties. These operating conditions may have application to production scale operations when the proper scaling factors are employed.

INTRODUCTION

The formation of poly(vinyl chloride) is an exothermic reaction liberating 25.1 kcal/mol polymer formed. One of the purposes of the reactor vessel is to provide the cooling surface for heat removal. The reactor size is limited by the ratio of reactor volume to cooling surface and the agitation system needed to maintain the monomer/water mixture at the proper monomer droplet size distribution. Commercial polymerization reactors of 25,000–50,000 gal capacity are standard for poly(vinyl chloride) industry. The reactor productivity will depend, in part, on the heat transfer capacity of the vessel, the higher the heat transfer capacity the more polymer that can be made per unit of time. The heat transfer capacity of a reaction vessel can be calculated using the following relationship:

$$Q = UA(\Delta T) \quad (1)$$

where Q is the total heat transfer capacity (BTU/h), A is the area of cooling surface (ft²), (ΔT) is the temperature differential between the reactor contents and the fluid in the jacket (°F), and U is the heat transfer coefficient of the cooling surface (BTU/ft² · °F · h).

Increasing any of these factors will increase the Q for the reaction vessel. Efforts to maximize the heat transfer capacity of the reactor vessel have been directed at reactor configurations¹⁻³; reactor wall fouling reduction^{4,5}; reactor cleaning procedures^{6,7}; temperature step processes.^{8,9} There has been a great deal of effort directed at optimization of the polymerization reactor configuration during the past 10 years. Large stainless steel reactors equipped with reflux condensers and multiple turbine agitators have been

developed for the manufacture of polyvinyl chloride resin. The efforts to increase the Q for large reactors have focused on the following factors: cooling surface area to volume ratio; reflux condenser utilization; temperature of the cooling fluid in the jacket.

A reflux condenser functions by condensing vapor to liquid and removing the latent heat of vaporization from the system. In large reactors, a reflux condenser is the most effective way to increase the available cooling surface without increasing the length to diameter ratio of the reaction vessel. The use of a reflux condenser to provide additional cooling capacity in vinyl chloride polymerization was discussed by Terwiesch¹⁰ for reactors of 50,000 gal capacity. A Conoco patent¹¹ describes the installation and use of a reflux condenser. In a recent patent, Shinetsu¹² indicates that the reflux condenser should only be used after 5% of the monomer is converted to polymer, because utilization of the reflux condenser before 5% conversion results in extensive reflux condenser fouling and a coarser resin.

The reflux condenser operation envelop (amount of reflux, startup time for reflux) will depend on the ability of the reactor agitation system to reincorporate the refluxed monomer effectively into the polymerizing mass and on the foaming tendency of the polymerization recipe. Venting procedures have been described¹³ to remove the noncondensable gases from the vapor phase of the reactor and reflux condenser. The level of noncondensable gases in the reactor vapor phase will be affected by the quality of the monomer, how well the reactor has been evacuated prior to polymerization, and whether the polymerization process generates an inert gas. The use of azo initiator will result in the formation of nitrogen as a by-product of the initiator decomposition. In addition, a carbonate buffer system will produce CO_2 gas if the aqueous phase becomes acidic. Both situations will result in the generation of inert, noncondensable gases which will reduce the efficiency of the reflux condenser. The effective operation of the reflux condenser is a key element in preparing high quality PVC resin in an economical fashion.

The use of laboratory scale equipment to simulate production scale operations offers economical alternatives to analyse process variables. Recently Johnson and co-workers^{14,15} have examined the effects of agitation on the particle properties of poly(vinyl chloride) prepared by suspension systems in different-size reactor vessels. They found that the agitation in the reactor vessel, as determined by a modified Weber number, could be used to predict bulk density and median particle size. This technique of using laboratory scale equipment was used to identify how reflux condenser process variables could affect the particle morphology of suspension polymerized vinyl chloride resin. These laboratory scale results can be applied to production scale equipment, when the proper scaling factor is employed.

EXPERIMENTAL

Raw Materials

Water. Tap water was passed through deionization column and then double distilled under a nitrogen purge.

Suspension Agent. Hydroxypropyl methyl cellulose (HPMC, type 2) from Dow Chemical was used as received.

Initiator. Lupersol-10 (75% active *t*-butyl perneodecanoate) supplied by Lucidol was used as received. Lupersol-188 (75% active α -cumyl perneodecanoate) supplied by Lucidol was used as received.

Vinyl Chloride Monomer. CP-grade vinyl chloride obtained from Air Products Specialty Gas was used as received.

Polymerization Procedure

Reactor. 14-Lr stainless steel reactor equipped with internal cooling coil in the vapor phase and bottom entering agitator, manufactured by Pressure Products of Hatboro, Pa. Equipped with flow meter and differential temperature indicators on the jacket and coil.

Test Procedures

IPTU (ASTM D-3367) a measure of porosity (g DOP plasticizer/100 g polymer); HPMC concentration (Air Products analytical method—based on procedures supplied by Dow Chemical); particle size, screen analysis (ASTM A1921-75).

Recipe

(1) Water 3000 g; (2) vinyl chloride, 2000 g; (3) HPMC, variable level; (4) Lupersol 10 and Lupersol 188—total 1.5 g; polymerization temperature 55°C; polymerization time 5.0 h. This initiator combination gave a uniform heat release polymerization with completion within ± 0.15 h.

Temperature Control Equipment

Flow rates for the reflux coil and the jacket were set so as to insure reflux ratios set within the experimental design limits. Flow rates were controlled by standard pneumatic valves. Differential temperatures were recorded to $\pm 0.01^\circ\text{C}$.

Charging Procedure

Components 1 and 3 were added to the reactor under a nitrogen purge and stirred at room temperature until dissolved. The reactor was sealed and the monomer was added at room temperature. The reactor content was heated to 55°C. The initiators were added to the reactor through a special addition port after thermal equilibrium had been established and base line readings for the jacket and cooling coil were set. The initiators were flushed into the reactor with 50 mL of water at 55°C.

Experimental Design and Data Analysis

The interaction between the independent and dependent process variables was studied in an experimental design developed by the Air Products-Statistics Department. The data were analyzed and reduced to linear equations with second order interactions. In all cases the experimental program was

TABLE I
Experimental Design and Results

Experiment no.	HPMC (PHM)	Reflux (%)	On time (h)	BD (lb/ft ³)	IPTU (%)	Cumulative on screens										MPS (μ m)
						PS20	PS30	PS40	PS60	PS80	PS100	PS140	PS170	PS200	PAN	
1	0.060	0	5	30.4	19.6	0.0	0.0	0.4	11.6	50.9	79.6	97.2	99.2	99.6	100.0	180
2	0.060	0	5	34.5	15.6	1.4	3.4	7.0	16.9	51.8	75.9	96.2	99.2	99.8	100.0	180
3	0.060	50	5	31.9	17.6	0.2	1.2	5.2	20.8	57.9	81.0	97.2	99.4	99.8	100.0	190
4	0.060	50	4	32.9	18.4	0.0	0.4	2.8	13.8	43.3	67.8	91.7	97.0	99.0	100.0	170
5	0.060	0	5	32.3	18.4	0.0	0.2	1.4	14.6	49.7	72.4	93.0	97.2	98.6	100.0	180
6	0.060	25	5	32.7	19.6	0.0	0.6	4.4	19.9	53.5	77.7	95.0	98.6	99.6	100.0	185
7	0.060	25	4	34.9	17.6	0.0	0.8	4.4	16.8	47.0	69.4	91.4	96.8	98.8	100.0	180
8	0.060	50	4	35.4	19.2	7.4	23.0	34.4	51.6	78.4	89.2	96.4	98.0	99.0	100.0	250
9	0.060	0	5	38.4	18.8	1.8	11.4	22.8	36.0	62.0	79.8	95.8	98.6	99.4	100.0	210
10	0.060	75	5	34.5	22.0	4.2	13.4	24.8	63.2	77.4	91.6	97.8	98.8	99.4	100.0	300
11	0.060	75	4	34.7	20.0	2.6	15.4	27.0	37.2	67.0	87.6	97.6	98.6	99.4	100.0	220
12	0.075	38	4	40.5	16.0	17.8	32.4	40.6	49.2	61.4	73.8	90.0	95.0	97.8	100.0	250
13	0.075	38	4	36.9	16.0	0.6	8.8	21.4	37.0	51.2	67.6	89.8	96.2	97.8	100.0	180
14	0.075	38	4	36.6	18.0	2.0	17.4	30.4	43.0	58.2	77.0	94.8	98.0	99.2	100.0	220
15	0.090	0	5	44.4	16.0	0.4	9.2	26.0	42.2	48.6	55.2	75.8	84.8	91.8	100.0	170
16	0.090	0	5	42.1	16.4	0.6	9.8	26.6	43.6	51.4	57.8	76.0	83.6	91.0	100.0	180
17	0.090	50	5	39.3	16.8	0.4	5.4	26.6	44.2	53.0	62.4	81.2	87.8	93.8	100.0	200
18	0.090	50	4	39.9	18.0	0.6	10.8	36.2	50.8	57.0	66.0	84.8	90.2	95.8	100.0	250
19	0.090	25	5	39.6	16.0	16.6	40.6	52.0	62.8	69.6	76.6	89.0	93.4	96.2	100.0	450
20	0.090	25	4	37.9	14.0	0.2	5.0	16.8	34.2	44.6	55.8	79.6	88.4	93.4	100.0	165
21	0.060	25	3	35.9	13.6	0.0	1.0	8.4	21.6	52.3	77.4	95.2	98.0	99.4	100.0	185
22	0.090	25	3	39.6	12.0	1.2	18.2	36.8	47.8	54.4	63.4	79.4	86.8	93.4	100.0	225
23	0.060	50	3	32.0	20.4	0.2	1.4	9.8	24.8	58.3	81.8	95.4	97.4	99.0	100.0	200
24	0.090	50	3	37.6	12.4	0.2	1.2	11.0	26.4	36.2	49.2	74.6	84.0	92.8	100.0	150
25	0.060	50	5	33.8	17.6	0.2	1.8	8.8	22.4	53.6	75.8	92.8	96.2	98.6	100.0	190
26	0.060	50	4	34.6	16.8	1.2	8.2	18.0	26.4	52.6	75.4	93.4	96.8	98.8	100.0	185
27	0.060	100	5	32.7	21.6	0.0	0.2	1.8	21.2	61.6	84.8	98.2	99.6	100.0	100.0	—
28	0.060	100	3	34.0	22.0	1.4	5.4	12.6	24.2	59.8	82.4	96.0	98.0	99.2	100.0	—
29	0.060	100	5	33.9	20.0	7.8	13.8	21.8	44.2	78.4	91.0	97.8	99.0	99.8	100.0	—
30	0.060	100	3	36.1	16.0	5.8	15.0	23.0	33.6	67.8	87.0	97.0	98.4	99.9	100.0	—

intended to determine how the input variables of (1) percent reflux and (2) condenser "on" time would affect the output resin properties of (1) particle size distribution, (2) porosity, (3) resin bulk density, (4) reactor fouling, and (5) conversion. The percent reflux is defined as the rates of heat removed by the condensing coil to the total heat removed, i.e., the coil plus the jacket. The condenser "on" time is defined as the total time in hours the coil being used for heat removal. A 3 h on time means the coil was switched on 2 h after reaching the temperature of polymerization and remained on for 3 h. The total polymerization time was kept constant at 5 h for all the experiments. The levels of input variables are as follows: Percent reflux: 0%, 25%, 50%, 75%, 100%; on time (h): 0, 3, 4, 5. HPMC levels: 0.060, 0.075, 0.090 (PHM). The details of the experimental program are summarized in Table I.

RESULTS

Particle Size/Particle Size Distribution (PSD)

The experimental PSD data described in Table I were analyzed using several empirical formulas composed of linear, interactive, and higher-order terms. The criterion of an F test greater than 10% was used to accept or reject terms. This technique led us to a linear equation [eq. (1)] which, with three independent terms, was able to predict the level of cumulative resin on the 60-mesh screen with a correlation coefficient squared (R^2) of 0.52. This value of R^2 indicates that the independent variables chosen in this study can account for about half of the experimental variation in particle size when HPMC level is maintained of 0.06/HM. The predictive equation for cumulative particle size on the 60 mesh is

$$X = K_1 + K_2 [\text{on time}] + K_3 [\% \text{ reflux}] + K_4 [\text{on time}] [\% \text{ reflux}] \quad (2)$$

where X = % on 60 mesh screen (coarse fraction), $K_1 = 12.0$, $K_2 = -9.24 \times 10^{-2}$, $K_3 = -1.38 \times 10^{-1}$, and $K_4 = -4.33 \times 10^{-2}$.

A contour plot based on eq. (1) presented in Figure 1 indicates the following general trends in laboratory scale reactors:

1. The level of particles on 60-mesh screen is decreased by reducing both percent reflux and "on time." This agrees with previous literature citations.
2. The level of particles on 60-mesh screen in this laboratory study is not affected by the condenser operation under the conditions of refluxing loading of up to 100% with 3 h on time, i.e., a 2-h delay before the condenser is switched on in a 5-h polymerization time. In a separate series of experiments we determined that the typical conversion was $31.0 \pm 2.4\%$ at 2 h. The effect of full reflux (100%) and increasing "on time" up to 5 h results in a larger fraction on the 60-mesh screen. No general trends could be identified for the "on time" of 4-5 h and ramped reflux.

Using the total data base of 30 experiments covering all levels of HPMC, a similar empirical model was developed to predict the level of resin on the 60-mesh screen for the entire experimental set. This particular contour plot is depicted in Figure 2. The similarity of Figures 1 and 2 indicate the rather

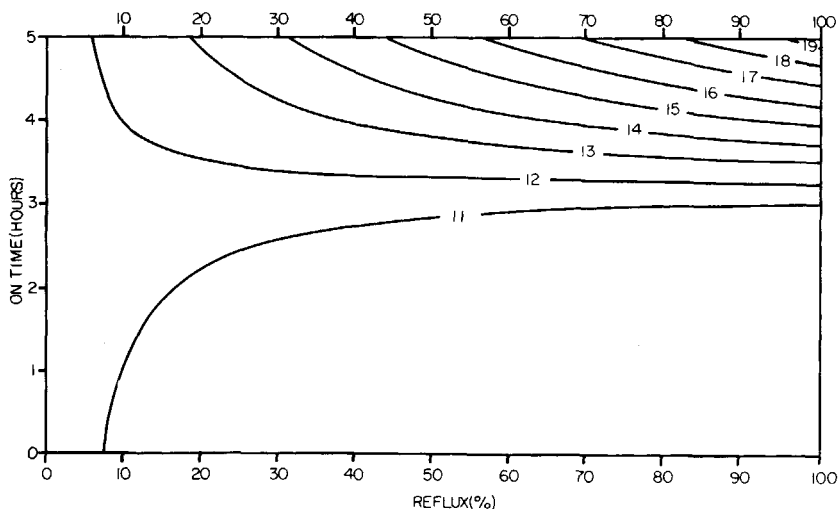


Fig. 1. Contour plot of P60 Model (on time and reflux terms) at HPMC = 0.060.

low sensitivity of HPMC level to coarse fraction of resin within the parameters of the experimental design which we utilized.

The particle size distribution for the data in Table I was plotted in a log-probability form using in one case the "on time" (Fig. 3) and in another case the reflux level (Fig. 4) as the experimental variable. These two figures depict graphically the trend that high levels of reflux and on time have on the median particle size and on the PSD within this experimental envelop.

Porosity/Bulk Density

The resin porosity is one of the important resin physical properties, affecting the efficiency of monomer stripping and the plasticizer absorption.

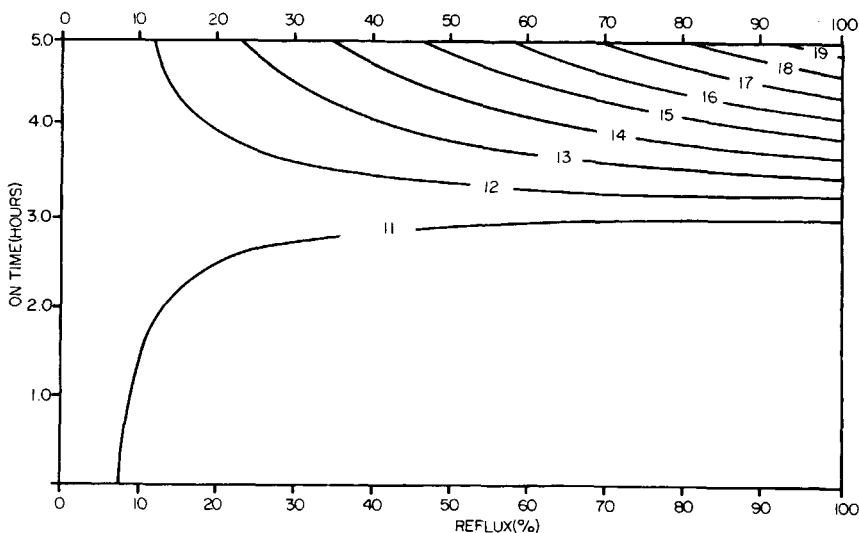


Fig. 2. Contour plot of P60 Model at all HPMC levels (on time, reflux, and HPMC terms).

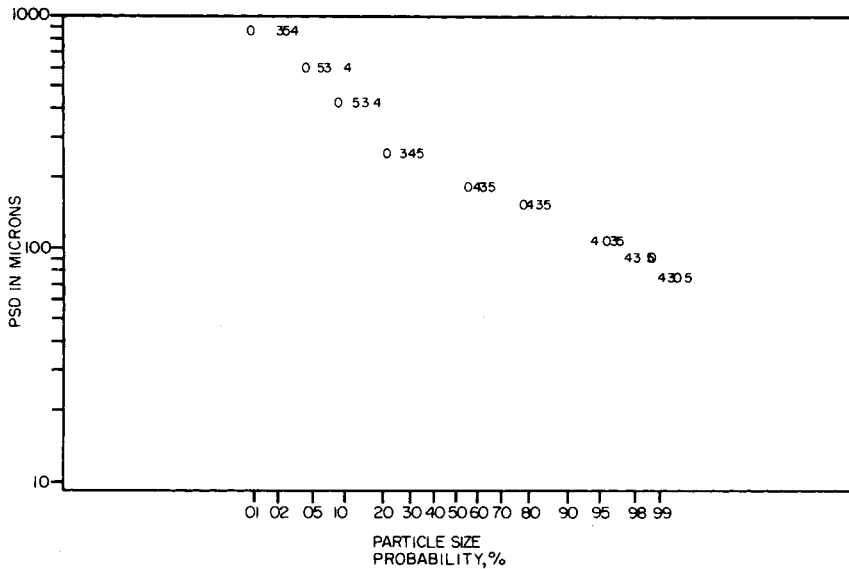


Fig. 3. Reflux condenser simulation—probability plot. Variation of on time (h): (0) 0; (3) 3; (4) 4; (5) 5. HPMC concn = 0.060.

Porosity is a measure of total pore volume per unit weight including voids of inter- and intraparticles. The porosity is commonly determined by mercury porosimetry or the IPTU (irreversible plasticizer take up) method, of which the latter has been adopted for this study. There is a linear correlation between data obtained by those two methods. The effect of monomer refluxing on resin porosity is shown in Figures 5 and 6 at two levels of HPMC. The general trend appears to be that the porosity, as measured by IPTU,

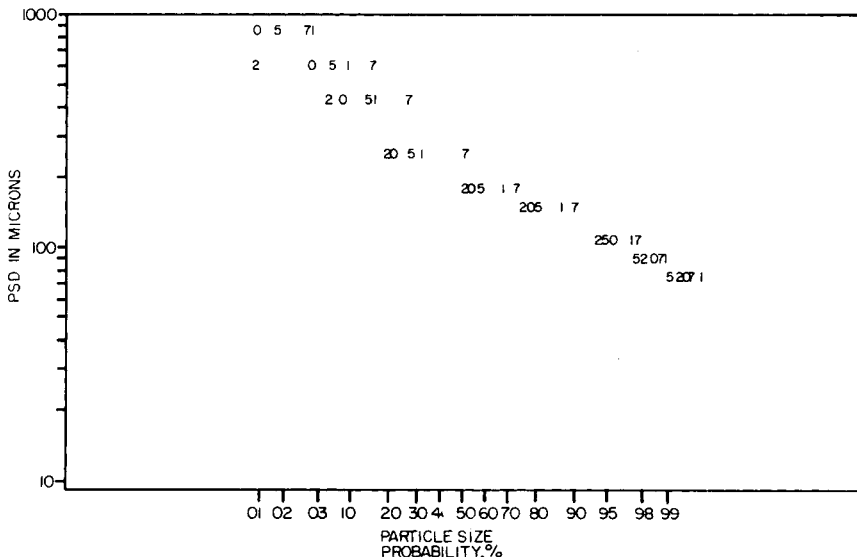


Fig. 4. Reflux condenser simulation—probability plot. Variation in % reflux: (0) 0; (2) 25; (5) 50; (7) 75; (1) 100. HPMC concn = 0.060.

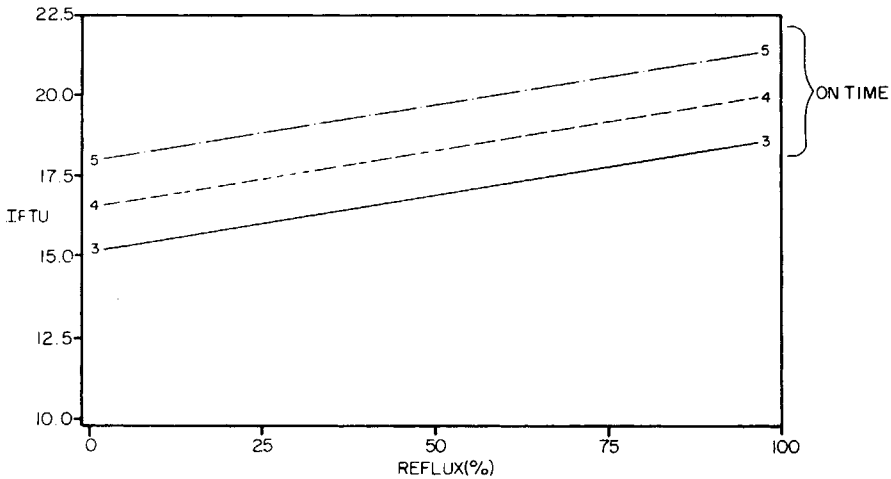


Fig. 5. IPTU vs. reflux at HPMC = 0.060.

increases with increasing reflux and condenser "on" time. The equation, with R^2 of 0.66, takes the form of

$$P = K_1 + K_2 [\text{HPMC}] + K_3 [\text{reflux}] + K_4 [\text{on time}]$$

where P = porosity (IPTU), $K_1 = 16.0651$, $K_2 = -8.69 \times 10^{-1}$ (HPMC) (phm), $K_3 = 3.94 \times 10^{-2}$ [reflux] (%), and $K_4 = 1.41 \times 10^0$ [on time] (h). The correlation of bulk density with R^2 of 0.67 is given by

$$B = K_1 + K_2 [\text{HPMC}] \quad (3)$$

where B = bulk density (lb/ft³), $K_1 = 22.0$, and $K_2 = 2.02 \times 10^{-2}$ [HPMC] (phm). Apparently the bulk density of homopolymer depends only on the concentration of HPMC unaffected by either refluxing or on time (Fig. 7).

Both the porosity and bulk density empirical models [eqs. (2) and (3)] can account for only two thirds of the experimental variations between the

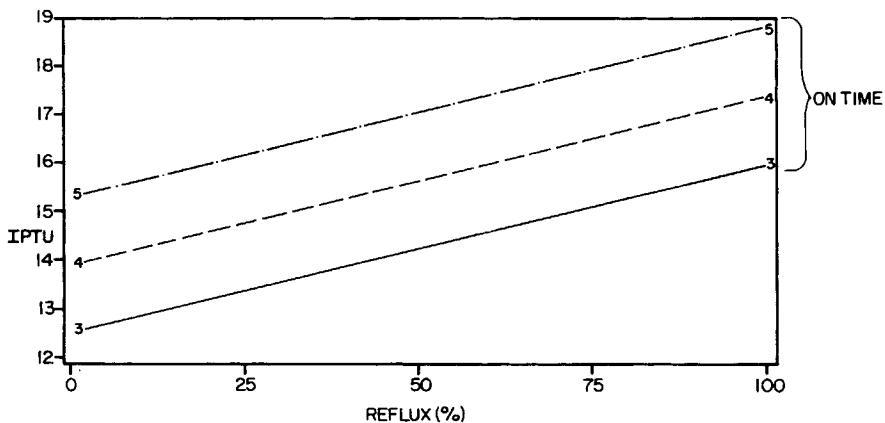


Fig. 6. IPTU vs. reflux at HPMC = 0.090.

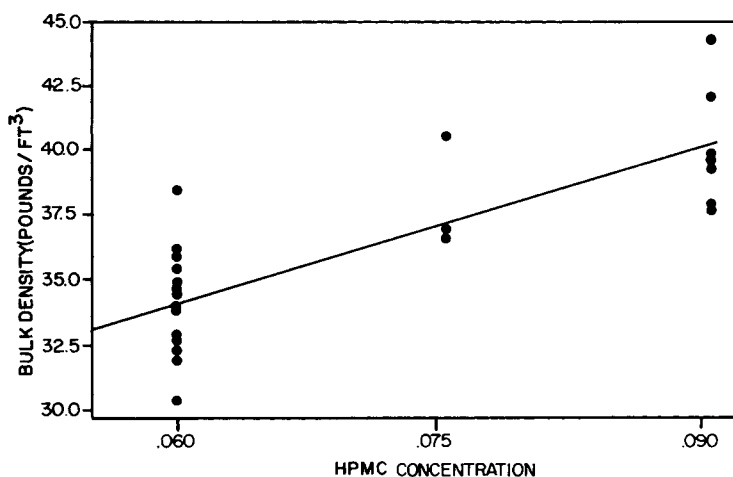


Fig. 7. Bulk density vs. HPMC level.

dependent and independent variables. These two equations are qualitatively consistent in that increasing the HPMC level increases the resin bulk density and decreases the resin porosity.

Reactor Fouling/Conversion

Reactor fouling is a common phenomenon concerning polymer buildup on internal of a reactor which has adverse effect on productivity. The analysis of fouling, which was based on 13 polymerization runs, resulted in a simple two-term equation. The level of fouling was found proportional to a level of reflux and inversely to HPMC concentration, independent of the condenser "on" time as shown below (Fig. 8). The R^2 was 0.78:

$$F = K_1 + K_2 [\text{reflux}] + K_3 [\text{HPMC}] \quad (4)$$

where F = fouling per batch (g), $K_1 = 5.49$, $K_2 = 1.36 \times 10^{-2}$ [reflux] (%), $K_3 = 2.51 \times 10^{+1}$ [HPMC] (phm). An analysis of conversion data failed to indicate any correlation to the experimental variables of reflux condenser operation.

The empirical equations developed for these experiments are based on a process using a single HPMC primary suspension agent. Experimental evidence indicates that the use of binary (or higher) suspension systems, and in particular where one of the components is a porosity modifier¹⁶ significantly alters the nature of these empirical equations.

MECHANISM FOR DROPLET STABILIZATION

The particle size distribution of polymer is determined by the size distribution of monomer droplets and the degree of agglomeration during polymerization. Both of which are, in turn, controlled by three major factors: (1) shear field the droplets are subject to; (2) T_g or viscosity/modulus of the polymerizing droplet at the temperature of polymerization; (3) characteristics of the interface. In normal production the first two factors are kept

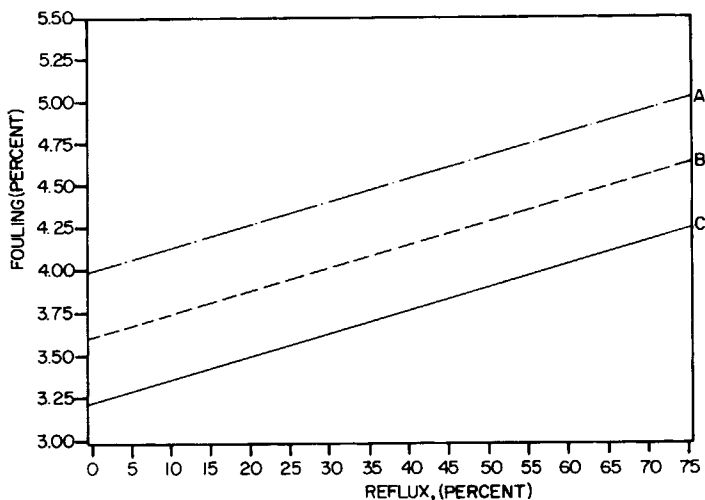


Fig. 8. Fouling vs. reflux: (A) 0.060; (B) 0.075; (C) 0.090. Points at ends of lines indicate line level.

constant while the dynamics of interface is significantly affected by the action of monomer refluxing. The complication of monomer refluxing on PSD appears to have been caused by the shifting of the dynamic equilibrium of HPMC molecules distributed among the three phases^{17,18}:



where $[C_s]$ = concentration of suspending agent, a = aqueous phase, I = interface, and m = monomer phase. The percent distribution at zero conversion was estimated to be 20% in aqueous phase, 45% at interface, and 35% in monomer phase when HPMC was used.

The experimental evidence indicates that the concentration of HPMC in aqueous phase reaches a steady-state only after 25% conversion which supports the following implications:

1. After 25% conversion, the nucleation stage has completed and no new particle forms thereafter. The surface of droplet is immobilized by a structural layer of modified cellulose through grafting, complexing or adsorption mechanism, and the polymerization is restricted to within the boundary of the particles. Therefore, the transport of monomer in and out of the droplet, as a result of refluxing, will have no effect whatsoever in the established particle size distribution.

2. When the reflux is introduced at the early stage of polymerization (before 25% conversion), the particle dimension has not formed well and the disturbance created by monomer movement will induce particle size changes. A high reflux rate is expected to generate greater turbulence both in magnitude and frequency. Whether such disturbance will alter the particle size depends largely on the structural stability of the particle, which increases with percent conversion.

3. Regardless of the state of conversion, the fate of refluxed monomer can be considered as:

- a. The refluxed monomer forms new, inert droplets under agitation. No polymerization occurs in those droplets because they do not contain initiator molecules or free radicals. Its size distribution is governed by the instantaneous concentration of HPMC in the aqueous phase. To maintain such a state is very difficult.
- b. The other alternative, which is thermodynamically favored, appears that those inert droplets return to the existing polymerizing droplets by diffusion/mixing process, losing their own identity.

PARTICLE MORPHOLOGY

Scanning electromicrographs were taken of representative samples of resins to determine the effect of reflux operations on the particle morphology. We use the samples noted in Table II. The following observations can be made:

1. Experiment 1—zero reflux [Figs. 9(a), 9(b)]: The particle surface is well defined; particle shapes are relatively uniform. The internal structure is well defined.
2. Experiment 3—50% reflux 5 h [Figs. 9(c), 9(d)]: The particle surface is convoluted, particle shapes are elongated. The internal pore structure is fused and poorly defined.
3. Experiment 23—50% reflux, 3 h [Figs. 9(e), 9(f)]: Particle surface and particle shapes are apparently unaffected by reflux; the internal pore structure is not completely distinct.

The refluxing of VCM at the start of the polymerization (experiment 3) can affect both the particle shape and internal pore structure. Refluxing after 2 h (experiment 23) does not affect the particle shape but does affect the internal pore structure.

CONCLUSIONS

In laboratory scale equipment using a single HPMC suspending agent.

1. The particle properties of vinyl chloride homopolymer are significantly affected by the operation of the reflux condenser. Severe particle coarsening, which is undesirable, has been observed when reflux is employed at 0% conversion. The percent coarse fraction is proportionally increased with both increasing refluxing rate and the start time of refluxing; the earlier refluxing is started, the higher the percent coarse fraction.
2. The particle coarsening effect is reduced to a negligible level when the refluxing process is introduced after 30% conversion. At this point, the particle boundary has been well formed and the growth is confined within the established final agglomerates. Both safe operating and correlation equations have been developed.

TABLE II
Effect of Reflux Operations on Particle Morphology

Experiment no.	Reflux level	On time
1	0	0
3	50	5
23	50	3

3. A 25% increase in reactor fouling is observed as the level of reflux is changed from 0% to 75%.

4. The porosity of homopolymer as measured by the IPTU test, increased by 2–3 units with an increasing level of reflux.

5. The bulk density of homopolymer, which is not affected by monomer refluxing, increases only with increasing concentration of the suspending agent.

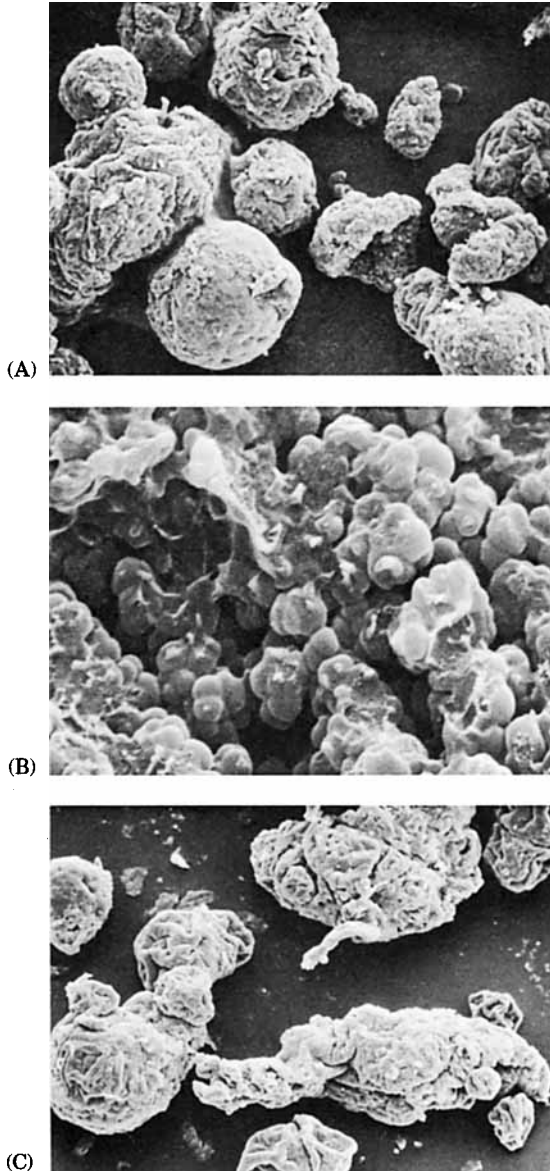


Fig. 9. Scanning Electron Micrographs. Experiment 1, zero reflux: (A) 114 \times ; (B) 3120 \times . Experiment 3, 50% reflux for 5 Hours: (C) 120 \times ; (D) 3060 \times . Experiment 23, 50% reflux for 3 Hours: (E) 120 \times ; (F) 2940 \times .

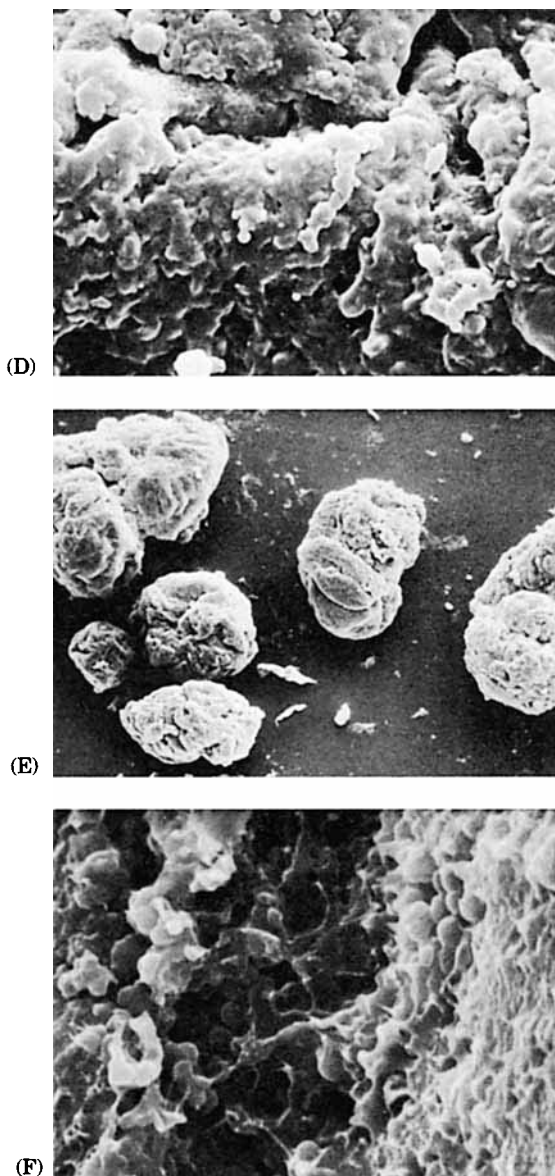


Fig. 9. (Continued from the previous page.)

APPENDIX: NOMENCLATURE

- A* area of cooling surface (ft²)
B bulk density (lb/ft³)
C concentration of suspending agent
F fouling per batch (g)
HPMC hydroxypropylmethylcellulose
K formula constant
P Porosity (%)
Q total heat transfer capacity (BTU/h)
 ΔT temperature differential (°F)

U heat transfer coefficient (BTU/ft² · °F · h)

X % on 60-mesh screen (%)

Subscripts

a aqueous phase

I interface

m monomer phase

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