Effect of Vinyl Chloride Injection on the Morphology of Suspension-Polymerized PVC

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ABSTRACT

The mechanism of growth of PVC granules was investigated by injecting additional vinyl chloride monomer into a conventional suspension polymerization process at two different conversions. Polymerization was sustained for long periods in both cases, with the injection before pressure drop producing a more rapid decrease in properties such as porosity and surface area. With injection after pressure drop, additional polymer growth produced a structure with noticeably inferior plasticizer absorption and gelation properties, even though porosity and surface area values were higher. A discussion of the growth mechanism of PVC granules under the two injection systems is presented and related to the conventional suspension process.

INTRODUCTION

It is well known that in the suspension polymerization of vinyl chloride monomer (VCM) a particular morphological and kinetic

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profile typifies the average process. The polymer precipitates from the monomer at very low conversion, and the number of primary particles (0.1-0.2 μm) is fixed below 2% conversion. These primary particles aggregate together as they grow and increase in size with conversion. A progressive fusion also occurs between the particles in an aggregate, particularly after pressure drop when unconverted monomer is present solely in the swollen gel phase.

The phase separation step present in VCM polymerization has a fundamental effect on the kinetics. In the case of a typical azo- or peroxydicarbonate-initiated recipe at 50-60°C, the reaction rate versus time profile is typified by a relatively slow initial rate followed by autoacceleration with a significant rate peak between 60 and 85% conversion.

It occurred to us that an investigation of the morphological and kinetic features of the process in the regions before and after pressure drop by continuous injection of fresh monomer could prove useful in increasing our understanding of the processes controlling the morphology of granular PVC.

EXPERIMENTAL

The experiments were carried out in a stainless steel reactor equipped with an agitator. The monomer was injected via a dip leg which reached well below the liquid level in the autoclave and close to the tip of the agitator to ensure good dispersion. Suspending agent (PVA) and initiator (alkyl peroxydicarbonate) concentrations typical of a straightforward granular polymerization of vinyl chloride at 50°C were used. Additional vinyl chloride monomer was injected either shortly after pressure drop (PD) or before the expected pressure drop point.

For a typical post-pressure drop injection, the polymerization was allowed to pass through the pressure drop stage ($\sim$70% conversion) and once the pressure had fallen some 5-8 psi the injection of fresh VCM began. For a typical injection before pressure drop, when the process is still under saturated vapor-pressure conditions, the injections commenced when the conversion was estimated to be 50%. In both systems a near linear injection/polymerization rate was maintained for up to 4 hr, at which point reactions were terminated (Fig. 1). During the injection period of the post-pressure drop system the conversion rate was of the order of 24-28%/hr; in the saturated system before pressure drop it was 15-18%/hr, whereas in the normal suspension process it is 13-14%/hr overall.
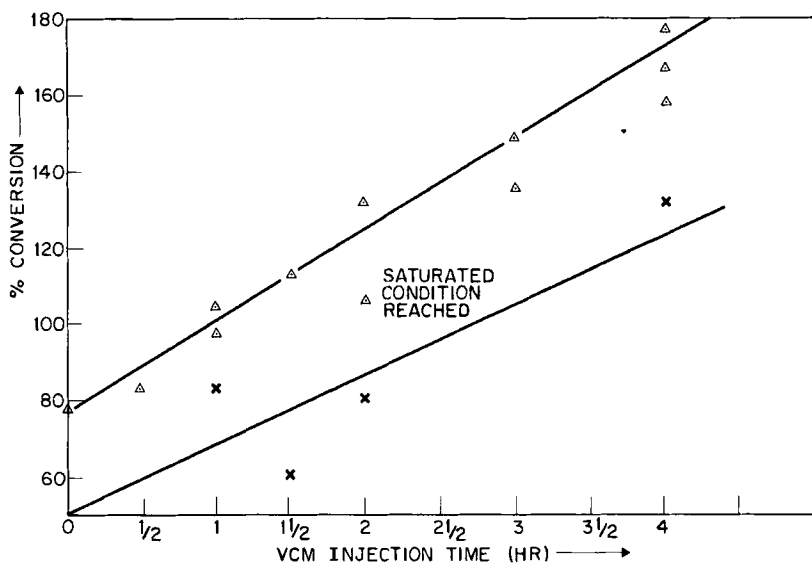
FIG. 1. Increase in conversion with injection time: (△) after pressure drop; (×) before pressure drop.

RESULTS AND DISCUSSION

Injection after pressure drop produced a linear increase in mean granule size (Fig. 2) and packing density (Fig. 3) and a steady decrease in surface area (Fig. 4), while the polymer molecular weight (K value) [1, 2] increased rapidly at first but then reached an asymptotic level at about 100% conversion (on initial monomer charged) (Fig. 5). When injecting before pressure drop there was no systematic change of mean size with conversion (Fig. 2), but packing density again increased linearly but at a higher rate (Fig. 3). Surface area was higher initially but decreased more rapidly (Fig. 4), while K value increased linearly with conversion (Fig. 5). The porosity of both sets of polymers fell linearly with conversion but more rapidly for those with vinyl chloride injection before pressure drop (Fig. 6).

While it is clear that the two injection techniques produce polymers with different powder properties, these results give no clear indication as to how this is achieved. If we consider the relationship between per cent porosity and packing density (Fig. 7) it is clear that
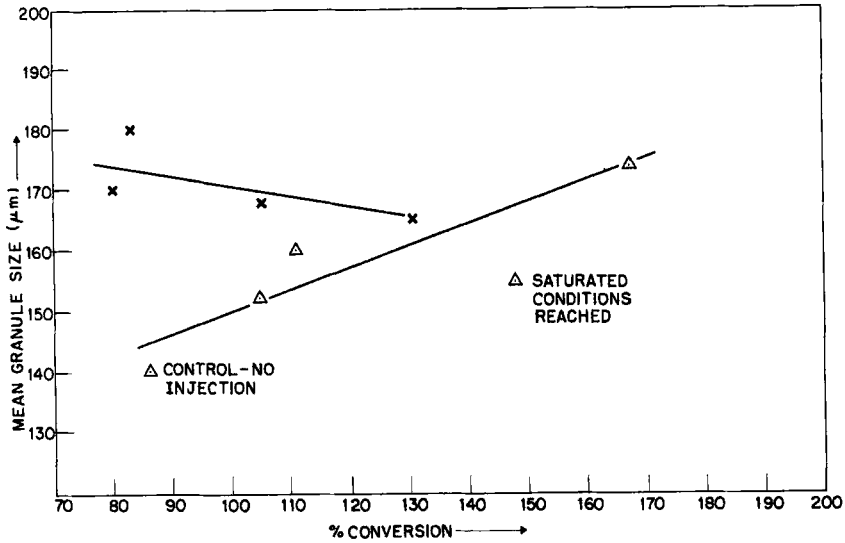
FIG. 2. Effect of injection conditions on mean granule size:
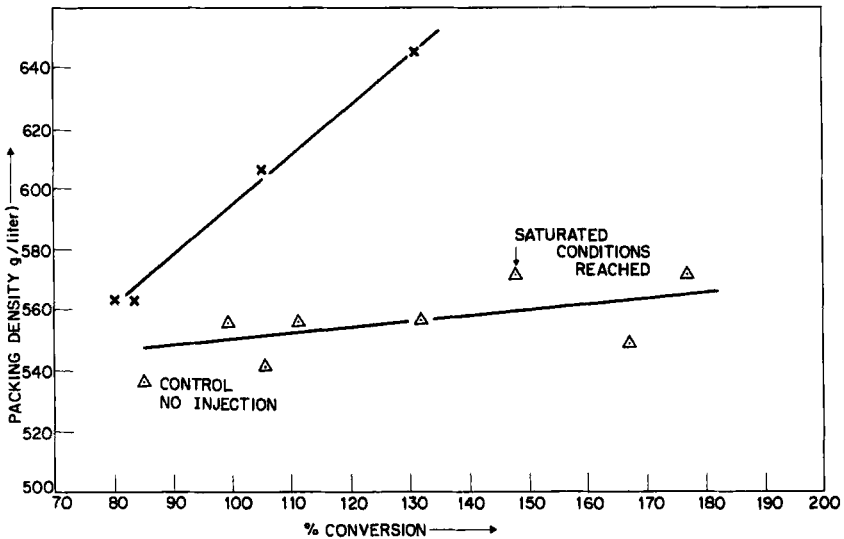(△) after pressure drop; (×) before pressure drop.

FIG. 3. Effect of injection conditions on packing density: (△)
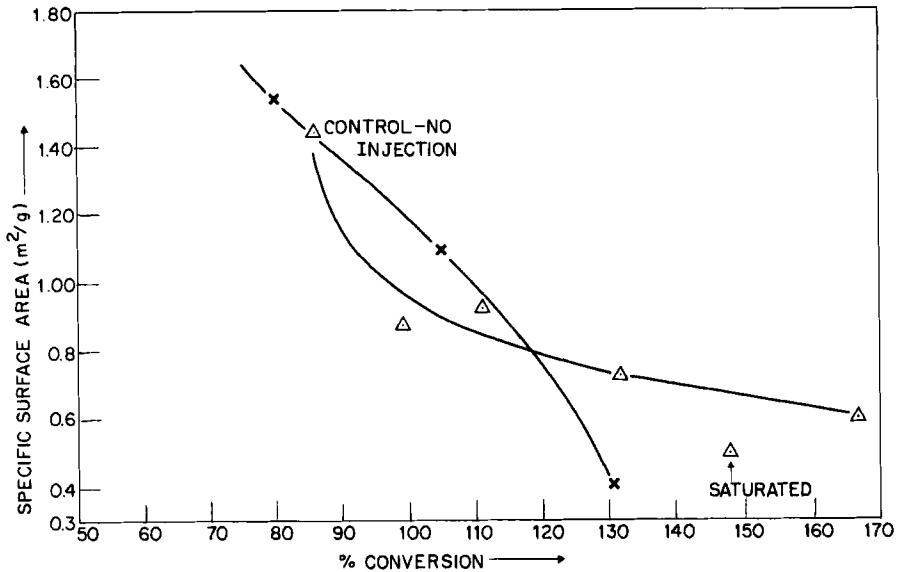after pressure drop; (×) before pressure drop.

FIG. 4. Effect of injection conditions on specific surface area:
(△) after pressure drop; (×) before pressure drop.

there is a fundamental difference in the growth mechanism of PVC
granules in the two systems. For a given level of porosity the
packing density of the polymers is quite different, and this suggests
that the shape and/or density of the granules produced differs sig-
nificantly.

However, the most informative results from the point of view of
understanding the mechanism of particle growth in the two areas
under investigation came from an examination of the pore size
distributions of polymers from each system. Typical results are
presented in Figs. 8 and 9. The level of porosity in small pores is
lower in the post-pressure drop than in the pre-pressure drop case,
where the porosity change is spread more evenly.

The relationship between the two injection systems is clearly
demonstrated by reconsidering Figs. 1, 4, 5, and 6, since these plots
contain at least one experimental point which has resulted from a
partial pressure injection system reaching saturated conditions as
a consequence of too rapid an injection rate. It is noticeable in all
cases that there is a shift in the property concerned towards that
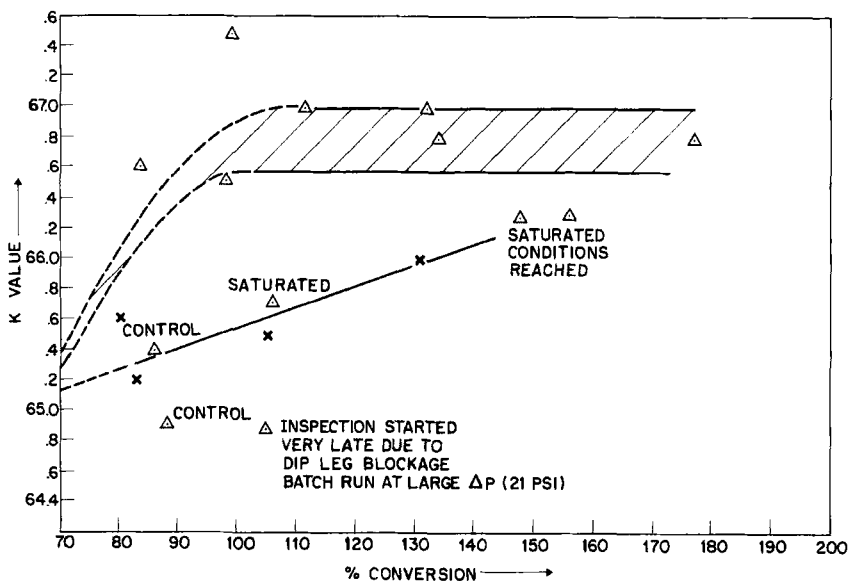achieved in the pre-pressure drop injection system.

FIG. 5. Effect of injection conditions on K value: (△) after
pressure drop; (×) before pressure drop. Note very expanded K
value scale.

These experiments clearly show that in a normal suspension
polymerization the decreasing polymerization rate after pressure
drop is due to monomer starvation, since the quantity of initiator
used in a conventional recipe is quite capable of converting at least
twice the quantity of monomer normally used. If fresh monomer is
injected immediately after pressure drop a high rate of reaction
can be maintained for long periods, producing material of increased
molecular weight, but unfortunately accompanied by a marked de-
terioration in certain polymer properties. Before pressure drop
an equally long period of polymerization can be maintained, albeit
at a lower rate, but with only a gradual change in properties.

We postulate that in a vinyl chloride polymerization the reactive
zone encompasses only the surface and immediate subsurface regions
of the phase-separated PVC. The depth of this reactive zone will
increase with conversion, but, once the macroradicals associated
with the original nuclei are terminated, the center region of the pri-
mary particles is essentially dead and merely acts as a monomer
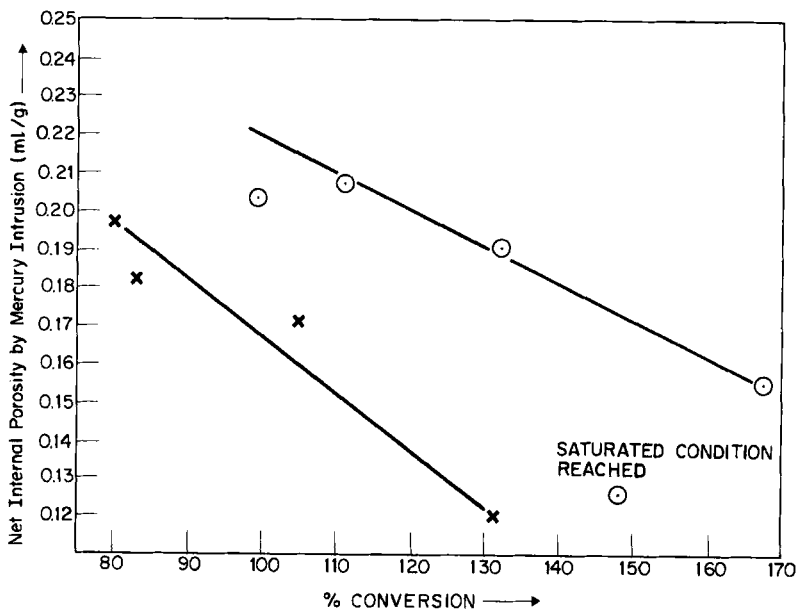
FIG. 6. Effect of injection conditions on polymer porosity (by Hg intrusion): (⊙) after pressure drop (×) before pressure drop.
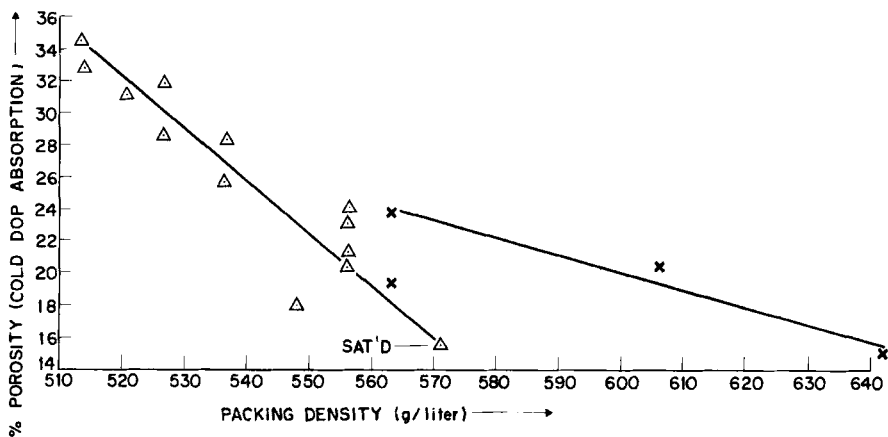

FIG. 7. Relationship between packing density and porosity: (▵) after pressure drop; (×) before pressure drop.
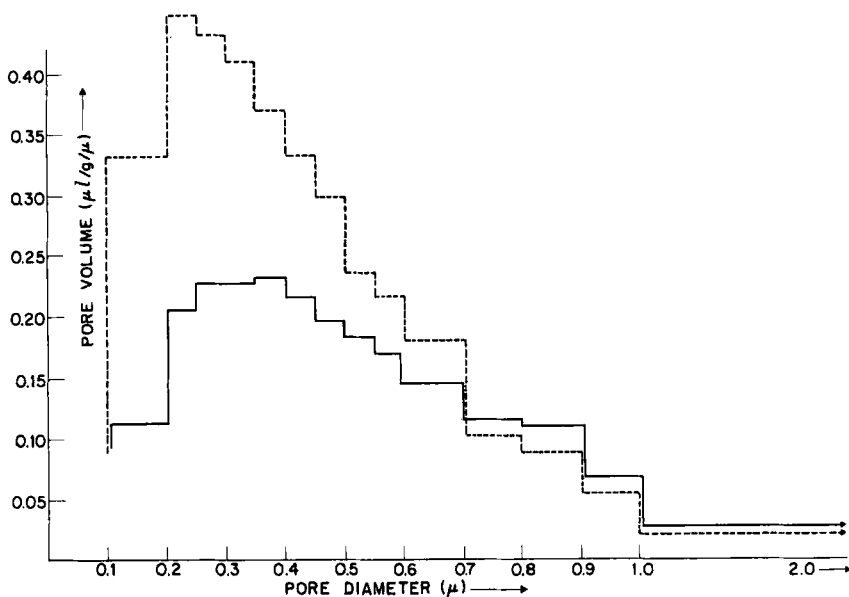
FIG. 8. Porosity histogram for VCM injection polymers with injection before pressure drop: (—) injection time, 0; conversion 86%, net internal porosity 0.248 ml/g, mean pore diameter 0.39 μm; (--) injection time 2 hr, conversion 132%, net internal porosity 0.191 ml/g, mean pore diameter 0.49 μm.

reservoir. Although the kinetic differences observed in these injection experiments can be explained by alternative theories, we suggest that the observed morphological changes are best explained by invoking the surface polymerization model.

The changes in polymer properties, particularly those involving polymer-liquid interaction are a direct result of the morphological differences produced by polymerizing under pre- or post-pressure drop conditions. The reason for this is the nature of the interface between the growing primary particle aggregates and the surrounding medium. When the latter is liquid monomer containing undecomposed initiator, the precipitating PVC nuclei are accreted by the existing primary particle surfaces which advance almost geometrically towards one another. This is responsible for the decrease in the degree of porosity at the large pore size end of the spectrum.
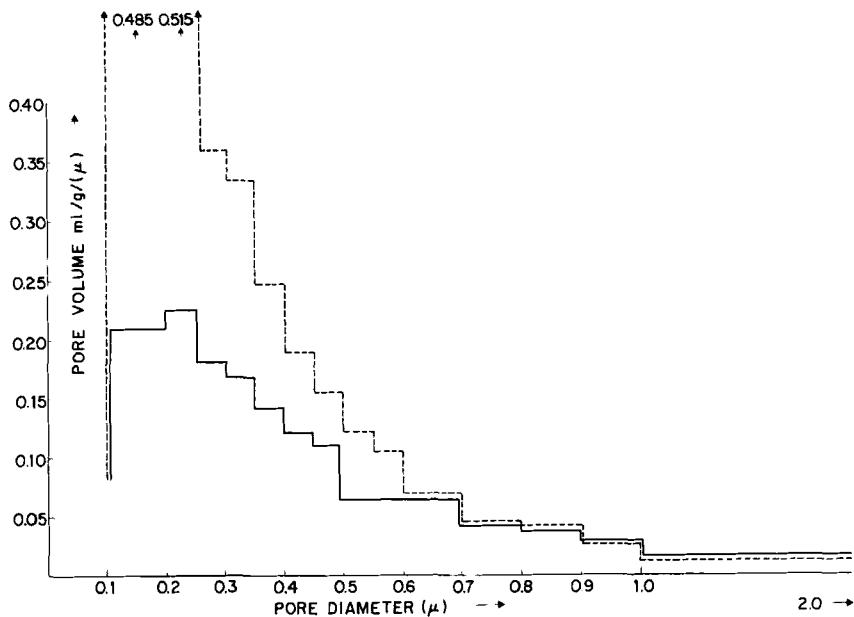
FIG. 9. Porosity histogram for VCM injection polymers with injection after pressure drop: (--) injection time 4 hr; conversion 131%, net internal porosity 0.120 ml/g, mean pore diameter 0.37 μm; (—) injection time 2 hr, conversion 80%, net internal porosity 0.197 ml/g, mean pore diameter 0.28 μm.

When the polymerization approaches pressure drop, the liquid monomer film is contracting and increasing in initiator concentration. As the system dries-up, the initiator precipitates onto the surface of the primary particle aggregates, particularly in small pores, the last region in which liquid monomer would be expected to persist. The post-pressure drop polymerization is typified, therefore, by an increased level of polymerization in the smaller pores of the material. These pores will fill with new PVC, the growth of which will cement together the particulate structures already present. It is for this reason that growth under partial pressure conditions after pressure drop is damaging to polymer properties.

In the conventional suspension polymerization process, the granules are seen to collapse to some extent as the pressure drop point
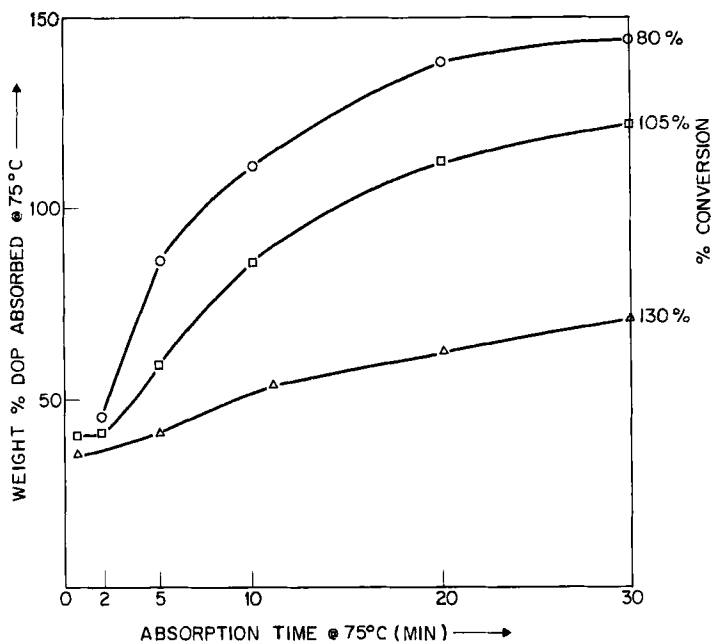
FIG. 10. Effect of VCM injection on plasticizer absorption behavior at 75°C with injection before pressure drop: (o) 2 hr injection; (□) 3 hr injection; (△) 4 hr injection.

is reached. Injecting VCM before this point maintains the fully swollen and symmetrical granules state inside which growth continues geometrically as discussed above. Therefore the granules retain their basically smooth spherical shape in which the pore volume steadily fills with new polymer, and this accounts for the systematic changes in powder properties described above. However, after pressure drop, when the granule collapse has taken place, we have a granule with a much more irregular surface topography. Polymer growth occurs in small pores, but as these can only accept a certain quantity of new polymer, the continuum of primary particles and aggregates is forced to expand to accommodate the new growth. The net effect of this difference in growth mechanism is best appreciated in the relationship between per cent porosity and packing density with conversion. The more regular granule surface and infilling growth mechanism gives polymers from the pre-pressure drop injection
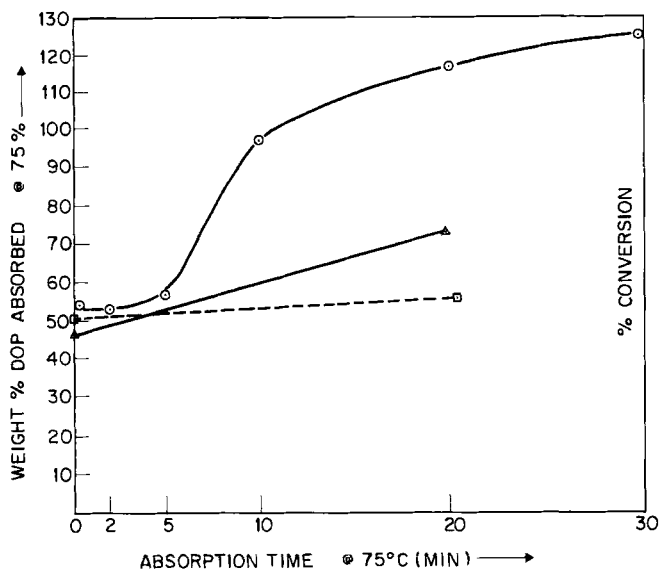
FIG. 11. Effect of VCM injection on plasticizer absorption behavior at 75°C with injection after pressure drop: (⊙) control, no injection, conversion 86%; (△) 1.5 hr injection, 111% conversion; (□) 2 hr injection, 132% conversion.

system a higher packing density for a given level of porosity or conversion. In fact, in the post-pressure drop system the expansion required to accommodate further growth will always limit the packing density achievable.

The importance of the morphological changes resulting from the two injection techniques can be gauged by considering the plasticizer absorption at 75°C (Figs. 10 and 11). Injection after pressure drop gave rise to a rapid deterioration in absorption behavior. Before pressure drop, the injection did not affect absorption behavior appreciably until the conversion exceeded 105%, and even 130% converted material was similar to 99% in the post-pressure drop system. The remarkable difference produced by the two injection tenchiques is best seen by making the comparison shown in Table 1.

However, the observed changes in porosity and surface area cannot alone account for the short-term plasticizer absorption behavior seen in Table 1. Instead, it would appear that there is a subtle morphological difference between material produced by

TABLE 1. Effect of Injection Conditions on Polymer Properties

	Injection before pressure drop		Injection after pressure drop	
Injection time (hr)	3	4	0.5	1.5
Conversion (% on initial monomer change)	105	130	86	111
Specific surface area (m^2/g)	1.09	0.40	1.44	0.92
Porosity (ml/g)	0.17	0.12	0.25	0.21
Plasticizer absorbed in 10 min at 75°C (wt %)	94	57	52	60

initiator in the free monomer phase and that adsorbed on the surface of the polymer.

CONCLUSIONS

The two VCM injection procedures give rise to polymers with a distinct range of powder properties. The explanation of how these arise can be fully satisfied by invoking the surface polymerization model. When the polymers are subsequently used in compounding processes such as plasticized dry blending, their performance cannot be explained solely in terms of their surface area and porosity. Instead a subtle morphological difference resulting from polymerization with and without the presence of a liquid VCM phase would appear to be present. These conclusions apply equally well to polymer formed in the conventional suspension polymerization process.

ACKNOWLEDGMENTS

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