

# Size Distribution of Suspension-Polymerized Unsaturated Polyester Beads

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## Synopsis

Thermosetting polyester beads in the size range of 200 to 2000  $\mu\text{m}$  were prepared in a PVAI stabilized suspension polymerization system from a commercial unsaturated polyester resin. Bead size distribution curves were determined and the average surface mean diameter  $D_m$  was calculated. Agitation speed, resin volume fraction in the reaction medium and PVAI concentration were varied and their effect on  $D_m$  was studied.

## INTRODUCTION

The process of suspension polymerization has been described in detail by several authors.<sup>1</sup> Vinyl-type monomers such as styrene, methyl methacrylate, vinyl chloride, and others possess properties suitable for suspension polymerization. The technique can also be used for preparation of crosslinked beads by polymerization of monomer mixtures containing a divinyl comonomer such as divinyl benzene.<sup>2</sup> The purpose of the present work was to produce clear beads from a thermosetting polyester. Literature search has shown that Buzbee and Lake<sup>3</sup> used suspension polymerization for unsaturated polyester as described in their German patent. During the course of the present work it was found that unsaturated polyester represented an interesting and convenient case study for suspension polymerization. Some of the results related to the size of the beads are presented in this paper.

## THEORY

Mechanical agitation of two immiscible liquids creates a two-phase system consisting of small droplets dispersed in a continuous phase. These droplets tend to coalesce so that if a constant rate of shear is maintained, a dynamic equilibrium will rapidly be established. The equilibrium droplet size distribution depends on many factors including physical properties (density, interfacial tension, and viscosity), geometric parameters (vessel, agitator, and baffles), and operational parameters (agitation speed and temperature). Vermeulen, Williams, and Langlois<sup>4</sup> have provided a quantitative formula expressing the mean droplet size  $D_m$  as follows:

$$\frac{D_m}{L} = K \left( \frac{N^2 L^3 \rho}{\sigma} \right)^{-0.6} \quad (1)$$

The term in parentheses is equal to the dimensionless Weber number. Scully<sup>5</sup> has modified the previous equation by taking into account the volume fraction  $\phi$  of the dispersed phase, proposing the following equation:

$$\frac{D_m}{f(\phi)L} = K \left( \frac{N^2 L^3 \rho}{\sigma} \right)^{-0.6} \quad (2)$$

where

$$f(\phi) = 1 + 3.3\phi \quad (3)$$

Hopff, Lussi, and Gerspacher<sup>6</sup> have used dimensional analysis combined with experimental data of suspension polymerization of methyl methacrylate and found the following correlation:

$$\frac{D_m}{L} = ARe^{0.5}We^{-1}(\eta_M/\eta_w)^{0.1} \quad (4)$$

where  $Re$  is the Reynolds number given by  $(L^2 N \rho \eta_w^{-1})$  and  $We$  is the Weber number. These authors report that from a practical point of view the size of the beads is determined at the beginning of the polymerization process. This conclusion implies that experimental bead size may be compared with theoretical droplet size. If this were not the case, a theory dealing with the initial system (whose properties will change dramatically by polymerization and crosslinking) would be expected to be poorly correlated to experimental bead size.

The effect of suspension stabilizers has not been treated theoretically. As a first approximation, however, they can be taken into account by consideration of the changes in viscosity and interfacial tension. The suspension polymerization of unsaturated polyester represents a case where an organic syrup is being used rather than a low-viscosity monomer. The tendency of the polyester syrup is to form larger droplets, see eq. (4), exposing less surface area which needs protection. The amount of protective suspension stabilizer required is thus reduced in this case. The range of PMMA bead size covered by Hopff et al.<sup>6</sup> was approximately 15 to 100  $\mu$  (1% to 5% PVAI), while in the present work the polyester bead size is in the range of 200 to 2000  $\mu$  (0.05% to 0.6% medium-viscosity PVAI).

## EXPERIMENTAL RESULTS

All polymerization experiments were carried out in a 2-liter glass reactor provided with a Teflon blade agitator (speed range from 100 to 200 rpm). The bath temperature was maintained at 50°C, and the duration of polymerization was 4 hr. A commercial general-purpose styrenated polyester (Makteshim Ltd., Israel) was used, catalyzed with 2% methyl ethyl ketone peroxide in the presence of 0.085% cobalt naphthenate. The water-to-polyester weight ratio was varied from 8:1 to 2:1. The ranges studied (concentrations, speed, etc.) were selected after considerable experimentation and roughly represent practical limits beyond which poor results are obtained.

Each batch of dry polyester beads was characterized by sieve analysis to determine the particle size distribution. Some typical distributions are shown in Figure 1(a). The average surface mean diameter  $D_m$  of the beads was calculated using the following equation:

$$D_m = \frac{\sum \Delta W}{\sum \Delta W/D} = \frac{1}{\sum \Delta W/D} \quad (5)$$

where  $\Delta W$  is the weight fraction and  $D$  is the mean diameter of this fraction.

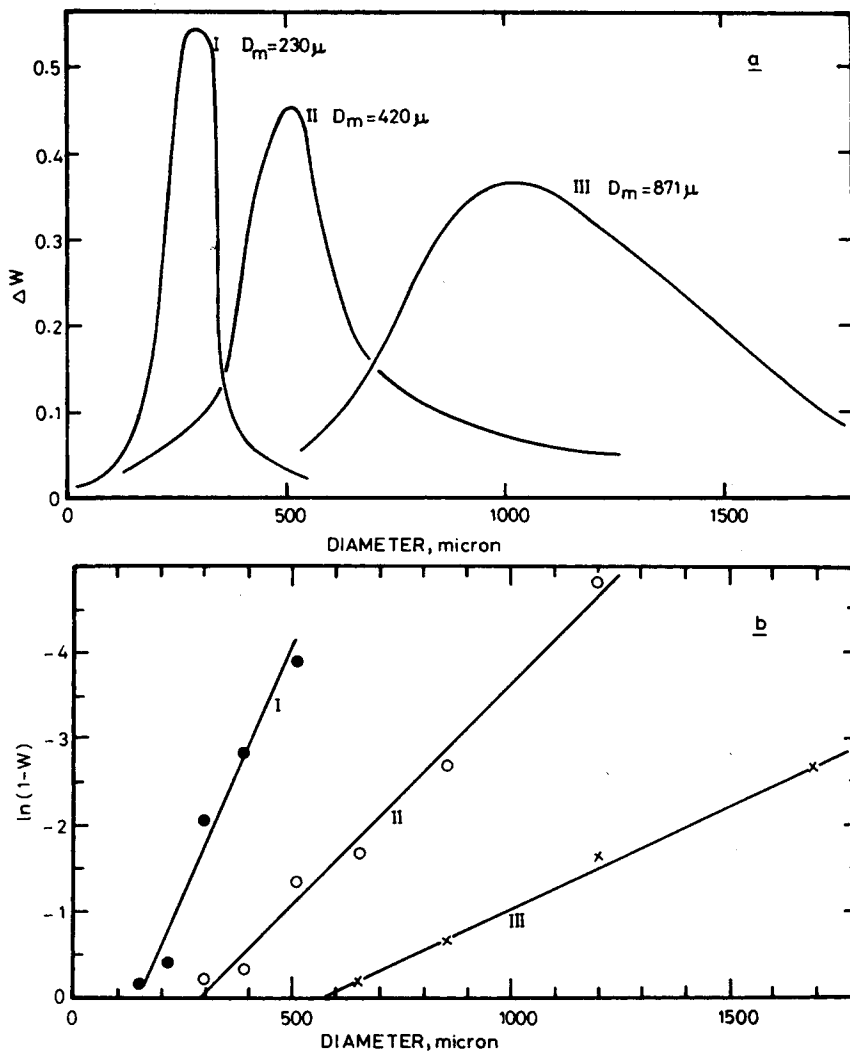


Fig. 1. Typical bead distribution curves (a) and cumulative representation (b).

Further analysis of the distribution curves has shown that they can be described approximately by

$$W = 1 - e^{-aD+b} \quad (6)$$

where  $W$  is the cumulative weight fraction and  $a$  and  $b$  are empirical constants. Equation (6) can be expressed as

$$\ln(1 - W) = -aD + b \quad (6')$$

and this relation is plotted in Figure 1(b) for the distribution curves shown in Figure 1(a). Equation (6) does not hold for very low or high values of  $W$  ( $W$  approaching zero or unity). The data of the extreme values of  $W$  are thus omitted in Figure 1(b).

A series of experiments where the mixing speed  $N$  was varied while all other parameters were kept constant is shown in Figure 2. A calculated least-squares

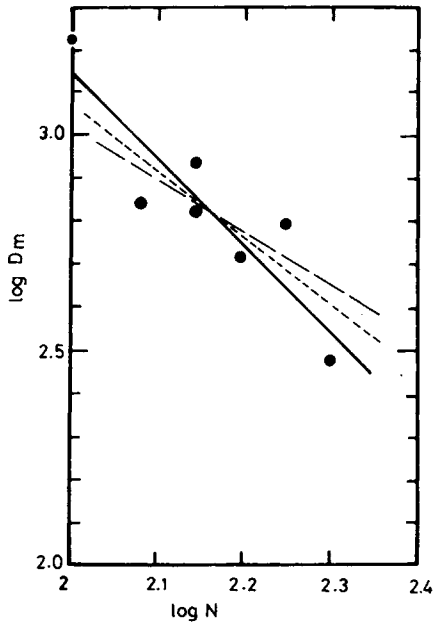


Fig. 2. Effect of agitation speed  $N$  (rpm) on bead average diameter  $D_m$  (microns). Water/polyester weight ratio 4/1; suspending stabilizer 0.3%: (—) least-squares method; (· · ·) Hopff; (- - -) Scully.

line whose slope is about  $-2$  is obtained by correlating  $\log D_m$  with  $\log N$ . Two other lines are also plotted in this figure, both passing arbitrarily through the center of gravity of the data, conforming to Eq. (1) (slope =  $-1.2$ ) and eq. (4) (slope =  $-1.5$ , obtained by grouping the  $Re$  and  $We$  numbers). Because of the high degree of scatter, the slope as measured in Figure 2 cannot be considered exact. However, the figure does show a clear decrease of  $D_m$  with  $N$  and it seems to agree better with Hopff's proposed equations than with that of Vermeulen.

Figure 3 shows the effect on  $D_m$  of changing the water-to-polyester ratio (as expressed by the polyester volume fraction  $\phi$ ).  $D_m$  clearly increases with  $\phi$ , in agreement with Scully.<sup>5</sup> The calculated least-squares line is given by

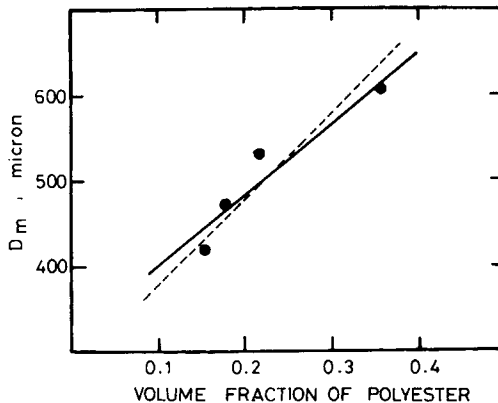


Fig. 3. Effect of volume fraction of polyester  $\phi$  on bead average diameter  $D_m$ .  $N = 160$  rpm; suspending stabilizer 0.3%: (—) least-squares method; (· · ·) Scully.

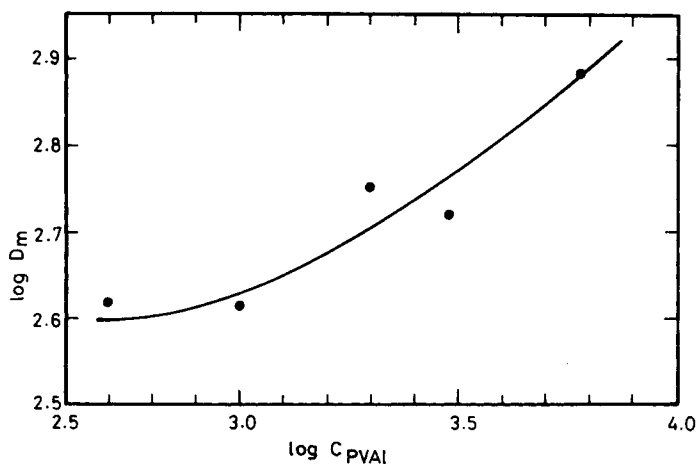


Fig. 4. Effect of suspending stabilizer  $C_{PVAI}$  (ppm) on bead average diameter  $D_m$  (microns).  $N = 160$  rpm; water/polyester weight ratio 4/1.

$$D_m = 314.4 + 842.5\phi \quad (7)$$

or

$$D_m = 314.4(1 + 2.7\phi) \quad (7')$$

Thus,

$$f(\phi) = 1 + 2.7\phi \quad (3')$$

The coefficient of 2.7 in eq. (3') is in surprisingly good agreement with Scully's coefficient of 3.3 in eq. (3).

The effect of the concentration of the poly(vinyl alcohol) suspending agent on  $D_m$  is shown in Figure 4. As mentioned earlier, a theoretical prediction of dependence of  $D_m$  on  $C_{PVAI}$  is not available. Experimental results on this effect can be found, however, in Hopff's work<sup>6</sup> showing a decline of  $D_m$  with increasing PVAI concentration. This conclusion apparently contradicts the behavior shown in Figure 4 of the present paper. One should note, however, that PVAI ranges covered by Hopff and this work are 1–5% and 0.05–0.6%, respectively. This and consideration of other parameters (MMA versus polyester, different PVAI grades, etc.) imply that the effect of the suspending agent can be complex, probably giving a maximum  $D_m$  at a certain dose of the PVAI.

In conclusion, within the ranges studied in the present work, agitation is the main parameter in the determination of  $D_m$ . The effects of  $\phi$  and  $C_{PVAI}$  are roughly of the same order.

#### NOMENCLATURE

$D$	mean diameter of a fraction
$D_m$	average surface mean diameter
$K$	shape factor
$L$	diameter of agitator
$N$	agitator rpm

$\Delta W$	weight of a fraction
$\rho$	mean density of phases
$\sigma$	interfacial tension
$\phi$	volume fraction of dispersed phase
$\eta_M$	viscosity of dispersed phase
$\eta_w$	viscosity of continuous phase

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