

Effect of Reaction Parameters on the Particle Sizes of Crosslinked Spherical Phenolic Beads by Suspension Polymerization of Phenol and Formaldehyde

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ABSTRACT: The crosslinked spherical phenolic beads (PB) were prepared with phenol and formaldehyde in alkaline medium by suspension polymerization technique. Poly(vinyl alcohol) (PVA) hexamethylenetetramine (HMTA), and triethylamine (TEA) were used as stabilizer, crosslinking agent, and basic catalyst respectively. The resulting PB with higher yield (82.5%) and relatively uniform particle size range (0.2–1.8 mm) were formed at 95–97°C, 550 rpm for 4 h, by using varied amounts of PVA as a stabilizer. The particle size and its distribution could be adjusted by selecting a suitable polymerization medium, consisting of mono-

mer added to water, and by varying their relative amounts, mechanical agitation and stabilizer concentration. The yield % of PB was also varied with the concentration of stabilizer, agitation rate, and monomer-to-water ratio. The effects of concentration of the stabilizer, agitation rates, and monomer-to-water ratio on PB formation and morphology are described. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2323–2330, 2006

Key words: phenolic resin; suspension polymerization; stabilizer; crosslinking agent; polymer particles

INTRODUCTION

Phenolic resins were the first thermosetting resins to be synthesized, in 1907. The reaction mechanisms in the synthesis of these resins and their reactions with other substances have been the subject of particularly intense study.^{1–12} Phenolic resins are formed from the acid- or base-catalyzed reaction of formaldehyde with phenol.^{1,13} The prepolymers obtained in the first stages, whether novolac or resole, are thermoplastic resins of low molecular weight and they must be further polymerized to become thermosetting resins. When the molar ratio is greater than 1 and the reaction is base catalyzed, the resulting product is called a resole-type resin. Today, numerous reports have been published about modification of the original reaction of Bakelite.¹⁴ Some researchers tried to use aldehydes other than formaldehyde,¹⁵ whereas others used different phenols and still others tried to modify the polymerization conditions.¹⁶ The base-catalyzed reaction between phenol and formaldehyde can be carried out in two separate steps. The first step involves the formation of a low molecular weight fusible, soluble resin and the second step involves curing reaction, which is a result of a controlled reaction between a

phenol and formaldehyde to give polymeric products.¹⁷

Crosslinked polymer resins are useful in a wide range of chemical applications, such as solid-phase synthesis.^{18–20} There are other important uses of crosslinked polymer: polymer-supported reagents,²¹ ion-exchange resins,²² molecular imprinting,^{23–25} and molecular sensors.²⁶ In many applications, it is advantageous to produce crosslinked resins in the form of regular microspheres of controlled particle size, which can be obtained by using heterogeneous polymerization techniques, including suspension, dispersion, and emulsion polymerization.²⁷ Suspension polymerization^{28,29} technique is useful for preparation of crosslinked polymer beads in the size range 10–2000 μm . A typical oil-to-water procedure involves the suspension of an immiscible, oil-soluble monomer in water, often with the addition of a porogen for highly crosslinked macroporous resins.^{30,31} The suspension is polymerized with stirring to form spherical particles directly, and the initiators are soluble in monomer phase.^{32,33} Recently, the scope of suspension polymerization has been broadened by the development of staged template technique, which allows the formation of large monodisperse, macroporous beads by a multistage swelling process.³⁴

The synthesis of phenolic resin using different techniques, covered under patents, has been shown by Hatori et al. and Mastuo and coworkers^{35–38} and

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TABLE I
Data for Polymerization of Phenol-Formaldehyde Monomer^a

Entry	Stabilizer	Yield ^b (%)	D_n^c (mm)	PSD ^d
1	None	— (viscous resin)	—	NA ^e
2	PVA	82.5	1.2	1.03

^a Reaction conditions: 50 g of phenol, 65 mL of formaldehyde, 1.9 mL of TEA, 250 mL of water, 3.7 g of PVA, 3.0 of HMTA, 550 rpm, 95–97°C, and 4 h.

^b Yields were determined gravimetrically and the spherical beads were weighed (there was free-flowing powder of about 12.3%, which could not be taken into account for size calculation).

^c D_n , mean particle diameter.

^d PSD, dispersity index of particle size distribution D_w/D_n .

^e NA, not applicable.

appears to be a promising method for preparing phenolic resin having an average particle size of 160 μm . Recently, the same group³⁹ described the formation of spherical phenolic resins, especially those with wide diameters (10%, <212 μm ; 36%, 212–1000 μm ; and 54%, >1000 μm). The broadening in the particle size distribution may be caused by either the extended particle nucleation or the initial formation of broadly dispersed nuclei that preserve their broad distribution during the growth. The particle size and the particle size distribution⁹ depend upon the type and concentration of stabilizer, the type and agitation speed, and monomer-to-water ratio.

In the present work, the effects of type and concentration of stabilizer, type and agitation speed and monomer-to-water ratio on particle size and its distribution were investigated. We describe the use of this suspension polymerization process in preparing spherical phenolic beads (PB) of desired size range by changing the aforementioned parameters.

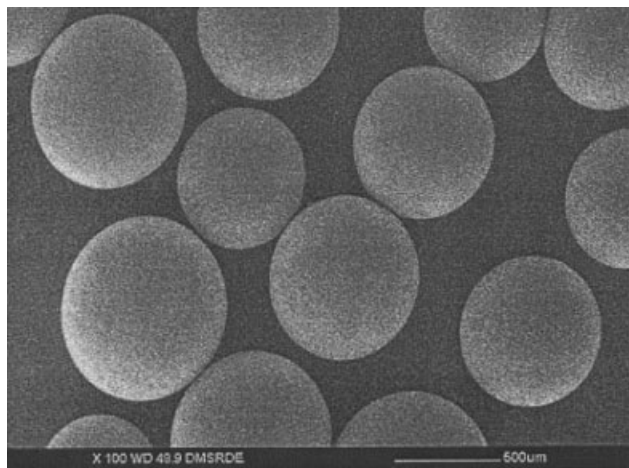


Figure 1 SEM micrographs of PB using PVA as stabilizer.

TABLE II
Data for Polymerization of Phenol-Formaldehyde Monomer^a (with Different Grades of PVA)

Entry	Stabilizer	Yield ^b (%)	D_n^c (mm)	PSD ^d
1	¹ PVA	— (ppt)	NA ^e	NA
2	² PVA	89.4 (Powder)	—	—
3	³ PVA	82.5	1.2	1.02
4	⁴ PVA	81.0 (<180 μm)	—	—

¹ PVA, partially hydrolyzed grade 88.0% (PVA; M_w = 8800) supplied by Acros Organics.

² PVA, normal grade (PVA; M_w = 25,000 and partially hydrolyzed grade <88.0%) supplied by SD fine-Chem., Ltd.

³ PVA, suspension grade (PVA; M_w = 25,000 and partially hydrolyzed >88.0 %) supplied by SD fine-Chem., Ltd.

⁴ PVA, hydrolyzed grade 95.0% (PVA; M_w = 9500) supplied by Acros Organics.

^a Reaction conditions were the same as in experimental Table I.

^b Yield was determined gravimetrically and the PB were weighed (there was free-flowing powder (about 7–14%), which could not be taken into account for size calculation).

^c D_n , mean particle diameter.

^d PSD, dispersity index of particle size distribution D_w/D_n .

^e NA, not applicable.

EXPERIMENTAL

Materials

The phenol (Ranbaxy Laboratories Ltd., Chemical Division, S.A.S. Nagar, Mumbai, India), aqueous formaldehyde solution 37–41% (w/v) LR (SD fine-Chem Ltd., India), poly(vinyl alcohol) (PVA; M_w , 25,000) (SD fine-Chem), Acros Organics (PVA; M_w = 8800 and 9500), (Kurary Co. Ltd.), triethylamine (TEA) 99% (Lancaster Synthesis, Eastgate, White Lund, Morecaube, England), Hexamine LR (hexamethylenetetramine) (HMTA; SD fine-Chem), and acetone AR (Samir Tech-Chem Pvt. Ltd., India) were used as received.

Apparatus and procedure

The polymerization was conducted in a 1000-mL glass reactor with a mechanical stirrer, a reflux condenser, and thermocouple. For a typical polymerization, 50 g of phenol was polymerized with 65 mL aqueous solution of formaldehyde, in the presence of 1.9 mL of TEA, followed by dispersing the resulting mixture in distilled water (10–35 wt %) by stirring. The reactor was charged with the above mixture at various amounts of PVA concentration (2.5–12.5 wt %) at temperature 95–97°C for 40 min. Then, 3.0 g of crosslinking agent (HMTA) was added to the reaction vessel and polymerization was carried out at the same temperature for 4 h.

At the end of the reaction, the reactor was cooled, and isolation became easy as this involved only filtration of beads and removal of the surface active agents

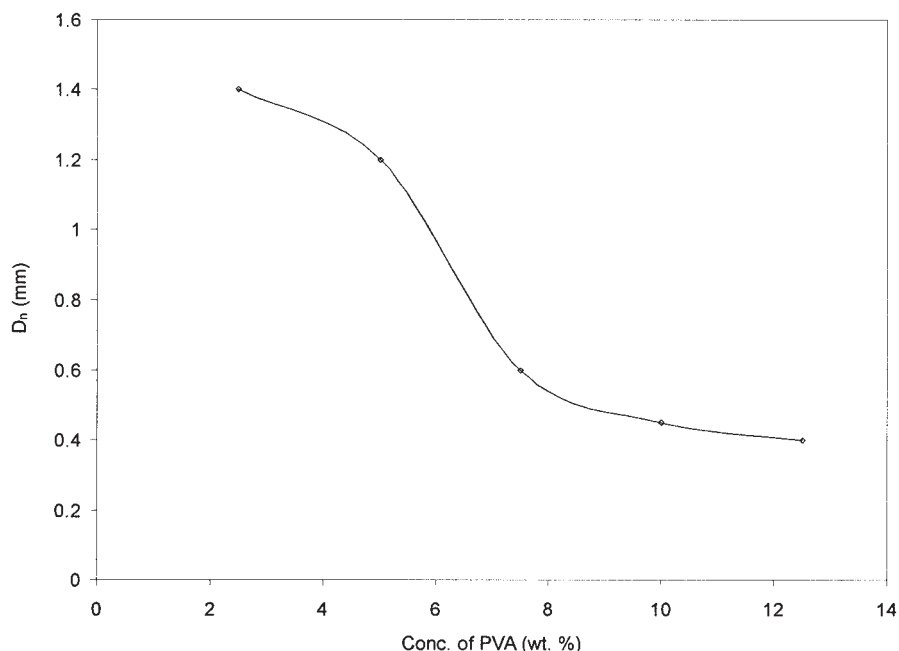


Figure 2 Dependence of PB diameter (D_n) on the stabilizer concentration in polymerization mixture containing phenol, formaldehyde, TEA, water, PVA, and HMTA at 95–97°C, 550 rpm, and 4 h. The PVA concentration in the mixture, 2.5–12.5 wt %; M_w , 125,000.

and protective colloids by washing with water. Finally, they were washed with acetone and dried to get the end product. The polymer conversion was determined gravimetrically. The weight of the stabilizer was subtracted from the total mass of product to obtain the weight of PB.

Characterization

Particle size and particle size distribution were measured using sieves of different mesh size. The surface morphology of the particle was studied using a JEOL scanning electron microscope (SEM). The samples were sputter coated with gold before analysis. The mean particle size of beads⁴⁰ was calculated from each sample micrographs by computerized image analysis manually. Two types of mean particle size were calculated: number-average (D_n) and weight-average (D_w), ($D_n = \sum D_i / N$, $D_w = \sum D_i^4 / \sum D_i^3$), where N is the number of particles. Particle size distribution was characterized by polydispersity index (PDI) calculated as a ratio of weight-average to number-average particle diameter.

RESULTS AND DISCUSSION

The preparation of PB entailed suspension polymerization of phenol with formaldehyde in the presence of TEA as initiator, water as the dispersing medium, PVA as the stabilizer, and HMTA as crosslinking agent. Under the effect of interfacial tension, the

monomer formed spherical droplets. The polymerization occurred with each spherical droplet and the polymer was obtained in the form of beads, which were easily collected and dried. The results are shown in different sets to demonstrate the effects of the type and concentration of the stabilizer, the type and agitation speed, and the monomer-to-water ratio.

Effect of stabilizer

Many commercially important polymers and copolymers are manufactured by suspension polymerization process.^{28,29} PVA is a copolymer of vinyl acetate and vinyl alcohol and used as a stabilizer in different industrial fields: textiles, adhesives, and coatings. It has been established that the stabilizing properties of PVA depend on the concentration, the degree of hydrolysis of poly(vinyl acetate), and the molecular weight. The stabilizing properties were also dependent on the stage of the phenol–formaldehyde polymerization when the PVA was added.

Data for the polymerization of phenol–formaldehyde with and without added stabilizer are summarized in Table I. The polymerization conducted in the absence of the stabilizer resulted in a highly viscous resin, which fouled the reactor and proceeded to undesirably low conversions. In contrast, the reactions carried out in the presence of the added stabilizer resulted in the formation of spherical PB instead of viscous resin. The SEM image in Figure 1 shows that PB have a spherical shape and smooth surface. No

pores were found on the surface of these particles on SEM images even at higher magnification, which conformed the absence of macropores.

Commercial grades (type) of stabilizer (PVA)

The basic properties of PVA depend on its degree of polymerization, degree of hydrolysis, and distribution of the degree of hydrolysis. With the expansion of commercial application, many grades of PVA⁴¹ have been made available, and it is now almost impossible to list all of them. The principal grade PVA produced can be classified as fully hydrolyzed (97.7–99.5% (degree of hydrolysis) and partially hydrolyzed (87.0–89.0% hydrolysis). In general, fully hydrolyzed grades of PVA are mainly used in paper coating, in textile warp sizing of hydrophilic fibers such as cotton and rayon staple yarns, and in laminating film in safety glass, while partially hydrolyzed grades⁴² are mainly used in protective colloids in emulsion, in remoistenable adhesives, in textile warp sizing for rayon filaments and polyester fibers, and in printing plates.

Data for polymerization of the phenol–formaldehyde with PVA supplied by different companies are summarized in Table II. The polymerization conducted in the presence of stabilizer of normal grade (entries 1 and 2) resulted in precipitation of the resulting polymer. In contrast, the reactions that were carried out in presence of suspension stabilizing grade (entries 3 and 4) resulted in the formation of PB with higher yield. The PVA in entry 3 is a protective colloid grade for suspension polymerization with same degree of hydrolysis and polymerization as that of PVA entry 2, which is an ordinary grade differing in the distribution of acetyl groups.

It is clear that PB formed in route 3 entry (Table II) were of uniform bead sizes (1.0–1.4 mm) with a higher degree of uniformity, which we had not seen in the previous study.³⁹

Effect of the stabilizer concentration

In the suspension polymerization of phenol–formaldehyde monomer using PVA as a stabilizer, the PB diameter is affected by the stabilizer concentration, as shown in Figure 2. The size of the beads decreased with increase in the concentration of stabilizer. Although the decrease in bead sizes with increasing PVA concentration did not appear monotonic, the average mean size of beads decreased from 1.4 to 0.4 mm when the concentration of PVA was increased from 2.5 to 12.5 wt %. The SEM images of PB with various amounts of PVA added are shown in Figure 3.

Inverse proportionality between the stabilizer concentration and the size of beads was given by an important role of the particle formation step; when the concentration of the PVA was increased, the viscosity of medium, the rate of adsorption of stabilizer mole-

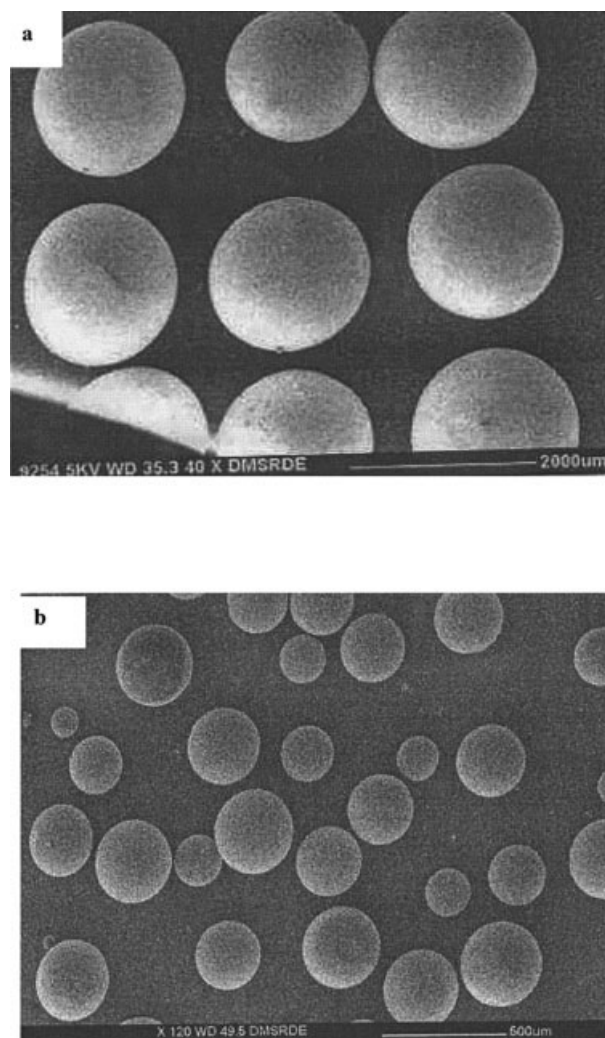


Figure 3 SEM images of PB from reactions, with (a) 2.5 wt % and (b) 12.5 wt % of stabilizer; values are taken weight/weight percent to organic phase.

cules, and the number of nuclei increased, and as a result, the extent of nuclei aggregation was reduced, the number of stable nuclei increased, and correspondingly, smaller size of PB [Fig. 3(b)] were produced. A sharp distribution is always an indication that the initial nuclei were formed within a short time period and the subsequent particle growth took place without the formation of new nuclei and without agglomeration of particles. The broadening in the particle size distribution may be caused by either the extended particle nucleation or the initial formation of broadly dispersed nuclei that preserve their broad distribution during the growth. The particle size distribution of samples became narrower if they were prepared with higher concentration of PVA in the system (Fig. 2). Here, the stable spherical beads formation stages became short, thus reducing the nucleation time and resulting in narrow size distribution samples. The preferable concentration of PVA in the

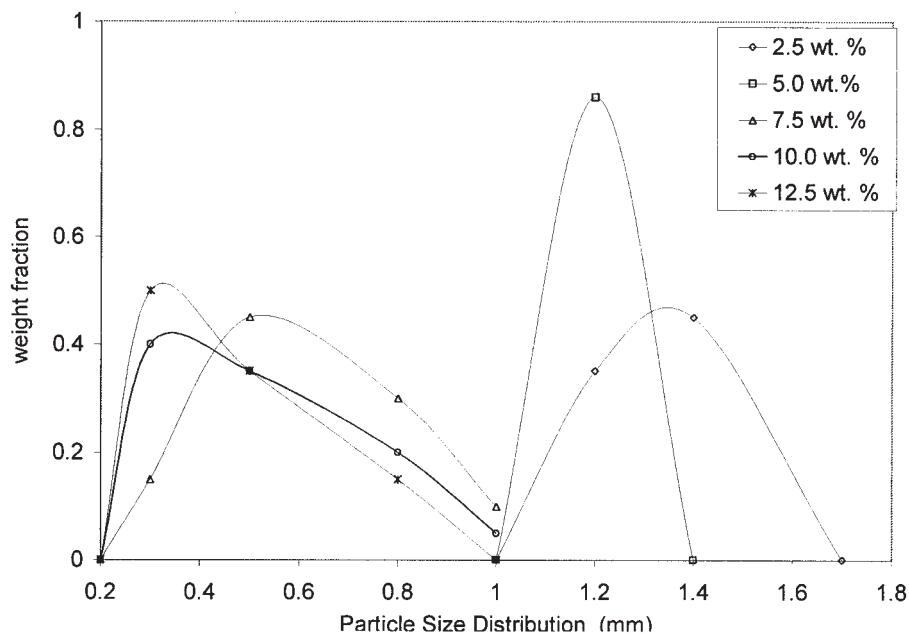


Figure 4 The particle size distribution of PB at different concentrations of the stabilizer.

polymerization mixture affording nearly uniform PB (1.0–1.4 mm) equaled 5.0–6.0 wt %. PB of irregular shape were formed when the concentration of the stabilizer was less than 3.0 wt %. The particle size distribution at different concentrations of stabilizer is shown in Figure 4.

The second notable trend was a strong dependence of yield of polymer (Fig. 5). The yield percent of PB decreased with increase in the concentration

of stabilizer (PVA). In some experiments, there was a residual population of small particles, which might have been produced by collapse of a few beads, during the polymerization, with the wall of reaction vessel. These materials are not taken into account for yield percent calculation. Free-flowing powder of size below $180\ \mu\text{m}$ was obtained (Fig. 6), which was also not taken into account for average bead size calculation.

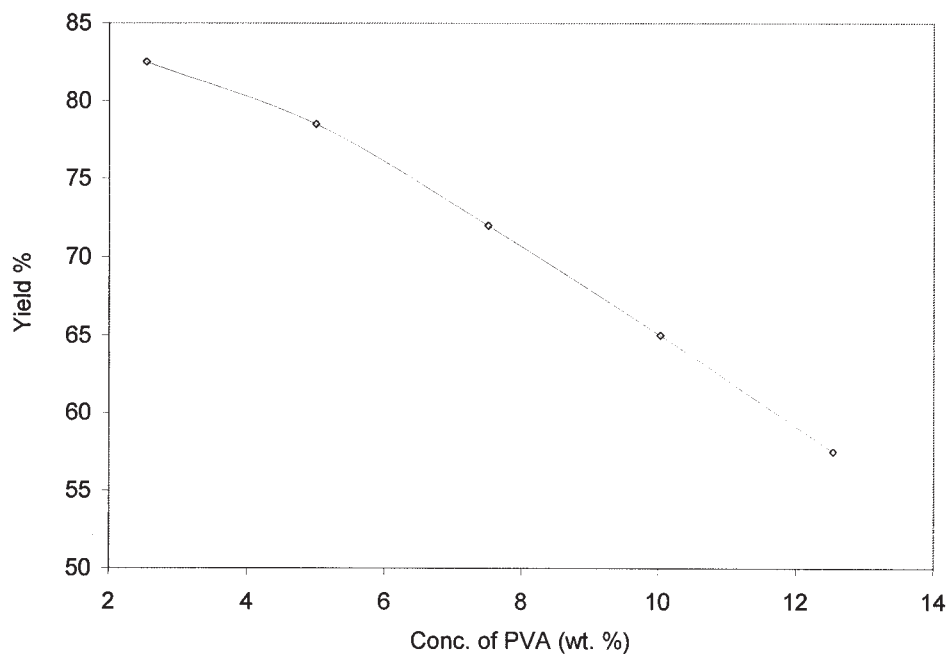


Figure 5 Effect of the stabilizer concentration on yield (%) of PB.

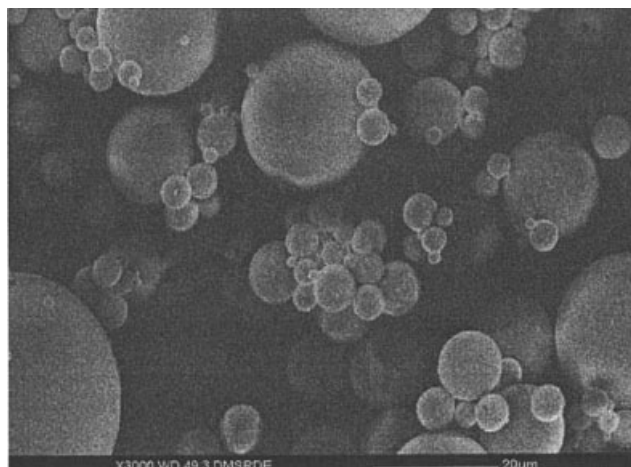


Figure 6 SEM micrographs of PB having size $< 200 \mu\text{m}$.

Type of mechanical stirrer

Many studies have shown that the size of the beads in heterogeneous polymerization is influenced by the type of stirring, the agitation speed of the stirrer, and the general design of the polymerization apparatus.^{36,37} We have investigated the effect of stirring on the polymerization reaction of phenol and formaldehyde in the presence of basic catalyst. The results have shown (Table III) that stirring does indeed have a profound influence on polymer yield, particle size, and particle morphology. The reaction conducted by using an impeller stirrer (three blades) resulted in partial agglomeration of particles with diameter 200–1400 μm . On the other hand, we observed that no such aggregation of particles was formed in reactions that were stirred with a rotary impeller stirrer (teflon two blades) at stirring speeds of 400–750 rpm. The particles formed from polymerization in the presence of the rotary impeller stirrer showed (entry 2, Table III) a higher yield and uniform particle size distribution. The SEM images of PB prepared using different types of stirrers are shown in Figure 7. Figure 7(a) shows the partial agglomeration of PB with diame-

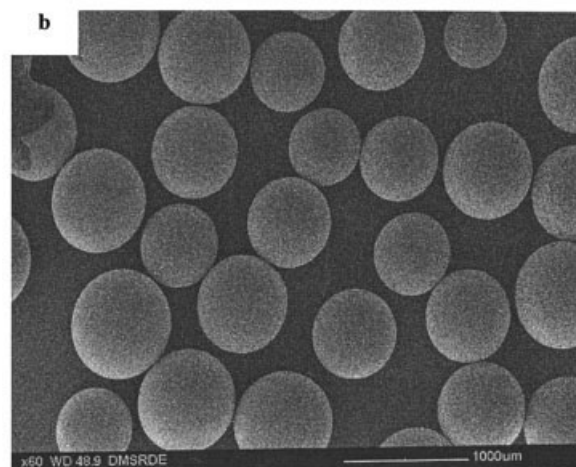
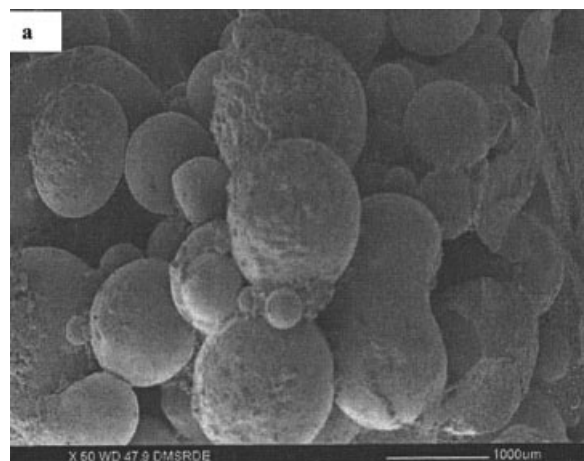


Figure 7 SEM images of PB prepared using different types of stirrers: (a) impeller stirrer, three blades; (b) impeller stirrer, teflon two blades.

ters 200–1400 μm and a broad particle size distribution. It indicates that the reaction was not effectively stirred under these conditions. In contrast, the reaction that was carried out by using a rotary impeller stirrer (teflon two blades) gave narrow particle size distribution without the aggregation of particles, as shown in Figure 7(b).

TABLE III

Effect of Agitation Rate on Polymerization of Phenol-Formaldehyde Monomer^a

Entry	Stirrer	Yield ^b (%)	D_n ^c (mm)	PSD ^d
1	¹ M	62.5	0.84	1.45
2	² M	80.0	1.25	1.03

¹ M: impeller stirrer, three blades.

² M: impeller stirrer, teflon two blades.

^a Reaction conditions were the same as in experimental Table I.

^b Yield was determined gravimetrically and the PB were weighed (there was free-flowing powder of 12.6% (entry 2), which could not be taken into account for size calculation).

^c D_n , mean particle diameter.

^d PSD, dispersity index of particle size distribution D_w/D_n .

Effect of mechanical agitation

The agitation speed was found to have a remarkable influence on particle and particle size distribution. The size of beads decreased on increasing the agitation rate, as shown in Figure 8. A low agitation rate, for example ≤ 400 rpm, gave an irregular particle size distribution (Fig. 9). As the agitation rate was increased to 475 rpm, we obtained 80–90% of spherical beads, while an agitation rate of 550 rpm resulted in spherical PB with particle size distribution of 1.0–1.4 mm. At higher agitation rate, the number of nuclei

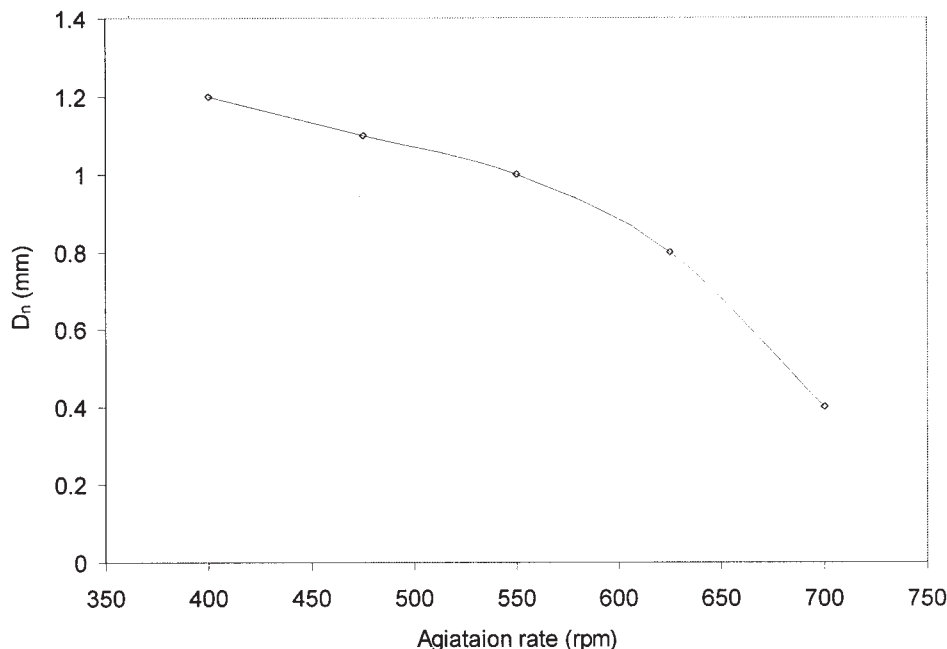


Figure 8 Effect of agitation rates on the particle sizes in polymerization reaction of 50 g of phenol, 65 mL of formaldehyde, 1.9 mL of TEA, 250 mL of water, 3.7 g of PVA, and 3.0 g of HMTA, at 95–97°C and 4 h. Agitation rate, 400–700 rpm.

increased, which reduced the extent of aggregation and thus smaller beads were obtained. So, an optimum agitation rate (about 500–600 rpm in our study) was a necessity for preparing uniform spherical beads of desired size range.

The size of monomer droplets depends on the mechanical force acting across the drop. At low force obtained at low agitation rate, the resultant drop size distribution was irregular for an average drop size of 1000 μm or large. Deformation of drop becomes evident when the radius of the drop is approximately greater than 1800 μm ,⁴³ and the various stages of deformation have been discussed by Ivahov and and Dimitrov.⁴⁴ At

very high agitation, the breaking up of monomer drops occurred, which gave rise to a number of nuclei and as a result, the bead sizes decreased below 0.5 mm.

Effect of the concentration of monomer

The overall polarity of the polymerization mixture depends on the fractions of individual components. Therefore, it is also influenced by the concentration of the monomer dissolved in the dispersing medium. The polymerization of the phenol–formaldehyde mixture was carried out over a wide range of monomer concentrations. Two general trends were observed. The first trend was dependent on bead size, which slightly increased with the concentration of the monomer in the polymerization mixture increasing from 10.0 to 35.0 wt % (Table IV). When the monomer concentration in the reaction mixture was 35.0 wt %, more irregular particles were found, probably because of large changes in the medium polarity as monomers were consumed during polymerization. Since it appeared that the most uniform, spherical beads were obtained with around 22.0–28.0 wt % monomer concentration, subsequent experiments were carried out at this concentration. The second notable trend was the dependence of polymer yield on monomer concentration. The polymer yield slightly increased with increasing monomer concentration (Table IV).

CONCLUSIONS

We have studied experimentally the effects of three parameters—concentration of stabilizer, mechanical

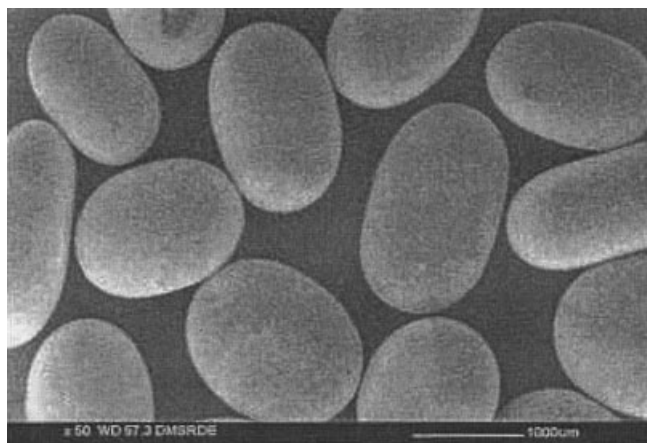


Figure 9 SEM images of PB at a low agitation rate of 400 rpm.

TABLE IV
Effect of Monomer Concentration on Polymerization of Phenol-Formaldehyde Monomer^a

Entry	Monomer Concentration (wt %)	Yield ^b (%)	D_n ^c (mm)	PSD ^d
1	10.0	75.3	0.7	1.14
2	15.0	74.5	0.8	1.35
3	20.0	73.0	0.9	1.45
4	25.0	72.1	1.2	1.04
5	35.0	67.2	1.3	1.03

^a Reaction conditions were the same as in experimental Table 1.

^b Yield was determined gravimetrically and spherical beads were weighed (there was free-flowing powder (14–29%), which could not be taken into account for size calculation).

^c D_n , mean particle diameter.

^d PSD, dispersity index of particle size distribution D_w/D_n .

agitation, and monomer-to-water ratio—on the suspension polymerization of phenol-formaldehyde mixture. The resulting PB have diameter from 0.2 to 1.8 mm for stabilizer concentration of 2.5 to 12.5 wt %. The size of beads was found to decrease with increase in the concentration of stabilizer. The corresponding polymer beads prepared in aqueous medium with 5.0 wt % concentration of stabilizer were also affected by the concentration of monomer. The size of beads was found to increase with increase in the concentration of monomer and optimal concentration of monomer was 22.0–28.0 wt %. Finally, an appropriate agitation rate (about 550 rpm in our study) was a necessity for preparing PB in spherical form. In our work, the size of beads was found to decrease with increase in the agitation rate from 400 to 700 rpm. The conversion percent of spherical beads increased on increasing the agitation rate from 400 to 700 rpm.

The prepared bead sizes are useful in many applications such as preparation of selective resins, supports for solid phase chemistry, electrodes, and activated carbon spheres.

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