

# Synthesis of Resole-Type Phenolic Beads from Phenol and Formaldehyde by Suspension Polymerization Technique

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**ABSTRACT:** The phenolic beads (PB) in macrosize range were obtained by mixing phenol and formaldehyde in the presence of basic catalyst by suspension polymerization. In this reaction, the triethylamine (TEA), poly(vinyl alcohol), and hexamethylenetetramine (HMTA) were used as initiator, stabilizer, and crosslinking agent, respectively. The resulting PB within size range 0.1–2.0 mm was obtained in this polymerization reaction, carried out at temperature  $96^{\circ}\text{C} \pm 1^{\circ}\text{C}$  with agitation rate 475 rpm for 4 h. The effects of different variables such as, formaldehyde to phenol ratio ( $F/P$ ) by mole, initiator concentration, concentration of crosslinking agent, and temperature on the particle sizes of PB and its formation were investigated. The particle size and its distribution were shown to be dependent on the  $F/P$  ratio, initiator concentration, and temperature. The average

particle size of PB increased with increasing  $F/P$  ratio by mole in the reaction mixture. The average particle size of PB decreased with increasing TEA concentration. The particle size distribution of PB became narrow in size range 0.9–1.3 mm with 86% of yield of 1.0% by weight. As far as the crosslinking is concerned, the uncured phenolic resin was formed in the reaction solution when the reaction was performed in the absence of HMTA at  $96^{\circ}\text{C} \pm 1^{\circ}\text{C}$  for 4 h. The amount cured PB formed increased with increase in the concentration of HMTA. The surface morphology, shape and size of PB were studied using scanning electron microscopy. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1005–1011, 2009

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

## INTRODUCTION

Phenolic resins are one of the oldest commercial synthetic resins, which have been studied for over past 100 years and are still popular in many industrial applications.<sup>1</sup> These resins are used extensively in the production of surface coating, wood products, and aerospace components.<sup>2</sup> In constructing aerospace components, the most important use of phenolic resins is in the manufacturing of high-performance composites. Phenolic resins are also used for matrix system for composites, sports industries, and construction,<sup>3</sup> which enable them to withstand high corrosive environment. These resins are widely utilized because of their excellent thermal and chemical resistance at elevated temperatures and low smoke density with low toxicity.<sup>4</sup> However, the use of phenolics has historically been limited due to the lack of understanding of its mechanical properties and fracture mechanics as well as health concerns.<sup>5,6</sup> The mechani-

cal and structural properties of phenolic resins depend on molar ratio of  $F/P$  as well as concentration of catalyst, reaction temperature, and curing time.<sup>7</sup> The relationship between synthesis conditions, structure and mechanical properties is not yet fully understood. Although, detailed research work has been done in the fields of kinetic characteristics,<sup>8,9</sup> reactor modeling,<sup>10,11</sup> flammability,<sup>12,13</sup> thermal analysis,<sup>14–16</sup> degradation,<sup>17–19</sup> and mechanical performance<sup>20</sup> and chemical analysis.<sup>21,22</sup>

Recently, the use of cured phenolic beads (PB) is increasing as precursor materials to produce porous carbon beads for removal of toxic organic chemical warfare agents.<sup>23–26</sup> The prepolymers obtained in the first stages, whether novolac or resole, are thermoplastic resins of low molecular weight, fusible and soluble resin, which can be given a particular shape before polymerization to become thermosetting resins. The preparation of various types of copolymers with well-defined porous structure is useful as it supports in chromatography, ion changers, or for selective removal of organic solvents. Porous copolymer beads are produced usually by suspension copolymerization in the presence of an inert diluent.<sup>27</sup>

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Another method to produce the porous material is by polymerization in the presence of inorganic matrix of desired shape, porosity, and surface area in reacting mixture.

The porosity of porous carbons depends on structural properties of precursors. Many authors have reported the influence of  $F/P$  molar ratio in the presence of alkaline medium to the formation phenolic resin. Few studies have reported to prepare cured PB from phenol and formaldehyde in alkaline catalyst which have covered under patents.<sup>28–30</sup> In these studies, each author has used different techniques to prepare PB with low conversion. Suspension polymerization<sup>31,32</sup> is one of the techniques for the preparation of crosslinked polymer beads in the size range 10–2000  $\mu\text{m}$ . In our earlier studies, the cured PB<sup>33</sup> with desired particle size was obtained by controlling the concentration of stabilizer, agitation rate, and concentration of monomer. PB were further carbonized and activated to produce microporous-activated carbon spheres.<sup>34</sup> They are outstanding materials used for the purification and separation of gases and liquids.

In the present study, influence of  $F/P$  ratio by mole, initiator concentration, crosslinking agent, and temperature on particle size of PB and its formation were investigated. The shape and particle size of PB were evaluated using scanning electron microscopy (SEM) technique.

### Reaction mechanism

The reaction mechanism of the resole-type phenolic resin is highly complicated.<sup>2,35</sup> It is obtained by condensation polymerization reaction of phenol and formaldehyde in the presence of basic catalyst. In the first step, the addition of formaldehyde occurs at ortho- and para-position of phenol. In the second step, two types of condensation reaction results: first reaction between hydroxyl phenols themselves to produce ether bridge and the second reaction between hydroxyl phenols and phenol free position to produce methylene bridge in phenol ring. In the basic aqueous solution, formaldehyde exists primarily as methyl glycol as shown in Figure 1(a). This methylene glycol is attached to ortho- and para-group of phenol ring to form hydroxyl methyl compounds as shown in Figure 1(b). The hydroxyl methyl groups on these compounds can further condense with unreacted phenol rings to form methylene bridge or hydroxyl methyl groups of different phenolic rings can condense together to form methylene bridge between aromatic ring as shown in Figure 1(c) or hydroxyl methyl groups of different phenolic rings can condense together to form methylene bridge between aromatic rings with elimination of formaldehyde. Figure 1(d) shows that the condensation of hydroxyl methyl

groups can occur to form dibenyl ether linkage, which is favorable near neutral or acid conditions. Most studies revealed that concentration of ether bridge can be negligible.<sup>36</sup>

The curing behavior of phenolic resin depends on the temperature of the polymerization reaction. The crosslinking (curing) of the resole-type phenolic resin is carried out by heating at temperature 180°C. The reaction of phenol and formaldehyde in alkaline condition resulted in the formation of methylene and ether bridge between benzene rings to yield a network structure of type Figure 1(e). In this polymerization reaction, the curing occurs by adding curing agent (hexamine) at temperature 95°C to the formation of both methylene and benzyl amine crosslinking bridge between benzene ring. The crosslinked network is pictured in Figure 1(f). It is reported in our previous studies of CHNS analyses<sup>34</sup> that PB have nitrogen contents (1.5), indicating the incorporation of nitrogen to PB from hexamine during the polymerization reaction.

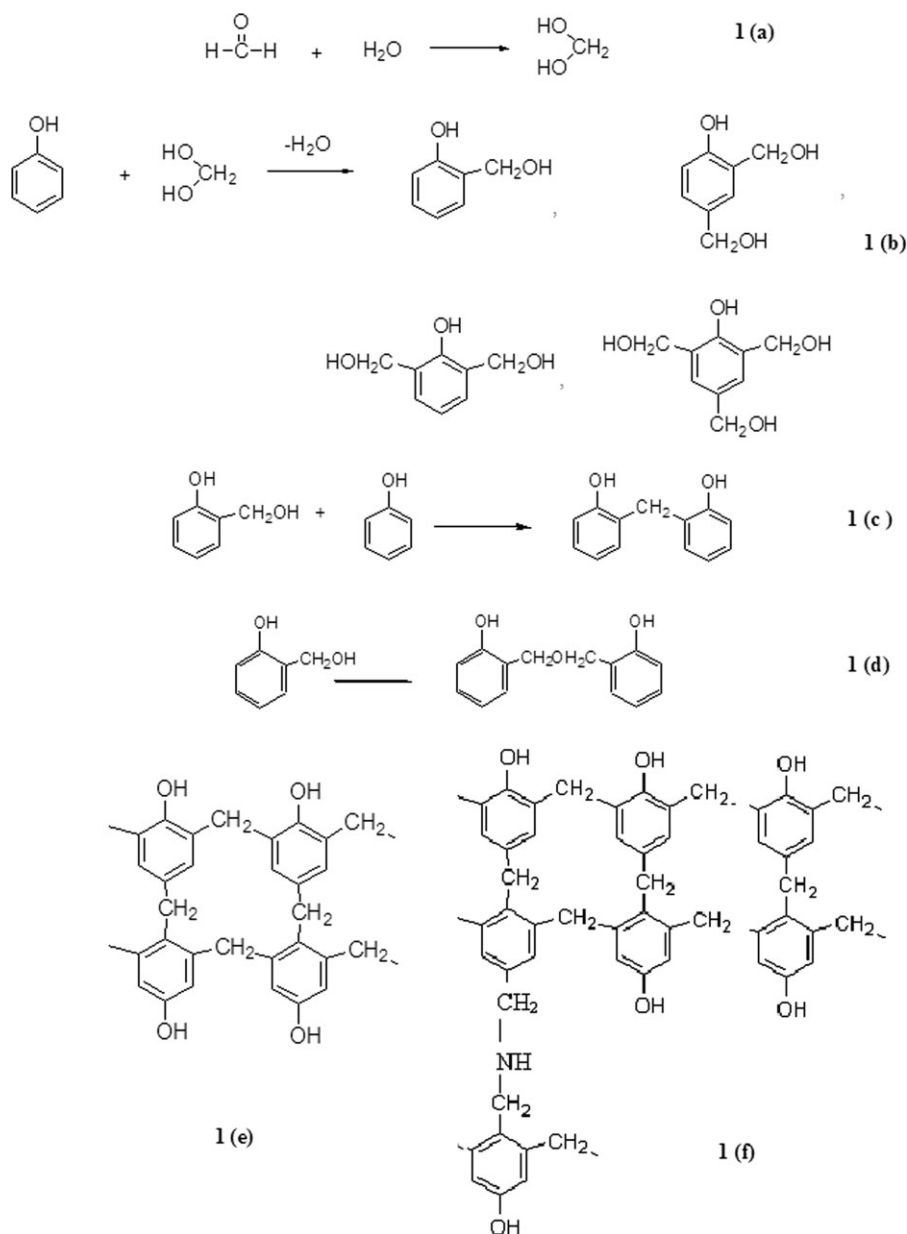
## EXPERIMENTAL

### Materials

The phenol (Chemical Division, Ranbaxy Laboratories, Mumbai, India), aqueous formaldehyde solution (37–41% w/v LR, S. D. Fine Chemical, Mumbai, India), poly(vinyl alcohol) (PVA, weight-average molecular weight = 125,000; S. D. Fine Chemical, Mumbai, India), triethylamine (TEA, 99%; Lancaster Synthesis, Morecaube, England), Hexamine LR (hex-methylene tetraamine) (HMTA) (S. D. Fine Chemical), and acetone AR (Samir Tech-Chem, Gurgaon, India) were used as received.

### Apparatus and procedure

The polymerization reaction was conducted in 1000-mL round-bottomed four-neck reaction vessel with a Teflon stirrer, a reflux condenser, and a thermocouple. In this reaction, the phenol and 37–41% aqueous formaldehyde at varying  $F/P$  molar ratios (1 : 1, 2 : 1, 3 : 1, and 4 : 1) were mixed in the presence of TEA (0.5–2.5 wt %), which were further followed by dispersing the resulting mixture into 230 mL of water by stirring. The stabilizer, 5.0 wt % PVA, was added to the above mixture at 96°C  $\pm$  1°C by stirring at 475 rpm for 30 min. Then, crosslinking agent, 3–7 wt % HMTA, was added to reaction vessel and polymerization reaction was carried out at same temperature for 4 h. At the end of the reaction, the reactor was cooled and isolation become easy as this involved only filtration of beads. The polymer conversion was determined gravimetrically.



**Figure 1** The reaction mechanism of resole-type phenolic resin obtained from phenol and formaldehyde in the presence of alkaline medium.

### Characterization

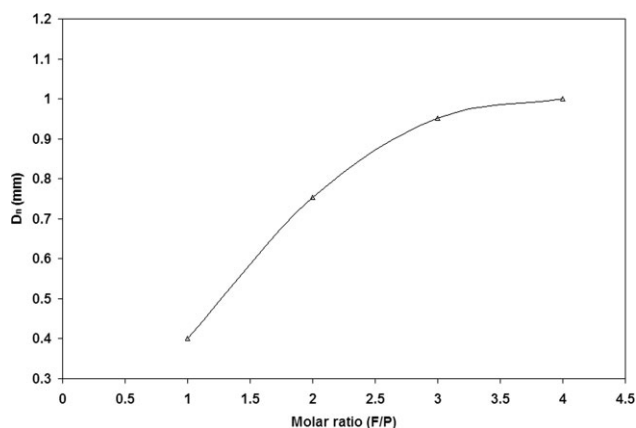
Particle size and its distribution were measured using Mesh Sieves of different sizes. The surface morphology of particle was studied using a SEM (Carlo ZEISS). The samples were sputter coated with gold before analysis. The mean size and particle size distribution was calculated by measuring diameter of 120–130 particles. The mean particle size of beads was calculated from each sample micrographs by image analysis manually. Two types of mean particle size were calculated: number-average ( $D_n$ ) and weight-average ( $D_w$ ), ( $D_n = \Sigma D_i / N$ ,  $D_w = \Sigma D_i^4 / \Sigma D_i^3$ ) where  $N$  is the number of particles and  $D_i$  is diameter of the particle  $i$ .

### RESULTS AND DISCUSSION

The PB were synthesized in aqueous medium of phenol–formaldehyde resin in the presence of TEA, PVA, and HMTA as initiator, stabilizer, and cross-linking agent, respectively. The results were shown in different sets to demonstrate the effect of  $F/P$  ratio by mole, initiator concentration, concentration of crosslinking agent, and temperature.

#### Effect of $F/P$ molar ratio

The relative size and the shape of the reacting molecules and the position of the relative sites largely determine the physical properties of the resulting

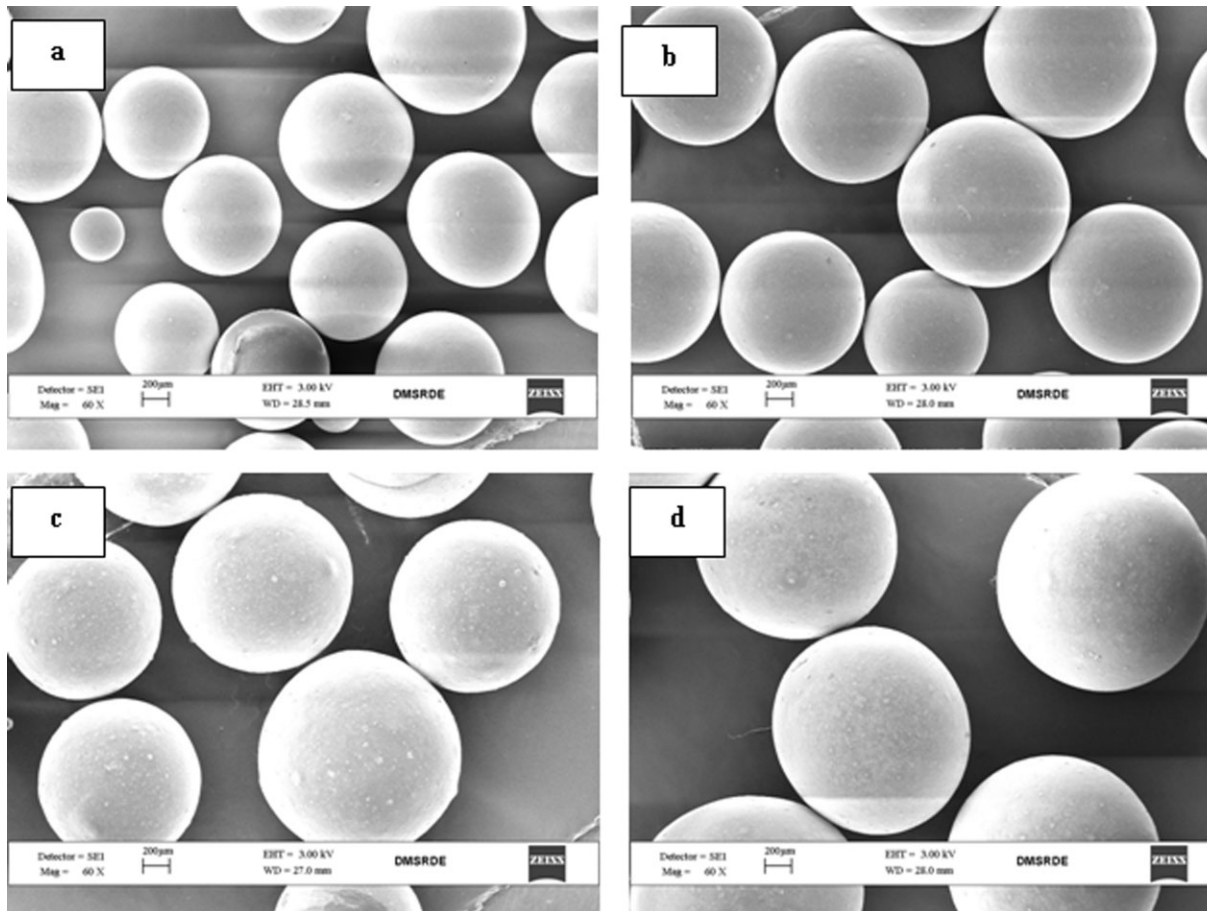


**Figure 2** Dependence of average size of PB on  $F/P$  molar ratio in polymerization reaction of phenol and formaldehyde.

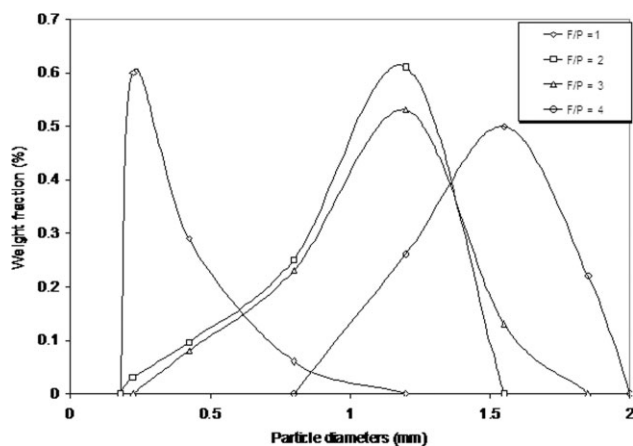
polymer. The physical properties of phenolic resins are determined by numerous interrelated factors,  $F/P$  ratio also one of them. It has been reported that particle size and its distribution<sup>20,33</sup> strongly depend on type and concentration of stabilizer, type and agitation rate, and concentration of monomer. The particle size of PB prepared from phenol and formaldehyde is

affected by the molar ratio of  $F/P$ . Figure 2 showed that average particle size was found to increase with increase in the  $F/P$  ratio by mole. Although the increasing average particle size with  $F/P$  molar ratios was not monotonic, the average size of PB increased from 0.4 to 1.0 mm when molar ratio of  $F/P$  increased from 1 to 4 mol. The reaction of 1 mol of phenol with a small excess of formaldehyde (1 to 3 mol) gave rise to sharp increase in average particle size. A further increase of formaldehyde 3 to 4 mol resulted in slight increase in average particle size. It is seen from Figure 2 that there is maximum change in average particle size of PB when  $F/P$  ratio varied between 1 and 2 and after  $F/P = 2$ , there was slight change in average particle size with increase in molar ratio of  $F/P$ .

The SEM images of PB prepared from phenol and formaldehyde at different  $F/P$  ratio by mole are shown in Figure 3(a–d). The effect of  $F/P$  ratios on particle size and its distribution may be clearly observed from SEM images. Figure 3(a,b) shows that particle size varied from 0.2 to 1.0 mm when  $F/P$  ratio varied from 1 to 2 by mole. However, Figure 3(c,d) shows the large particle size and its distribution of the range 1.0–1.7 mm. The SEM photographs exhibited that relative particle size and its distribution increase



**Figure 3** SEM photographs of PB obtained at different molar ratios of  $F/P$ .



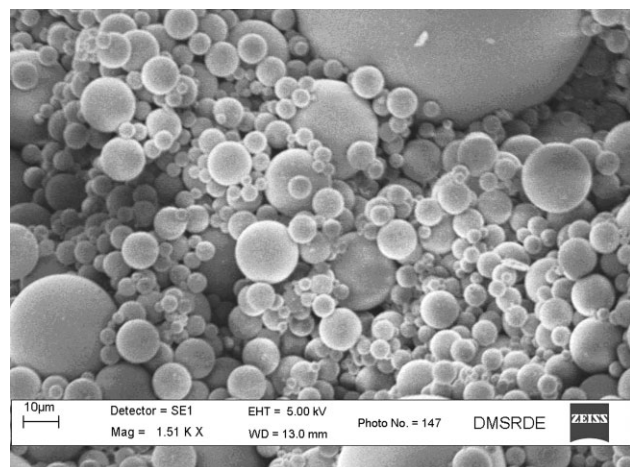
**Figure 4** Particle size and its distribution of PB prepared at different molar ratios of  $F/P$ .

with increasing  $F/P$  ratio. Moreover, SEM images exhibited that they are spherical in shape and have a smooth surface. Figure 4 shows the particle size and its distribution of PB prepared at different  $F/P$  molar ratio.

It is clearly seen that particle size and its distribution of PB increase with increasing  $F/P$ . The particle size of PB varied from 0.18 to 2.0 mm when  $F/P$  ratio varied from 1 to 4 by mole. The broadening in particle size distribution of PB may be either due to the extended particle nucleation or the initial formation of broadly dispersed nuclei. The free flowing powder of PB having particle size below 180  $\mu\text{m}$  (about 10–30%) was obtained, which was not taken into account for average size calculation.

The SEM photograph of phenolic resin obtained in powder form of size below 180  $\mu\text{m}$  is shown in Figure 5. SEM photograph shows the free flowing powder of PB.

The second notable trend was a strong dependence on yield of polymer. It is seen from Figure 6 that the



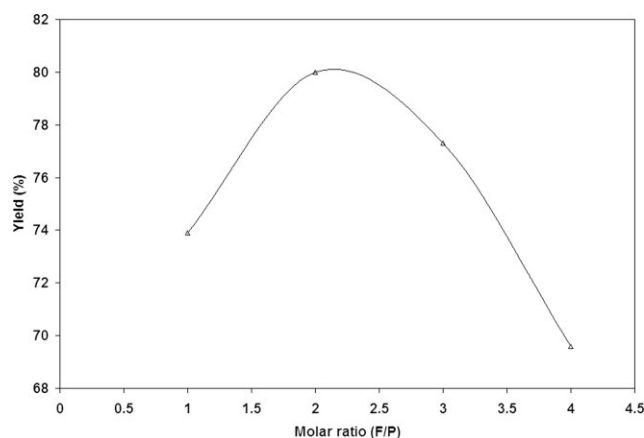
**Figure 5** SEM photographs of PB having size 180  $\mu\text{m}$  which were not taken in average particle size calculation.

yield (%) of PB initially increased with increasing  $F/P$  molar ratio, but above  $F/P = 2$ , the yield of PB was found to decrease with increasing  $F/P$  molar ratio. It clearly indicates that inhibition of polymerization occurs by excessive  $F/P$  ratio, which results in unreacted phenols in solution. If the content of formaldehyde falls to 1 mol, the PB was found to have low conversion, which was due to the fact that monomer formed had a high content of free phenol. The polymerization conducted in the presence of excess of formaldehyde resulted in agglomeration of resultant polymer at walls of reaction vessel, which fouled the reactor. In few experiments, the phenolic resin was formed at walls of reaction vessel that were not taken into account for yield percent.

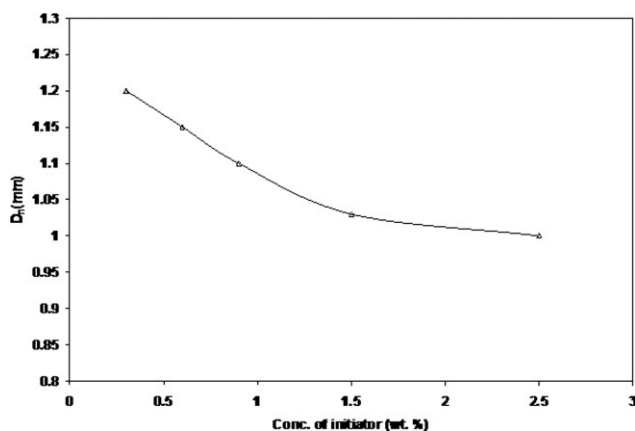
### Effect of initiator concentration

In the past, many authors have reported the influence of initial  $F/P$  ratio for resins catalyzed with alkaline catalysts, such as sodium hydroxide, barium hydroxide, ammonia, and some tertiary amines.<sup>9,22,37,38</sup> The choice of the catalyst has influence on the cost, the efficiency, and its separation. Sodium catalysts are normally not separated from the products, whereas oxides and hydroxides of alkaline earth metals are usually precipitated as sulfates and removed by filtration. Both ammonia and TEA appeared to be suitable because they are soluble in the monomer. The preliminary studies revealed that TEA resulted in the formation of PB from phenol and formaldehyde by polymerization reaction.

The rate of conversion of the monomer to PB with time at different initiator concentration is shown in Figure 7. The rate of conversion of PB initially increases with the increase in TEA concentration and the 86.0% PB was obtained at 1.0 wt % TEA concentration. But above 1.0 wt % concentration of TEA, the rate of conversion to PB decreased with increase in TEA



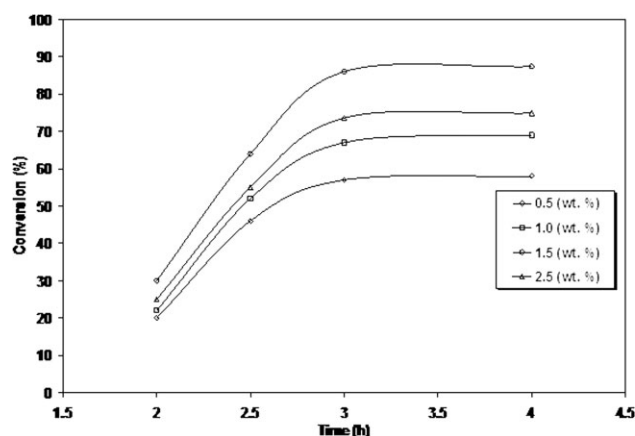
**Figure 6** Dependence of yield (%) of PB on the  $F/P$  ratio varied from 1 to 4 by mole in polymerization reaction.



**Figure 7** Effect of initiator concentration on the size of PB in polymerization reaction of phenol and formaldehyde.

concentration. So, an appropriate initiator concentration (about 1.0 wt %) was necessary for formation of monomer, which were further converted into PB.

It is seen from Figure 8 that the average size of the PB decreased with increase in the TEA concentration. The average diameter of PB decreased from 1.2 to 0.9 mm when TEA concentration increased from 0.5 to 2.5 wt %, which may be due to the fact that the concentration of ionic groups increases with increasing initiator concentration. Then, at the early stage of the polymerization, more polymer chains of lower molecular weight were formed. Because the suspension polymerization mechanism requires the polymer chains reach a critical size before nucleation can occur, and fewer of the chains reach this critical size, fewer of the sites are available. Therefore, fewer particles of large diameter are produced at higher concentration of initiator, number of ionic groups involved in the stabilization of lattices increased, resulting in the formation of smaller particles. The narrow particle size distribution (0.9–1.3 mm) of PB was obtained when they were prepared at TEA con-



**Figure 8** The amount of PB at different concentration of initiator in polymerization reaction of phenol and formaldehyde.

centration of 1.0 wt %. Here, the stable spherical beads formation stages became short, thus reducing the nucleation time and resulting in narrow particle size distribution.

### Effect of the crosslinking agent

By preference suspension polymerization of phenol and formaldehyde at temperature below 100°C, at least one crosslinking agent<sup>30,33</sup> is required to obtain cured crosslinked structure of phenolic resin. The polymerization conducted in the absence of HMTA resulted in a highly viscous resin. In contrast, the reaction that was carried out in the presence of the added HMTA resulted in the formation of cross-linked PB structure.

The crosslinked structure of PB in this polymerization reaction is strongly affected by the concentration of HMTA. Table I shows that the amount of cross-linked PB obtained were increased by increasing the concentration of HMTA. The amount of crosslinked PB formed in the reaction increased from 1 to 100% when the concentration of HMTA varied from 0 to 7.0 wt %. In addition to PB, the viscous resin was formed in the system when the concentration of HMTA was less than 5.0 wt %.

### Effect of temperature

Table II summarizes the temperature dependence of particle size and its formation, when other parameters, such as  $F/P$  ratio, concentration of PVA, monomer, TEA, and HMTA, are kept constant. Table II shows that the average particle size slightly decreased with increase in temperature. The diameter of PB decreased from 1.2 to 1.0 mm when the temperature of polymerization reaction increased from 70 to 98°C.

**TABLE I**  
Data for Polymerization of Phenol–Formaldehyde Monomer<sup>a</sup> at Different Concentration of Crosslinking Agent

Entry	Concentration of HMTA (wt %)	Yield <sup>b</sup> (%)	$D_n$ <sup>c</sup> (mm)	$R$ <sup>d</sup> (%)
1	4.0	65.8	1.3	82
2	5.0	78.8	1.2	98
3	6.0	80.2	0.9	100
4	7.0	81.6	1.15	100

<sup>a</sup> Reaction conditions: 50 g of phenol, 65 mL of formaldehyde, 1.9 mL of TEA, 230 mL of water, 5.0 g of PVA, 475 rpm, 96°C  $\pm$  1°C, and 4 h.

<sup>b</sup> Yields were determined gravimetrically and PB were only weighed (there are uncured phenolic resin, which are not taken in to account for yield %).

<sup>c</sup>  $D_n$ , number-average size of beads.

<sup>d</sup>  $R$ , crosslinked particles which were taken for percentage account.

**TABLE II**  
**Data for Polymerization of Phenol-Formaldehyde Monomer<sup>a</sup> at Different Temperature**

Entry	Temperature (°C)	$D_n^b$
1	80	1.1
2	90	1.0
3	98	1.0

<sup>a</sup> Reaction conditions were same as taken in Table I.

<sup>b</sup>  $D_n$ , number-average size of beads.

It is also seen from Table II that the curing behavior of phenolic resin depends on the temperature of the polymerization reaction. The reaction carried out at and below 80°C resulted in the formation of uncured phenolic resin. The PB formed at and below 80°C were soluble in methanol. But, the reactions that were performed at and above 90°C resulted in cured PB. The amount of cured PB formed in the reaction increased from 0 to 100% when the temperature of reaction increased from 80 to 100°C.

### CONCLUSIONS

We have studied experimentally the effect of reaction parameters, such as  $F/P$  ratio, initiator concentration, concentration of crosslinking agent, and temperature on particle size and its formation in the polymerization reaction of phenol and formaldehyde. The resulting PB exhibited particle size within range of 0.2–2.0 mm with 40.0–86.0% yield when the reaction was carried at different  $F/P$  ratio by mole (1 to 4) at temperature of 96°C ± 1°C with agitation rate 475 rpm for 4 h. The particle size of PB increased from 0.4–1.0 mm with a varying  $F/P$  ratio from 1 to 4 mol, while the yield percent of PB was initially increased and, maximum value obtained at  $F/P$  ratio 2 and then it was found to decrease with increase in  $F/P$  ratio. The average particle size of PB was found to decrease with the increase in the TEA concentration. The yield of 86.0% of PB with narrow particle size (0.9–1.3 mm) diameters was obtained at 1.0 wt % TEA concentration. The other parameter is crosslinking agent, which also plays an important role for thermosetting the phenolic resin. The polymerization conducted in the absence of HMTA resulted in the formation of viscous resin. The amount of PB in the crosslinked structure was found to increase with the increase in the concentration of HMTA. The temperature of about 96°C ± 1°C was necessary to obtain PB in cured form. The prepared PB may find useful application as polymeric precursor for the preparation of activated carbon spheres.

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