

Study on Phenolic Resin Beads: Effect of Reaction Parameters on the Properties of Polymeric Beads

Smriti Shrivastava, Avanish Kumar Srivastava, Beer Singh, D. Shah, A. K. Verma, P. K. Gutch

Defence Research and Development Establishment, Gwalior 474002, Madhya Pradesh, India

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ABSTRACT: Well-sized spherical beads of phenolic resin (0.3–1.2 mm) with an extremely high compressive strength (>8 kg/1.0 mm bead) and hardness ($>98\%$) were synthesized via suspension polymerization of phenol and formaldehyde. Barium hydroxide was used as a catalyst (1.68–10.13 wt %) to get larger size of resin beads. Poly(vinyl alcohol) (5.0–12.5 wt %) and hexamethylene tetramine were used as stabilizing agent and crosslinking agent, respectively. Comprehensive studies elucidated a specific relation between the reaction parameters and properties

of the resin beads. Yield was found proportional to catalyst concentration and inversely proportional to stabilizing agent concentration. Particle size distribution curves got contracted and shifted toward a lower size range with higher concentration of catalyst and stabilizing agent. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3741–3747, 2012

Key words: suspension polymerization; phenolic resin; synthesis; stabilizing agent; particle size distribution

INTRODUCTION

As a family of resins originally developed in the early 20th century, the nature and potential of phenolic resins have been explored thoroughly to produce an extensive body of technical literature.¹ Work on this first commercially important polymeric product was initiated by Baekeland in the year 1905. Since their introduction, the relatively inexpensive and highly versatile family of phenolic resins has played a vital role in construction, automotive, electrical, and appliance industries as well as in the field of aerospace. Owing to their inherently higher flame retardancy, these are classified as charring polymers.^{2,3} Phenolic resins offers a high degree of purity and low ash content^{4,5}; thus, carbon materials derived from these precursors are expected to have a high-specific surface area and well developed porosity compared to the carbon derived from coal and hence are preferred over coal.⁶ Among various polymers available, phenolic resins have been preferred, because they are easy to prepare in desired physical forms (powder, granules, and fibers) with a comparatively large size range.^{7,8} Effects of variation in the concentration of catalyst, reaction temperature, and formaldehyde to phenol (F/P) ratio during the kinetic studies via high-performance liquid chromatography technique have been studied.^{9–11} Precursor

materials other than formaldehyde and phenol such as resorcinol and *m*-cresol have also been explored.^{12,13} Bajia et al.¹⁴ developed a method for microwave-assisted synthesis of phenolic resin. The effects of concentration and grade of stabilizing agent on the properties of the resin have been discussed by Singh et al.,¹⁵ who later used phenolic resin beads to prepare activated carbon spheres.¹⁶ Yang and co-workers¹⁷ also reported phenolic resin as precursor for the preparation of activated carbon spheres.

A number of studies have been executed using sodium hydroxide¹⁸ and ammonium hydroxide as a catalyst^{4,19}; therefore, it was thought to explore alkaline earth metal hydroxides to prepare phenolic resin beads. Barium hydroxide [Ba(OH)₂] is the first alkaline earth metal hydroxide attempted in the series, as its basic nature and solubility indicate this to be an appropriate one for making large-sized/suitable/polymeric beads. It produces required alkalinity of the medium in a very short time being highly basic. This results into faster nuclei formation that later grows into a bigger size of beads. The resin may be prepared in different physical forms. It is frequently preferred to obtain the polymers in the form of beads because of the obvious convenience of their storage, transportation, and easy handling.

Phenolic resins have been prepared either as powdered materials or in the form of microspheres. To make activated carbon spheres to be used in the air purification filters for defense purposes, the precursor, that is, phenolic beads must have bigger size, a definite particle size distribution, and high mechanical strength. As-prepared activated carbon spheres

Correspondence to: B. Singh (beerbs5@rediffmail.com).

posses enough hardness to avoid dust formation during filling and packing in the filters and canisters. Hence, it was imperative to synthesize a precursor, with a bigger size and a particular particle size distribution, having low level of inorganic impurities, high mechanical strength, and spherical shape, without sharp edges. The major objective of prepared phenolic resin beads was to make activated carbon spheres out of it through carbonization and activation. To achieve the targeted precursor, efforts have been made to synthesize spherical phenolic resin beads with large size (0.3–1.2 mm) using $\text{Ba}(\text{OH})_2$ as a catalyst. The effects of variation in the concentration of catalyst and stabilizing agent on the particle size distribution, degree of conversion, and properties of the prepared resin have also been studied. The synthesized resin beads were characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), compressive strength, elemental analysis, and surface area analysis. Compressive strength, particle size distribution, hardness, moisture content, and bulk density were also measured using standard methods.

EXPERIMENTAL

Materials

Phenol crystals [S.D. Fine Chemicals, India, AR Grade], aqueous formaldehyde solution (37–41%, w/v) [S.D. Fine Chemicals, AR Grade], $\text{Ba}(\text{OH})_2$ [Sigma Aldrich, USA], poly(vinyl alcohol) (PVA; MW : 14,000) [S.D. Fine Chemicals], hexamethylene tetramine (HMTA) [S.D. Fine Chemicals, LR grade], and acetone [S.D. Fine Chemicals, AR grade] were used as received without further purification.

Apparatus and procedure

Phenol–formaldehyde resin beads were synthesized using formaldehyde to phenol ratio 1.5 : 1.0. $\text{Ba}(\text{OH})_2$ and PVA were used as basic catalyst and stabilizing agent, respectively. Suspension polymerization was conducted in a four-necked round-bottomed flask with 1-L capacity (Fig. 1). Phenol (50 g) and formaldehyde (65 mL) were charged to the flask equipped with a reflux condenser, a mechanical stirrer, and a thermocouple. pH of the medium was maintained nearly 8.0 by $\text{Ba}(\text{OH})_2$ (6.75 wt %), added as catalyst. The resulting mixture was dispersed into distilled water (250 mL). PVA (5.0 wt %) was added to this mixture as a stabilizing agent. Resulting mixture was stirred at 500 rpm, and temperature was set at 95°C. After maintaining the reaction temperature at 95°C for 40 min, HMTA (4.05 wt %) was added to it. Finally, the reaction was allowed

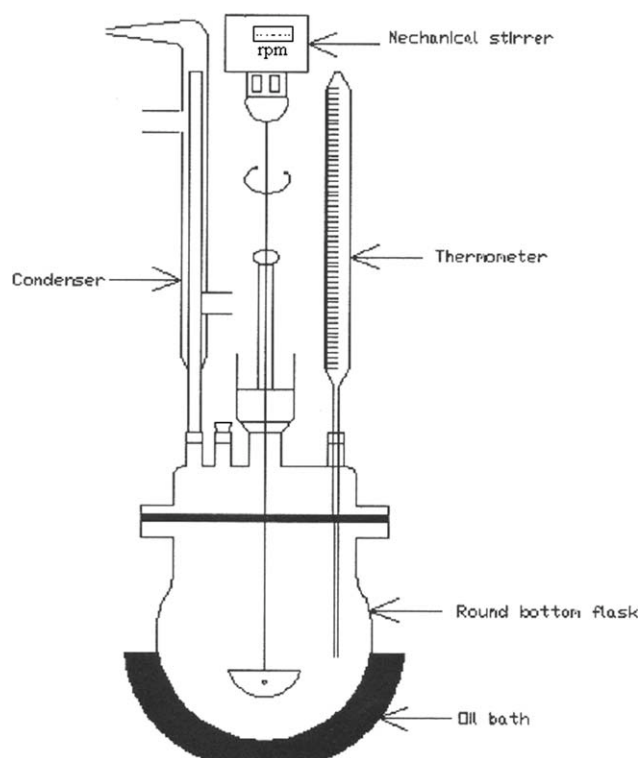


Figure 1 Assembly for polymerization reaction.

to proceed for 4 h, and resulting mixture was cooled. Finally, the two phases were separated, washed with distilled water followed by acetone, and beads were then allowed to dry. Concentration of the crosslinking agent was set to the optimum value considering maximum size to be obtained without any aggregation of beads. To study the effects of catalyst and stabilizing agent, several experiments were conducted with different concentration ranging from 1.68 to 10.13 and 5.0 to 12.5 wt % of catalyst and stabilizing agent, respectively. Results indicated that optimized beads were obtained with 6.75, 5.0, and 4.05 wt % of $\text{Ba}(\text{OH})_2$, PVA, and HMTA, respectively. This is important to mention here that, due to the highly exothermic reaction, it is preferred to carry out the reaction in small batches, though water is being used as a heat transfer medium in the reaction.²⁰

Characterization

Elemental analysis of resole beads was performed with Thermo Electron CHNS Analyzer Flash EA 1112 Series. Compressive strength was determined using Testometric Micro 350, and hardness of the material was determined by using vibrating machine. Shape and surface morphology of resole beads were characterized, performing SEM. For SEM analysis, beads were first mounted on brass stubs using double-sided adhesive tape and then gold

TABLE I
Elemental Analysis of Resole Beads

S. No.	Sample			Carbon (wt %)	Nitrogen (wt %)	Hydrogen (wt %)	Oxygen (wt %)
	Ba(OH) ₂ (wt %)	PVA (wt %)	HMTA(wt %)				
1	1.68	5.0	4.05	72.05	1.68	5.84	20.43
2	10.13	5.0	4.05	68.81	0.85	5.23	25.11
3	6.75	5.0	4.05	67.07	1.16	5.78	25.99
4	6.75	12.5	4.05	67.89	0.96	5.69	25.46
5	6.75	5.0	1.35	66.88	0.71	5.63	26.78
6	6.75	5.0	4.05	67.07	1.16	5.78	25.99

coated for 8 min using ion sputter JEOL, JFC 1100 coating unit. Images were recorded using FEI ESEM Quanta 400 instrument. Surface area was measured by nitrogen adsorption at 77 K using Autosorb1C from Quantachrome Instruments, USA, using Brunauer–Emmett–Teller (BET) method. Particle size distribution of the synthesized phenolic resin beads was measured with sieves of different mesh sizes. Bulk density was measured by weighing a known volume (25 mL) of the material and expressed in gram per milliliter. Moisture content of the material was determined by heating a known amount (10 g) of sample in an oven at 120°C for 6 h followed by cooling in desiccator for 20 min and finally weighing to a constant weight. The weight loss in sample per 100 g was taken for determining moisture content of the material. FTIR spectra were recorded on Perkin–Elmer spectrum BX FTIR spectrophotometer. For analysis, a few of the particles of powder resole beads were mixed with 200 mg of potassium bromide, ground to make pellet, dried, and, finally, IR spectrum was recorded. Spectrum was recorded in the wavelength range between 4000 and 600 cm⁻¹ at a resolution of 8 cm⁻¹. Thermal stability of the beads was determined by performing TGA under nitrogen atmosphere using TA 2950 instrument at a heating rate of 20°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Elemental analysis

Elemental analysis of resole beads (optimized) showed the carbon, hydrogen, nitrogen, and oxygen contents of 67.07, 5.78, 1.16, and 25.99%, respectively (Table I). The oxygen content was obtained from the difference in the weight of elements. Results indicated the presence of nitrogen in the synthesized beads, which is due to the incorporation of nitrogen from HMTA during crosslinking reaction. Table I clearly indicates that with the increase in concentration of HMTA from 1.35 to 4.05 wt %, the nitrogen content increased from 0.71 to 1.16%. Nitrogen content was also found to be varied with other parameters. Use of HMTA as a crosslinking agent imparts a

hydrophobic nature to the resole beads,²¹ which is considered as an important factor for the precursor for making activated carbon spheres.

Mechanical and compressive strength

To justify their applicability under the areas of crucial conditions like mechanical and physical pressures, the beads were characterized for their compressive strength and hardness, which came out to be >98% and >8 kg/1.0 mm bead. This much high mechanical strength was attributed to the well developed crosslinking present in the beads.

Surface morphology, surface area, bulk density, and moisture content

To go through the structural properties, the beads were characterized by SEM analysis, which showed the outer surface of the beads to be smooth and without any pores, while the internal structure was found with a dense network of pores present inside [Fig. 2(a,b)]. These pores may get opened by suitable physical and chemical activation. This fact promotes to further proceed the work for preparing activated carbon using this material as a precursor. Bulk density of the beads was calculated to be 0.7 g/mL. A high bulk density is indicative of good carbon yield; hence, such materials are proved as a better precursor for the preparation of activated carbon.²² The average moisture content of the beads was nearly 10% (Table II).

FTIR spectra and TGA

To analyze the surface functional groups present there in the resin beads, Fourier transform infrared spectroscopy (FTIR) study was performed on the resole beads (Fig. 3). The obtained peaks were compared to the reference data available to confirm the functional groups present in the structure.^{23–25} Figure 3 shows a broad band at ~ 3400 cm⁻¹, which is assigned to the hydroxyl group-stretching mode of intermolecular hydrogen bonding. In phase stretching, vibration of —CH₂— alkane is shown by a peak at 2923 cm⁻¹. Peak at ~ 2851 cm⁻¹ is assigned due to the out of phase stretching vibration of —CH₂— alkane.

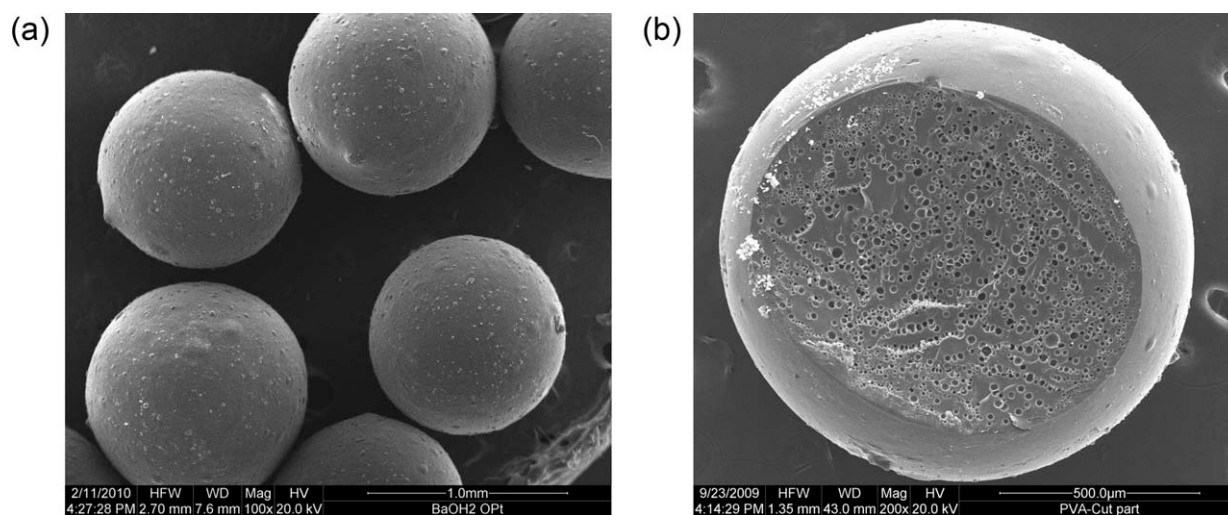


Figure 2 (a) SEM images of optimized resole beads. (b) SEM images of optimized resole beads (cross sectioned).

Peaks at 1634, 1605, and 1510 cm^{-1} are due to C=C aromatic ring vibration. Peak at 1384 cm^{-1} belongs to O—H in-plane deformation vibrations. Further peaks at 878 and 756 cm^{-1} represent the peak for CH— out of plane bending vibrations for isolated hydrogen and para substituted hydrogen, respectively. FTIR spectrum of the sample shows a peak at $\sim 1472 \text{ cm}^{-1}$ showing the presence of —CH₂— methylene bridge formed during the crosslinking reaction of resole beads.²⁶ There also appears a peak at $\sim 1168 \text{ cm}^{-1}$, which is indicative of C—O—C ether bridges. The major conclusion drawn from the data are that methylene bridges are predominant in the resin composition, while ether bridges are also present in the resin beads.

Thermal degradation behavior of the resole beads synthesized with different concentrations of catalyst was investigated by TGA (Fig. 4). The weight loss data as a function of increasing temperature were collected and used to interpret the thermal stability of resole beads. Beads started decomposing initially at about 230°C leading to a 10% weight loss during

the temperature range of 460–480°C. The final decomposition took place at about 510°C leading to a sharp weight loss, continuing up to a temperature of 530°C. Finally, at about 800°C, there appeared a plateau indicating the completion of carbonization process at the temperature.²⁷ Figure 4 shows an increase in residue content with increasing concentration of the catalyst.

Effect of catalyst and stabilizing agent on yield% and particle size distribution

Effect of catalyst on yield%

A profound relationship was observed between the concentration of catalyst and yield%. We observed a direct proportionality between the concentration of catalyst and % yield of the polymeric beads, which was found in accordance with the facts reported by Gupta et al.²⁸ During the polymerization process, concentration of catalyst was varied from 1.68 to 10.13 wt %. As shown in Figure 5, when the concentration

TABLE II
Bulk Density, Moisture, and Surface Area of Resole Beads

S. No.	Sample			Bulk density (g/mL)	Moisture content (%)	N ₂ -BET surface area (m ² /g)
	Ba(OH) ₂ (wt %)	PVA (wt %)	HMTA (wt %)			
1	1.68	5.0	4.05	0.74	8.0	2.82
2	3.38	5.0	4.05	0.67	8.5	2.79
3	6.75	5.0	4.05	0.66	8.5	2.76
4	10.13	5.0	4.05	0.67	8.7	2.72
5	6.75	5.0	4.05	0.66	8.5	2.82
6	6.75	7.4	4.05	0.66	8.4	2.83
7	6.75	10.0	4.05	0.69	8.5	2.84
8	6.75	12.5	4.05	0.69	8.0	2.84
9	6.75	5.0	1.35	0.70	8.5	2.84
10	6.75	5.0	2.7	0.70	8.5	2.83
11	6.75	5.0	4.05	0.66	8.6	2.83

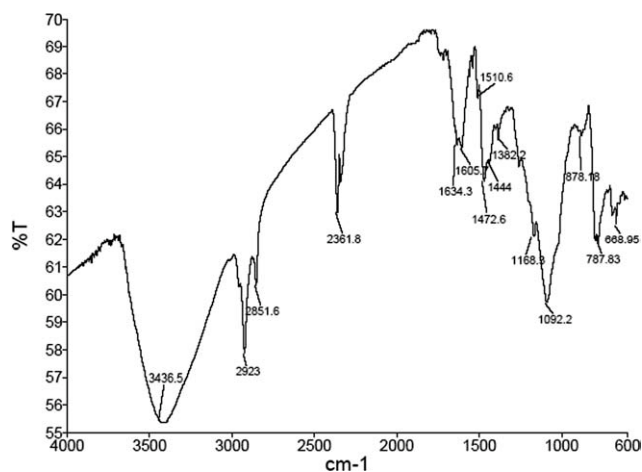


Figure 3 FTIR spectrum of resole beads.

of catalyst was initially 1.68 wt %, the yield was 3.19% only. As the concentration of the catalyst got increased, % yield correspondingly increased showing maxima of 53.81 at a highest catalyst concentration value of 10.13 wt %. Polymeric yield is a function of alkalinity of the medium, which is maintained by catalyst. During the process of polymerization, initially, phenolate ions are formed under the influence of hydroxyl ions available in the medium. At the highest concentration of catalyst, there appeared a plateau, showing a maximum of polymeric yield.

Effect of catalyst on particle size distribution

During the process of suspension polymerization under the influence of interfacial tension between the two phases, initially, droplets of polymeric nuclei develop. Rate of nuclei formation is a function of alkalinity of the medium. Catalyst maintains the alkalinity of the medium, hence governs the rate of nuclei formation, and, as a result, it controls the particle size distribution. When the catalyst concentration was 1.68 wt %, the particle size covered the size range from 0.3 to 1.2 mm, which later contracted in

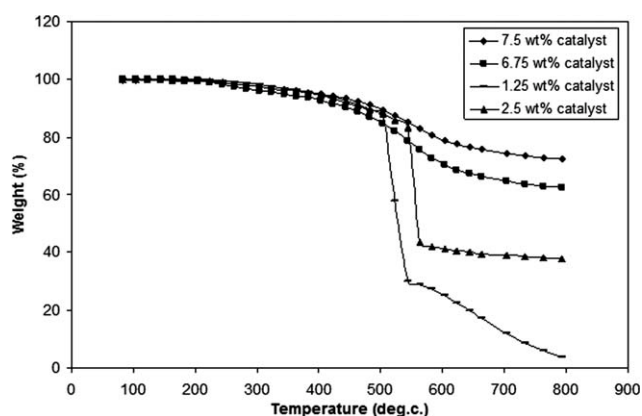


Figure 4 TGA curve of resole beads.

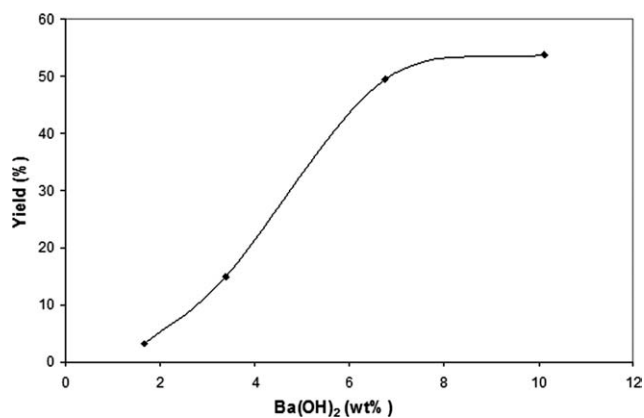


Figure 5 Effect of concentration of $\text{Ba}(\text{OH})_2$ on yield % of resole beads.

case of 10.13 wt % of catalyst and showed a maxima of 55.6% yield of 0.6 mm beads (Fig. 6). Increased concentration of catalyst leads to enhanced alkalinity of the medium. This results into a smaller nucleation period and finally smaller-sized nuclei get formed within a narrow period, leading to further solidification giving rise to smaller particle size distribution of the beads. Hence, a larger number of beads of smaller size is formed, which maintain their identity throughout the reaction period leading to sharp particle size distribution.

Effect of stabilizing agent on yield%

During suspension polymerization, nature and concentration of stabilizing agent are extremely crucial parameter, which maintains the overall viscosity of the reaction medium,¹⁶ which dominates the extent of nuclear aggregation and hence results in the variation of physical properties of the polymeric product. In the present study, PVA was being used as stabilizer. It has been preferred over other stabilizers because of its easy availability, economic viability, easy handling characteristics, and solubility in

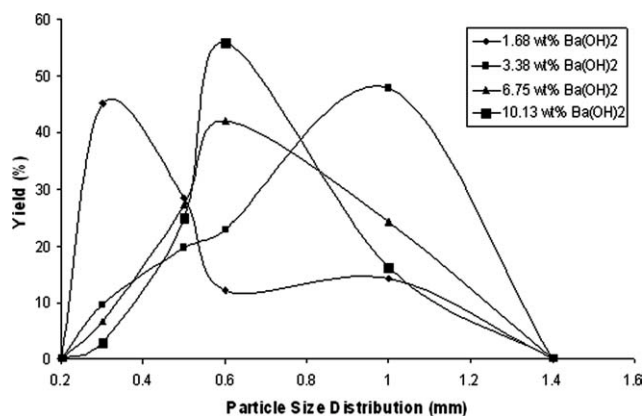


Figure 6 Effect of concentration of $\text{Ba}(\text{OH})_2$ on particle size distribution of resole beads.

water.²⁹ Concentration of PVA was varied from 5.0 to 12.5 wt % and effect on particle size distribution and yield% has been discussed. Figure 7 shows the yield % of beads obtained with different concentrations of PVA, which indicates a decrease in the yield% of the resulting polymer with increasing concentration of stabilizer. When the concentration of the PVA was 5.0 wt %, the yield of the resin obtained was 49.45%, while it decreased to 27.32% with 12.5 wt % PVA. This inverse proportionality between the concentration of stabilizing agent and yield% may be described as a function of viscosity of the medium.³⁰ Hence an optimized concentration of PVA is required, so as to maintain the required viscosity of the medium. A minimal concentration of PVA is required for beads to oil out from the reaction mixture, while enhanced viscosity leads to extreme powdered resin, which is not considered for yield calculation (below 0.1 mm).

Effect of stabilizing agent on particle size distribution

There is a marked effect of concentration of stabilizing agent on the particle size and its distribution. Concentration of stabilizing agent has been varied from 5.0 to 12.5 wt %. With lower concentration of stabilizing agent, particle size distribution obtained was 0.3–1.2 mm, covering a large range, while this distribution contracts to a range of 0.3–0.8 mm when higher concentration of stabilizing agent was used (Fig. 8), whereas the optimized concentration of stabilizing agent was found to be 5.0 wt %. This is attributed to the increased viscosity of reaction medium with increasing concentration of stabilizing agent. When the stabilizing agent's concentration was less, reaction mixture was not enough viscous, and probability of nuclear aggregation was higher, leading to an increase in the size of the beads.¹⁶ Similarly, there was a possibility of greater particle size distribution, as during a large period of time, the

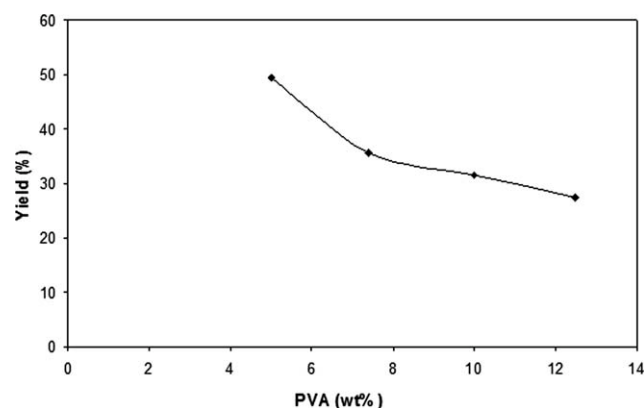


Figure 7 Effect of concentration of PVA on yield % of resole beads.

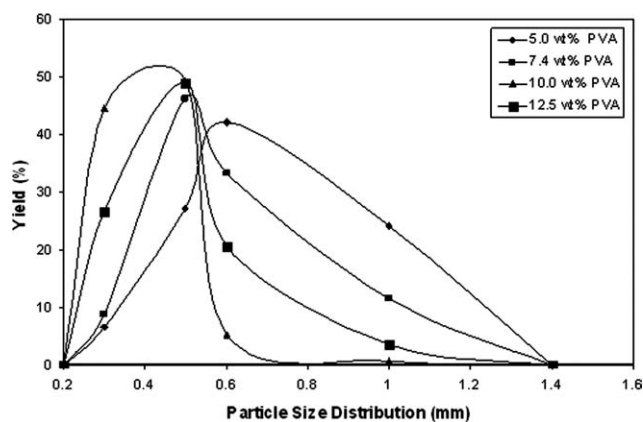


Figure 8 Effect of concentration of PVA on particle size distribution of resole beads.

dispersion and nuclei aggregation was allowed. At higher concentration of stabilizing agent viscosity of the medium, rate of adsorption of stabilizing agent molecule and the numbers of nuclei get increased and, as a consequence, the extent of nuclear aggregation gets decreased. Figure 8 indicates that there is an inverse proportionality between the concentration of stabilizing agent and particle size.³¹

CONCLUSIONS

Spherical beads of phenolic resin synthesized using 6.75 wt % of $\text{Ba}(\text{OH})_2$ as a catalyst 5.0 wt % of PVA as stabilizing agent and 4.05 wt % of HMTA as crosslinking agent were reported in the size range of 0.3–1.2 mm with an extremely high compressive strength (>8 kg per 1.0 mm bead) and enough hardness (98.5%). The beads were found to be thermally stable up to a temperature of 510°C. Investigation on the effects of parameters like concentration of catalyst and stabilizing agent on polymerization was performed. Catalyst and PVA at a concentration of 6.75 and 5.0 wt % gives a good polymeric yield (49.45%), and particle size remains mainly in between 0.5 and 1.0 mm range; hence, this concentration of PVA was found to be the optimum one. Closed porosity was observed by SEM images and high carbon content as investigated by the elemental analysis; therefore, it can be inferred that these phenolic beads may certainly be used as a precursor for preparing activated carbon spheres to be used for defense purposes.

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