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Effect of Adding Conditions of Polyvinyl Alcohol on the Reaction Behavior and Particle Characteristics of Spherical Phenol-formaldehyde Resin Beads

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Phenol-formaldehyde resin (PF) is the oldest synthetic resin. Through the design of synthesis conditions, PF resins with different characteristics can be provided, which are widely used in molding materials, adhesives and impregnation. Spherical PF beads are a hardened resin prepared by a special synthesis method. In this study, a mixture of phenol and formaldehyde was added with triethylamine, polyvinyl alcohol (PVA), and hexamethylenetetramine as a catalyst, granulating agent, and hardening agent, respectively. Spherical PF beads were prepared by a three-stage suspension polymerization in a large-

scale water system, and the effects of PVA addition conditions on the reaction behavior and particle characteristics were discussed. The results show that formalin with a concentration of 14% can be used as a formaldehyde raw material to prepare spherical PF beads by suspension polymerization. The largest spherical PF beads can be obtained with a reactant-liquid ratio of 2/1, a stirring speed of 300 rpm, and an addition amount of BF-04 of 2%. The particle size of 14–20 mesh accounts for 83.9% and has the average particle size of 1016 μm .

Introduction

PF resin is the first synthetic resin to be used, and PF resins with different properties can be obtained by changing the synthesis conditions.^[1] Resol-type PF resin is prepared by reacting phenol with excess formaldehyde under alkaline conditions. Among them, water-soluble resol-type PF resin is synthesized with a strong base as a catalyst, and is mainly used as an adhesive. While the alcohol-soluble resol-type PF resin is synthesized with a weakly basic catalyst, it gradually loses its hydrophilicity and is insoluble in water during the growth of the resin molecule. The obtained resin uses alcohol as a solvent, and is mostly used in the manufacture of resin impregnated materials. Both resol-type PF resins are thermosetting resins. On the other hand, the reaction of phenol with insufficient amount of formaldehyde in an acidic environment forms a thermoplastic novolac-type PF resin, which is mainly used as a molding materials.^[2]

Because PF resin has the characteristics of high strength, good thermal stability, water and weather resistance, and relatively inexpensive. It is widely used in different manufacturing fields such as the construction, automobiles, electrical appliances and aerospace. The cured PF resin has high temperature resistance and high carbon conversion rate. Therefore, it is regarded as a precursor of carbon materials, and the carbonized PF resin is classified as a charring polymer. PF resin-


derived carbon materials have the characteristics of high purity, low ash content, high specific surface area and developed porosity, which can be further activated to produce activated carbon.^[3–6]

The synthetic resin becomes a block resin after hardened, and the fragments obtained by crushing the block resin are irregular particles. The spherical resin can only be obtained through special preparation procedures. Cao et al.^[7] pointed out that spherical particles offer greater advantages over than that of other shapes because they are less prone to break or damage other materials during processing, and their regular shape and size provide the particles to be tightly and orderly stacked, and their spherical shape can give the best fluidity. Romero-Anaya et al.^[8] indicates that the morphology of the activated carbons is very important for their final application. Spherical activated carbons have the characteristics of good wear resistance, high mechanical strength, well adsorption performance, high purity with low ash content, good fluidity, large micropore volume, and more controllable pore size. However, their pore distribution and adsorption capacity are affected by the shape of the sphere and the conditions of carbonization or activation.^[9–11] Wickramaratne and Jaroniec^[12] made spherical resin by reacting resorcinol and formaldehyde with ammonia as catalyst, and pointed out that the carbonized sphere is superior CO₂ adsorbents. Wang et al.^[13] indicated that carbonized microspheres made of this series of resins can be used as the anode materials of potassium ion batteries.

Generally, PF resins form prepolymerized resins in the synthesis stage, and real hardened resins complete their polymerization by heating or adding hardeners in the use stage. While in the production of spherical PF beads, spheroidization and polymerization need to be completed simultaneously in the synthesis process to form independent hardened

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PF resin beads, which makes the control of the reaction conditions more complicated. Yang et al.^[14] and Ye et al.^[15] used novolac-type PF resin and hexamethylenetetramine as raw materials to prepare spherical PF beads. The spheroidization reaction is carried out in methanol liquid with sodium lauryl as emulsion agent under high-speed stirring and high-temperature heating. Sun et al.^[16] dissolved novolac-type PF resin and hexamethylenetetramine in methanol and mixed with an aqueous solution of PVA to produce spherical PF beads. They pointed out that activated carbon made from these spherical PF beads is an excellent CO₂ adsorbent. However, the reaction needs to be carried out in an autoclave in order to provide the high temperature required for the polymerization of the novolac-type PF resin.

Suspension polymerization is often used to prepare water-insoluble resins in the water phase. During the synthesis of alcohol-soluble PF resin, if a granulating agent is added, the suspended molecular chains in the system can aggregate to form spherical particles. Subsequent addition of hardener can make it directly form hardened PF resin in the reaction system.^[17,18] This reaction has the advantage that it can be carried out under normal pressure. Shrivastava et al.^[19] prepared spherical PF beads via suspension polymerization of phenol and formaldehyde with barium hydroxide, PVA and hexamethylenetetramine as a catalyst, stabilizer and cross-linking agent, respectively. The results show that a well-sized spherical PF beads can be made. Singh et al.^[20] used different molar ratios of phenol and formaldehyde as raw materials to prepare spherical PF beads by suspension polymerization. They pointed out that these PF beads can be used as precursors of activated carbon, and the performance of these spherical activated carbons is better than that of powdered and granular activated carbon. Hahn et al.^[21] indicated that the particle size of spherical PF beads increases with the increase in the molar ratio of phenol to formaldehyde and the basicity of the catalyst. Lee et al.^[22] used phenol liquefied-bamboo as a raw material to prepare spherical PF beads by a suspension polymerization in a two-step process and discussed the influence of synthesis conditions on the particle size distribution of spherical PF beads obtained. Huang et al.^[23] used bamboo tar instead of petroleum phenol and prepared PF beads by suspension polymerization under weak alkaline conditions. The results show that 35% of the PF beads obtained have a particle size between 9 and 16 mesh. After carbonization and activation, the activated PF beads are suitable for the adsorption and recovery of VOC gases. Talreja et al.^[24] prepared PF beads by suspension polymerization. These PF beads can be used as carbon sources to fabricate activated carbons with controlled pore size by combined metal templating and physical/chemical activation approach, and can become supercapacitors with high energy and power density.

When making spherical PF resin by suspension polymerization, the second stage of granulation is a key step. At this stage, the pre-polymerized resin dispersed in the reaction system will aggregate with each other to form spheres. In the process of increasing the volume of the sphere, in addition to

maintaining the shape of the sphere, it is also necessary to prevent the sphere from colliding and fusing to form clumps.

Formalin is one of the most important raw materials for synthesizing PF resin beads. The concentration of formalin used in our previous study^[25] and other researchers^[17–24] was 37%. However, due to environmental and safety considerations, the concentration of formalin currently used in Taiwan is limited to less than 14%. This greatly changes the environment of the reaction system during PF bead granulation. Therefore, the relevant synthesis parameters must be re-established and confirmed. In this study, formalin with a concentration of 14% was used as the formaldehyde raw material, and the liquid ratio, stirring speed and PVA addition conditions (including polymerization degree, addition amount and addition method) used in the second stage of spherical PF bead preparation were changed. The influence of these synthesis parameters on their reaction behavior and product properties was explored, and the most suitable synthesis method when using low concentration formalin was confirmed.

Results and Discussion

Effect of PVA addition conditions on synthesis of spherical PF beads

In this study, formaldehyde and phenol with a molar ratio of 1.5/1 were reacted in a system containing triethylamine catalyst and a large amount of water to form a water-insoluble resin. Subsequently, PVA was added as a granulating agent to agglomerate the suspended prepolymerized resin to form spherical particles. Finally, hexamethylenetetramine was added to form hardened spherical PF beads. In the suspension polymerization system, the reactants can be aggregated to form spherical droplets by the effect of the interfacial tension of the granulating agent, and the polymerization occurs within the droplets. The mechanism of particle generation is to form nuclei first, and then gradually expand the particles during the nucleation process to increase the size of the particle. During the process, the molecular chain length of the prepolymer, the type and amount of granulating agent, the stirring speed will all affect the particle size and size distribution of the formed beads.^[17,18,25]

The spherical PF beads currently produced by the suspension polymerization are formed by the reaction of phenol and formalin with a concentration of 37%. However, formalin with a concentration of more than 14% is regulated and restricted in Taiwan. Therefore, we tried to use 14% formalin as raw material to make spherical PF beads. Table 1 shows the reaction conditions of the second stage during the synthesis of PF beads and the final synthesis result. Among them, the synthesis conditions (No.1 ~ No.5) with a liquid ratio of 2/1 and a stirring speed of 300 rpm can be used to obtain spherical PF beads. Figure 1 shows the appearance of the product. Figure 1(a) displays that it is a yellow liquid when the reaction is terminated. Figure 1(b) indicates that the resin particles settle to the bottom after standing. Figure 1(c) shows these spherical PF beads obtained after filtered through a 200 mesh screen

Table 1. Reaction conditions in the second stage and the result of spherical PF resin.

Sample code	Liquid ratio ^[a] (wt/wt)	PVA Type	Dosage (%) ^[b]	Stirring speed (rpm)	Reaction time (min)	Result ^[e]
1	2/1	BF-26	3	300	60	○
2	2/1	BF-17	3	300	60	○
3	2/1	BF-04	4	300	60	○
4	2/1	BF-04	3	300	60	○
5	2/1	BF-04	2	300	60	○
6	2/1	BF-04	3	250	60	×
7	2.5/1	BF-04	3	250	60	×
8	3/1	BF-04	3	250	60	×
9	2.5/1	BF-04	2	300	45	×
10	2.5/1	BF-04	3	300	45	×
11	2.5/1	BF-04	4	300	60	○
12 ^[c]	2.5/1	BF-04	4	300	60	○
13 ^[d]	2/1	BF-04	2	300	–	○

[a] The weight ratio of water to the total weight of phenol and formaldehyde. [b] The percentage of the total weight of phenol and formaldehyde. [c] Dissolve PVA into an aqueous before adding to the reaction system. [d] PVA was added in the first stage and reacted for 120 min. [e] ○ means that spherical particles can be formed, and × means that gelation has occurred during the synthesis process.

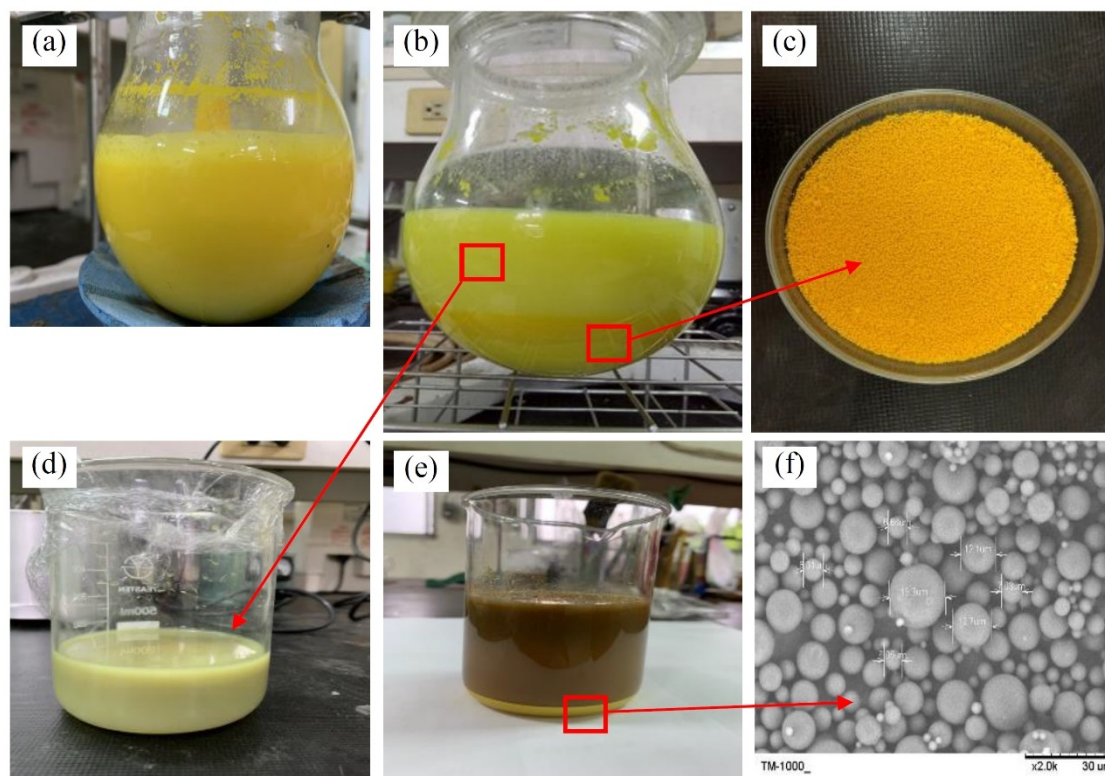


Figure 1. The appearance of the synthesized product; (a) reactant, (b) reactant after standing, (c) spherical resin in the lower layer, (d) filtrate in the upper layer, (e) re-precipitate, (f) precipitate particles.

and heated in an 135 °C oven for 1 h. Figure 1(d) shows the liquid in the upper layer. Figure 1(e) indicates that the liquid gradually turned brown during standing, and then precipitates appeared again. Figure 1(f) shows a 2000x magnified image of the precipitate. The photo shows that the composition is fine particles with a diameter of less than 20 μm. There were no precipitates appeared after the brown liquid was separated by the centrifuge.

Lee et al.^[22] pointed out that using a slower stirring speed during the synthesis process will result in larger resin particles. In order to increase the size of the spherical PF beads, the stirring speed at the second stage of the reaction was reduced to 250 rpm (No. 6). However, the reactants gelled during the reaction process (as shown in Figure 2). This is because the shear force in the reaction system is reduced at a low stirring speed, which causes the colliding resin to aggregate and

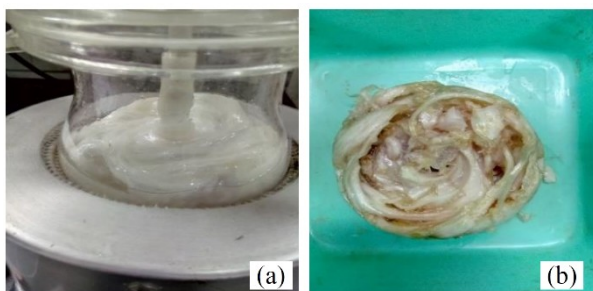


Figure 2. Resin that gelled during the reaction.

become agglomerates, which in turn leads to gelation. To avoid this phenomenon, additional water was added to dilute the reaction solution, the liquid ratio of the reactants was changed

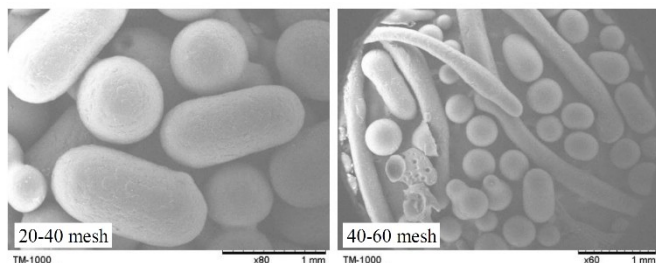


Figure 3. The appearance of particles of resin No.11.

from 2/1 to 2.5/1 (No.7) and 3/1 (No.8). However, this gelation phenomenon still occurs in the second stage of the reaction process.

In order to confirm the relationship between the liquid ratio of the reactants and the gelation phenomenon, the stirring speed was maintained at 300 rpm, and the reactant liquid ratio was adjusted to 2.5/1 for reaction. Among them, No. 9 and No. 10 that prepared with 2% and 3% PVA still show gelation, while No. 11 that with 4% PVA can get granular resin. However, about half of the particles are elliptical or elongated as shown in Figure 3. From the above results, it can be concluded that the granulation reaction should be carried out at a lower liquid ratio (2/1) with a higher stirring speed (300 rpm).

In order to improve the convenience of the synthesis operation, No. 12 refers to the preparation conditions of No. 11, but the PVA powder is dissolved into an aqueous with the additional water scheduled for the second stage, and then dropped into the reaction system with a separatory funnel. This method can also obtain granular resin, and can reduce the proportion of elliptical particles. No. 13 added PVA to the reaction system together with phenol and formaldehyde in the first stage for reaction. This method can simplify the reaction steps while obtaining typical spherical PF beads.

The particle size distribution of spherical PF beads

In this study, a suspension polymerization was used to prepare spherical PF beads. The results show that prepared spherical PF beads are a mixture of particles with different sizes. Figure 4 shows the microscopic appearance of spherical PF beads in

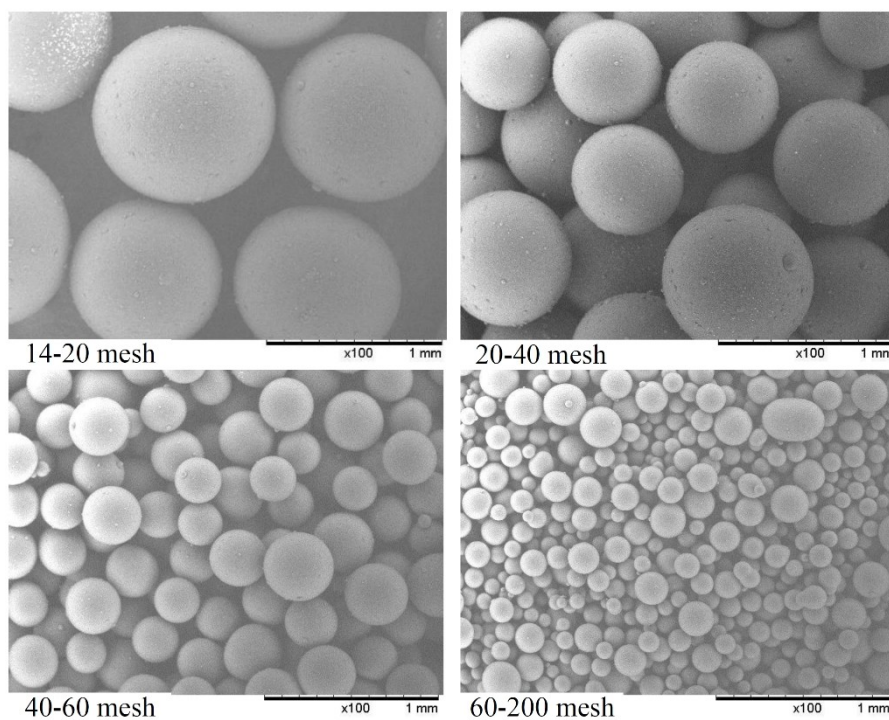


Figure 4. The appearance of spherical PF resin with different particle sizes.

particle sizes range of 14–20 mesh, 20–40 mesh, 40–60 mesh and 60–200 mesh. It can be seen from the figure that beads of various sizes are mainly composed of spherical particles. However, in resin No.5, No.11 and No.12, some beads with a particle size of 14–20 meshes are shown as elliptical particles, as shown in Figure 3. This is because the spherical PF beads are formed by the interfacial tension generated by the PVA molecules. For large-sized beads, more PF resin accumulates inside, which weakens the interfacial tension on the outside of the beads. Therefore, under the action of the shearing force generated by the stirring, these beads are easy to flow and deform to form an elliptical elongated strip.

Figure 5(a) shows the particle size distribution of spherical PF beads obtained by using PVA (BF-04, BF-17 and BF-26) with different degrees of polymerization as the granulating agent and reacted under the condition of a liquid ratio is 2/1, a PVA addition amount of 3%, and a stirring speed of 300 rpm. As the degree of polymerization of PVA increases, the average diameter of PF beads decreases. Among them, those with BF-04, BF-17 and BF-26 as granulating agents have the average diameter of 766 μm , 715 μm and 397 μm , respectively. This trend is the same as the results of Chang et al.^[25] Comparing their particle size distribution, in the spherical PF beads prepared with BF-04 as the granulating agent, 51.6% of the beads have a size of 14–20 mesh, and 44.0% of the beads have a size of 20–40 mesh. As the degree of the polymerization of PVA increases, the proportion of larger-sized beads decreases,

while the proportion of smaller-sized beads increases. For the PF resin prepared with BF-26 as a granulating agent, there are many small beads, and the particle size is mainly 20–40 mesh, and 14–20 mesh particles do not appear.

Lee et al.^[22] pointed out that the dosage of PVA played an important role in deciding the yield and the diameter of beads, the higher dosage of PVA resulted in a small beads diameter. Figure 5(b) shows the particle size distribution of spherical PF beads produced with different amounts of PVA (BF-04). It can be seen that the spherical PF beads prepared by adding 2% PVA have the largest average diameter (1016 μm), and 83.9% of the beads have a particle size of 14–20 mesh. With the PVA addition amount increased, the proportion of beads with a particle size of 14–20 mesh gradually decreases, while those with 20–40 mesh increase. When the amount of PVA is 4%, the spherical PF beads mainly have a particle size of 20–40 mesh, and its weight percentage reaches 65.1%. This is because the greater the amount of PVA added, the more the number of initial nuclei in the reaction system, and more crystal nuclei undergo adsorption at the same time, which causes the pre-polymerized resin to be consumed faster and reduced the degree of aggregation of crystal nuclei. Therefore, a stable crystal nucleus is formed faster, and the growth of particles is reduced to make its size smaller.^[17,19]

Figure 5(c) compares the influence of the liquid ratio of the reactants (2/1 and 2.5/1) and the type of PVA (solid and solution) on the particle size distribution of spherical PF beads

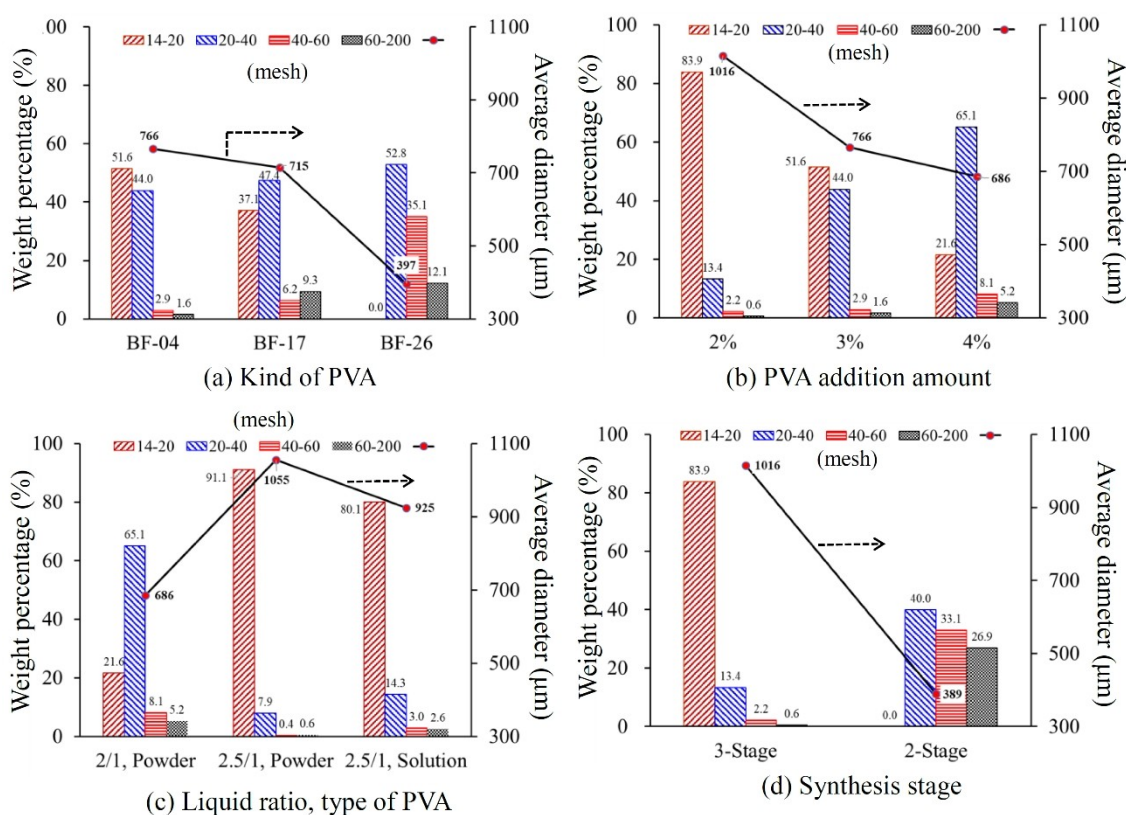


Figure 5. Particle size distribution of spherical PF beads prepared with different PVA (a), PVA dosage (b), liquid ratio and PVA type (c) and synthesis stages (d).

prepared by adding 4% of BF-04. The previous content has pointed out that although increasing the liquid ratio of the reaction system can reduce the concentration of the reactants, but the phenomenon of gelation is prone to occur during the reaction, and when the liquid ratio is 2.5/1, the amount of PVA added must be increased to 4%. Under the condition of 4% PVA addition and a liquid ratio of 2/1, the spherical PF beads produced have an average diameter of 686 μm , of which 20–40 mesh is the main one. When the liquid ratio is 2.5/1, the average diameter can be increased to 1055 μm , of which 14–20 mesh particles account for 91.1%. However, about half of the resin particles formed elliptical strip instead of the typical round shape. This phenomenon is similar to Chang et al.^[25] When PVA is first dissolved into an aqueous solution and then added to the reaction system, the resulting resin particles are mainly 14–20 mesh larger particles.

Figure 5(d) shows the particle size distribution of spherical PF beads prepared by adding PVA to the reaction system together with phenol and formaldehyde in the first stage for reaction. It can be seen that under the same reaction conditions, the size of the particles obtained by the two-stage synthesis process is relatively low. Its average diameter is only 389 μm , and particles distributed in 14–20 mesh did not appear.

Table 2 shows the average diameter of each size grade of spherical PF beads obtained under different preparation conditions. The hole diameter of the 14, 20, 40, 60, 200 mesh screens are 1410, 840, 420, 250 and 75 μm , respectively. The spherical PF beads prepared under different synthesis conditions have different average diameters on the same size screen. Among them, the spherical PF beads with a larger weight average diameter have a larger average diameter in each screen grade. For example, the average particle size of 14–20 mesh beads in resin No. 5 and No. 11 is larger than other spherical PF beads, which are 1057 μm and 1078 μm , respectively. Similarly, the average particle diameter of 20–40 mesh is also relatively large. On the other hand, resin No.1 and No.13 with a smaller weight average diameter does not show beads with a particle size of 14–20 mesh, and beads with a particle size of 20–40 mesh are also smaller. Their average diameters are 488 μm and 473 μm , respectively.

Compression properties of spherical PF beads

Figure 6(a) shows the fracture load of spherical PF beads prepared with different conditions under compression. The sample size is 20–40 mesh and the diameter is 700–800 μm . It can be seen that the fracture load of spherical PF beads

Table 2. Average diameter of each size grade for spherical PF beads prepared with different conditions.

Sample code	Liquid ratio ^[a] (wt/wt)	PVA ^[b] Type	Dosage (%)	Average diameter (μm)				Weight average diameter (μm)
				14–20 (mesh)	20–40 (mesh)	40–60 (mesh)	60–120 (mesh)	
1	2/1	BF-26	3	0 \pm 0	488 \pm 45	328 \pm 31	199 \pm 36	397
2	2/1	BF-17	3	933 \pm 67	695 \pm 150	365 \pm 40	181 \pm 36	715
3	2/1	BF-04	4	874 \pm 44	705 \pm 110	348 \pm 44	194 \pm 36	686
4	2/1	BF-04	3	859 \pm 75	707 \pm 80	339 \pm 40	173 \pm 39	766
5	2/1	BF-04	2	1057 \pm 164	891 \pm 74	364 \pm 44	198 \pm 36	1016
11	2.5/1	BF-04	4	1078 \pm 94	884 \pm 62	421 \pm 76	222 \pm 32	1055
12 ^[c]	2.5/1	BF-04	4	996 \pm 85	780 \pm 185	438 \pm 46	220 \pm 30	928
13 ^[d]	2/1	BF-04	2	0 \pm 0	473 \pm 62	420 \pm 32	225 \pm 23	389

[a] The weight ratio of water to (phenol + formaldehyde). [b] The percentage of the total weight of phenol and formaldehyde. [c] Dissolve PVA into an aqueous before adding to the reaction system. [d] PVA was added in the first stage and reacted for 120 min.

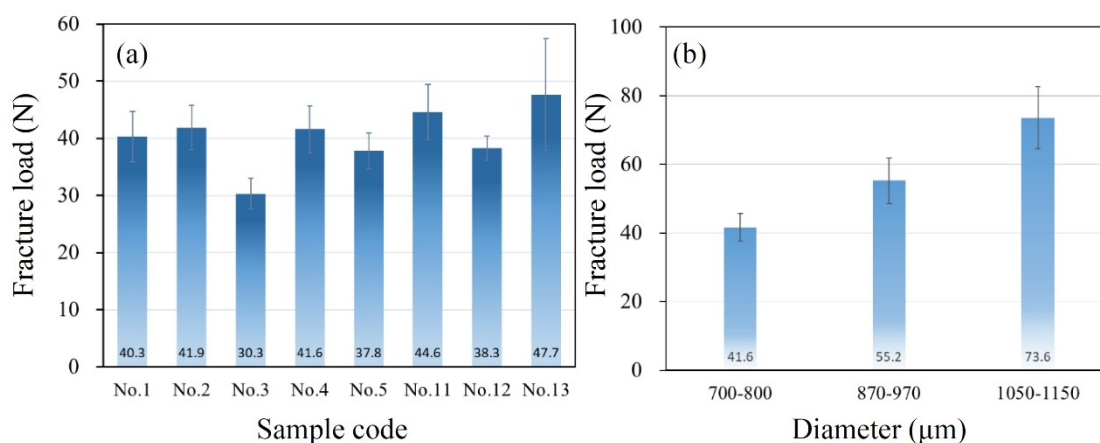


Figure 6. Compressive load of spherical PF beads; (a) different sample, (b) different bead diameter.

prepared with different production conditions has no obvious change trend. Among them, spherical PF beads prepared with 4% of BF-04 as granulating agent have the lowest fracture load, while No.13, which added PVA in the first stage has a larger fracture load. Figure 6(b) shows that as the particle diameter increases, the fracture load of the spherical PF beads tends to increase.

TGA of spherical PF beads

PF resin can be processed at high temperature to obtain a carbon material with a high yield and a special pore structure. Therefore, PF resin can be used as a precursor of synthetic carbon. The pyrolysis mechanism of PF resin includes complex reactions such as molecular chain breaking, rearrangement and re-condensation. Figure 7(a) shows the TG and DTG curves of spherical PF beads prepared with different conditions. All PF

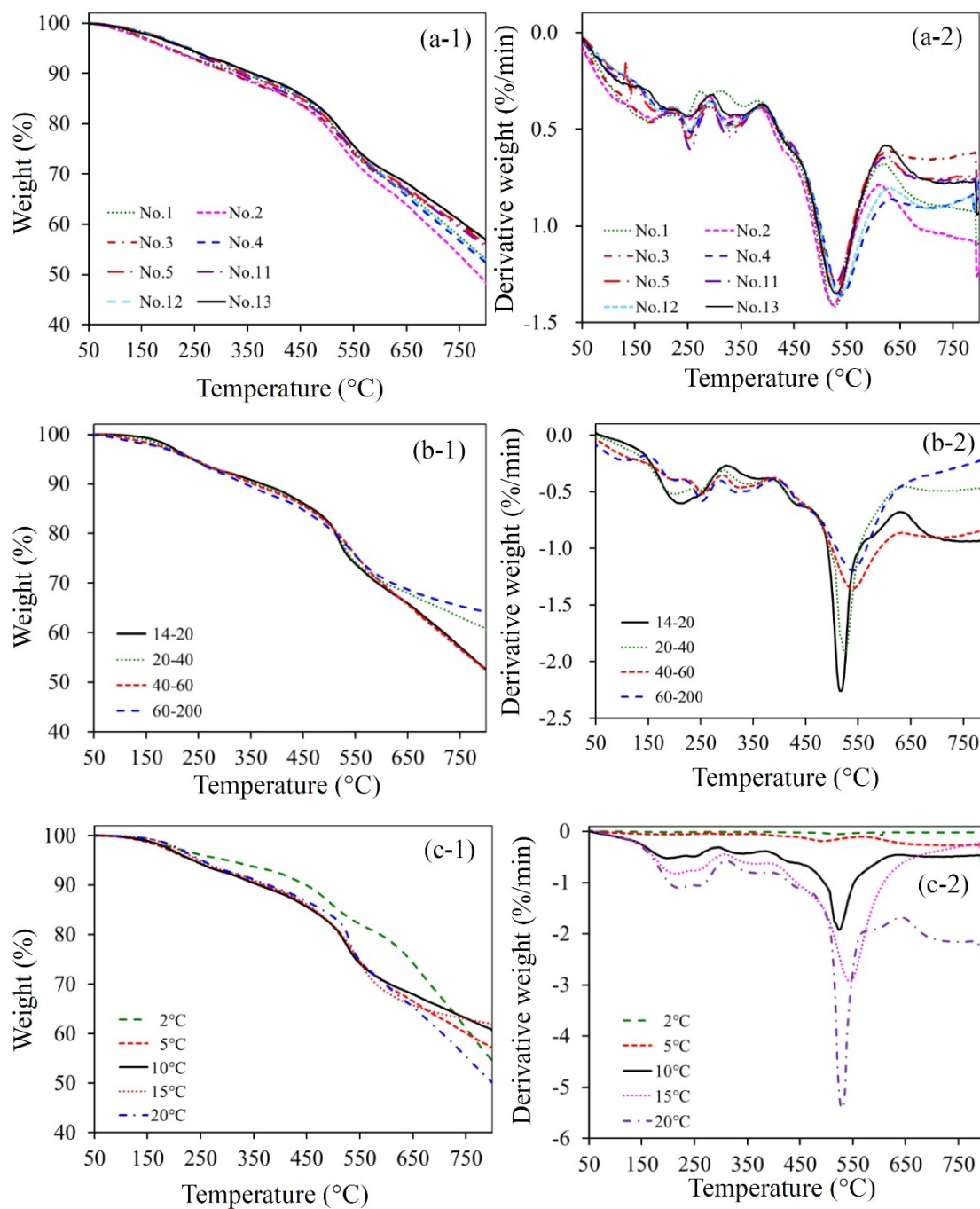


Figure 7. TG and DTG curves of spherical PF beads; (a) with different preparation conditions, (b) with different dimensions, (c) with different heating rates.

resin beads have similar thermal weight loss curves as shown in Figure 7(a-1), indicating that they have the same thermal degradation behavior.

Figure 7(a-2) shows that there are multiple peaks in the DTG curves before heating to 400 °C. The weight loss at this stage includes the volatilization of absorbed water and unreacted formaldehyde, as well as the destruction of methylol groups to release formaldehyde, the reaction with phenol to release condensation water, and the cleavage of the methylene links to release low molecular weight components, such as phenol, methyl phenol, dimethyl phenol, trimethyl phenol.^[26–28]

The obvious DTG peak between 400–600 °C also includes a series of complex reactions. Jiang et al.^[29] pointed out that both the methylene and phenolic hydroxyl groups in the PF resin structure are active functional groups. Therefore, the weight loss includes the etherification reaction between the two phenolic hydroxyl groups or the reaction between the phenolic hydroxyl group and the methylene group to form C–H to connect three benzene rings and release water. In addition, the OH radicals stripped from the phenolic hydroxyl groups provide the oxidation of methylene groups and produce CO and CO₂. The C–H link can react with methylene at higher temperatures to release H₂ and form a C–C link between the benzene rings. The further interaction of condensed water and hydrogen with methylene can release gases such as CO₂ and CH₄. The weight loss above 600 °C is caused by the continuous dehydrogenation reaction of the polycyclic structure after carbonization.

The relevant data obtained by TGA analysis of spherical PF beads can be found in Table 3. For particles prepared under different synthesis conditions (sample code 1–13 with 40–60 mesh in particle size and 10 °C/min in heating rate), the temperature at which 10% weight loss occurs is 319–361 °C. The most intense thermal degradation temperature is 524–541 °C, which corresponds to a thermal weight loss rate of 1.287–1.419%/min. When heated to 800 °C, the char yield is 48.4–56.9%, and the diameter shrinkage is 14.2–52.3%.

Figure 7(b) takes No.4 spherical PF beads as an example to compare the influence of particle size on the thermal degradation behavior. The TG curves show that spherical PF bead of different sizes have similar thermogravimetric loss curves before 600 °C. The DTG curves show that the larger the particle size, the greater the peak height in the two temperature ranges of 150–200 °C and 450–600 °C, indicating that their thermal degradation is more intense. Table 3 shows that the peak temperature and peak height of spherical PF beads with a particle size of 60–200 mesh are 544 °C and 1.199%/min, respectively. For larger particle sizes (14–20 mesh), the peak temperature shifts to the low temperature side to 515 °C, and the peak height increases to 2.260%/min, but the diameter shrinkage less after heating to 800 °C is smaller.

Figure 7(c) also takes No. 4 spherical PF beads as an example to compare the effect of heating speed on the thermal degradation behavior. The TG curves show that the spherical PF beads heated with a slow heating rate of 2 °C/min has lower weight loss than that of faster heating rate at temperature before 700 °C. For using a heating rate above 5 °C/min, different heating rates have similar weight loss curve before 600 °C. But the DTG curves show that the faster the heating rate, the greater the weight loss rate per unit time. This is because the weight loss rate is measured in minutes. Within a certain heating temperature range, the slower the heating rate, the longer the residence time, and therefore the lower the weight loss rate per unit time. This result also shows that in the thermal degradation process, the effect of heating temperature is greater than heating time. It can be seen from Table 3 that in addition to the greater weight loss rate, the peak temperature of the weight loss rate tends to shift to the higher temperature side for those with a higher heating rate.

Table 3. TGA thermal analysis parameters of spherical PF beads prepared with different conditions.

Sample code	Particle size (mesh)	Heating rate (°C/min)	10% Weight loss (°C)	Peak Temperature (°C)	Height (%/min)	800 °C Char yield (%)	Diameter shrinkage (%)
1	40–60	10	339	528	1.419	52.9	16.8
2	40–60	10	321	524	1.412	48.4	25.6
3	40–60	10	319	531	1.287	56.9	18.2
4	14–20	10	371	515	2.260	52.4	1.7
4	20–40	2	448	492	0.193	54.3	22.3
4	20–40	5	366	521	0.820	57.0	1.9
4	20–40	10	359	524	1.917	60.6	6.5
4	20–40	15	372	545	2.940	61.9	2.6
4	20–40	20	379	530	5.416	50.0	4.4
4	40–60	10	352	541	1.361	52.4	18.0
4	60–200	10	338	544	1.199	64.1	27.6
5	40–60	10	344	525	1.342	56.0	14.2
11	40–60	10	334	526	1.302	55.5	33.5
12	40–60	10	353	541	1.367	52.9	52.3
13	40–60	10	361	530	1.352	56.9	28.2

The appearance and internal microstructure of spherical PF beads

Figure 8 shows the external appearance and internal cross-sectional microstructure of No.4 spherical PF beads with a particle size of 20–40 mesh. Figure 8(a) shows that spherical PF beads have an uneven surface structure. After 800 times magnification, Figure 8(b) shows that the surface is composed of fused resin and granular resin. Figure 8(c)(d) shows the

internal microstructure of this particle is mainly composed of resin, but it contains many circular cells. This is similar to the results of Shrivastava et al.^[20] It indicates that during the granulation process, small particles continuously aggregate, fuse, and accumulate outward, forming larger spherical PF beads.

Figure 9 shows the appearance of carbonized spherical PF beads obtained at different heating rates. The spherical PF beads remain spherical after being heated at 800 °C, but the

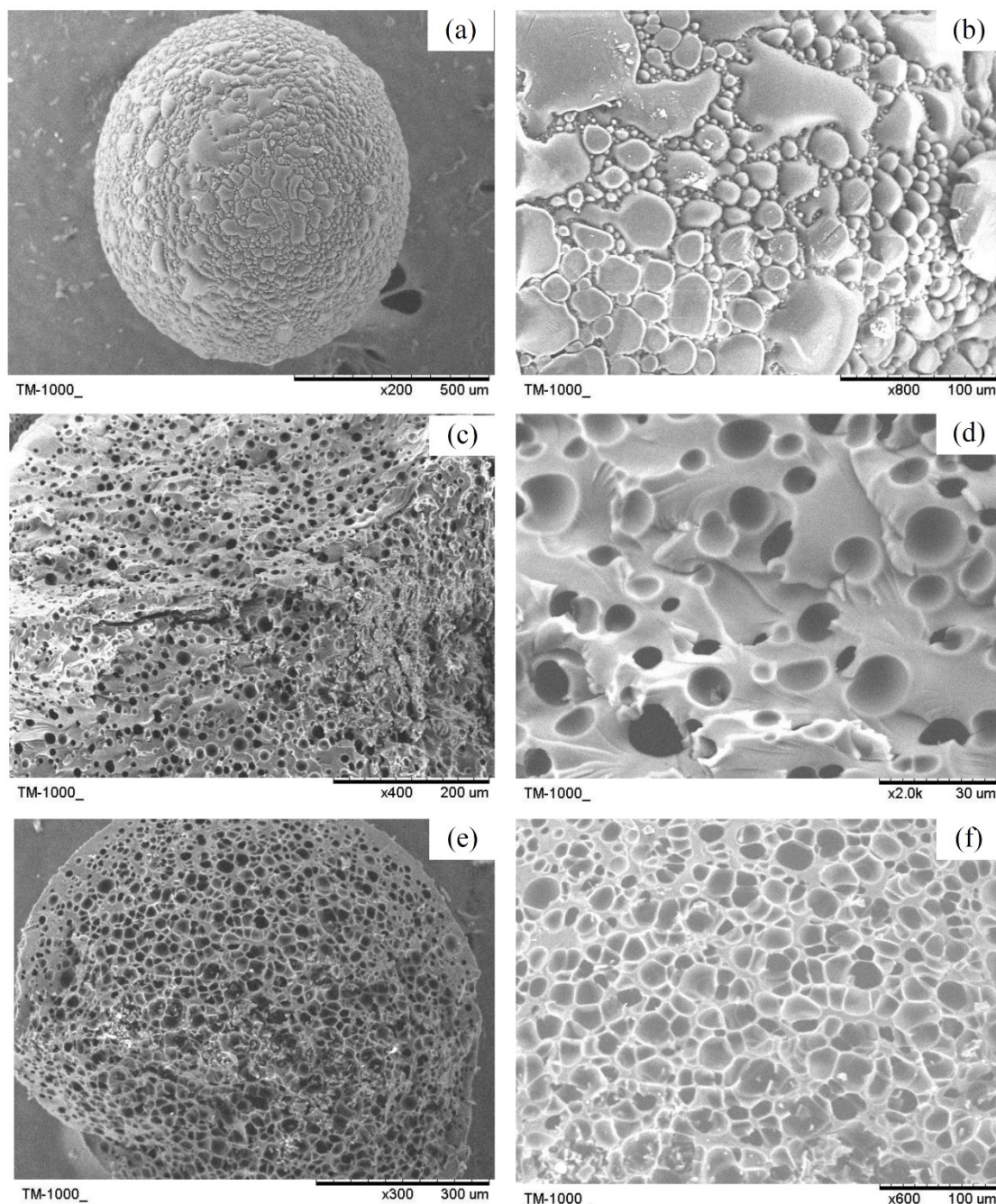


Figure 8. The microstructure of spherical PF bead (No.4, 20–40 mesh, 10 °C /min); (a) and (b) are the external appearance, (c) (d) and (e)(f) are the internal cross-sectional microstructure before and after carbonization, respectively.

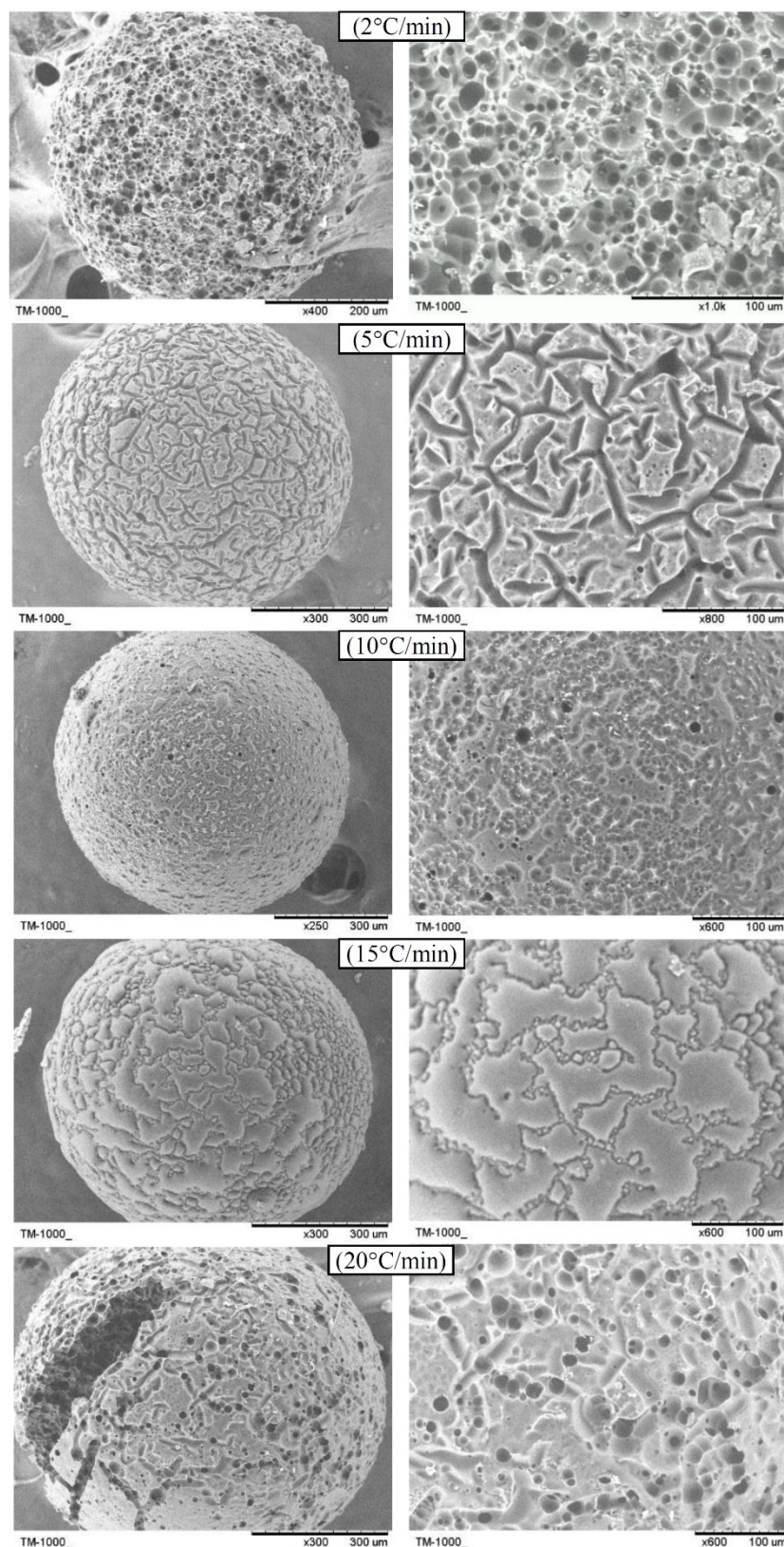


Figure 9. The microstructure of spherical PF bead carbonized at different heating rates. (No.4, 20–40 mesh)

appearance of the carbonized resin beads obtained at different heating rate is different. The appearance of the carbonized spherical PF bead heated at 15°C/min is similar to that of unheated PF bead, as shown in Figure 8(a). When the heating rate is reduced to 10°C/min, many tiny round holes appear on the surface of the carbonized PF beads. Except for round pores, deep groove-like surface appears when heating at 5°C/min. The surface of the spherical PF bead heated at 2°C/min presents a porous cell like structure.

On the other hand, the carbonized spherical PF bead obtained by rapid heating at a speed of 20°C/min has many grooves and bubble holes on the surface, accompanied by the phenomenon of sphere cracking. This is because the rapid rise in temperature leads excessive thermal cracking products to be generated in a short period of time, and rapid shrinkage is formed inside the sphere, resulting in greater internal stress, which leads to cracking the sphere.^[16]

The internal microstructure of the PF bead after carbonization is shown in Figure 8(e)(f). Compared with Figure 8(c)(d), the interior of the unheated beads is mainly composed of resin, while the carbonized bead is transformed into parenchyma cells as the main structure.

Conclusions

In this study, spherical PF beads were produced by a three-stage suspension polymerization, and the influence of the PVA addition conditions in the second stage was discussed. The results show that formalin with a concentration of 14% can be used as a formaldehyde raw material to prepare spherical PF beads by suspension polymerization. The appropriate reactant-liquid ratio in the granulation reaction stage is 2/1, and the stirring speed is 300 rpm. The polymerization degree and addition amount of PVA affect the average diameter and particle size distribution of spherical PF beads. Using PVA with a lower degree of polymerization or adding a smaller amount of PVA result in the prepared spherical PF beads with a larger average diameter. The average diameter of spherical PF beads obtained by adding 2% of PVA-04 as a granulating agent is 1016 μm, of which the particle size of 14–20 mesh accounts for 83.9%. The spherical PF beads obtained by the two-stage synthesis process of adding PVA in the initial reaction stage have a small particle size. The spherical PF beads prepared under various conditions have similar thermal degradation behavior. The surface of the spherical PF bead is a concavo-convex structure composed of fused resin and granular resin, and its internal structure is mainly resin and has many circular cells. The appearance of carbonized PF beads varies depending on the heating rate. After carbonization, the internal main structure changes from a resin matrix to thin-walled cells.

Supporting Information Summary

Detailed material and experimental procedures are provided in the supporting information.

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Conflict of Interest

The authors declare no conflict of interest

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Aggregation · phenol-formaldehyde resin · polyvinyl alcohol · spherical PF bead · suspension polymerization

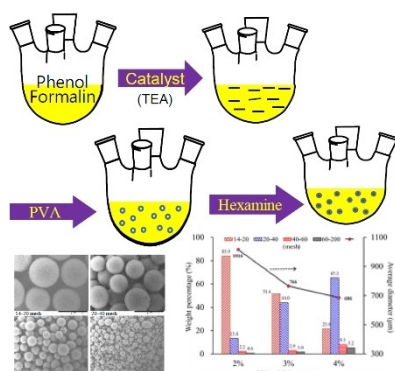
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RESEARCH ARTICLE

Spherical PF beads were prepared by reacting phenol with formaldehyde by a three-stage suspension polymerization. TEA, PVA and hexamine were used as catalyst, granulating agent and hardening agent, respectively. Formalin with 14% concentration can be used as the raw material. The largest PF beads obtained with a reactant-liquid ratio of 2/1, stirring speed of 300 rpm, and BF-04 addition amount of 2%. The particle size of 14–20 mesh accounts for 83.9% and has the average particle size of 1016 μm .



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1 – 12

Effect of Adding Conditions of Polyvinyl Alcohol on the Reaction Behavior and Particle Characteristics of Spherical Phenol-formaldehyde Resin Beads



Author Contributions

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