Scalable preparation of hollow polymer and carbon microspheres by spray drying and their application in low-density syntactic foam

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Abstract

Monodispersed hollow polymer microspheres (HPMs) and hollow carbon microspheres (HCMs) are prepared by a low-cost and rapid spray-drying technique using resorcinol-formaldehyde as precursors. By spraying the precursor solution into a high-temperature chamber, micrometer-scale hollow structure can be immediately obtained. To achieve the required morphology, the factors of influencing the products morphology and purity are systematically optimized. The as-obtained HPMs have a low bulk density of 0.089 g/cm^3 , narrow particle size distribution of 15 to $80\text{ }\mu\text{m}$ with a mean size of $37\text{ }\mu\text{m}$, a high floatation ratio of 96.3% and high mechanical strength. Followed by a simple carbonization, HCMs with a bulk density of ca. 0.1 g/cm^3 and a mean size of $23\text{ }\mu\text{m}$ are achieved. This spray-drying strategy could drastically reduce their production times and costs, enabling continuous and scalable synthesis of hollow microspheres for practical use. As a proof-of-concept application, a series of syntactic foam consisting of HPMs and HCMs as fillers and phenolic resin as matrix are prepared via a hot-press molding. The resulting composite materials have low bulk densities but improved mechanical properties, which highlights the possibility for the manufacturing of light-weight materials using these kinds of hollow microspheres.

Keywords: Chemical synthesis; Polymer; Composite materials; Mechanical properties

1. Introduction

Over the past decade, extensive research has been undertaken in the preparation of hollow microspheres, because their special characteristics such as the interior void space, low density and good flow ability [1]. These materials have been successfully used as fillers for low-weight, mechanically and thermally stable engineering materials, such as metal matrix syntactic foams (MMSFs) [2-7], thermal insulators and structural foams in the aerospace thermal protection system [8, 9]. They also are attractive materials as high-performance biomaterials (e.g. controlled release capsules for drug) [10], gas storage media [11], catalyst supports [12, 13] and electrode materials [14, 15] and so on. So far, many types of hollow microspheres such as silica [16, 17], metal oxide (Al_2O_3 , SnO_2 , TiO_2) [18, 19], polymer and carbon [20-22] has been developed. Among such systems, hollow carbon microspheres (HCMs) are very attractive owing to their unique properties, including high specific surface area, good electrical conductivity, outstanding thermal stability, chemical inertness and satisfactory oxidation resistance at moderate temperature [23], which make them technologically important in a wide range of potential applications. This promise has motivated intense research efforts seeking to develop general routes for synthesizing HCMs.

The state-of-the-art approach for the production of HCMs is relied on templating method [19, 24, 25]. For instance, monodisperse silica or polyester (PS) microspheres are usually used as hard templates, because they are readily available in a wide range of sizes [26, 27]. However, the synthesis procedure is complicated and time consuming, since the hard templates should be synthesized beforehand and then introduce the carbon precursor coating on surface of the templates and finally remove the templates.

Like templating method, emulsion processing is also one option to fabricate hollow microspheres [28]. The difference between them is that the droplets are used as the “templates” in emulsion processing. However, the reaction is not easily controlled, resulting in the formation of aggregated microspheres. Other approaches such as arc discharge approach [29], hydrothermal reduction [30], and self-assembly [31] have been also reported to synthesize HCMs. However, all of these approaches have more or less disadvantages such as low yield, time-consuming and complex fabricating process, that greatly limit their practical applications. Hence, how to fabricate this kind of materials more easily and feasibly still remains a great challenge despite intense attention paid on them nowadays. It is highly essential to explore economical and high-throughput methods for the synthesis of HCMs with high mechanical properties amenable to practical use.

Spray drying is a most widely used industrial process involving particle formation and drying, which has been applied in many areas including the food, pharmaceutical, ceramic, polymer, and chemical industries [32-35]. Many researchers used spray drying method to fabricate various sophisticated particles such as hydroxyapatite powders, chitosan microspheres and metal–organic frameworks [36-38]. The products have usually two structures which are solid or hollow, respectively, and the size distribution of them is relatively narrow that ranges from a few microns to several decades of microns. As the most common used precursor to prepare microspheres, the phenolic precursor had a high yield during the carbonization process and a low-cost. So far, there are few literatures about preparation of phenolic polymer based microspheres through a

spray-drying method to the best of our knowledge.

Here, we exploit the spray-drying technique for the scalable preparation of monodispersed hollow polymer microspheres (HPMs) and HCMs. The basic idea of this synthesis is relied on spraying a phenolic precursor solution into a high-temperature chamber and then rapid removing the solvent from the formed liquid droplets. Since spray drying depends upon many interacting variables and operating conditions, systematic studies are carried out for optimizing the product morphology of the HPMs. Followed by a simple carbonization of optimized HPMs, HCMs can thus be obtained. The present method can improve the efficiency and save the time to some extent, and thus should be of great interest for practical use. To highlight the real application prospect, these low-density microspheres are used as fillers for lightweight and highly rigid syntactic foam, which is the core material in sandwich structures used in aerospace, transportation and deep sea submersibles. The mechanical properties of syntactic foams have been tested, promising this kind of hollow microspheres with tailored physical and chemical properties for further practical applications.

2. Experimental section

2.1 Preparation of the hollow microspheres

The formation process of hollow microspheres is shown in Fig.1. Aqueous solutions of the precursor were prepared by mixing resorcinol (R), formaldehyde (F) and a small amount of Polyvinyl Alcohol (PVA) in the presence of NaHCO_3 . Briefly, the dissolved PVA ($\text{Da}=75000$) were added into the resorcinol and formaldehyde (RF) solution, with

continuous magnetic stirring after which the sol was further diluted with distilled water to the desired content (% w/v). The mixed solution was stirred for 2 h at 45 °C, followed by sodium bicarbonate (NaHCO_3) was dissolved in distilled water and was added to the solution under magnetic stirring. Then the prepared precursor solution was spray-dried using a spray-dryer (OPD-8, Shanghai ohkawara dryers Co., Ltd). The solution was pumped into the atomizer at the rate of 3000 mL/h, together with a constant spray air flow. The inlet temperature was set to 200 °C, generally the outlet temperature was in the range of 100-110 °C. HPMs were discharged continuously from the drying chamber and then collected using a cyclone separator. The prepared HPMs were then carbonized in a nitrogen flow at a certain temperature for 3 h with a heating rate of 2 °C min^{-1} . Finally, the HCMs were obtained and denoted as HCM-x, where x represents the carbonization temperature (600 °C, 800 °C and 1000 °C).

Fig. 1. Formation process of the HCMs using a spray drying method

2.2 Preparation of syntactic foams

HPMs and HCMs with different filler content were added to the phenolic resin

solution slowly, and with stirring of the mixture to minimize gas bubbles in the resin. In order to avoid agglomeration, the microspheres were added in multiple steps to the phenolic resin solution [39]. Then the mixture desolventize was carried out in a vacuum drying oven by vacuum evaporation with 24 h. After that, the mixture was molded using a mold coated with a silicone release agent. The molding operation was carried out in a heated press by raising the temperature from 110 °C (the melting temperature of the phenolic resin) to 180 °C during one hour. The mold was kept at 180 °C for additional one hour under 0.5 MPa to hold the volume unchanged during the curing process. By adding different amounts of microspheres to the phenolic resin matrix, syntactic foams with various properties were thus prepared and were machined to blocks of 25.00×25.00×12.00 mm³ for compression testing.

2.3 Characterization

The morphology of the hollow microspheres was examined by scanning electron microscope (SEM) (a Hitachi S-570, Japan). The particle size distribution and mean particle size were measured using a LS13320 Laser Diffraction Particle Size Analyzer (Beckman-Coulter, America) and distilled water was employed as the dispersion medium.

The flotation ratio and hydrostatic strength were obtained by the follow steps according to the China Standard GJB3594-99: a certain weight (M) of hollow microspheres were immersed in ethanol to separate the integrated hollow microspheres. After separating completely, the floating hollow microspheres were collected and dried,

followed by weighing the mass (m), and the flotation ratio was obtained as m/M (%). In order to obtain the hydrostatic strength, a certain amount of hollow microspheres (M_1) were immersed in ethanol in an autoclave at a constant pressure of 2 MPa. The hollow microspheres that were not destroyed by pressure would float in ethanol and then were collected, dried and weighed (m_1), and the hydrostatic strength was obtained as m_1/M_1 (%).

The syntactic foam samples were evaluated by density and uniaxial compressive strength measurements in the majority of cases. Densities were obtained from the weights and dimensions of the samples. Compression testing of syntactic foams was conducted on a universal testing machine (Instron 3367) at a crosshead speed of 0.5 mm/min for each diameter and procedure based on ASTM Standard C365/C 365M – 05.

3. Results and discussion

3.1 Preparation and morphology control of the HPMs

Fig. 2. The possible formation process of hollow structure during rapid spray drying.

The possible forming mechanism of HPMs is illustrated in Fig. 2. The precursor solution is firstly prepared by mixing resorcinol (R), formaldehyde (F) and a small

amount of PVA in the presence of NaHCO_3 . The spray-drying process starts with atomization of the precursor solution into droplets using a rotating nozzle (Fig. 1). This step is accomplished by simultaneously injecting the solution at a certain feed rate and compressed air at another flow rate. Thus, each precursor droplet is suspended by a gas stream heated to a certain inlet temperature, resulting in the water to begin evaporating and inducing the precursors to diffuse radially to the droplet surface (Fig. 2). This is because the time of the solute diffusing is longer than that of water in the droplets evaporating during the drying process. Then a solid polymer shell appears on the surface, and so the internal pressure increases because the decomposed CO_2 gas from NaHCO_3 and the moisture cannot be released instantly. With the assistance of flexible PVA, the pressure can be released slowly from the RF shell and the expanded hollow structure thus form. This process is continuous with a yield of ca. 240 g per hour through a commercial mini spray dryer (80% yield), and could easily amplify on a large scale by an industrial instrument. The as-obtained HPMs are further carbonized in the nitrogen atmosphere to obtain HCMs.

After a RF polymer shell has formed on an evaporating droplet, it is likely to be deformed by internal pressure, due to pressure differences and changes in material properties caused by thermal polymerization. This period of particle formation process will determine whether a dry particle remains a hollow sphere, forms dimples, or folds on itself. Because the type of morphology affects important particle properties such as density, mechanical properties, cohesiveness or dispersibility, it is desirable to obtain the required spherical morphology. Therefore, the factors including the precursor

composition (RF concentration, PVA content and NaHCO_3 content) and process conditions (inlet temperature, feed speed) were systematically investigated. Two key indicators, morphology and flotation ratio are used to assess the results and are shown in Table 1. The form is overserved directly by SEM, while the latter is evaluated by the mass fraction of floating HPM (weight of hollow product)/ (weight of crude solid collected in the spray dryer), which refer to the purity and yield of hollow microspheres.

Table 1. Experimental design grid and results pertaining to production.

Batches	NaHCO ₃ content	PVA content	RF concentrat ion	Inlet temperature (°C)	Feed speed (mL/min)	Flotation ratio	Morphology from SEM
1	0.1%	3%	7%	200	50	10.2%	Poor-collapsed, wrinkled
2	0.15%	3%	7%	200	50	65.4%	Fair-collapsed, some spherical
3	0.2%	3%	7%	200	50	96.3%	Good-spherical, intact
4	0.3%	3%	7%	200	50	50.6%	Poor-spherical, broken
5	0.2%	1%	7%	200	50	8.5%	Poor-collapsed, capsules
6	0.2%	2%	7%	200	50	16.2%	Poor-collapsed, capsules
7	0.2%	4%	7%	200	50	82.5%	Fair-spherical, broken
8	0.2%	3%	7%	140	50	20.7%	Poor-collapsed, capsules
9	0.2%	3%	7%	240	50	65.1%	Fair-spherical, broken
10	0.2%	3%	3%	200	50	--	No production
11	0.2%	3%	10%	200	50	--	No production
12	0.2%	3%	7%	200	35	95.2%	Good-spherical, intact
13	0.2%	3%	7%	200	65	--	No production

Fig. 3. SEM images of HPMs obtained with different NaHCO_3 contents, (a) 1# (batch number, same below) 0.1%, (b) 2# 0.15%, (c) 3# 0.2% and (d) 4# 0.3%.

The NaHCO_3 is a strong basic catalyst which would promote the polymerization reaction of R-F. More importantly, it is a common inorganic gas forming agent that could be decomposed into CO_2 at a temperature of ca. 60 °C. In our preliminary experiments, we found that other basic catalysts such as Na_2CO_3 , NaOH , KHCO_3 , KOH and $\text{NH}_3\cdot\text{H}_2\text{O}$ could not achieve HPMs. This should be due to insufficient vaporization of water inside the droplet during very fast drying process (about 0.1 s). Thus, the screen of NaHCO_3 is one of prerequisites to promote the formation of hollow structure, which could provide additional gases to blow the microspheres. Furthermore, the content of NaHCO_3 in the precursor solution also plays an important role on the product morphology. As shown in Fig. 3 and Table 1, when the content of NaHCO_3 is low as 0.1%, most of products are wrinkled with only flotation ratio of 10.2%,

suggesting insufficient vaporization. On the contrast, at a high NaHCO_3 content of 0.3%, the microspheres are mostly broken due to overflow of excess gas. Only an appropriate amount of NaHCO_3 (0.2%) could form hollow structure without obvious collapses or fractures, and with a high flotation ratio of 96.3%.

Fig. 4. SEM images of HPMs obtained with different PVA contents, (a) 5# 1%, (b) 6# 2%, (c) 3# 3% and (d) 7# 4%.

Under a strong basic condition, resorcinol can easily react with formaldehyde to form substituted hydroxymethyl resorcinol, which can further condense and crosslink to form a branched network polymer. However, owing to the rigid and fragile characteristic of thermosetting phenolic resin, the RF shell cannot bear the huge volume expansion driven by external CO_2 and vapor, making it impossible to obtain hollow microspheres. Herein, linear PVA with a molecular weight of 75000 Da was employed as a proper additive to modify the viscosity and flexibility of polymer shell. At low PVA

concentrations of 1% and 2%, the collected products are mostly dimpled or wrinkled particles with floatation ratios of only 8.5% and 16.2%, respectively (see Fig. 4 and Table 1). Increasing the PVA concentration to 3%, the obtained polymer microspheres possess good spherical shape with a high floatation ratio of 96.3%. However, excessive PVA causes a reduction in floatation ratio due to the formation of holes on the microspheres. Therefore, a compromise of flexibility and mechanical properties should be necessary for polymer shell to preserve a hollow spherical structure.

Also, the total polymer concentration in the solution is crucial for product morphology. A low concentration of less than 2 % is not effective for sphere formation, while a high concentration of ca. 10% will cause the formation of viscous polymer aggregate adhered on the wall of spray dryer. Solid hollow spheres can be only formed at an appropriate concentration range of 5-7 wt. %.

Fig. 5. SEM images of HPMs obtained with different inlet temperatures, (a) 8# 140 °C, (b) 3# 200 °C, and (c) 9# 240°C.

The product morphology is also strikingly depended on process conditions such as inlet temperature and feed speed, of which the first-named is more important. High temperature will accelerate the droplet evaporation and so the solvent on the surface runs away quickly. However, while the inlet temperature is up to 240 °C, fractured

structure will appear as evaporation rates are so fast (Fig. 5). But if the inlet temperature is less than 140 °C, the water cannot be evaporated immediately, so the products are wrinkled with a low flotation ration of 20.7%. Thus, the inlet temperature for the hollow microsphere is selected to be 200 °C. The feed speed has also important effect on the product morphology, in which only a moderate feed could produce well-fine HPMs.

Thus, by controlling the parameters of the spray-drying method, one can prepare hollow microspheres with optimized morphology and purity. In this particular study, the parameters are used to a NaHCO₃ concentration of 0.2%, a PVA concentration of 3%, a polymer concentration of 7%, an inlet temperature of 200 °C, and feed flow of 25 mL/min. The obtained polymer microspheres are pink powders (See Fig. S1), with the size from 15 to 80 μm and a floatation ratio of 96.3%. The bulk density is determined to be ca. 0.089 g/cm³. The mechanical property of polymer microspheres, evaluated with the number of microspheres not destroyed at a certain hydrostatic pressure (2 MPa), is as high as 75%, guaranteeing their real applications especially in processing of composite materials by pressure casting, extrusion, or other methods.

3.2 Characterization of the HCMs

After preparation of the HPMs with the optimized conditions, the HCMs could be easily obtained by a simple carbonization at different temperatures. As show in Fig. 6, it is obvious that the HCMs could retain very well their spherical shape without fracture, but their particle size seems to decrease after carbonization. This could be further confirmed by DSL measurement and shown in Fig. 7. The size of pristine HPMs size

locates in the range of 15–80 μm with a mean size of 37 μm . After carbonization, the size distribution curve shifts to a lower region of 10–60 μm with a mean size of 23 μm , which should be due to the shrinkage during the carbonization process.

Fig. 6. SEM images of HPMs (a) and corresponding HCMs at different carbonization temperatures, (b) 600 °C, (c) 800 °C, (d) 1000 °C.

Fig. 7. Particle size distribution of HPMs and HCMs with different temperature.

Fig. 8. Nitrogen adsorption–desorption isotherms (a), and the resulting NL-DFT pore size distribution curves (b) of HCMs.

During the carbonization, the micropores could be created by the release of volatile that is dependent on the carbonization temperature. Fig. 8 shows the N_2 adsorption-desorption isotherms and the resulting DFT pore size distributions of the HCMs. All isotherms exhibit type I with a sharp increment at low relative pressure, responding to the presence of considerable micropores. The detailed porosity parameters are summarized in Table S1. The specific surface areas (S_{BET}) and total pore volumes (V_{total}) for HCM samples are relatively low as 350-500 m^2/g and 0.15-0.24

cm³/g, respectively. However, the introduction of micropores does not affect significantly the flotation ratios of hollow microspheres, possibly due to the poor connectedness of these micropores. As listed in Table 2, the flotation ratios of HCMs are 94.2%, 92.6% and 90.4% for different carbonization temperatures of 600 °C, 800 °C and 1000 °C, respectively, which are very close to the flotation ratio of pristine HPMs. Furthermore, the buoyancy properties, evaluated by the mass fraction of floating HCMs in the acetone, are still up to 85%, ensuring their applications as syntactic foam fillers in different liquid medium. However, the hydrostatic strength of HCMs are significantly lower than that of HPMs, due to more rigid and fragile of carbon framework than polymer framework. In addition, the hydrostatic strength decreases gradually with the carbonization temperature increasing. This point should be paid more attention during molding or other processing.

Table 2. Flotation ratio of HCMs with different temperatures.

Sample	Bulk density ^a (g/cm ³)	Flotation ratio ^b (%)	Hydrostatic strength ^c (%)	Average particle size ^d (μm)
HPM	0.089	96.3	75	37
HCM-600	0.095	94.2	73.3	23.7
HCM-800	0.099	92.6	71.9	23
HCM-1000	0.11	90.4	69.7	22.8

^{a,b} obtained by the method in GJB3594-99; ^c measured using DSL measurement.

3.3 Preparation of the syntactic foam

Like glass hollow microbeads, HPMs and HCMs with low bulk densities have great potential as highly efficient fillers for low-density syntactic foams [40]. As a proof-of-concept application, a series of syntactic foams consisting of HPMs and HCMs (HCM-800) as fillers and phenolic resin as matrix are prepared via a simple hot-press molding. The content of the fillers changes from 10 to 30 wt. % in the syntactic foams, and the resultant bulk density and properties of the syntactic foams are summarized in Table 3. Apparently, with the increase of the content of the fillers, the density decreases remarkably from 1.28 g/cm³ of phenolic resin block to 1 g/cm³ of syntactic foam with 10 wt. % filler and further to 0.48 g/cm³ with 30 wt. % filler.

Table 3. The densities and mechanical properties parameters of the syntactic foams.

Content	Density		Compressive strength		Young's modulus	
	(g/cm ³)		(MPa)		(MPa)	
	HPM	HCM	HPM	HCM	HPM	HCM
Pure resin	1.28		122.3		2017	
10 wt. %	1.04	1.06	69.3	100.2	1420	1289
20 wt. %	0.69	0.69	27.4	29.3	404	953
30 wt. %	0.48	0.50	18.6	19.4	244	504

Fig.9. Morphology of the syntactic foams of HPMs (a) 10 wt. %, (b) 20 wt. %, (c) 30 wt. %, and HCMs (d) 10 wt. %, (e) 20 wt. %, (f) 30 wt. %.

The SEM images of these syntactic foams are shown in Fig. 9. It can be observed that the syntactic foams contain three phases: the hollow microspheres, the phenolic resin matrix, and the internal voids. The latter is an incidental part of the syntactic foam and not easy to avoid their formation. Due to their good dispersion, the microspheres could well dispersed into phenolic resin matrix to form a relatively compact structure. However, when the filler content increases to 30%, the resin could not fully fill the space between the microspheres, so lots of internal voids are left. Thus, the measured density values are significantly lower than the calculated ones ($\sim 0.55 \text{ g/cm}^3$). The existence of these voids could reduce the density of the syntactic foams, but may at a cost of mechanical properties.

Fig. 10. Compressive strain-compressive stress curves of syntactic foams with different content HPMs and HCMs.

The compressive stress-strain curves of these syntactic foams are shown in Fig. 10. At a low filler content of 10 wt. %, the curves show an initial linear elastic loading segment and end quickly when the syntactic foams reach the maximum compressive strengths, just like the curve of pure resin, of 69.3 MPa for the HPM syntactic foams and 100.2 MPa for the HCM syntactic foams, lower than the pure resin (122 MPa). The compressive strength represents the point at which fracture initiate, and the shape of the curve suggests that the hollow microspheres of the foams do not get crushed prior to the peak stress. The higher compressive strength of HCM-derived foam should be due to the rigid structure of carbon framework which could bear higher loading. However, the curves of the foams with high filler content are obviously different, in which a plateau regime following the maximum compressive strength could be easily observed, indicating to the stress becomes nearly constant for further compression [41]. This is

the implosion and densification stage when hollow microspheres are crushed exposing their internal hollow volume, while microsphere debris and matrix resin could occupy this volume under the compression. The maximum compressive strength decrease significantly to 27.4 MPa and 29.3 MPa for 20 wt. % HPM syntactic foams and 20 wt. % HCM syntactic foams, respectively. Further increasing the filler content to 30 wt. %, even no definite fracture point is observed during the compression of syntactic foams. And the maximum compressive strength decrease to only ca.19 MPa. On the other hand, the Young's modulus of the syntactic foams are decreasing with the increase of hollow microspheres content (shown in Table 3), indicating that the syntactic foams have a good property of toughness.

Fig. 11. SEM images of the syntactic foams after compression testing, of HPMs (a) 10 wt. %, (b) 20 wt. %, (c) 30 wt. %, and HCMs (d) 10 wt. %, (e) 20 wt. %, (f) 30 wt. %.

After the compression testing, fractured surfaces were examined by SEM as shown in Fig. 11. For low filler content the failure is matrix dominated, since the microspheres

remain substantially unbroken, being the same with the original morphology. It could be deduced that the crack initiated from an internal void will propagate towards the nearest internal void and grow through the interface between the microspheres and the resin, resulting in the rupture of resin matrix and partial debonding of the microspheres. Apparently, the rigid HCMs could sustain high loading, while the flexible HPMs show large distortion. Further increasing the filler content, the internal void increases greatly and resin matrix becomes fragile. Extra energy will concentrate to break the interfacial force, leading to the fracturing of microspheres as observed by SEM images. The observed fractured microstructure is in good agreement with the results of the compression testing. Combined the results of low bulk density and high mechanical properties, it is believed these microspheres should exhibit great potential for the manufacturing of light-weight materials with the increase of the filler content.

4. Conclusions

In conclusion, we demonstrate a general, rapid and low-cost method for preparing hollow polymer and carbon microspheres via a spray-drying system by using resorcinol-formaldehyde as precursors. This spray-drying strategy could drastically reduce their production times and costs, and enables continuous and scalable synthesis of hollow microspheres for practical use. Effects of precursor compositions and operating conditions on the morphology and purity of the microspheres are studied to determine the best method of producing HPMs. Following a simple carbonization, high-quality HCMs are achieved. Using these HPMs and HCMs, having a lower

density compared to the matrix material, allows for the manufacturing of light-weight materials with the increase of the filler content. Given the availability of huge quantities by the spray-drying method, these hollow polymer and carbon microspheres should have great potential for numerous applications, including catalysis, adsorption, electrode materials, drug delivery, packing materials for high performance liquid chromatography and so forth.

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