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Preparation of mesocarbon microbeads from coal tar

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Mesocarbon microbeads (MCMB) was prepared from coal tars with various primary pyridine insoluble fraction (PI) contents from 0 to 3.7 wt %, through heat treatment at 430–480 °C for different time under autoginious pressure. The heat treated coal tars were filtered under 150 °C and the residue was rinsed with pyridine. MCMB was obtained as the pyridine insoluble fraction. Both yield and diameter of MCMB increased with the increasing of reaction temperature and holding time. It was found that primary PI also had strong influence on the formation of MCMB, which restricting coalescence between mesophase spheres by sticking on the surface of mesophase spheres or dispersing in the matrix. Low temperature, short reaction time and high PI content resulted in the MCMB with small diameter and narrow size distribution. Carbon block with 1.75 g/cm^3 density could be easily obtained from the MCMB after molded under 100 MPa and carbonized at 1000 °C.

1. Introduction

It is well known that aromatic hydrocarbons, such as coal tar, heavy oil residue and pitch can gradually transform into mesophase during liquid phase carbonization [1]. Mesophase pitch has been used to prepare high performance pitch based carbon fiber for many years [2, 3]. However, before bulk mesophase forms, the mesophase exists as a large number of mesophase spheres. Such spheres, after separated from matrix, are generally called mesocarbon microbeads [4, 5], which have been expected to be an excellent candidate raw material for high density carbon [6], column packing material [7], super active carbon [8] and electrode material of lithium ion rechargeable battery [9]. Several methods have been established and industrial scale production has also been started for some years [10, 11, 12], But the MCMB derived from emulsion and suspension methods needs to be stabilized before carbonization. Superior to it, the MCMB prepared by heat treatment shows the character of insoluble and infusible, except low yield and wide diameter distribution. The key factor to get MCMB with high yield and narrow size distribution is to prevent mesophase spheres from coalescing during heat treatment. Carbon black was reported to be a good additive to control the polymerization reaction and the diameter of MCMB [13], but it is difficult to disperse the carbon black thoroughly into raw materials. Some organic metal substances, such as phthalocyanine, ferrocene were also found to be beneficial to increase the yields of MCMB and to have effects preventing coalescence between mesophase spheres [14, 15], but the metals would remain in the MCMB, which may be harmful to some kind of usage like electrode for battery. The primary PI particles in coal tar was reported to disperse in coal tar evenly and consist of carbon black-like substances [16]. The influence of primary PI upon the development of mesophase, particularly with reference to the nucleation, growth and coalescence of mesophase, has been previously reported [17–22]. According to the results of Brooks' [17] and Marsh's [18], primary PI (or QI) affects the development of the mesophase in two ways. Initially, it acts as nucleation sites, and later restricts the growth and coalescence of mesophase. Yamada [4] and Tillmanns [19], on the other hand, concluded that addition of extracted primary PI accelerated the formation of mesophase. Staddlehofer [20] and Twigg [22], however, believed that additions of up to 10 wt % primary quinoline insoluble fraction (QI) do not affect the rate of mesophase formation. Marsh has studied the structure and behavior of QI [20], also suggesting that the primary acts to restrict mesophase to coalesce, where the derived mesophase spheres extracted from heat treated pitch distorted from extraction. Therefore, the present study aims to seek a method by which MCMB can be obtained with high yield and narrow size distribution as well as easy separation.

2. Experimental

2.1. Raw material

A coal tar (CT0) with 3.7 wt % PI was used as the raw material, and some properties of the coal tar and the

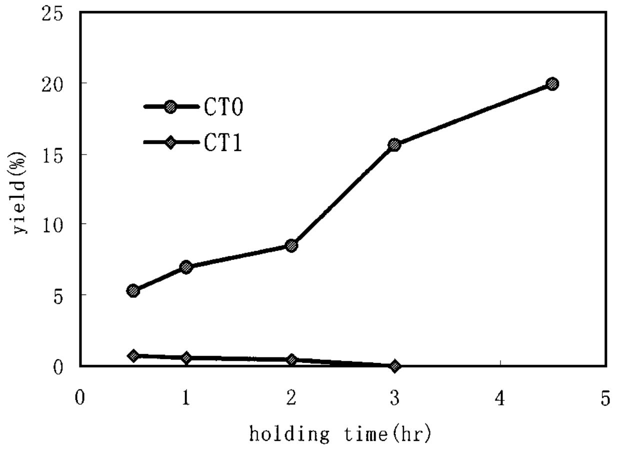
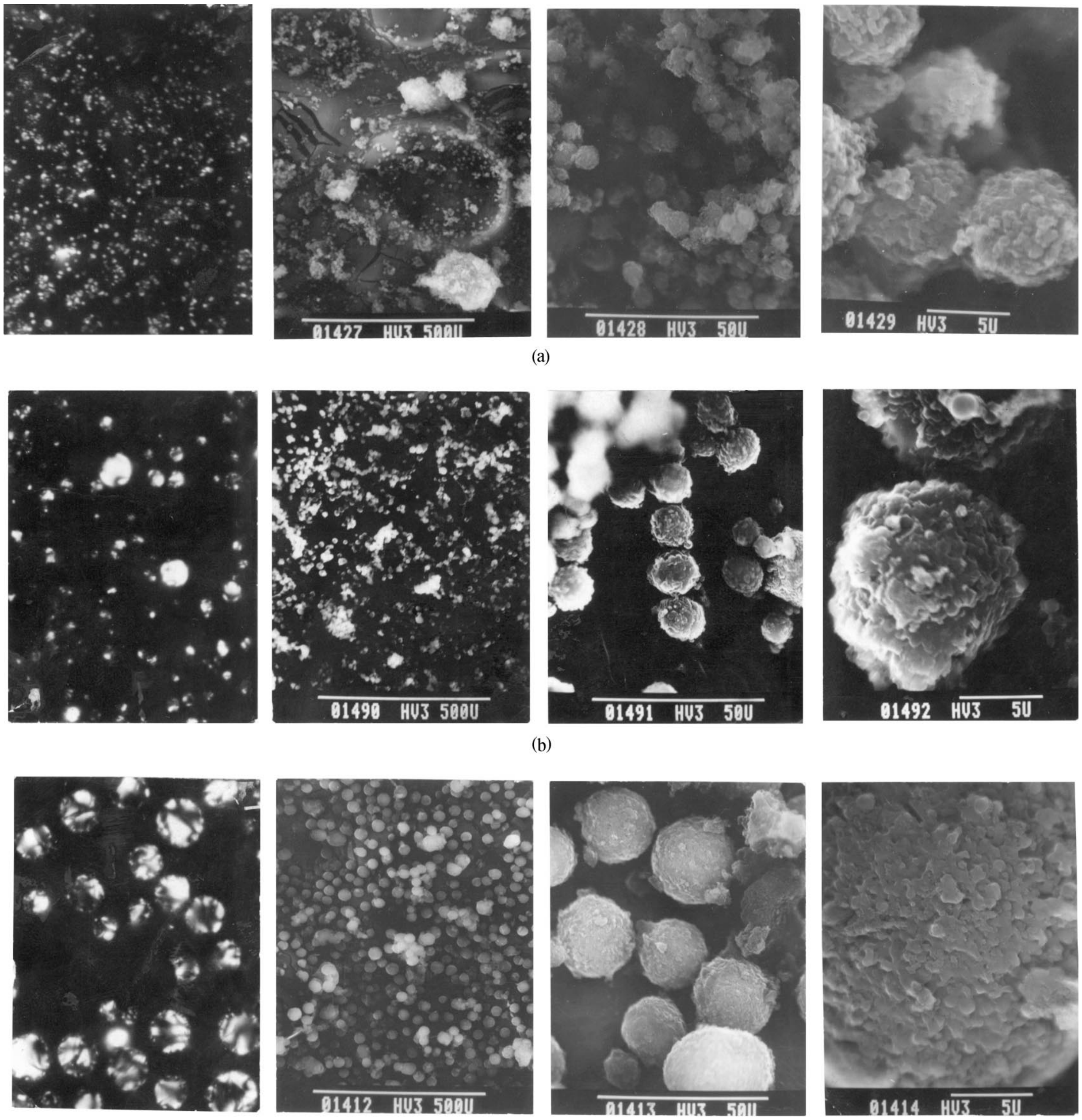


Figure 1 The yield of MCMB separated from CT0 and CT1 heat treated at 450 °C for different time.

primary PI are listed in Table I. CT0 was also filtered at 150 °C, to remove PI and get a PI-free coal tar (CT1). Coal tars with different PI contents (0.3–1.85 wt %) was prepared by mixing CT0 and CT1 in various proportion.

2.2. Preparation of MCMB

The coal tars were heat treated firstly at 250 °C in an autoclave under N_2 blowing to remove volatile fractions, and then carbonized at 435–480 °C for 0.5–4.5 h under autogenous pressure. The products were filtered at 150 °C, and the residues were extracted in Sohlet extraction using pyridine. After dried at 50 °C under vacuum, MCMB was obtained as the pyridine insoluble fraction.



(a)

(b)

(c)

Figure 2 The optical texture of heat treated coal tars and SEM micrographs of MCMB derived from CT0(a–d) and CT1(e) carbonized at 450 °C for different time. a: 1 h, b: 2 h, c: 3 h, d: 4.5 h, e: 2 h. (*Continued*)

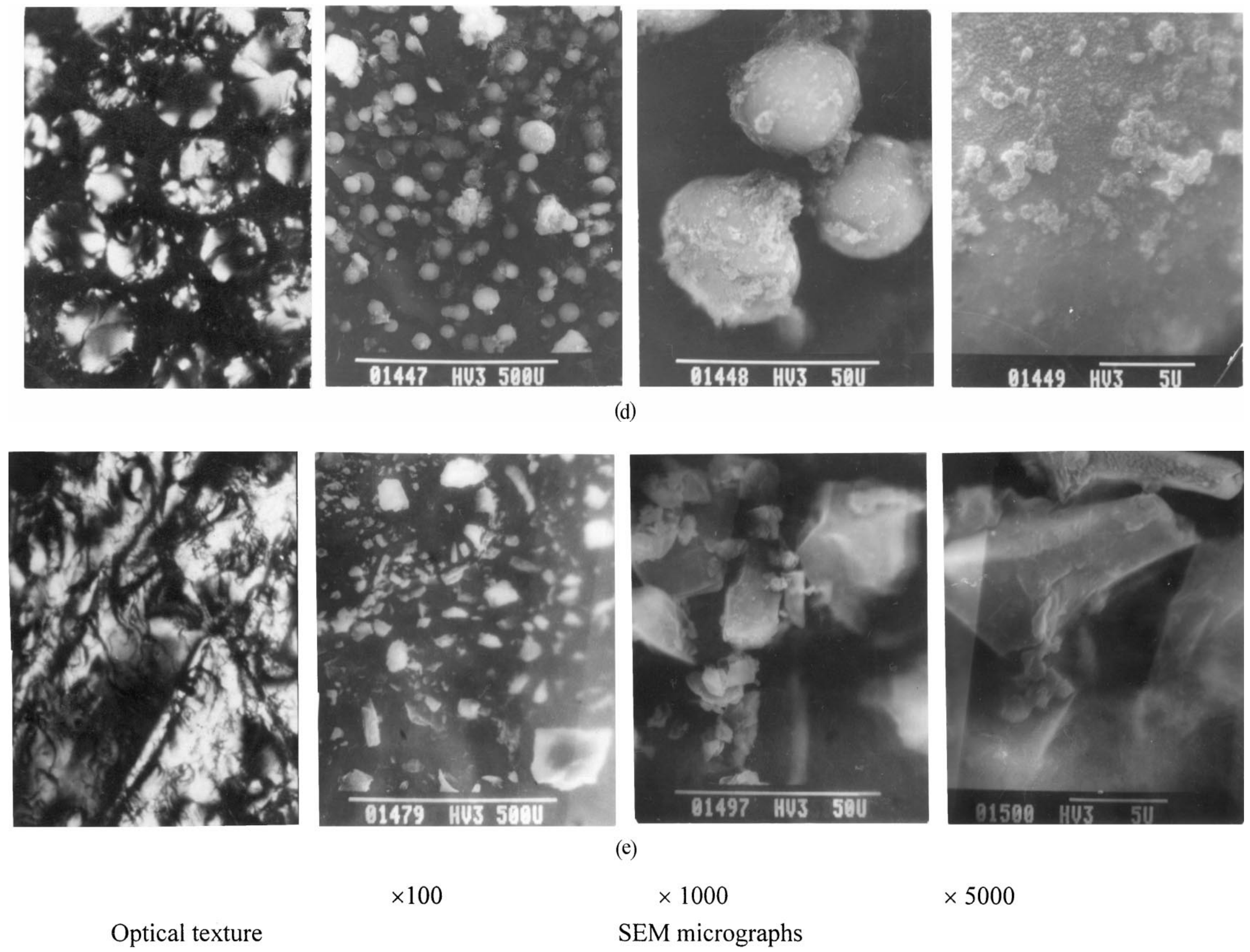


Figure 2 (*Continued*).

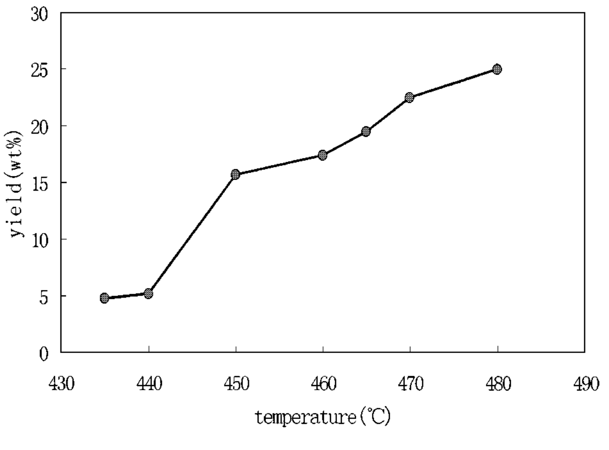


Figure 3 Yield of MCMB from CT0 carbonized at various temperatures for 2 h.

2.3. Observation of MCMB

The mesophase spheres in heat treated coal tars were observed under a polarized optical microscope (Leitz Vario Orthomat) after polishing. The MCMB was also bserved under a scanning electron microscope (SEM) (Hitachi H-600).

2.4. Preparation of carbon block

The MCMB derived from CT0 carbonized at 480 °C for 3 hours was molded under pressure of 100 MPa. Carbon blocks were obtained by carbonization of green solids at 500–1000 °C for 30 min. The heating program was 1.0 °C/min below 600 °C, and 10 °C/min above 600 °C.

3. Results

3.1. The influence of reaction time on the MCMB

Fig. 1 shows the relationship between the yield of MCMB and reaction time at 450 °C. The yield of MCMB increases from 5 to 20 wt % as holding time prolongs from 0.5 to 4.5 h. MCMB could not be obtained from CT1 under the same conditions due to serious coalescence. Fig. 2a–d shows the optical and SEM micrographs of the MCMB from CT0. A lot of fine particles, probably being the primary PI, are observed adhering to the surface of MCMB. The optical texture of the pitch prepared from CT1 is also illustrated in Fig. 2e. It can be observed that the MCMB from CT0 became large after long reaction time. However some irregular spheres appeared after soaking for 4.5 h due to partial coalescence between spheres as showed in Fig. 2d.

3.2. Influence of reaction temperature on MCMB

Fig. 3 gives the relationship between the yield of the MCMB derived from CT0 and reaction temperature, where the reaction time is 3 h. The yield of MCMB

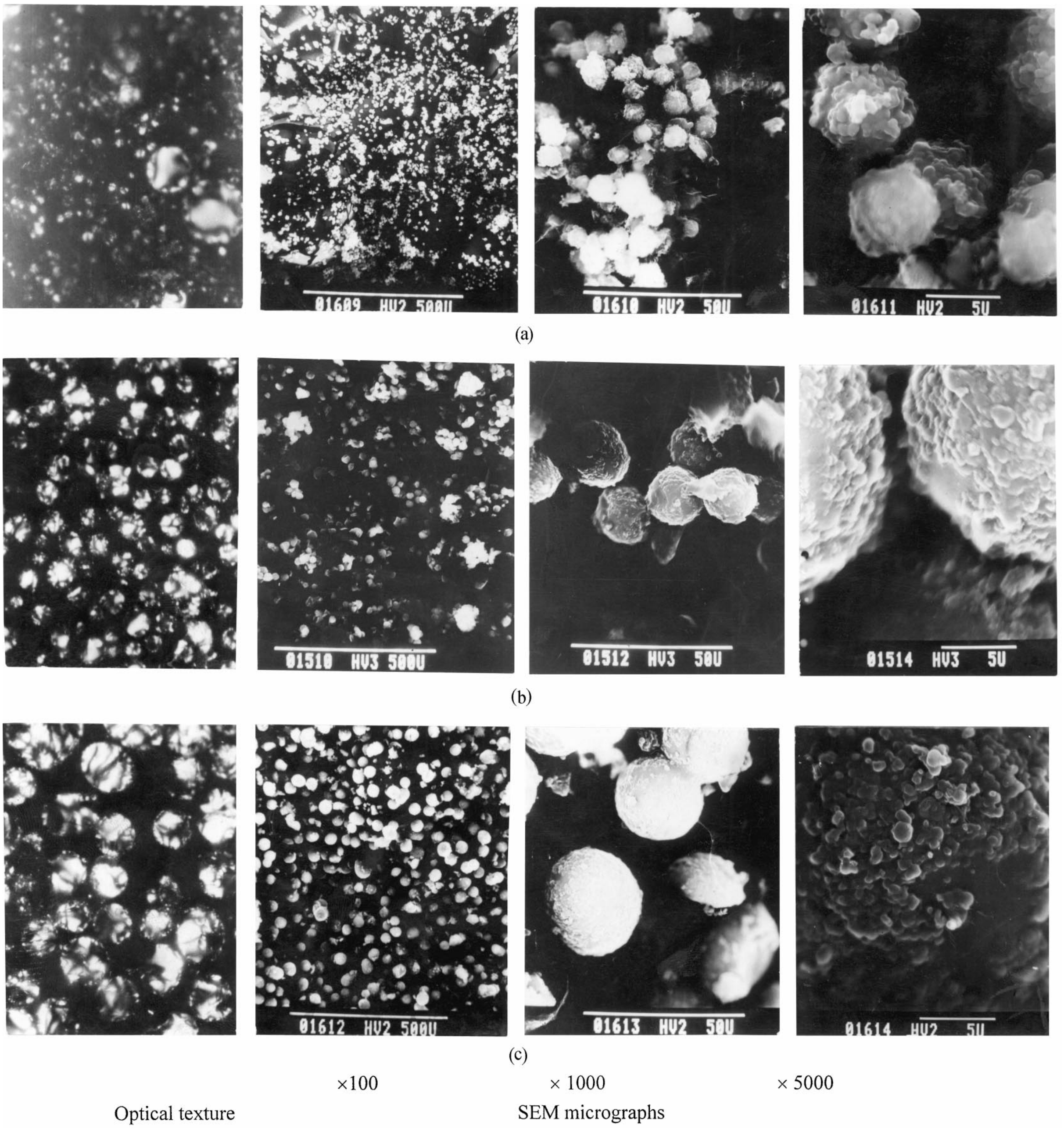


Figure 4 The optical texture of heat treated coal tars and SEM micrographs of MCMB derived from CT0 carbonized at different temperatures for 3 h. a: 440 °C, b: 460 °C, c: 480 °C.

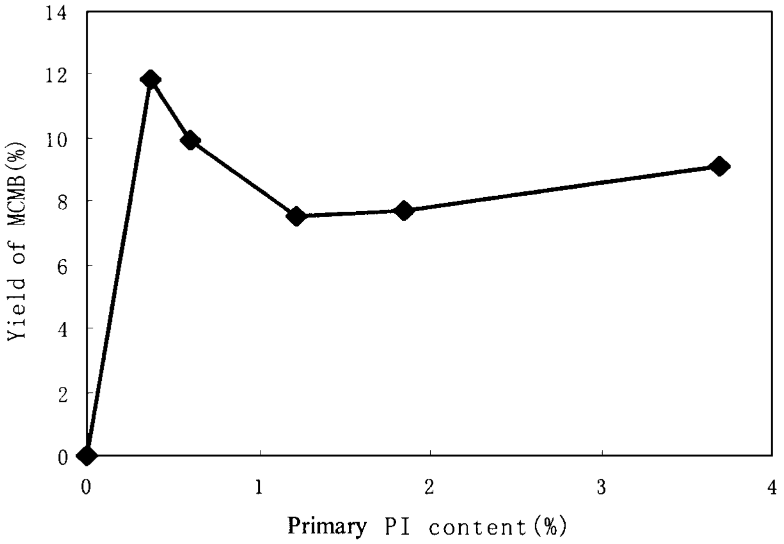


Figure 5 The yield of MCMB from different PI content coal tars carbonized at 450 °C for h.

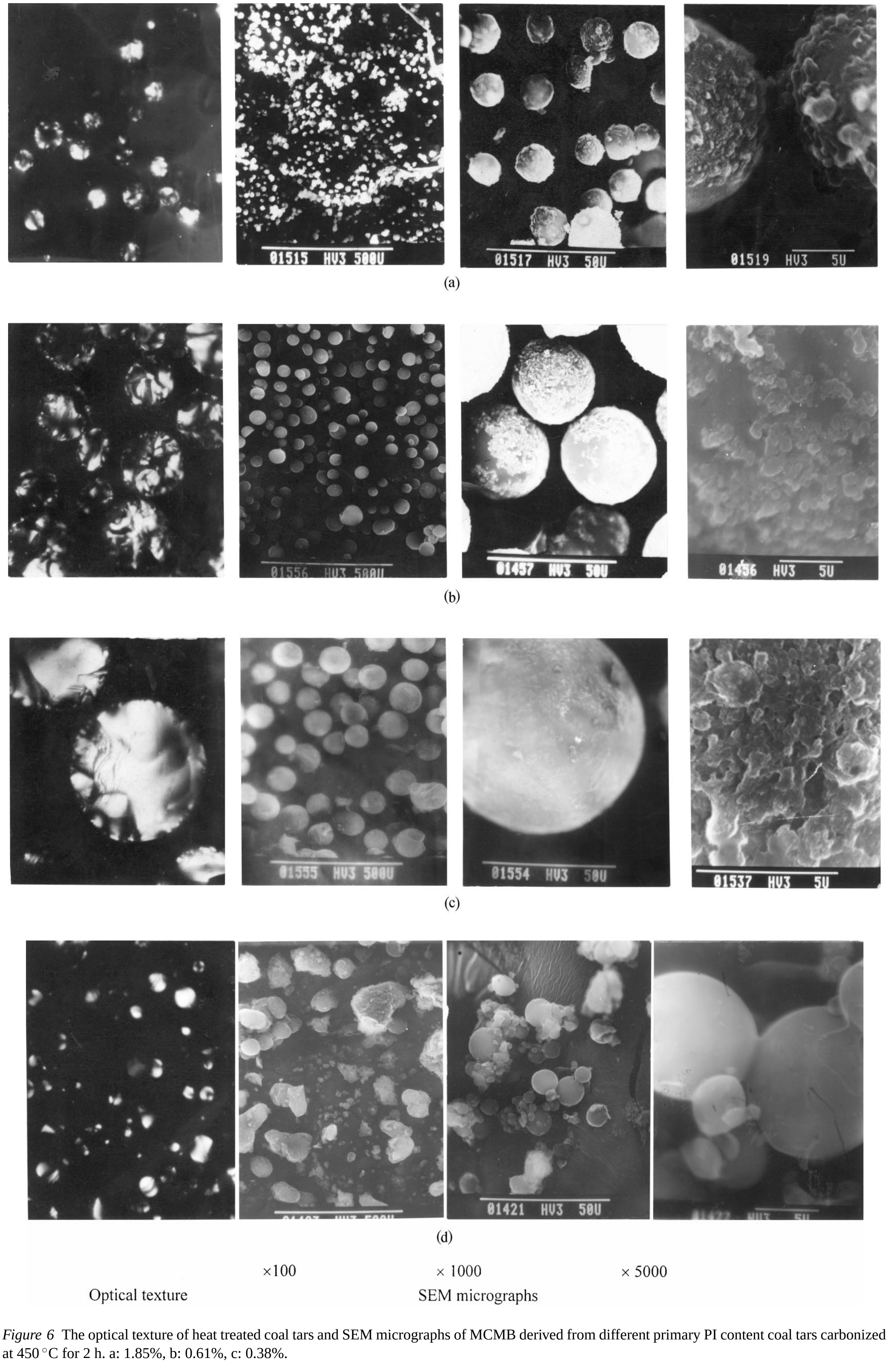


Figure 6 The optical texture of heat treated coal tars and SEM micrographs of MCMB derived from different primary PI content coal tars carbonized at 450 °C for 2 h. a: 1.85%, b: 0.61%, c: 0.38%.

also increases with the rising of reaction temperature, reaching 24.5 wt % at 480 °C. It indicates that reaction temperature has much more influence on the yield of MCMB than holding time does. It may be due to that the small molecule components such as benzene soluble fraction (BS), which is stable at low temperature, probably takes part in the reaction at high temperature. Fig. 4 shows the optical texture of heat treated coal tars and SEM micrographs of separated MCMB prepared from CT0 under various reaction temperatures. As anticipated, the diameter of MCMB becomes large at high temperatures. Also a lot of small particles adhere to the surface of the MCMB.

3.3. Influence of primary PI content on MCMB

Fig. 5 reveals the relationship between the yield of MCMB and primary PI content of coal tars. The yield of MCMB decreases sharply with the increasing of primary PI contents from 0.38 to 1.23 wt %, and becomes very stable with further high primary PI contents up to 3.7%. Fig. 6 illustrates the optical texture of mesophase spheres existing in pitch SEM micrographs of MCMB prepared from coal tars with various primary PI contents. The diameter of MCMB decreases with increasing of primary PI content. MCMB with a rather low yield of 2 wt % was also obtained from CT1 under a high reaction temperature of 480 °C, short time of 5 min and a high quench rate of 200 °C/min to room temperature. The optical texture of the pitch and the corresponding SEM micrographs of MCMB were shown in Fig. 6d. It can be observed that the surface of this MCMB is very smooth.

3.4. The diameter distribution of MCMB

Fig. 7 shows the diameter distributions of the MCMB prepared under various conditions. The coal tars with 1.23–3.7 wt % primary PI generated very narrow size distribution of MCMB, ranging between 5–20 μ. However, as primary PI contents further decreases to 0.61–0.38 wt %, the diameter distribution become quite wide varying from 10–65 μ and 20–140 μ, respectively. MCMB larger than 100 μ appeared from the coal tar with primary PI of 0.38 wt %.

The reaction time for CT0 at 450 °C are also found very influential on the diameter distribution. Below 3 h, the diameters distributes in the range of 5–30 μ. The diameter range of MCMB extends to 5–60 μ when the holding time is 4.5 h.

In comparison to reaction time and primary PI, the reaction temperature has weaker influence on the diameter distribution of MCMB, although the diameters of MCMB also become large at high temperature. The diameters distributed in the range of 5–10, 10–30, 10–40, 20–50 and 20–50 μ, respectively, for the temperatures of 440, 450, 460, 470, 480 °C.

The relationships between average diameter and primary PI contents, holding times and reaction temperatures are illustrated in Figs 8–10, respectively. It can also be seen that the average diameter of MCMB is sensitive to the reaction conditions as well as primary PI contents.

3.5. Carbon block from the MCMB

Fig. 11 shows the relationship between the bulk density of carbon blocks and the carbonization temperature. The bulk density of the carbon block that made from the

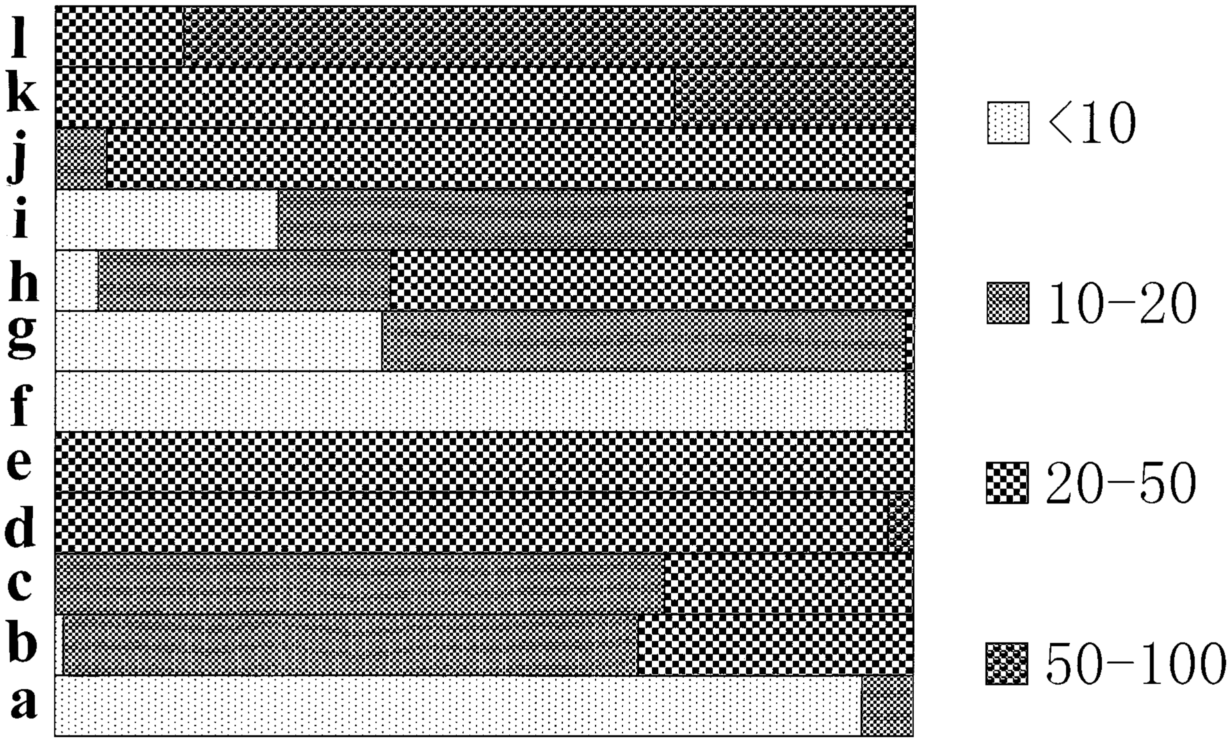


Figure 7 The diameter distribution of MCMB(μ). Conditions: a: CT0, 440 °C, 3 h; b: CT0, 450 °C, 3 h; c: CT0, 460 °C, 3 h; d: CT0, 470 °C, 3 h; e: CT0, 480 °C, 3 h; f: CT0, 450 °C, 1 h; g: CT0, 450 °C, 2 h; h: CT0, 450 °C, 4.5 h; i: 1.85%PI, 450 °C, 2 h; j: 1.23%PI, 450 °C, 1 h; k: 0.61%PI, 1 h; l: 0.38%PI.

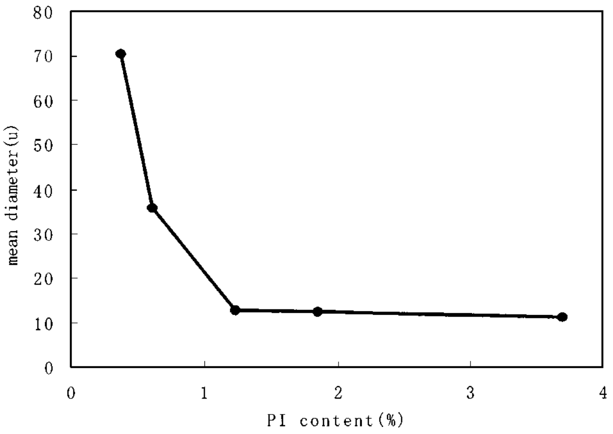


Figure 8 The influence of primary PI content on the average diameter of MCMB. Carbonization condition: 450 °C, 2 h.

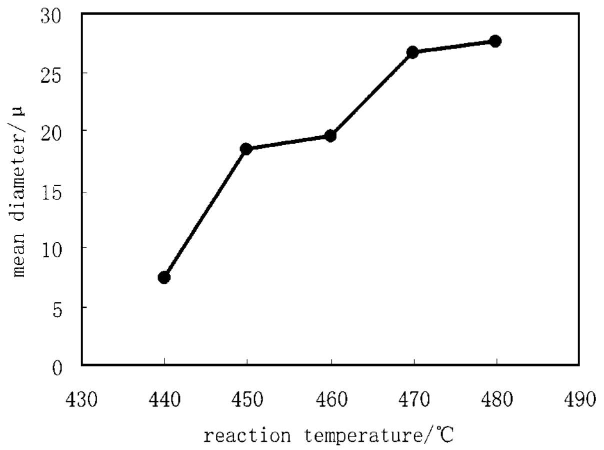


Figure 9 The influence of temperature on the average diameter of MCMB from CT0 carbonized for 3 h.

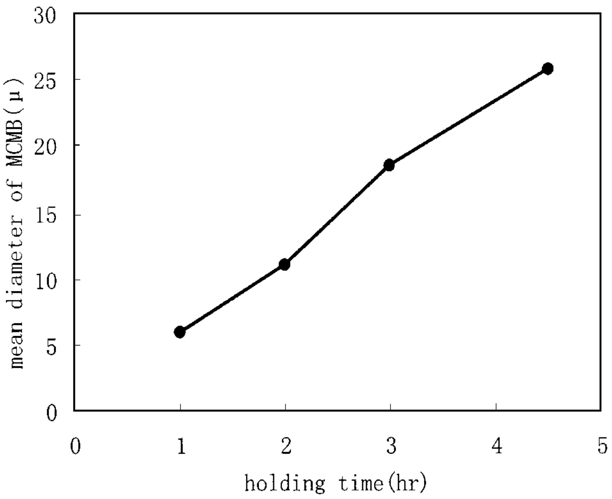


Figure 10 The influence of holding time on the average size of MCMB derived from CT0 carbonized at 450 °C.

MCMB derived from CT0 polymerized at 480 °C for 3 h increases from 1.25 g/cm^3 for green block to 1.65 g/cm^3 for carbonized solid at 1000 °C. While the density of the carbon block made from the MCMB derived from the coal tar with PI of 1.85 wt % reaches 1.75 g/cm^3 after carbonization of 1000 °C, and increases to 1.92 g/cm^3 after heat treatment of 2500 °C. The optical textures of the former green and the 1000 °C carbonized blocks are shown in Fig. 12. Obvious volume shrinkage can be observed after carbonization. No crack was formed on the carbonized solid although the MCMB was not stabilized through oxidization before carbonization.

4. Discussion

The present study reveals that the yield, diameter as well as the diameter distribution of MCMB can be controlled by adjusting the PI content in coal tar and reaction conditions. The primary PI plays a very important role in the preparation of MCMB. No MCMB but domain mesophase was obtained from CT1 carbonized at 450 °C for 3 h due to the serious coalescence, while MCMB could be easily obtained from coal tars with primary PI contents of 0.38–3.7 wt %. These indicate that the primary PI particles existing in the coal tar restricted the coalescence between mesophase spheres. The reason maybe as following, which was suggested previously [21]. As a new phase of mesophase appears, it owns very high surface energy, making the spheres have strong tendency of coalescence. The primary PI particles adsorbed on the surface of the spheres discharge the surplus surface energy effectively to prevent the spheres from coalescing. Meanwhile the primary PI particles sticking on the surface of MCMB also limited the adsorption of small molecular components onto the aromatic layers of MCMB, thus, depressing the griwth of mesophase spheres, resulting in the MCMB with small diameter. No clear evidence in present study shows that primary PI acted as nucleation sites as reported before [17,18].

The MCMB with a rather low yield was obtained from CT1 when it was carbonized at high temperature for short time with very rapidly quenching. Nevertheless, there were still some coalescence due to absence of fine PI particles, which again proved the importance of primary PI particles.

Reaction temperature and holding time are certainly influential on the yield as well as the diameter of MCMB. High reaction temperature and long holding time are beneficial to generation of mesophase spheres, and to the spheres adsorbing more small aromatic molecules, resulting in high yield and large diameter of MCMB. However, excessive high temperature and long holding time makes spheres coalesce, destroys the form of spheres, and thus reduces the yield of MCMB.

MCMB was obtained with a yield as high as 25 wt % from CT0 after heat treatment at 480 °C for 3 h. It means that the cost of MCMB can be reduced in comparison with emulsion method through which the MCMB derived needs to be stabilized before successive carbonization process.

Carbon block with bulk density of 1.75 g/cm^3 can be easily obtained from the present MCMB after molded under 100 MPa and carbonized at 1000 °C. The self-sintering property was excellent for the MCMB since no crack was found on the carbon blocks.

At present, the remained problem is the relative low yield for MCMB with small diameter that is strongly demanded by electrode industries and high density carbon. It is possible to select the reaction conditions and primary PI content in the view to control the yield and diameter of MCMB. The yield of MCMB increases at

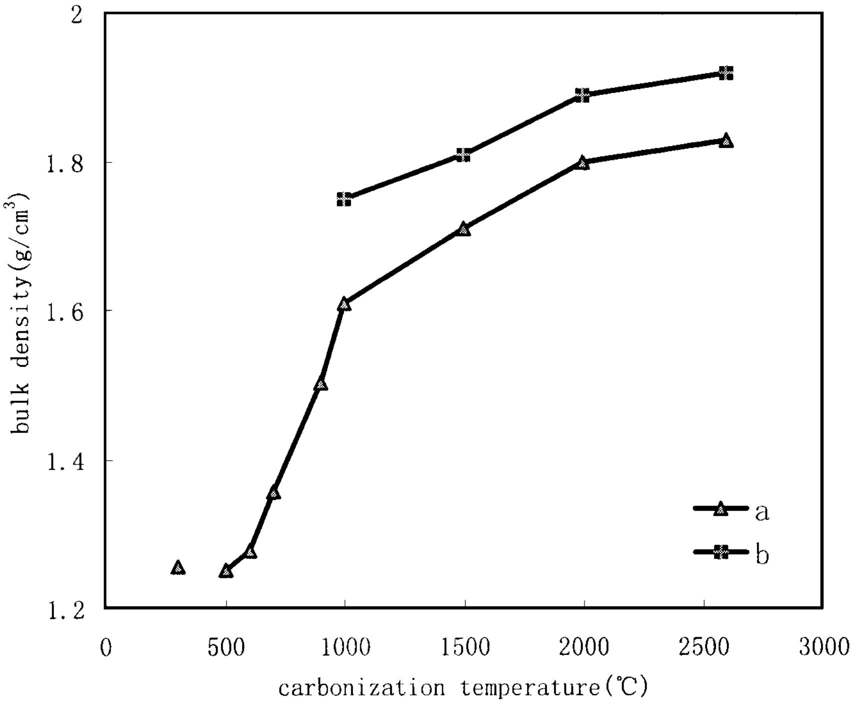


Figure 11 The influence of heat-treatment temperature on the weight loss, volume shrinkage and bulk density of carbon solids.

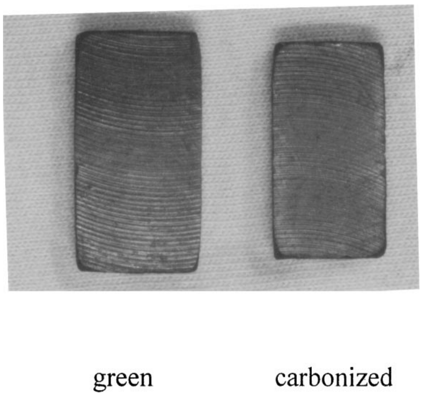


Figure 12 The optical texture of green solid and carbonized one at 1000 °C.

high reaction temperature, since more active sites will appear at high temperature to generate more spheres, while adding more primary PI particles or enhancing quench rate can restrict coalescence of spheres. Nevertheless, to get MCMB with higher yield and controllable diameter distribution is still a major work for its wide application as excellent candidate for advanced materials. The terminal destination is that the heat treatment conditions and the primary PI content in coal tar can be previously determined for a required size MCMB of high yield.

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