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Letter to the editor

Observation of “in-contact” characteristics of Brooks–Taylor mesophase spheres obtained by high-temperature centrifugation

A B S T R A C T

The “in-contact” mesophase spheres were obtained successfully by separating from mesophase sphere-containing pitches at a relatively low temperature of 220 °C using high-temperature centrifugation. The optical and scanning electron microscopies were employed to examine the characteristics of mesophase pitch samples. The results indicated that strong interactions between mesophase spheres started at relatively low temperature, with the contact point(s) occurring three dimensionally around spheres. The mesophase layers between different spheres appeared to dock with each other behind the scene, as these spheres came close enough and their lamellae at the contact point were orientated parallel with each other.

Since the discovery of the carbonaceous mesophase in the early 1960s by Brooks and Taylor [1], many workers have investigated the structural features of Brooks–Taylor mesophase spheres, kinetics and mechanism of the formation of mesophase pitches [2–6]. It is widely believed that the coalescence process of mesophase spheres includes: individual spheres before contact, just contacting, shortly after contact and contact incomplete to a large sphere [1,2]. Most have focused on the structural features of single mesophase spheres before coalescence, the coalesced mesophase and bulk mesophase. However, little is known about the coalescence itself, particularly at the very moment of contact. Normally mesophase spheres coalesce and grow up in a very short time, especially for thermally condensed mesophase pitches where the process temperature of 330–450 °C is required [1], making it very difficult to observe directly. In this paper, high-temperature centrifugation was employed to successfully capture the moment when mesophase spheres get in contact with each other at a reduced temperature, enabling us to look into how the lamellae components start to establish their bonding and develop the anisotropic mesophase.

The high-temperature centrifugation was operated under the centrifugal conditions of 220 °C and 50 G (the gravity $G = 9.8\ m/s^2$) to separate a mesophase pitch derived from petroleum pitch. Both the parent pitch and the enriched mesophase pitch were examined by polarized light microscopy. The pitch samples essentially containing mesophase spheres were obtained by solvent extraction using N-methyl pyrrolidone (NMP) to remove the isotropic pitch after centrifugation. Subsequently, the extracted mesophase particles were treated at 300 °C for 30 min in air flow, and then carbonized at 1200 °C for 30 min in nitrogen atmosphere. The oxidative step was to stabilize the mesophase spheres in order to prevent them from melting or fusion in the subsequent heat treatment. The carbonized samples were examined by scanning electron microscope (JSM-6700F).

The optical micrographs of sphere-enriched samples by centrifugation were shown in Fig. 1. It is interesting to note that the mesophase spheres with diameter of 10–20 μm, appeared to be just contacted with each other in an intact situation, rather than separated originally (micrographs of the parent pitch provided as Supplementary data), although it was difficult to judge any interactions existed between the spheres at this point. The periodic changes in extinction contour by rotating the stage indicated that these spheres belonged to the Brooks–Taylor type [5]. However, some mesophase spheres next to each other have the same color (or the shade of gray) in both sides of the contact point. And such phenomena remain unchanged (e.g. pairs of O_2 and O_3, O_3 and O_4, O_5 and O_6 in Fig. 1), no matter how the stage rotates. This observation indicated that the orientation of mesophase stacking layers probably was the same, which can be schematically depicted in Fig. 2. While for many other in-contact mesophase spheres, the colors of the two sides of the contact point were different, including the pairs of O_5 and O_7, O_1 and O_8, O_1 and O_9.

The NMP solvent extraction easily removed isotropic pitches and allowed individual mesophase spheres to be separated from pitch matrix around, as shown in Fig. 3. The in-contact mesophase spheres with 10–20 μm in diameter were retained in an agglomeration form (Fig. 3a). The agglomerated mesophase spheres actually formed a three-dimensional structure and some mesophase spheres had scars and debris on the out-surface as in a closer view in Fig. 3b (positions A and B). The size of scars was indicative

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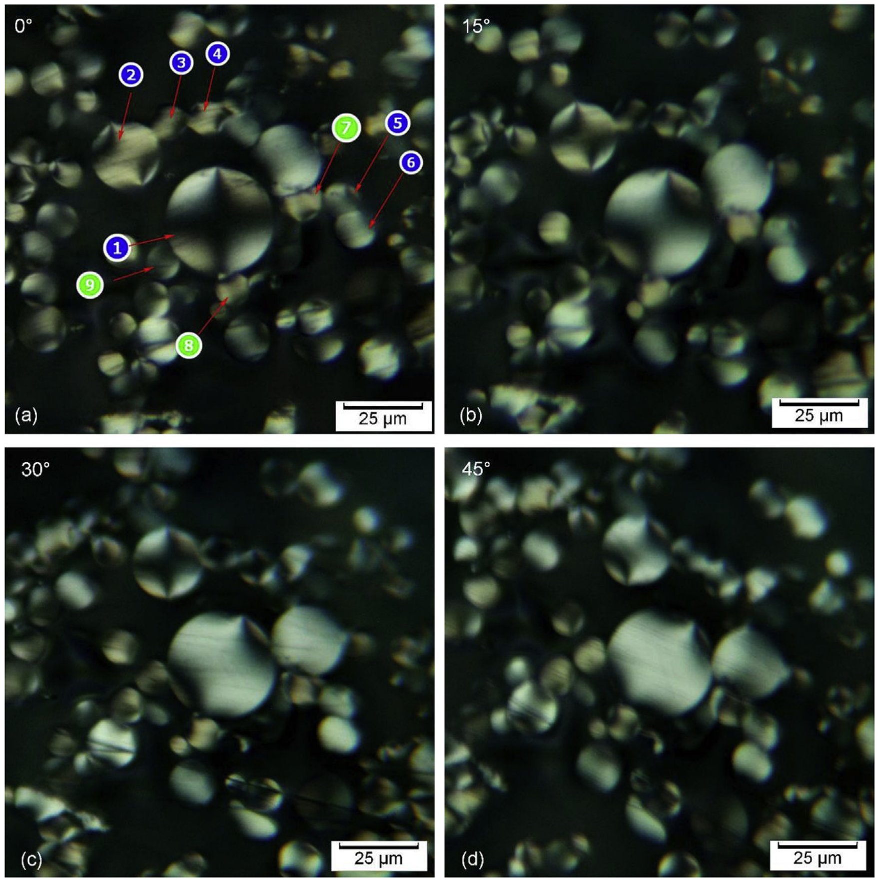

Fig. 1. Changes of polarized-light extinction contours of in-contact mesophase spheres separated by centrifugation and observed at varied rotation angles, with the central large sphere sectioned near to its polar diameter. (A color version of this figure can be viewed online.)

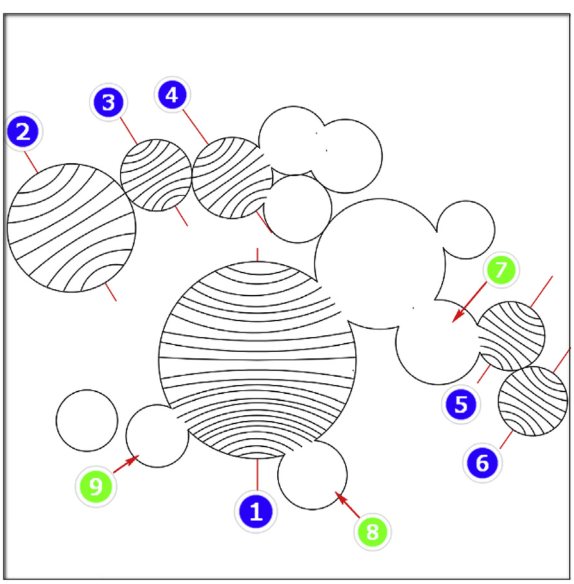

Fig. 2. A schematic illustration of different "in-contact" mesophase spheres shown in Fig. 1. (A color version of this figure can be viewed online.)

of the small contact area, and a few of debris might suggest a quite strong bonding. Therefore, certain interactions between mesophase spheres had already occurred as they were concentrated by centrifugation at relatively low temperature, although little change in morphology could been noticed on these mesophase spheres externally.

The lamellae stacking of the in-contact mesophase spheres after carbonization were clearly observed with three dimensional impressions by SEM (Fig. 4). A closer view (Fig. 4b) displayed the spacial conformation of a mesophase sphere (marked O_1) with its neighbor spheres (O_2 and O_3). The structural features, in terms of micro-crystalline lamellae, for individual mesophase spheres, such as O_1 and O_2, were also revealed (Fig. 4b). These mesophase spheres are axis-symmetric, and their mesophase lamellae were parallel to define the polar axis and their edges were perpendicular to the outsurface of the sphere, exactly as Brooks–Taylor's mesophase sphere model [1–3]. Also Fig. 4 showed the key characteristics of in-contact mesophase spheres. Firstly, mesophase spheres were in contact randomly with others in different locations of lamella stacking. For example, the sphere O_1 was in contact with both spheres O_2 and O_3 at its equator (marked M) and its polar area (marked N), respectively. The angles between the axes of two contacted spheres were also variable. Secondly, a mesophase sphere may be in contact with more than one sphere. For instance, the O_1 was actually in contact with three different spheres, while the O_2 had only one. Thirdly, the number of mesophase layers in the contact point may vary as well, from a few to many, as shown in Fig. 4a and b. Although there were clear distinctions between the in-contact mesophase spheres in terms of relative locations along each polar axis, angle between polar axes, and thickness of layers bonded, they had one thing in common. That is, the contact area between mesophase spheres was relatively small to their diameters, and the mesophase layers of two spheres to be bonded