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Observation of carbonaceous mesophase behaviors in phenolated sawdust using polarized light microscopy

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Abstract The phenolated sawdust had been proved to be a new kind of carbon precursor with excellent self-sintering ability. As a part of research on characterizing the structure and composition of the new kind of carbon precursor, the self-made sinterable phenolated sawdust was observed with polarized light optical microscope in this paper. It was found that the derivative contained some mesocarbon microbead-like optical anisotropic phase which might flow under pressure. The phenolated sawdust was also observed with hot-stage polarized light optical microscope. The results showed that anisotropic phase could be further formed from the phenolated sawdust and then transformed into carbon during the heat treatment. According to the observed results, it was concluded that the self-sinterable phenolated sawdust contained carbonaceous mesophase and component being transformable into carbonaceous mesophase. To some extent, the phenolated sawdust could be described as a new kind of carbonaceous mesophase.

Introduction

As the most abundant biomass resource on the earth, lignocellulosic resource was considered as the most hopeful substitute of petroleum and coal [1]. Many researchers focused on the utilization of lignocellulosic resources, for example, preparing bio-oil, biomass derived polymers, organic chemical products, composites, and so on [2–6].

In our previous research, phenolated sawdust was prepared and proved to be a kind of self-sinterable carbon precursor [7]. It was noticed that in carbon precursors, only few of chemicals such as carbonaceous mesophase had good self-sintering ability. Carbonaceous mesophase had been developed as main binder for preparing carbon matrix composites [8, 9]. In addition, some special carbonaceous mesophase such as mesocarbon microbead (MCMB) was still looked as the best raw material of anode of lithium-ion rechargeable battery [10], separating media in liquid phase separation chromatogram, and super high specific surface area activated carbon [11]. The traditional carbonaceous mesophase was mainly formed and separated from pitch of petroleum and coal [8]. Until now the efficiency of manufacturing the traditional carbonaceous mesophase materials was still low, so that the prices of the carbonaceous mesophase products were too expensive to be used widely. The situation would not be changed easily because its raw materials, petroleum and coal, were being more and more expensive. Therefore, it made us be very interested in studying further on its characterization and application that the self-sintering ability of the phenolated sawdust was very similar to that of the traditional carbonaceous mesophase. In our previous research, the phenolated sawdust was mixed with sawdust and then press-molded into shaped precursor, which was further carbonized into porous carbon monolith. Some particles in ball shape and ball-like shape could be found in the SEM photos of the samples [12]. In this paper, the phenolated sawdust was characterized by static and hot-stage polarized light optical microscope. The results showed that the phenolated sawdust contained some

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MCMB-like substance and component being transformable into mesophase. The phenolated sawdust was possibly a new kind of carbonaceous mesophase.

Experimental

Preparation of the self-sinterable phenolated sawdust

Sawdust of a kind of pine tree (Pinus Elliottii) was selected as raw material. The sawdust passed sieve of 400 meshes was used to react with phenol and sulfuric acid. About 60 g of phenol was mixed with 0.8 g of sulfuric acid (98 wt.%) and 20 g of the sawdust powder, and then stirred at 150 °C for 3 h. The formed black liquid was then washed with excess distillated water for several times until purple powder was obtained. The purple powder was filtered, dried and further ball-milled into fine powder smaller than 63 μm.

Preparation of the samples for polarized light optical microscopic observation

Sample 1# was prepared as follows: 0.2 g of the phenolated sawdust was well mixed with 2.0 g of epoxy resin E51 and 0.2 g of curing agent 2-ethyl-4-methyl-imidazole. The mixture was poured into a cylinder plastic mold, and then cured in air at room temperature for 12 h, further cured in drier at 80 °C for 12 h. Surface of the cured sample was polished for polarized light optical microscopic observation.

Sample 2# was prepared as follows: 1.0 g of the phenolated sawdust was mold-pressed under 100 MPa for 1 min into pellet (diameter 1.0 cm). Its surface was polished for polarized light optical microscopic observation.

Polarized light optical microscopic observation

The samples 1# and 2# were observed by polarized light optical microscope (Leica DM LP). The phenolated sawdust was observed with hot-stage polarized light optical microscope for in-situ observation from room temperature to 400 °C. The heating rate is 10 °C/min.

Results and discussion

MCMB-like optical anisotropic phase contained in the phenolated sawdust

As shown in Fig. 1A, the phenolated sawdust particles of different shape and size were dispersed in cured epoxy resin. Within the particles, only those in ball shape (particles marked 1, 6, and 7) could be observed under 90° crossed polarized light (as shown in Fig. 1B). The particle marked 5 was also in ball shape, however, it could not be seen in Fig. 1B. It must be an air hole instead of optical anisotropic substance. Therefore, possibly the phenolated sawdust was composed of optical anisotropic MCMB-like substances such as the particles marked 1, 6, and 7 and non-crystal substance such as the particles marked 2, 3 and 4. Figure 2 showed the 400 amplified photos of the MCMB-like particles.

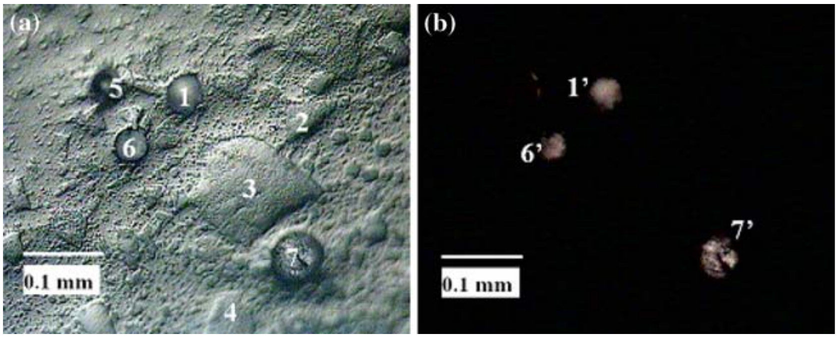


Fig. 1 Optical microscopic photos of some particles in sample 1#. (**A**) Without polarized light; (**B**) with 90° polarized light

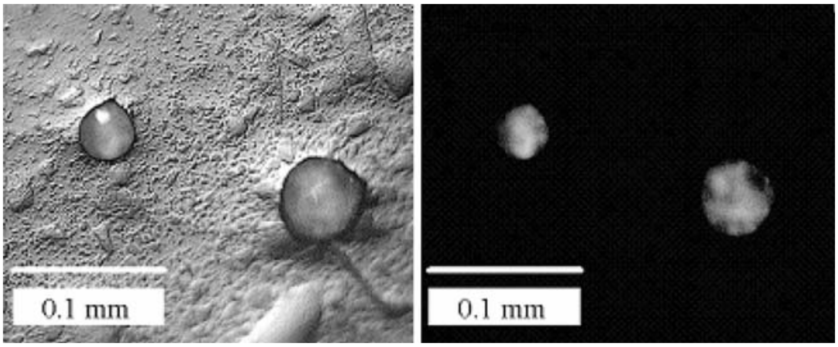


Fig. 2 MCMB-like substance observed in the optical microscopic photos of sample 1#. (**A**) Without polarized light; (**B**) with 90° polarized light

Fluidity of the anisotropic phase in sawdust derivative

MCMB and other carbonaceous mesophase were usually dispersed in resin for polarized light optical microscopic observation [13]. In this paper, the sawdust derivative had very good self-adhering ability, so it could be mold-pressed into shaped bulk material without using additional binder. The surface of the shaped bulk material was polished to be very smooth for polarized light optical microscopic observation.

As shown in Fig. 3, net-like optical anisotropic substance instead of MCMB-like crystal existed in the sample. The phenomenon showed the fluidity of the anisotropic phase in the phenolated sawdust. It was possible that the MCMB-like optical anisotropic substance deformed under pressure and further flowed into net-like shape. Figure 4 illustrated the possible forming mechanism of the net-like optical anisotropic phase in the mold-pressed sample.

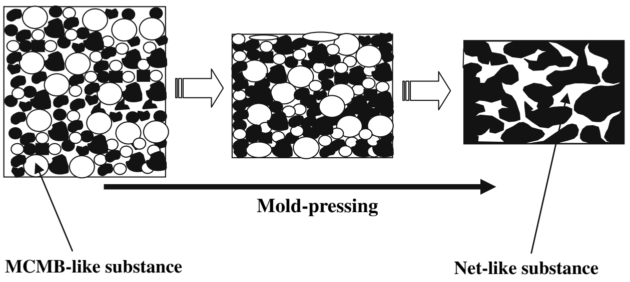


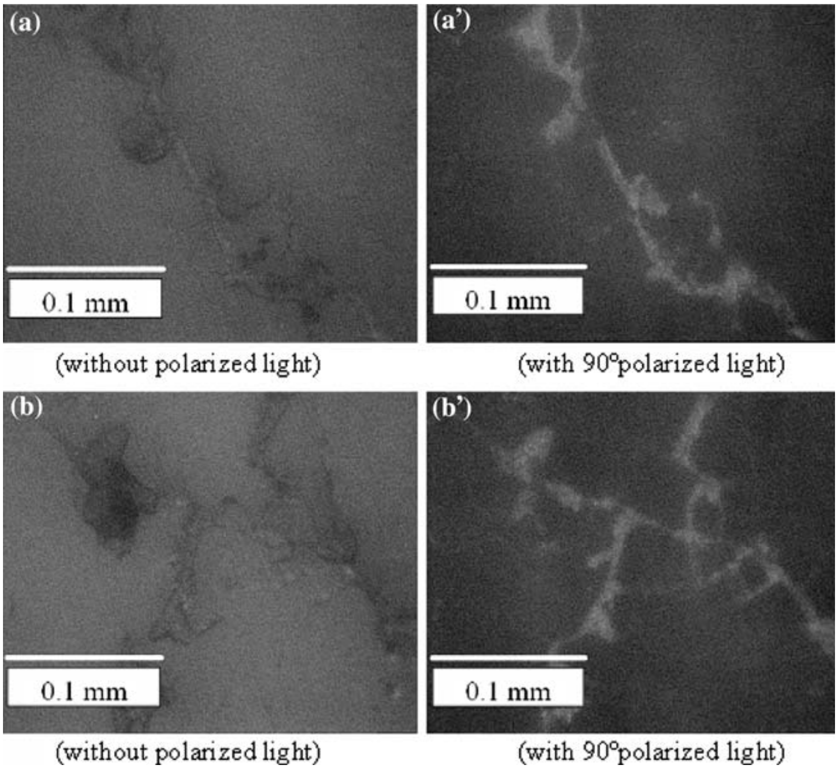
Fig. 4 Illustration to the forming mechanism of the net-like anisotropic phase

In-situ observation on hot-stage polarized light optical microscope

The distances between the particles and the lens would change with the physical and chemical transition of the samples during the process of being heated; therefore, focus need to be adjusted continuously for in-situ observation. The samples for the observation were made in two ways. One way was dispersing the powders directly on the surface of glass slide. Another way was painting the ethanol solution of sawdust derivative on the surface of glass slice and then drying it.

Figure 5 showed the optical microscopic photos taken at different temperatures. The photos 5A–D were taken without polar light. The photos 5A′–D′ were taken under 90° crossed polarized light. When the temperature was raised from 25 to 300 °C, as shown in Fig. 5A–D, a large amount of powders decomposed or melted into transparent liquid. At 25 °C, almost no optical anisotropic phase could be observed, but as shown in Fig. 5C′ and D′, some optical anisotropic phases could be observed at 250 and 300 °C. It could be concluded that under heating treatment, some components of the phenolated sawdust were melted or decomposed, and some components were transformed into optical anisotropic phase.

Fig. 3 Optical microscopic photos of net-like substance observed in sample 2#. (**A**) Without polarized light; (**B**) with 90° polarized light



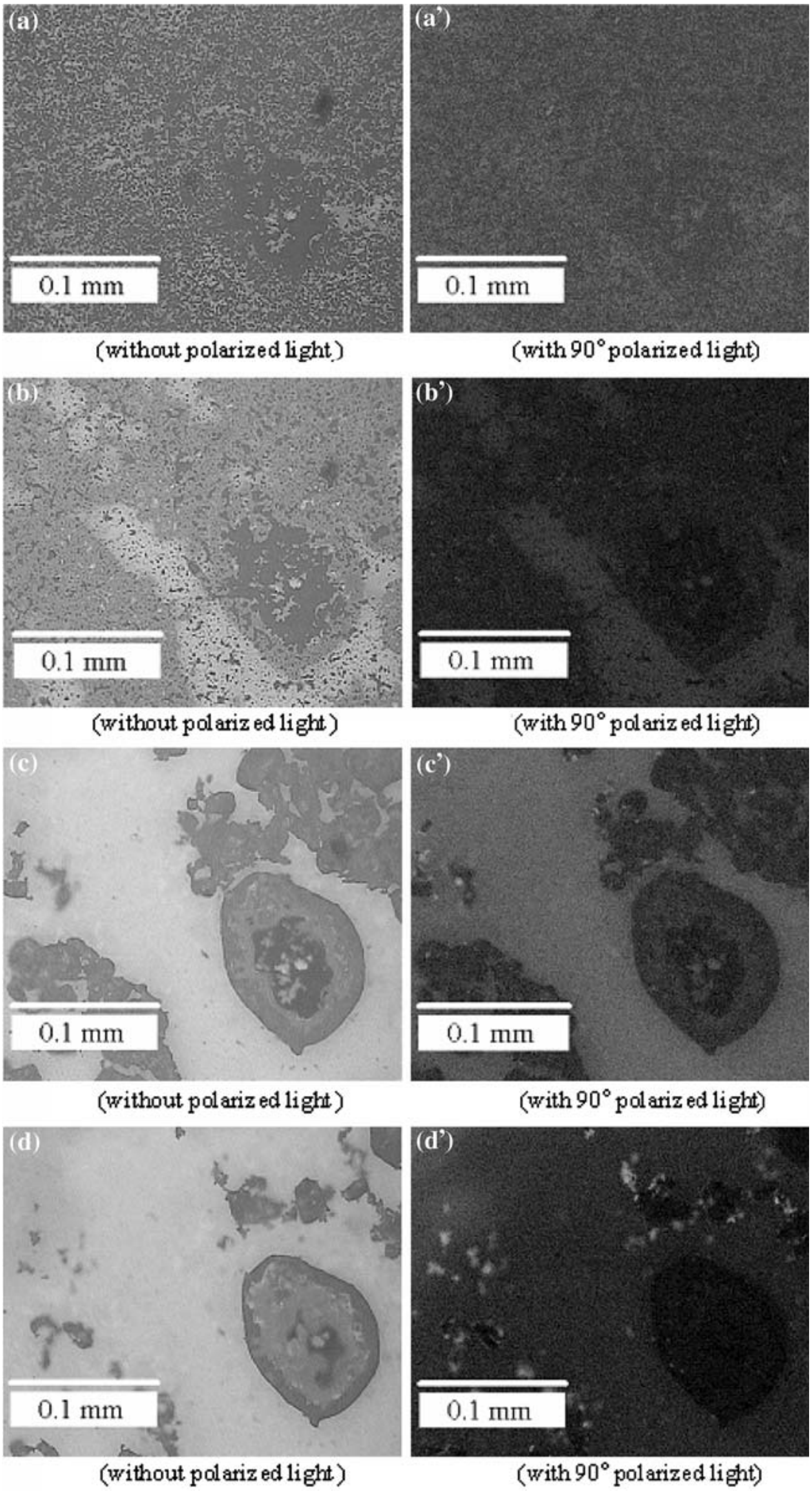
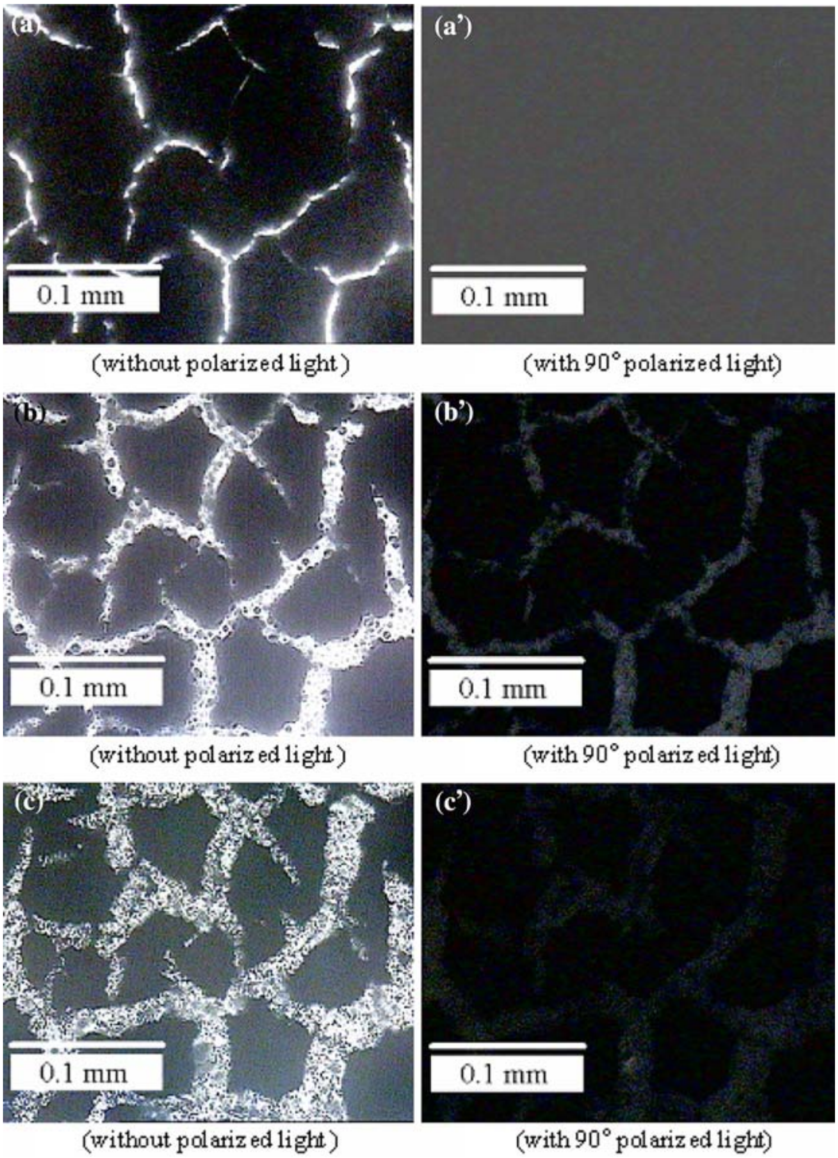


Fig. 5 In-situ optical microscopic photos of the phenolated sawdust powder. (**A**) Without polarized light, (**A′**) with 90° polarized light—25 °C; (**B**) without polarized light, (**B′**) with 90° polarized light—150 °C; (**C**) without polarized light, (**C′**) with 90° polarized light—250 °C; (**D**) without polarized light, (**D′**) with 90° polarized light—300 °C

Fig. 6 In-situ optical microscopic photos of the ethanol soluble phenolated sawdust film. (**A**) Without polarized light, (**A′**) with 90° polarized light—25 °C; (**B**) without polarized light, (**B′**) with 90° polarized light—150 °C; (**C**) without polarized light, (**C′**) with 90° polarized light—250 °C; (**D**) without polarized light, (**D′**) with 90° polarized light—300 °C; (**E**) without polarized light, (**E′**) with 90° polarized light—350 °C; (**F**) without polarized light, (**F′**) with 90° polarized light—400 °C

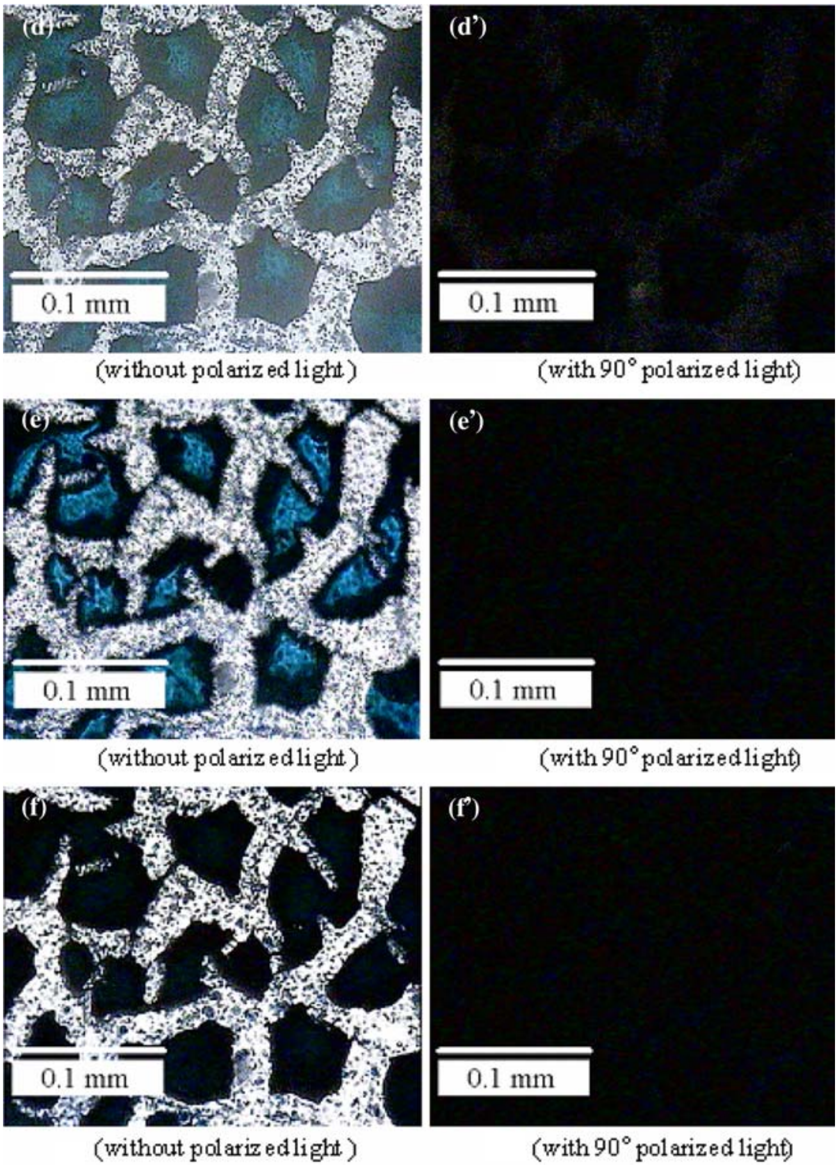


In former section, optical anisotropic phase had been found in the sample 1# and 2# at room temperature. It was contradicted with the result as shown in Fig. 5A and A′. One explanation was that the MCMB-like particles were the congeries of very small liquid crystals. If the liquid crystals were too small, they could not be observed clearly by the polarized light optical microscope of low amplitude. When the small liquid crystals were mixed with epoxy resin and curing agent, they might accumulate each other and form ball shape in larger size to be seeable with polarized light optical microscope. Further research is necessary to explain the phenomena.

Figure 6 showed the optical microscopic photos of the film of the ethanol soluble phenolated sawdust under different temperatures. The formed film was so thick that only the cracks could be distinguished clearly with optical microscope (as shown in Fig. 6A).

As shown in Fig. 6, with the increase of the temperature, some components of the phenolated sawdust were melted or decomposed, which enlarged the transparent part between the black blocks. Furthermore, the color of the block parts changed from black to purple to blue, and turned back into black again. During the process, the blocks became smaller gradually. Because the block parts were too thick to be transmitted by light, the optical anisotropic phases could only be observed in the transparent parts between the blocks. It was found that the optical anisotropic phases increased firstly and then disappeared with the temperature. The change in color of the blocks might also be attributed to some components in the phenolated sawdust being

Fig. 6 continued



transformed into optical anisotropic phases and finally into carbon.

Until now, it could be concluded that the phenolated sawdust was composed of at least two parts. One part was a new kind of carbonaceous mesophase, which could flow under pressure, and appeared as MCMB-like substance or very small liquid crystals. Another part was precursor of carbonaceous mesophase, which was non-crystal, and could be partly transformed into carbonaceous mesophase under heat treatment. The mesophase part endowed the phenolated sawdust with self-sintering ability, while the non-crystal part endowed the phenolated sawdust with excellent self-adhering ability. The composition of the phenolated sawdust was similar to traditional carbonaceous mesophase, which was composed mainly of mesophase and β-phase [8]. Therefore, to some extent, the phenolated sawdust could be described as sawdust derived carbonaceous mesophase, although its content of mesophase might be not as high as traditional carbonaceous mesophase. The sawdust derived carbonaceous mesophase might be very small liquid crystals which could combine with each other into different morphologies in different environments. The observed MCMB-like substances should be typical morphology of the sawdust derived carbonaceous mesophase, which was very easy to be changed with pressure and solvent.

Conclusions

According to the results discussed above, the following conclusions could be drawn. The phenolated sawdust was composed of carbonaceous mesophase and non-crystal substance. The carbonaceous mesophase could appear in MCMB-like morphology, and showed very good fluidity under pressure. Under heat treatment, part of the non-crystal substance could be transformed into mesophase, and finally all the mesophase would lose the properties of the liquid crystal and be transformed into carbon. To some extent, the phenolated sawdust could be described as a kind of sawdust derived carbonaceous mesophase.

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