

Comparative Study of the Modification of Coal Tar Pitch for Higher Carbonization Yield and Better Properties^{*}

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Abstract Parent coal tar pitch (CTP) was modified with boric acid (BA), cinnamaldehyde (CMA) and the mixture of BA and CMA, respectively. The parent CTP and three modified CTPs were characterized by elemental analysis, thermogravimetric analysis, Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy. The four samples were carbonized at different temperatures and resultant carbonized products were characterized by FT-IR spectroscopy, X-ray diffraction and polarized-light microscopy. The results show that the morphologies and carbonization behaviors of the parent CTP and modified CTPs are quite different. The carbonization yield of the CTP modified with the mixture of BA and CMA is higher than that of CTP modified with BA or CMA only. In addition, the modification of CTP with 7 g of BA and 10 ml of CMA results in an increase in carbonization yield by 5.64%. During the pyrolysis of modified CTPs, the dehydration of BA or the distillation of CMA occurs at the temperature lower than 300 °C, and methyl and methylene groups of the modified CTPs disappear gradually as temperature rises. Furthermore, the modification of CTP by the mixture of BA and CMA results in more intensive mesophase spheres than other modified CTPs, and the modified CTP is easier to be carbonized to form graphitic carbon.

Keywords coal tar pitch, cinnamaldehyde, boric acid, carbonization

1 INTRODUCTION

Coal tar pitch (CTP) is a kind of complex materials consisting of aromatic compounds with a broad molecular mass distribution [1]. It has been a quite promising candidate for the production of carbon materials and carbon-carbon composites for its low cost and the ability to generate graphitizable carbons [2]. However, the application of CTP is greatly restricted due to its low carbon yield, low density and high pore volume of its resultant coke, which necessitates subsequent densification by a series of impregnation/carbonization steps under high pressure. Thus, the processing of carbon materials or carbon-carbon composites with CTP as the matrix precursor becomes time consuming and expensive [3]. Therefore, it is a striking point that specific treatments should be applied to improve the carbon yield of CTP to simplify the preparation process and to reduce costs [4].

It is well known that the carbonization yield of CTP can be improved by physical separation and chemical modification. Physical separation (*i.e.*, fractional distillation and solvent extraction) can be used to separate components with different average molecular weights from CTP [5]. On the other hand, chemical modifications are involved in chemical reactions between CTP and polystyrene, rosin, phenolic resin, and lignin/silica hybrid, *etc* [6–9]. Compared to physical separation, chemical modification is superior in saving resources, reducing waste disposal and simplifying the preparation procedure. Therefore, it has been the typical approach to improve the carbonization yield of CTP.

Cinnamaldehyde (CMA) is a major bioactive compound isolated from the leaves of *Cinnamomum osmophloeum* kaneh [10]. It is a α,β -unsaturated aldehyde in which the benzene ring is conjugated with C=O and C=C groups. So, it is a potential natural cross-linking agent [11] and hydrogenation reactions can take place in both C=O and C=C groups [12, 13]. Hence, in this work, CMA was used to modify CTP in the presence of boric acid (BA). The purpose of this paper is to compare the characteristics and carbonization behaviors of the CTPs modified with BA, CMA and the mixture of BA and CMA, respectively.

2 EXPERIMENTAL

2.1 Materials

CTP was purchased from the Wuhan Steel Co. Ltd. (Wuhan, China). CMA and BA were of analytical grade reagents. Some properties of the CTP are included in Table 1.

The modified CTPs are defined as B_mC_n , where m is the amount of BA and n is the dosage of CMA. For example, CTP B_7C_{10} indicates that 100 g of parent CTP is modified with 7 g of BA and 10 ml of CMA. So, the four pitches mentioned in this paper are B_0C_0 (parent CTP), B_0C_{10} , B_7C_0 and B_7C_{10} , respectively.

2.2 Procedures

2.2.1 Modification of CTP

100 g of CTP and certain amount of BA were mixed in a 500 ml round bottom three-neck flask

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Table 1 Physical properties of the four CTPs

	SP ^① /°C	CV ^② /%(by mass)	TI ^③ /%(by mass)	QI ^④ /%(by mass)	Elemental analysis/% (by mass)			C/H
					N	C	H	
B ₀ C ₀	120	57.75	55.95	7.90	2.50	93.07	4.09	1.90
B ₀ C ₁₀	92	55.72	47.46	5.30	1.89	87.01	4.53	1.60
B ₇ C ₀	117	62.50	45.89	10.06	1.81	92.27	3.76	2.04
B ₇ C ₁₀	114	67.58	46.42	14.62	1.78	85.46	4.29	1.66

① Softening point; ② Coking value; ③ Toluene insolubles; ④ Quinoline insolubles.

equipped with a motor driven stirrer. It was started at 100 °C at a speed of 90 r·min⁻¹ and CMA was added slowly into the flask. Then, the speed of the stirrer was raised to 200 r·min⁻¹ at 150 °C and held for 3 h under a nitrogen flow of 50 ml·min⁻¹.

2.2.2 Carbonization

Carbonization of the four CTPs (B₀C₀, B₀C₁₀, B₇C₀ and B₇C₁₀) was carried out in a tube furnace. About 1 g of sample was heated to designated temperature at a rate of 10 °C·min⁻¹ and kept at the set temperature for 2 h. The N₂ stream was introduced into the tube furnace throughout the carbonization. The resultant carbonized products are denoted as C_x, where *x* is the final carbonization temperature.

2.3 Analysis

2.3.1 Characteristics of CTP and modified CTPs

The compositions of parent CTP and modified CTPs were analyzed using the following standard methods: softening point (SP), ASTM D36-66; coking value (CV), ISO 6998; toluene insolubles (TI), ISO 6376-96; quinoline insolubles (QI), ISO 6791-81.

2.3.2 Measurements

Elemental analysis of C, H and N was performed on a Vario EL-III analyzer. Fourier transform infrared (FT-IR) spectroscopy was acquired on a Bruker Tenser-27 FT-IR spectrometer with thin films of KBr in the range 4000–400 cm⁻¹. Thermogravimetric analysis (TG-DTG) was performed on a Mettler-Toledo 851^e thermal analyzer under N₂ atmosphere with a heating rate of 10 °C·min⁻¹.

The morphologies of parent CTP and modified CTPs were examined using FEI Sirion 200 scanning electron microscopy (SEM). Optical textures of the semi-cokes were observed from the polished surfaces using OLYMPUS-B061 polarized-light microscope. X-ray diffraction (XRD) was measured on a PANalytical X'Pert PRO X-ray Diffractometer with CuK_α (λ = 0.15406 nm) radiation at 40 kV and 35 mA.

3 RESULTS AND DISCUSSION

3.1 Characteristics of the four CTPs

The physical properties of the four CTPs are

listed in Table 1. It can be observed that the three modified CTPs (B₀C₁₀, B₇C₀ and B₇C₁₀) have lower softening points than that of parent CTP (B₀C₀). When CTP is modified with only CMA or BA, the data of B₀C₁₀ and B₇C₀ shows different trends (see Table 1). B₀C₁₀ has lower CV, QI content and C/H ratio than that of parent CTP, while B₇C₀ has higher CV, QI content and C/H ratio than that of parent CTP. However, when CTP is modified with the mixture of BA and CMA, the highest value of CV can be obtained. The order of CV is consistent with the following TG results.

3.2 TG-DTG analysis

TG as well as DTG is frequently used for studying pitches to determine the extent and rate of mass losses and the temperature ranges in which these take place [14, 15]. The TG curves of parent CTP and three modified CTPs are shown in Fig. 1. It can be observed that both parent CTP and modified CTPs decompose in one single mass loss stage in the temperature range of 25–800 °C. The mass loss is mainly due to the removal of light compounds and gases generated via thermal polymerization and cracking of side chains of aromatic rings [1]. The carbonization yields of B₀C₀, B₀C₁₀, B₇C₀ and B₇C₁₀ are 41.04%, 40.90%, 44.50% and 46.68%, respectively. It can be seen that the carbonization yields of B₇C₀ and B₇C₁₀ are higher than that of parent CTP (B₀C₀). The carbonization yield of B₀C₁₀ is lower than that of B₀C₀ possibly because of the distillation of CMA for its low boiling point (248 °C) [16].

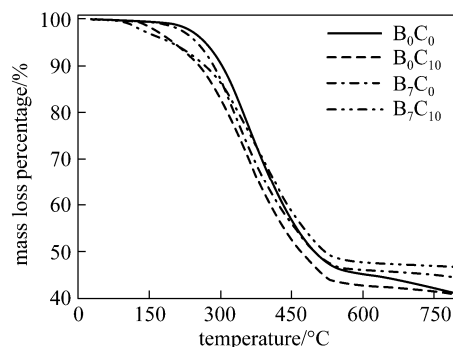


Figure 1 TG curves of the four CTPs

The carbonization yield of B_7C_0 is higher than that of B_0C_0 . The possible reason could be that BA can react with the organic compounds containing functional groups of hydroxyl group, amines amino, *etc.* [17–19], which increases the carbonization yield of CTP. It is found that the carbonization yield of B_7C_{10} is the highest. This result could be rationalized as follows: the aldehyde group in the chemical structure of CMA reacts with small molecules of CTP in the presence of BA to produce large molecules [20], which decreases the removal of light compounds and increases the carbonization yield.

The DTG curves of the four CTPs are quite different as shown in Fig. 2. The DTG profile of B_0C_0 is characterized by a single peak centered at 362 °C, which indicates that the mass loss rate reaches the maximum value at this temperature. However, there are two new peaks in the DTG profile of B_0C_{10} : one at about 200 °C attributed to the distillation of CMA and the other at 520 °C related to the thermal reactions [21]. For B_7C_0 and B_7C_{10} , the small peaks at about 160 °C are due to the dehydration of BA [22] and the peak corresponding to the thermal polymerization in B_7C_0 and B_7C_{10} is broader than that of B_0C_0 . In addition, there are two small peaks at about 370 °C in the profile of B_7C_{10} , and the temperature corresponding to the maximum mass loss rate shifts to higher temperature compared to those of other three CTPs, indicating the better thermal stability of B_7C_{10} . Based on the above analysis, it can be expected that the modification of CTP, either by BA or CMA or their mixture, mainly influence the subsequent process of pyrolysis.

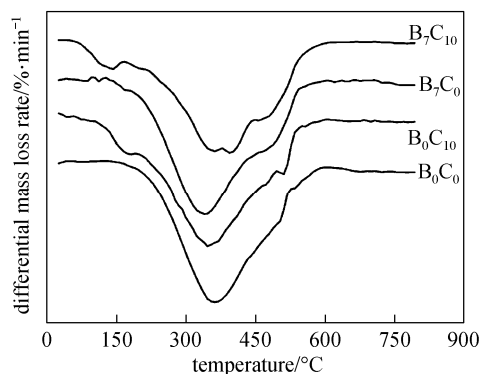


Figure 2 DTG curves of the four CTPs

3.3 FT-IR analysis

FT-IR spectra of the four CTPs and their carbonized products at different temperatures are shown in Fig. 3. The spectrum of B_0C_0 shows the following regions of interest. The peaks at 3030 cm^{-1} and 2915 cm^{-1} are due to aromatic C—H stretching vibration and aliphatic C—H stretching vibration, respectively. The aromatic C=C stretching vibration is at about 1600 cm^{-1} . The peak at 1441 cm^{-1} is attributed to C—H bending vibration of methyl and methylene. In addition, the peaks in the range of 700–900 cm^{-1} are related to the aromatic out-of-plane C—H vibration with different substitution patterns in the aromatic structures [23].

Compared with the characteristic peaks of B_0C_0 ,

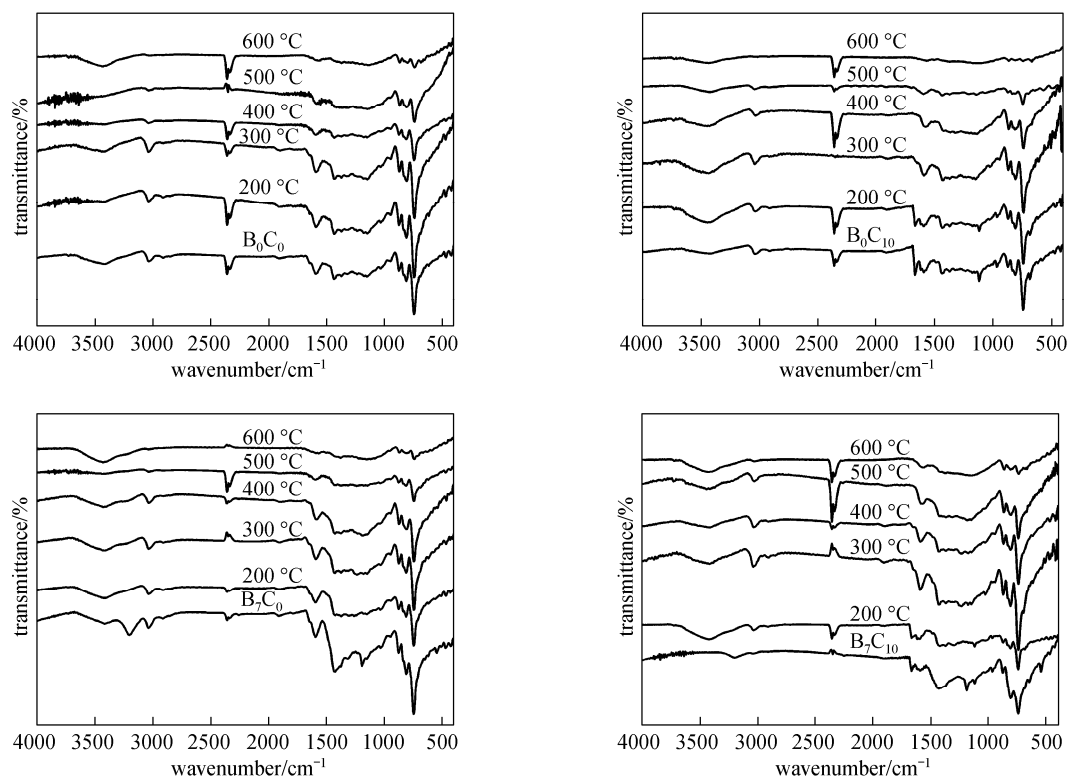


Figure 3 FT-IR spectra of the four CTPs and their carbonized products

three new peaks appear in the FT-IR spectrum of B_0C_{10} , which locate at 1670 cm^{-1} , 1120 cm^{-1} and 700 cm^{-1} and are respectively assigned to the peaks of CMA [24]. As to B_7C_0 , there are new peaks at 3200 cm^{-1} (O—H stretching vibration) and 1192 cm^{-1} (asymmetric stretching vibration of the tetrahedral BO_4) [25]. It can also be observed in B_7C_0 that the peak at 1441 cm^{-1} is broader than that of B_0C_0 and B_0C_{10} , which may be caused by the overlap of the parent CTP peaks and the asymmetric stretching of trigonal BO_3 peak in BA. Regarding to B_7C_{10} , both the peaks of B_0C_{10} and B_7C_0 can be observed.

The products of the four CTPs carbonized at different temperatures are also shown in Fig. 3. It can be observed that methyl and methylene groups (see the peak at 2915 cm^{-1} and 1441 cm^{-1}) of all the CTPs disappear gradually as temperature rises, which is caused by the demethylation of methyl and methylene. In addition, it can be observed in the FT-IR spectra of B_0C_{10} and B_7C_{10} that the peaks at 1670 cm^{-1} and 1120 cm^{-1} , which are the characteristic peaks of CMA, disappear when the modified CTPs are heated to temperature higher than $300\text{ }^\circ\text{C}$. The results are in agreement with the DTG analysis. In addition, the peaks at 3200 cm^{-1} in the FT-IR spectra of B_7C_0 and B_7C_{10} disappear at $200\text{ }^\circ\text{C}$, which is due to the dehydration of BA. So, the FT-IR spectra confirm the TG-DTG results.

3.4 SEM analysis

The SEM images of the four CTPs are shown in Fig. 4. There are some white spots in the morphology of B_0C_0 , which results from the inorganic material (ash) and gold sprayed over the pitch sample [20]. For B_0C_{10} , the morphology is almost the same with B_0C_0 [see Fig. 4 (a) and 4 (b)]. However, the morphology

changes greatly when the parent CTP is modified by BA [see Fig. 4 (c)]. Some particles distribute on the surface of CTP. For B_7C_{10} , the particles are agglomerated, which could be the larger products generated *via* the reaction between CTP and CMA in the presence of BA.

3.5 Optical texture of resultant semi-cokes

Optical texture observed with polarized light optical microscope is one of the most relevant characteristics of carbon materials because it is closely related to their conductivity, thermal expansion, mechanical strength and graphitizability [26, 27]. When CTP is heated to temperature higher than $350\text{ }^\circ\text{C}$, its optical texture will appear mesophase spheres, which are excellent precursor for high performance carbon materials [28]. In this paper, the four CTPs were heated to $400\text{ }^\circ\text{C}$ and held for 1 h to study the effect of modification on the development of mesophase spheres. The optical textures are shown in Fig. 5. It can be observed that the shape and number of mesophase spheres change greatly after modification. In parent CTP, the spheres are little and small [see Fig. 5 (a)]. For B_0C_{10} and B_7C_0 , the spheres are much bigger than that in B_0C_0 but distribute widely [see Fig. 5 (b) and 5 (c)]. As for B_7C_{10} , the spheres are more intensive than the other three CTPs [see Fig. 5 (d)]. The reason for this could be due to the reaction between CMA and the small molecules of CTP in the presence of BA, which decreases the small molecules in CTP and consequently reduces the resistance caused by the small molecules in the formation process of mesophase spheres. So, the results indicate that the modification of CTP by the mixture of BA and CMA favors the formation of mesophase spheres.

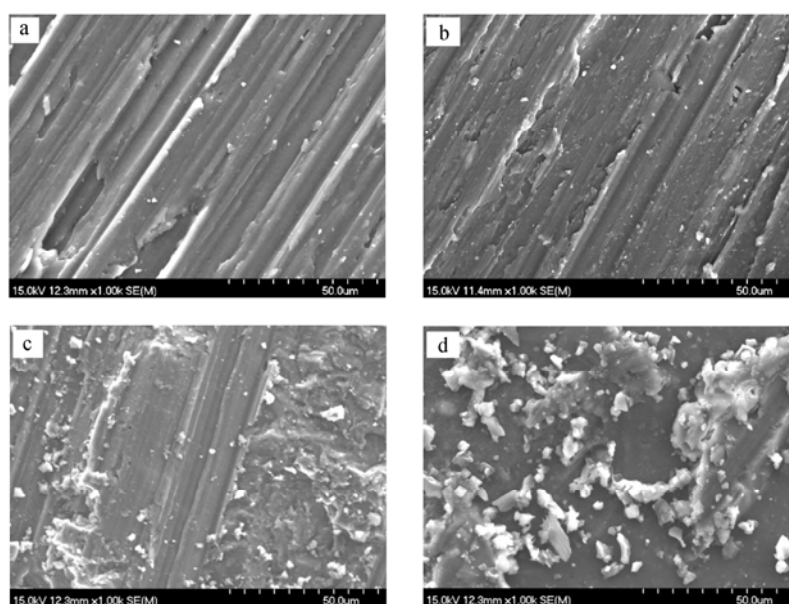


Figure 4 SEM images of B_0C_0 (a), B_0C_{10} (b), B_7C_0 (c) and B_7C_{10} (d)

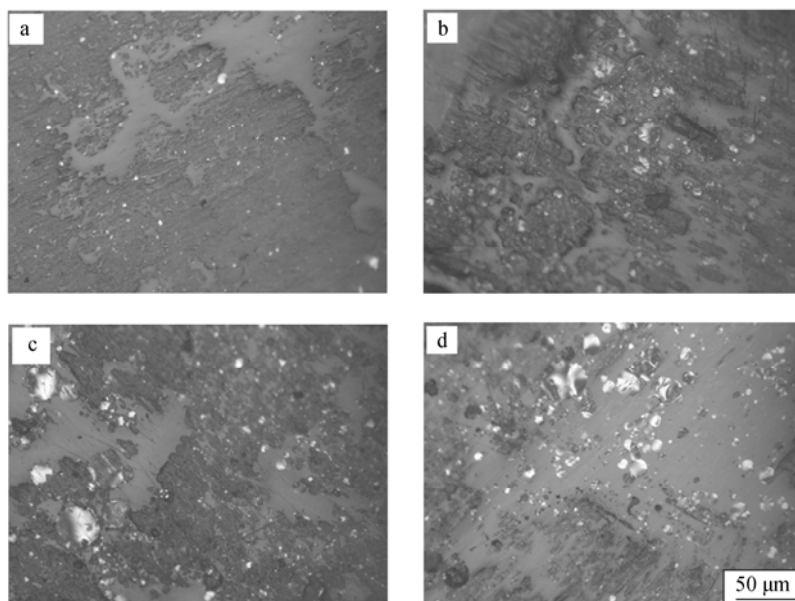


Figure 5 Optical micrographs of pyrolysis products B_0C_0 (a), B_0C_{10} (b), B_7C_0 (c) and B_7C_{10} (d) obtained from the four CTPs carbonized at 400 °C for 1 h

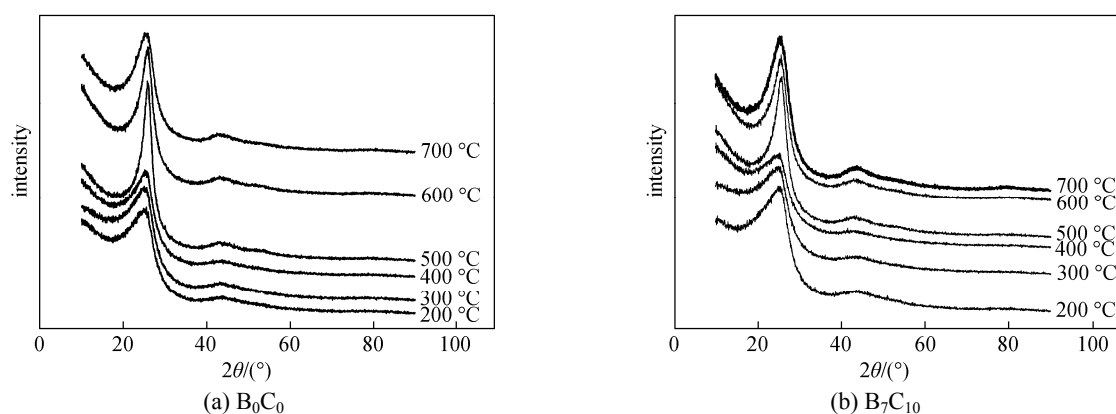


Figure 6 XRD patterns of B_0C_0 and B_7C_{10} carbonized at different temperatures

3.6 XRD analysis

Since the higher carbonization yield and better thermal stability of B_7C_{10} , the effect of thermal treatment on the XRD patterns of B_0C_0 and B_7C_{10} has also been studied, which are shown in Fig. 6. All the samples exhibit two diffraction peaks centered at 25° and 43°, which can be generally indexed to (002), (100) diffraction of graphite [29]. It can be seen that with increasing temperature, the intensity of the two peaks increase slightly, suggesting the crystallite growth of the carbonized products.

Table 2 lists the XRD parameters of B_0C_0 and B_7C_{10} . It is worthwhile to note that the 2θ angle increases with increasing carbonization temperature, consequently, the d -spacing of carbonized CTPs decrease with increasing carbonization temperature. In addition, the d_{002} values of B_7C_{10} are smaller than the corresponding data of B_0C_0 , indicating that B_7C_{10} has better graphitizability than B_0C_0 .

Table 2 XRD parameters of B_0C_0 and B_7C_{10}

	B_0C_0		B_7C_{10}	
	$2\theta_{002}/(^{\circ})$	d_{002}/nm	$2\theta_{002}/(^{\circ})$	d_{002}/nm
C_{200}	24.5	0.363	25.0	0.356
C_{300}	24.8	0.359	25.1	0.355
C_{400}	25.1	0.355	25.3	0.352
C_{500}	25.5	0.349	25.6	0.348
C_{600}	25.7	0.346	25.8	0.345
C_{700}	25.8	0.345	25.9	0.344

4 CONCLUSIONS

The modification of CTP has great effect on its characteristics, carbonization behavior and morphology. The carbonization yield of the CTP modified with the mixture of BA and CMA is higher than that of CTP modified with BA or CMA only. In addition, the

modification of CTP with 7 g of BA and 10 ml of CMA results in an increase in carbonization yield by 5.64%. The results of FT-IR analysis show that during the pyrolysis of modified CTPs, the dehydration of BA or the distillation of CMA occurs at the temperature lower than 300 °C, and methyl and methylene groups of the modified CTPs disappear gradually as temperature rises. Furthermore, the modification of CTP by the mixture of BA and CMA results in more intensive mesophase spheres than the other modified CTPs and the modified CTP is easier to be carbonized to form graphitic carbon.

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