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Thermodynamic Study on the Synthesis of Coal Pitch-based Mesophase by Catalytic Polycondensation

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As an important chemical raw material, the coal pitch-based mesophase is extensively used in national defense, industry and life. Taking refined coal-tar pitch as the raw material, this paper examines the thermodynamic changes in the synthesis of coal pitch-based mesophase by catalytic polycodensation. The optical microstructures, yield, and softening points of the mesophase pitch at different synthesis temperatures and holding times are investigated through a catalytic pyrolysis experiment, providing the theoretical guidance for preparation of high quality coal pitch-based mesophase.

1. Introduction

First discovered by Brooks and Taylor in the study of coal coking, the coal pitch-based mesophase is a discotic nematic liquid crystal formed by parallel arrangement of planar aromatic molecules (Ciampi et al., 2016). The concept of carbonaceous mesophase refers to the intermediate liquid crystal state during the transition of bituminous organic matters to solid semi-coke (Korai et al., 1997). The mesophase pitch is a polymer composed of various discotic polycyclic aromatic hydrocarbon with relative molecular mass of 370~2000. It is resulted from the physicochemical reaction of organic matters at a moderate temperature (Bonnamy, 1999; Mukhopadhyay and Monda, 2016; Pi, 2016; Popoola et al., 2016; Dogaru, 2016). In the liquid phase of the pitch pyrolysis system, any easily calcined organic matter has to go through a series of structural changes like the appearance, growth, melting, fusion and deformation of mesophase small spheres before becoming highly graphitized carbon.

The formation conditions of high-quality mesophase pitch include: the size of aromatic hydrocarbon units, the flatness of molecules, and the continuity or completeness of the carbon atom arrangement in the molecule. However, the arrangement of small spheres within the intermediate phase might be disrupted by the direct thermal polycondensation reaction, making it difficult to obtain high quality mesophase pitch (Corriu et al., 1994). Owing to the difference in raw materials and processing technologies, the mesophase pitch can be produced by different methods and the mesophase products are of varying quality.

The research and preparation of high-quality mesophase pitch have captured much attention from scholars with its status as an important raw material for high-performance carbon materials (Sibilio et al., 2016). This paper carries out a chemical experiment with purified coal tar as the raw material, adopts the catalytic polycondensation method with the addition of anhydrous $ALCL_3$ (Okabe et al., 2011), and analyzes the thermodynamic changes in the preparation of coal pitch-based mesophase. In the end, the best thermal polymerization temperature and the ideal holding time are acquired to improve the yield, optical microscopic micromorphology, softening point and other characteristics.

2. Raw materials, devices and contents of the experiment

2.1 Raw materials and devices of the experiment

The raw materials for the experiment are refined coal-tar pitches produced by the Taiwanese company China Steel Chemical Corp. The chemical composition is shown in Table 1.

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Table 1: Analytical data of refined coal tar pitches

C%	H%	N%	Others	H/C	SP(°C)	TS%	TI-PS%	PI%
93.0	4.4	1.4	1.2	0.56	60	62.46	16.98	21.56

In the above table, SP stands for soft point, TS refers to toluene solution, PS represents pyridine soluble, and PI means pyridine insoluble.
The experimental devices mainly consist of: 1. Coal tar heat treatment instrument, featuring constant speed and stable temperature control program. 2. Self-made softening point test device, including the heat-gathering thermostatic oven, ceramic crucible, meldometer, needle pin, self-made glass softening point test tube. 3. Olympus BX51M polarized light microscope.

2.2 Experimental contents

The refined coal-tar pitches were ground and then relocated to the heat treatment instrument for thermal transition experiment (Hirao et al., 2009; Mukhopadhyay, 2016; Hossain et al., 2016; Nayak, 2016; Mukhopadhyay and Mondal, 2016). The experiment involves the following steps: Set a fixed stirring speed, add the Lewis acid catalyst $AlCl_3$, set different temperatures and holding times for the thermodynamic reaction, and observe such features of thermodynamic changes as morphological structure, yield and soft point. The process parameters of the thermal polymerization reaction are listed in Table 2, including the heating rate, the heat polymerization temperature, and the settings of the constant temperatures and holding times (Mathew and Singho, 2015).

Table 2: The process parameters of the thermal polymerization reaction

No	Heating rate (room temperature - 250°C)	heating rate≥250°C	Treatment temperature	Holding time
D_1	6°C/min	3°C/min	295	6
D_2			310	5
D_3			320	5
D_4			330	5
D_5			345	5
D_6			360	2

The thermally polymerized pitch prepared with the above parameters was rinsed to obtain purified asphalt, and a series of property analysis were conducted for the purified asphalt (Muñoz, D. M et al., 2007).

2.2.1 Effect of catalytic thermal polymerization temperature on morphological structure of mesophase

The morphological structure of the thermally polymerized pitch mesophase (Choudhury and Das, 2016) in the coal tar reaction still was observed by the polarizing microscope (Wakioka et al., 2013) under different treatment temperatures and holding times. The results are shown in Figure 1.
As shown in the above figure, it is possible to obtain relatively dense mesophase spheres at 310°C-5h. With the increase of temperature, the mesophase spheres are changed and fused to reach the mesophase micromorphology, featuring high degrees of fusion (Eisch et al., 2002). The polarized-light micrograph of the polymerizate at 295°C-6h is completely black (Habibi and Nasrollahzadeh, 2012). Under this condition, the product is isotropic pitch, the softening point is 183°C, and the yield of the polymerizate is 92.6%. Relatively big mesophase spheres are formed at 310°C-5h (the black part of the micrograph stands for isotropic pitch). At 320°C-5h, the mosaic structure is formed (radius≤ μm) with some of the spheres melted and fused into streamline mesophase texture (radius≤ 60μm); in this case, the mesophase content can reach 60%. The condition of 330°C-5h is characterized by the formation of mesophase optical anisotropic coarse stream body and euryzonal stream body. Under this condition, the mesophase content grows to around 85%. When into comes to the condition of 345°C-5h, the euryzonal mesophase structure appears everywhere (radius≥μm). At 360°C-2h, the mesophase enters the semi-coke state and becomes difficult to soften. The above polarized-light micrographs give a vivid illustration of the entire process from the formation of mesophase spheres to the generation of the euryzonal mesophase (Nicoletti et al., 2016).

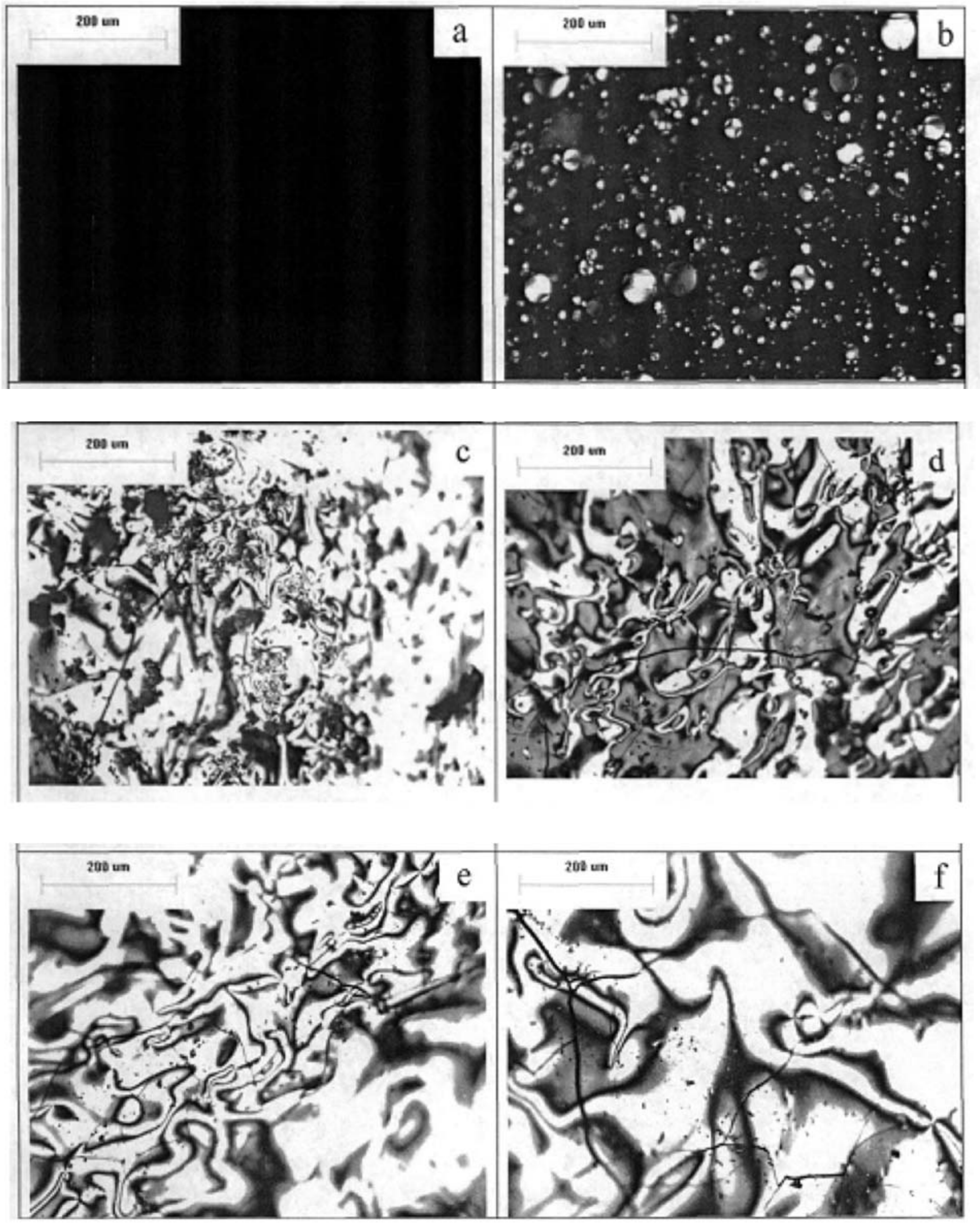

Figure 1: Polarized-light micrographs of mesophase pitches at different treatment temperatures and holding times for coal-tar pitch reaction/°C (a)295°C-6h; (b)310°C-5h; (c) 320°C-5h; (d) 330°C-5h; (e) 345°C-5h; (f) 360°C-2h

2.2.2 Effect of catalytic thermal polymerization temperature on mesophase yield and softening point

Table 3 displays the mesophase contents of thermally polymerized pitch at different treatment temperatures (295°C-360°C) under the action of catalyst. The table reveals that the mesophase content gradually climbs up with the increase of treatment temperature. When the temperature rises to 345°C, the mesophase content reaches 100%. Any further temperature increase only results in the coking of mesophase rather than the lowering of the softening point.

The yield and softening point variations of the mesophase in the polymerization process are further analyzed, and the temperature-induced changes to the yield and softening point in the experiment are shown in Figures 2 & 3, respectively.

Table 3: Yield, softening point and content of mesophase pitch

No	Treatment temperature (°C)	Holding time (h)	Anisotropic content
D_1	295	6	0
D_2	310	5	≤ 40
D_3	320	5	≤ 60
D_4	330	5	85
D_5	345	5	100
D_6	360	2	100

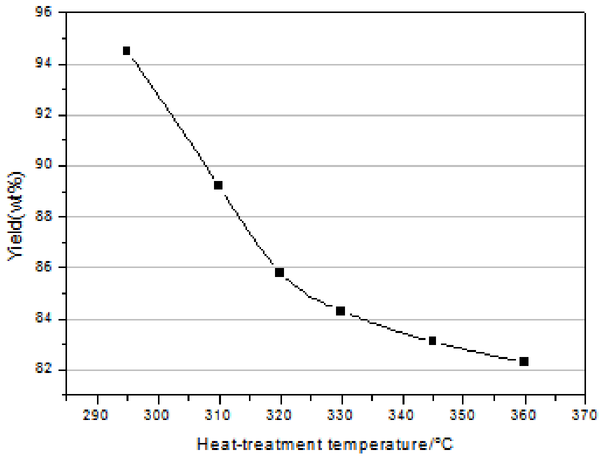

Figure 2: Effect of reaction temperature on the yield of mesophase pitch

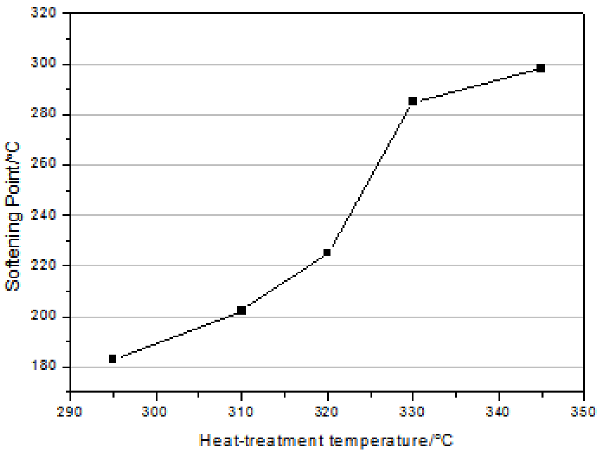

Figure 3: Effect of reaction temperature on the softening point of mesophase pitch

It can be seen from Figure 2 that the yield of mesophase polymerized pitch gradually falls as the temperature increases. The relationship is attributable to the growth of mesophase microcrystals and substantial growth in the number of mesophase small spheres throughout the experiment. In Figure 3, however, the softening point keeps rising with the temperature. The upward trend is most pronounced from 320°C to 330°C. The analysis shows that the yield decrease is mainly caused by the large number of light components produced during cracking as the temperature increases, while the gradual increase in softening point from 310° to 445°C is explained by the fact that mesophase pitch is at the mutual fusion stage. Any further temperature increase only results in the coking of mesophase rather than the lowering of the softening point.

2.3 Summary of the experiment

1. Based on the observation of changes to mesophase morphological structure, it is concluded that the catalytic polymerization process encompasses three stages: the formation of mesophase microcrystals, the accumulation of mesophase microcrystals and the fusion of mesophase small spheres.
2. Temperature has an important effect on thermal polymerization reaction. Despite shortening the time it takes to generate mesophase pitch, high temperature results in lower yield and rapid increase of softening point and insoluble. The temperature of catalytic polymerization should be controlled to prevent excessive dehydrogenation and excessive polymerization during the reaction. In this way, mesophase small sphere will form in good order, contributing to the control of mesophase morphology.
3. After the catalytic polycondensation with refined coal pitch as the raw materials and $AlCl_3$ as catalyst, it is possible to obtain an anisotropic photocatalytic structure of 83.3% yield and low softening point by holding the temperature at 345°C for 5h.

3. Conclusion

For better understanding of the thermodynamic changes in the preparation of coal pitch-based mesophase, this paper carries out a catalytic polymerization experiment with refined coal pitch as the raw material. The results show that the temperature and holding time of thermal polymerization are key influencing factors on the form, yield and softening point of coal pitch-based mesophase; the catalyst chloride $AlCl_3$ is an ideal additive for the preparation of coal pitch-based mesophase because it can effectively lower the thermal polycondensation temperature and shorten the reaction time.

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