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Mesophase formation of coal-tar pitches used for impregnant of C/C composites①

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[Abstract] By a polarized light optical microscopy with a hot stage, liquid-phase nuclear magnetic resonance ^{13}C-NMR and ^{1}H-NMR, X-ray diffractometry and scanning electron microscopy (SEM), the factors that affect the formation of mesophase in C/C composites, such as pressure, quinoline insolubles (QI) and heterocylic compounds, were analyzed. Further, the graphitizability of the resultant carbon was discussed. The results indicate that to some degree, QI contents accelerate the formation of mesophase at atmospheric pressure; while at high pressure, the coalescence and growth of mesophase spherules are impeded and the resultant coke produced from higher QI content pitch is harder to be graphitized. This is in agreement with the transfer of microstructure from domain anisotropy to fine-grained mosaics.

[Key words] C/C composites; coal-tar pitch; mesophase; quinoline insolubles; graphitization
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1 INTRODUCTION

Carbon fiber reinforced composites (C/C composites) are important for engineering and scientific applications in aerospace industry because of their unique properties. Currently, besides being used as aircraft brakes, they are also used as refractory material, corrosion resistant material and biocompatible material, etc[1~4]. But fabrication methods of C/C composites are hitherto time-consuming and cost-intensive, which limits the use of this material. Among the fabrication methods, pitch impregnation/carbonization is one of the best choices from the viewpoint of all criteria (i. e. high carbon yield, minimal density change and a graphitic carbon matrix)[5~8]. In the case of pitch impregnation, mesophase appears inevitably during pyrolysis process. The formation, coalescence and orientation of basal planes of mesophase have been studied for a long time[9~16] since these processes will affect the graphitizability, mechanical, thermal, frictional properties of the resultant C/C composites[17~19]. The objective of this paper is to assess the influence of quinoline insolubles, pressure and heterocylic compounds of N, S and O on the formation and growth of mesophase, and on the microstructure and graphitizability of resultant coke from two different pitches.

2 EXPERIMENTAL

The coal-tar pitches used in this study were from Taiyuan Iron and Steel Plant (TY pitch) and Wuhan Iron and Steel Plant (WH pitch). Some characteristics of these two pitches are presented in Table 1.

Different kinds of carbon and hydrogen atoms were analyzed with VARIN FT-80A spectrum nuclear magnetic resonance apparatus (^{13}C-NMR and ^{1}H-NMR).

The formation of mesophase from the parent pitches was monitored by Leitz hot-stage microscopy. The pitches were heated at a rate of 10 ℃/min under an argon flow. The texture of the resultant carbon was qualitatively determined by scanning electron microscopy.

Carbonization and graphitization were carried out in QIH-3 hot isostatic press furnace made in Sweden and ZGSJ-100-28 vacuum-pressure sintering furnace respectively. The efficiency of the graphitization was determined by X-ray diffraction (XRD) on a Rigaku D/MAX-3C diffractometer with CuK_α radiation. The degree of graphitization was calculated from Maire and Mering's equation[20]:

$$\bar{g} = \frac{3.44 - d_{002}}{3.44 - 3.354} \times 100\% \quad (1)$$

3 RESULTS AND DISCUSSION

3.1 ^{13}C-NMR and ^{1}H-NMR spectrum analyses

The distribution of carbon and hydrogen atoms in TY pitch and WH pitch characterized by ^{13}C-NMR and ^{1}H-NMR spectrum analyses is listed in Table 2.

The aromatic characteristics show that TY pitch is largely composed of polyaromatics even though the element component fraction and $x(C)/x(H)$ ratio

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Table 1 Some properties of coal-tar pitches

Sample	Softening point/ ℃	w (Element) / %						w (Ash) / %	w (Components) / %		
		C	H	O	N	S	C/H		TS	TI-QS	QI
TY pitch	108	92.58	4.99	0.958	0.89	0.49	1.55	0.092	62.86	37.14	11.21
WH pitch	78	92.32	4.90	0.927	0.99	0.66	1.57	0.103	77.41	22.59	5.9

TS—Toluene solubles; TI—Toluene insolubles; QS—Quinoline solubles; QI—Quinoline insolubles

Table 2 Distribution of carbon and hydrogen atoms in two pitches (mole fraction, %)

Sample	Aliphatic carbon	Aromatic carbon			Aliphatic hydrogen			Aromaticity index
		Proton aromatic carbon	Bridged carbon	Substituted aromatic carbon	H_α	H_β	H_γ	
TY pitch	7.24	54.37	17.64	20.75	7.09	3.57	1.41	92.76
WH pitch	29.46	52.31	7.88	10.35	5.22	7.70	0.52	70.54

of the two pitches are almost the same. In addition, mole fraction of bridged carbon and substituted aromatic carbon of TY pitch are nearly two times those of WH pitch. Generally, aliphatic carbon consists of light mass molecules or volatiles in pitches, so the NMR analyses is in agreement with group components distribution. Consequently, the softening point and viscosity of TY pitch are much higher than those of WH pitch. Accordingly, the impregnating temperature of these two pitches should be distinguished.

3.2 Hot-stage microscopy investigation

Hot-stage microscopy investigation is a suitable method to monitor the formation and growth of mesophase in pitches. The main characteristics of the two pitches during heating are listed in Table 3.

Table 3 Results from hot-stage microscopy investigation

Temperature/ ℃	TY Pitch
250	Isotropic black powder existed
300	Some volatiles produced
360	Anisotropy nuclei appeared
420	Mesophase spherules grew and coalesced
500	Bubbles ascended and small domains formed
Temperature/ ℃	**WH pitch**
40	Isotropic black powder existed
200~ 400	Lots of volatiles rose from isotropic parent pitch
460	Intensive mesophase spherules came up
520	Bubbles rose and medium-flow anisotropy formed

It can be inferred from the hot-stage microscopy investigation that at temperature above 375 ℃, cracking reactions take place, releasing aliphatic fragments because the side chains to the polyaromatic molecules which remain in the fluid are severed. The evaporation of low molecular mass species disrupts the micellar structure of the pitch; the solubility of the polyaromatics is reduced; and they separate out to form an anisotropic liquid crystalline phase, the carbonaceous mesophase. Fig. 1 shows the development of mesophase through pyrolysis. Spherules with a lamellar arrangement of the disc-like molecules appear firstly. They coalesce, grow, and gradually increase in concentration until the mesophase becomes dominant and then almost the only phase in the pyrolysis residue. Beyond the phase inversion point, when the mesophase becomes the continuous phase, the viscosity increases very rapidly and eventually the material solidifies.

In heterocylic compounds, O and S appear to act as cross-linking species[21]. They cause an isotropic pitch develop into three-dimensional network structure and increase the viscosity of the whole system, which prevents the formation of carbonaceous mesophase. In addition, the resultant coke will be graphitizable. N has similar effect upon mesophase formation. Since both pitches have almost equal amounts of N, S and O, there are not much difference upon the formation and coalescence of mesophase spherules. Comparatively, quinoline insolubles (QI) have stronger influence upon that course.

QI can be categorized into two types, primary QI and secondary QI. This paper mainly discussed the influence brought out by primary QI. It is established that the development of mesophase during pitch impregnation/ carbonization and the structure of resultant cokes are significantly influenced by the presence of QI. Taylor et al[11] stated that the presence of QI accelerated the formation of mesophase, while Romovacek et al[12] got the contrary conclusion. Taylor[11] indicated that when QI contents were less than 10% (mass fraction), they had no accelerating effects at the initial stage of mesophase formation.

In the experiment, mesophase spherules appeared much earlier in TY pitch than in WH pitch. This means that in the range of 5% ~ 10% (mass fraction), QI content is favorable in nucleation of mesophase, or at least has no retardant effect. In TY pitch, the relatively higher QI content tends to agglomerate during heating process before mesophase nucleation, and this results in inhomogeneity in the liquid system, then some large mass molecular polyaromatics aggregate and collide with each other. Polymerization and condensation reactions take place between the various planar aromatic molecules, where aromatic planes are stacked approximately parallel to

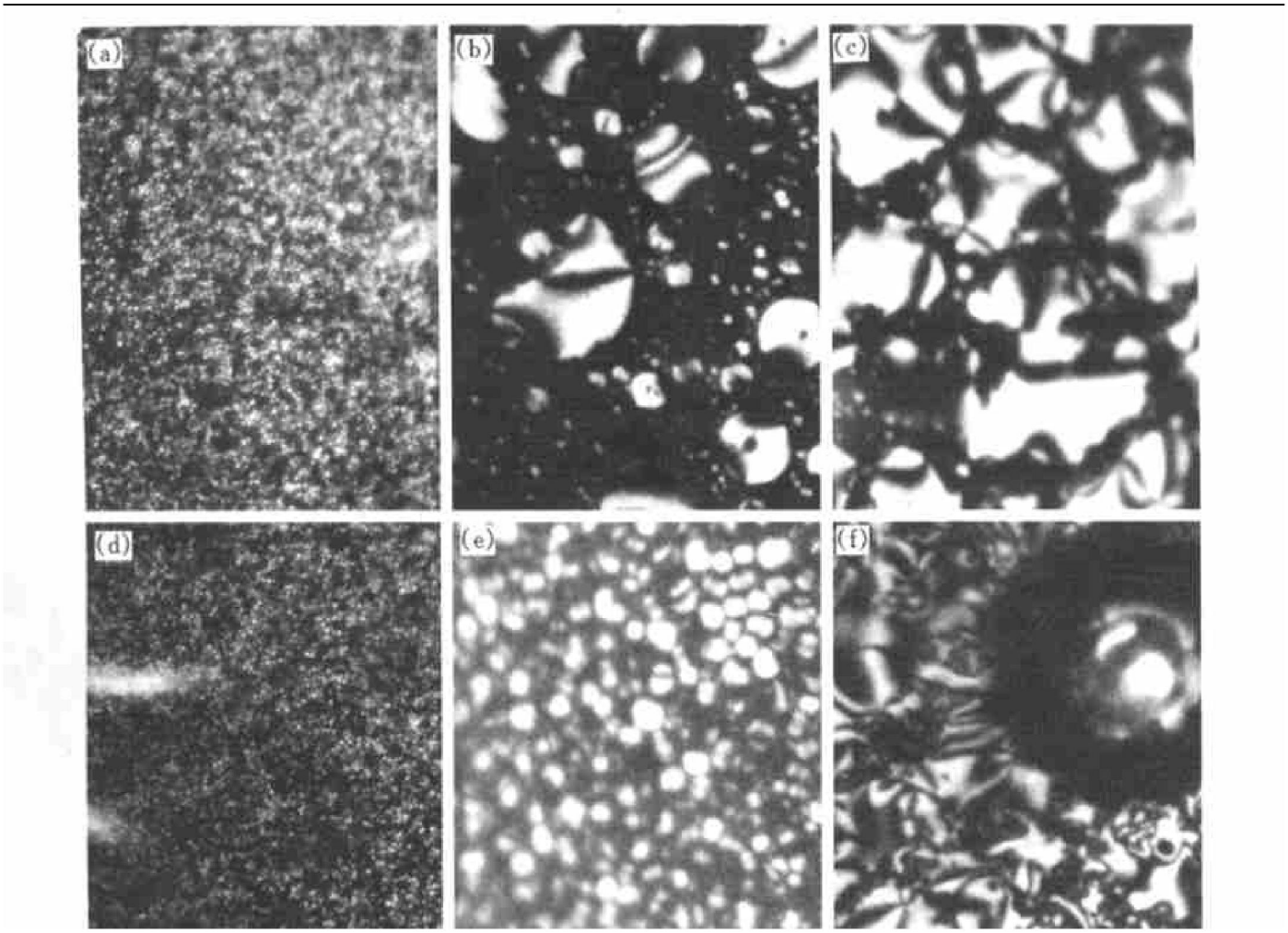

Fig. 1 Formation of mesophase in TY pitch (a~ c) and WH pitch (d~ f)
(a), (d) —Nucleation and spherules formed; (b), (e) —Growth and coalescence of spherules;
(c), (f) —Small domains and medium-flow anisotropy formed

each other, then nematic liquid crystal forms, mainly composed of aromatic oligomers. To some extent, nucleation is induced by this mechanism and QI particles have a catalytic effect on the polymerization of molecules in the isotropic phase. Contrastively, the WH pitch, in spite of small amount of QI content, does not nucleate until 460 ℃. This might be ascribed to the high ratio of volatiles, and the ascension of lots of volatiles from parent pitch intensifies convection in the liquid system. Consequently, the force between molecules can not fix them to laminar crystal phase. From this point of view, QI in some situation can accelerate nucleation of mesophase.

Secondly, it is easy to find small beads agglomerating around the margin of big spheres, especially in TY pitch (as shown in Fig. 1(c)). Because of high QI content, at early stage of mesophase formation, the mesophase spherules may be coated by QI and this prevents their further coalescence because of the "pin" effect of QI. Hence the later formed spherules grow much faster than the initially formed ones do (as shown in Fig. 1(b)), and this inference is proved by hot stage microscopy investigation. This result is in correspondence with Taylor and Figueiras' research[10,11]. The change of orientation of layer planes will surely affect the bonding of fiber/matrix of C/C composites.

Besides QI content, other effects, such as pressure, also affect the formation of mesophase. Because the morphology of mesophase can maintain in the resultant cokes, it is reasonable to deduce the effect of pressure on the mesophase formation by analyzing the resultant coke carbonized under pressure. Fig. 2 shows the SEM micrographies of cokes for TY pitch and WH pitch. The resultant cokes from WH pitch are mainly elongated flow type domains with pressure increasing from 7 MPa to 100 MPa. While carbonization of TY pitch under 86 MPa leads to a botryoidal structure.

On one hand, as for WH pitch, with the increase of carbonization pressure, more and more volatile material is retained, which not only causes higher carbon yield (as listed in Table 4), but also increases the solubility of large mass molecules because of increased "solvents". The viscosity of the liquid system decreases, so the growth and coalescence of mesophase spherules are encouraged.

On the other hand, the other effect of pressure on liquid system is to increase its viscosity. As for TY pitch, when viscosity induced by pressure increasing

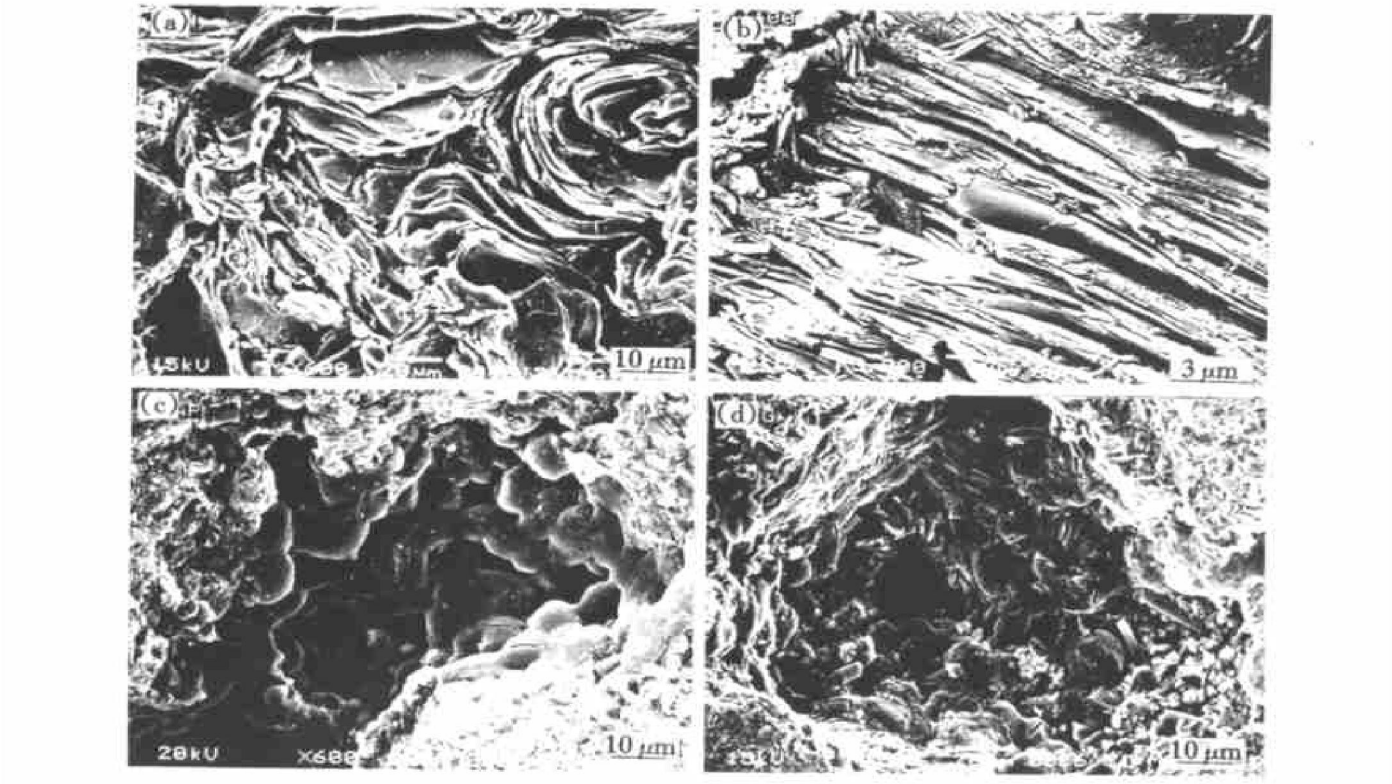

Fig. 2 SEM images of resultant cokes from TY pitch and WH pitch
(a) —WH pitch, 7 MPa; (b) —WH pitch, 100 MPa; (c) —TY pitch, 86 MPa; (d) —TY pitch, graphitized, 2400 ℃

Table 4 Results of carbonization (at 1000 ℃) and graphitization

Sample	Carbonization pressure/ MPa	Carbon yield/ %	Graphitization degree/ %	
			2400 ℃	2600 ℃
TY pitch	86	90.1	65.3	81.1
WH pitch	7	80.3	76.2	88.8
WH pitch	100	89.4	77.0	86.3

outweighs the effect of volatile retention, the viscosity of liquid pitch is increased. As a result, coalescence and growth of mesophase spherules are impeded. This can be proven by the semi-coalesced botryoidal structures of cokes from TY pitch (as shown in Fig. 2(c)). The different effects of carbonization pressure upon these two pitches may be ascribed to their different group components, especially the QI contents. This result is in agreement with the study of Forrest et al[22].

As for C/C composites, the graphitizability of resultant coke is very important. Obviously, the graphitizability of these two cokes is different, although the carbon yields of the two pitches under high pressure are nearly equal (as listed in Table 4).

Results in Table 4 show that if judged only by carbon yield, TY pitch is more suitable as impregnant of C/C composites. Increasing carbonization pressure from 3MPa to 100MPa is not economically feasible in case of little improvement of carbon yield, but when combined with densification efficiency, things will be in another way.

Because of high QI content in TY pitch, under high carbonization pressure, coalescence of mesophase spherules is impeded and three-dimensional network structures forms which is different from the flake shaped graphitizable cokes from WH pitch. After graphitization, some cracks generates in TY pitch (as shown in Fig. 2(d)).

4 CONCLUSIONS

1) Under atmospheric pressure, QI contents accelerate the nucleation of mesophase or at least have no obvious retardant effects.

2) Coalescence of mesophase spheres will be impeded under high carbonization pressure if QI contents are relatively high (> 10%, mass fraction).

3) QI contents affect the graphitizability of resultant cokes. The coke produced from TY pitch is less graphitizable.

4) As for impregnant of C/C composites, coal-tar pitches should be paid more attention to about modification considering different conditions of C/C composites.

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