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Oxidation properties of mesophase pitch prepared by a heterogeneous nucleation method

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Mesophase pitches prepared by a heterogeneous nucleation method from various mixtures of coal tar-derived isotropic pitch and petroleum-derived mesophase pitch (MP-P) were oxidatively stabilized, and the dependence of chemical reactivity and stabilization rate on their chemical structure was investigated. The rate and amount of oxygen uptake of the mesophase pitch fibres, revealed by thermogravimetry, increased under given conditions of oxidation with the amount of added MP-P, but the rate of stabilization showed a reverse trend. The lower chemical reactivity of coal tar-derived mesophase pitch (MP-C) appears to induce a slower rate of oxygen uptake, while the higher content of pyridine-insoluble fraction and higher aromaticity of MP-C may result in a lesser content of oxygen being required for stabilization, as compared with MP-P.

1. Introduction

Mesophase pitch has been recognized as a precursor of high-performance carbon fibre, and several methods of preparation of mesophase pitch have been reported [1–5]. Some modifications of mesophase pitch by blending polymeric substances have also been examined [6, 7]. Park and Yoon [8] prepared mesophase pitch using a heterogeneous nucleation method from various mixtures of mesophase pitch and isotropic pitch. They found that the method was very effective to prepare mesophase pitch in a shorter time and at a higher yield compared with the preparation from a simple heat-treatment of isotropic pitch alone. A modification of pitch components may be also possible, if the starting pitches and their composition are properly designed.

The manufacture of carbon fibre from mesophase pitch requires oxidative stabilization of pitch fibre for the prevention of melting, sticking and loss of fibrous shape during successive carbonization [9–11]. As the stabilization process has a strong influence on the cost and performance of the resultant carbon fibre [12], some of the chemical reactions and the thermodynamic and kinetic natures of the step have been investigated [9–16]. However, the stabilization scheme in relation to the chemical structure of mesophase pitch components was not fully understood.

In the present work, in order to compare the stabilization behaviours of mesophase pitch samples with different chemical structures, the oxidation properties of mesophase pitch fibres prepared by the heterogeneous nucleation method from mixtures of coal tar-based isotropic pitch and petroleum-based mesophase pitch were investigated, and also compared to those prepared from coal tar pitch or petroleum pitch alone.

2. Experimental procedure

A coal tar-derived isotropic pitch (IP-C), prepared after heat treatment under pressure, and a petroleum-derived mesophase pitch (MP-P), prepared from residues of fluidized catalytic cracking decant oil (FCC-DO), were used as raw materials in this work. Table I shows some analytical data for IP-C and MP-P. Various mixtures of IP-C and MP-P were weighed in a Pyrex tube with a side arm and heated at a rate of 5 °C min^{-1} to a desired temperature, and were maintained with an inert gas sparge to produce mesophase pitches.

The mesophase pitch was spun into fibres of 20 to 30 μm diameter using a spinnerette with a nozzle diameter of 0.3 mm. The applied pressure of nitrogen was 1.1 to 1.3 kg cm^{-2}.

A part of the spun pitch fibres was slightly milled to less than 1 mm in length. Thermal analysis of the milled pitch fibre was carried out by thermogravimetry (TG) and differential. scanning calorimetry (DSC) under air flow.

Bundles of pitch fibres were stabilized under air flow at 270 °C for 30 min. The heating rate was 10 °C min^{-1}. The stabilized fibres were then carbonized at 1300 °C for 1 h under an argon atmosphere at a heating rate of 10 °C min^{-1}. The cross-sectional views of the stabilized fibre and the carbonized one were examined using a polarized light microscope to evaluate the extent of thermosetting.

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TABLE I Some properties of the pitches

Sample	Carbon aromaticity, f_a	H/C	Softening point (°C)	Anisotropy content (vol %)	Solubility (wt %)*		
					BS	BI–PS	PI (QI)
IP-C	–	0.57	105	0	90	10	0 (0)
MP-P	0.81	0.55	258	100	19	29	52(31)

*BS = benzene-soluble, BI = benzene-insoluble, PS = pyridine-soluble, PI = pyridine-insoluble, QI = quinoline-insoluble.

TABLE II Some properties of mesophase pitches

Sample	Carbon aromaticity, f_a	H/C	Softening point (°C)	Anisotropy content (vol %)	Solubility (wt %)		
					BS	BI–PS	PI (QI)
MP-C	0.95	0.48	315	100	5	28	67(55)
MP-20	0.91	0.51	272	100	22	12	66(47)
MP-30	–	0.51	273	100	28	17	55(47)
MP-50	0.87	0.53	267	100	23	21	56(51)
MP-70	0.85	0.53	262	100	–	–	–

Some of the pitch fibres were stabilized at a higher temperature of 350 °C using a heating rate of 10 °C min^{-1} for complete thermosetting and then carbonized at 1300 °C for 1 h at heating rate of 10 °C min^{-1}. The carbonized fibres were observed using a scanning electron microscope (SEM).

3. Results

Table II summarizes some analytical results for mesophase pitches. Coal tar-derived mesophase pitch (MP-C) shows a higher softening point and lower solubilities due to a higher degree of aromaticity than those of MP-P. The analytical values for the mesophase pitches prepared from mixtures of IP-C and 20, 30, 50 and 70 wt % MP-P (denoted by MP-20, MP-30, MP-50 and MP-70, respectively) approach that of MP-P itself with increasing content of MP-P.

Fig. 1 illustrates TG curves of mesophase pitch fibres when heated at 10 °C min^{-1} to 430 °C in air flow. Each curve shows a parabolic pattern with an initial weight gain to a maximum value followed by a subsequent weight loss, which may result from internal oxygen uptake and surface burn-off [9, 10], respectively. The weight gain of MP-C fibre reaches a maximum of 5.8 wt % at 380 °C, whereas the weight gain of MP-P increases more rapidly than that of MP-C and reaches a maximum of 8.6 wt % at 350 °C. The maximum gains of MP-30 and MP-50 are 7.2 and 7.8 wt %, respectively. The rate and maximum value of weight gain of the mesophase pitch fibres increase and finally approach those of MP-P fibre as the content of MP-P (in the mixture) increases.

Fig. 2 shows TG curves of mesophase pitch fibres during heat-treatment at 270 °C for 90 min in an air flow. The weight gain increases rapidly between 20 and 40 min for all samples, but the fibres gain more weight in this range as the content of MP-P increases. In the DSC analysis illustrated in Fig. 3, the oxidation of mesophase pitches prepared by addition of MP-P begins to occur at lower temperatures than for MP-C.

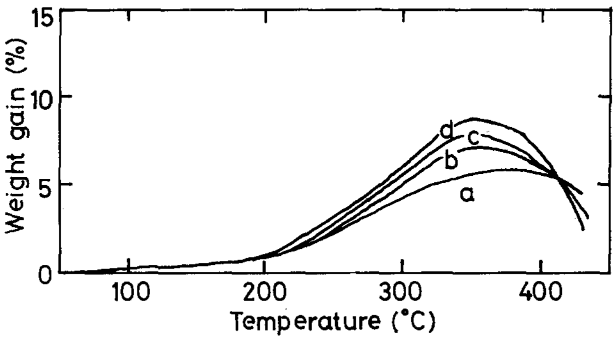

Figure 1 TG curves of mesophase pitch fibres heated at a rate of 10 °C min^{-1} under air flow of 16.6 cm^3 min^{-1}. (a) MP-C, (b) MP-30, (c) MP-50, (d) MP-P.

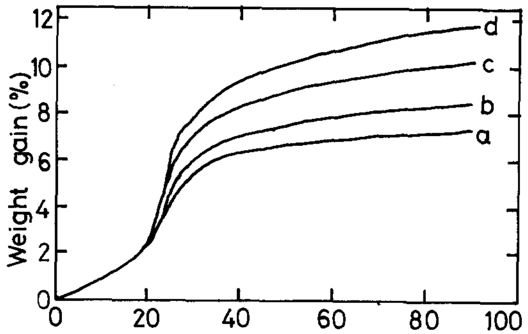

Figure 2 TG curves of mesophase pitch fibres heated at 270 °C under air flow. (a) MP-C, (b) MP-30, (c) MP-50, (d) MP-P.

Fig. 4 shows optical micrographs of pitch fibres oxidized at 270 °C for 30 min in air and then carbonized at 1300 °C for 1 h. MP-C fibres were found to be completely stabilized and maintained their fibrous shapes without sticking. Mixed mesophase pitch fibres, MP-30 and MP-50, show a fusion of the core

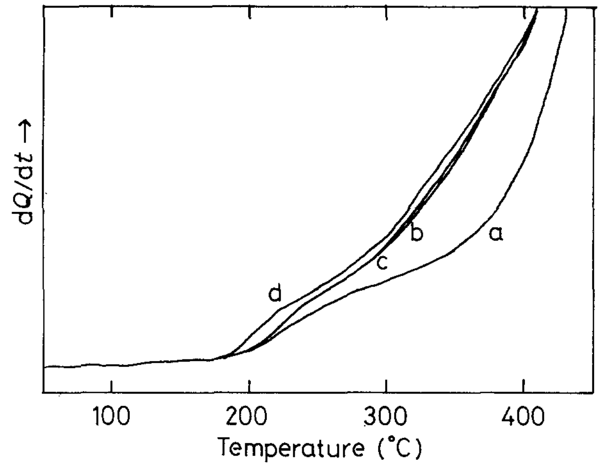

Figure 3 DSC curves of mesophase pitch fibres heated at a rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ under air flow. (a) MP-C, (b) MP-30, (c) MP-50, (d) MP-P.

region. MP-P fibres were also fused in the core region and even adhered to each other.

Fig. 5 shows scanning electron micrographs of mesophase pitch-based carbon fibres prepared by oxidation at 350 °C and successive carbonization at 1300 °C for 1 h, all of which were completely stabilized and show skin–core structure. The skin of MP-C fibre shows a very fine mosaic texture in transverse section and has an average thickness of about 6 μm. As the amount of added MP-P increases, the thickness of skin decreases and its texture becomes coarse.

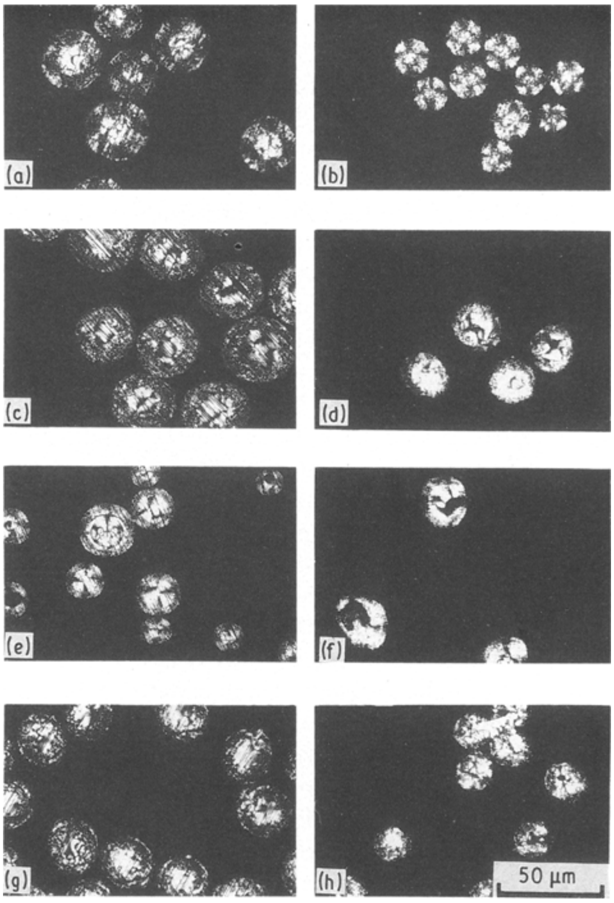

Figure 4 Optical micrographs of stabilized fibres (a, c, e and g) and carbonized fibres (b, d, f and h). Stabilization conditions $10\,^{\circ}\mathrm{C\,min^{-1}}$, 270 °C, 30 min; carbonization conditions $10\,^{\circ}\mathrm{C\,min^{-1}}$, 1300 °C, 1 h. (a, b) MP-C, (c, d) MP-30, (e, f) MP-50, (g, h) MP-P.

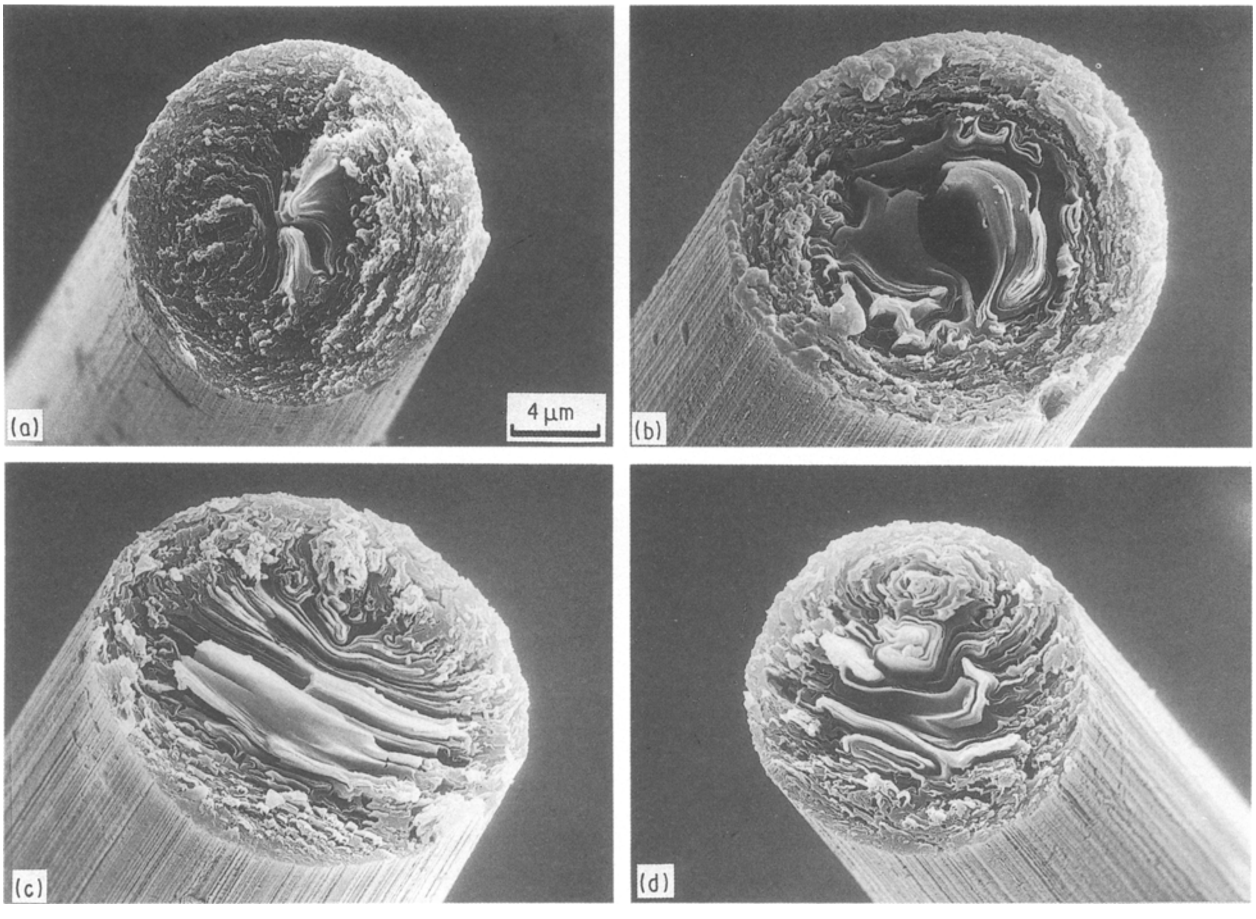

Figure 5 Scanning electron micrographs of carbonized fibres. Stabilization condition $10\,^{\circ}\mathrm{C\,min^{-1}}$, 350 °C; carbonization condition $10\,^{\circ}\mathrm{C\,min^{-1}}$, 1300 °C, 1 h. (a) MP-C, (b) MP-30, (c) MP-50, (d) MP-P.

4. Discussion

Oxidative stabilization of mesophase pitch involves the diffusion of oxygen to reaction sites and oxidative reaction at those sites [9]. Some authors [9, 13] have reported that oxygen diffusion was the rate-determining step of the stabilization process. Mochida *et al.* [17, 18] showed that the rate of stabilization was also influenced by the chemical reactivity of the precursor pitch, which depends on its composition and chemical structure.

The rate of oxygen uptake of MP-P fibre was faster than that of MP-C fibre as shown in Figs 1 and 2. The oxygen contents of MP-C, MP-30, MP-50 and MP-P were 5.5, 6.0, 7.2 and 7.9 wt % (see Fig. 1), respectively, when they were oxidized at 270 °C for 30 min. However, only MP-C fibre was completely stabilized in spite of having the lowest content of oxygen, as shown in Fig. 4. This means that 5.5 wt % of oxygen uptake is sufficient to stabilize MP-C fibres but more than 7.9 wt % is required to stabilize MP-P fibres.

The stabilization of pitch fibres is assumed to be achieved through oxygenation and oxidative dehydrogenation–condensation [19]. The former reduces the solvent ability of fusible pyridine-soluble (PS) material and the solubility of non-fusible pyridine-insoluble (PI) material in the fusible PS fraction, while the latter converts fusible PS material to a non-fusible form [18]. As MP-C has a higher content of PI fraction and a higher aromaticity than MP-P as shown in Tables I and II, MP-C requires a lesser content of oxygen for stabilization than MP-P and could be more rapidly stabilized under given conditions.

For the mesophase pitches from mixtures of IP-C and MP-P, the PI fraction and the aromaticity decrease and approach those of MP-P itself with increasing amount of added MP-P. Therefore, the stabilization rate increased in the order of MP-P $<$ MP-50 $<$ MP-30 $<$ MP-C. The structural distribution of the mixed MP should be further investigated in detail.

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