

AR mesophase pitch prepared by co-carbonization of methyl-naphthalene and naphthalene with aid of HF/BF₃ as a catalyst

Seong-Ho Yoon, Hidetoshi Oka, Nobuyuki Takano, Yozo Korai, Isao Mochida, Takashi Kojima*, and Makoto Komatsu*

Institute of Advanced Material Study, Kyushu University, *Mitsubishi Gas Chemical Co.

1. INTRODUCTION

The present authors prepared AR-mesophase pitch through co-carbonization of methyl-naphthalene and naphthalene in order to obtain the better tensile properties of the resultant carbon fiber. The structure and properties of co-carbonized mesophase pitch were characterized and compared to reveal the role of methyl groups on the mesogenic aromatic plane with the methyl-naphthalene, naphthalene, and melt-blended AR mesophase pitches. The molecular structure, aromatic molecular stacking, flow properties and stabilization reactivities of the co-carbonized mesophase pitch as a precursor for the carbon fiber were principally examined. Tensile properties of the resultant carbon fibers from homo- or co-carbonized AR mesophase pitches were also examined.

2. EXPERIMENTAL

Co-carbonized mesophase pitch (mNP/NP(co)) was prepared from the mixture of methyl-naphthalene and naphthalene by 3/7(wt/wt) with aid of HF/BF₃. Blended mesophase pitch (mNP/NP(mix)) was prepared by melt-blending of mNP and NP by weight ratio of 7/3.

Mesophase pitches were characterized using ¹H-NMR, ¹³C-NMR, FD-Mass, X-ray diffractometer, and Model Capirograph 1B capillary rheometer. The mesophase pitch was spun into fiber of ca. 9 - 12 μm in diameter using laboratory scale mono-filament spinning apparatus. Oxidation reactivity of as-spun mesophase pitch fibers were estimated by differential scanning calorimetry. The stabilized fibers were carbonized at 1000°C for 0.5 hs at a heating rate of 10°C/min and graphitized at 2500°C for 2 min at a heating rate of 100°C/min.

3. RESULTS AND DISCUSSION

Softening point, anisotropic contents, solubility, H/C ratios, and X-ray properties of mNP, NP, mNP/NP(co), and mNP/NP(mix) mesophase pitches are summarized in Table 1. Co-carbonized pitch of mNP/NP(co) shows very similar softening point, solvent solubility, and H/C atomic ratio with NP, while blended pitch of mNP/NP(mix) shows lower softening point, more solubility to benzene, and larger H/C ratio that are very similar with that of mNP.

M/Z peaks ranged from 250 to 1200 which corresponds to dimers to decamers of the naphthalene units in the spectrum of mNP/NP(co) as shown in Fig.1. MNP/NP(co) shows non-Gaussian and continuous molecular weight distribution, exhibiting lower molecular components compared to NP.

The results of ¹H-NMR and ¹³C-NMR are summarized in Table 2. The NP and mNP/NP(co) carried more aromatic hydrogens and higher carbon aromaticity than mNP and mNP/NP(mix). MNP/NP(co) and mNP/NP(mix) shows much larger value of methyl carbons of 3.1 and 3.6, respectively, than that NP. The amount of methyl carbon of mNP/NP(co) was a little smaller than calculated one, while that of mNP/NP(mix) well agreed with calculated

one.

X-ray C(002) diffraction parameters of mesophase pitches are also listed in Table 1. D002 of mNP/NP(co) and mNP/NP(mix) were 0.3532 nm and 0.3531 nm, respectively, which is similar with that of NP. Lc(002) of mNP/NP(co) and mNP/NP(mix) were 3.6 nm and 4.0 nm, respectively. Lc(002) of mNP/NP(mix) well agreed with the calculated value of 4.0 nm, while that of mNP/NP(co) appeared a little lower.

The shape of viscosity-shear rate correlation curve of MNP/NP(co) was similar to that of NP, while the MNP/NP(mix) was similar to mNP.

The peak appeared at the lower temperature(P1) indicated the oxidation of naphthenic and alkyl groups as shown in Fig. 2. The larger peak at the higher temperature(P2) indicated the oxidation of aromatic carbons. The locations of P1 peaks of each pitch fiber shifted to higher temperature in the order of mNP, mNP/NP(mix), mNP/NP(co), and NP, reflecting the low glass transition temperatures of mNP and mNP/NP(mix). However, the location of P2 peaks of each pitch fibers shifted vice versa, reflecting lower aromaticity of mNP and mNP/NP(mix). The endothermic heat of the oxidation of the aromatic carbon appeared increasing in the order of mNP, mNP/NP(mix), mNP/NP(co), and NP.

All fibers show the degree of preferred orientation in the range of 75 - 85 %. MNP fiber shows the highest preferred orientation. The degree appeared increasing in the order of NP, mNP/NP(co), mNP/NP(mix), and mNP, well agreed with the value of Lc(002) of them.

The graphitized fiber from mNP/NP(co) showed totally radial orientation in the all transverse area. Long and multi-bent domains were aligned from the outer to the center parts.

Table 3 shows the tensile properties of the resultant graphitized fibers. The graphitized fiber from mNP/NP(co) heat treated at 2500°C for 2 min shows the highest tensile strength and Young's modulus of 4750MPa and 975GPa respectively. Especially, it shows the largest value of ultimate elongation of 0.5%, reflecting that it has a best and unique tensile properties inheriting from the structure of mesophase pitch precursor.

The tensile strength and Young's modulus of the graphitized fibers from mNP and NP shows 2050 and 4050 MPa, and 960 and 800 GPa, respectively. The ultimate elongation of the graphitized fibers from mNP and NP shows 0.3 and 0.4 %, respectively. The fiber from the mNP was characterized with higher Young's modulus and smaller ultimate elongation compared to the fiber from NP.

The co-carbonized pitch with methyl-naphthalene and naphthalene and the mixed mesophase pitch with mNP and NP show both characteristics of mNP and NP that is induced from the methyl groups pentanted on the aromatic carbons. Higher stackings in mNP/NP(co) and mNP/NP(mix) are believed to be the major reason for the higher preferred orientation and better mechanical properties.

Table 1 Some properties of mesophase pitches

Sample code	Softening point(°C)	Anisotropic contents(vol%)	Solubility(wt%)		H/C	X - ray properties	
			BS	BI		d002(nm) ^{a)}	Lc(002)(nm) ^{b)}
NP	237	100	45.7	54.3	0.65	0.3532	3.0
mNP	205	100	55.3	44.7	0.70	0.3545	6.5
mNP/NP(co)	235	100	45.7	54.3	0.65	0.3532	3.6
mNP/NP(mix)	228	100	56.0	44.0	0.65	0.3531	4.0

a) Interspace distance. b) Height of crystalline

Table 2 Hydrogen and carbon distributions of BS in mesophase pitches

Sample	¹ H - NMR				¹³ C - NMR					fa
	H(a)	H(1)	H(2)	H(3)	C1	C2	C3	C4	C5	
NP	54.4	34.3	9.0	2.3	33.3	21.3	38.9	5.6	0.9	0.935
mNP	46.4	39.7	11.3	3.0	28.5	19.5	43.8	3.7	4.5	0.918
mNP/NP(co)	52.8	33.7	11.1	2.5	27.7	20.3	44.3	4.6	3.1	0.923
mNP/NP(mix) measured	47.8	36.0	13.3	3.0	26.6	19.8	44.4	5.6	3.6	0.908
mNA/NA(mix) calculated	52.0	35.92	9.7	2.5	31.7	20.8	40.4	5.0	2.0	0.930

H(a): Aromatic hydrogen, H(1): α -hydrogen, H(2): β -hydrogen, H(3): γ -hydrogen.

C1: Substituted aromatic carbon, C2: Outer quaternary aromatic carbon C3: Unsubstituted aromatic carbon, C4: Methylene carbon, C5: methyl carbon

Table 3 Mechanical properties of graphitized fibers heat treated at 2500 °C for 2min.

Designation	Precursor pitch	Diameter (μ m)	UE ¹⁾ (%)	YM ²⁾ (GPa)	TS ³⁾ (MPa)	DO ⁴⁾ (%)
mNP-GF	mNP	11.1(1.6)	0.3	960(154)	2050(501)	95.5(0.8)
NP-GF	NP	8.9(0.9)	0.4	800(120)	4050(440)	94.8(0.4)
mNP/NP(co)-GF	mNP/NP(co)	9.0(0.5)	0.5	975(60)	4750(303)	95.0(0.3)

1) Ultimate elongation, 2) Young's modulus, 3) Tensile strength, 4) Degree of preferred orientation. *() means the standard deviation.

