Recovery of Stacking Height of Mesophase Pitch Fiber by Solid-Phase Annealing

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The solid-phase annealing at temperatures higher than glass transition temperature (T_g) was found effective to recover or further improve the stacking of naphthalene and methylnaphthalene mesophase pitch fibers, maintaining the morphology of their fiber form. Thermal behaviors of mesophase pitches were examined to describe thermal changes of molecular stacking in its solid state and to clarify their significance on their nanoscopic structure.

Synthetic mesophase pitch derived from naphthalene has been highly appreciated as a precursor of carbon fiber of high graphitizability.[1–3] High tensile modulus, high capacity of Li ion and high thermal conductivity of the graphitized fiber have enlarged its application. The graphitizability of the mesophase pitch fiber has been reported to depend on not only the cluster dimension of mesophase pitch but also the spinning process.[4] The clusters of mesophase pitch lose their stacking at the spinning temperature.[5] The strong shear from the wall of spinning capillary forces shear thinning, to reduce also the stacking to a significant extent. The reduced stacking is not recovered through the quenching after commercial spinning.[6]

It is well-known with thermoplastic polymer that the glass transition phenomena can control the crystalline/amorphous dimension by the annealing at higher temperatures than T_g.[7–9] The mesophase pitch has not been reported to show obvious crystalline/amorphous structure. The annealing at higher temperature than T_g can be a key to recover the stacking of the pitch fiber reduced by spinning while the fiber shape and molecular orientation along fiber axis must be maintained when the stacking is attempted to be improved.

In the present study, the solid-phase annealing was attempted to recover or improve the stacking in the mesophase pitch fiber. Solid-phase annealing at a temperature between the glass transition and softening temperatures is expected to adjust the planar arrangement in the pitch fiber, retaining the fiber form.

AR mesophase pitches (Mitsubishi Gas Chemical Co.) synthesized from naphthalene (NP), and methylnaphthalene pitches (mNP 1, 2) using a HF/BF_3 were used for this study.[1–3] Some representative properties of mesophase pitches are summarized in Table 1. Thermal analysis was performed to measure the glass transition temperature (T_g) and softening temperature (T_s) of mesophase pitches, using a Thermal Mechanical Analyser (TMA, Seiko 5200). The heating rate was 10 °C/min.

Table 1. Representative properties and glass transition temperature (T_g), softening temperature (T_s) of naphthalene (NP) and methylnaphthalene (mNP) pitches

		NP	mNP 1	mNP 2
H/C (mol ratio)		0.65	0.69	0.67
Aromaticity (fa)		0.95	0.86	0.90
Lc002/nm		3.0	4.1	4.0
Annealing temperature/°C		206	190	200
TMA	T_s/°C	228	211	225
	T_g/°C	163	143	144
	T_g/K/T_s/K	0.87	0.86	0.84

AR mesophase pitches were spun under nitrogen pressure through a circular shaped spinning nozzle (diameter = 0.3 mm, length = 0.9 mm). Spinning was carried out using a laboratory scale mono-filament spinning apparatus at 300 °C for naphthalene pitch fiber (NPF) and 290 and 300 °C for methylnaphthalene pitch fibers 1 and 2 (mNPF 1 and 2), respectively. The spinning rate was 230 m/min which was comparable to that applied in the current industry of carbon fiber manufacture. The average diameters of NPF, mNPF 1 and mNPF 2 were 10.4, 13.7 and 16.4 μm. As-spun fibers were annealed at the temperatures of $(T_g + 2T_s)/3$, which are suggested in Table 1. The annealing time was 1–72 h. In some experiments annealing was repeated several times.

Stacking height (Lc002) was measured by an XRD apparatus (Rigaku Geigerflex, 40 kV, 30 mA, CuKα) and calculated by JSPS method.[10]

Figure 1 shows the TMA profiles of several mesophase pitches. Magnified profile suggests the glass transition point. The abrupt increase of slope can be observed at the glass transition point. NP showed relatively small increase of the slope, whereas mNPs showed larger change of slope. Table 1 shows the T_g, T_s and their ratio of mesophase pitches measured by TMA. T_gs of mNP 1 and mNP 2 were lower than that of NP. T_g was about 84–89% of T_s, being relatively high despite low molecular weight, compared with common thermoplastic polymers which show T_g/T_m (melting point) of 1/2–2/3.[11]

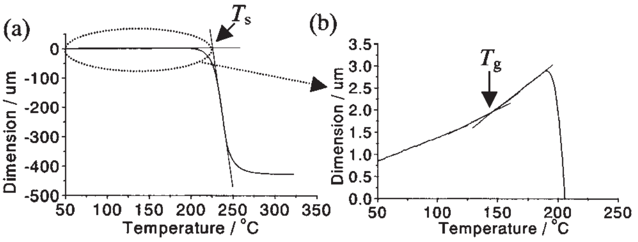

Figure 1. TMA profile of methylnaphthalene pitch (a) and its magnified profile (b) (mNP 2, 10 °C/min).

Figure 2 shows the stacking height of naphthalene and methylnaphthalene mesophase pitches, pitch fibers as-spun and annealed under different conditions. Spinning decreased the stacking height of NP from 3.0 nm to 1.6 nm. Lc002 values of mNP 1 and mNP 2 decreased from 4.1 nm, 4.0 nm to 3.8 nm,

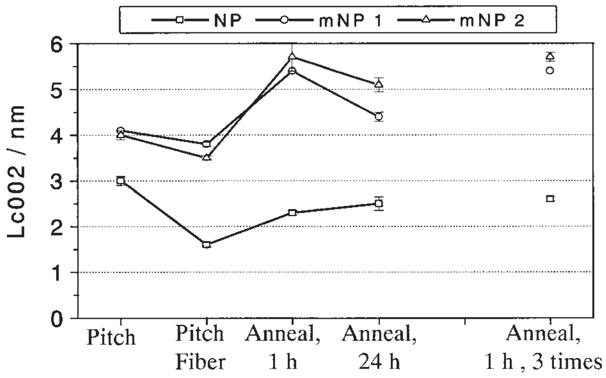

Figure 2. Stacking height (Lc002) of naphthalene and methylnaphthalene pitches, pitch fibers as-spun and annealed at different condition.

3.5 nm, respectively. Solid-phase annealing recovered definitely the reduced stacking height. Lc002 value of NPF increased to 2.3 nm by annealing for 1 h. Longer annealing for 24 h increased the Lc002 value to 2.5 nm, however, further annealing did not increase further. Lc002 increased by repeated annealing to 2.6 nm. The stacking of the mNPFs was more improved by annealing, Lc002 increasing to 5.4 and 5.7 nm, however, longer time annealing or repetition hardly improved stacking. The different kinds of mNPs showed the similar results.

The mesophase pitch consists of a mixture of aromatic oligomers that have relatively small molecular weights of 400–4000.[12] It is well-known that such oligomers are stacked to form a series of discotic clusters of dispersed stacking height, which includes larger and smaller aromatic ring compounds.[1–6,12] The stacking height is defined by the temperature of solidification as well as the molecular structure and composition.[13] When the pitch is spun and quenched, because of the rapid spinning and cooling of the fiber, the stacking height is governed by the spinning temperature.[14–16]

Above T_g, smaller molecules in the cluster obtain molecular mobility which may assist the finite rearrangement of larger molecules to increase the stacking height. Such a controlled mobility or flexibility of molecules in the fiber may allow the overall improvement of molecular stacking without any deformation of the fiber shape.

Lc002 of mNPFs was observed to be recovered and further improved by annealing regardless of annealing condition, which is higher than Lc002 of mNPs. Whereas Lc002 of NPF was recovered partially. The mNPs were made into pallet under shear stress in production process although it is smaller than that in spinning process. Therefore the provided pitch is thought to show no maximum stacking height. It may be a reason why solid-phase annealing was observed to improve the stacking height of mNPF.

Discotic molecules of the mesophase pitch in the π-π stacking form may require high energy for molecular relaxation. This explains why the glass transition temperature of the mesophase pitch was very high in spite of rather smaller molecular weight, compared with that of the thermoplastic polymer.

In conclusion, the stacking heights of mesophase pitch fibers were recovered and further improved by solid-phase annealing above T_g in the fiber form. Controlled mobility of large aromatic rings assisted by smaller rings above T_g can improve the discotic stacking without any deformation of the fiber shape.

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