Microvoids Present in Anisotropic Mesophase Pitch, Their As-spun and Annealed Fibers

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The sizes of free volumes in the mesophase pitches, as-spun and annealed fibers were measured by positron annihilation lifetime spectroscopy (PALS). The size of free volume increased with increasing of methyl groups in the mesogen molecules. Spinning increased the free volume while annealing after the spinning decreased it to similar value of the starting pitch.

Anisotropic mesophase pitch fiber has been appreciated as an excellent precursor for high performance carbon fibers of high graphitic extent which carries the best properties as essential parts in energy storage and thermo-management.[1–3] The high graphitizability is believed to originate from the hexagonal stacking in the cluster units of the mesophase pitch and their alignment along the fiber axis. The stacking inherits that in the anisotropic pitch and the units aligned during the spinning, reflecting the stacking and fluidity or deformability of microdomain units, and mesoscopic unit of the cluster aggregates in the mesophase pitch.[4,5]

The present authors found that the melt spinning reduces the stacking height of the cluster unit in the mesophase pitch and that the stacking reduced by spinning is recovered or even improved by annealing after the spinning.[6–8] The annealing temperature must be above the glass transition temperature but below softening temperature for effective improvement without any deformation of fiber form. The preferred orientation along fiber axis measured by XRD is not particularly improved.

The free volume, which reflects the microvoids of nano or subnano scale in the plasitic, has been believed to be present among the polymer chains, being very subjective to their chain folding structure. The crystalline region tends to have less volume than the amorphous region.

The mesophase pitch is a kind of oligomers and its free volume must reflect the stacking extents of hexagonal planes in their assembly. However, the free volume of mesophase pitches is difficult to quantify by DSC since melting occurs in a broad temperature range to overlap partly with the glass transition phenomenon.

In the present study, a series of mesophase pitches, their as-spun fibers and their annealed forms were measured by positron annihilation lifetime spectroscopy (PALS) to quantify their free volume since positron annihilation lifetime reflects the free volume. PALS can analyze the microvoids of subnano-nanometer scale which cannot be analyzed by other methods such as adsorption, Hg porosity, and small angle XRD. The lifetime and intensity of ortho-positronium (*o*-Ps) are related to the size of free volume and content of amorphous region respectively, since it is preferentially localized in the free volume holes. The free volume in the pitch is expected to give further insight into the structure of higher order in the mesogen assemblies.

Naphthalene, methylnaphthalene, and dimethylnaphthalene pitches were provided from Mitsubishi Gas Chemical. The as-received pitches, their as-spun and annealed fibers were measured. Pitch fibers were annealed at ca. 200 °C, higher than the glass transition temperature of the pitches.

Free volume properties were measured with PALS. Its theories, details and application to polymer can be found in the references.[9–13] The positron lifetime (τ_3) was measured at room temperature with a time resolution of 380 ps and a channel width of 20.9 ps. The specimens were formed into platelets of 20 mm diameter and 2 mm thickness. For each experiment, a 1.8 MBq positron source (^{22}Na) was sandwiched between two identical samples, which was precipitated from carrier-free ^{22}NaCl solution.

Table 1 summarizes *o*-Ps lifetime, τ_3, its intensity, I_3, spherical radius and volume, R_3 and V_3 of the free volume of mesophase pitches, as-spun and annealed fibers. I_3 indicates the number concentration of free volume, that is to say, the proportion of τ_3 component when the total positron annihilated is 100%. *o*-Ps is assumed to reside in a simple spherical potential space of radius R_3 and volume V_3, which were calculated by the following semiempirical equations.[14,15]

$$\tau_3 = 0.5[1 - R_3/R_o + (0.5/\pi)\sin(2\pi R_3/R_o)]^{-1}$$
$$R_o = R_3 + \Delta R, V_3 = 4\pi {R_3}^3/3$$

Table 1. The *o*-Ps lifetime τ_3, its intensity and free volume size of mesophase pitches, as-spun and annealed fibers

	Starting Molecules	Code	τ_3[a] /ns	R_3[b] /Å	V_3[c] /Å^3	I_3[d] /%
Pitch	naphthalene	NP	1.56 (±0.04)	2.41	58.8	4.4 (±0.2)
	methyl-naphthalene	mNP	1.60 (±0.03)	2.46	62.0	5.7 (±0.2)
	dimethyl-naphthalene	dimNP	1.65 (±0.04)	2.51	66.3	4.3 (±0.2)
Pitch Fiber	naphthalene	NPF	1.62 (±0.03)	2.48	64.1	6.2 (±0.2)
	methyl-naphthalene	mNPF	1.70 (±0.02)	2.56	70.1	8.7 (±0.2)
Pitch Fiber (Annealed)	naphthalene	NPFA	1.57 (±0.05)	2.43	59.7	3.2 (±0.2)
	methyl-naphthalene	mNPFA	1.63 (±0.03)	2.48	64.1	5.8 (±0.2)

a) *o*-Ps lifetime. b) The radius of free volume. *o*-Ps is assumed to be in a simple spherical potential well of radius R_3. c) The spherical volume. d) The intensity of *o*-Ps lifetime.

$\Delta R = 1.656$ Å is the thickness of the homogeneous electron layer in which the positron annihilates.[16]

First of all, the mesophase pitches showed similar but still meaningfully different values of τ_3, R_3 and V_3. I_3s were definitely

different. The increasing orders of NP < mNP < dimNP for $V_3(R_3)$, and dimNP ≤ NP < mNP for I_3 were observed reflecting the molecular structure of the mesogen, stacking of aromatic sheet in the cluster and the alignment of clusters in the microdomain.

The melt spinning and rapid quenching into thin fiber increased τ_3, $R_3(V_3)$, and I_3, indicating large increase of free volume. Disorder to induce free volume was certainly increased by the spinning. The annealing of spun fiber reduced significantly τ_3, $R_3(V_3)$, and I_3. It is noted that I_3 of annealed NP fiber was smaller than that of the starting pitch while that of annealed mNP fiber was still larger than that of starting pitch. Additionally, it must be noted that the mesophase pitch showed much smaller intensity than that of common thermoplastic polymer such as PS or PMMA. Highly aromatic natures of the mesophase pitch may reduce the intensity.

The mesophase pitches were first proved by PALS to carry free volume, which must reflect the molecular structure of mesogen, the height of hexagonal stacking in the cluster unit and their packing in the microdomain. The volume, V_3, may reflect the number of methyl groups, increasing in the order of NP, mNP and dimNP. Their free rotation may define the V_3. I_3 reflects the stacking height of the crystalline region and content of amorphous region. The latter is ascribed to the remaining volatile component, of which content is strongly subjective to the volatilization extent at the pitch synthesis. More extensive study is necessary to establish the correlation between free volume and structural parameters of mesophase pitches.

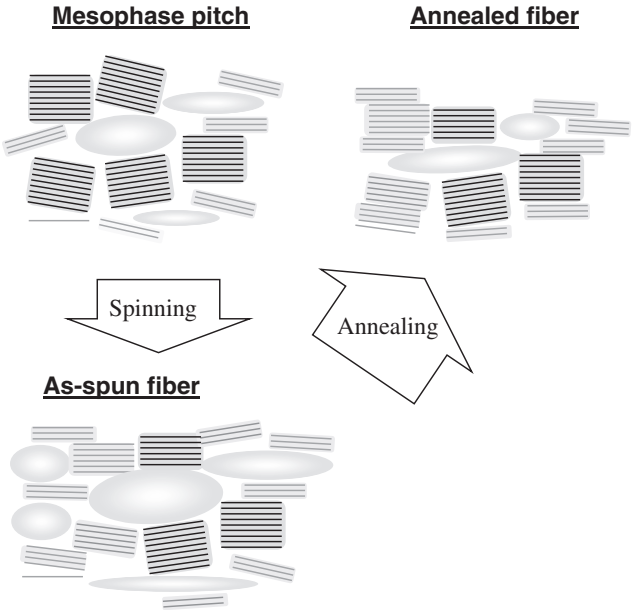

Figure 1. Schematic diagram for the change of stacking order and free volume by spinning and solid-phase annealing (Ellipse indicates free volume).

Spinning of the mesophase pitch certainly increased free volume in terms of both V_3 and I_3, probably reflecting stacking in the cluster and the alignment of clusters in the crystalline region in the mesophase pitch. Annealing recovers the stacking and alignment to reduce the free volume. Large recovery with NP may reflect larger contribution of crystalline region. Such situations about stacking order and free volume are schematically illustrated in Figure 1.

The present study describes a structural characteristic of the mesophase pitches, their as-spun and annealed fibers through measuring changes of their free volume. The free volume must intimately correlate with the structural orders of hexagonal planes in the cluster and microdomain, suggesting the importance of nanoscopic structure in terms of nanovoids as well as nano carbon body.

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