Quantitative Determination of Anisotropic Domain Size in Mesophase Pitch

by

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Introduction

Anisotropic domain size, defined as the average spacing between extinction contours observed during microscopic examination with crossed polarizers, is known to be an important characteristic of mesophase pitch. For example, mesophase pitches employed in the production of carbon fibers must be capable of forming a large domain size when heated under quiescent conditions.[1] The qualitative relationship between mesophase viscosity and domain size, namely, a large domain size reflecting a low mesophase viscosity and vice versa, was inferred initially by Brooks and Taylor[2] and confirmed by hot-stage microscopy.[3] Typical domain size versus time behavior derived from hot-stage observations is illustrated schematically in Figure 1. At a given temperature, the time (Point A) required for the less viscous mesophase (I) to reach a given domain size after agitation is less than the time (Point B) required by the more viscous mesophase (II) to reach the same domain size. This method can be used to estimate domain size, but it is time-consuming and subjective.

The paper describes a "constant time" procedure in which the domain size is the measured quantity. In this method, the mesophase is reduced to a uniformly small domain size, heated (annealed) for an appropriate length of time at a constant temperature, and then examined by polarized light microscopy. For this procedure, the domain size (Point C in Figure 1) of the less viscous material (I) is larger than the domain size (Point B) of the more viscous mesophase (II).

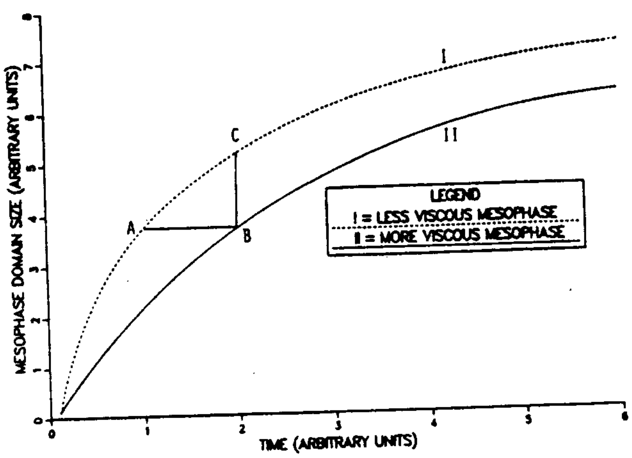

Figure 1. Schematic Plot of Domain Size Versus Time at Constant Temperature.

Experimental

Mesophase Pitch Preparation

Any suitable method can be used to prepare the mesophase pitch. The only requirement is that the product contain more than approximately 30% mesophase. This requirement precludes the case where the true "inherent" domain size might be larger than the small size of the coalesced regions in a low mesophase content pitch.

Annealing

The "annealing" procedure employed here is essentially identical to that used previously for the quantitative measurement of mesophase content.[4] Briefly, a representative powder sample (-200 mesh) of the mesophase pitch is placed in a loosely covered ceramic boat and heated in an inert atmosphere at the desired temperature (usually 325°-400°C) for a convenient time, e.g., 0.5 or 1.0 hours. Since the individual powder particles are randomly oriented with respect to each other in the sample holder, they develop a uniformly small domain size when they begin to melt during the initial heat-up portion of the annealing step. After annealing, several intact vertical cross-sections are mounted and polished for microscopic examination using the procedure described previously.[4]

Quantitative Evaluation of Domain Size

Domain size measurements can be made manually on photomicrographs by using a line segment method. This procedure involves counting the number of extinction contours which intersect a series of equally-spaced parallel lines drawn across the micrograph. A number average domain size is calculated from this data after correcting for any isotropic phase regions or voids which are present.

Preferably, domain size measurements can be automated with a Quantimet 720 Image Analyzer (IA). This technique can be applied to photomicrographs or used directly on polished specimens. The magnification is selected to ensure that the apparent size of the domains is within the resolution and frame size limits of the IA. Analogous to the manual procedure, an electronic mask was fitted to the IA to convert the actual image into a series of narrow bands. For direct IA analyses on specimens, eight representative areas which are free of voids and large isotropic regions are selected for measurement.

Table I shows the distribution of segment lengths by the IA for a typical sample. A logarithmic base has been used for the segment length size intervals to equalize the number of segment lengths detected in each interval. The first column lists the average segment length (P_i) in a size interval, and the second column gives the number of segment lengths (n_i) in that interval. The number average domain size calculated from the distribution for this sample was 10.9 µm. In developing this procedure, it was found that for some samples the number average was a poor measure of domain size because of the large number of small lengths. Therefore, a higher moment average was used. The relationship developed was:

$$W.D.S. = \frac{\Sigma n_i (P_i)^3}{\Sigma n_i (P_i)^2}$$

The weighted average domain size (W.D.S.) evaluated by the IA program from the above expression is 21.8 µm for the sample in Table I. The time required for the automated IA analysis is 10-15 min. per sample, after calibration of the IA.

Table 1. Domain Size Distribution for a Typical Sample

P_i (µm)	n_i
1.6	23
2.3	92
3.2	203
4.5	419
6.3	609
8.6	686
12.3	580
17.3	350
23.9	283
33.3	102
51.2	12

Results

We have used our measurement techniques to determine the average anisotropic domain size in a variety of mesophase pitch systems. Two examples are presented in this section.

Domain Size of Mesophase Derived from Different Precursors

The mesophase domain size is useful for characterizing carbon raw materials. As an example, Table II includes typical values for some commercial and model pitch precursors, which had been heat treated to produce 30-60% mesophase and then annealed at 400°C for 0.5 hours. The W.D.S. varies with the nature of the precursor, ranging from 10 µm for the resid to 200 µm for the petroleum pitch.

Table 2. Weighted Average Domain Size (W.D.S.) in Mesophase Derived from Different Precursors by IA on Polished Specimens

Precursor	W.D.S. (µm)
Vacuum Resid	10
Ethylene Tar	30
Dimethylnaphthalene	60
Naphthalene	170
Decant Oil	190
Q.I. Free Coal Tar Pitch	190
Ashland Petroleum Pitch	200

Domain Size of Mesophase Derived from Blends

The measurement technique can be used to determine the domain size derived from carbon precursor blends. Table III presents results for mesophase prepared from blends of a petroleum resid and a thermal tar. The resid produces a heterogeneous, relatively small-domain mesophase, while the thermal tar produces a large-domain mesophase. The blends were heat treated for 6 hours at 400°C and then annealed at 400°C for 0.5 hours. The measurements were made using the IA method on photomicrographs. As expected, the W.D.S. increases with increasing amounts of thermal tar in the blend.

Table 3. Weighted Average Mesophase Domain Size (W.D.S.) for Resid-Thermal Tar Blends by IA on Photomicrographs

Vol. % Resid	W.D.S. (µm)
100	13
73	29
53	46
22	141
0	238

Conclusions

A quantitative procedure has been developed for measuring an average anisotropic domain size for mesophase pitch. The quantitative determination of mesophase domain size can provide a very useful parameter for characterizing precursor pitches and for examining mesophase interactions in blends.

References

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