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Changes in the yield and size distribution of mesophase spheres on suppressing convective motion in a fused coal tar pitch

R. Moriyama[a,*], J.-i. Hayashi[b], R. Goda[b], T. Chiba[b]

[a] *The Institute of Applied Energy, Shinbashi SY Bldg., 14-2 Nishishinbashi 1-chome, Minato-ku, Tokyo 105-0003, Japan*
[b] *Center for Advanced Research of Energy Conversion Materials, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo 060-8628, Japan*

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Abstract

Upon heating of a coal tar pitch at 703 K, vaporization of the tar was promoted to a degree of 15–20 wt.%, either by increasing the free surface of the fused pitch exposed to a N_2 atmosphere or by jetting N_2 onto the surface. Enhanced viscosity of the pitch matrix by removing tar combined with restricted convection of the matrix prevented mesophase spheres from frequent coalescence and maintained a high interfacial area between the spheres and the matrix. The high interfacial area allowed a rapid increase in yield and sphere size. Sphere yields were up to 30 vol.% of the residual pitch, which lacked a bulk mesophase, and in which the average sphere radius was 2–4 μm.

Keywords: Liquid crystals; Crystallization; Optical microscopy; Microstructure

1. Introduction

When coal- or petroleum-derived pitch is heated to above 650 K, anisotropic mesophase spheres are generated in the isotropic matrix. These grow in size by absorbing material from the matrix, and coalesce. Progressive coalescence generates larger spheres and leads to a wide distribution in sphere size when coalescence proceeds in a random fashion. In order to produce meso-carbon microbeads (MCMB), the coalescence must be stopped before the spheres transform into a continuous bulk mesophase. When pitch is heated for a short period or at lower temperatures in order to avoid formation of the bulk mesophase, the yield of MCMB is generally low, only 5–20 wt.% of the heat-treated pitch [1]. In addition, the MCMB particles range from 1 to 100 μm, unless a chemically modified or synthetic pitch is used as the initial constituent [2]. Three elemental rate processes are involved in mesophase sphere formation: nucleation, growth, and coalescence, and the wide distribution in sphere size is attributed to a protracted period of nucleation and/or frequent coalescence [3,4]. Therefore, it is important to ascertain the factors that determine the rates at which these three elemental processes proceed in order to narrow the sphere size distribution, and increase the yield of mesophase spheres.

At the temperatures at which mesophase formation occurs, the vaporization of lighter components, referred to as tar, occurs concurrently with polymerization. The promotion and suppression of tar release may alter the relative concentration of heavier materials in the pitch, and hence its properties, such as the viscosity of the pitch [5–8] and the distribution of the anisotropic spheres. Both factors are considered crucial in determining the frequency of sphere coalescence. Bhatia et al. [5] investigated the formation of mesophase spheres from the toluene-insoluble portion of a coal tar pitch. They found that sphere coalescence was enhanced by diluting the toluene-insoluble portion with toluene-soluble material, thereby reducing the viscosity of the isotropic pitch matrix. The precursors of the mesophase are thought to consist of the heavier pitch fraction, rather than the lighter fraction, and variation in the proportions of each fraction produces variation in the rates at which the spheres nucleate or grow. Santamaria-Ramirez et al. [8] explored the effects of depressurizing the carboniza-

* Corresponding author. Tel.: +81 3 4435 8284; fax: +81 3 3501 8021.
E-mail addresses: moriyama@iae.or.jp, ryo.moriyama@nifty.com (R. Moriyama).

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tion reactor used to heat treat a petroleum-derived pitch on mesophase sphere formation. They found that depressurization increased the yield of mesophase spheres with radii of 5–50 μm, and reduced the proportion of bulk mesophase formed. They attributed these results to suppression of the frequency of sphere coalescence brought about by the enhanced release of volatiles and a resultant increase in the viscosity of the pitch matrix.

In this work, we attempted to use simple techniques to control the rate and extent of tar release while heating a coal tar pitch and examined the effects that this had on the process of mesophase sphere formation under conditions where no bulk mesophase was formed. We then analyzed the time-dependent changes in the number-based concentration, volume-based concentration, and radius distributions of the spheres.

2. Experimental

2.1. Sample

Coal tar pitch (CTP) which contained no quinoline-insoluble material was used as the sample. The elemental compositions and softening point temperatures of the sample are summarized in Table 1.

2.2. Heat treatment of CTP and product analysis

A known mass of CTP, m_0, from 0.05 to 3.5 g, was placed in a Pyrex cup with an internal diameter of 16.5 mm and a depth of 37 mm. The cup was placed in a 20 mm dia. coaxial vertical tubular reactor and heated at a rate of 10 K min^{-1} from ambient temperatures to the holding temperature of 703 K. The temperature was maintained for t_h ranging from 0 to 65 min while the sample was subjected to a flow of N_2 directed downward at a rate of 100 ml-STP min^{-1}; atmospheric pressure was maintained by venting the reactor. The sample was then cooled to ambient temperature at a rate that exceeded 70 ± 10 K min^{-1}, which is sufficient to prevent spheres from growing during the cooling process [9]. In additional experiments, 1.0 g of CTP was heated while a jet of N_2 was directed onto its free surface from a nozzle aligned with the central axis of the reactor. The 1000 ml-STP min^{-1} flow rate of N_2 corresponded to a velocity of about 0.6 m s^{-1} (STP) at the nozzle tip. The yield of volatile matter that consisted mainly of tar, Y_{vm}, in a given t_h was defined as

$$Y_{vm} = \frac{m_0 - m}{m_0} \quad (1)$$

where m_0 and m are the masses of CTP present initially and at time t_h, respectively. After recovery from the reactor, the cylindrical mass of residual CTP was sliced into two equal half-cylinders and examined using a polarized reflected-light microscope at 400× magnification. Height of the cylinder was in a range from 0.15 to 6.0 mm depending on m_0 and Y_{vm}. Images of the visual fields, each with an area of 45,000 μm^2, were taken with a digital camera. In each field, mesophase spheres appeared as optically anisotropic circles with radii of 1 μm or greater. An area of at least 260,000 μm^2 was observed for each sample in order to reduce deviations of analytical data. Details of the microscopic observations have been reported previously [3,4].

Mesophase sphere formation was also observed in situ in another reactor. A small amount of CTP (0.02 g) was placed in a platinum pan with an internal diameter of 7 mm and a depth of 0.7 mm. The pan was placed in an optical cell and heated at 10 K min^{-1} to a temperature of 723 K while subject to a flow of N_2 at atmospheric pressure. The top surface of the fused pitch was monitored with a microscope during both heating and cooling of the sample.

The radii of the anisotropic circles observed in a cut section differed from those of the original mesophase spheres, and the former radii were converted into the latter ones. The radius distributions of the anisotropic circles were represented in a geometrically discretized form by using the length as the internal coordinate. Circles with radii between r_{i-1} and r_i ($i = 1, 2, 3, \ldots 136$ and $r_0 = 1$ μm), where $r_i - r_{i-1} = 0.2$ μm, are contained in the i-th interval, denoted I-i, with the representative radius of $\bar{r}_i = (r_i + r_{i+1})/2 = r_{i-1} + 0.1$ μm. The conversion of the radii of the observed circles into those of spheres requires assumptions concerning the homogeneous dispersion of spheres within the isotropic matrix, and the random sectioning of the spheres [3,4,10]. Details of the conversion are given in Appendix A. The residual-CTP-based total population and volume densities of the mesophase spheres, n_T, and v_T, respectively, were calculated as

$$n_T = \sum_i n(i) \quad (2)$$

$$v_T = \sum_i v(i) = \frac{4\pi}{3} \sum_i n(i)(\bar{r}_i)^3 \quad (3)$$

where $n(i)$ and $v(i)$ are the population and volume densities of the spheres in I-i, respectively. The details concerning the estimation of $n(i)$ and $v(i)$ are also presented in Appendix A. The initial-CTP-based total population density, N_T, and the total volume density, V_T, of spheres can also be given by assuming that the specific volume of the CTP remains unchanged throughout heating.

Table 1
Properties of CTP

Sample	CTP
C (wt.%)	92.9
H (wt.%)	5.1
O (difference) (wt.%)	0.24
N (wt.%)	1.1
S (wt.%)	0.66
H/C	0.055
SP (K)	353