POSTER

CONTROL OF MESOPHASE PITCH PROPERTIES BY SUPERCRITICAL FLUID EXTRACTION

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Introduction

Supercritical fluid (SCF) extraction has been investigated for the production of mesophase pitch, the liquid-crystalline precursor of high performance carbon fibers. Mesophase is produced by extracting an isotropic, heat-soaked petroleum pitch with supercritical toluene. An experimental design was used to explore the effect of temperature, solvent-to-pitch ratio, and solubility parameter on the softening point and yield of the mesophase-containing pitch. Temperatures of 320°C to 360°C, solvent-to-pitch ratios of 2.5 to 3.5, and solubility parameters of 3.7 to 5.0 $(cal/cc)^{1/2}$ were chosen to conform to a two-level factorial experiment (1).

In this paper, we report on our investigation of the effect of operating conditions on the properties of the mesophase pitch fractions produced by SCF extraction.

Experimental

A continuous-flow apparatus, shown in Figure 1, had been previously constructed for measuring fluid-phase equilibria at temperatures and pressures up to 400°C and 350 bar respectively (2). This flow apparatus allows residence times for the material of a few minutes and large-scale production for subsequent analysis and spinning. A 50/50 by weight homogeneous mixture of isotropic pitch and toluene is pumped indirectly using a high pressure cylinder. This cylinder contains a floating piston displaced by toluene used as a working fluid. Additionally, pure toluene is pumped independently at a predetermined flow rate to obtain a specified solvent-to-pitch ratio. The two streams are preheated and combined through a mixing coil before reaching the equilibrium cell, which functions as a phase separator. The preheating, mixing, and separation steps are performed in an isothermal nitrogen bath. The heavy and light phases are collected independently through the bottom and the top of the cell, respectively. The interface in the equilibrium cell is monitored by an electrical capacitance technique described elsewhere (2). The pressure control is insured by the top-phase valve using a computer-controlled servo motor, and the bottom-phase valve is used for level control in the cell. All sample lines exiting the nitrogen bath are wrapped by electrical heating tapes and insulated. After expansion to atmospheric pressure, both samples are collected.

The top phase is mainly toluene (about 80 percent by weight) and a low molecular weight portion of the pitch. In contrast, the bottom phase consists of about 20 percent toluene by weight and 80 percent pitch. The bottom phase is then dried at 150 °C and 1.5 torr in a vacuum oven for one hour to eliminate the residual toluene. The resulting bottom phase, solid at ambient temperature consists of up to 100 percent mesophase.

Results and Discussion

The dried bottom-phase samples were analyzed to determine their softening point along with the percentage of mesophase present. Figure 2 shows a plot of percent mesophase vs. softening point of these bottom-phase fractions. As a greater fraction of the feed pitch is extracted by the solvent, the high molecular weight species concentrate in the bottom-phase. As a result, the softening point increases, and a higher percent of mesophase is formed. The fact that several fractions containing 100 percent mesophase were produced with a wide range of softening points is of particular interest because the mesophase will be subsequently melt-spun into fibers.

During melt-spinning, the mesophase precursor (bottom-phase fraction) must have a viscosity near 40 Pa.s (3). As a result, Figure 3 shows a plot of the spinning temperature vs. softening point. Testing has confirmed that a temperature 60°C above the softening point allows melt-spinning of the bottom-phase sample.

Figure 4 shows that an increase in the solubility parameter produces a significant increase in both the softening point of the mesophase pitch and the extraction yield (4).

Finally, Figure 5 illustrates that an increase of the solvent-to-pitch ratio results in a smaller fraction extracted from the parent pitch.

Therefore, supercritical toluene can be seen as an antisolvent for petroleum pitch (4).

Conclusion

The properties of mesophase pitch produced by supercritical extraction can be modified by changing the operating conditions of the extraction process. The results found show that both the softening point of the mesophase pitch and the yield of the pitch can be increased simultaneously.

References

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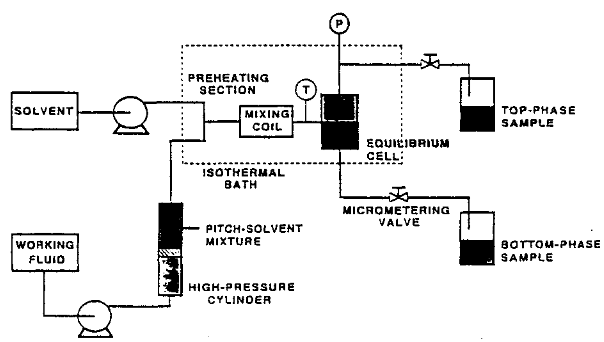

Figure 1. Schematic diagram of the experimental apparatus.

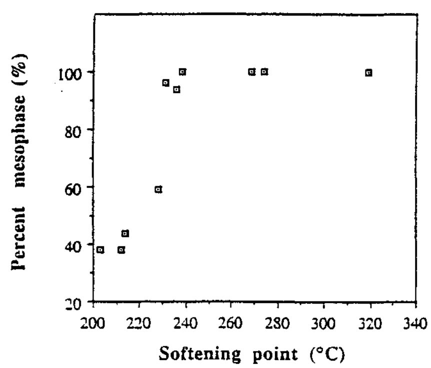

Figure 2. Percent mesophase vs. softening point for bottom-phase samples.

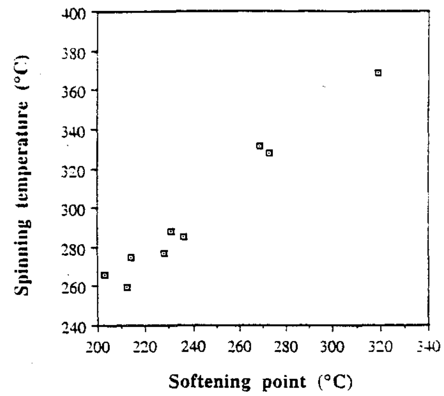

Figure 3. Spinning temperature vs. softening point for bottom-phase samples.

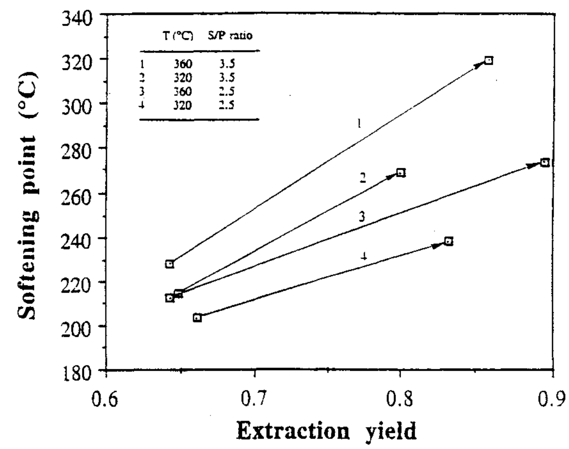

Figure 4. Variation in softening point and extraction yield when the solvent solubility parameter is increased from 3.7 to 5.0 $(cal/cc)^{1/2}$.

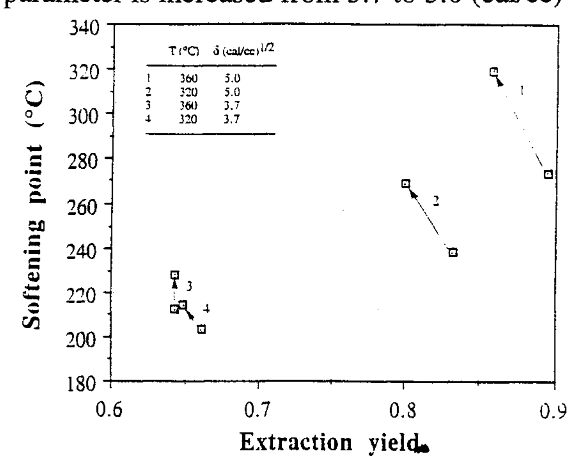

Figure 5. Variation in softening point and extraction yield when the solvent to pitch ratio is increased from 2.5 to 3.5.