

SYNTHESIS OF ISOTROPIC CARBON FIBERS FROM PITCH PRECURSORS

Frank Derbyshire, Rodney Andrews, Adam Berkovich, David Jacques,
Marit Jagtoyen & Terry Rantell

University of Kentucky Center for Applied Energy Research,
2540 Research Park Drive, Lexington, KY. 40511-8410, USA

KEYWORDS: Isotropic pitch, coal extracts, carbon fibers.

1. INTRODUCTION

Pitch is used extensively as a binder and as an impregnant in the production of bulk carbon and graphite materials. Traditionally, coal tar pitch, a coke oven by-product, has been the major source of such materials. However, the range of carbons that can be obtained from coal is considerably expanded through the derivation of high molecular weight liquids or pitches by solvent extraction, hydrolysis, direct liquefaction as well as coking, each of which effectively serves to liberate the coal structural units. The composition of the liquids can be altered to a greater extent through the selection of the coal and reaction parameters, allowing considerable latitude in the preparation of precursors for different end products. The heavy liquid products and bottoms from crude oil processing represent an alternative source of these materials.

Relatively small quantities of both petroleum and coal tar pitch are also used as precursors for the production of carbon fibers. General purpose carbon fibers are produced by melt blowing isotropic pitch and high performance carbon fibers by melt spinning mesophase pitch. For isotropic pitch fibers, the principal steps involve the removal of entrained particulates by a solids separation process and elevation of the softening point. The ability to produce fine filaments from a pitch (spinnability) is very sensitive to the rheological properties of the pitch. For isotropic pitches exhibiting Newtonian flow properties, the glass transition temperature, T_g , and softening point can be used as characterization parameters. Once formed, the "green" pitch fibers need to be rendered infusible, or stabilized, to prevent the fibers melting and sticking together during carbonization.

In this paper the synthesis of carbon fibers from a range of isotropic pitch precursors of different origins have been examined to ascertain their suitability for fiber production. The overall aims were: to investigate the basic relationships between the composition and properties of the precursors and the ability to form fibers by melt spinning and to elucidate the mechanisms and kinetics of fiber stabilization and carbonization. The structure and properties of the carbon fibers were determined.

2. EXPERIMENTAL

Starting materials for the pitch precursors were obtained from several sources. Two coal tar pitches originating from industrial coking plants were obtained, both derived from bituminous coals (EF4 & 60FDR4). A third coal tar pitch was the by-product from the gasification of a North Dakota lignite (DR8). Several laboratory-prepared coal extracts were produced by the solvent extraction of coal under a range of conditions. These included the liquefaction of a West Virginia bituminous coal in tetralin under a high-pressure hydrogen atmosphere (FO79) and the extraction of a North Dakota lignite in a hydrogen donor solvent (47FDR). A third coal extract was produced by the dissolution of a Kentucky bituminous coal in a high boiling coal-derived solvent (7FDR2). Reaction temperatures in these tests were around 400°C with residence times of 60 minutes. Coal conversions were all high at >90%daf coal. In addition, some coal extracts were prepared by the solvent extraction of coal under very mild conditions (ACKy, ACPa & ACWy). Here, bituminous coals from Western Kentucky and Pittsburgh, and a Wyoming subbituminous coal, were extracted in anthracene oil at temperatures of around 350°C and residence times of 60 minutes. Extraction yields were correspondingly lower, ranging from 40 to 70%daf coal depending upon coal type. Two other feedstocks were used: a pitch derived from shale oil asphaltenes (F2DR) and a petroleum pitch (A500) that is used commercially to produce general purpose carbon fibers and activated carbon

fibers. The origins and the principal characteristics of these starting materials represent a diverse range of properties, Table 1. via soxhlet extraction

It is important to minimize the amount of particulate solids present in the feedstocks since their presence can disrupt the fiber forming process, result in non-uniform fiber production and also provide a source of weakness within the product carbon fiber. Where necessary, solids were removed by filtration or by extracting a soluble fraction from the reaction products using tetrahydrofuran (THF) or N-methyl pyrrolidone (FO79). For most of the precursors it was necessary to elevate the softening point of the solids-free feedstock to fall within the preferred range for fiber spinning, 230 to 260°C. This was generally achieved by vacuum distillation. Softening points were determined using a Mettler Apparatus (ASTM D3461-85, 1989). The solubility of the pitches in both quinoline and THF were determined to provide a guide to the molecular weight distribution. The pitches were also characterized by measurement of the elemental composition and by Fourier transform infrared spectroscopy (FTIR) and solid state ^{13}C nmr spectroscopy. The FTIR transmittance spectra were acquired using a Nicolet 20 SX spectrometer at 4 cm^{-1} resolution. The samples were mixed with KBr to give a 0.5% concentration in KBr and pressed into a pellet for analysis. The solid state ^{13}C nmr measurements were carried out at the University of Strathclyde using a Bruker MSL100 instrument with MAS at 5.0kHz. Once suitable pitches had been prepared, fibers were produced as single filaments by extruding the pitch through a die and drawing the diameter down into a fine filament by winding up on a rotating drum. Tows of fiber were cut into convenient lengths and stabilized by heating in air at rates of between 0.1 and $5^\circ\text{C}/\text{min}$. The process of stabilization by air oxidation serves to cross-link the fiber structure, rendering it infusible and preventing softening during subsequent heat treatment. The stabilized fibers were then carbonized by heating in an inert atmosphere to a temperature of 1100°C for 60 minutes. The yield and linear dimensions of the fibers were measured after each stage to monitor the major changes that were occurring during stabilization and carbonization. The physical properties of the carbonized fibers - diameter, tensile strength, elastic modulus (ASTM D3379, D638M) and electrical resistivity were also determined.

3. RESULTS and DISCUSSION

Broadly, these studies have confirmed that, the higher the softening point of the pitch from any one source, the higher the heating rate that can be used for fiber stabilization without incurring problems of fiber deformation or fusing. It is also clear that the maximum effective heating rate decreases with increasing fiber diameter, a result that was not unexpected when diffusional limitations are considered. However, it was apparent that some precursors can be stabilized significantly faster than others despite their exhibiting a similar or even lower softening temperature, Figure 1.

The processes that occur during stabilization include a small loss of volatile matter (depending upon the softening point and boiling point distribution), the uptake of oxygen, and possibly some loss of carbon as CO_2 , with a consequential change in the mass of the fibers. A contraction in the fiber dimensions is also observed. For most of the precursors, the uptake of oxygen compensates for volatile loss, and there is a net weight gain that can be as much as 10%. However, for the oil shale fibers there was a net weight loss of similar proportions. Not surprisingly, an inverse correlation between weight increase and the contraction in fiber length is observed, where a positive weight gain corresponds to a smaller dimensional change. These phenomena can be related to the precursor composition. In particular, there is a general trend of increasing weight gain and decreasing linear contraction, as the carbon content of the pitch increases. This implies that the uptake of oxygen primarily involves its combination with carbon, and these cross-linking reactions reduce volatile loss. The loss of labile hydrogen and heteroatom-containing species will contribute to the liberation of volatiles that increase the weight loss (or reduce the net gain) and increase the extent of dimensional contraction.

These same observations translate to the subsequent step of carbonization. In this case, there is always a weight loss of between approximately 20 to 45% with a corresponding net carbon yield from pitch feedstock to carbon fiber of between 50 and 86%. The corresponding overall linear

contraction was between 28 and 12%. The net carbon yield increases with precursor carbon content, (and decreases with the content of H, N, O and S), while the overall dimensional contraction follows an inverse trend. If such fibers were incorporated into a brittle matrix, the change in axial dimensions upon further thermal processing can introduce significant internal stresses. Therefore, careful selection of fiber and matrix for compatibility is necessary.

The mechanical and electrical properties of carbon fibers are, to some extent, controlled by the distribution of flaws and defects in the fibers. However, the tensile strength has been found to increase with precursor carbon content and carbon yield, Figure 2. The values for the materials studied here range from about 0.1 to 1.1 GPa. Pitches derived from bituminous coals via coking or solvent extraction produce fibers that are generally stronger than those from petroleum pitch. In contrast, the fibers derived from low-rank coals and oil shale were relatively weak. Similarly, the fibers generated from low rank coals with low aromaticities tend to have higher electrical resistivities.

The pitches derived from bituminous coal and the petroleum pitch sample are all strongly aromatic, while the pitches derived from low rank carbonaceous deposits are highly aliphatic. The lignite and shale oil samples were the most aliphatic and, significantly, were also the two samples for which it was not possible to increase the softening point by distillation to a value in the preferred temperature range, 230-260°C. The coal tar pitch DR8, is rich in oxygen groups, with both C-O bonds and carbonyl groups present. This may be expected since its lignite precursor will also be rich in oxygen. Two other pitches derived from low rank sources, 47FDR4 (lignite) and F2DR (shale oil) are also rich in C-O bonds. The elemental analysis data confirm the high oxygen contents of these pitches, ranging from 2.5 to 4.8%, compared with 0.5% or less for the pitches from higher rank sources.

4. CONCLUSIONS

Feedstocks suitable for generating isotropic carbon fibers were prepared from a wide range of pitch precursors. The differences in the properties and chemical composition of the feedstocks have been related to the processing and properties of the resultant carbon fibers:

- The higher the softening point of the pitch, the greater the stabilization rate at which the fibers could be processed. However, this can be offset by an increase in fiber diameter, which reduces the maximum achievable rate. For some of the feedstocks, (shale oil, subbituminous coal extract and petroleum pitch) significantly higher stabilization rates could be obtained compared to other feedstocks of similar softening point.
- During stabilization, weight gain increases with increasing carbon content in the precursor pitch, and correspondingly, the axial contraction is less for those fibers from pitches of higher carbon content. These changes are related to the uptake of oxygen and formation of cross-links within the pitch structure, reducing the loss of volatiles.
- The combined effects of stabilization and carbonization gave carbon yields of between 50 to 86% of the green fibers, with a corresponding overall axial contraction between 28 and 12%. The net carbon yield on conversion from pitch to carbon fiber was found to increase with carbon content of the parent pitch. This implies that the pitches with higher heteroatom content suffer greater loss of material due to gasification. Similar relationships were found between axial contraction and carbon content, and axial contraction and heteroatom content.
- The tensile strength of the derived fibers ranged from 0.1 to 1.1 GPa. The strength increased with aromaticity, increasing molecular size, and decreasing heteroatom content in the precursor, while the electrical resistivity of the fibers tended to decrease with these properties.

ACKNOWLEDGEMENTS

The authors wish to thank Paige Presler and Beverly Moore who diligently performed much of the characterization work and Peter Stansbury and John Zondlo at West Virginia University for supplying the FO79 pitch. Financial support was provided by the University of Kentucky Center for Applied Energy Research and the Commonwealth of Kentucky and also by Dept. of Energy contract DE-AC22-91PC91040.

Table 1: Analysis of Prepared Pitch

Source	Sample No.	Ultimate Analysis (wt%, daf)					Insolubility (wt%)		Softening point (°C)	Car / Cal (FTIR)	f_{ar} ($^{13}C_{ar}$)
		C	H	O	N	S	QI	THFI			
Coal Tar Pitch	EF4	93.6	3.7	0.5	1.6	0.6	0.5	38	245	35.1	>0.99
Coal Tar Pitch	60FDR4	94.4	3.9	0.0	1.3	0.5	0.2	31	240	29.9	>0.99
Coal Tar Pitch	DR8	88.4	6.5	3.4	1.3	0.3	0.5	0.5	225	0.05	0.65
Coal Extract	FO79	-	-	-	-	-	3.7	-	213	-	-
Coal Extract	47FDR	87.9	5.3	4.8	1.4	0.5	0.5	6	240	0.03	0.66
Coal Extract	7FDR2	90.2	4.3	2.5	1.8	1.1	0.1	58	260	0.59	0.91
Coal Extract	ACKy	91.1	4.5	1.7	1.7	1.0	<0.1	<0.1	230	-	-
Coal Extract	ACPa	-	-	-	-	-	<0.1	<0.1	230	-	-
Coal Extract	ACWy	85.7	5.8	6.8	1.4	0.3	<0.1	<0.1	220	-	-
Shale Oil	F2DR	84.9	6.6	3.6	2.3	2.5	0.6	1.3	210	0.04	0.61
Petroleum Pitch	A500	92.9	4.6	0.3	0.3	1.9	0.0	22	258	0.60	0.91

Oxygen by difference; QI = Quinoline insolubles; THFI = Tetrahydrofuran insolubles.
 f_{ar} is the fraction of aromatic carbon relative to the total carbon content.

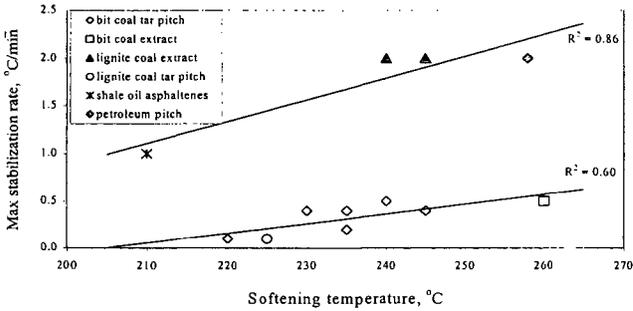


Figure 1 Dependence of Stabilization Rate on Pitch Softening Point

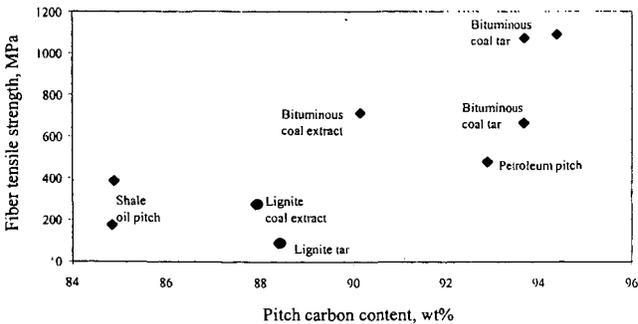


Figure 2 Tensile Strength of Fibers as a Function of Pitch Carbon Content