

## AN IMPREGNATED ACTIVATED CARBON FOR THE SEPARATION OF VOC MIXTURES INTO THEIR INDIVIDUAL COMPONENTS

J.P. Boudou,

Université Pierre et Marie Curie - Case 124, CNRS, 4, Place Jussieu, 75252 Paris, France

F. Payot

Laboratoire de Chimie du Solide Minéral, Université Henri Poincaré BP 239

54506 Vandoeuvre les Nancy, France

Deposition of impregnation chemicals on the internal surface of suitable activated carbon optimizes the existing properties of the activated carbon for the chemisorption of certain gas pollutants giving a synergism between the chemicals and the carbon. Various qualities of impregnated activated carbon are available and have been used for many years in the fields of gas purification, civil and military gas protection and catalysis. For the manufacture of impregnated activated carbon, an activated carbon of suitable quality for the particular application is impregnated with solutions of salts or other chemicals which, after drying or other after-treatment steps, remain on the internal surface of the activated carbon. Usually, homogeneous distribution of the impregnating agents on the internal surface without any blocking of the micropores and macropores is considered to be important to keep the impregnation agent accessible for the reactants. However, in this case, the impregnated activated carbon is not selective: the adsorptive removal of further gas impurities can also take place.

In this work, we propose a new impregnated activated carbon for the selective removal and the fractionation of VOC's mixtures in exhaust humid gas. One seeks to separate by adsorption and thermodesorption on activated carbon four organic solvents: chlorinated (dichloromethane : DCM, 1,2-dichloroethane : DCE) and oxygenated (methanol : MET, methylethylketone : MEK) present in low concentration ( $< 0.5 \text{ mole/m}^3$ ) in wet air (c. 70% of relative humidity). While seeking to avoid any degradation, the solvents must be selectively trapped at ambient temperature and selectively thermodesorbed by electric heating under a flow of nitrogen. Thermodesorption must perfectly regenerate the activated carbon in order to make it possible to apply a sequence of cycles of adsorption-desorption modulated in temperature. That implies a high selective adsorption capacity and a fast desorption at low temperature.

A preliminary work undertaken on carbon adsorbents chemically activated with phosphoric acid (SA 1817 from Atochem and Picazine from Pica), or on activated carbon oxidized by a mixture of nitric and sulfuric acid, showed us that, after washing, the residual mineral acid (acid phosphoric or acid sulfuric) gave a beginning of selectivity to the carbonaceous supports: the chlorinated solvents (DCM, DCE) tend to be better retained on the acid loaded support than the oxygenated ones (MET, MEK). We took benefit from this observation by impregnating the carbonaceous support (activated carbons in grains or fiber) with a mineral substance ( $\text{ZnCl}_2$ ) having acid properties by simple cold agitation in aqueous concentrated solutions (c.  $1.25 \text{ g ml}^{-1}$ ). Electron microscopy showed that the grains are coated with the product of impregnation and the adsorptiometry put in evidence that the impregnation plugs the whole porosity of the carbonaceous material. However the effect of the support is very important. Various supports were tested (powdered /granular from coal or coconut, carbon cloth). The best results were obtained with the most mesoporous activated carbons - for instance with a granular activated carbon prepared with the lignite of Lubstov (Poland) at the University of Wroclaw (Table 1).

The most remarkable result is that on the  $\text{ZnCl}_2$  impregnated CA, the DCM and the DCE are not retained at all, whereas methanol and MEK are trapped and completely desorbed by isothermal heating at  $100^\circ\text{C}$  during a few minutes under a flow of nitrogen, while on the non-impregnated support, the peaks of desorption of the oxygenated VOC "strongly tails". The impregnated support remains perfectly stable during more than 15 cycles of adsorption in a flow of air charged with 70% moisture followed by a thermodesorption at  $150^\circ\text{C}$  under a nitrogen flow (Figure 1). The disadvantage of the method lies in the fact that the impregnation's product is toxic, corrosive and hygroscopic. That implies constraints of storage, and requires to use reactor protected from corrosion and to work in short cycles of adsorption-desorption. In fact, MEK breakthrough appears before that of methanol and water. The improvement of the process is currently in hand by seeking a better acidic substance of impregnation for the selective removal of ppm concentration of various VOC's and HAP's in humid effluents.

Table 1. Porosity parameters of the activated carbon (AC) before and after impregnation

	Pore volume, $\text{cm}^3 \text{g}^{-1}$			BET $\text{m}^2$
	Micropores	Mesopores	Micro+Meso	
Non-impregnated AC	0.205	0.504	0.709	740
ZnCl <sub>2</sub> impregnated AC	0.028	0.057	0.085	17

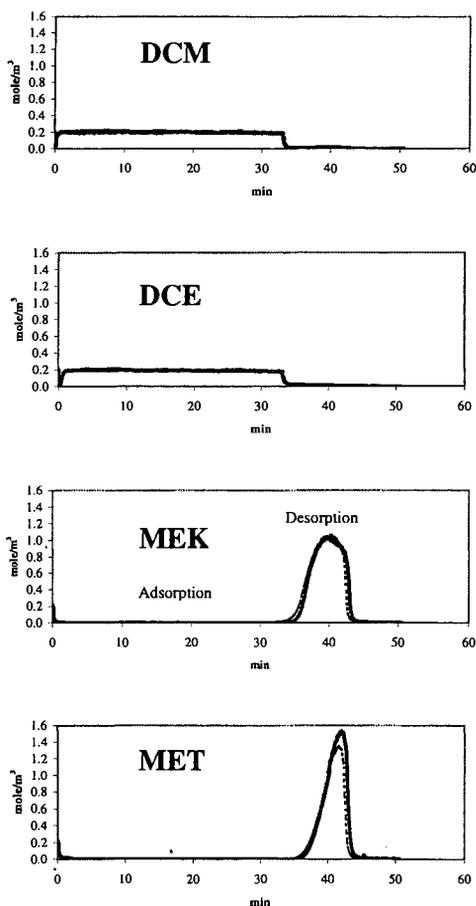


Figure 1. Profile of dynamic adsorption at 25°C and desorption at 150°C of a mixture of dichloromethane (DCM), 1,2-dichloroethane (DCE), methylethylketone (MEK) and methanol (MET) (individual VOC concentration : 0.2 mole /m<sup>3</sup>, water vapour concentration : 70% of the saturation pressure at 25°C, flow rate : 20 ml/min) on a column filled with 83 mg of ZnCl<sub>2</sub>-impregnated activated carbon (impregnation rate : c. 50 wt %, dashed line : 2<sup>nd</sup> adsorption-desorption cycle, solid line : 15<sup>th</sup> adsorption-desorption cycle). The adsorption stage is stopped at the breakthrough point of MEK.

# ACTIVATED CARBON FIBERS AND FILMS PREPARED FROM POLY(VINYLDENE FLUORIDE) BY USING A CHEMICAL CARBONIZATION

Junya Yamashita\*, Toyonari Hirano, Masatoshi Shioya, Takeshi Kikutani and  
Toshimasa Hashimoto

Department of Organic and Polymeric Materials, Tokyo Institute of Technology,  
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

\* Present address: Carbon Materials Division, Energy Resources Department, National  
Institute for Resources and Environment,  
16-3 Onogawa, Tukuba-shi, Ibaraki 305-8569, Japan

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## 1. INTRODUCTION

Activated carbons with excellent adsorptive properties have been used in many fields such as separation of mixtures and removal of contaminant impurities. The granular activated carbons have been produced mainly from palm shells and coal. As compared with the granular activated carbons, activated carbon fibers prepared from synthetic fibers have an advantage to process into various shapes such as fabrics and papers. Furthermore, high adsorption-desorption rate of activated carbon fibers is also advantageous. The activated carbon fibers produced by conventional methods, however, are microporous and they are insufficient for the purpose of adsorbing large molecules.

Recently, several attempts have been made to introduce mesopores into carbons. For example, mesoporous carbons have been obtained by steam activation of the carbons derived from mixtures of pitch and metal complexes [1-3]. It is considered, however, that the metal residues in these carbons bring about unfavorable effects for the application to catalyst supports. Thus, new methods to prepare the mesoporous carbons free from metal complexes are required.

The present authors have obtained carbon fibers and films with various average pore sizes by applying a combination of dehydrofluorination and high-temperature heat-treatment to poly(vinylidene fluoride) (PVDF) [4]. In this study, PVDF-based carbons derived with this method were further activated. The porous structure and adsorptive properties of the resulting activated carbons were investigated by using nitrogen gas and methylene blue as adsorbates.

## 2. EXPERIMENTAL

The PVDF fibers with small diameters in a range of 7-10  $\mu\text{m}$  were prepared by firstly spinning bicomponent fibers which consisted 261 continuous filaments of PVDF core fibers and polystyrene matrix and secondly dissolving the matrix. The bicomponent fibers were spun using a melt-spinning technique with the spinning temperature at 290°C and the take-up velocity of 100 m min<sup>-1</sup>. For dissolving the matrix, the bicomponent fibers were soaked in tetrahydrofuran at 50°C for 90 min. Then, obtained PVDF fibers were washed in methanol and dried under reduced pressure.

PVDF films with a thickness of about 120  $\mu\text{m}$  were prepared by hot-pressing PVDF pellets at 200°C and quenching them between steel plates at room temperature. The films were cut into the sizes of 7.5 mm by 10 mm.

The dehydrofluorination of PVDF fibers and films were carried out by using one of the strongest organic base, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), under a swollen state. The degree of swelling was controlled by using a mixture of a swelling solvent, dimethylformamide (DMF), and a nonsolvent, ethanol (EtOH), with a volume ratio of DMF/EtOH = 2/3. The PVDF fiber bundles and films by the amounts corresponding to the number ratio of DBU/(vinylidene fluoride unit) = 4/1 were soaked in a DMF-EtOH solution of 1.0 M DBU at 70°C. During this treatment, a slight tension was applied to the fiber bundle. After the treatment, the fibers and films were washed in methanol for 1 h and

dried under reduced pressure. In the following, 'untreated PVDF' will refer to the PVDF that was not dehydrofluorinated.

The dehydrofluorinated fibers and films were heated at a rate of  $2^{\circ}\text{C min}^{-1}$  up to desired temperatures below  $1300^{\circ}\text{C}$  in a nitrogen atmosphere. During the heat-treatments, the fibers were slightly tensioned, and the films were held between two graphite plates in order to reduce wrinkling. The untreated PVDF films were also heat-treated under the same conditions by placing them on a glassy carbon plate in order to avoid adhesion of the products to the substrate.

The carbonized fibers and films were activated using carbon dioxide gas. First, the specimens were heated at a heating rate of  $10^{\circ}\text{C min}^{-1}$  up to  $850^{\circ}\text{C}$  under nitrogen gas flow. Then, the flowing gas was changed to carbon dioxide and the specimen was activated at  $850^{\circ}\text{C}$  for a desired duration. The flowing gas was changed back to nitrogen, and the specimen was left to cool in the furnace down to room temperature. The flow rate of both nitrogen and carbon dioxide gasses was  $500\text{ cm}^3\text{ min}^{-1}$ . The duration of activation was determined so that the mass loss during activation relative to the carbonized PVDF ( $\Delta M_{act}/M_{heat}$ ) reached about 70% for all the specimens.

The pores developed in the carbon fibers and films were characterized with small-angle X-ray scattering (SAXS) by using a diffractometer (Rigaku), the PSPC and pinhole-collimated  $\text{CuK}\alpha$  radiation. Specimens were prepared by aligning the carbon fibers and stacking the carbon films. The specimen-to-detector distance was 360mm and a height-limiting slit with 0.43 mm gap was attached at the X-ray entrance of the PSPC. Since SAXS of the pores in the PVDF-based carbon fibers and films was isotropic, it was possible to convert the SAXS profiles into those obtainable with an infinitely-long-slit collimation of the incident X-ray beam. From the converted profiles, the radius of gyration ( $R_g$ ) of the pores was estimated according to a method proposed by the present authors [5,6]. If the pores are of spherical shape, their diameter  $D$  is given by  $(28/3)^{1/2} R_g$ . If the pores are of cylindrical shape, aligned in parallel to each other, and  $R_g$  is estimated with this analysis method from the equatorial intensity distribution of the cylinders, their diameter  $D$  is given by  $81/2 R_g$ .

The nitrogen gas adsorption-desorption isotherm was measured at 77K using an automatic gas adsorption apparatus (Autosorb-1, Quantachrome). From the isotherms measured, BET surface area, total pore volume and average pore diameter were calculated. Pore size distribution was determined from the desorption isotherm by applying the Barrett-Joyner-Halenda method to the desorption isotherm [7].

Adsorptive properties against methylene blue (MB) adsorbate which is accessible to the pores with diameters larger than 1.5 nm [8] was measured. The MB dye used showed 13.0% mass loss when heated at  $135^{\circ}\text{C}$  for 12 h under reduced pressure due to evaporation of water. By taking into account the degree of hydration of MB, aqueous solutions of MB with various concentrations in a range of 25-500  $\text{g m}^{-3}$  were prepared. The carbon specimen of about 10 mg, dried at  $135^{\circ}\text{C}$  for 12 h under reduced pressure, was mixed with the solution of MB of  $10\text{ cm}^3$  in a test tube and shaken at  $30^{\circ}\text{C}$  for 24 h. The concentration of MB in the solution sampled by using a hypodermic syringe was measured. The adsorption of MB per unit mass of the specimen was calculated from the difference in the concentrations of MB in the solution before and after the specimen was added to the solution. The concentration of MB was determined by measuring the optical absorbance of the solution with a visible spectrometer (UV-2200, Shimadzu) and using a calibration curve which had been constructed based on Beer's law.

### 3. RESULTS AND DISCUSSION

#### 3.1. Dehydrofluorinated fibers and films

As dehydrofluorination progresses, the color of PVDF fibers and films was turned from white into black initially at the surface of the materials and eventually over the entire cross section. From the masses of the specimen before and after dehydrofluorination, the

mass loss during dehydrofluorination relative to the mass of the starting PVDF ( $\Delta M_{chem}/M_{PVDF}$ ) was calculated. With increasing dehydrofluorination time, the  $\Delta M_{chem}/M_{PVDF}$  value decreases and at a dehydrofluorination time of 12 h, these values reached 16 and 13%, respectively, for the fibers and films [4]. With the increase of  $\Delta M_{chem}/M_{PVDF}$ , the fluorine content decreased and the carbon content increased almost linearly [4]. Thus,  $\Delta M_{chem}/M_{PVDF}$  will be used as the measure of the degree of dehydrofluorination.

### 3.2. Heat-treated fibers and films

During heat-treatment, untreated PVDF melted and only granular carbon was derived. On the contrary, dehydrofluorinated PVDF maintained its macroscopic precursor geometry during heat-treatment even though  $\Delta M_{chem}/M_{PVDF}$  was as small as 2%. As a result, carbon fibers and films could be obtained without causing wrinkling and/or fragmentation. It is considered that multiple C-C bonds were introduced into the PVDF molecules by dehydrofluorination, which prevented fusion of PVDF during high-temperature heat-treatment.

During heat-treatment, rapid decomposition took place in the temperature range of 300-400°C, and the pores were formed in this temperature range. The change of the pore size with increasing heat-treatment temperature above 400°C was small.

The  $R_3$  values of the pores in PVDF-based carbon fibers and films carbonized at 1300°C are plotted against  $\Delta M_{chem}/M_{PVDF}$  in Fig. 1. For comparison,  $R_3$  values of the pitch-, polyacrylonitrile- and phenol-based carbon fibers prepared in our laboratory at the carbonization temperature of about 1300°C were 1.2, 0.8 and 0.9 nm, respectively. In these cases,  $R_3$  values represent the size of the pore cross section perpendicular to the fiber axis. For the commercial activated carbon granule derived from palm shells,  $R_3$  value was 2.1 nm. By applying a slight dehydrofluorination, the pore size of the PVDF-based carbon increases as compared with that of the carbon derived from untreated PVDF. By applying an intensive dehydrofluorination, on the other hand, the pore size decreases. Thus, the pore size of the PVDF-based carbon can be controlled in a range of 0.3-2.3 nm by changing the degree of dehydrofluorination.

From the nitrogen gas adsorption, it was obtained that the PVDF-based carbon granule derived from untreated PVDF by heat-treatment at 1300°C had BET surface area of 761 m<sup>2</sup> g<sup>-1</sup>, total pore volume of 0.46 ml g<sup>-1</sup> and average pore diameter of 2.41 nm. On the other hand, the PVDF-based carbon prepared by dehydrofluorination to a  $\Delta M_{chem}/M_{PVDF}$  value of 7% and heat-treatment at 1300°C did not adsorb detectable amount of nitrogen gas. Thus, the pores detected with SAXS have closed structure. In order to make the pores in PVDF-based carbons accessible with adsorbate, activation was carried out.

### 3.3. Activated carbon fibers and films

In the nitrogen gas adsorption-desorption isotherms of PVDF-based activated carbon films shown in Fig. 2, a steep increase of the amount of adsorption is found at low relative pressure region. This indicates that micropores are developed in the PVDF-based activated

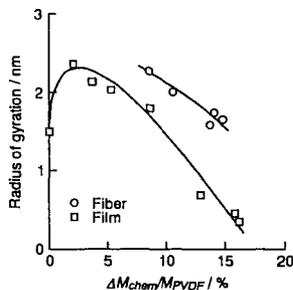


Fig. 1 Radius of gyration ( $R_3$ ) of pores in PVDF-based carbon fibers and films versus  $\Delta M_{chem}/M_{PVDF}$ . Heat-treatment temperature was 1300°C. At the value of  $\Delta M_{chem}/M_{PVDF}$  of 0%, film was pulverized during heat-treatment.

carbons. For the activated carbon films which were prepared by applying dehydrofluorination to a  $\Delta M_{chem}/M_{PVDF}$  value of 2%, the isotherm has a large hysteresis loop indicating the existence of mesopores. The hysteresis loop gradually diminishes and disappears at  $\Delta M_{chem}/M_{PVDF}$  of 13%.

Pore size distributions of PVDF-based activated carbon films are shown in Fig. 3. Mesopores with a diameter of 2-4 nm are developed even though dehydrofluorination is not applied. In this case, however, the material is granular. By applying dehydrofluorination to a  $\Delta M_{chem}/M_{PVDF}$  value of 2%, noticeable amount of mesopores with a diameter of 4-8 nm are formed. Intensive dehydrofluorination decreases the amount of mesopores.

As shown in Fig. 4, the average pore diameter, determined by nitrogen gas desorption, of PVDF-based activated carbon films is almost in proportion to the  $R_3$  value determined by SAXS for the carbon films before activation. Therefore, the pore structure of the PVDF-based activated carbon films reflected that of the carbon films before activation.

Adsorption of MB, at equilibrium concentration of  $3.0 \times 10^{-4}$  mol l<sup>-1</sup>, on PVDF-based activated carbon fibers and films are plotted against  $\Delta M_{chem}/M_{PVDF}$  in Fig. 5. For comparison, the MB adsorption properties of various activated carbon granules cited from literature [2] are shown in Table 1. PVDF-based activated carbons exhibit superior adsorptive properties against MB. With appropriate preparation conditions, MB adsorption of  $1.7 \times 10^{-3}$  mol g<sup>-1</sup> was achieved.

#### 4. SUMMARY

By using a combination of chemical dehydrofluorination and high temperature heat-treatment, the PVDF-based activated carbon fibers and films were highly mesoporous and showed superior adsorptive properties against MB.

The advantage of PVDF-based activated carbon prepared in the present study is that it does not contain impurity such as metal particles. This will be preferable for the application of activated carbons to catalyst supports or electrodes of electric double-layer capacitor.

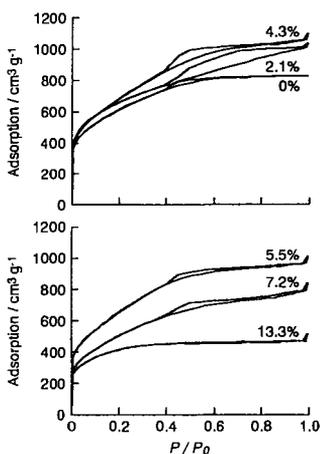


Fig. 2 Nitrogen gas adsorption-desorption isotherms at 77K, of PVDF based activated carbon films. The value of  $\Delta M_{act}/M_{heat}$  was about 70% for all specimens. Values of  $\Delta M_{chem}/M_{PVDF}$  are shown in the figure. At the value of  $\Delta M_{chem}/M_{PVDF}$  of 0%, film was pulverized during heat-treatment.

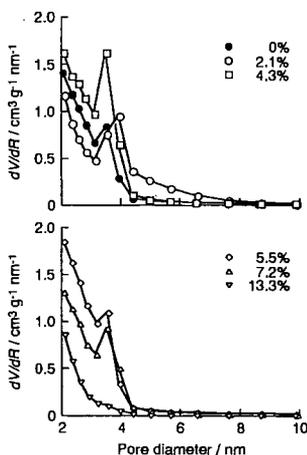


Fig. 3 Pore size distributions of PVDF based activated carbon films. The value of  $\Delta M_{act}/M_{heat}$  was about 70% for all specimens. Values of  $\Delta M_{chem}/M_{PVDF}$  are shown in the figure. At the value of  $\Delta M_{chem}/M_{PVDF}$  of 0%, film was pulverized during heat-treatment.

Furthermore, the pore size is controllable in a wide range by changing the degree of dehydrofluorination. The good processability of PVDF into various geometries is also advantageous for applications.

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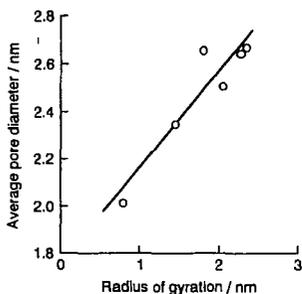


Fig. 4 Average pore diameter of PVDF based activated carbon films versus radius of gyration of PVDF based carbon films before activation.  $\Delta M_{act}/M_{heat}$  was about 70% for all specimens. At the value of  $\Delta M_{chem}/M_{PVDF}$  of 0%, film was pulverized during heat-treatment.

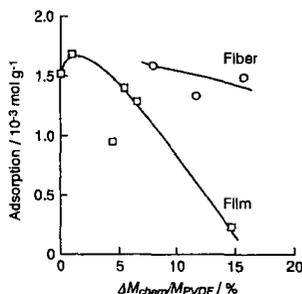


Fig. 5 Adsorption of methylene blue at equilibrium concentration of  $3.0 \times 10^{-4} \text{ mol l}^{-1}$  at  $30^\circ\text{C}$ , on PVDF based activated carbon fibers and films versus  $\Delta M_{chem}/M_{PVDF}$ . The value of  $\Delta M_{act}/M_{heat}$  was about 70% for all specimens. At the value of  $\Delta M_{chem}/M_{PVDF}$  of 0%, film was pulverized during heat-treatment.

Table 1 Adsorption of methylene blue on various granular activated carbons.

Precursor	Adsorption / $10^{-3} \text{ mol g}^{-1}$
Palm shell	0.12
Coconut husk	0.20*
Bituminous coal	0.55*
Pitch	0.10*
Pitch/Y(naphthoate) <sub>3</sub>	0.15*
Pitch/Y(OiPr) <sub>3</sub>	0.16*

\*Values were cited from reference [2].

# 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  $^{13}\text{C}$ nmr spectroscopy. The FTIR transmittance spectra were acquired using a Nicolet 20 SX spectrometer at  $4\text{ cm}^{-1}$  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  $^{13}\text{C}$ 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  $1100^\circ\text{C}$  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  $\text{CO}_2$ , 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.

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Table 1: Analysis of Prepared Pitch

Source	Sample No.	Ultimate Analysis (wt%, daf)					Insolubility (wt%)		Softening point (°C)	Car / Cal (FTIR)	$f_{ar}$ ( $^{13}C_{org}$ )
		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.

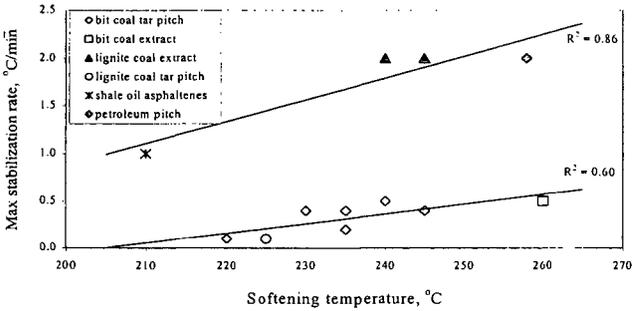


Figure 1 Dependence of Stabilization Rate on Pitch Softening Point

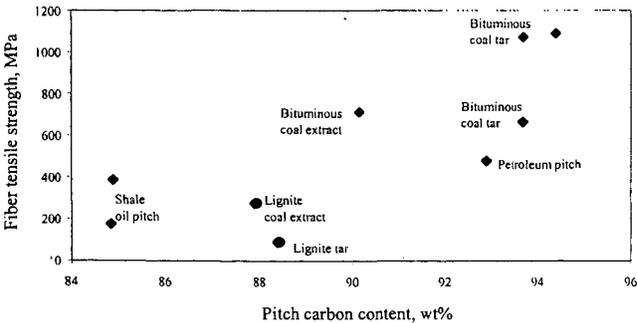


Figure 2 Tensile Strength of Fibers as a Function of Pitch Carbon Content