

Physical and chemical properties of pitch fluoride prepared by direct fluorination

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(Received December 16, 1991; accepted March 2, 1992)

Abstract

Various physical and chemical properties of pitch fluoride such as chemical composition, molecular weight, specific gravity, dielectric constant, and water- and oil-repellency have been investigated as functions of the fluorination temperature between 30 °C and 130 °C. Bulk properties such as chemical composition, molecular weight, specific gravity and interlayer spacing vary according to the reaction temperature, while the surface properties are independent from it. Each property may be summarized as follows: chemical compositions were between $CF_{1.00}$ and $CF_{1.59}$; molecular weights were in the range 2070–4300; specific gravity was *c.* 2.00; refractive index was in the range 1.36–1.39; dielectric constant was *c.* 2.0. The contact angle of water was almost constant at *c.* 143°, demonstrating the excellent water-repellency.

Introduction

Recently we reported that the mesophase pitch derived from coal tar reacted with elemental fluorine over the temperature range 50–130 °C to yield pitch fluoride having a composition between $CF_{1.30}$ and $CF_{1.59}$ [1]. This material has a similar structure to graphite fluoride, $(CF)_n$, with a low crystallinity as shown in Fig. 1. A fluorine atom is bonded to each carbon from above or below the carbon ring network to form chair-type condensed cyclohexane structures. Such condensed cyclohexane ring compounds are crosslinked by perfluoromethylene bridges and stacked lamellarly along the *c*-axis where the interlayer spacing is *c.* 6.4–6.9 Å. Although the ideal structure for pitch fluoride is illustrated in the model shown in Fig. 1, some defects occur in the bulk material with some carbon atoms being linked by double bonds.

It is widely known that fluorocarbons have unique properties such as low surface energy, low refractive index and excellent insulating capabilities which are not observed in hydrocarbons with a similar structure arising from the strong C–F bond, the high electronegativity, the small van der Waal's radius and the low polarizability of the fluorine atom. Nowadays, these unique

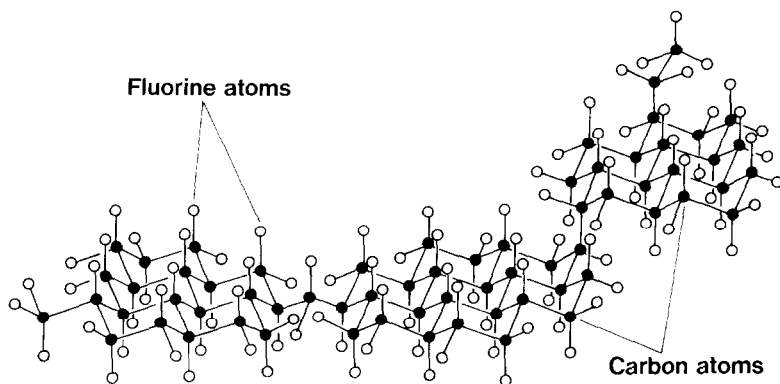


Fig. 1. The average structure of the pitch fluoride.

properties are applied in many fields, e.g. optical fiber materials, surface coating materials, solid lubricants, etc. [2, 3]. Since pitch fluoride is regarded as being an intermediate compound between graphite fluoride, $(CF)_n$, and polytetrafluoroethylene (PTFE), from the stoichiometry, the common properties of fluorocarbons should also be expected for it.

In the present study, the physical and chemical properties of pitch fluoride such as chemical composition, molecular weight, specific gravity, water- and oil-repellency, chemical resistance, dielectric constant and refractive index have been examined as a function of the fluorination temperature.

Experimental

Preparation of mesophase pitch and pitch fluoride

Preparation of the mesophase pitch and the pitch fluoride were carried out in the same manner as described elsewhere [1]. The fluorination reaction was carried out at the temperatures between 30 °C and 130 °C. The particle size of the pitch as a starting material and after being subjected to fluorination at various temperatures is listed in Table 1. Hereafter, the fluorinated mesophase pitch will be abbreviated to MP-F followed by its fluorination temperature, e.g. 'MP-F90' for the specimen fluorinated at 90 °C.

Analyses of the pitch fluoride

Grading analysis was carried out using Coulter Multisizer (Coulter Electronics Ltd.) with ethanol as the dispersing solvent. Elemental analysis was carried out by the conventional oxygen flask method. Molecular weights were measured using a vapor pressure osmometer (117 type osmometer Corona Denki K.K.) with hexafluorobenzene as a solvent. Specific gravities were measured at 30 °C according to the testing methods employed for carbon (Japanese Industrial Standard R 7212) except that ethanol was used instead of butanol. X-ray diffraction measurements were made via a JEOL diffractometer (DX-G0-S). Contact angle measurements were carried out using a

TABLE 1

Particle sizes of starting pitch and pitch fluorides prepared at several temperatures

Sample	Particle size distribution ^a (μm)		
	D25	D50	D75
Starting pitch	2.82	4.14	5.43
MP-F30	3.12	4.91	6.99
MP-F50	3.00	4.57	6.24
MP-F70	2.91	4.40	5.90
MP-F90	3.12	4.73	6.46
MP-F110	3.02	4.55	6.09
MP-F130	2.99	4.67	6.42

^aD25, D50 and D75 indicate the particle diameter of the 25%, 50% and 75% median, respectively.

CA-A type contact angle meter (Kyowa Kaimenkagaku Co. Ltd.) as a means of estimating the water- and oil-repellency. The liquids used for contact angle measurements were distilled water, glycerol, formamide, 1,4-butandiol, hexadecane and a 17% NaOH solution. The surface free energy of pitch fluoride was estimated from the contact angle of water and formamide according to the method developed by Owens and Wendt [7]. The refractive index was measured at 30 °C with an Abbé refractometer (Atago Co. Ltd. type 3T); the D line of the Na spectrum (589.3 nm, Atago Co. Ltd., type SL-NaB) was used as the light source. Methanol and ethylene glycol were used as standard solutions for refractive index measurements. The dielectric constant was estimated from the refractive index results using the equation

$$\epsilon = n^2 \quad (1)$$

where ϵ and n are the dielectric constant and refractive index, respectively. The oxidizing ability of fluorine in pitch fluoride was measured by iodometry; a constant amount of pitch fluoride was dispersed in a mixed solution of ethanol and 1 mol l⁻¹ KI solution (1:1 volume ratio), and stirred for 2 d. After that time, the iodine liberated in the solution was titrated by 0.01 mol l⁻¹ sodium thiosulfate solution. Guaranteed reagent potassium iodide and sodium thiosulfate (Kanto Chemical Co. Inc.) were used. The chemical resistance of pitch fluoride was investigated via the color and weight change before and after immersion in 35% hydrochloric acid, 40% nitric acid, 28% aqueous ammonia or 1 N sodium hydroxide solutions, or in methanol, ethanol, acetone or benzene. The immersion test was carried out for 5 d at room temperature.

Results and discussion

Particle size distribution of pitch fluoride

It is preferable to use pitch fluorides having the same particle sizes for measuring properties in order to avoid size effects on the properties. For

this reason, grading analysis of pitch fluorides was undertaken. All the results obtained are listed in Table 1 together with those for the starting pitch. The particle size increased somewhat during the fluorination reaction. The diameters of the resulting compounds were $4.7 \pm 0.3 \mu\text{m}$ for D50 (diameter of the 50% median), with no dependence on the fluorination temperature apparent.

Appearance of the pitch fluoride

The color of the pitch fluoride varied from yellowish white to white with increasing reaction temperatures. MP-F30, 50, 70 and 90 were yellowish white, while MP-F110 and 130 were almost white. As mentioned in the Introduction, pitch fluorides contain some residual carbons which do not bond to fluorine. Such 'unreacted' carbons exist inside the condensed 'cyclohexane' rings linked by double bonds, and their concentrations decrease with increasing fluorination temperatures [1]. As a result, the pitch fluorides become more yellow in color with decreasing reaction temperature.

Chemical composition, molecular weight, interlayer spacing and specific gravity of pitch fluoride

Table 2 lists data for the chemical composition, molecular weight, interlayer spacings and specific gravities of pitch fluorides prepared at several temperatures. As far as the composition of pitch fluoride is concerned, there is a clear tendency for the F/C atomic ratio to increase from 1.29 to 1.59 with increasing fluorination temperature. In contrast, the molecular weight decreased from 4300 to 2070 with an increase in the reaction temperature. As the fluorination temperature increases, the extent to which elemental fluorine interacts with pitch increases. As a result, the CF_2 bridges crosslinking the condensed cyclohexane rings are cleaved at higher temperatures leading to a lowering of the molecular weight.

TABLE 2

Stoichiometry, molecular weight, specific gravity and an X-ray diffraction parameter for pitch fluoride

Sample	F/C ratio	Molecular weight	Specific gravity	Interlayer spacing (\AA)
MP-F30	1.29	4300	—	6.85
MP-F50	1.27	—	—	6.86
MP-F70	1.39	2700	1.98	6.74
MP-F90	1.41	—	2.03	6.51
MP-F110	1.49	2070	2.07	6.42
MP-F130	1.59	—	2.07	6.41
$(\text{CF})_n$	1.00	—	2.68 ^a	5.85 ^b
PTFE	2.00	—	2.1	—

^aValue for $(\text{CF})_n$ prepared from natural graphite, quoted from ref. 4.

^bValue for $(\text{CF})_n$ prepared from natural graphite, quoted from ref. 5.

The specific gravity and interlayer spacing also vary as a function of the reaction temperature. The interlayer spacing of pitch fluoride, as estimated from X-ray diffraction patterns, decreases with increasing fluorination temperature. The change in the specific gravity coincides with the change in the interlayer spacing, with a decrease in the interlayer spacing accompanying an increase in the density. As mentioned in detail below, samples prepared at low relative temperatures, e.g. MP-F30 and MP-F50, exhibit an oxidizing ability. For this reason, the specific gravity of these samples could not be measured because the ethanol used as a solvent in such measurements was oxidized.

Water- and oil-repellency

Previous studies using elemental analysis and ^{19}F NMR spectroscopy have revealed that the F/C ratio and the proportion of CF_3 groups in pitch fluoride increase with increasing fluorination temperature as a result of the ring-opening reactions which occurs at higher temperatures yielding CF_3CF_2 groups at the periphery of the cyclohexane rings [1]. Hence, in view of the enhanced surface tensions of compounds having CF_3 end groups, the water- and oil-repellency might be expected to be improved with increasing reaction temperature. However, as shown in Table 3, the contact angles remain unchanged and are independent of the reaction temperature. This suggests that the surface conditions remain virtually the same even if the composition is altered. The dominant appearance of many CF_3 groups on the surface would be necessary for a significant improvement in the oil-repellency to be observed.

On the basis of the theoretical considerations of Owens and Wendt [7], the surface free energy can be expressed as follows:

$$\gamma_{\text{lv}} = \gamma_{\text{l}}^{\text{d}} + \gamma_{\text{l}}^{\text{h}} \quad (2)$$

where the superscripts h and d refer to components arising from hydrogen bonding and dispersion forces, respectively. Using the Young equation, Owens

TABLE 3

Contact angles for pitch fluoride and other samples with various liquids at 30 °C

Sample	Water	17% NaOH	Glycerol	Formamide	1,4-Butanediol
MP-F30	143.3	139.3	146.3	135.2	penetrated
MP-F50	142.4	136.7	142.9	138.5	115.9
MP-F70	142.1	137.9	142.3	137.2	115.6
MP-F90	143.6	137.4	141.1	135.2	115.8
MP-F110	143.2	138.6	143.5	138.3	120.6
MP-F130	141.3	139.1	140.2	137.1	117.2
$(\text{CF})_n^{\text{a}}$	143 ± 3	139 ± 2	151 ± 2	128 ± 3	103 ± 2
PTFE ^a	109 ± 2	114 ± 3	105 ± 2	95 ± 1	86 ± 2

^aAll values quoted from ref. 6.

and Wendt have also derived an equation for the contact angle of a liquid on a solid, thus enabling each contribution to be calculated, i.e.

$$1 + \cos \theta = \frac{2(\gamma_s^d)^{1/2}(\gamma_l^d)^{1/2}}{\gamma_{lv}} + \frac{2(\gamma_s^h)^{1/2}(\gamma_l^h)^{1/2}}{\gamma_{lv}} \quad (3)$$

The value of γ_l^h can be determined from the values of γ_{lv} and γ_l^d via eqn. (2). By measuring θ for two different liquids relative to a given solid, homogeneous equations are obtained which can be solved for γ_s^d and γ_s^h . An approximate value for the total solid surface free energy can then be obtained by summing these two components as in eqn. (2). On the basis of this theory and the γ_l^d and γ_l^h values for water and formamide which have already been published [8, 9], the surface free energies of pitch fluoride, $(CF)_n$ and PTFE have been calculated. The results obtained are listed in Table 4. Calculations using eqn. (3) gave a surface free energy of 0.95–2.02 mJ m⁻² for pitch fluoride, 7.01 mJ m⁻² for $(CF)_n$ and 15.88 mJ m⁻² for PTFE. The surface free energy for pitch fluoride is much lower than that for $(CF)_n$ and PTFE. As graphite fluoride and PTFE gave few CF₃ groups, their surface energies would be larger than that of pitch fluoride.

Oxidizing ability of fluorine and the nature of the C–F bond in pitch fluoride

When some samples of pitch fluoride were kept in a glass ampoule for a few weeks, the inside of the glass tube became frosted. This indicates that a small amount of hydrogen fluoride or other fluorine species possessing oxidizing ability is entrapped the pitch fluoride. The oxidizing ability of fluorine in pitch fluoride has been measured by iodometry. Samples prepared at temperatures above 70 °C exhibited little oxidizing ability, with only MP-F30 and MP-F50 appearing to contain a fluorine species exhibiting an oxidizing ability. The content of such fluorine species for these two samples was 0.1 wt.% and 0.09 wt.%, respectively.

On the other hand, an interesting result was obtained from an F_{1s} ESCA measurement. The binding energies of the pitch fluorides prepared at temperatures above 70 °C were found to lie between 689.0 and 690.0 eV, while

TABLE 4

Components of the surface energy for pitch fluoride

Sample	γ^d (mJ m ⁻²)	γ_s^h (mJ m ⁻²)	γ_s (mJ m ⁻²)
MP-F30	2.02	6.75×10^{-3}	2.02
MP-F50	0.67	0.28	0.95
MP-F70	0.95	0.19	1.14
MP-F90	2.12	1.87×10^{-3}	2.12
MP-F110	0.89	0.16	1.05
MP-F130	0.79	0.29	1.08
$(CF)_n$	6.59	0.43	7.02
PTFE	15.07	0.81	15.88

those of MP-F30 and MP-F50 were 688.1 and 688.7 eV, respectively. The chemical shifts of the F_{1s} electron binding energy can be taken as a relative indication of the ionic or covalent character of C–F bonds, and from this viewpoint the covalent character of the C–F bond increases with increasing F_{1s} electron binding energy from 685.6 eV in LiF to 689 eV for the covalent bond in graphite fluoride. Since the binding energies of pitch fluoride prepared at temperatures above 70 °C were higher than those of MP-F30 and MP-F50, the covalent character of the C–F bonds appear to be more pronounced in the former.

Refractive index of pitch fluoride

It is well known that the refractive index decreases with increasing fluorine content in a polymer because of the small polarizability of fluorine. Hence, most fluorine compounds have low refractive indices. Table 5 lists the refractive index values for pitch fluoride prepared at several temperatures. As the reaction temperature increases, the refractive index tends to decrease. This tendency is in good agreement with that of the F/C atomic ratio listed in Table 2.

On the basis of Maxwell's theory of electromagnetism, the refractive index is related to the dielectric constant at a fixed frequency as expressed by eqn. (1) above. Accordingly, the dielectric constant of pitch fluoride can be estimated by measuring its refractive index. The results obtained from the use of eqn. (1) are listed in column 3 of Table 5, and show that the dielectric constant also decreases slightly with an increase in the fluorination temperature.

Chemical resistance of pitch fluoride

The pitch fluoride exhibited excellent resistance towards HCl and HNO_3 solutions, whilst it reacted with alkaline solutions such as aq. NH_3 and NaOH. On immersion of samples in such alkaline solutions, the color of the sample changed and the solutions turned to black and brown, respectively. In particular, such changes occurred rapidly in aq. NH_3 just after sample immersion.

TABLE 5

Refractive index of pitch fluoride and the corresponding dielectric constant as estimated from the same

Sample	Refractive index	Dielectric constant
MP-F50	1.390	1.93
MP-F70	1.380	1.90
MP-F90	1.373	1.89
MP-F110	1.368	1.87
MP-F130	1.365	1.86
PTFE	1.35 ^a	<2.1

^aQuoted from ref. 10.

Resistance against organic solvents was also excellent, as far as samples prepared at temperatures above 70 °C were concerned. However, with MP-F30 and MP-F50 the organic solvent turned yellow on sample immersion. This could have resulted from attack on the solvent by the absorbed fluorine species exhibiting oxidizing ability as detected by iodometry.

Conclusions

All the results associated with the properties investigated in the present study have been summarized in Table 6 together with those for $(CF)_n$ and PTFE. Properties such as composition, molecular weight, specific gravity and interlayer spacing, which reflect the bulk characteristics, changed as functions of the fluorination temperature. On the other hand, surface energy, and water- and oil-repellency, which reflect the surface conditions, were independent of the fluorination temperature.

The results obtained for surface free energy and refractive index were almost the same as expected from general observations of fluorocarbons, indicating the low surface energy and refractive index. As far as physical parameters obtained in this study such as specific gravity, molecular weight and interlayer spacing are concerned, there was no inconsistency with the proposed structure of the pitch fluoride depicted in Fig. 1 based on the structures of the pristine pitch and graphite fluoride.

TABLE 6

Various physical and chemical properties of pitch fluoride, graphite fluoride and PTFE

Property	Pitch fluoride	$(CF)_n$	PTFE
Particle size in D50 (μm)	4.3–5.0	–	–
F/C atomic ratio	1.15–1.59	1.00	2.00
Molecular weight	4300–2070	–	–
Specific gravity	c. 2.0	2.68	2.1
Interlayer spacing (Å)	6.4–6.9	5.85	–
Color	yellowish white or almost white	white	white
Contact angles ($^\circ$)			
Water	141–143	143	109
17% NaOH	137–140	139	114
Glycerol	140–146	151	105
Formamide	135–139	128	95
1,4-Butanediol	115–121	103	86
Surface energy (mJ m^{-2})	1.0–2.0	7.01	15.88
Refractive index	1.36–1.39	–	1.35
Dielectric constant	c. 1.9	–	<2.1
Acid resistance	excellent	– excellent –	

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