Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: F. Moguet, S. Bordere, L. Rabardel, A. Tressaud, F. Rouquerol & P. Llewelly (1998): Deintercalation Process of Fluorinated Carbon Fibres. Part I - Controlled Rate Evolved Gas Analysis, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 310:1, 111-118

To link to this article: http://dx.doi.org/10.1080/10587259808045323

Mol. Cryst. Liq. Cryst., 1998, Vol. 310, pp. 111–118
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Deintercalation process of fluorinated carbon fibres. Part I - Controlled rate evolved gas analysis

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The intercalation of fluorine into graphite leads to graphite intercalation compounds (F-GICs) exhibiting potential properties such as the storage and transport of fluorine. Stage-1 compounds with $C_{2.5}F$ to C_4F compositions are obtained by fluorination treatments at room temperature of ex-pitch, high-temperature treated carbon fibres under 10 bars F_2 pressure in the presence of, gaseous HF. The deintercalation process of fluorine species has been studied by evolved gas analysis : the F-GICs are decomposed using the Controlled transformation Rate Thermal Analysis (CRTA) method. The thermal analysis curve obtained for stage-1 F-GICs exhibits three decomposition steps. The first two steps correspond to a simultaneous deintercalation of atomic fluorine F and gaseous HF and the third step (above 460°C) to the degradation of the compound with formation of C_2F_4 and CF_4 which further dissociate in the spectrometer to CF_n ($1 \leqslant n \leqslant 3$) species.

Keywords : carbon fibres ; fluorine intercalation ; deintercalation ; controlled transformation rate thermal analysis ; mass spectrometry

INTRODUCTION

The peculiar reactivity of fluorine with graphite can be illustrated by the competition between the formation on the one hand of covalent *C-F* bonding, as in covalent graphite fluorides $(CF)_n$ and $(C_2F)_n$, and the

intercalation on the other hand of fluorine in between the graphene layers, leading to graphite intercalation compounds (F-GICs), in which the sp^2 C electronic structure is preserved and semi-ionic C-F bonding occurs [1-3]. Whereas the covalent compounds are stable up to about 500°C, the intercalated compounds are quite unstable even at lower temperatures. It therefore seemed worthwhile to investigate the thermal stability of the intercalated compounds keeping in view a possible application of the products for the storage and transport of fluorine and fluorinating gases. Several studies on the thermal stability of these compounds have been recently carried out on different types of carbon host materials using differential thermal analysis (DTA) and thermogravimetry (TG) techniques [4-7]. However, using these techniques, an overlapping of the successive stages of the decomposition could not be avoided. In addition, no information was available on the gaseous species formed during the process. We have therefore chosen to study the decomposition mechanism of fluorine-intercalated carbon fibres of composition C_xFH_5 using evolved gas analysis. The host carbon materials were high-temperature treated ex-pitch fibers, whose high degree of graphitization allowed the intercalation to proceed steadily up to stage-1 compounds with C/F ratios equal to 4 to 3. The Controlled transformation Rate Thermal Analysis (CRTA) was used in order to obtain a better separation of the decomposition steps and to send the whole gas flow in the quadruple gas analyser with no risk of overpressing.

In the following the different steps of the deintercalation/decomposition of the F-GICs will be investigated using the CRTA technique. In a second part, the activation energies associated with each step will be determined by the rate-jump method and a kinetical study of the deintercalation/decomposition process of the F-GICs will be proposed [8].

EXPERIMENTAL PROCEDURE

Starting carbon fibres, fluorination procedure and structural characterization

Pitch-based carbon fibres (P75, P120) obtained from AMOCO, USA were used. The fibres were high temperature treated (3000°C HTT) at Le Carbone Lorraine, France, prior to experiments. The fibres were intercalated in a conventional fluorination set up previously described [9]. 10 bar F_2 gas +0.1 bar HF gas were introduced in contact with the fibres in a nickel container and the reaction was carried out at room temperature

for one day. The rough composition of the intercalated fibres was estimated from the weight uptake. The main structural features, i.e. stage number and c-axis repeat distance were deduced from X-ray diffraction patterns. In the above experimental conditions, stage-1 compounds with I_c ~ 0.5 nm were obtained. The corresponding C/F ratio ranged from 4 to 3 [9]. The nature of the C-F bonding was determined by XPS. Due to the high degree of graphitization of the host fibers, the main components in both C1s and F1s spectra could be attributed to the semi-ionic type, i.e. to intercalation (F-GICs) compounds [9, 10].

Thermal analysis

The thermal analyses were carried out under conditions of Controlled transformation Rate Thermal Analysis (CRTA). The evolved gas were analysed using a quadrupole gas analyzer. This equipment has been described in [11] and is interesting for its analytical and kinetical possibilities. The possibility of controlling both the rate of reaction and the pressure at the reacting zone allowed to obtain favourable conditions for a clear separation of the successive steps. Moreover, due to a slow rate control, the whole gas flow was sent to the quadrupole analyzer, avoiding overpressure and gas discrimination.

Controlled Rate Evolved Gas Analysis

The Controlled transformation Rate Thermal Analysis (CRTA) was effected on pitch-based carbon fibres after treatment at high temperature. We selected 23 mg of HTT P120 fibres, fluorinated under 10 bar F_2 + 0.2 bar HF and having a composition $C_{3.4}F$. The X-ray crystallographic study had shown that it was mainly a stage-1 compound (I_c = 0.54 nm) containing a small amount of stage 2 (I_c = 0.94 nm). The decomposition, effected at a constant pressure of 10^{-2} mbar was carried out at a rate of about 0.03 h^{-1}. The obtained thermogram, as well as the pressure imposed during the thermolysis are shown in Fig. 1 a : three decomposition steps are observed. The gas species produced during thermolysis were analyzed by mass spectrometry for relative molecular weights (m/e) in the range 1 to 100. It is possible to observe between -30 and 150°C, i.e. before reaching the start of the first stage, an abrupt increase in the H_2O partial pressure (m/e = 18). Note that a fragmentation of H_2O in the mass spectrometer causes the formation of OH species (m/e = 17) and O species (m/e = 16) whose respective signals have the same appearance as that of H_2O in partial pressure ratios, respectively equal to 3 (p_{H2O}/p_{OH})

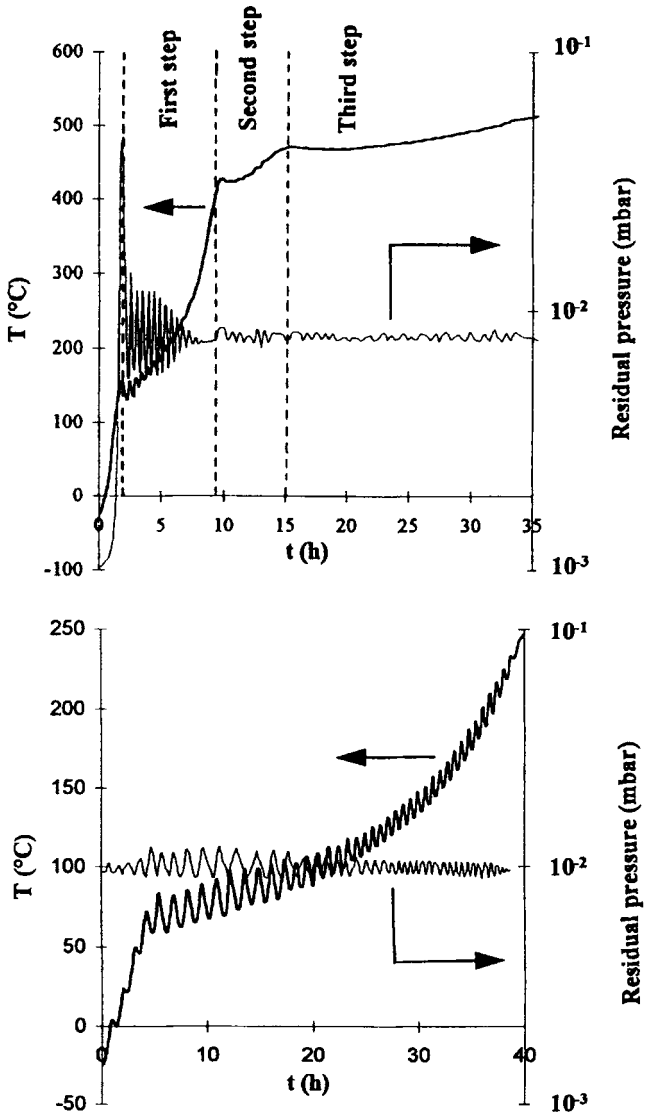

FIGURE 1 - CRTA of the F-GICs $C_{3.4}F$ (P120 HTT fibres)[a] and $C_{10}F$ (natural graphite)[b] under a total pressure of 10^{-2} mbar, and a reaction rate of $0.03h^{-1}$.

and 10 (p_{H2O}/p_O). This loss of water may correspond to the desorption of water molecules adsorbed on the surface of the fibres during contact with the atmosphere after the fluorination. Note that the elemental analysis of the fibres $C_{3.4}F$ (P120 HTT), carried out at the CNRS Central Analysis Laboratory, clearly indicates that the water content in this compound is less than 0.1% (by weight).

First step - The first step of decomposition between 150 and 430°C (see Figure 1a) shows a simultaneous loss of atomic fluorine (m/e = 19) and hydrogen fluoride HF (m/e = 20). This step thus corresponds to the deintercalation of fluorine species and notably fluorine. The relative intensities of the gaseous species formed during this step are reported in Table I. Note that molecular fluorine F_2 (m/e = 38) is completely dissociated in the spectrometer : this is the reason why only atomic fluorine (m/e = 19) is observed.
The X-ray diffraction pattern obtained after this first step is typical of an interstratification compound (mainly of stage-2, with the presence of higher stages) with the presence of graphitic domains. Furthermore, a large width of the lines (00l) indicates that this decomposition product is characterized by smaller crystallites than in the starting material $C_{3.4}F$. Thus, the average dimension of these crystallites along the c axis, calculated using the Scherrer relation, is estimated to be 2.5 nm, whereas that in the $C_{3.4}F$ compound is 5.6 nm. The partial loss of fluorine thus causes an increase in the structural disorder by breaking the graphene planes.

Second step - The thermolysis continues through a second step between 430 and 460°C during which the HF and F contributions are similar to those in the first step : this step, like the first one, corresponds to the deintercalation of fluorine species.
Note that in the total of the first two steps (deintercalation steps), the quantity of HF detected by mass spectrometry is greater than that of fluorine. From the composition $C_{3.4}F_{1-d}(HF)_d$ with d in the range 3.4/10 to 3.4/15 [9], the HF contained in this compound is much less than that of fluorine. The major portion of the HF detected by the spectrometer would thus be formed by a post-deintercalation reaction of the fluorine. In order to confirm this hypothesis, we carried out a CRTA of natural graphite treated with pure fluorine. The compound $C_{10}F$ obtained, characterized by an intercalation stage greater than 3, does not contain any HF (or least

only traces). Note that we have chosen natural graphite because of its high structural organization which favors the intercalation. The thermogram of the compound $C_{10}F$ shows a major deintercalation stage between 60 and 250°C (Figure 1b). As in the case of the compound $C_{3.4}F$, the HF signal (m/e = 20) comprises the major portion. The relative intensities are summarized in Table I. Since the compound $C_{10}F$ contains no (or very little) HF, this observation shows that essentially all the HF detected is formed by a parasitic reaction between the fluorine which is liberated by deintercalation and the traces of water which are initially present in the apparatus and which were also produced by desorption from the surface of the material.

Third step - The third step which starts at 460°C involves the appearance of signals relating to fluorocarbon groups CF_3 (m/e = 69), CF_2 (m/e = 50), CF (m/e = 31) and C_2F_4 (m/e = 100) and to carbon (m/e = 12). These signals increase at the same time as those for F and HF decrease, which marks the transition between the deintercalation of the fluorine species and the degradation step of the material as evidenced by the presence of fluorocarbon groups. The relative percentages of the gaseous species detected in this step are given in Table I. The results from this third step thus indicate the presence of a significant quantity of fluorine bonded by covalent bonds, a type of bond which was present as minor component only in the starting material (F-GIC of stage 1). This leads to the possibility that these C-F bonds were formed during the intercalation steps. Previous DSC measurements have shown that below 200°C the presence of an exothermic peak could be associated with the reaction between evolving fluorine and defects [7]. TEM observations of stage-2 GICs [9, 12] also indicate that the intercalation process caused structural disorder inducing the creation of numerous defects. These defects thus appear to be preferred sites for the formation of covalent CF_n groups ($1 \leqslant n \leqslant 3$) by reaction of fluorine with the carbon atoms.

This third step would thus be characterized by the loss of these groups through rupture of the C-C bonds which, by recombination, give CF_4 and C_2F_4 molecules. It is also possible to consider the formation of C_2F_6 and C_3F_8 although these species are not detected because their relative weight is greater than 100. As was previously shown, CF_4 is finally dissociated in the spectrometer into CF_n groups ($1 \leqslant n \leqslant 3$) and into atomic fluorine [13, 14]. Consequently, this third step corresponds to the degradation of

TABLE I : Comparison of the relative intensities of the gaseous species formed during the decomposition of $C_{3.4}F$ fibres (P120 HTT) and of the compound $C_{10}F$(natural graphite).

Type of compound	Nature of the decomposition step	F	HF	CF_4	CF_3	CF_2	CF	C	C_2F_4	H_2O
$C_{3.4}F$ (P120 HTT)	First deintercalation step (between 150 and 430°C)	53	100	0	3.3	1.8	4.1	6.7	2.8	7.8
	Second deintercalation step (between 430 and 460°C)	48	100	0	7.8	2.4	3.3	5.6	1.5	5
	Degradation step (between 460 and 510°C)	8.6	7	0	100	9.7	25.3	7	7.5	2.2
$C_{10}F$ (Natural graphite)	Deintercalation step	36	100	0	0	0	0	7.4	0	1.6

the compound by formation of CF_4 and C_2F_4 and thus presents similarities with the decomposition of graphite fluorides $(CF)_n$ and $(C_2F)_n$, since it was shown by infrared that these latter compounds decomposed with formation of the same species [15, 16].

In summary, the investigations by CRTA of the decomposition of $C_{3.4}F$ fibres has shown that are observed three steps :

- *two deintercalation steps* during which the quantities of fluorine deintercalated are of the same order of magnitude (because the duration of the two stages and the partial pressures of HF and F are practically equal),
- *a third degradation* step of the compound with formation of CF_4 and C_2F_4 which dissociate in the spectrometer into CF_n species ($1 \leqslant n \leqslant 3$).

With the identification of these three distinct steps, it is possible to consider a study of the decomposition kinetics of fibres in which fluorine has been inserted. The activation energies associated with each of these

steps will be determined by the rate-jump method and reaction mechanisms will be proposed.

Acknowledgements - L. Lozano is acknowledged for assistance in fluorination experiments.

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