Letters

Study of the intercalated carbon formed by electrochemical reduction of polytetrafluoroethylene

The reduction of polytetrafluoroethylene (PTFE) only occurs under very vigorous conditions e.g. with sodium in liquid ammonia[1] or sodium naphthalenide in tetrahydrofuran[2]. An alternative is the electrochemical reduction briefly described by Brewis, Dahm and Konieczko[3]. This involved either reduction by electrochemically generated intermediates or by direct contact of PTFE with a cathodically polarized electrode in an aprotic solution of tetraalkyl ammonium ions. Since then considerable work has been done on the direct contact method and in this communication the nature of the reduced surface will be described.

Early work on the chemical reduction showed that a black coherent film was formed on the polymer surface which was described as a 'carbonaceous' layer formed by defluorination of PTFE[2]. Later, two sets of workers[4,5] applied X-ray photoelectron spectroscopy (X.p.s. or e.s.c.a.) to the problem and found that the surface consisted of carbon and oxygen in a ratio of $\sim$1:0.3, but with no fluorine. Since the incorporation of oxygen in the reaction mixtures was not feasible it was concluded that oxidation occurred on exposure to air and hence that the carbon in its initially formed state was highly reactive; one group of workers[4] were able to apply X.p.s. analysis to an unoxidized film and found it consisted of 'carbon radicals and carbon–carbon double bonds'. The reduction of PTFE with alkali metal amalgams[6] has been studied independently and in this work it was shown that the products consisted of an 'amorphous' carbonaceous component interspersed with solid alkali metal fluoride.

Our work has shown that the electrochemical reduction also produces a coherent, black, carbonaceous product. X-ray diffraction studies have shown that, on reduction, the lines due to PTFE disappear and are replaced by a single broad band at a low angle indicating that the carbon formed has little three-dimensional order.

X.p.s. analysis of the carbon has shown it to be similar to that obtained on chemical reduction, although it is apparently more readily oxidized than the chemically formed material since we have as yet been unable to observe an unoxidized film, even when glove box techniques were used for sample preparation (Brecht, Mayer and Binder[4]). However, it has been possible to obtain information indirectly, prior to oxidation, from the resistance behaviour of the film. Thus a freshly-formed carbonaceous film had a resistivity, measured in a single compartment vacuum cell, of between 10^{-1} and $10^{-2}\ \Omega$ cm. However, the resistance rapidly increased by several orders of magnitude when the film was exposed to air or washed with methanol or water. A rather slower rise in resistance occurred on exposure to a nitrogen atmosphere or to a vacuum of $\sim 10^{-4}$ mmHg, probably indicating reaction of the film with residual oxygen and/or water vapour in the system.

Results from coulometric analysis have shown that reduction of each $-(C_2F_4)-$ unit required between 4.1 and 4.5 electrons. This has been interpreted as further reduction of the carbon to give a species of the form $-(C_n)-^-R_4N^+$ where n = 4–16. This is analgous to tetraalkyl ammonium intercalation compounds of graphite produced under conditions identical to our own[7,8].

The presence of such species explains a number of previous observations, e.g. the use of an excess of alkali metal in the amalgam reduction of PTFE[9] and the highly reactive nature as indicated by the X.p.s. and resistance experiments. However, comparison of our material and intercalated graphite shows: (a) that the former has a much less ordered structure (although this does not necessarily preclude intercalation as shown by the insertion of alkali metal cations into non-graphitizing and even glassy carbons[10]); (b) that it is more densely intercalated with one R_4N^+ cation per 4 to 16 carbon atoms compared to a ratio of between 1:400 and 1:100 reported by Simonet and Lund for graphite; and (c) whereas Simonet and Lund were able to recover $\sim$94% of the cathodic charge on a subsequent anodic pulse, we could only obtain $\sim$40%. This last point may be related to the increase in resistivity of several orders of magnitude also observed on discharge.

The dependence of conductivity on the intercalated nature of the carbon presents an alternative explanation for the resistance increase *in vacuo.* Thus it may be due not only to reaction with traces of oxygen and water but also to decomposition of the intercalated cations or discharge via continued reaction with the PTFE substrate. The changes in resistance on charge and discharge are related to the semiconductor nature of the intercalated carbon which again has been reported for graphite intercalation products[11,12]. A further change which accompanies the charge and discharge is the appearance and disappearance of a metallic sheen to the surface; similar effects are well known for alkali metal intercalation compounds of graphite[12].

Another factor pertinent to the film's reactivity is its porosity, which has been calculated from its double layer charging behaviour on application of a potential pulse[13]. The porous nature of the film was reflected in the slow response of the resulting current transient[14]. Thus using a value for the double layer capacity of $\sim 10\ \mu F/cm^2$ [15] a surface area of $\sim 1000\ m^2/g$ was obtained. This value is similar to that of very finely divided carbons e.g. some carbon blacks[16], or those obtained by evaporation[17].

Scanning electron microscopy has shown that there are no significant textural differences between the blackened surface and PTFE; it does, however, reveal the presence of islands of material joined by fibrils. Since the formation of carbon from PTFE must result in a volume decrease these fibrils are probably formed during the accompanying contraction. However, their composition is not known at present.

This work and other surface studies will be published in more detail at a later date.

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Intensities of longitudinal acoustic modes and their structural implications

It is now commonly known that an intense longitudinal acoustic mode (*LAM*) can be observed in the low frequency Raman spectra of linear paraffins and polyethylene. However, the higher orders of the *LAM* in polyethylene are relatively weaker than for paraffins. Whereas up to 31 orders have been reported for n-tetranonacontane[1] only the 3rd order has been detected for polyethylene[2]. It has been suggested that the relative weakness of the *LAM* in polyethylene arises because of perturbations brought about by the fold surface[3], although this has been challenged on the basis of degradation studies[4]. In this Letter it will be shown that a further consideration of the factors controlling intensity as a function of wavenumber calls for a reappraisal of conclusions based on intensity measurements.

Schaufele and Shimanouchi[1] used a form of the theoretical Raman intensity in which for a given length of paraffin chain the *LAM* intensity depends upon $1/\tilde{\nu}_m$ where $\tilde{\nu}_m$ is the wavenumber shift of the *LAM* in the mth order. Because $\tilde{\nu}_m$ is directly proportional to m through the *LAM* equation

$$\tilde{\nu}_m = \frac{m}{2Lc}\left(\frac{E}{\rho}\right)^{1/2}$$

it was suggested that the *LAM* intensity should depend upon $1/m$. Here E is Youngs Modulus, ρ is density, L is length of paraffin chain and c is the speed of light. However, multiplication of the observed intensities of the higher orders in n-hexatriacontane by m did not reveal this dependence. *Table 1* shows these results and others from this laboratory.

A full treatment of Raman intensities as given in standard texts[5,6] shows that the intensity depends not only upon $1/\tilde{\nu}$ but also upon the scattering efficiency of the radiation and upon the population of vibrational energy levels, which give rise respectively to terms in $(\tilde{\nu}_0 - \tilde{\nu})^4$ and $[1 - \exp(-h\tilde{\nu}c/kT)]^{-1}$. Here $\tilde{\nu}_0$ is the absolute wavenumber of the exciting radiation, h is Planck's constant, and T is absolute temperature. The term in $[1 - \exp(-h\tilde{\nu}c/kT)]$ results from summing the population of vibrational energy levels. Assuming that the potential is harmonic, these levels are equally spaced and transitions between them give rise to Raman lines at the same wavenumber. Since kT/hc has a value of 200 cm^{-1} at room temperature the *LAM*s fall in the range where this term has a significant effect on their relative intensities. Although the dependence upon 4th power of absolute wavenumber is important when comparing intensities obtained using different exciting lines, it has a small effect, of the order of 10%, for a given exciting line over the range out to 500 cm^{-1}. Consequently, this

Table 1 *LAM* data for n-hexatriacontane (n-$C_{36}H_{74}$) and n-tetranonacontane (n-$C_{94}H_{190}$). n, number of carbon atoms; m, *LAM* mode order; $\tilde{\nu}_m$, wavenumber shift of mth order *LAM*; I, integrated intensity. Intensities are normalized to that of the first order throughout. The data for n-$C_{36}H_{74}$ are those of Schaufele and Shimanouchi in ref 1. The data for n-$C_{94}H_{190}$ were obtained in this laboratory

n	m	$\tilde{\nu}_m$	I	$I.m$	$[1 - \exp(h\tilde{\nu}c/kT)]$	$I.m.[1 - \exp(h\tilde{\nu}c/kT)]$
36	1	65.9	1.0	1.00	0.28	1.00
	3	189	1.7×10^{-1}	0.51	0.61	1.11
	5	306	9.2×10^{-2}	0.46	0.78	1.28
	7	403	4.8×10^{-2}	0.34	0.87	1.06
	9	473	2.8×10^{-2}	0.25	0.91	0.81
94	1	27.9	1.0	1.00	0.13	1.00
	3	74.5	1.6×10^{-1}	0.48	0.31	1.15
	5	122.2	5.2×10^{-2}	0.26	0.46	0.92

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