ELSEVIER

Thermochimica Acta 286 (1996) 17–24

thermochimica
acta

X-ray diffraction and thermoanalytical investigations of amorphous carbons derived from C_{60}

J.A. Nisha *, J. Janaki, V. Sridharan, G. Padma, M. Premila, T.S. Radhakrishnan

Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam-603 102, Tamil Nadu, India

Received 28 October 1995; accepted 28 February 1996

Abstract

We have synthesized two kinds of amorphous carbon products starting from C_{60}, one by low-temperature oxidation and the other by vacuum-annealing in a sealed tube at 900°C. Our characterization studies indicate that the former has a nominal composition C_5O and consists of two amorphous phases one of which has an amorphous C_{60} structure, and may perhaps be a C_{60} polymer, whereas the other has an amorphous graphitic carbon structure. The product obtained by vacuum-annealing of C_{60} has a negligible oxygen content and is single phase with an amorphous graphitic carbon structure. The TG–DTA thermograms of both these materials in oxygen exhibit close similarity with respect to their ignition temperatures and the two-step burning process. However, their heats of combustion differ. The TG–DTA studies in a helium atmosphere followed by X-ray characterization of the residue indicate that although vacuum-amorphized C_{60} is stable and remains amorphous up to 1000°C the amorphous product C_5O exhibits appreciable volatility perhaps due to oxygen-induced instability. The volatilization proceeds in two steps and the gas phase may contain carbon clusters. Together with volatilization, crystallization of amorphous C_5O also occurs.

Keywords: Fullerenes; Amorphization; XRD; TG–DTA

1. Introduction

Since the discovery and availability of C_{60} in large quantities, understanding carbon in its various forms, their thermal stabilities and reactivities, has been of much interest.

---

* Corresponding author.

PII: S0040-6031(96)02936-X

The possibility of amorphization of C_{60} to give amorphous carbon products [1, 2] has created further interest in the field of carbonaceous materials. Thermoanalytical and structural studies on these different forms of amorphous carbon derived from fullerenes are of great significance as they may have structures related to fullerenes and may exhibit volatility on heating to give carbon clusters.

Recent studies on fullerenes have thrown light on their interesting chemistry [3]. They are known to undergo a wide range of reactions characteristic of alkenes, e.g. additions, cycloadditions etc. Although as many as 24 hydrogen atoms and several methyl groups and halogen atoms can be added to fullerenes while maintaining the basic fullerene network intact, the reaction of fullerenes with oxygen leads to cage-opening and ultimate fragmentation of the molecule. The oxidation reaction of C_{60} leads to different products depending upon the conditions of the reaction. In the case of photochemical oxidation in solution the product is the epoxide $C_{60}O_n$ ($n = 1, 2 \ldots 5$) [4, 5]. Gas-phase photo-oxidation of C_{60} films leads to the formation of the dioxetane derivative which is unstable and decomposes to give dicarbonyl compounds [6]. Thermal oxidation of C_{60} has been investigated by IR as well as by TG–DSC studies and mass spectrometric analysis [1,7]. They indicate fragmentation of the molecule on oxidation, without the formation of any fullerene-based intermediate, as is evidenced by TGA [1]. The product is a carbon–oxygen compound with a C:O ratio of 5:1, henceforth this will be called C_5O. It has an amorphous structure and is believed to be a polycondensate containing cyclopentanone rings [1]. However, detailed phase characterization and study of the thermal behaviour of this product have not yet been carried out.

Amorphization of C_{60} can also take place in the absence of oxygen by application of pressure and temperature. Non-hydrostatic compression above 15 GPa at room temperature induces a transformation of C_{60} to polycrystalline diamond embedded in a bulk sp^3 amorphous matrix [8]. On the other hand a quasihydrostatic pressure of 6–7 GPa at a temperature of 1000°C yields an amorphous graphitic sp^2 phase [8]. Crystalline phases of carbon involving cross-linked C_{60} cages have also been synthesized from pure C_{60} under quasihydrostatic pressure of 5 GPa and at a lower temperature between 300 and 600°C; they are however metastable [9]. The products obtained therefore depend sensitively on the conditions. Our previous studies [2] indicate that an amorphous carbon product can also be obtained by thermal annealing of C_{60} in a sealed quartz tube at 900°C. The detailed evolution of this product has been reported earlier [2] and it has also been observed starting from very pure single crystals of C_{60}.

In our present work we have carried out a comparative thermal analysis study of two kinds of amorphous carbon derived from C_{60}. This has been coupled with X-ray diffraction studies.

2. Experimental

Thermal analysis has been carried out on two samples of amorphous carbon under identical conditions of heating rate and gas flow so as to make comparative studies possible. The samples were synthesized starting from pure and well characterized C_{60}.

One was prepared by isothermal annealing of C_{60} in an oxygen flow at 220°C in a thermobalance. The other was prepared by vacuum-annealing of the C_{60} in a sealed quartz tube at 900°C for 24 h in a constant temperature zone of the furnace. The thermal analysis equipment used was a simultaneous thermal analyser model PL STA-1500 which gave combined thermogravimetry and differential thermal analysis data. Runs were carried out in helium and oxygen atmospheres. All the samples were studied in platinum crucibles with Al_2O_3 as the reference material. The gases used were of high purity and the sample chamber was evacuated to a pressure of 60 microbars before purging with gas. The system was checked for leaks by measuring the weight loss of a sample of high purity graphite at 900°C over a period of 20 h. This was found to be 0.92 $\mu g\ min^{-1}$ which is of the same order as indicated in the instrument specifications [10]. The gas flow rates were maintained at 100 $mL\ min^{-1}$ for helium and around 20 $mL\ min^{-1}$ for runs in oxygen. The heating rates were maintained at 5°C min^{-1} for helium runs and 1°C min^{-1} for runs in oxygen.

The X-ray diffractograms were taken using a Siemen's model D-500 diffractometer and zero background specimen holder comprising a Si (911) single crystal wafer specially developed in our laboratory [11]. The slit dimensions were reduced to 0.3° in order to minimise background due to air scattering.

3. Results and discussion

The amorphization of C_{60} is effected by isothermal oxidation at 220°C on the thermobalance. The corresponding thermogram is shown in Fig. 1. The weight gain is

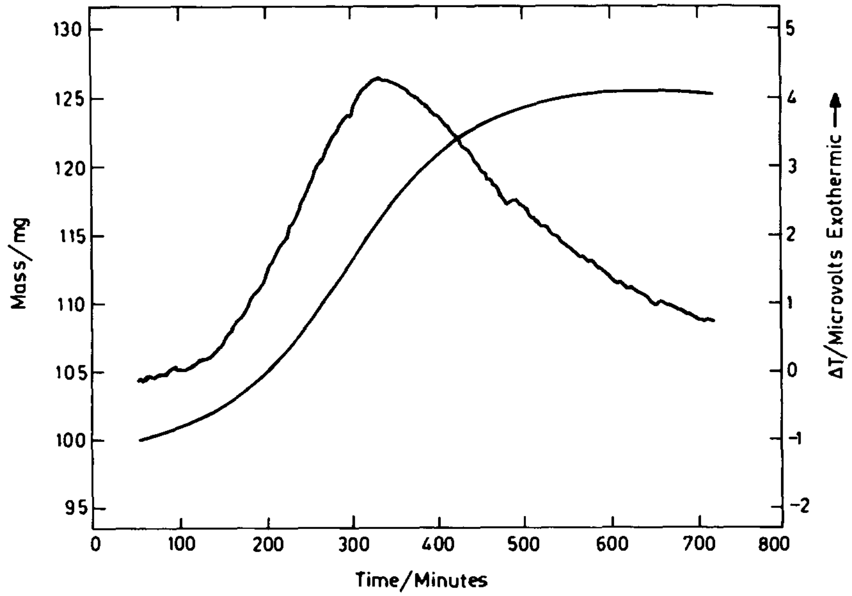

Fig. 1. Isothermal TG–DTA of C_{60} in oxygen at 220°C.

about 26% which corresponds to the product stoichiometry of C_5O. This oxide of nominal composition C_5O is essentially a mixture of two amorphous phases as can be seen from the two broad peaks in the X-ray diffractogram in Fig. 2b. The first peak, which occurs at $d = 15.5$ Å, corresponds to the correlation distance in C_{60} solid (14.2 Å) and the second peak, at $d = 3.80$ Å, corresponds to the c-axis correlation distance in graphite (3.4 Å). The sample is therefore biphasic with one phase having an amorphous C_{60} structure which may be a C_{60} polymer formed by condensation with oxygen and the second phase having an amorphous graphitic carbon structure.

A different amorphous carbon product was obtained by vacuum-annealing of pure C_{60} in a sealed quartz tube at 900°C for 24 h. Weight measurements before and after the amorphization using a semi-micro balance indicate that there is no appreciable weight gain and the product is essentially pure carbon. The X-ray diffractogram (Fig. 2c) shows that it had a single broad peak only at $d \sim 4.5$ Å corresponding to a graphite-like structure and is therefore a single-phase material. While both the amorphous carbons derived from C_{60} have a graphite-like phase there appears to be differences in detailed structural features of this phase as observed by the differences in the peak positions ($d = 3.8$ and 4.5 Å, respectively). This may be investigated in greater detail from analysis of the radial distribution function which is in progress.

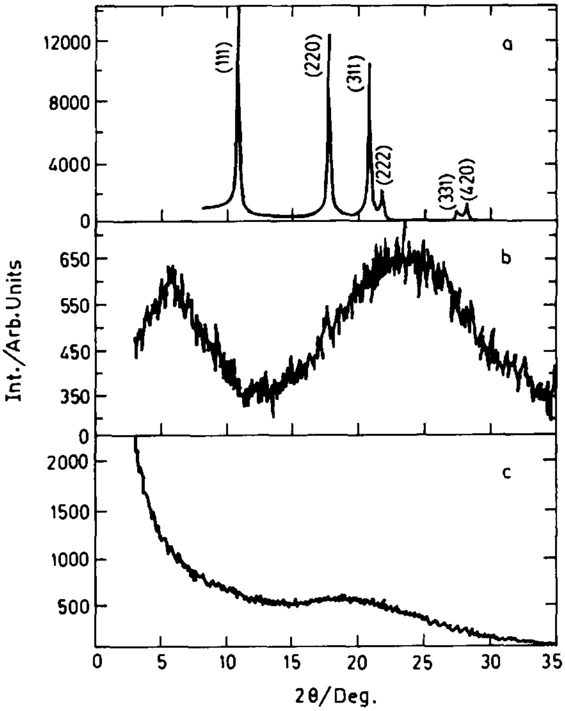

Fig. 2. X-ray diffractogram of (a) pure C_{60}, (b) amorphous carbon derived by low temp. oxidation of C_{60} (C_5O) and (c) amorphous carbon derived by vacuum-annealing of C_{60}.

The thermal analysis of the two types of amorphous carbon in helium and oxygen atmospheres has been carried out; the TG–DTA curves in oxygen at a heating rate of 1°C min^{-1} are presented in Fig. 3. Both these samples exhibit two-step burning processes with a satellite peak whose inception temperature is about 280°C followed by the main peak centred around 450–500°C. This similarity in oxidation reaction temperature may be attributed to their similarity in structure. It is apparent that the ignition temperature of activated charcoal with an amorphous graphitic carbon structure is 450°C [12, 13]. This is in broad agreement with the two kinds of amorphous carbon studied. The two-step oxidation is observed in both kinds of amorphous carbon and may be due to the presence of two kinds of active sites. Detailed STM and other studies of oxidation may throw light on these aspects. The enthalpic change on oxidation of vacuum-amorphized C_{60} is $-19.55\ \text{kJ g}^{-1}$. This was measured from the area under the curve and comparing it with a standard sample of aluminum metal whose heat of fusion was known. The enthalpic change due to burning of C_5O is $-13.50\ \text{kJ g}^{-1}$ which is less than that of vacuum-amorphized C_{60}. This is expected since the former is already partially oxidized relative to the latter.

The comparative TG–DTA plots in helium at a heating rate of 5°C min^{-1} are shown in Fig. 4. The X-ray diffraction pattern of the residue left on the thermobalance after completion of the thermal analysis is presented in Fig. 5. While the amorphous carbon derived from vacuum-amorphized C_{60} is stable and does not undergo either weight loss or crystallization on heating (Figs. 4a and 5a), C_5O exhibits appreciable volatility and the residue is crystalline (Figs. 4b and 5b). Two weight loss steps are observed in the

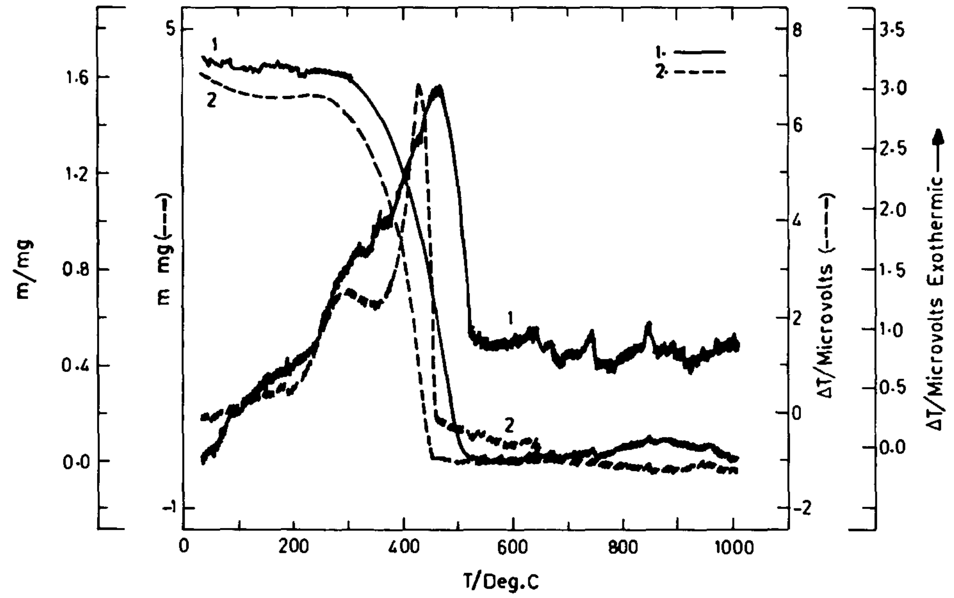

Fig. 3. Comparative thermal analysis study in oxygen atmosphere of two kinds of amorphous carbon: (1) derived by vacuum-amorphization of C_{60}; (2) derived by low-temperature oxidation of C_{60} (C_5O).

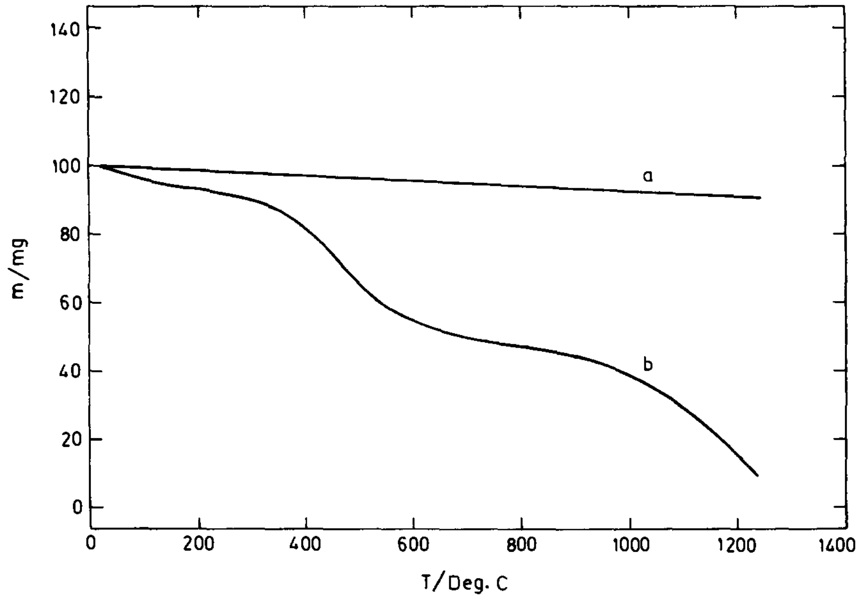

Fig. 4. Comparative TG curves in helium atmosphere of two kinds of amorphous carbon: (a) derived by vacuum amorphization of C_{60}; (b) derived by low temperature oxidation of $C_{60}(C_5O)$.

thermogram of C_5O with inception temperatures about 350 and 850°C (Fig. 4b). This may be due to the volatilization of the two phases. It leads us to believe that oxygen induces thermodynamic instability and volatility of the two phases. The oxygen content of the sample is too low to cause decomposition of the entire sample to CO. The gaseous phase must therefore contain, apart from CO, an appreciable fraction of carbon clusters. The first weight loss step at approximately 350°C may correspond to the volatilization of fullerene-like clusters and the second step at 850°C may correspond to volatilization of smaller clusters, e.g. C_2. Mass spectroscopic studies are in progress to study the composition of the gaseous phase.

Crystallization has also been observed concurrently with volatilization in the case of the amorphous carbon product C_5O, as the residue left on the TG balance at the end of the experiment is crystalline (Fig. 5b). This residue constitutes only 12% of the total weight, and exhibits very sharp diffraction peaks indicating a high degree of crystallinity. It is interesting to note that the first diffraction peak occurs at a low angle of $2\theta = 6.55$ indicating that it may be long-chain linear polymeric carbon.

The heat of vaporization can be calculated from the TGA curve of C_5O in helium (Fig. 4b) by the Langmuir method [14]. Such a calculation has been reported in the literature for the sublimation of C_{60} [15]. Assuming that the two-step weight loss observed on heating C_5O in helium arises due to the volatilization of two distinct phases and does not correspond to any chemical reaction one can compute the ΔH_S for the two phases. As the second step is incomplete we have calculated ΔH_S corresponding

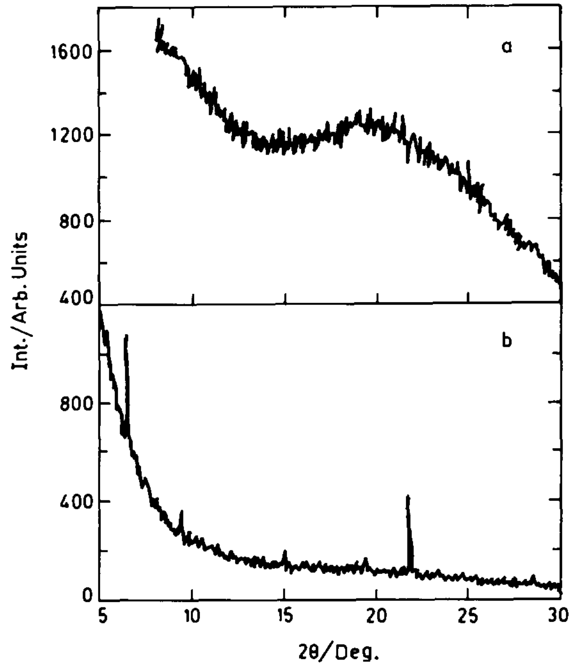

Fig. 5. X-ray diffractogram of the residue left on the thermobalance after the thermal analysis in helium of the two amorphous carbon products: (a) derived by vacuum annealing of $C_{60}(C_5O)$; (b) derived by low temp. oxidation of $C_{60}(C_5O)$.

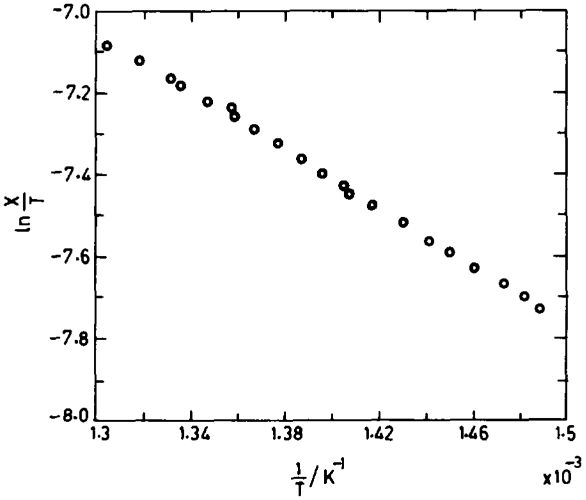

Fig. 6. ln X/T vs $1/T$ plot for the first step of sublimation of biphasic C_5O in helium.

to the first step of sublimation by adopting the equation given by Chen et al. [15].

$$X = \frac{KRT}{\alpha \Delta H_S} \exp \frac{-\Delta H_S}{RT}$$

where X is fraction of weight lost, K is a constant and α the heating rate. The heat of sublimation ΔH_S has been determined from the slope of the $\ln (X/T)$ vs $1/T$ curve (Fig. 6) and is around 30 kJ mol^{-1}. This is lower than the value of 150 kJ mol^{-1} for crystalline C_{60} [15].

References

[1] H.S. Chen, A.R. Kortan, R.C. Haddon, M.L. Kaplan, C.H. Chen, A.M. Mujsce, H. Chou and D.A. Fleming, Appl. Phys. Lett., 59 (1991) 2956.

[2] C.S. Sundar, A. Bharathi, Y. Hariharan, J. Janaki, V. Sankara Sastry and T.S. Radhakrishnan, Solid State Commun., 84 (1992) 823.

[3] R. Taylor and D.R.M. Walton, Nature, 363 (1993) 685.

[4] A.B. Smith, III, J.P. McCauley Jr, D.R. Jones and R.T. Gallagher, J. Am. Chem. Soc., 114 (1992) 1103.

[5] J.M. Wood, B. Kahr, S.H. Hoke II, L. Dejarme, R.G. Cooks and D. Ben-Amotz, J. Am. Chem. Soc., 113 (1991) 5907.

[6] C. Jalioni, G. Ruoni, R. Zamboni, R. Danieli, S. Rossini, V.N. Demisov, V.M. Burlakov, F. Negri, G. Orland and F. Zorbatte, J. Chem. Soc. Chem. Commun., (1993) 220.

[7] A.M. Vassallo, L.S.K. Pang, P.A. Cole-Clarke and M.A. Wilson, J. Am. Chem. Soc., 113 (1991) 7820.

[8] J.L. Hodeau, J.M. Tonnerre, B. Bouchet-Fabre, M. Nunez Regueiro, J.J. Capponi and M. Perroux, Phys. Rev. B, 50 (1994) 10311.

[9] Y. Iwasa, T. Arima, R.M. Fleming, T. Siegrist, O. Zhou, R.C. Haddon, L.J. Rothberg, K.B. Lyons, H.L. Carter Jr, A.F. Hebard, R. Tycko, G. Dabbagh, J.J. Krajewski, G.A. Thomas and T. Yagi, Science, 264 (1994) 1570.

[10] Stanton Redcroft Technical Information Paper No. TG/10.87/508.

[11] G.V.N. Rao, V. Sankarasastry, V. Seshagiri and T.S. Radhakrishnan, Powder Diffraction, in print.

[12] Fang Li and J.S. Lannin, Phys. Rev Lett., 65 (1990) 1905.

[13] E.L. Charsley, J.A. Rumsey, S.B. Warrington, J. Robertson and P.N.A. Seth, Thermochim. Acta, 72 (1984) 251.

[14] I. Langmuir, Phys Rev, II (1913) 329.

[15] H.S. Chen, A.R. Kortan, R.C. Haddon and D.A. Fleming, J. Phys. Chem., 96 (1992) 1016.