Experimental verification of the dominant influence of extended carbon networks on the structural, electrical and magnetic properties of a common soot

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Abstract. Common soots are disordered carbonaceous materials containing several per cent of heteroatoms. A question of some importance is to what extent pure carbon networks dominate the properties of common soots. Here, we report the results of a comparative study of fullerene soots which are a form of pure partially ordered carbon and those formed from flaming polystyrene combustion which contain a few per cent of oxygen atoms, using electron diffraction, electron spin resonance (ESR), infra-red transmission and measurements of electrical conductivity. It has been found that despite some important characteristic differences, the annealed fullerene soot and flaming polystyrene soot have a number of important structural, electrical and magnetic features in common, provided that the flame and annealing temperatures are the same. This suggests that the graphitic layer and fullerene related tubular structures found in these materials dominate the electrical properties of these soots regardless of the presence of small quantities of heteroatoms in the soot derived from the flaming combustion of polystyrene.

1. Introduction

Sooting flames, which were the original focus of work by Kroto and co-workers [1–3] provide a rich source of graphitic and fullerene-type structures [4–6]. A major unresolved question in this field is to what extent disordered pure carbon structures dominate the properties of common smoke and soot. Fullerene soot is a form of pure carbon and is free of heteroatoms. It is generated in the gas phase and deposited during the electrical discharge in a Krätschmer–Huffman carbon arc fullerene generator [7]. Following the work of Krätschmer *et al* and many other subsequent studies [1–9], it is now known that this form of pure carbon typically contains a few per cent of extractable fullerenes of which C_{60} is dominant and, in a recent publication [10], a comprehensive characterization of the electrical, magnetic and structural properties of fullerene soots was presented.

In this paper the electrical and magnetic properties of a pure annealed fullerene soot are compared with a soot deposited by the flaming combustion of polystyrene. The latter material appears to be structurally related to the annealed fullerene soot but also contains a

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few per cent of oxygen and hydrogen atoms. The key result is that combustion of a common polymer under 'open fire' conditions leads to a material closely related in structure and electrical properties to a fullerene soot annealed at the same temperature as the combusting polymer, and that these properties of this chemically heterogeneous polystyrene soot are dominated by the structural features which they share with annealed fullerene soots.

As well as the intrinsic interest of the fundamental observation that these two types of soot have deep similarities, our work suggests that fullerene soots, which are a form of pure carbon, may provide a good model system for studying the important problem of smoke and will perhaps allow features associated with the chemically heterogeneous nature of common soots to be identified in future work.

2. Soot preparation and structural characterization

The fullerene soot used in this study was prepared using the now standard Krätschmer–Huffman technique [7, 10, 33]. Helium was used as the quenching gas at a pressure of 50 Torr. For annealing, the fullerene soot samples were placed in quartz boats which were then loaded into a pyrolysis tube and heated at 1273 K under flowing argon at atmospheric pressure. The heat treatment was applied for seven hours, after which time the samples were allowed to cool under argon flow.

The soot formed from the flaming combustion of polystyrene was prepared by supplying incident radiant heat flux of a known intensity (30 kW m^{-2}), to a sample of non-expanded polystyrene, and collected by passive sedimentation in air. The flame temperature was monitored with a thermocouple and found to be close to 1273 K. Such soots were hence formed under conditions which simulate an 'open fire' environment.

Electron micrographs of the soots were taken using a JEOL 1200 electron microscope operating at 120 keV. A TEM of a fullerene soot is shown in figure 1, where it can be seen that the soot is made up of irregular shaped balloons of typical dimensions of about 50 nm. During the discharge of a carbon arc, defective carbon 'onions' of different radii will form by an icospiral mechanism [1–14]. Gas phase aggregation of such polarizable 'onion' structures is also probable. The coagulation of fullerene soot particles has been observed by Ugarte [11, 13, 14], and our TEMs are similar in form to those reported by him for soots prepared at 100 Torr He pressure. It has been suggested [10] that the shape of the fullerene soot particles is that of encapsulated aggregates of defective carbon 'onions' [11–15] with a range of radii. Selected area electron diffraction indicates that the fullerene soot is largely disordered, yet an extensive search showed a diffraction pattern indicative of the existence of randomly oriented graphitic microcrystallites in the material [10]. An interpretation of the origin of such a spot pattern is given in [10] which suggests that it arises from graphitic microcrystallites embedded in the unannealed fullerene soot [10, 15, 16].

The 100 Torr fullerene soot studied by Ugarte [11, 13, 14], when annealed at about 2000 K for 1 hour, undergoes a spectacular structural transformation. Transmission electron diffraction indicates that the annealed fullerene soot is inhomogeneous and contains regions with submicrometre sized particles, disordered regions and partially crystalline regions discussed in detail in [10]. Figure 2(a) captures an intermediate stage in the formation of a nanotube from annealing the fullerene soot, and shows nanostructures contained in the interior of other submicrometre sized structures, suggesting that collapse of the material on the inside of the balloon-like structures, shown in figure 1, occurs on annealing. It can be seen from the presence of inner walls in the tube that collapse of the walls between coagulated particles occurs at a late stage. Figure 2(b) shows a TEM of a flaming polystyrene
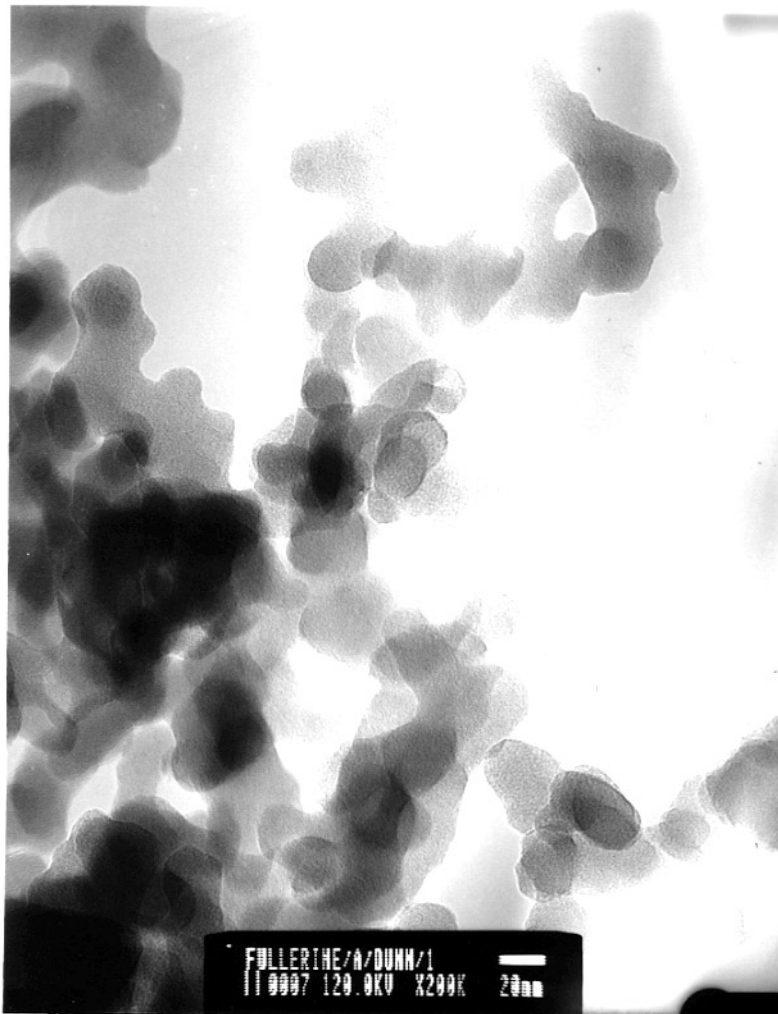
Figure 1. Transmission electron micrograph of 50 Torr He fullerene soot showing coagulated balloons which are suggested to be sealed containers of defective free radical material (defective carbon onions). Notice that the shape of the particles suggests that the balloons contain several structures held together initially by Van der Waal's forces and then sealed by a number of coats of carbon atoms in the gas phase.

soot, in which a tubular structure is depicted, which is very similar to the fullerene soot annealed at the same temperature as the polystyrene combustion flame, shown in figure 2(a).

Selected area electron diffraction from the annealed fullerene soot clearly shows graphitic crystalline regions as shown in figure 3(a). Selected area electron diffraction from the soot formed by the flaming combustion of polystyrene also showed the presence of ordered graphitic material, where the ring spacings shown in figure 3(b) are the same as those of graphite and similar to those in the annealed fullerene soot. Some regions of the soot formed from the flaming combustion of polystyrene produced a selected area electron diffraction pattern with a satellite structure. A detailed interpretation has been undertaken using the CERIUS [17] electron diffraction simulation package. The essential features of
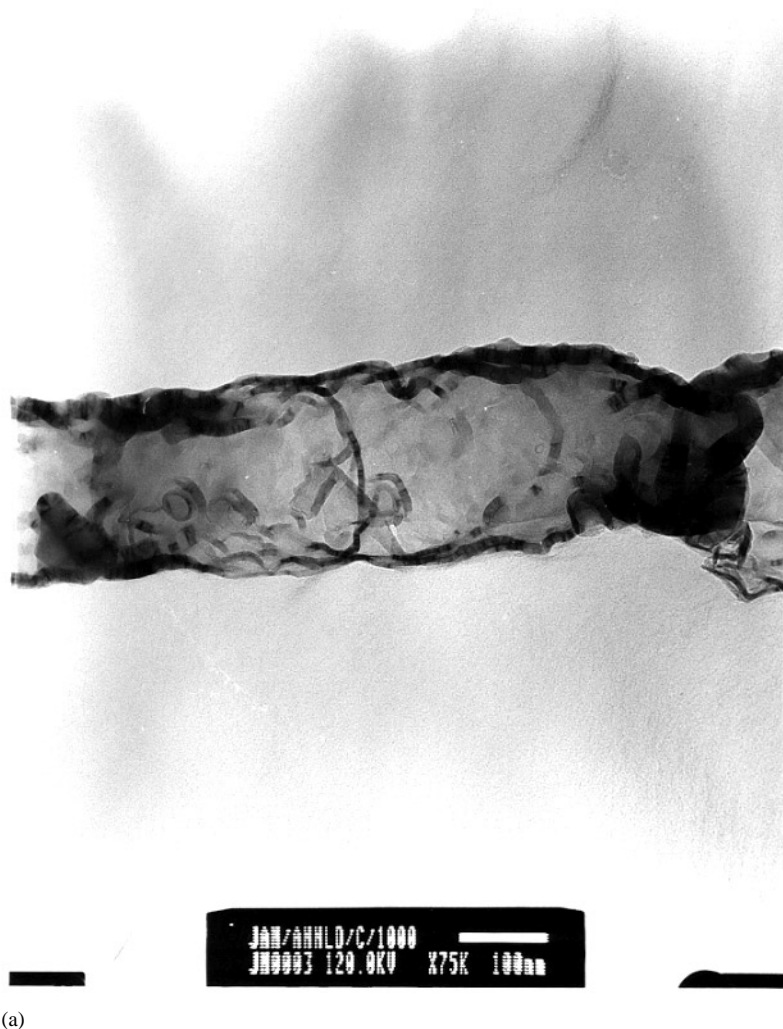
Figure 2. (a) Partial formation of a nanotube formed by annealing fullerene soot (7 hours at 1273 K in flowing argon). Note the disordered material and wall in the interior of the tube. (b) Similar tubular structure in flaming polystyrene soot.

the selected area pattern and satellite structure can be reproduced by twisted AB graphitic layers. Full details of the analysis will be given elsewhere.

3. Electron spin resonance (ESR) investigations

The ESR absorption characteristics of the fullerene and polystyrene soot samples were measured on a Bruker ESP 300 ESR spectrometer, operating at X-band and at 5–10 mW microwave power to avoid saturation. Figure 4 depicts a set of typical ESR spectra obtained from the soot samples at 300 K. All the signals recorded were almost symmetric; this contrasts with the asymmetric lineshapes that have been observed from polycrystalline graphites where the resonance is due to conduction electrons [18, 19].

(b)

Figure 2. (Continued)

An estimate of the spin concentration in the fullerene soot is very roughly 10^{21} g^{-1} which corresponds to approximately one spin for every 10–100 carbon atoms. An estimate of the spin concentration in the material formed from the flaming combustion of polystyrene is 10^{19} spins g^{-1}. Since it is expected, as supported by results described below, that the unannealed soots are essentially sealed containers with free radical material inside, we attribute the ESR signals to unsatisfied valencies at the edges of carbon fragments in the interior. The ESR g-factor for the fullerene soot before annealing in the temperature range 100–300 K is close to 2.0023 and the peak-to-peak linewidth was close to 2×10^{-4} T over the same temperature range. The g-factor of the resonance for the material formed from the flaming combustion of polystyrene is 2.0028, and the linewidth is close to 5×10^{-4} T.

In amorphous carbons, prepared by the thermal decomposition of organic materials, paramagnetic centres, which give rise to ESR signals, can be observed at the onset of charring [18–22]. An analysis of the g-factors for a range of chars [20–25] indicates
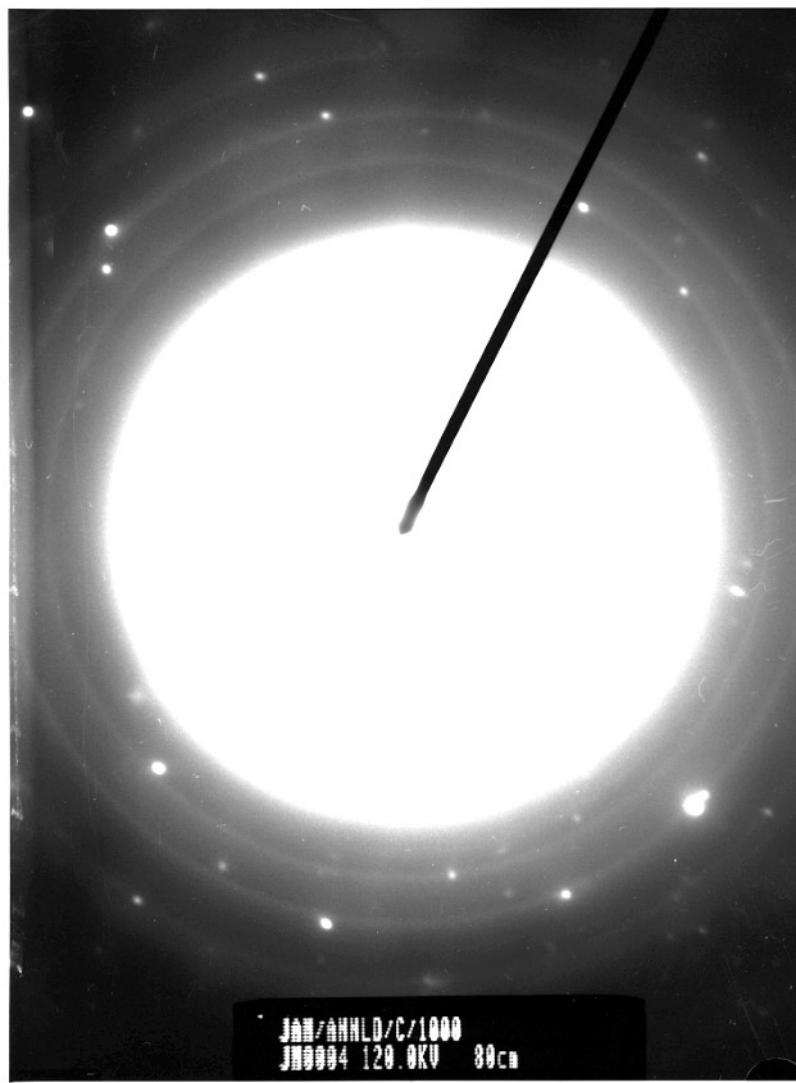
(a)

Figure 3. (a) Small-aperture transmission electron diffraction from annealed fullerene soot indicative of quasi-crystalline order in small regions of the annealed fullerene soot. (b) Small-aperture transmission electron diffraction of soot formed from the flaming combustion of polystyrene. Both (a) and (b) indicate highly ordered graphitic regions are present in the soots.

that these are typically in the range 2.0030–2.0034; values consistent with odd-alternate π-radicals. Hence, it appears that the radicals in fullerene soots and polystyrene soots are not of the same type as found in chars.

In marked contrast to chars [19–23], the linewidths of the fullerene soot and polystyrene soot resonances did not change to any significant degree when the samples were subjected to oxygen. In chars, the interaction with paramagnetic oxygen molecules causes a dramatic broadening effect shown in figure 5. Neither the fullerene soot nor the polystyrene soot showed an 'oxygen effect' which is discussed in the next paragraph. The absence of an
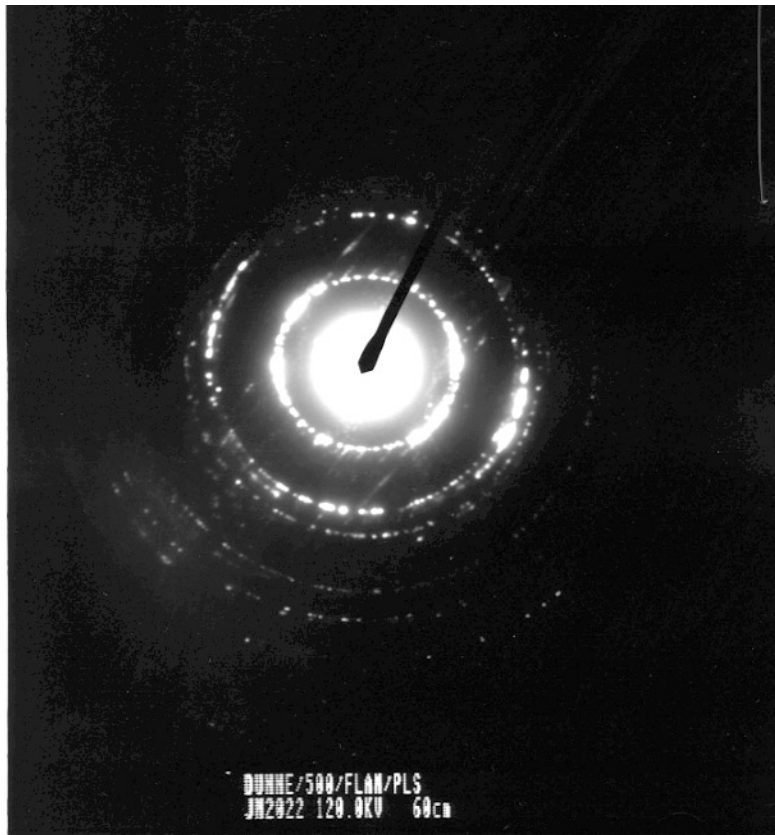
(b)

Figure 3. (Continued)

oxygen effect and closeness of the g-factor to the fullerene soot suggests that the soots prepared from the flaming combustion of polystyrene contain radicals similar to those in the fullerene soot, which are probably broken or dangling bonds buried deep inside a protective carbon overcoat. The absence of such an 'oxygen effect' is significant since it indicates that the spin centres in the fullerene and polystyrene soots are inaccessible to the paramagnetic oxygen molecules, which are likely to cause dipolar broadening of the ESR absorption [10]. A plausible explanation is that in fullerene and polystyrene soots, the free radicals are encapsulated.

On the other hand the annealed fullerene soot, prepared at 50 Torr He pressure, did not show ESR signals, which is consistent with the complete satisfaction of free valencies during structural rearrangements caused by annealing, as discussed above. It is possible that ESR activity in the annealed fullerene soot has been undetected due to relaxation effects, such as collisions with impurities, or with the edges of crystallite, which have broadened the resonances beyond detection. Charge carrier ESR absorption has been observed in nanotubes with quite similar characteristics to the ESR absorption in graphite [18–26]. In some fullerene soots annealed under different conditions, an ESR signal with very weak temperature dependent intensity has been observed, which is characteristic of charge carrier Pauli paramagnetism. With respect to ESR characteristics the material formed from the
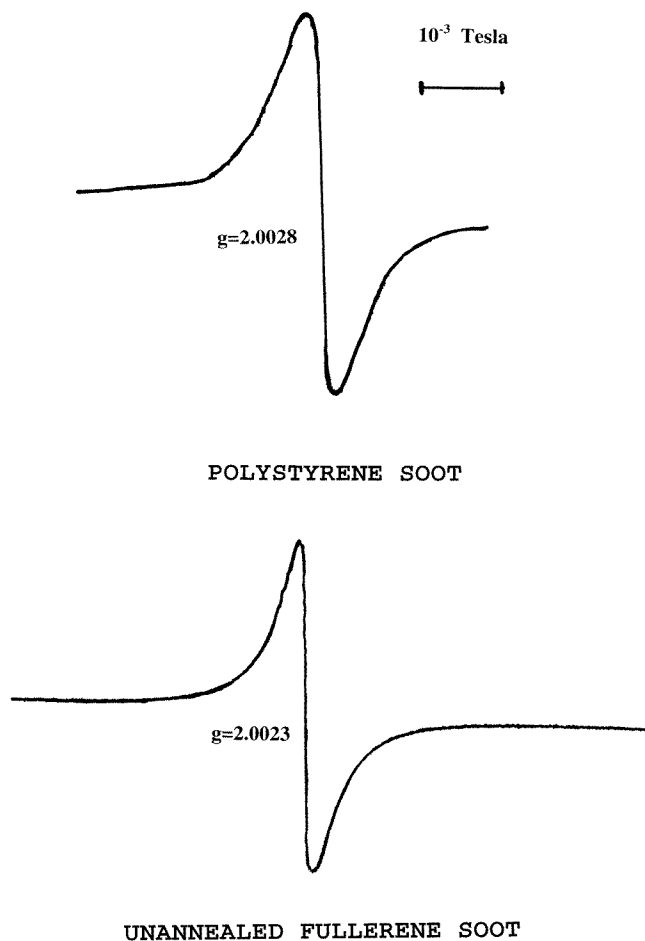
POLYSTYRENE SOOT

UNANNEALED FULLERENE SOOT

Figure 4. Typical ESR spectra of fullerene soots and soot formed from the flaming combustion of polystyrenes.

flaming combustion of polystyrene appears to be quite similar to an incompletely annealed fullerene soot.

4. Electrical conductivity measurements

Electrical conductivity measurements were carried out on discs of fullerene soot and soot formed from the flaming combustion of polystyrene compacted with polyvinyl chloride (PVC) as a binder (binder concentration 15% by mass), by the Van der Pauw method [27]. For the fullerene soot, the conductivity at room temperature of an unannealed sample is 5×10^{-6} Siemens cm^{-1}, and that of an annealed sample is 2×10^{-5} Siemens cm^{-1}. The compaction was carried out at 1248 kg cm^{-2}. The conductivity as a function of temperature, $s(T)$, was thermally activated, and found to give a good fit to the form $s(T) = s(0)\exp(-bT^{-1/2})$, as shown in figure 6. The fitting correlation coefficient (r) is typically 0.990 for the fullerene soots and 0.975 for the material formed from the flaming combustion of polystyrene. Such a functional form for the temperature dependence
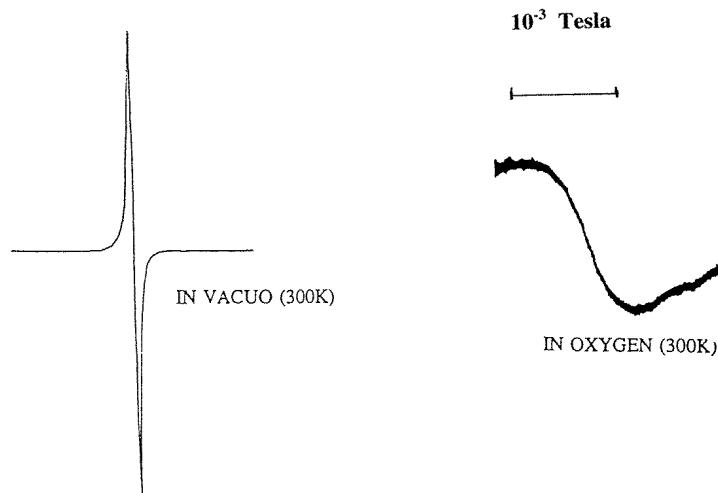
10⁻³ Tesla

IN VACUO (300K)

IN OXYGEN (300K)

Figure 5. The oxygen effect in the ESR absorption signal obtained from an amorphous carbon char (sulphanilic acid) decomposed in argon at 900 K; described in detail in [23]. Note that the signal broadens by a factor of about 20 on exposure to oxygen, suggesting that the spin centres are exposed to paramagnetic oxygen molecules. No such effect is observed in fullerene soots or the material formed from the flaming combustion of polystyrene which suggests that oxygen cannot access the spin centres.

of the electrical resistance is characteristic of percolation of charge carriers tunnelling through a matrix of conducting particles [28, 29]. We should point out that a plot of $\ln(s)$ versus $1/T$ is also roughly linear, but the correlation is inferior ($r = 0.974$ and 0.965 for fullerene and polystyrene soots respectively) to the fit proposed above. The conductivity of the compacted soot formed from the flaming combustion of polystyrene at 300 K was 4.7×10^{-5} Siemens cm⁻¹, and the conductivity as a function of temperature was again found to give a good fit to the form $s(T) = s(0)\exp(-bT^{-1/2})$, as shown in figure 6. It is noteworthy that the slopes of the plots in figure 6 are unaffected by the annealing process. In a percolation process, charge carriers seek pathways offering minimum resistance. Qualitatively, it would appear that similar pathways exist in all materials, but that the concentration of these in the material formed from the flaming combustion of polystyrene is higher. The conductivity for the unannealed fullerene soot sample, extrapolated to infinite temperature, is 5.5×10^{-4} Siemens cm⁻¹, which is consistent with a mechanism involving tunnelling or hopping between localized states [28]. For the annealed soot the corresponding value is 2.8×10^{-3} Siemens cm⁻¹, and for the soot formed from the flaming combustion of polystyrene the infinite-temperature conductivity is roughly 10^{-4} Siemens cm⁻¹. Hall mobility measurements for the fullerene soot indicate that the charge carriers are holes with densities of approximately 1.4×10^{18} m⁻³ for the unannealed sample, 2.6×10^{19} m⁻³ for the annealed sample and 1.6×10^{19} m⁻³ for the soot formed from the flaming combustion of polystyrene. It is useful to compare these values with the ambient-temperature conductivity of 730 Siemens cm⁻¹, and a charge carrier density, 3×10^{24} m⁻³ for semi-metallic graphite [31, 32]. These increased values reflect the significantly higher structural order in extended graphitic material. The mobility values for the fullerene soots are 2.25×10^{-3} m² V⁻¹ s⁻¹ for the unannealed sample, 4.9×10^{-4} m² V⁻¹ s⁻¹ for the annealed and 1.4×10^{-3} m² V⁻¹ s⁻¹ for the soot formed from the flaming combustion of polystyrene.
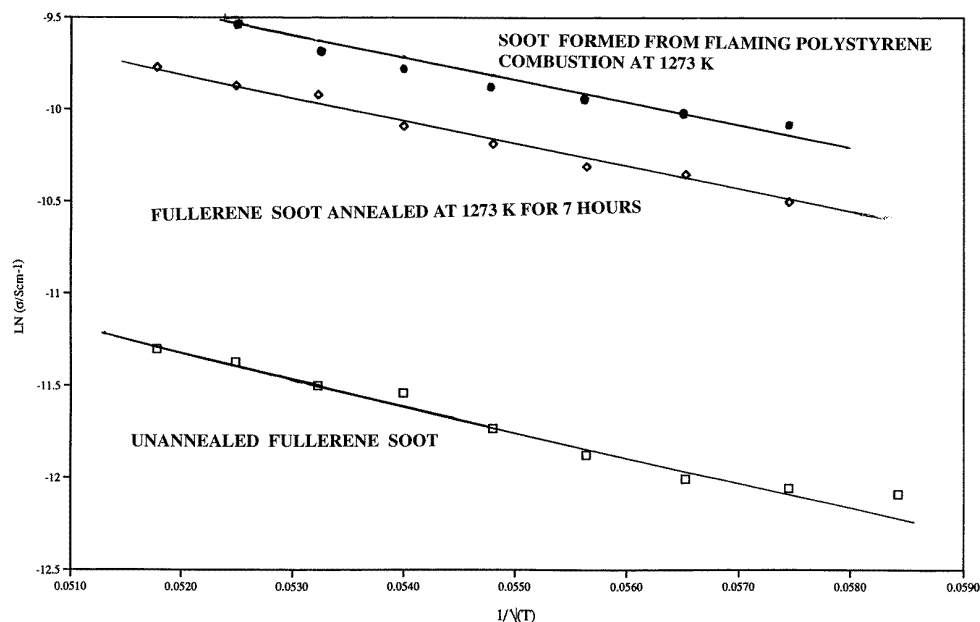
Figure 6. Temperature dependence of the electrical conductivities of unannealed and annealed (7 hours at 1273 K in flowing argon) fullerene soots, and soot formed from the flaming combustion of polystyrenes showing an activated conduction of the form $s(T) = s(0) \exp(-bT^{-1/2})$, indicative of tunnelling between metallic islands in the materials.

These mobility values are too large to be associated with carriers hopping below a mobility edge, and it seems more likely that the carrier wavefunctions are only very weakly localized [10, 30]. The conductivity of both the annealed and the unannealed fullerene soot samples, and soot formed from the flaming combustion of polystyrene, are roughly independent of frequency up to about 10 MHz. The rise in conductivity in this high-frequency region is highly suggestive of hopping/tunnelling between conductive islands in these materials.

The electrical conductivity studies reported here have yet to be explained by a detailed theoretical model, but they are consistent with carriers which tunnel between conductive islands. Such conductive islands are presumably graphitic, and from the carrier densities the concentration of such ordered graphitic regions rises by about a factor of ten on annealing the fullerene soot. The electrical conductivity of the soot formed from the flaming combustion of polystyrene, and fullerene soots, showed very similar features indicative of the transport of charge by electron tunnelling between graphitic metallic islands in the materials.

5. Infrared transmission studies

In electrically conducting materials infrared absorption due to inter-band electronic transitions may be observed which for many crystalline semiconductors enables the band gap to be determined spectrometrically. Many amorphous semiconductors show frequency (ω) dependent optical absorption $a(\omega)$, of the power law form given by [22, 28] $a(\omega) = K(h\omega - h\omega_0)^n/h\omega$, where K is a constant [10, 24, 30] and n is typically in the range 1–3. $h\omega_0$ is the energy gap for electronic transitions. This allows a band gap to be measured
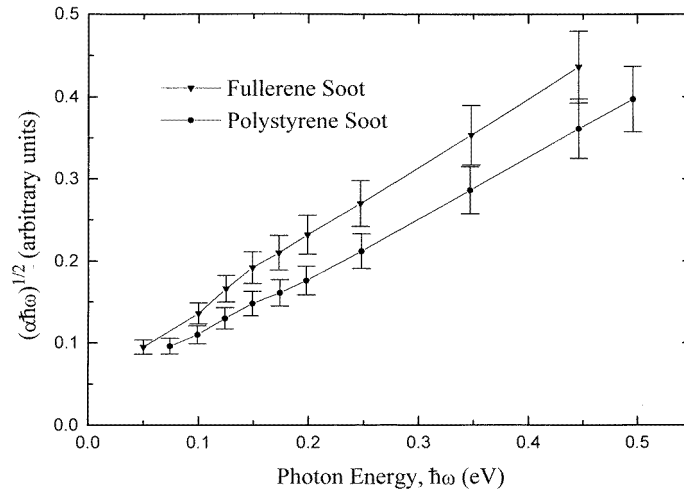
Figure 7. Plot of $(a(\omega)h\omega)^{1/2}$ against photon energy for a thin film of fullerene soot prepared at a pressure of 50 Torr He and similar plot for soot formed from the flaming combustion of polystyrene.

optically. In figure 7 the fullerene and polystyrene soots are shown to follow the above law quite well when $n = 2$. It is evident that the plot is linear and, subject to the small experimental errors, extrapolates through the origin. The implication of this observation is that it strongly supports the notion that all these soots contain metallic islands which are likely to be due to extended layers of carbon atoms containing delocalized electronic states. The optical absorption and electrical conductivity of the fullerene soots and flaming polystyrene soots is hence consistent with the presence of metallic islands with zero optical gap in the materials.

6. Discussion

On the basis of the evidence presented above we are now able to make some inferences about the comparative structures and properties of fullerene and polystyrene soots. Fullerene soots are formed by nucleation of a carbon plasma. However, little is known about the detailed mechanism of the process or of the corresponding process in a flame. The studies described here can be rationalized if the interiors of unannealed fullerene soots are composed of characteristic structures similar to those shown in figure 8(a), or those discussed in [10] (figure 14) in which carbon layers contain voids or defects at a level which is consistent with the ESR result—namely approximately 1 spin per 10 carbon atoms. The bonds at the edges of the defects, so-called dangling bonds, appear to give rise to the experimentally observed ESR signals. The lack of any observable effect of oxygen in the ESR spectra of the unannealed soot, together with the TEM images, indicates that the spin carrier phase is encapsulated inside effectively closed carbon cages. It seems unlikely that the interior of the soot particle is entirely covalently bonded. During the gas phase formation of such carbon structures, aggregation may occur by van der Waal's interactions, which will be strong between such essentially metallic molecules with large polarizabilities. On annealing, it appears that several processes occur all involving the removal of the defect voids in the defective carbon onions. In a sooting flame the annealing process is incomplete and hence
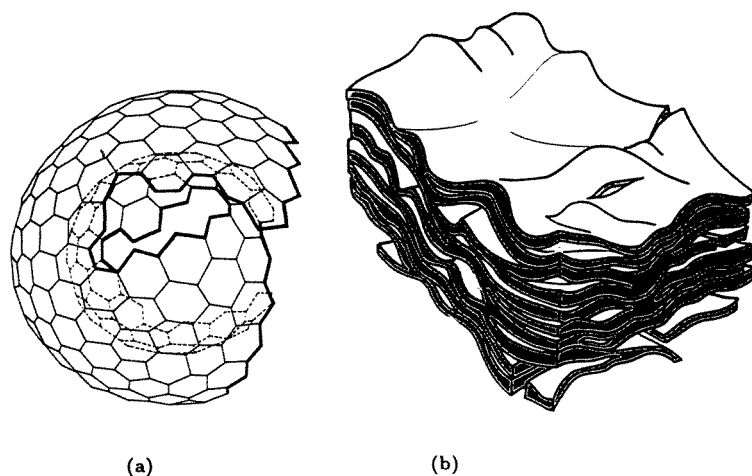
(a)   **(b)**

Figure 8. (a) Suggested structure and typical contents in the interior of an unannealed fullerene soot particle. The balloon type structures shown in figure 1 are thought to be effectively sealed containers of such defective metallic structures [10, 33]. (b) Voids in buckled graphitic layers.

this gives rise to ESR absorption in the polystyrene soots. The rise in the conductivity on annealing the fullerene soot samples is attributed to an increasing concentration of metallic islands in the material. The annealing process studied here appears to involve the removal of the walls of the coagulated, unannealed particles to produce a new form of nanostructured material which is also seen in the material formed from the flaming combustion of polystyrene. The driving force for the annealing process is the need for unstable defective carbon networks to eliminate the large number of dangling bonds trapped at defect sites in carbon sheets, by the most expedient locally accessible network extending process. This process appears to be incomplete in the polystyrene soot. The walls of the tubular structure in the polystyrene soot may contain voids of the type shown in figure 8(b) and these may encapsulate free radical material.

The polystyrene soots appear to have electrical and magnetic properties very closely related to the fullerene soots annealed at the same temperature as the polystyrene combustion temperature because of the structural features, which are essentially those of pure disordered carbon, which they have in common. Although heteroatoms in polystyrene soots may be important for chemical interactions such as surface adsorption of gases they appear to be less important for bulk physical properties. The study of other soots [34] along the lines of this paper would seem well worthwhile.

Acknowledgments

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