

Fullerene-like models for microporous carbon

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Abstract Microporous carbons are important in a wide variety of applications, ranging from pollution control to supercapacitors, yet their structure at the molecular level is poorly understood. Over the years, many structural models have been put forward, but none has been entirely satisfactory in explaining the properties of the carbons. The discovery of fullerenes and fullerene-related structures such as carbon nanotubes gave us a new perspective on the structure of solid carbon, and in 1997 it was suggested that microporous carbon may have a structure related to that of the fullerenes. Recently, evidence in support of such a structure has been obtained using aberration-corrected transmission electron microscopy, electron energy loss spectroscopy and other techniques. This article describes the development of ideas about the structure of microporous carbon, and reviews the experimental evidence for a fullerene-related structure. Theoretical models of the structural evolution of microporous carbon are summarised, and the use of fullerene-like models to predict the adsorptive properties of microporous carbons are reviewed.

Introduction

The adsorptive properties of charcoal have been known for thousands of years. Egyptian papyri from 1500 BC record the application of charcoal to adsorb odorous vapours from putrefying wounds, while Hindu documents from 450 BC refer to the use of sand and charcoal filters for the

purification of drinking water [1]. In the eighteenth century, charcoal began to be used industrially for the decolourization of sugar syrups, while in the First World War the deployment of poisonous gases created an urgent need for adsorbent carbons suitable for use in respirators. Today, activated microporous carbon is used on an enormous scale for the purification of air and water [2, 3]. It is still used widely in respirators, as well as in air-conditioning systems and in the clean-up of waste gases from industry. In the liquid-phase, its largest single application is the removal of organic contaminants from drinking water. Many water companies in Europe and USA now filter all domestic supplies through granular activated carbon filters, and household water filters containing activated carbon are also in widespread use. Other applications include decontamination of groundwaters and control of automobile emissions. Microporous carbon is also an important support material in heterogeneous catalysis, and is used in lithium ion batteries and supercapacitors. As a result of its commercial importance, charcoal has been the subject of a huge amount of research in both industrial and academic laboratories. Despite this, many important questions remain, not least about its detailed atomic structure.

The primary aim of this article is to discuss the idea, first put forward by the present author and Tsang in 1997 [4, 5], that charcoal, or char, has a structure related to that of the fullerenes. In order to put this in context, a brief outline of earlier work in the field is included. The article begins with a brief description of the characteristics of graphitizing and non-graphitizing carbons, and highlights the work of Rosalind Franklin in establishing the distinction between these two forms of carbon. Some of the structural models which have been put forward for non-graphitizing carbons are then discussed, beginning with Franklin's original models, which were based on cross-linked graphitic

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domains. Subsequent workers suggested that sp^3 -bonded carbon atoms might be present in the cross-links, while later workers interpreted transmission electron microscopy (TEM) images of microporous carbon in terms of a ribbon-like structure. The studies which led to the proposal of the fullerene-related model are then outlined, and experimental support for this structure is discussed. The strongest experimental support comes from studies carried out in the past 4 years using aberration-corrected TEM and electron energy loss spectroscopy (EELS). Both the techniques provide evidence for the presence of pentagonal carbon rings in microporous carbon.

In the subsequent section, some attempts to model the structural evolution of microporous carbon are reviewed. It is notable that in each case these modelling exercises lead to structures which contain non-hexagonal rings. Finally, using fullerene-like models of microporous carbons to predict their adsorptive properties is summarised.

Graphitizing and non-graphitizing carbons

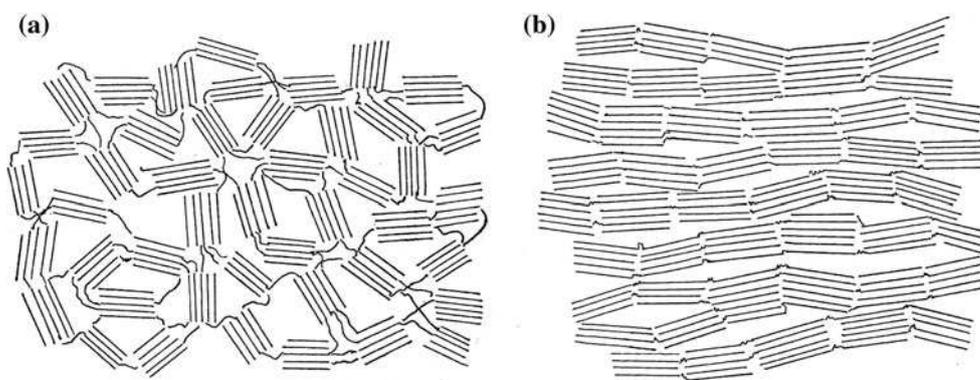
In the early part of the twentieth century it was established that carbons formed by the pyrolysis of organic materials fall into two distinct classes, cokes and chars. The two types of carbon have quite different physical properties. Cokes are relatively dense and soft, whereas chars are hard, low density materials. Although cokes may be porous, this porosity is on a relatively large scale. Chars, on the other hand, have a high degree of microporosity, although some of this porosity is usually inaccessible to gases. The internal surface area can be enhanced by activation, i.e. mild oxidation with a gas such as carbon dioxide, steam or air. In this way, surface areas of the order of $2000 \text{ m}^2 \text{ g}^{-1}$ can be achieved. There is another key distinction between cokes and chars: the former can be converted into graphite by high-temperature annealing while the latter cannot. It is not entirely clear when this was first demonstrated, but it was certainly known in the 1940s. In a major review article published in 1948 [6], Emmett describes work carried out

by H. F. Johnston and G. L. Clark, who showed that 'charcoals sinter and turn into graphite much less readily than does petroleum coke'. Unfortunately this study only seems to have been published in the US government reports. The first detailed study of this topic to appear in the open literature is Rosalind Franklin's classic 1951 paper [7]. Franklin prepared carbons from a wide range of organic materials, including sugar, polyvinylidene chloride (PVDC), polyvinyl chloride (PVC) and pitch. She then used X-ray diffraction to investigate the effect of heat treatment, up to a temperature of $3000 \text{ }^\circ\text{C}$, on the structure of these carbons. She found that some of the carbons, including those prepared from PVC and pitch could be graphitized by heat treatments above about $2200 \text{ }^\circ\text{C}$, while others, such as those prepared from sugar and PVDC, could not be transformed into crystalline graphite, even at $3000 \text{ }^\circ\text{C}$. Instead, they formed a porous, isotropic material which only contained tiny domains of graphite-like structure. Franklin coined the terms 'graphitizing' and 'non-graphitizing' to describe these two classes of carbon.

Structure of non-graphitizing carbon: early work

In his 1948 review, Paul Emmett stated that 'There are very few things about which we can be sure as regards the structure of charcoal'. However, he goes on to express the view that 'The X-ray results taken as a whole constitute strong evidence that much of the carbon in charcoal is arranged in platelets'. Emmett's idea seems to be that char consists of tiny flakes of graphene approximately aligned with each other, giving a structure in which the pores have a slit-like shape. This picture of porosity in carbon as a system of interconnecting slits has proved extremely tenacious. In fact, it is still used in theoretical studies of adsorption and permeability of carbons [8, 9]. However, there is little experimental evidence that the pores in non-graphitizing carbon are generally slit-like in shape. Franklin's 1951 X-ray diffraction study demonstrated rather the opposite, as can be seen from Fig. 1, which

Fig. 1 Franklin's representations of **a** non-graphitizing and **b** graphitizing carbons [7]



shows her models for non-graphitizing and graphitizing carbons. In these models, the basic units are small graphitic crystallites containing a few layer planes, which are joined together by cross-links. For the non-graphitizing carbon (Fig. 1a), the structural units are oriented randomly, so that the structure is isotropic, while in the graphitizing carbon (Fig. 1b) the units are approximately parallel to each other. It is clear that the structure in Fig. 1b is more amenable to transformation into graphite.

Franklin's ideas on graphitizing and non-graphitizing carbons are probably broadly correct, but they are in some regards incomplete. For example, the nature of the cross-links between the graphitic fragments is not specified, so the reasons for the sharply differing properties of graphitizing and non-graphitizing carbons are not explained. Some authors have suggested that the 'cross-links' envisaged by Franklin might in fact be sp^3 -bonded atoms [10]. The presence of diamond-like domains would be consistent with the hardness of non-graphitizing carbons, and might also explain their extreme resistance to graphitization. A problem with these models is that sp^3 carbon is unstable at high temperatures: diamond is converted to graphite at 1700 °C. Therefore, the presence of sp^3 atoms in a carbon is unlikely to explain the resistance of the carbon to graphitization at high temperatures, although the presence of small amounts of sp^3 carbons cannot be ruled out. It should also be noted that diffraction studies of non-graphitizing carbons have found no evidence for the presence of sp^3 -bonded atoms [11].

TEM began to play a major role in the structural study of carbon in the 1970s, when improvements in lens design meant that the interlayer (0.34 nm) graphitic spacing could be readily resolved [12]. In 1975, Ban, Crawford and Marsh described a lattice-resolution TEM study of non-graphitizing carbons derived from PVDC [13]. The structures of the carbons following heat treatments at temperatures in the range 530–2700 °C were investigated. Images of these carbons apparently showed the presence of curved graphite sheets, typically two- or three-layer planes thick, enclosing voids. These images led Ban et al. to suggest that heat-treated non-graphitizing carbons have a ribbon-like structure. A rather similar model for the structure of glassy carbon had been proposed by Jenkins and Kawamura in 1971 [14]. However, models of this kind have serious weaknesses. Such models consist of curved and twisted graphene sheets enclosing irregularly shaped pores. However, graphene sheets are known to be highly flexible, and would therefore be expected to become ever more closely folded together at high temperatures, to reduce surface energy. Indeed, tightly folded graphene sheets are quite frequently seen in carbons which have been exposed to extreme conditions. Thus, structures like the ones envisaged by Jenkins, Ban and their colleagues would be

unlikely to be stable at very high temperatures. It has also been pointed out by Oberlin [15] that the ribbon-like models are based on a questionable interpretation of the electron micrographs. In most micrographs of graphitized carbons, only the {002} fringes are resolved, and these are only visible when they are approximately parallel to the electron beam. Therefore, such images tend to have a ribbon-like appearance. However, as only a part of the structure is being imaged, this appearance can be misleading, and the true three-dimensional structure may be more cage-like than ribbon-like.

Structure of non-graphitizing carbon: fullerene-related models

The discovery of the fullerenes [16–18] and subsequently of related structures such as carbon nanotubes [19, 20] and nanohorns [21, 22] has given us a new paradigm for solid carbon structures. We now know that carbons containing pentagonal rings, as well as other non-six-membered rings, among the hexagonal sp^2 carbon network, can be highly stable. This new perspective prompted a number of groups to take a fresh look at well-known forms of carbon, to see whether any evidence could be found for the presence of fullerene-like structures.

The first studies to consider the idea that non-graphitizing, microporous carbon might have a structure related to that of the fullerenes were published in 1997 [4, 5]. A series of subsequent papers developed the idea further [23–26]. In the original studies, some non-graphitizing carbons were examined using TEM before and after heat treatments at very high temperatures (up to 2600 °C). For comparison, graphitizing carbons treated in a similar way were also examined. Typical TEM micrographs of non-graphitizing and graphitizing carbons prepared at 1000 °C are shown in Fig. 2. The insets show diffraction patterns recorded from areas approximately 0.25 μm in diameter. The image of the non-graphitizing carbon shows the structure to be disordered and isotropic, consisting of tightly curled single carbon layers, with no obvious graphitization. The diffraction pattern shows symmetrical rings, confirming the isotropic structure. The appearance of graphitizing carbon, on the other hand, approximates much more closely to that of graphite. In this case, the structure contains small, approximately flat carbon layers, packed tightly together with a high degree of alignment. The fragments can be considered as rather imperfect graphene sheets. The diffraction pattern for the graphitizing carbon consists of arcs rather than symmetrical rings, confirming that the layers are preferentially aligned along a particular direction. The bright, narrow arcs in this pattern correspond to the interlayer {002} spacings, while the other reflections appear as broader, less intense arcs.

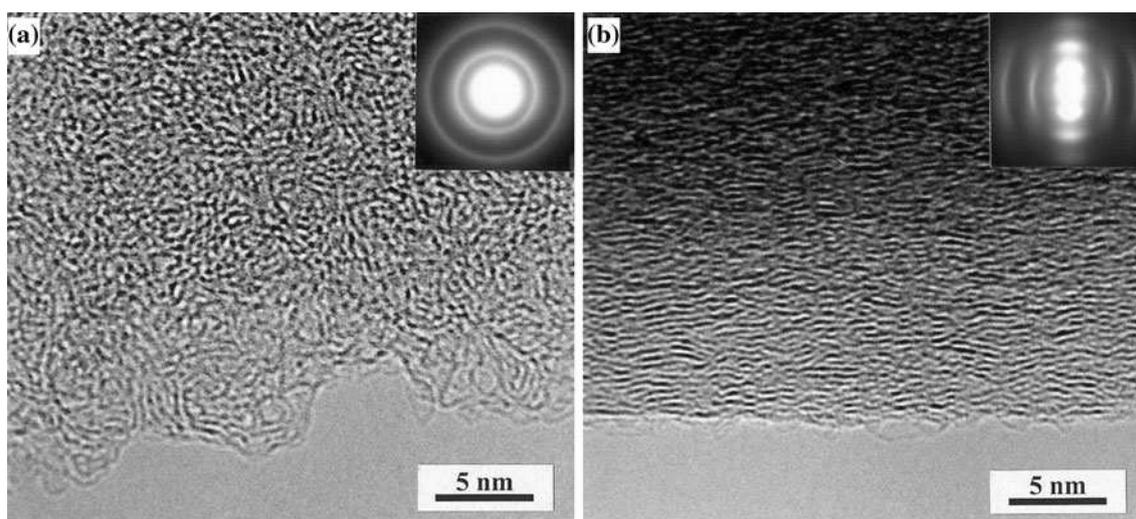


Fig. 2 **a** High-resolution TEM image of carbon prepared by pyrolysis of sucrose in nitrogen at 1000 °C, **b** carbon prepared by pyrolysis of anthracene at 1000 °C. *Insets* show selected area diffraction patterns [23]

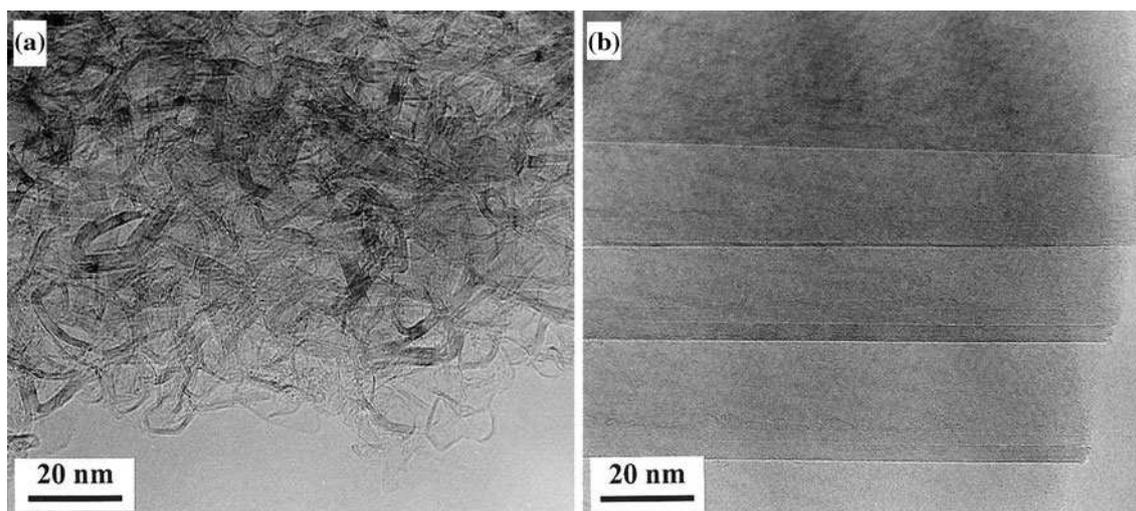


Fig. 3 Micrographs of **a** sucrose carbon and **b** anthracene carbon following heat treatment at 2300 °C [24]

Micrographs showing the effect of high-temperature heat treatments on the structure of non-graphitizing and graphitizing carbons are shown in Fig. 3 (note that the magnification here is much lower than for Fig. 2). In the case of the non-graphitizing carbon, heating at 2300 °C in an inert atmosphere produces the disordered, porous material shown in Fig. 3a. This structure is made up of curved and faceted graphitic layer planes, typically 1–2 nm thick and 5–15 nm in length, enclosing randomly shaped pores. A few somewhat larger graphite crystallites are present, but there is no macroscopic graphitization. In contrast, heat treatment of the anthracene-derived carbon produces large crystals of highly ordered graphite, as shown in Fig. 3b.

More detailed analysis of the heat-treated non-graphitizing carbons showed that they often contained closed nanoparticles; examples can be seen in Fig. 4. The particles were usually faceted, and often hexagonal or pentagonal in shape. Sometimes, faceted layer planes enclosed two or more of the nanoparticles, as shown in Fig. 4b. Here, the arrows indicate two saddle-points, which are indicative of heptagonal rings, as pointed out by Iijima et al. [27]. The closed nature of the nanoparticles, their hexagonal or pentagonal shapes, and other features such as the saddle-points strongly suggest that the particles have fullerene-like structures. Indeed, in many cases, the particles resemble those produced by arc-evaporation in a fullerene generator although in the latter case the particles usually contain many more layers.

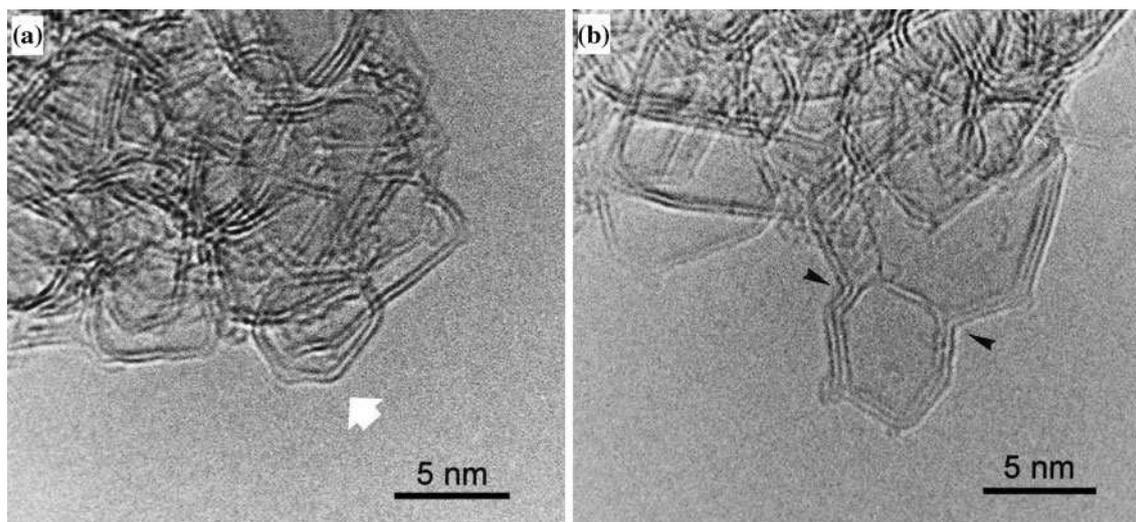


Fig. 4 **a** Micrograph showing closed structure in PVDC-derived carbon heated at 2600 °C, **b** another micrograph of same sample, with *arrows* showing regions of negative curvature [4]

The observation of fullerene-related nanoparticles in the heat-treated carbons suggested that the original, freshly prepared carbons may also have had fullerene-related structures. This prompted the present author and colleagues to propose a model for the structure of non-graphitizing carbons which consists of discrete fragments of curved carbon sheets, in which pentagons and heptagons are dispersed randomly throughout networks of hexagons, as shown in Fig. 5. It should be noted that this representation of the structure is intended as an illustration, rather than a full, three-dimensional model. In subsequent work, discussed in section ‘Modelling adsorption using fullerene-like models for microporous carbon’ three-dimensional structures have been created from the curved fragments, and have been used to model adsorption.

Experimental evidence for fullerene-related structure of non-graphitizing carbon

The micrographs shown in Figs. 2, 3 and 4 were recorded using conventional TEM. The resolution achievable with such microscopes is typically around 0.18 nm. In the past 10 years or so, a new generation of TEMs has become available with resolutions of 0.05 nm or better. This has been achieved through the use of aberration-correctors, which compensate for the inherent defects of electron lenses [28]. These microscopes are capable of resolving carbon atoms in graphene, where the atomic spacing is 0.142 nm [29, 30]. In 2008, Suenaga and co-workers applied this technique for the first time to a microporous carbon [31]. The carbon studied was a commercial activated carbon, Norit GSX. Imaging was carried out in an aberration-corrected TEM operated at 120 kV, with a point

resolution of better than 0.14 nm. Obtaining atomic resolution images of the fresh carbon proved to be extremely challenging, and the images which were recorded were difficult to interpret. A typical example is shown in Fig. 6. At the edge of this fragment the individual rings of carbon atoms are resolved: the bright spots represent the centres of the rings. In some cases, pentagonal arrangements of spots can be discerned: an example is arrowed. However, the images of the fresh carbon were not of sufficient quality to provide definite proof of the presence of pentagons.

Much better quality images could be obtained from carbon samples which had been heated at high temperature, to increase the crystallinity. An image from a carbon sample which had been heated in Ar to 2000 °C is shown in Fig. 7a. Here, there is a clear evidence for the presence of five-membered rings. The area enlarged in Fig. 7b shows an arrangement of five bright spots surrounding a central spot. A good match was obtained with the simulated image in Fig. 7c, which was obtained from the structure in Fig. 7d using a standard multi-slice procedure. Here, the pentagon is oriented approximately parallel to the plane of the image. A second area which contains a pentagonal structure is shown in Fig. 7e. In this case, the central pentagonal ring is not visible, apparently because the ring is tilted away from the plane of the image. Support for this comes from the reasonable match which can be seen between the image and the simulated image in Fig. 7f, obtained from the structure in Fig. 7g. Images of this kind provide convincing evidence for the presence of pentagonal carbon rings in the heat-treated carbon.

In addition to high-resolution imaging, TEM can also probe the structure of material using EELS. In 2011, Zhang et al. [32] used EELS to investigate the structure of a non-graphitizing

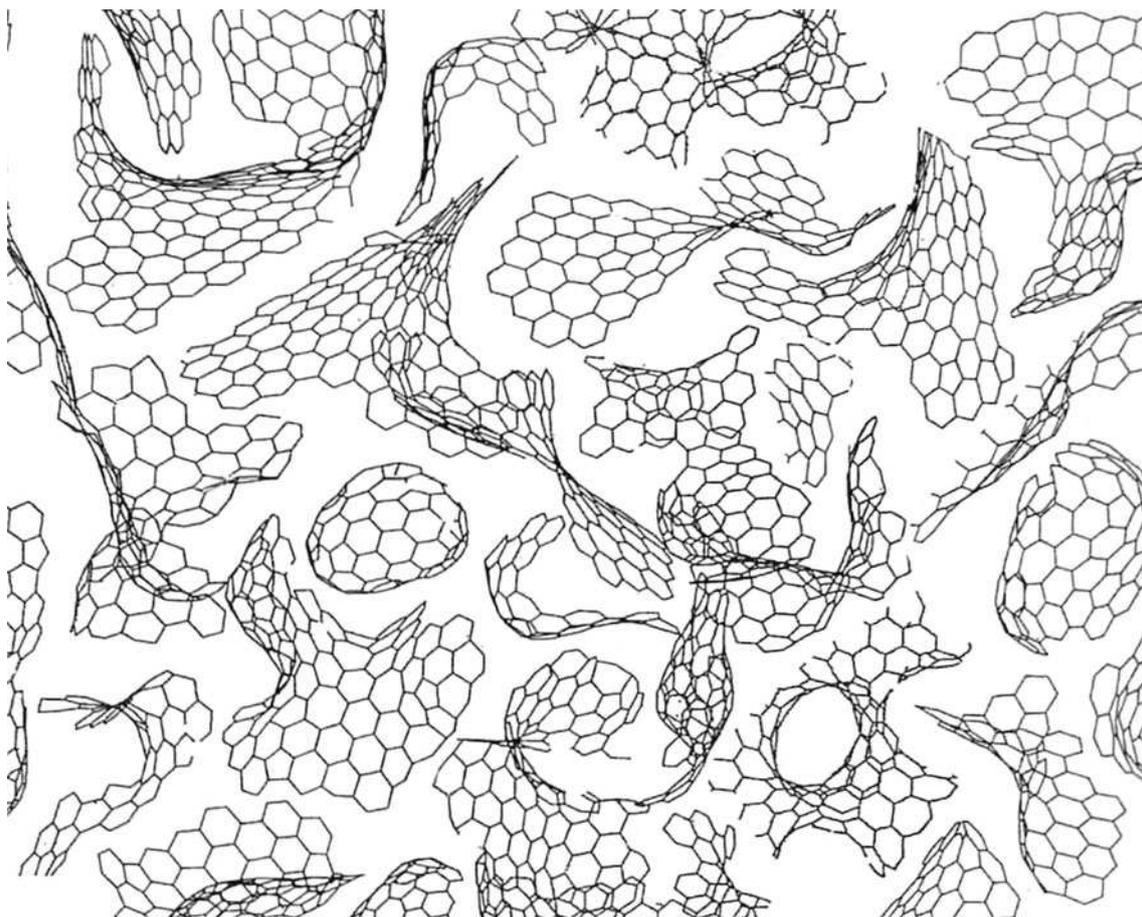


Fig. 5 Schematic illustration of a model for the structure of non-graphitizing carbons based on fullerene-like elements

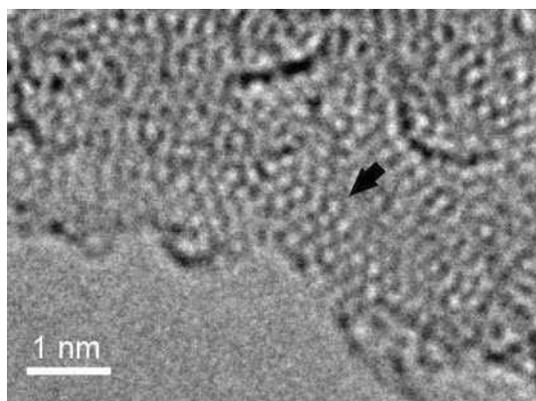


Fig. 6 Aberration-corrected HRTEM micrograph of fresh activated carbon, with *arrow* indicating possible pentagonal arrangement of carbon rings [31]

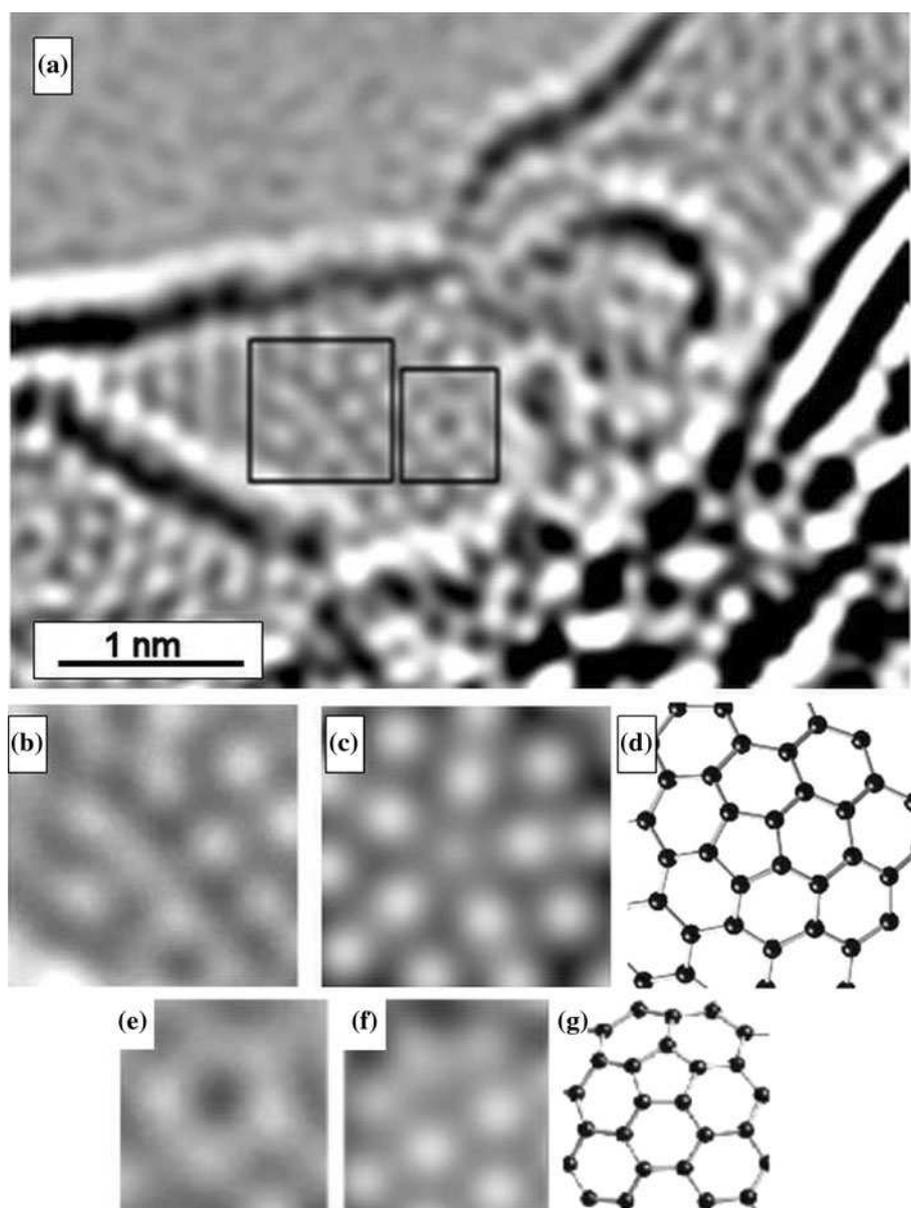
carbon derived from phenolic resin. In this study, a detailed analysis was carried out of the carbon K-edge spectrum. When the C=C π^* , C-C σ^* and C=C σ^* components were removed from the spectrum, a residual feature was found between 286

and 288 eV. A similar feature is observed in spectra recorded from crystalline C₆₀ [33] and could therefore be interpreted as evidence for five-membered rings. As Zhang et al. point out further, theoretical modelling would be valuable in confirming this interpretation.

Evidence for fullerene-like structures in microporous carbons has also been found using Raman spectroscopy. Burian et al. [34, 35] have used this method to analyse carbons prepared from sucrose, heat treated at temperatures from 1000 to 2300 °C. The Raman spectra showed clear evidence for the presence of fullerene- and nanotube-like elements in the carbons.

X-ray and neutron diffraction studies have generally been less useful than microscopy and spectroscopy in establishing whether microporous carbons have a fullerene-related structure, as the interpretation of diffraction data from these highly disordered materials is not straightforward. Burian and co-workers [36, 37] have published a number of studies in this area and have found that the results are consistent with the presence of non-six-membered rings, but other interpretations may also be possible.

Fig. 7 **a** Aberration-corrected micrograph of activated carbon heated to 2000 °C. **b** Enlarged region showing pentagonal arrangement of spots. **c** Simulated image of structure shown in **(d)**. **e** Second region showing pentagonal arrangement. **f** Simulated image of structure shown in **(g)** [31]



Modelling the structural evolution of microporous carbon

The formation mechanism of microporous carbon is not well understood at the atomic level. A number of groups have attempted to model the process, and in several cases these modelling exercises have produced structures which contain fullerene-like elements. One of the first such exercises was reported by Acharya et al. in 1999 [38]. In this study, the carbon was assumed to be derived from polyfurfuryl alcohol. The starting point for the simulation was a series of all-hexagon fragments, terminated with hydrogens, as shown in Fig. 8a, while Fig. 8b–d illustrates the evolution of the structure as the H/C ratio is reduced (i.e. the temperature is increased). During

this evolution, pentagons and heptagons are formed as well as hexagons, resulting in the formation of curved fragments.

In a later study, Kumar et al. [39] used Monte Carlo (MC) simulations to model the evolution of a polymer structure into microporous carbon. Again polyfurfuryl alcohol was chosen as the precursor, and in this case the starting structure was the polymer itself rather than hexagonal fragments of carbon. Simulations were carried out with a number of different polymer starting structures and different pre-defined densities. In each case, the final carbon was made up of a hexagonal network with 10–15 % non-hexagonal rings (pentagons and heptagons). The properties of the simulated carbons appeared to be generally consistent with experimental results.

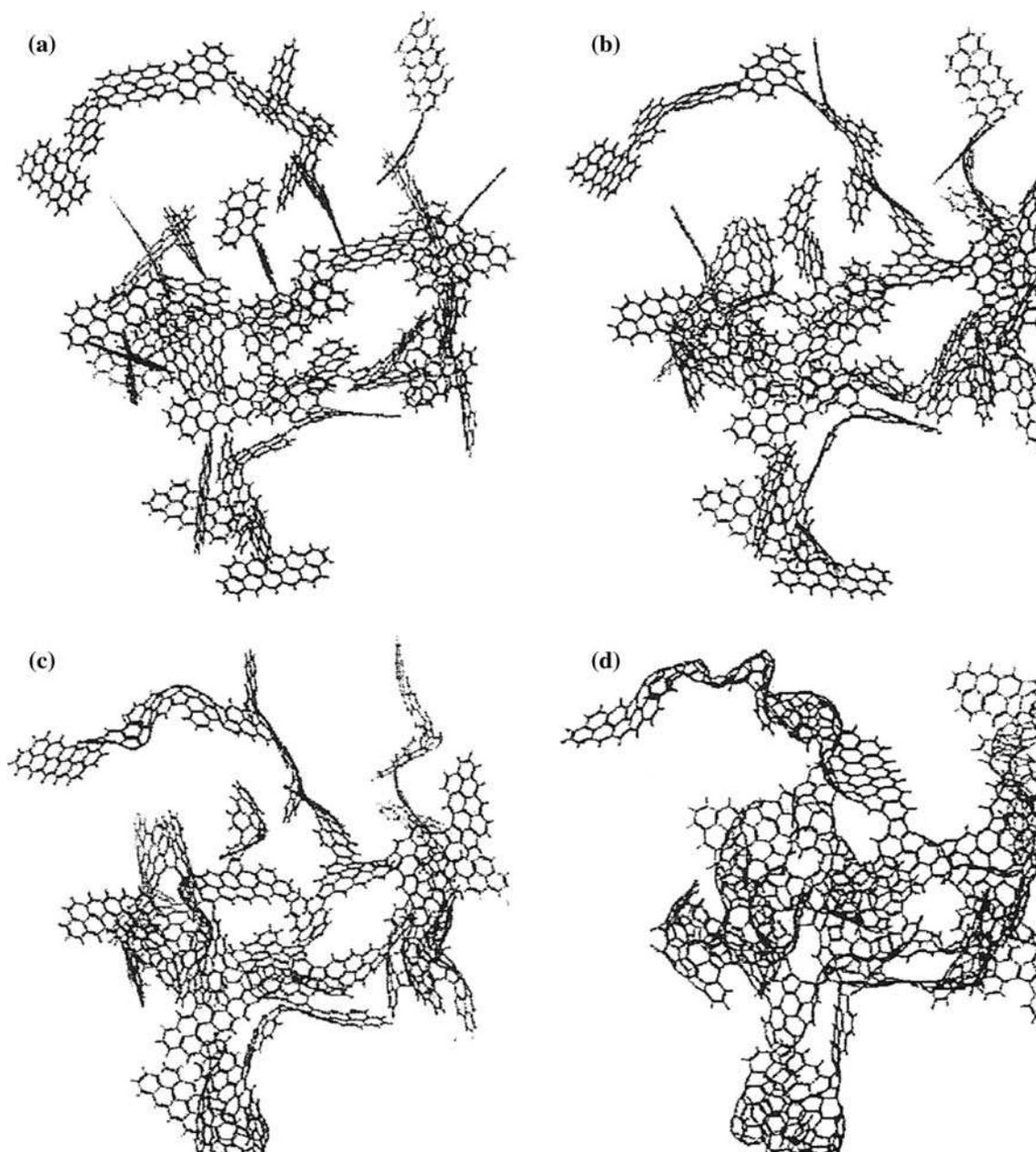


Fig. 8 Structural evolution of microporous carbon modelled by Acharya et al. [38]. The sequence of images **a–d** represent decreasing H/C ratio (or equivalently, increasing temperature)

A different approach to modelling the evolution of microporous carbon was used by Shi [40]. Here, the initial system consisted of carbon gas atoms at very high temperature. This choice of initial condition was intended to represent the high-temperature state in a pyrolysis process after the polymer chains break down and most other elements have evaporated. The temperature was then decreased so that the atoms ‘condensed’ to form a porous structure composed of curved and defected graphene sheets, in which the curvature was induced by non-hexagonal rings.

In 2009, Powles et al. [41] described a comprehensive molecular-dynamics study of the self-assembly of carbon nanostructures. The precursor for these simulations was highly disordered amorphous carbon, which was generated by rapid quenching of an equilibrated liquid sample. It was found that, under certain conditions, annealing the amorphous carbon at high temperature could lead to the highly curved sp^2 sheet structure shown in Fig. 9. The resemblance between this and the structure shown in Fig. 5 is very striking.

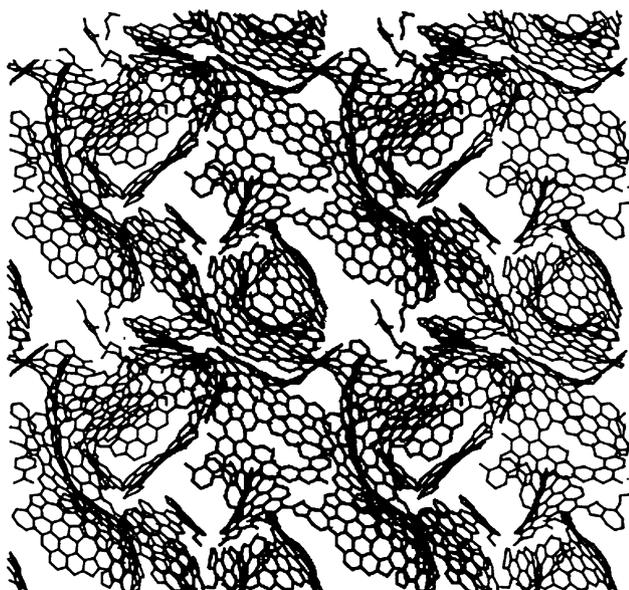
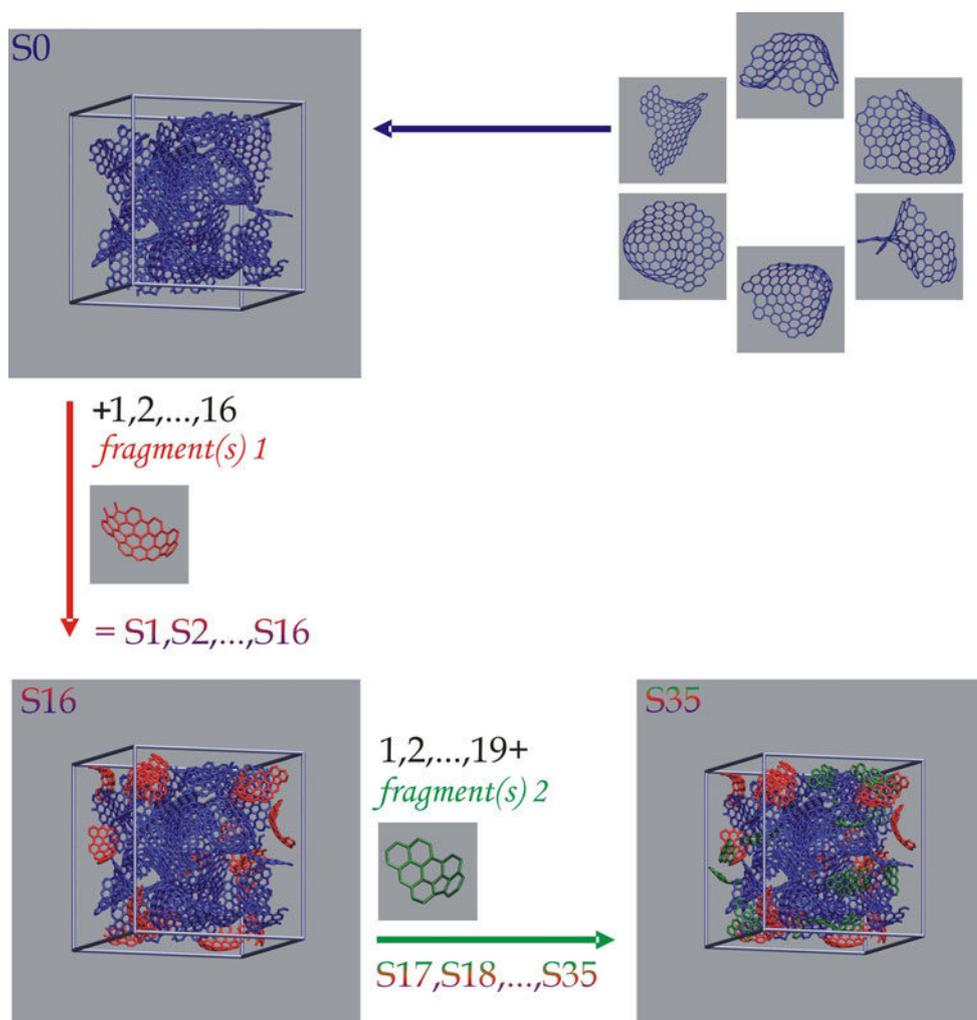


Fig. 9 Curved sp^2 sheet structure produced in molecular-dynamics simulations by Powles et al. [41]

Modelling adsorption using fullerene-like models for microporous carbon

To date, there have been relatively few attempts to use fullerene-like models to predict the adsorptive and other properties of microporous carbons. By far the most ambitious programme of work in this area has been carried out by Terzyk and colleagues [42–49], whose results have been published in a series of papers beginning in 2007. In the first of these [42], 36 different carbon structures with increasing microporosity, labelled S0–S35, were generated. The initial microporous structure, named S0, is shown in Fig. 10 (top left). Fragments were then progressively added to create the 36 structures labelled S0–S35. Pore size distribution (PSD) curves for the structures were calculated using the method of Bhattacharya and Gubbins (BG) [50]. This involves determining the statistical distribution of the radii of the largest sphere that can be fitted inside a pore at a given point. A selection of the PSD curves determined in this way is shown in Fig. 11. It can be seen that the most ‘crowded’

Fig. 10 Illustration of the construction of microporous structures S0, S16 and S35 from fullerene-related fragments. These structures are used by Terzyk et al. to simulate adsorption properties [42]



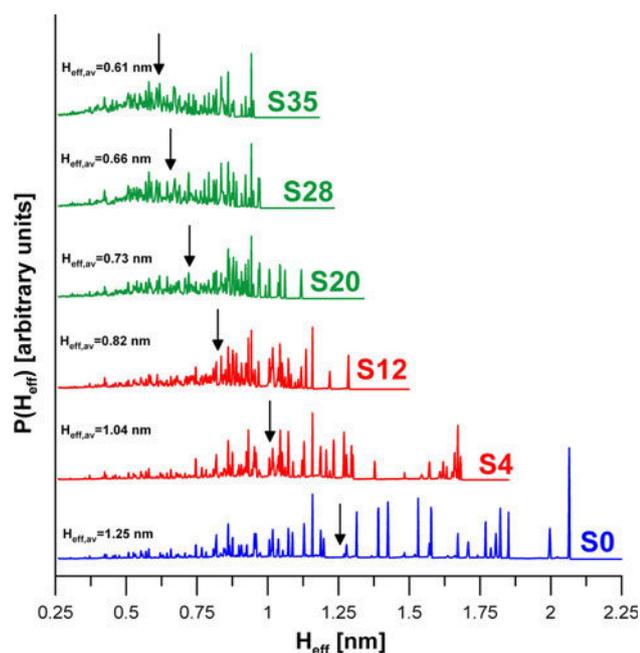


Fig. 11 PSD curves for some of the model structures created by Terzyk et al. [42]

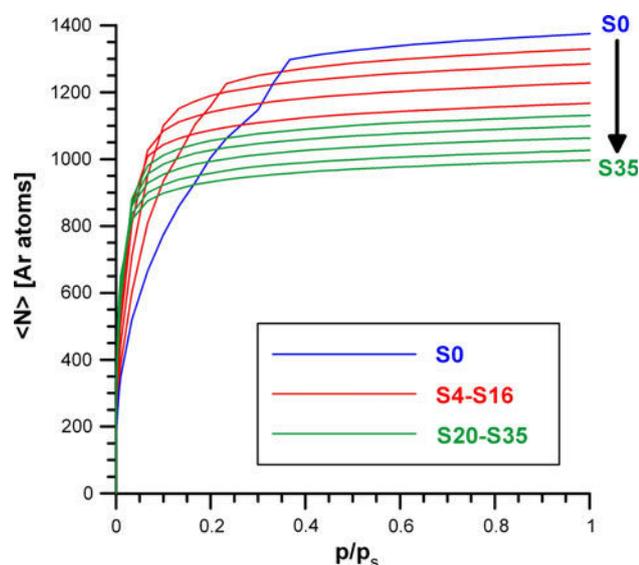


Fig. 12 Argon adsorption isotherms for model structures [42]

structure, S35, has a much narrower range of pore sizes than the initial S0 structure. Argon adsorption isotherms were simulated for these structures using the parallel tempering MC simulation method developed by Yan and de Pablo [51]. Some of these isotherms are shown in Fig. 12. These show that the gradual crowding of the S0 structure (leading finally to S35) leads to a decrease in the maximum number of adsorbed molecules. On the other hand, the S0 structure exhibits less adsorption at low pressures than the more crowded ones because the average micropore diameter is

larger. Also notable is the increasing ‘sharpness’ of the inflection point in the isotherms, a feature which is often reported for experimental systems [52]. The simulated isotherms were then used to determine PSD curves, using a range of widely used methods, with the aim of checking the validity of these methods. Good agreement was found between the PSDs determined from the isotherms and the PSDs from the BG method. This confirms the validity of various methods for calculating PSD curves from adsorption data. It would also seem to confirm the validity of the fullerene-related model for microporous carbon.

In the next paper of this series [43], Terzyk et al. began with three structures constructed from fullerene-like fragments, as shown in Fig. 13. The densities of these structures were calculated, and values in the range $2.18\text{--}2.24\text{ g cm}^{-3}$ were found, consistent with typical densities of non-graphitizing carbons. Once again, PSDs for the structures were determined using the BG method. As in the previous paper, the simulated isotherms were used to determine PSD curves, using a range of widely used methods. Good agreement was found between the PSDs determined from the simulated adsorption data and the original PSDs from the BG method. This is illustrated in Fig. 14, where the PSD curve determined from the Bhat-tacharya–Gubbins method is compared with results from the Horvath–Kawazoe method [53].

In a further paper [44], the adsorption of Ne, Ar, Kr, Xe, CCl_4 and C_6H_6 on the S0 and S35 carbons was modelled. The simulated data were compared with the predictions of the Dubinin–Radushkevich [54] and Dubinin–Astakhov [55] adsorption isotherm equations, and a good fit was found for the S35 carbon. For the S0 carbon the Dubinin–Izotova (DI) equation [56] gave a better fit because the micropores in this model have a wide distribution of diameters. The simulated isotherms exhibited a number of features similar to those seen in experimental results. For example the isotherms for CCl_4 and C_6H_6 were temperature invariant, as observed experimentally. It was also noted that the isotherms obeyed Gurvich’s rule, which states that the larger the molecular collision diameter the smaller the access to micropores, as well as other empirical and fundamental correlations developed for adsorption on microporous carbons.

The effect of oxidising the carbon surface on porosity was analysed in a paper published in 2009 [45]. A ‘virtual oxidation’ procedure was employed, in which surface carbonyls were attached to carbon atoms located on the edges of the fragments. It was assumed that the structure of the carbon skeleton remained unchanged. PSDs, determined using the BG method were found not to be greatly affected by oxidation. Simulated isotherms for Ar, N_2 , and CO_2 were calculated using the GCMC method. For Ar, the effect of oxidation on the isotherm was relatively small. However, for

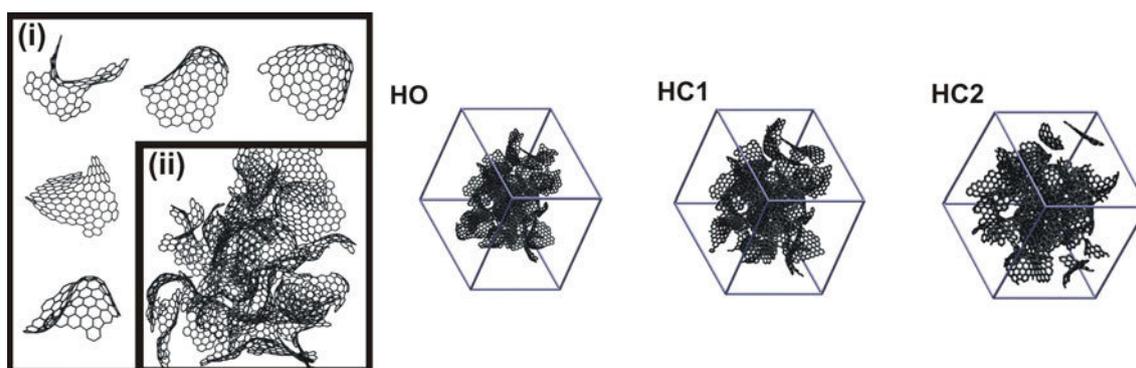


Fig. 13 Illustration of the construction of microporous-mesoporous structures, from the work of Terzyk et al. [43]. **i** Individual fullerene-related fragments, **ii** A 2D structure constructed from these fragments.

HO is the initial 3D structure produced from the fragments; HC1 and HC2 were created by cutting boxes from this structure

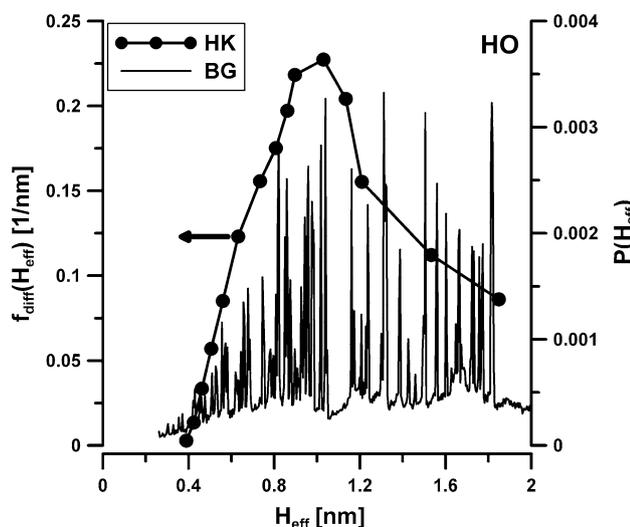


Fig. 14 Comparison of PSD curves for the HO structure determined using the Bhattacharya-Gubbins and the Horvath-Kawazoe method [43]

N_2 and CO_2 there were significant changes in the isotherms, due to electrostatic interactions between N_2 and CO_2 and the surface carbonyl groups. As a consequence of this, PSDs calculated from the simulated isotherms for N_2 and CO_2 differed markedly from those originally determined from the BG method. An important conclusion from this is that experimental PSDs determined using CO_2 (or using N_2 if there is a large oxygen content) may be unreliable. A further study looked at the influence of carbon surface oxygen groups on Dubinin-Astakhov equation parameters calculated from CO_2 isotherms [46]. It was concluded that porosity parameters calculated by fitting the DA model to experimental CO_2 adsorption data may be questionable.

Terzyk and co-workers have published a number of other studies in which fullerene-like models have been used to predict the properties of microporous carbons [47–49], but the results summarised above are sufficient to demonstrate the utility of such models.

Discussion

The structure of microporous carbon has been a subject of uncertainty for decades, and a wide range of different structural models have been proposed. The idea discussed in this review, that microporous carbon has a structure related to that of the fullerenes, is by no means universally accepted, and will remain controversial until unequivocal experimental evidence is obtained. The best hope of achieving such proof probably lies with aberration-corrected TEM. As discussed in section ‘Experimental evidence for fullerene-related structure of non-graphitizing carbon’, the advent of this new form of TEM has meant that directly imaging the ring structure of graphitic carbons is now a practical possibility. Initial studies using this technique [31] have produced convincing evidence for pentagonal rings in carbon heated to 2000 °C, but further work is needed to achieve clear images of pentagons in ‘fresh’ carbon. This is clearly a considerable experimental challenge, but not beyond the capabilities of current microscopes.

While direct imaging probably provides the best hope of finally determining the structure of microporous carbon, other techniques can give valuable corroborative information. We have seen that careful analysis of electron energy loss spectra has revealed features that can be ascribed to five-membered rings [32]. More work in this area, involving both experimental studies and theoretical analysis would be welcome, as would further studies using techniques such as Raman spectroscopy and X-ray and neutron diffraction.

If experimental evidence for a fullerene-related structure appears to be growing, theoretical studies of the formation of microporous carbon also point in the same direction. It is surely significant that four separate modelling studies, all using slightly different methods and starting systems [38–41], each produce structures containing non-hexagonal rings. Particularly notable is the resemblance between the structure of Powles and colleagues (Fig. 9), and the

structure inferred from TEM observations shown in Fig. 5. There is clearly scope for further modelling work on the evolution of carbonaceous material into carbon, as there is still much that we do not understand. In particular, the question of why some materials yield non-graphitizing carbon while others give graphitizing carbon is not at all well understood at the molecular level.

A fullerene-like model for microporous carbon could be of great value in understanding its adsorptive properties. It is widely recognised that the slit pore model has serious deficiencies [57–61], and it has been known for some time that the profile for small-angle (X-ray or neutron) scattering does not correspond to the model predictions for slit scattering. However, a widely accepted alternative model has not yet emerged. Theoretical studies by Terzyk and co-workers [42–49] have shown that fullerene-like models can replicate reasonably well the densities, PSDs and adsorption isotherms observed experimentally, and it would be valuable if other groups were to carry out similar studies. One way in which the modelling work could be extended would be by employing larger fragments. It is very difficult to determine accurately the size of the individual fragments in microporous carbon, but recent work by Kyotani and co-workers [62] has suggested that they may be larger than generally thought. In this study, the amount of hydrogen in carbon materials heat-treated to 1000 °C and above was measured. The crystallite sizes were then determined by assuming that all the edge sites were terminated by hydrogen atoms. In this way, it was found that a non-graphitizing carbon prepared from polyfurfuryl alcohol by heating to 1000 °C had a crystallite size of 12 nm, much larger than the size estimated from X-ray diffraction (1 nm). This is understandable, as XRD measurements assume planar crystallites, and the structures in a non-graphitizing carbon are of course highly curved. A graphene crystallite with a diameter of 12 nm would contain approximately 4500 atoms, whereas the fragments employed by Terzyk et al. generally had fewer than 500 atoms. It is quite possible that structures constructed from larger fragments would display similar behaviour to those made from smaller ones, but further modelling studies are needed to confirm this.

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References

- Derbyshire F, Jagtoyen M, Thwaites M (1995) In: Patrick JW (ed) Porosity in carbons: characterization and applications. Edward Arnold, London, p 227
- Patrick JW (ed) (1995) Porosity in carbons: characterization and applications. Edward Arnold, London
- Marsh H, Rodriguez-Reinoso F (2006) Activated carbon. Elsevier, Oxford
- Harris PJF, Tsang SC (1997) *Philos Mag A* 76:667
- Harris PJF (1997) *Int Mater Rev* 42:206
- Emmett PH (1948) *Chem Rev* 43:69
- Franklin RE (1951) *Proc R Soc A* 209:196
- Lim YI, Bhatia SK (2011) *J Membr Sci* 369:319
- Sitprasert C, Zhu ZH, Wang FY, Rudolph V (2011) *Chem Eng Sci* 66:5447
- Ergun S, Tiensuu VH (1959) *Acta Crystallogr A* 12:1050
- Burian A, Ratuszna A, Dore JC, Howells SW (1998) *Carbon* 36:1613
- Ban LL (1972) In: Roberts MW, Thomas JM (eds) *Surface and defect properties of solids*, vol 1. Chemical Society, London, p 54
- Ban LL, Crawford D, Marsh H (1975) *J Appl Crystallogr* 8:415
- Jenkins GM, Kawamura K (1971) *Nature* 231:175
- Oberlin A (1989) In: Thrower PA (ed) *Chemistry and physics of carbon*, vol 22. Dekker, New York, p 1
- Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE (1985) *Nature* 318:162
- Krätschmer W, Lamb LD, Fostiropoulos K, Huffman DR (1990) *Nature* 347:354
- Kroto HW (1992) *Angew Chem* 31:111
- Iijima S (1991) *Nature* 354:56
- Harris PJF (2009) *Carbon nanotube science*. Cambridge University Press, Cambridge
- Harris PJF, Tsang SC, Claridge JB, Green MLH (1994) *J Chem Soc, Faraday Trans* 90:2799
- Iijima S, Yudasaka M, Yamada R, Bandow S, Suenaga K, Kokai F, Takahashi K (1999) *Chem Phys Lett* 309:165
- Harris PJF, Burian A, Duber S (2000) *Philos Mag Lett* 80:381
- Harris PJF (2003) In: Radovic LR (ed) *Chemistry and physics of carbon*, vol 28. Dekker, New York, p 1
- Harris PJF (2004) *Philos Mag* 84:3159
- Harris PJF (2005) *Crit Rev Solid State Mater Sci* 30:235
- Iijima S, Ichihashi T, Ando Y (1992) *Nature* 356:776
- Erni R (2010) *Aberration-corrected imaging in transmission electron microscopy: an introduction*. Imperial College Press, London
- Hashimoto A, Suenaga K, Gloter A, Urita K, Iijima S (2004) *Nature* 430:870
- Meyer JC, Kisielowski C, Erni R, Rossell MD, Crommie MF, Zettl A (2008) *Nano Lett* 8:3582
- Harris PJF, Liu Z, Suenaga K (2008) *J Phys: Condens Matter* 20:362201
- Zhang Z, Brydson R, Aslam Z, Reddy S, Brown A, Westwood A, Rand B (2011) *Carbon* 49:5049
- El-Barbary AA, Trasobares S, Ewels CP, Stephan O, Okotrub AV, Bulusheva LG, Fall CJ, Heggie MI (2006) *J Phys: Conf Ser* 26:149
- Burian A, Dore JC (2000) *Acta Phys Pol, A* 98:457
- Burian A, Daniel P, Duber S, Dore JC (2001) *Philos Mag B* 81:525
- Hawelek L, Koloczek J, Brodka A, Dore JC, Honkimaki V, Burian A (2007) *Philos Mag* 87:4973
- Hawelek L, Brodka A, Dore JC, Honkimaki V, Burian A (2008) *Diam Relat Mater* 17:1633
- Acharya M, Strano MS, Mathews JP, Billinge JL, Petkov V, Subramoney S, Foley HC (1999) *Philos Mag B* 79:1499
- Kumar A, Lobo RF, Wagner NJ (2005) *Carbon* 43:3099
- Shi YF (2008) *J Chem Phys* 128:234707
- Powles RC, Marks NA, Lau DWM (2009) *Phys Rev B* 79:075430
- Terzyk AP, Furmaniak S, Gauden PA, Harris PJF, Włoch J, Kowalczyk P (2007) *J Phys: Condens Matter* 19:406208
- Terzyk AP, Furmaniak S, Harris PJF, Gauden PA, Włoch J, Kowalczyk P, Rychlicki G (2007) *Phys Chem Chem Phys* 9:5919
- Terzyk AP, Furmaniak S, Gauden PA, Harris PJF, Włoch J (2008) *J Phys: Condens Matter* 20:385212

45. Furmaniak S, Terzyk AP, Gauden PA, Kowalczyk P, Harris PJF (2009) *J Phys: Condens Matter* 21:315005
46. Furmaniak S, Terzyk AP, Gauden PA, Harris PJF, Kowalczyk P (2010) *J Phys: Condens Matter* 22:085003
47. Terzyk AP, Gauden PA, Furmaniak S, Wesółowski RP, Harris PJF (2010) *Phys Chem Chem Phys* 12:812
48. Gauden PA, Terzyk AP, Furmaniak S, Harris PJF, Kowalczyk P (2010) *Appl Surf Sci* 256:5204
49. Furmaniak S, Terzyk AP, Gauden PA, Kowalczyk P, Harris PJF (2011) *J Phys: Condens Matter* 23:395005
50. Bhattacharya S, Gubbins KE (2006) *Langmuir* 22:7726
51. Yan QL, de Pablo JJ (1999) *J Chem Phys* 111:9509
52. Kruk M, Jaroniec M, Gadkaree KP (1999) *Langmuir* 15:1442
53. Horvath G, Kawazoe K (1983) *J Chem Eng Jpn* 16:470
54. Dubinin MM, Radushkevich LV (1947) *Dokl Akad Nauk SSSR* 55:327
55. Dubinin MM, Astakhov VA (1971) *Izv Akad Nauk SSSR Seriya Khimicheskaya* 1:5
56. Izotova TI, Dubinin MM (1965) *Zh Fizicheskoi Khimii* 39:2796
57. McEnaney B, Mays TJ, Chen XS (1998) *Fuel* 77:557
58. Thomson KT, Gubbins KE (2000) *Langmuir* 16:5761
59. Biggs MJ, Buts A, Williamson D (2004) *Langmuir* 20:7123
60. Do DD, Do HD (2006) *J Phys Chem B* 110:17531
61. Palmer JC, Moore JD, Brennan JK, Gubbins KE (2011) *J Phys Chem Lett* 2:165
62. Kashihara S, Otani S, Orikasa H, Hoshikawa Y, Ozaki J, Kyotani T (2012) *Carbon* 50:3310