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Importance of fullerenic active sites in surface modification of carbon black by plasma polymerisation

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ABSTRACT

Carbon black is widely used as an active filler in rubber to improve the physical properties. The surface energy of carbon black is high compared to that of various elastomers like Styrene–Butadiene rubber, Butadiene rubber and Ethylene–Propylene Diene rubber. Reducing the surface energy and matching its surface chemistry will aid in compatibilising carbon black with various elastomers. Surface modification of carbon black by plasma polymerisation has been attempted earlier in order to reduce the surface energy of carbon black. These studies have shown that for effective surface modification of carbon black, there should be available a sufficient number of surface active sites. The present paper looks into the possibilities of utilizing the surface activity of a by-product of the production of fullerene, the fullerene soot for its use in a plasma modification process. Thermogravimetric analysis, wetting behaviour with various liquids of known surface tension, time of flight secondary ion mass spectrometry and transmission electron microscopy are used to characterise the carbon black before and after surface modification. The study shows that the fullerenic type structures present on the surface of fullerenic soot act as very active growth sites for the plasma polymer.

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1. Introduction

Carbon black is widely used as active filler to improve the physical properties of rubbers [1]. Dispersion and distribution of carbon black in the rubber matrix are important factors to achieve optimum physical properties. In order to have a good compatibility, the surface energy difference between the filler and the rubber should be low. With a large surface energy difference between filler and rubber, the filler–filler interaction increases, which in turn has a negative influence on the stability of the dispersion state attained during mixing.

In the case of carbon black, the surface energy is high compared to that of various elastomers like Styrene–Butadiene rubber (SBR), Butadiene rubber (BR) and Ethylene–Propylene–Diene rubber (EPDM). In rubber blends, this difference in surface energy leads to preferential wetting of one phase which eventually results in non-uniform distribution of the filler between the phases in the blend. The non-uniform distribution of filler is more prominent in the case of dissimilar rubber blends i.e., blends in which rubber components differ in their level of unsaturation/polarity. In order to have an appreciable influence on the dispersion and distribution properties of

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carbon black in rubber, there should be a significant reduction in surface energy of the filler. Reducing the surface energy of carbon black to the range of different rubbers may aid in compatibilising this filler with different rubber systems and improve the distribution between the phases in blends.

It is possible to tailor the surface properties of a filler by plasma polymerisation. This technology has emerged as a surface modification technique for metals, polymers and powders. The technique involves electric field bombardment of monomer molecules, thereby creating active monomer species, which then react with a surface to form a film over the substrate. As a result, the surface properties of the substrate change dramatically. By suitable selection of monomers, a substrate can either be made hydrophobic or hydrophilic. Plasma polymerisation can be carried out at ambient temperature and does not require any solvents for the process, making it a clean process.

Contrary to the vast amount of information available on the plasma deposition on flat surfaces [2,3], there are only few reports on the deposition on powder substrates. Powders are difficult to handle in plasma treatment, mainly because of aggregation and the large surface area per unit mass of the powder. Inagaki et al. [4] reported surface modification of polyethylene powders using a fluidised bed. Later, van Ooij et al. [5–7] reported surface modification of various powder substrates using different reactors, which included a vertical tubular reactor, a tumbler reactor and a fluidised bed reactor.

The extension of plasma polymerisation as a surface modification technique for fillers like carbon black and silica, for application in rubber happened quite recently. Nah et al. [8,9] reported plasma polymerisation on silica and its effect on rubber properties. Vidal et al. [10,11] reported modification of various rubber curatives like sulphur and cyclohexylbenzothiazole sulphenamide. Donnet et al. [12] has reported on the plasma treatment of graphitised carbon black using reactive gases. Their study showed that after plasma treatment the graphitised surface appeared to be more like that of regular carbon black than that of graphite. Akovali et al. [13] and Tricas et al. [14,15] reported the modification of carbon black by plasma polymerisation. The monomers used for the process were styrene, butadiene, and acrylic acid. Their findings led to the conclusion that carbon black was modified with the coating covering the whole surface. Kang et al. [16] also reported the modification of carbon black by plasma polymerisation and concluded that it is possible to manipulate the surface properties.

In a recent publication [17], we reported on the mechanistic aspects of surface modification of carbon black by plasma polymerisation with acetylene. For effective surface modification of carbon black, the distribution and stability of the active sites formed during the modification process are important. It is well known that, on a carbon black surface the active sites, which are mainly the crystallite edges and slit shaped cavities, are low in concentration. Hence surface modification of carbon black by plasma polymerisation is a difficult process, especially when aiming for a significant reduction in surface energy.

The evidence for fullerene-like structures on the carbon black surface has been reported in literature [18–22]. The development of plasma technology for the production of full-

erenes opened a new possibility to increase the concentration of fullerene active sites on the carbon black and graphite surfaces. The present work looks into the possibilities of utilizing the activity of fullerene sites on a carbon black surface for effective modification by plasma polymerisation. Fullerene soot, a by-product of the production of fullerenes with its surface being covered with large number fullerene-like residues, is used in the experiments. The monomer chosen for the plasma polymerisation is acetylene, as it deposits a hydrocarbon coating over the substrate surface.

2. Experimental

2.1. Materials

The type of regular rubber grade carbon black used for the modification experiments was carbon black N330 in the fluffy form, as supplied by Degussa AG, Germany. The surface area of the N330 carbon black was 83 m²/g (BET – nitrogen adsorption surface area). The fullerene soot (EP-P434) was supplied by Timcal S.A, Belgium. The fullerene production consists of vapourisation of carbon from a carbon precursor: carbon black or graphite, in an inert atmosphere: Helium or Argon, and their recondensation into fullerenes [23,24]. Part of the carbon vapour recondenses on the carbon precursor surface. The precursor material will then consist of the original precursor in its core and on its surface contain recondensed fullerenes or fullerene fractions. In the present case, the precursor material used was a standard conductive carbon black ENSACO[®] 250G (E-250 g) manufactured by the MMM process. The surface area of the fullerene soot was 69.8 m²/g. The monomer used for plasma polymerisation was acetylene (99.6% purity), as supplied by Prax Air, The Netherlands.

2.2. Methods

2.2.1. Plasma polymerisation

Plasma polymerisation on carbon samples was carried out in a radio frequency (RF) plasma vertical tubular reactor. A schematic representation of the reactor is shown in Fig. 1. The reactor consists of a round bottom flask attached with a long tubular region. The powders are kept at the bottom of the chamber and stirred with the help of a magnetic stirrer in order to expose the powder particles uniformly to plasma. The system is evacuated to a pressure of 4 Pa. The monomer is injected into the reaction chamber under steady flow conditions. The monomer flow is monitored by a mass flow controller (MKS-1179A) and the system pressure by a temperature regulated capacitance manometer (MKS-627B). Plasma is generated with the help of a 13.56 MHz radio frequency (RF) plasma generator (MKS-ENI ACG 3B). When sufficient monomer pressure is attained, RF power is applied. Carbon black N330, carbon precursor E-250 g and fullerene soot EP-P434 were all modified by plasma polymerisation. The conditions applied for the surface modification process are 27 Pa monomer pressure, 250 W RF power and a treatment time of 1 h. In one experiment N330 was treated for 4 h under similar conditions.

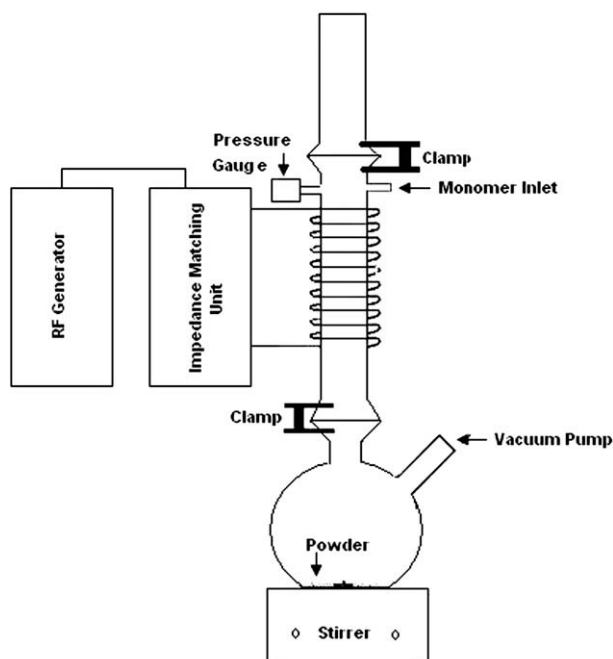


Fig. 1 – Schematic representation of a vertical tubular reactor for plasma polymerisation.

2.2.2. Thermogravimetric analysis

A Perkin-Elmer TGA was used for thermogravimetric analysis of the samples. The samples were heated from 50 to 800 °C at 10 °C/min in an air atmosphere. The thermal degradation behaviour of pure plasma polymerised acetylene was first studied. Pure plasma polymerised acetylene starts to decompose at 265 °C and the decomposition is complete at 600 °C. Based on this, the weight losses for the coated and uncoated carbon blacks were calculated in this region of decomposition of plasma polymerised acetylene. The difference in weight loss between the coated and uncoated samples corresponds to the amount of coating deposited on the surface of the carbon blacks.

2.2.3. Wetting behaviour with liquids of known surface tension

Wetting behaviour of the modified and unmodified powders with liquids of known surface tension was observed in order to semi-quantitatively characterise the degree to which the modification had taken place. For this purpose, 50 ml of liquid was put in a glass beaker and 1–2 g of sample was added to the liquid. Depending on the surface energy of the powder, it either sinks or floats on the liquid. The wetting behaviour gives an idea about the range over which surface energy has been reduced.

2.2.4. Time of flight secondary ion mass spectroscopy (ToF-SIMS)

In order to study the surface composition of the coated carbon blacks, ToF-SIMS measurements were carried out. The measurements were carried out in an Ion-ToF Cameca ToF-SIMS IV machine. The carbon black powder samples were deposited on an indium foil, which was then loaded on to the sample holder. The system vacuum was maintained between

10^{-7} and 10^{-9} mbar. Monoisotopic Gallium (^{69}Ga) ions were used as the primary ion source with an energy of 25 kV. The ion current was kept in the range 1.5–2.5 μA . The total integrated ion dose was $\approx 10^{10}$ ions/cm 2 .

2.2.5. Surface area measurements

A Micrometrics model 2280 nitrogen adsorption surface area analyser was used to determine the BET surface area of the fullerene soot sample before and after plasma modification. Procedures according to ASTM D-3037 were followed during the measurements.

2.2.6. Transmission electron microscopy (TEM)

Bright field TEM images of the plasma coated and uncoated fullerene soot were taken using a Philips CM300ST-FEG transmission electron microscope. The powder samples were ultrasonically dispersed in ethanol and then placed on a carbon grid using a micropipette. The samples were then viewed through the microscope.

3. Results

The TGA thermogram of plasma polymerised acetylene is shown in Fig. 2. The decomposition starts at 265 °C and is complete at 600 °C. The TGA thermograms of the coated and uncoated carbon black samples are shown in Fig. 3. The difference in weight loss of the coated and uncoated carbon black samples corresponds to the weight of the plasma polymerised acetylene film deposited on the surface. Carbon black N330 after 1 h plasma treatment gives only a deposition of 1.05 wt.% of polymerised acetylene and respectively the E-250 g carbon black sample gives 2.3 wt.% deposition on its surface. On the other hand, the fullerenic soot after 1 h plasma treatment gives a deposition of 14 wt.% of polymerised acetylene. The 4 h treated carbon black N330 gives an increased deposition of 17 wt.% indicating that substantial deposition can be formed on its surface when the treatment time is increased. The results are tabulated in Table 1.

For a liquid to wet a particular surface, the surface energy of the liquid has to be lower than that of the substrate. The

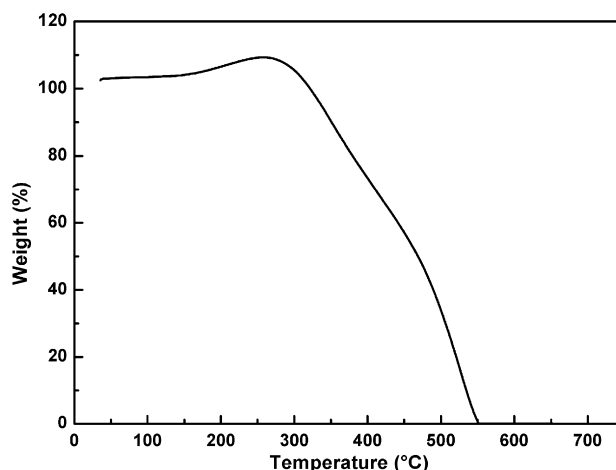


Fig. 2 – TGA thermogram of pure plasma polymerised acetylene.

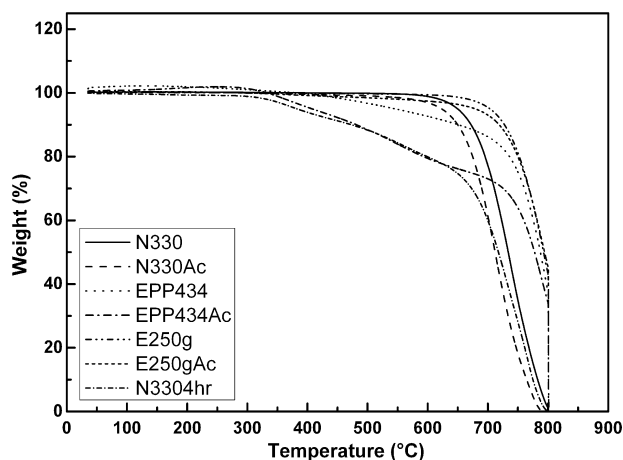


Fig. 3 – TGA thermogram of various coated and uncoated carbon black samples.

Table 1 – Calculated weight losses for various carbon black samples.

Sample code	Weight loss (%)
N330-Ac (N330 treated for 1 h)	1.05
E-250 g-Ac (E-250 g treated for 1 h)	2.3
EP-P434 – Ac (EP-P434 treated for 1 h)	14
N330-Ac 4 h (N330 treated for 4 h)	17

wetting behaviour of carbon black samples in liquids of known surface tension gives an indication about the range over which the surface energy has been reduced. The wetting behaviour of coated and uncoated carbon black samples are summarised in Fig. 4. After the formation of the plasma polymerised acetylene film, the surface of carbon black should show characteristics corresponding to the formed acetylene film: a lower surface energy. This also depends on the surface coverage of the film. Plasma treated carbon black N330 sample and E-250 g sample show a slight reduction in surface energy. The 1 h treated fullerene soot EP-P434 shows an appreciable reduction in surface energy, which corresponds with the substantial deposition, as already evident from the TGA results. Only the 4 h treated carbon black N330 shows a surface energy reduction similar to that shown by 1 h treated fullerene soot.

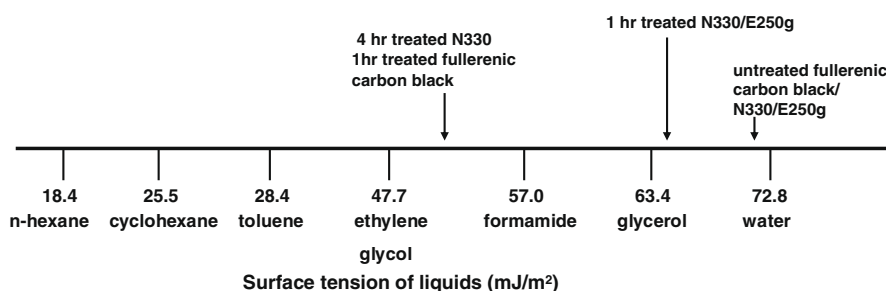


Fig. 4 – Schematic representation of the wetting behaviour of treated carbon black samples with liquids of known surface tension.

Plasma polymerisation of acetylene will result in the formation of a crosslinked hydrocarbon film. In a positive ToF-SIMS spectrum, such a hydrocarbon must show a cluster pattern of mass fragments, especially in the higher mass fraction regions [25]. A ToF-SIMS spectrum of a 1 h treated carbon black sample N330 is shown in Fig. 5. The spectrum shows less intense hydrocarbon peaks and shows only a small extent of cluster pattern in the higher mass fraction regions. The ToF-SIMS spectrum of 1 h treated fullerene soot is shown in Fig. 6. This spectrum shows intense hydrocarbon peaks and a good cluster pattern in the higher mass fraction regions. This observation, combined with the TGA results and the wetting behaviour, points towards the fact that the carbon black having fullerene active sites give a very good surface modification indeed. Whereas for the carbon black N330, the modification is minimal and the deposition might have happened only locally. On the other hand, after a long treatment time carbon black N330 also gave sufficient deposition on its surface as evident from the amount of deposition and its reduction in surface energy. Also it shows a better cluster pattern behaviour after 4 h treatment: Fig. 7.

It is clear from the above data that a plasma polymer film forms most readily on the surface of carbon black with fullerene active sites. In order to see whether the plasma coating affects the specific surface area, the BET surface area of the uncoated and plasma coated fullerene soot was measured. Before modification the fullerene soot had a surface area of 69 m²/g, whereas after the plasma polymer deposition, it reduced to 63.7 m²/g. TEM images were taken in order to visualize the plasma polymer coating over the surface of fullerene carbon black. Fig. 8 shows the TEM images of an uncoated fullerene carbon black. The image clearly reveals the surface with fullerene nanostructures, as reported earlier by Goel et al. [26]. It is worth mentioning that the fullerene structures are recondensed at the surface of the carbon black during the production of the fullerene, while towards the core the original structure is retained. The TEM image of the plasma coated fullerene carbon black is shown in Fig. 9. The image clearly shows the existence of the plasma polymer film over its surface. The average thickness of the coating was characterised to be in the range of 3–5 nm. In some regions, the thickness was in the range of 8–10 nm. These are areas which are exposed more to plasma, during the modification process. The TEM images also show that a total carbon black aggregate is encapsulated in a plasma polymer shell. This

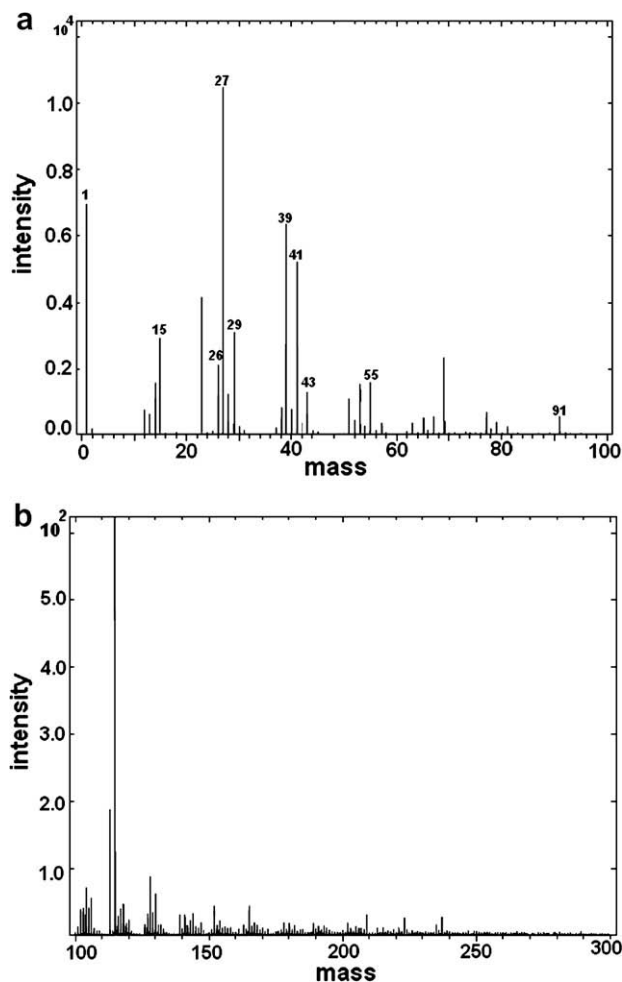


Fig. 5 – Positive ToF-SIMS spectrum of carbon black N330 treated for 1 h; (a) mass range 0–100; (b) mass range 100–300.

demonstrates that it is possible to deposit a plasma polymer film on irregular structures such as that of carbon black.

4. Discussion

It is clear that some modification has occurred on the surface of regular carbon black N330/E-250 g by deposition of plasma polymerised acetylene, but the extent of modification is little in comparison with the ease with which fullerene carbon black can be modified. The carbon black N330/E-250 g after 1 h treatment gave only a slight reduction in surface energy, whereas, the fullerene carbon black after 1 h treatment gave an appreciable reduction in surface energy. This difference in behaviour of these two carbon black is attributed to the different surface characteristics.

The surface of carbon black is known to consist of graphitic planes (site I), amorphous carbon (site II), crystallite edges (site III) and slit shaped cavities (site IV) [27]; Fig. 10. The conduction electrons associated with the graphitic structure play an important role in the amount of energy associated with these sites. Recently, Schroeder et al. [27–29] quantified the different energies at these sites on the surface

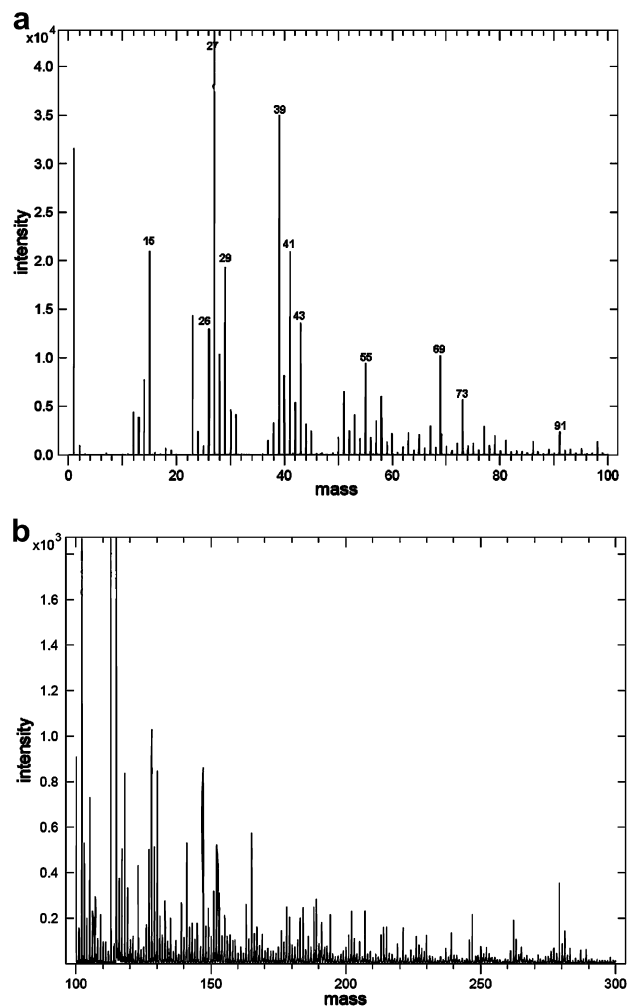


Fig. 6 – Positive ToF-SIMS spectrum of fullerene soot EP-P434 treated for 1 h; (a) mass range 0–100; (b) mass range 100–300.

of carbon black by analysing adsorption isotherms of various molecules. According to their analysis, particularly the crystallite edges (III) and slit shaped cavities (IV) on the surface of carbon black are the sites of high concentration of π -electrons. These sites are most important with respect to rubber filler and filler–filler interaction. Furthermore, the surface of carbon black is also covered with functional groups like carboxyl, phenol, lactones and quinonic groups. These are preferably located at the edges of the graphitic basal planes or at the crystallite edges. For furnace carbon blacks, the concentration of the active sites (II–IV) varies between 5 and 20% on the surface, and the other 95–80% is from graphitic planes (site I). Furnace carbon blacks with higher surface area and lower particle size have relatively higher fractions of these energetic sites (sites II–IV). As the surface area reduces and the primary particle size increases, the fraction of these sites decreases. Carbon black N330 has approximately 10% of type II, III and IV sites and the remaining 90% of the surface consists of graphitic planes.

In fullerenes and fullerene-like structures, the double bonds present are localised and weakly conjugated [30]. This is due to the strong deviation from planarity of the curved

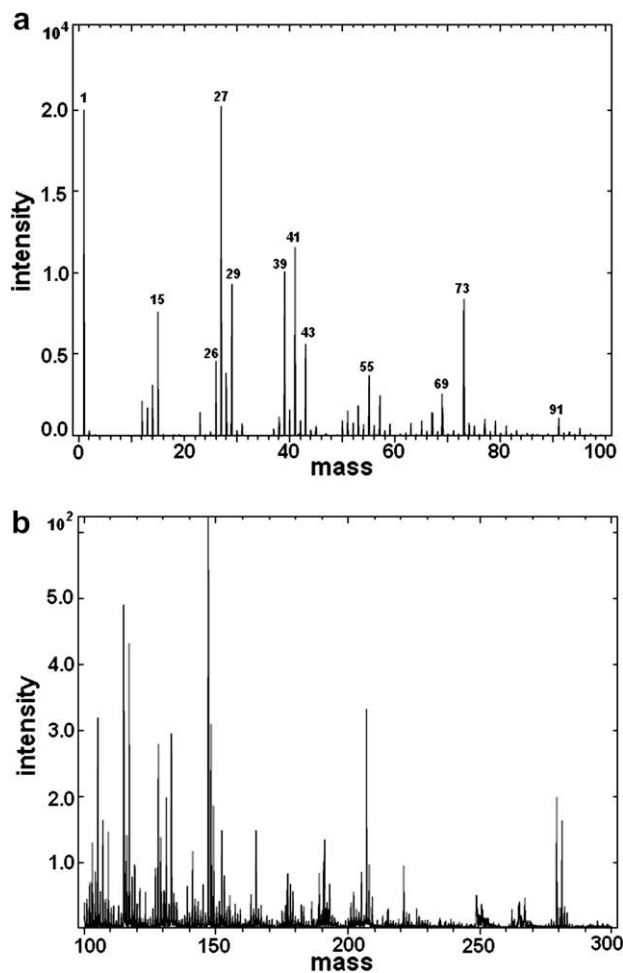


Fig. 7 – Positive ToF-SIMS spectrum of carbon black N330 treated for 4 h; (a) mass range 0–100; (b) mass range 100–300.

surfaces of these molecules (pyramidalisation). Fullerenes and their homologues have an unusually high electron affinity and have been defined as free radical sponges. The surface of fullerene carbon black contains these structures and con-

sequently makes the carbon material very reactive, which may be held responsible for the ease of plasma modification.

The excitation of gaseous molecules in the plasma generates active species like electrons, protons, excited molecules, ions etc. The energy required for the formation of a free radical is 3–4 eV, whereas the energy required for the formation of ions is 9–13 eV. The average electron energy in a low pressure discharge is in the range of 2–5 eV [31,32]. This energy is sufficient to break almost all types of bonds. Typical bond energies are given in Table 2. When the filler particles are exposed to the plasma atmosphere, the positive ions colliding on the substrate are capable of creating radical active sites on the surface, to which monomer active species can attach and further grow from there.

Therefore, when carbon black N330 is exposed to plasma, the following processes can happen:

1. C–C bond breakage in the graphitic planes. Due to breakage of these C–C bonds, radicals are generated on the graphitic planes. However, the graphitic structures are stabilised by resonance. As soon as radicals are generated, they will reform the bond and return to their stable state. In the present case, acetylene generates radicals of carbon as well. So the system will favour restructuring itself to its original state or to another favourable state by rearrangement. This reduces the chances of attaching a monomer active species on to the graphitic planes.
2. The breakage of C–O bonds and other functional groups, located at the crystallite edges. As soon as a C–O bond or another functional group located at the crystallite edges is broken, monomer active species can attach on to these sites, which is more favourable.

The thermodynamic feasibility of these processes can also be made clear on basis of the bond energy values: Table 2. The active sites formed on the graphitic basal planes are extremely short lived, so that they revert to their original state before the attachment of monomer active species has happened. Successful attachment of the monomer active species only happens at the sites generated at the crystallite edges, the sites generated by the bond breakage of the func-

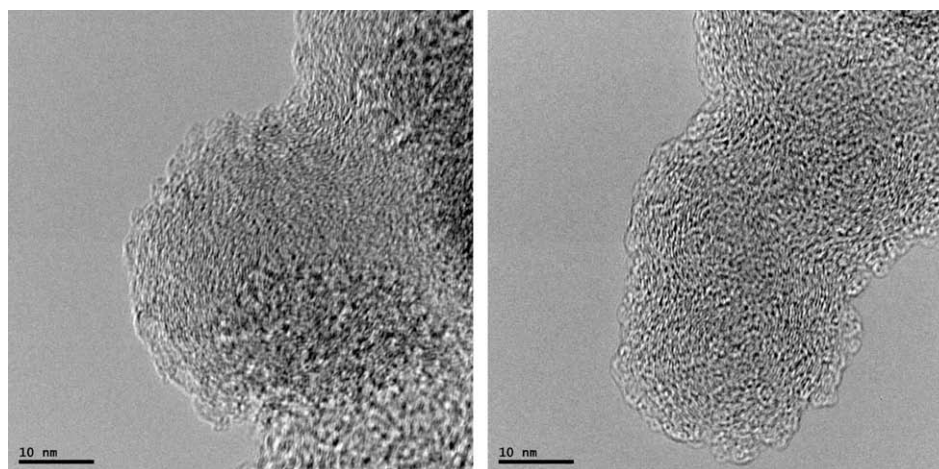


Fig. 8 – TEM images of fullerene carbon black.

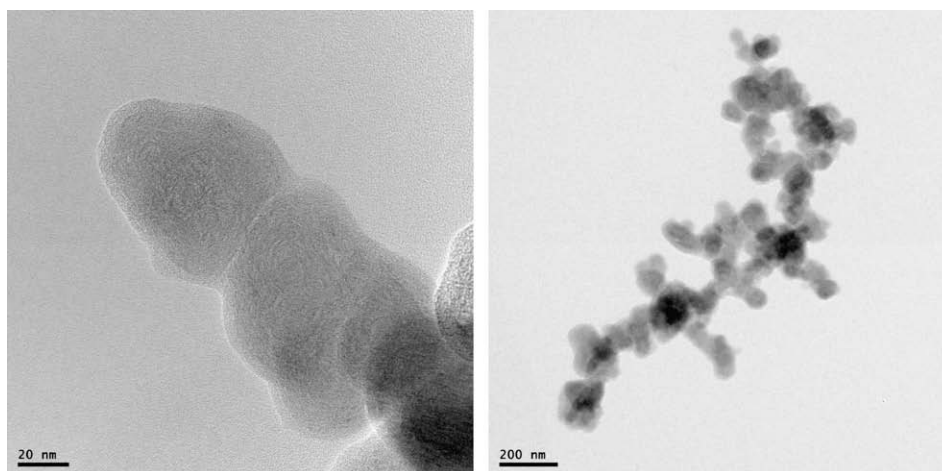


Fig. 9 – TEM images of plasma coated fullerene carbon black.

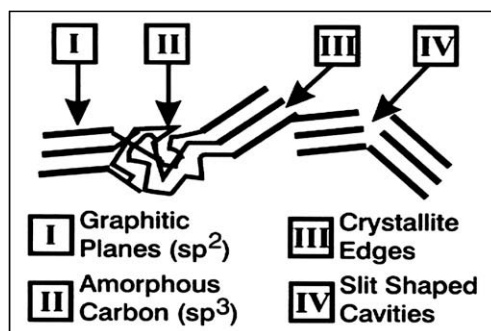


Fig. 10 – Schematic representation of various energetic sites on carbon black surface [27].

Table 2 – Bond energy values of typical bonds.

Bond type	Bond energy (kJ/mol)	Bond energy (eV/mol)
C–C	346	3.56
C=C	602	6.23
C≡C	835	8.65
C–O	358	3.70
C–F	458	4.73
C–H	411	4.25
C–S	272	2.80
Si–O	452	4.68
Si–C	318	3.28

tional groups. These sites represent somewhat higher bond energy, and cannot easily stabilise their radical nature by resonance. So it is only from these low concentrations of sites on the surface of carbon black that the plasma polymer can grow. That is the reason why so little plasma polymer coverage happens in the first place. In the case of fullerenic carbon black, fullerenic structures are present all over the surface. Hence during exposure to plasma, more stable active sites are formed. On to these sites monomer active species can attach and further grow from there. Also due to the fact that the stable active sites are formed all over the surface, the growing chains from neighbouring sites can link chemically, giving a good coverage within a short time.

5. Conclusions

Surface modification of two different categories of carbon blacks by plasma polymerisation was attempted using acetylene as monomer. Under the conditions applied, the amount of plasma polymer formed on the surface of regular carbon black N330 is very little in comparison with fullerenic carbon black. The thermodynamic feasibility of the attachment process is explained on the basis of bond energy values. Successful attachment of the monomer species on carbon black N330 takes place only at the low fraction crystallite edges. In the case of fullerenic carbon black, there is an abundant amount of fullerenic active sites all over the surface. Hence successful attachment of monomer species takes place on to these sites. Also due to the fact that the stable active sites are formed all over the surface, the growing chains from neighbouring sites are linked chemically giving a good coverage of the plasma polymer film over the carbon black surface.

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