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Effects of ozone oxidation on carbon black surfaces

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Surface effects of ozone treatment with a fluidized bed-type reactor on carbon black have been studied. It has been observed that the surface oxygen level is proportional to the total volume of ozone supplied per unit area of carbon black surface. The ozone treatment increases the acidity of the carbon black surface. A limiting pH value has been obtained at a surface oxygen concentration of around 6 at %. The surface oxygen introduced on the carbon black is most likely present as carboxylic acid groups as indicated by both high-resolution X-ray photoelectron spectroscopy and Fourier transform–infrared spectroscopy results. The ozone treatment of a carbon black decreases the tensile strength for a natural rubber (non-polar), but increases the tensile strength for a nitrile butadiene rubber (polar).

1. Introduction

The surface modification of carbon blacks has received much attention due to the great importance of their surface chemistry in a number of industrial applications. Where carbon black is used as a filler in rubber, good dispersion in the rubber matrix is necessary for optimum mechanical properties. Various oxidation methods, including nitric acid [1–3], ammonium persulphate [4], phosphorus pentoxide (P_2O_5) [3], potassium dichromate ($K_2Cr_2O_7$) [3], and plasma [5]. Although reports of surface modification of carbon black with ozone can be found in the literature [6–8], there is a lack of detailed investigation on the surface effects of this treatment. In this work, we studied the effects of ozone treatment on carbon black surfaces. Ozone treatment parameters were studied. X-ray photoelectron spectroscopy (XPS) and Fourier transform–infrared spectroscopy (FT–IR) were used to examine the oxidation level and functional groups introduced on the surface. The effects of this oxidation on the acidity of the carbon black and on the properties of carbon black-filled rubber were also investigated.

2. Experimental procedure

2.1. Materials

The carbon blacks used in this study were obtained from Cabot. Their specific surface areas, together with their surface elemental compositions (from XPS) are shown in Table I. It can be seen that untreated carbon blacks have very low levels of oxygen and sulphur.

2.2. Ozone treatment

Carbon blacks were treated with ozone in a laboratory-scale fluidized bed-type reactor, as schematically shown in Fig. 1. The carbon black was put in the reactor and oxidized with ozone by flowing the ozone/oxygen mixture through the reactor. The ozone concentration in the O_3/O_2 mixture varied between 0% and 3% by volume, depending on the ozonization voltage and the flow rate of oxygen through the ozonator (BA023, Wallace and Tieman Ltd).

The ozone concentration in the O_3/O_2 gas mixture was determined by iodometry. About 800 ml gas mixture containing ozone was directed into a 250 ml gas-washing bottle containing 200 ml 2% KI aqueous solution. Ozone was found to rapidly and completely react with the KI solution, because no further detectable reaction with KI of the gas emitted from the KI solution in the gas-washing bottle was found. The resultant KI solution was acidified with 20 ml 1 M H_2SO_4 and the iodine produced was titrated with 0.1 M $Na_2S_2O_3$ using 1 ml 1% starch aqueous solution as an indicator. 1 mol O_3 generates 1 mol I_2 [9] and therefore the ozone concentration in the gas mixture can be calculated from the amount of $Na_2S_2O_3$ used.

2.3. XPS and FT–IR analysis of carbon black

Treated and untreated carbon blacks were analysed with XPS and FT–IR. XPS was performed on a VG ESCALAB spectrometer using an AlK_α X-ray source (1486.6 eV) under a vacuum of 10^{-7} torr

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TABLE I Specific surface areas (from nitrogen adsorption) and surface elemental compositions (from XPS) of carbon blacks used in this study

Carbon black	Specific surface area ($m^2 g^{-1}$)	Surface elemental compositions (at %)		
		C	O	S
N115	139.5	98.9	0.6	0.5
N326	78.3	99.0	0.6	0.4
N330	78.0	98.6	0.9	0.5
N550	38.9	98.5	0.9	0.6
N762	32.2	98.4	1.1	0.5

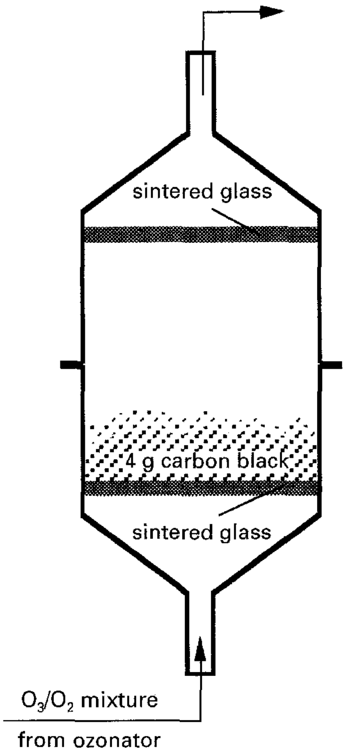

Figure 1 Fluidized bed-type reactor for ozone treatment.

(1 torr = 133.322 Pa). Survey scan spectra were recorded with a pass energy of 85 eV, while high-energy resolution spectra were recorded with a pass energy of 20 eV. Details of quantification can be found in a previous paper [10].

Transmission infrared analysis of carbon blacks was performed on a Nicolet DXC20 FT–IR spectrometer. About 0.4 g potassium bromide (KBr) was ground in an agate mortar with ~0.04 g carbon black for approximately 5 min. About 0.04 g of the ground mixture was further diluted with KBr to a carbon black concentration of 0.05% (by weight) and ground for 3 min. After pressing 0.400 g of the final mixture into a KBr disc (diameter 0.5 in, ~1.25 cm) it was dried for 2 h in a clean oven at ~120 °C before IR analysis. The atmospheric water spectrum was removed from the final IR spectra by subtraction.

2.4. Measurement of the pH value and rubber properties

The pH value was measured using a sonic slurry method according to ASTM D1512-84. 1.5 g carbon black was weighed into a 30 ml beaker into which 20 ml triple-distilled water (boiled and cooled to room temperature) was then added. Three drops of acetone (HPLC grade) were added to aid dispersion. The beaker was then agitated for 3 min in an ultrasonic bath. The pH value of the carbon black slurry was then measured using a Corning 220 pH meter which was calibrated using pH buffers of 4.0 and 7.0 before the measurement.

To examine the effects of ozone oxidation on the carbon black-filled rubber properties, both untreated and ozone-oxidized carbon blacks were compounded with a natural rubber (NR) or a nitrile butadiene rubber (NBR). Rubber mixing was carried out on a Haake Rheocord 90 [11]. The tensile strength of the cured rubber samples was measured according to BS 903.

3. Results and discussion

3.1. Ozone-treatment parameters

XPS has shown a strong O 1 s peak after the ozone oxidation. While the treatment significantly increases the surface oxygen concentration, it has been observed that it has little effect on the specific surface area as determined by nitrogen adsorption. For example, a specific surface area of 79.3 $m^2 g^{-1}$ has been found for the carbon black which was oxidized with ozone for 2 h at an ozonization voltage of 200 V and an oxygen flow rate of 50 $l h^{-1}$. This is very similar to that of the untreated carbon black (78.0 $m^2 g^{-1}$).

The effects of ozone-treatment parameters, i.e. ozonization voltage, oxygen flow rate, and the time of treatment, were investigated by using the carbon black N330. Each parameter was studied by keeping others constant.

With the increase of the ozonization voltage, the ozone concentration in the O_3/O_2 mixture increased and, as expected, the surface oxygen concentration of the carbon black also increased. Increasing the flow rate of oxygen decreased the ozone concentration but increased the carbon black surface oxygen concentration. This is attributed to the increase in total volume of ozone produced as higher flow rates are used. Carbon black surface oxygen concentration was significantly affected by treatment time. It increased steadily with treatment time when the ozonization voltage and the oxygen flow rate were kept constant.

The carbon black surface oxygen concentration is plotted against the total volume of ozone supplied in Fig. 2. Data points were calculated from those on the studies of the treatment parameters. It can be seen that there exists a complex relationship between carbon black surface oxygen concentration and total ozone supplied. Two plateaus exist at surface oxygen concentrations of around 6 and 11 at %.

Carbon blacks with various specific surface areas were oxidized with ozone. It has been found that under the same treatment conditions, the carbon black surface oxygen concentration decreases with increasing surface area, as shown in Fig. 3. It has already been found that for the same carbon black, the oxidation level is dependent on the volume of ozone

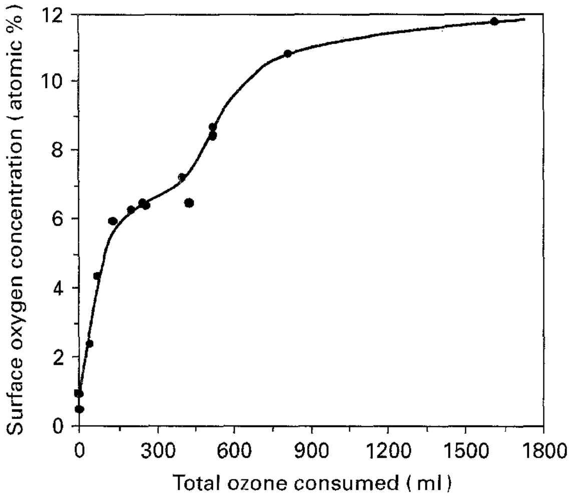

Figure 2 Effects of total volume of ozone supplied on carbon black (N330) surface oxygen concentration.

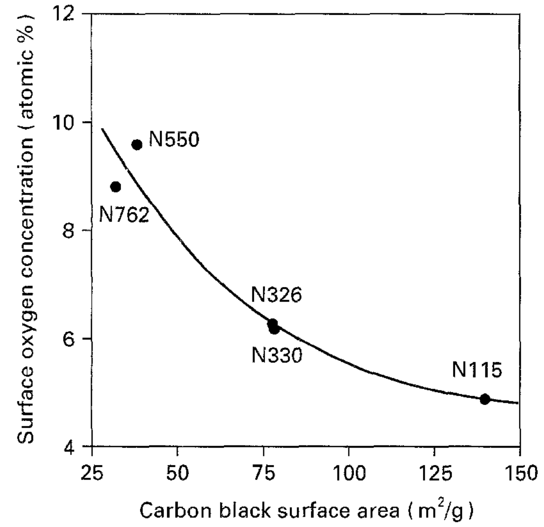

Figure 3 Effects of carbon black specific surface area on surface oxygen concentration by ozone treatment. Ozonization voltage 200 V, oxygen flow rate 50 l h^{-1}, treatment time 15 min.

supplied (Fig. 2). Therefore, it can be further concluded that the surface oxidation level is related to the volume of ozone supplied per unit carbon black surface area.

3.2. Effects of ozone oxidation on pH value

It has been found that the pH value of the carbon black aqueous slurry is reduced significantly by ozone oxidation. Fig. 4 shows a plot of pH value against carbon surface oxygen concentration. The pH value initially decreases significantly with increasing surface oxygen concentration and then reaches a limiting pH value of around 2.0 above a surface oxygen concentration of around 6 at %. The initial decrease can be attributed to the introduction of acidic oxygen-containing groups (e.g. carboxylic acid) on the carbon black surface by ozone treatment (see high-energy resolution XPS and FT–IR results below). It is interesting to note that the 6 at % oxygen concentration corresponds to the inflexion of the curve in Fig. 2. One possible explanation is that the 6% is related to the limiting monolayer oxidation level of the carbon black. Further increase in surface oxygen concentration can be attributed to the increase in oxidation level below the first monolayer, and therefore it does not affect the pH value. XPS detects the elemental compositions within a depth of around 80 nm of the carbon black, and it is less surface specific than the pH measurement because the pH is only determined by the chemistry of the outmost molecular layer on the carbon black surface.

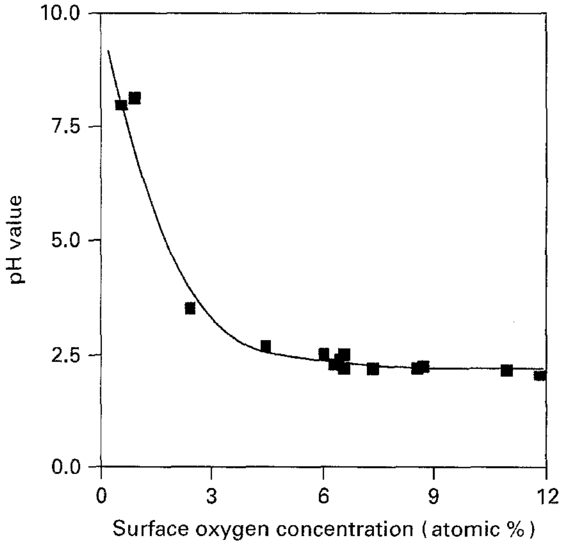

Figure 4 pH value of carbon black (N330) with various surface oxidation levels.

3.3. High-energy resolution XPS and FT–IR investigation

High-energy resolution XPS was used to study the chemical structure on the carbon black surface. Fig. 5 shows the C 1 s spectra of untreated and treated carbon black (N330). It clearly shows that a chemically shifted peak at 289.0 eV (equivalent to a chemical shift of 4.4 eV) which can be attributed to –C(=O)–O– groups (e.g. carboxylic acid, ester), the broad peak at around 6.7 eV is π–π* shake-up structure of the carbon black.

Fig. 6 shows transmission IR spectra of N330 before and after ozone oxidation. The ~1600 cm^{-1} peak can be attributed to quinone-like structures, and the ~1280 cm^{-1} peak is due to C–O in various chemical environments. These peaks are present on both carbon blacks. The most prominent change induced by the oxidation is the appearance of the peak at around 1720 cm^{-1} which can be attributed to either ketone (C=O) or carboxylic acid (–COOH) groups. Considering the high-energy resolution results, it is most probably due to carboxylic acid groups because no ketone groups (with a chemical shift of ~3.0 eV) were detected. It has also been found that the absorbance at 1720 cm^{-1} increases with the surface oxygen concentration detected by XPS (see Fig. 7).

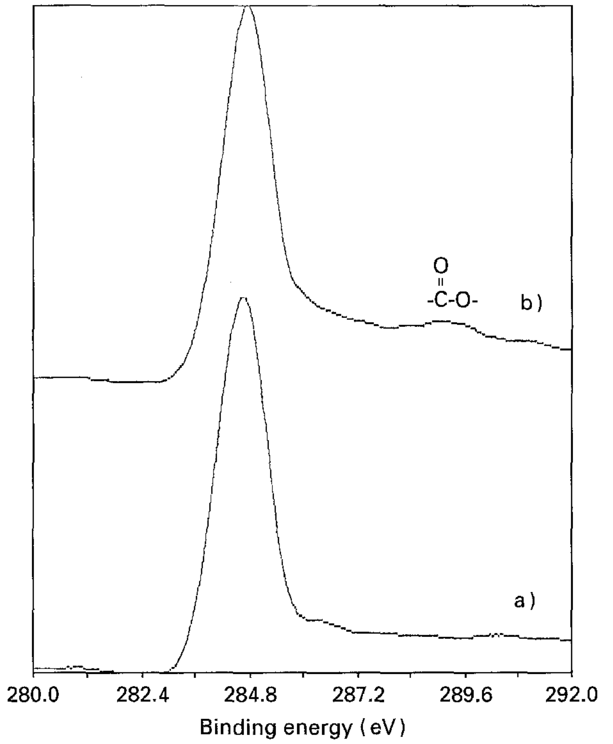

Figure 5 High-energy resolution C1 s XPS spectra of carbon black N330, (a) untreated, (b) ozone oxidized for 2 h at an ozonization voltage of 200 V and an oxygen flow rate of $50\,\mathrm{l\,h^{-1}}$.

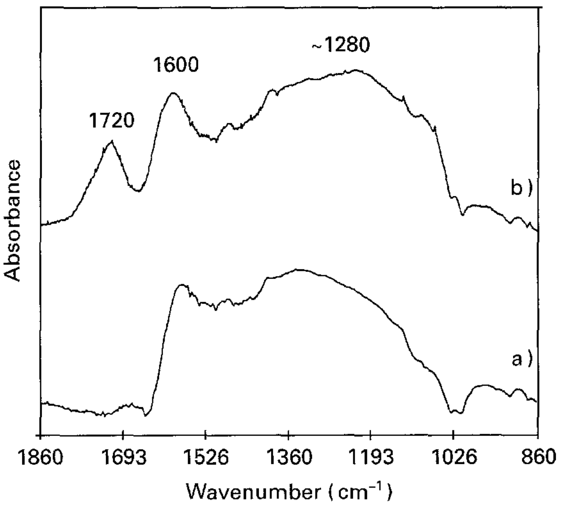

Figure 6 IR spectra of carbon black N330, (a) untreated, (b) ozone oxidized for 2 h at an ozonization voltage of 200 V and an oxygen flow rate of $50\,\mathrm{l\,h^{-1}}$.

3.4. Effects of ozone oxidation on rubber properties

Table II shows the effects of ozone oxidation on the tensile strength of carbon black-filled NR and NBR. It can be seen that the oxidation decreased the tensile strength for the non-polar rubber (NR), but increased the tensile strength for the polar rubber (NBR). The increase for the NR can be attributed to the perturbation of the carbon black surface graphitic structure by the ozone oxidation, resulting in a weaker carbon black–rubber interaction. The increase in tensile strength for the NBR can be attributed to the significant increase in surface polarity induced by the oxidation, resulting in a stronger polar–polar interaction between the carbon black and the polar rubber. Surface free energies of carbon blacks can be estimated from the heat of immersion calorimetry results which will be reported in a future paper.

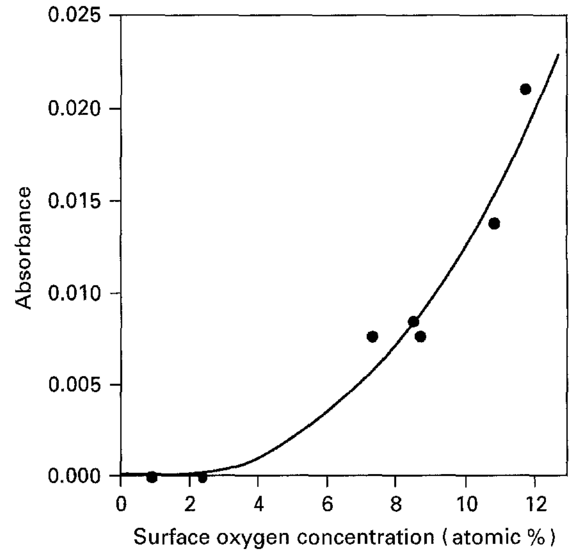

Figure 7 Relationship between IR absorbance at $1720\,\mathrm{cm^{-1}}$ and surface oxygen concentration from XPS of ozone oxidized carbon black N330.

TABLE II Tensile strength of carbon black-filled natural rubber (NR) and nitrile butadiene rubber (NBR)

Carbon black	NR	NBR
N330 untreated	25.0	16.4
N330 ozone oxidized[a]	22.0	22.2

[a] Ozone treatment conditions: 200 V, $50\,\mathrm{l^{-1}\,h}$, 1 h.

4. Conclusion

Effects of ozone treatment on carbon black surfaces have been studied. Surface oxygen concentration has been found to increase with ozonization voltage, oxygen flow rate, and the treatment duration. The oxidation level was found to depend on the total volume of ozone used and the surface area of carbon black. The pH value of the carbon black aqueous slurry was found to first decrease with carbon black surface oxygen concentration (determined by XPS) and then level off above 6 at %. High-energy resolution XPS and FT–IR results have shown that the dominant functional groups introduced by the oxidation were carboxylic acid groups. The ozone treatment of a carbon black decreases the tensile strength for a natural rubber (non-polar), but increases the tensile strength for a nitrile butadiene rubber (polar). The decrease in tensile strength for NR can be attributed to the perturbation of carbon black surface graphitic structure, and the increase for NBR can be attributed to the increased carbon black surface polarity by the ozone treatment.

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