

AN INVESTIGATION OF THE ACTIVITY OF CARBON BLACKS RECOVERED FROM ELASTOMER COMPOSITES

J. Azizi¹, D. Dollimore^{1}, G. R. Heal², W. A. Kneller³,
P. Manley¹ and C. C. Philip¹*

¹Department of Chemistry and College of Pharmacy, University of Toledo, Toledo, OH, USA

²Department of Chemistry and Applied Chemistry, University of Salford, Salford, UK

³Department of Geology, University of Toledo, Toledo, OH, USA

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Abstract

The activity of carbon blacks recovered from elastomer systems is determined by use of a temperature jump technique imposed on the carbon blacks in air using a TG unit. The elastomer composites were composed of styrene-butadiene rubber (SBR), fillers, activators, accelerators together with a number of different carbon blacks. The organic content was pyrolyzed away by heating in nitrogen, the atmosphere was changed to air and the activity of the carbons was assessed by the temperature jump method. This enables the Arrhenius parameters to be established for the gasification of the carbons in air. This data was compared with the oxidation rates of carbons before they were introduced into the elastomer system. Nitrogen adsorption surface areas based on a BET analysis showed that the surface area of the carbons was similar before and after incorporation into the composite. The kinetic parameters of the carbons were however somewhat altered by incorporation into the elastomer systems, but their order of activity towards the gasification process as assessed by their relative rate of gasification remained the same. This is explained by postulating that the higher rates of oxidation is associated with the presence of edge carbon atoms at the surface compared to the much slower oxidation rates of the 'basal' plane carbon atoms. It appears that this surface structure is largely retained in the composite carbon-elastomer system. This enables some speculation regarding the reinforcing action of certain carbon blacks in the composite system.

Keywords: elastomer composites, rubber

Introduction

In this investigation the oxidizing capacity of carbon blacks recovered from elastomer composites is compared with the oxidizing capacity of the same car-

* Author to whom all correspondence should be addressed:
Dr. David Dollimore, University of Toledo, Department of Chemistry,
Toledo, OH 43606, USA.

bons before incorporation. The method of determining kinetic parameters on carbon blacks by use of a temperature jump method using a TG balance has been reported in a previous study [1].

It is possible according to the literature to adopt an alternative method of identifying the carbon blacks after they have been incorporated. The method is based on determining the temperature in a TG experiment at which 15% of the black has been oxidized [2].

Carbon blacks are formed by the degradation of organic compounds from the vapour phase. They are used as reinforcing fillers in rubber. Carbon blacks usually contain 95–99% elemental carbon with oxygen and hydrogen making up the remaining major elements present. Carbon blacks differ from other carbons (e.g. graphite, charcoals, and coke) because they are composed of spherical particles and are quasi-graphitic in structure the primary particle size is found to be small (diameters 14 μm to 122 μm) with high largely external surface areas (up to 150 m^2g^{-1}) [3]. These differences have a profound effect upon the incorporation of carbon blacks into the rubber. The manufacture of carbon black is an important industrial process the majority of the production being incorporated into an elastomer and used in tire manufacture [4].

Experimental

Equipment

A Stanton-Redcroft thermogravimetric unit TG 1000 was used coupled with an Omnitherm computer workstation. The surface area determinations were achieved using a nitrogen volumetric BET unit [3].

Materials

The elastomer-carbon blends were prepared in accordance with ASTM D-3191. The recipe used here was prepared as follows and conforms to a typical blend, noted in Table 1. The various carbon blacks used in this study to make up a set of elastomer-composites differing only in the carbon black used are designated by the ASTM recommended method and are listed in Table 2.

The mixing of the elastomer composite was done in accordance with 'method A mill mixing of rubber' as described in ASTM D-3191.

The temperature jump on the carbon blacks before they were incorporated into the elastomer system has been described [1] and consisted of heating the sample in the TG unit to 450°C, changing the atmosphere to air and then raising the temperature in increments of 10°C for twenty minutes until 6 linear mass loss steps of mass against time were recorded. The carbons in the elastomer system were also subjected to a temperature jump oxidation after the organic content was pyrolyzed in a nitrogen atmosphere until the organic content was

Table 1 Ingredient of elastomer-composite blend

Ingredients	Parts per hundred	Recipe/g
Polybutadiene-styrene copolymer (SBR) 1502	100.00	400
Carbon Black	50.00	200
Zinc Oxide	3.00	12
Stearic Acid	1.00	4
N-tert-butyl-2-benzothiazole sulfenamide (TBBS)	1.00	4
Sulfur	1.75	7

- 1) SBR 1502 is the elastomer which is not oil extruded. This raw rubber was supplied by Copolymer Rubber and Chemical.
- 2) Zinc Oxide was used as an activator. It was 99.50% pure, designated CT-4 and supplied by G. and H. Chemicals.
- 3) Stearic acid was also used as an activator. It was labelled rubber makers grade and supplied by H. B. Chemicals.
- 4) TBBS was supplied by the Monsanto Chemical Company and also acts as an accelerator.
- 5) The sulfur was labelled rubber makers grade and supplied by Harvick Chemical Company.
- 6) Various carbon blacks were used as noted in Table 2.

Table 2 Carbon blacks used in this study

Grade ASTM specification	Supplier
N110	Cabot
N234	Columbian
N326	Columbian
N330	Columbian
N550	Witco
N650	Witco
N660	Cabot
N774	Columbian

lost. The sample was then allowed to cool to 400°C, heated on the TG unit to 470°C in air at a low rate of 10 mL per minute. The temperature was then raised 10°C for twenty minutes in incremental steps as described in the temperature jump test of the carbons before incorporation into the elastomer system. The nitrogen volumetric BET method was used to determine the surface area [3]. This however meant that larger quantities of the carbon freed from the elastomer system had to be obtained. The procedure was to employ an airtight furnace with a programmable heating rate. The samples were heated in a crucible in a nitrogen gas flow up to 615°C. The temperature was held constant at 615°C for

45 min and the samples of carbon recovered on cooling down to room temperature.

Results and discussion

The experimental determined nitrogen adsorption surface areas of the carbons before and after polymer burn off are given in Table 3. In most cases the carbon black still retained its original surface area after polymer burn off.

Table 3 Nitrogen adsorption data on carbon blacks

Grade	Surface area before polymer burn off/m ² g ⁻¹	Surface area after polymer burn off/m ² g ⁻¹
N110	141	116
N234	127	124
N326	84	80
N330	86	83
N550	48	49
N650	41	49
N660	35	45
N774	30	39

The temperature jump method has already been outlined. A typical plot of mass against time is shown in Fig. 1 for a carbon before burn off. Figure 2 shows similar data for another carbon but this time plotted as mass against temperature in Fig. 2. Similar data was collected for all carbon samples before they were incorporated into the elastomer system and those recovered from the elastomer composite. The methods of calculating the Arrhenius parameters from this data has been explained in detail in a previous study [1]. Table 4 shows the Arrhenius parameters for the carbon blacks before and after polymer burn off. It can be seen that the inclusion of the carbon black into the elastomer system does not alter the energy of activation very much except in a few cases but it does alter the pre-exponential term (the entropy of activation). This might have been expected for the process of inclusion in, and separation from the elastomer system would cause some reorganization of the carbon surface. It is possible to compare rates of oxidation of the carbon blacks at 743 K before and after polymer burn off (Table 5). The rates of oxidation of carbon blacks before inclusion in the polymer was determined at 774 K and at 794 K and the order of reactivity found to be similar at both temperatures. The interpretation of this kind of data is reported in detail in an earlier study [1]. In this study the order of reactivity on the reaction rates of the carbon separated from the elastomer composite was also determined at 763 K and found to be similar to that recorded at 743 K

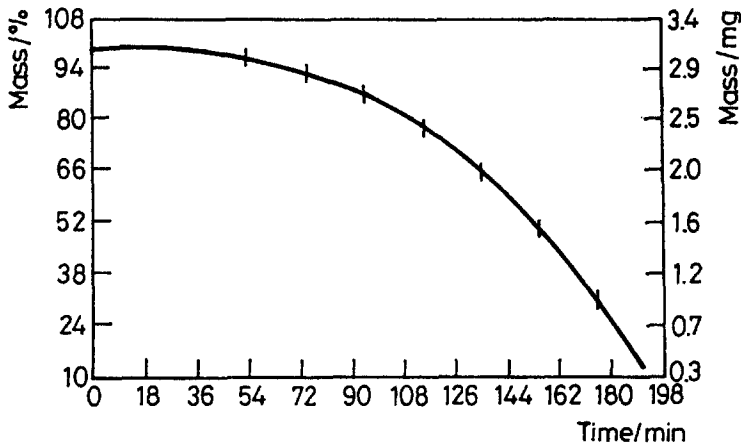


Fig. 1 Plot of mass vs. time in the temperature jump method for carbon black

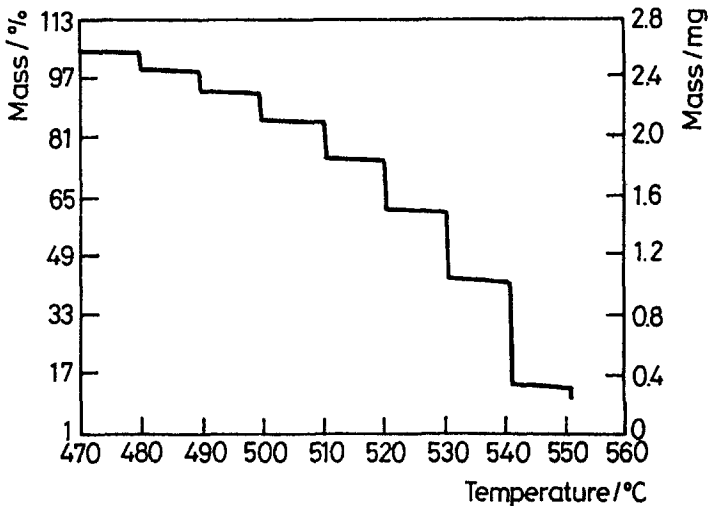


Fig. 2 Plot of mass vs. temperature in the temperature jump method for carbon black

shown in Table 5. The concept outlined in the earlier study was that the reaction of carbon with oxygen produces surface oxygen complexes which decompose to form gaseous products. Two components at the carbon surface were identified, one called the active surface associated with fast oxidation and gasification while the other component termed inactive was associated with relatively slow oxidation rates. This is the reason why the specific reaction rate quoted in Table 5 is referred to unit area using the BET surface area (Table 3).

The active sites for gasification by oxygen were identified with 'edge' carbon of the graphitic platelets forming the surface structure of the carbon black (for

Table 4 Arrhenius parameters for carbon blacks before and after burn off

Sample	Before burn off		After burn off	
	A/min^{-1}	$E/\text{kJ mol}^{-1}$	A/min^{-1}	$E/\text{kJ mol}^{-1}$
N110	$4.1 \cdot 10^{10}$	190.5	$3.8 \cdot 10^5$	183.0
N234	$4.4 \cdot 10^{10}$	128.8	$1.3 \cdot 10^5$	115.5
N326	$1.9 \cdot 10^7$	140.4	$4.1 \cdot 10$	67.2
N330	$2.0 \cdot 10^6$	125.4	$1.5 \cdot 10^4$	102.6
N550	$2.5 \cdot 10^{10}$	138.9	$6.2 \cdot 10^2$	83.2
N650	$1.6 \cdot 10^8$	152.5	$6.3 \cdot 10^4$	113.9
N660	$2.4 \cdot 10^8$	158.9	$1.3 \cdot 10^2$	72.7
N774	$1.0 \cdot 10^{10}$	182.2	$1.9 \cdot 10^3$	92.8

Table 5 Comparison of rates of oxidation of carbon blacks at 743 K before and after polymer burn off

Sample	$K/\text{surface area} \times 10^5$		$K/\text{unit area relative to carbon N774}$	
	Before burn off	After burn off	Before burn off	After burn off
N110	0.70	6.39	0.13	0.40
N234	3.44	7.33	0.66	0.45
N326	3.47	0.10	0.67	0.62
N330	2.45	0.11	0.47	0.69
N550	2.40	8.04	0.46	0.50
N650	5.37	0.11	1.03	0.70
N660	5.00	0.23	0.96	1.40
N774	5.20	0.16	1.00	1.00

schematic portrayal see Fig. 3). The inactive surface sites were identified with 'basal plane' atoms of the graphitic platelets (Fig. 3).

Grisdale [5] and Smith and Polley [6] showed that the rate of oxidation of carbon crystallites is about 17 times faster in the direction parallel to the basal planes (along their edge atoms described here as 'edge atoms') than perpendicular to them. From the previous publication [1] it was deduced that low surface area carbon blacks tended to have faster rates per unit area of surface than the higher area surface area carbons. The results here are in agreement with the earlier findings; the order of reactivity towards oxygen (from Table 5) is at 744 K.

$$N650 > N774 > N660 > N326 = N234 > N550 > N330 > N110$$

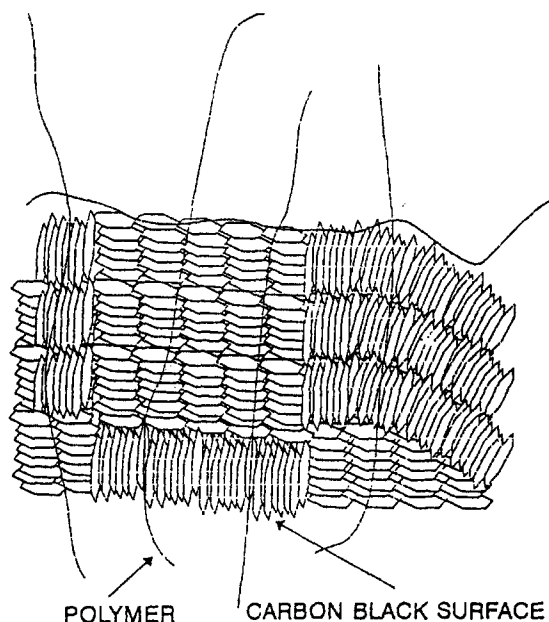


Fig. 3 Schematic portrayal of carbon black-polymer surface

At 774 K the order of reactivity is similar

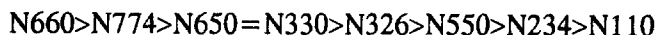


and at 794 K the reactivity sequence is

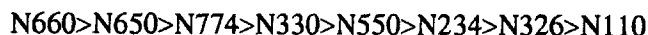


The conclusion from this data must be that lower surface area carbon blacks have a greater proportion of their surface consisting of 'edge' carbon atoms while the higher area carbon blacks expose a larger proportion of the relatively inactive basal plane carbon atoms.

The evidence to be drawn from the oxidation rates of carbons after separation from the elastomer matrix is that their oxidation rates at 743 K is



and at 763 K is



The conclusion is again that lower surface area carbon blacks have a greater proportion of their surface consisting of 'edge' carbon atoms while the higher

area carbons expose a larger proportion of the basal plane carbon atoms. Although the actual order of the oxidation reactivity is changed, the same trend is apparent in the carbons separated from the elastomer system then the reactivity of the carbons before inclusion into the polymer complex. It is known that smaller surface area carbon blacks act mainly as fillers in elastomer formulations while the higher area carbon blacks actually have reinforcing action [7]. It can therefore be a reasoned speculation that bonding between the carbon blacks and the elastomer concerns the 'basal' plane atoms of the carbon black graphitic structures and not the 'edge' atoms. A schematic portrayal of this situation in the elastomer carbon interface is provided in Fig. 3.

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