

OBSERVATIONS ON THE THERMOGRAVIMETRIC OXIDATION OF CARBON BLACKS IN VULCANIZATES*

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ABSTRACT

Thermogravimetric oxidation under isothermal conditions of carbon black residues from styrene-butadiene rubber vulcanizates was investigated as a method of identification of carbon black type. Although a relationship has been reported between the rate of oxidation and the surface area of the carbon black, we have found that this relationship holds only for some carbon blacks significantly separated in surface area. Further, we have found that the rate of oxidation can be quite different for the same type of carbon black produced by different manufacturers, and that the rate of oxidation of the carbon black residue from the pyrolyzed vulcanizate can depend on the procedure used for mixing and vulcanizing the rubber compound. This technique, therefore, cannot be recommended as generally suitable for identification of carbon black type in an unknown vulcanizate.

The isothermal oxidation technique used in conjunction with the derivative thermogram has been found to be useful in determining the amount of carbon black in carbonizing elastomers such as chloroprene and nitrile rubbers.

INTRODUCTION

Carbon black is the most important reinforcing agent used in the rubber industry. Reinforcing blacks consist of chains or three dimensional networks of primary particles, the spatial distribution of which defines the degree of structure. In the free state, carbon blacks are readily characterized by such properties as specific surface area, particle diameter and bulk density. Identification of the type of black present in a vulcanizate is more difficult. Methods which have been used involve the isolation of the carbon black either by breakdown of the vulcanizate with nitric acid or pyrolysis and subsequent characterization of the carbon black by light absorbance¹⁻³, reflectance^{4, 5} or adsorption⁶⁻⁸. The possibility of a simpler technique based on thermogravimetry was first suggested by Maurer⁹.

Thermogravimetry has been extensively used to determine the composition of vulcanizates⁹⁻¹² including the quantitative amount of carbon black present. The

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vulcanizate is heated at a given rate up to $\sim 550^{\circ}\text{C}$ in a nitrogen atmosphere and, provided the elastomeric components do not carbonize, the residue at 550°C consists of the original added carbon black and any inorganic component. If the elastomer is carbonizing, the residue at this stage also contains a carbonaceous residue which is formed by cyclization and/or condensation reactions of the polyene chains. Typically¹³, by 700°C the hydrogen/carbon ratio of this residue is ~ 0.15 . Introduction of an oxygen-containing atmosphere at greater than 500°C results in oxidation of the carbon black leaving only the inorganic material present in the original vulcanizate.

In analytical studies, Maurer⁹ reported that the rate of oxidation when the recovered black was heated dynamically, was a function of the surface area of the virgin carbon black. The temperature at which 15% of the carbon black was oxidized was compared for a wide range of carbon blacks recovered from butyl vulcanizates, varying in surface area from 20 to $120\text{ m}^2/\text{g}$. In later studies¹⁴, the rate of oxidation was determined under isothermal conditions and mixtures of FEF and SRF identified in EPDM/NR/SBR vulcanizates. Pautrat et al.¹⁵ applied the dynamic heating oxidation method for the identification of a wide range of blacks (MT, SRF, HAF and EPC) in NR, SBR, NBR, IIR and EPDM vulcanizates, and also found a linear relationship between oxidation rate and surface area. These authors also discussed the difficulty of determining the carbon black present in a carbonizing elastomer (NBR). Swarin and Wims¹⁰ reported no difficulty in separating FEF black from an NBR carbonaceous residue using the dynamic heating oxidation method.

In this paper, the isothermal oxidation method is applied to a much wider range of carbon blacks including those very similar in surface area but differing in structure. Using the isothermal method with a controlled diluted oxygen atmosphere and simultaneously recording the derivative thermogravimetric (DTG) thermogram offers advantages, although several black types cannot be differentiated. The method is also applied to carbonizing neoprene and NBR vulcanizates for the determination of carbon black content.

TABLE 1

CARBON BLACKS AND PROPERTIES

<i>ASTM</i>	<i>Type</i>	<i>Surface area^a</i>	<i>Comments^b</i>
N 110	SAF	153	Corax A, Statex 160
N 220	ISAF	128	
N 326	HAF-LS	105	
N 330	HAF	100	Printex, Statex R, Philblack O
N 347	HAF-HS	105	
N 550	FEF	80	Statex M, Corax 9
N 660	GPF	46	
N 770	SRF-HM	41	Furnex H, Durex O
N 990	MT		Philblack

^a Manufacturers' surface area value. Calculated from particle size, determined by electron microscopy.

^b All blacks Columbian Carbon Co. except where noted.

EXPERIMENTAL

Materials

All carbon blacks were used directly as received. Table I summarizes the types used. Throughout the text, the ASTM type designation¹⁶ will be used. Carbon blacks of similar type but from different manufacturers are identified, where necessary, by trade name. All vulcanizates were prepared by standard laboratory techniques¹⁷ following ASTM D-15. All carbon blacks were compared in an SBR 1500 formulation at the 50 phr level carbon black. A standard accelerated sulphur cure system was used throughout. Neoprene and nitrile rubber vulcanizates were prepared similarly; however, carbon black levels were varied and these are given in the text. Vulcanizates containing German-manufactured blacks were prepared in the Dunlop Research Centre, Hanau, Germany.

Thermogravimetry

A Dupont 951 thermogravimetric analyzer was used in conjunction with the Dupont 990 control module equipped with a $x-y-y'$ recorder and simultaneous derivative recording.

The heating program used to prepare the carbon black residue and the subsequent isothermal oxidation temperature was varied to suit the elastomer type. For SBR vulcanizates, 15–20 mg of vulcanizate was pyrolyzed in a nitrogen stream (200 ml/min) at 50°C/min up to 525°C, and then isothermal conditions established. The oxidizing atmosphere, 7% oxygen in nitrogen, was then admitted to the sample at 100 ml/min and the weight loss recorded as a function of time. The dilute oxygen (supplied by Matheson Canada Ltd.) was used to reduce the exothermicity of the oxidation which, in a richer atmosphere, often went out of control, destroying reproducibility. Rates of oxidation of different recovered blacks were compared using the time for 20% weight loss (t_{20}) from six runs after introduction of the oxidizing atmosphere.

Experimental conditions used with the neoprene vulcanizates were different to accommodate the rapid hydrogen chloride evolution in the 250–350°C range. Pyrolysis in nitrogen was carried out at 5°C/min up to 350°C and then at 20°C/min to 700°C. The latter temperature was chosen arbitrarily as the stop temperature, as even at 1000°C, weight loss still occurs from the carbonaceous residue. The 700°C residue was allowed to cool to 350°C in nitrogen and then heated to 540°C at which temperature the oxidizing atmosphere was admitted at 100 ml/min.

RESULTS AND DISCUSSION

SBR vulcanizates

Figures 1 and 2 illustrate the dependence of t_{20} upon the surface area and particle size of the carbon black. Surface area and particle size refer to the virgin blacks as reported by the manufacturer. The range of values found for t_{20} is shown by

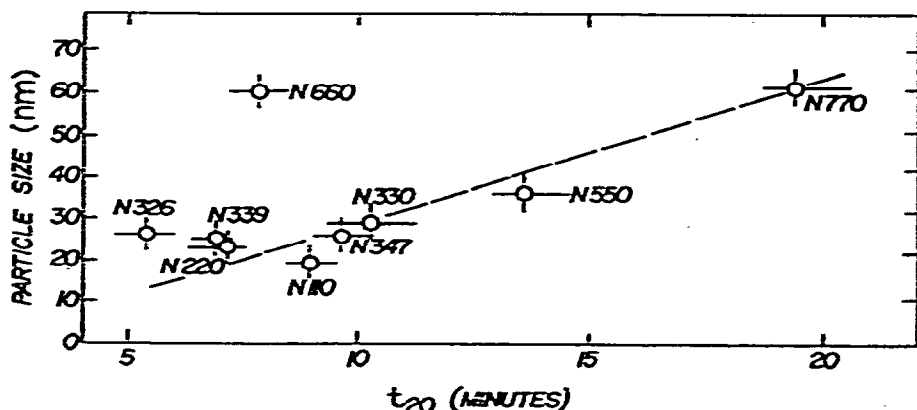


Fig. 1. Particle size of carbon black versus t_{20} for oxidation of carbon black recovered from SBR vulcanizates. Oxidation carried out isothermally at 525°C in 7% oxygen in nitrogen flowing at 100 ml/min.

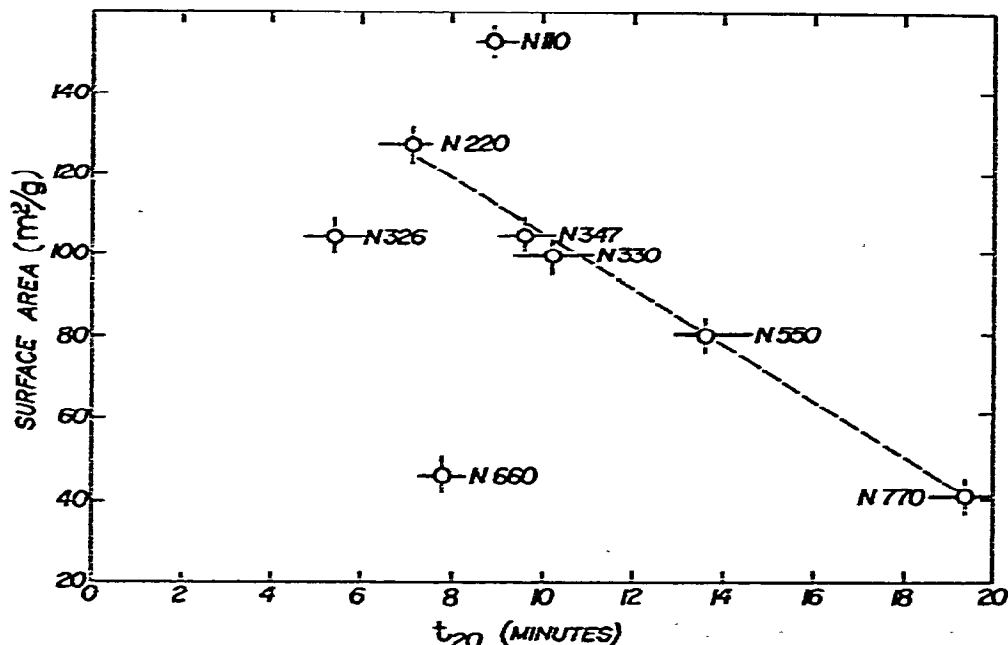


Fig. 2. Specific surface area of carbon black versus t_{20} for oxidation of carbon black recovered from SBR vulcanizates. Oxidation carried out isothermally at 525°C in 7% oxygen in nitrogen flowing at 100 ml/min.

the horizontal lines and the mean values indicated by the vertical line. The broken line in Fig. 2 is the least squares line excluding the results obtained for N 110, N 326 and N 660 types.

The results obtained are in good agreement with those in the literature^{14, 15} for carbon blacks with significant differences in surface area and particle size, i.e. N 770, N 550, N 330 and N 220. Clearly, a simple relationship between surface and oxidation rate does not hold for N 110, N 326 and N 660 carbon blacks. Further, because of the

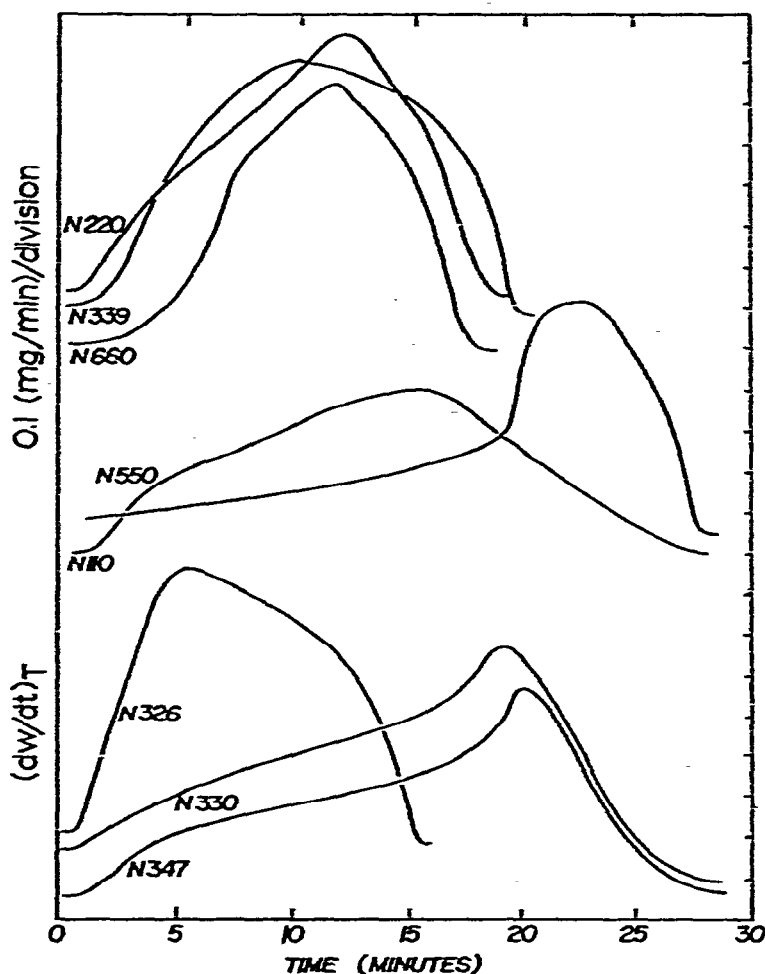


Fig. 3. Derivative curves for the oxidation of carbon blacks recovered from SBR vulcanizates. Oxidation carried out isothermally at 525°C in 7% oxygen in nitrogen flowing at 100 ml/min.

range of values and similarity of t_{20} for several black types, differentiation between N 220 and N 339 and N 110, N 347 and N 330 would be difficult on the basis of t_{20} alone.

Figure 3 illustrates the DTG thermograms for the carbon blacks recovered from SBR vulcanizates. The rate of weight loss is recorded directly and indicates the rate of oxidation as a function of time. The carbon blacks are arbitrarily grouped for ease of presentation. However, the N 326 (HAF-LS), N 330 (HAF) and N 347 (HAF-HS) have been grouped to illustrate the effect of structure. These three blacks have very similar surface area (Table 1). The oxidation profile of N 326 is very similar to that of N 220, N 339 and N 660 blacks which have both considerably higher (N 220) and lower (N 660) surface areas. Clearly, the oxidation rate dependence on surface area has no validity. N 110, the highest surface area black studied ($153 \text{ m}^2/\text{g}$) oxidizes much more slowly than N 220, N 326, N 339 or N 660.

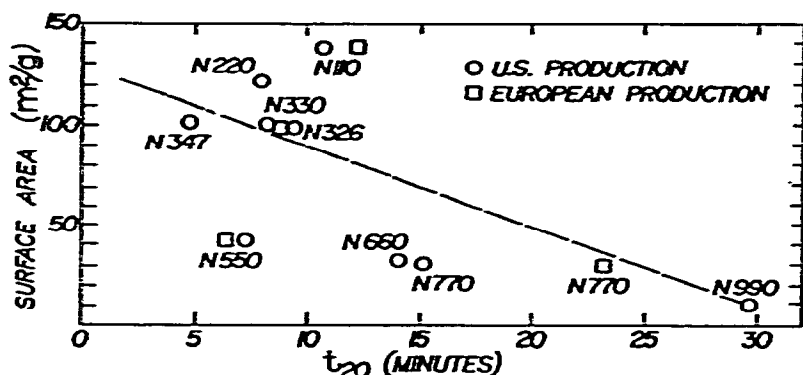


Fig. 4. Specific surface area of carbon black versus t_{20} for oxidation of virgin carbon blacks. Oxidation carried out isothermally at 600°C in 7% oxygen in nitrogen flowing at 100 ml/min.

The oxidation of the two small particle size blacks N 347 and N 330 as well as N 550 at 525°C is quite different from the other blacks. Oxidation starts immediately the oxidizing atmosphere is admitted and then, after a period of slow oxidation, the rate suddenly increases. N 770 black, the smallest surface area (41 m²/g) studied in SBR, is not illustrated; N 770 oxidized at a uniform rate until completely volatilized and t_{20} was 19.2 min.

Since we have used the specific surface area of the virgin blacks and assumed that there has not been any change during the mixing, curing and thermal degradation, it is of interest to compare t_{20} data for the virgin blacks. Figure 4 illustrates results obtained for t_{20} of virgin blacks as a function of surface area. Differences in t_{20} between virgin and recovered blacks are greater than the recovered blacks as reported by Maurer¹⁴. SBR is considered non-carbonizing as it leaves less than 1% carbonaceous residue. However, it appears that the small residue or the thermal treatment effectively makes the carbon black surface more reactive to oxidation. A large shift to shorter t_{20} is observed for virgin N 550 (FEF). Again, the results obtained for the virgin blacks suggest that the rate of oxidation does not correlate well with surface area.

The situation is complicated further when the same grades of carbon blacks produced in different locations are compared. Figure 4 contains data for North American and German manufactured N 110, N 326, N 550 and N 770 virgin blacks. Excellent agreement in t_{20} is found for all grades except N 770. Figure 5 illustrates results obtained using N 110, N 326, N 550 and N 770 of different manufacture in SBR vulcanizates. Vulcanizates were prepared in our laboratory using the North American material and in both our laboratory and Dunlop Research Centre, Germany, using the German manufactured blacks. Although agreement for the same grade is fair for N 110, problems are encountered with N 326, N 550 and N 770 grades. With the N 770 grade, wide variations are apparent not only between the manufacturers' product, but also in different laboratories' mixing these high particle size blacks. The results possibly suggest that particle size can alter during the mixing process which, if it occurs, makes the identification of carbon blacks in unknown samples very

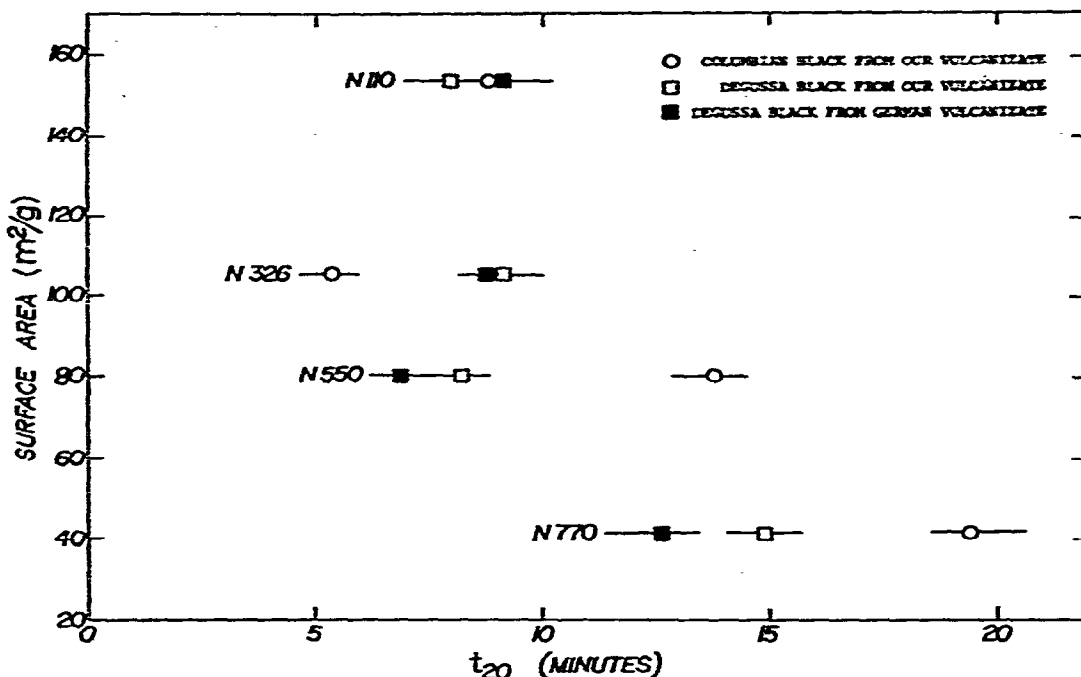


Fig. 5. Comparison of t_{20} for carbon blacks from two different sources recovered from vulcanizates. Oxidations carried out isothermally at 525°C in 7% oxygen in nitrogen flowing at 100 ml/min.

speculative. Also metal oxides are known to catalyze the oxidation of carbon black¹⁸, and the differences in rate that we observe may be due to the presence or absence of traces of metal oxides or salts.

The manufacturers' surface area data quoted in Table I was calculated from particle diameters determined by electron microscopy. Correlation of t_{20} with other measurements indicative of surface area such as dibutyl phthalate or iodine adsorption give results with similar scatter. A detailed discussion of carbon black structure is outside of the range of this paper. Hess and McDonald¹⁹ have made a careful study of the specific shapes of carbon particles in various grades and classified them into nine basic shapes. Little correlation could be found between t_{20} and the predominance of a given shape (e.g. spherical or fibrous) in a given grade of carbon black.

Neoprene and NBR vulcanizates

As previously mentioned, thermogravimetric analysis for carbon black in these carbonizing polymers is complicated by the formation of a carbonaceous residue. Presumably, carbon black recovered from the vulcanizates is coated with the carbonaceous residue which at 550°C is not pure carbon black but contains other elements. Pautrat et al.¹⁵ reported that N 110 and N 330 blacks oxidized at the same temperature as the residue from NBR, whereas the N 770 and N 990 blacks could be separated because of their higher oxidation temperature. Swarin and Wims¹⁰ reported that FEF black could be distinguished from the NBR residue. In both studies, a dynamic heating program was used with the oxidation.

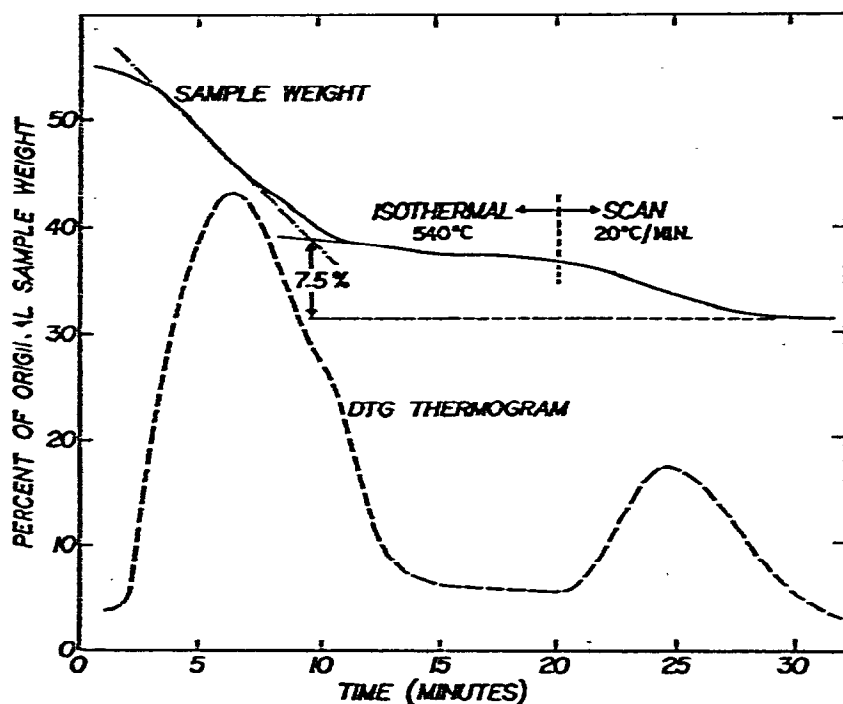


Fig. 6. Weight loss and derivative of weight loss curves for the oxidation of the residue remaining from the pyrolysis in nitrogen of a Neoprene W vulcanizate containing 9% of N 550 black and 36.5% inorganics. Oxidation carried out isothermally at 540°C in 7% oxygen in nitrogen flowing at 100 ml/min.

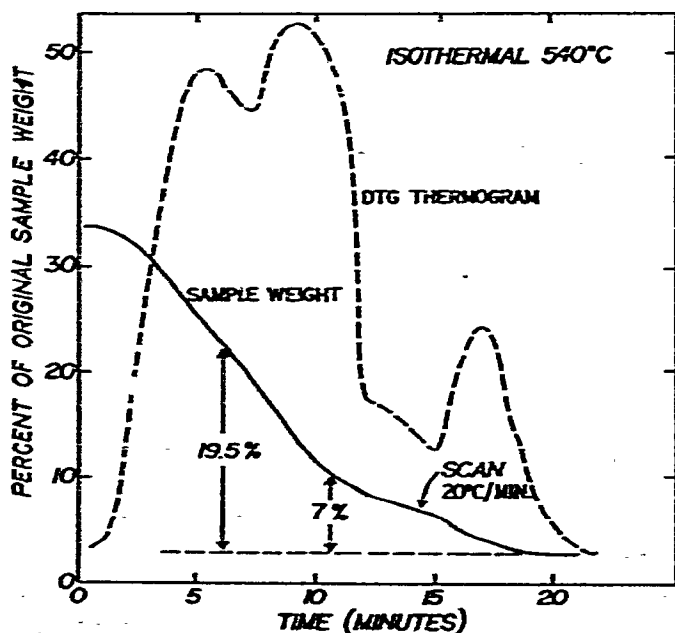


Fig. 7. Weight loss and derivative of weight loss curves for the oxidation of the residue from the pyrolysis in nitrogen of a 50:50 natural rubber/Neoprene WRT blend containing 13.5% N 326 and 6.7% N 990 carbon blacks. Oxidation was carried out isothermally at 540°C in 7% oxygen in nitrogen flowing at 100 ml/min.

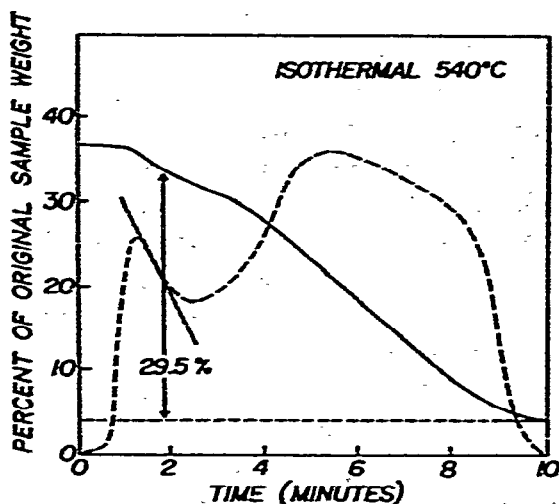


Fig. 8. Weight loss and derivative of weight loss curves/or the oxidation of the residue from the pyrolysis of a 85:15 34% NBR/EPDM blend containing 30% N 326 black. Oxidation was carried out isothermally at 540°C in 7% oxygen in nitrogen flowing at 100 ml/min.

The ability of the isothermal method to separate oxidation of the carbonaceous residue from the carbon black has been evaluated. Typical results for neoprene vulcanizates are shown in Figs. 6 and 7. Analysis of a Neoprene W vulcanizate containing 9% by weight N 550 black and a high loading of inorganic fillers is shown in Fig. 6. Oxidation of the carbonaceous residue at 540°C is much faster than the N 550 black. Note that to decrease analysis time after 20 min at 540°C, the sample was programmed at a heating rate of 20°C/min. The carbon black loading was calculated to be 7.5% in fair agreement with the added 9.0%.

Figure 7 illustrates the thermogravimetric results obtained with a more complex system containing NR and Neoprene WRT as well as a mixture of N 990 and N 326 blacks. The derivative thermogram is particularly useful in separating the oxidation of the carbonaceous residue and the N 326 black. Again, the sample was heated at 20°C/min to expedite oxidation of the N 990 black. The level of each black was determined as shown in Fig. 7 and gave 12.5% N 326 and 7% N 990, compared to the added values of 13.5% N 326 and 6.7% N 990. Similar results can be obtained with carbonizing NBR vulcanizates as illustrated in Fig. 8. The NBR vulcanizate contains 30% N 326 (HAF-LS) carbon black and the derivative separates the oxidation of the carbonaceous residue and the N 326, the latter showing a similar oxidation profile as N 326 recovered from SBR vulcanizates.

In the above, we have shown that by choice of an appropriate temperature and dilute oxygen atmosphere, the oxidation of medium particle size reinforcing blacks can be separated from the oxidation of the carbonaceous residue. Thus, derivative thermogravimetry can still be used with carbonizing polymers to determine carbon black loadings. Identification of carbon blacks similar in nature would still be a problem, as with SBR vulcanizates.

SUMMARY

The rate of oxidation of carbon blacks recovered from vulcanizates by pyrolysis in a nitrogen atmosphere has been determined for a wide variety of commercial carbon blacks. Although a relationship has been reported between the rate of oxidation and the surface area of the carbon black, it has been shown that this relationship only holds for some carbon blacks significantly separated in surface area. Two notable exceptions are N 110 (SAF) and N 660 (GPF) which exhibit very similar oxidation rates, yet are different in surface area by about a factor of four. Further, it has been shown that the rate of oxidation can be quite different for the same grade of carbon black produced at different locations, and that the rate of oxidation can depend on the location and procedure used for mixing and vulcanizing the compound.

It is our conclusion that extreme caution must be taken in using the thermogravimetric oxidation procedure to identify the type of carbon black used in an unknown vulcanizate. This does not negate the value of the method for determining the amount of carbon black present in an unknown vulcanizate, nor the use of the technique for regular "in-house" quality control.

The oxidation technique used in conjunction with the derivative thermogram has also been shown to be useful in determining the amount of carbon black in carbonizing polymer systems. By judicious choice of the isothermal oxidation temperature, the oxidation of medium and high surface area carbon blacks can be separated from that of the carbonaceous residue. As in the case of noncarbonizing polymers, the method would not be infallible in identification of the type of black.

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