

An electron spin resonance investigation of carbon black-filled polybutadiene

E. M. CASHELL, V. J. McBRIERTY

Physical Laboratory, Trinity College, University of Dublin, Dublin, Ireland

This paper describes an ESR investigation complemented with X-ray measurements, of *cis*-polybutadiene filled with a range of carbon blacks. The aim was to derive further insight into the rubber–carbon black interaction. There are two distinguishable free spin species in the carbon blacks; free spin carriers and localized free spins. There appears to be a correlation between the localized free spin concentration and defects concentrations in the carbon blacks as determined by X-ray measurements. The interpretation of experimental data emphasizes the importance of considerations of the “structure” parameter of the carbon blacks.

1. Introduction

The continuing interest in the reinforcement phenomenon in filled rubbers has focused latterly on the free-spin characteristics of these materials [1–3]. In particular ESR investigations of Sullivan and Wise [1] and of Waldrup and Kraus [3] on the one hand and those of Baugher and Ellis [2] on the other, into carbon black-reinforced rubber systems (SBR and natural rubber) have highlighted important differences in the various data obtained.

ESR studies on such filled systems are motivated by the fact that free–radical interactions between the polymer chains and the carbon black particles feature prominently in the development of bound rubber [4–6] which, in turn, bears a close correlation to reinforcement [7–9]. This idea gains support from the known free radical affinity of active carbon blacks [10] and also from the observation that the milling process leads to facile rupture of the polymer molecules to provide another free radical source [11].

Thus, Sullivan and Wise and Waldrup and Kraus reported a broad symmetric ESR resonance in filled SBR, at cryogenic temperatures ascribable to the incorporated active carbon black filler, with a superimposed narrow resonance which they attributed to free radicals produced in the masticated rubber by the milling process [11]. These free radicals are considered to be stabilized in the ensuing interaction between the elastomer chains

and the carbon black surface. In contradistinction, Baugher and Ellis [2] detected a broad asymmetric orientation-dependent resonance, also found in unfilled rubber and attributed to paramagnetic impurities, together with the carbon black signal. They found no trace of a narrow resonance and suggested that the free radicals responsible for the narrow signal may be unstable at the ambient temperature at which they conducted their experiment.

The detection of a resonance in unfilled and unmasticated SBR rubber [2] adds further complexity and shows the need for continued experimentation.

This paper describes an ESR investigation, complemented with related X-ray measurements, on the comprehensive series of filled *cis*-polybutadiene samples which were the subject of an earlier nmr study into the nature of the carbon black–rubber interaction [12]. These experiments, we believe, will provide further insight into the reinforcement mechanism and the apparent anomalies in the existing ESR data on other filled rubbers,

2. Experimental

Room temperature spectra were recorded on an X-band Bruker spectrometer (B-ER 420) employing a rectangular resonant cavity operating in the TE 102 mode. Spectra at other temperatures were obtained on a Varian X-band spectrometer

adapted for use with an Oxford Instruments continuous flow cryostat which provided temperature control to within ± 1 K from liquid nitrogen to room temperatures. A double-walled quartz inset permitted sample cooling without the necessity of cooling the complete cavity. X-ray data on the

carbon blacks were recorded on conventional Phillips X-ray diffraction equipment using $\text{CuK}\alpha$ radiation.

2.1. Sample preparation

Details of sample preparation are listed in Table I where the sample code broadly follows that used in the previous work [12]. An additional parameter studied here is the degree of milling which has been quantified in terms of the number of passes through the nip of a cold (water-cooled) open mill after removal from the internal mixer. The polymer studied throughout was a linear high ($> 96\%$) *cis*-polybutadiene of density 1.01 g cm^{-3} and the characteristics of the carbon blacks used are listed in Table II. Sample preparation was effected several months before analysis to ensure equilibrium of the bound rubber. The latter was obtained from each filled rubber composite by extraction with hot toluene under an atmosphere of nitrogen in a Soxhlet extractor. Samples were placed in a 2 mm internal diameter quartz tube and sealed under vacuum. Neat carbon black samples were lightly crushed to avoid possible skin effects [13–15].

2.2. Data acquisition and analysis

The parameters of importance in ESR spectra include linewidths, g values and signal source spin concentrations, the latter being the most difficult to assess. Spin concentration is proportional to the area under the resonant absorption curve which is obtained from double integration of the recorded first derivative ESR signal. A comparison is made with a reference of known spin content to arrive at an absolute measure of the spin concentration [16–18]. This procedure is attendant with considerable difficulties, particularly when there is more than one component present in the spectrum [13, 17, 19, 20]. Feher [21] and Poole [17] have considered the problem in detail and the results of their analysis may be expressed in the following simplified expression where the sample and the standard are run on the same spectrometer under comparable conditions [22, 23].

$$\frac{N_{\text{sample}}}{N_{\text{standard}}} = \frac{A_{\text{sample}} Q_{\text{standard}}}{A_{\text{standard}} Q_{\text{sample}}} \quad (1)$$

N is the number of spins per gram, A the area under the resonance absorption curve and Q is the loaded Q of the cavity. The standard used was the

TABLE I

Code	Filler	Loading (phr)	Milling (No.)	Mixing temp. (°C)
1	—	—	—	—
2	Purified BR + ISAF	50	30	~70
3	Statex GPF	100	30	84
4	Statex GPF	90	30	84
5	Statex GPF	80	30	84
6	Statex GPF	70	30	84
7	Statex GPF	60	30	84
8	Statex GPF	50	30	84
9	Statex GPF	40	30	84
10	Statex GPF	30	30	84
11	Statex GPF	20	30	84
12	Regal SRF	50	30	89
13	Statex GPF	50	30	86
14	Philblack A FEF	50	30	100
15	Statex R HAF	50	30	71
16	Vulcan 6 ISAF	50	30	79
17	Vulcan 6 ISAF	50	30	—
18	Statex GPF	100	3	84
19	Statex GPF	100	5	84
20	Statex GPF	100	10	84
21	Statex GPF	100	15	84
22	Statex GPF	100	20	84
23	Statex GPF	100	30	84
24	Statex GPF	100	40	84
25	Statex GPF	100	50	84
26	Statex GPF	100	60	84
27	Statex GPF	100	70	84
28	Vulcan 6	100	0	84
29	Vulcan 6	100	1	84
30	Vulcan 6	100	3	84
31	Vulcan 6	100	5	84
32	Vulcan 6	100	7	84
33	Vulcan 6	100	10	84
34	Vulcan 6	100	15	84
35	Vulcan 6	100	20	84
36	Vulcan 6	100	25	84
37	Vulcan 6	100	30	84
38	Vulcan 6	100	40	84
39	Vulcan 6	100	50	84
40	Vulcan 6	100	60	84
41	Vulcan 6	100	80	84
42	Vulcan 6	100	100	84
43	Vulcan 6	100	120	84
44	Vulcan 6	100	140	84
45	Vulcan 6	100	160	84
46	Vulcan 6	100	180	84
47	Vulcan 6	100	200	84

TABLE II Carbon blacks

Type	N ₂ (BET) Surface area (m ² g ⁻¹)	Em diam. (nm)	Mineral oil absorption (cm ³ g ⁻¹)	Apparent specific vol. at 734 psi (cm ³ g ⁻¹)
SRF	30.3	67–83	0.6–0.75	1.20–1.35
GPF	29.3	46–63	1.26–1.36	1.30–1.40
FEF	43.4	31–46	1.27–1.43	1.40–1.70
HAF	83.5	18–30	.98–1.05	1.45–1.60
ISAF	104.3	17–28	1.09–1.15	1.45–1.75
g HAF	62–88	26–35	.94–1.14	1.45–1.60
g GPF	25–30	50–65	1.26–1.36	1.30–1.40

Varian 3.3% pitch in KCl, equivalent to an estimated 10^{13} spins per cm of sample length, with a quoted accuracy of $\pm 25\%$ [16].

The area under the absorption curve was determined directly on a Nicolet 1074 analog computer interfaced to the spectrometer. The narrow line contribution was readily assessed by subtraction of the appropriate carbon black broad resonance signal from the total spectrum. A recurring feature of the carbon black resonance was the failure of the spectrum to return to the base line. This was partially compensated for by assuming a linear base line drift and subtracting an appropriate count from the estimated area. Because of the large error of $\pm 25\%$ quoted for the standard, the accuracy in the determination of absolute spin concentrations were accordingly limited. However, each spin assay was repeated a number of times with a reproducibility of $\sim 3\%$. Because the accuracy of the spin determination is dependent on the overall width of the spectrum, [15], errors were somewhat larger for the carbon black resonances.

3. Results and discussion

3.1. Carbon blacks

An understanding of the filled systems required an ESR characterization of those carbon blacks with which the polybutadiene was filled. The detailed analysis by Kraus *et al.* [13, 14] provided carbon black spin concentrations of 10^{19} to 10^{20} spins g⁻¹

and 10^{18} spins g⁻¹ for the graphitized material. Our ESR results are consistent with these observations (Table III) within an order of magnitude. In particular, we observe an unusually high spin concentration for the GPF black. This is consistent with measured linewidth which is much greater than those already reported in the literature [13–15, 24].

In considering the nature of the carbon black spin species it is pertinent first to examine related X-ray and electron microscope evidence [27]. Current interpretations envisage a paracrystalline microstructure for the carbon black particle with the layer of carbon atoms as the basic repeating entity [28–32]. The observed diffuseness of the X-ray diffractions is a manifestation of interdefect distances [27, 32, 33]. Indeed, the development of defects has been observed in other carbonaceous materials [34, 35].

In the interpretation of our X-ray diffraction data, we have expanded upon these notions to arrive at an estimate of the defect concentration per gram of carbon black in the hope that there will be some correlation with the observed free spin concentration. A hexagonal array of defects has been assumed in our calculation for which the results are presented in Table IV. Quantitatively there is rough comparability between the number of defects and the number of stable free spins (Table III). The polyaromatic character of the structure would certainly facilitate the stabil-

TABLE III ESR data on carbon blacks

Type	Total spin conc. per gram ($\times 10^{19}$)	Local spin conc. ($\times 10^{19}$)	Cond. spin conc. $\times 10^{19}$	Fraction local spins	ΔH_{vac} (G)	$\frac{\Delta H_{air}}{\Delta H_{vac}}$	g value
SRF	7.5	—	—	—	39	1.26	2.0133
GPF	57.0	13.0	44.0	0.22	~ 600	—	2.0142
FEF	10.2	7.0	3.2	0.69	60	1	2.0139
HAF	4.8	2.1	2.7	0.44	67	1.88	2.0086
ISAF	7.0	3.8	3.2	0.54	39	1.85	2.0077
g HAF	0.43	—	—	—	3.1	~ 1	~ 2
g GPF	0.61	—	—	—	5.2	~ 1	~ 2

TABLE IV

Carbon black	L_a^* (Å)	L_c^\dagger (Å)	No. defects per gram
SRF	28.1	12.3	1.3×10^{20}
GPF	22.9	11.2	2.2×10^{20}
FEF	29.2	11.8	1.3×10^{20}
HAF	26.2	10.8	1.7×10^{20}
ISAF	24.2	10.5	2.1×10^{20}

* L_a = Mean inter-defect distance in layer.

† L_c = Mean inter-defect distance perpendicular to parallel layer.

ization of free spins associated with defects through resonance configurations [13, 36].

Studies by Spackman [15, 25, 26] have led to the conclusion that some of the spins in carbon black may be due to charge carriers and this idea has gained support from observations of the temperature dependence of the ESR response in carbon black, complemented by Hall measurements [37–39]. Our ESR data in fact support this two-spin theory: in addition to the variation of signal intensity expected from a Curie-like temperature-dependent paramagnetism, assigned to local spin centres, we observe a Pauli-type paramagnetism, independent of temperature, which is assigned to hole carriers in the π -conduction band.

Following Mrozowski [37–39], the ratio R of the room temperature signal intensity to that at liquid nitrogen temperatures allows one to determine the relative concentrations of localized spins to conduction carriers according to

$$R = 0.88x + y(1 - x) \quad (2)$$

where x is the fraction of conduction carriers and y is the ratio of the temperatures. The factor 0.88 takes account of a slight temperature dependence in the Pauli paramagnetism.

The concentrations of the two types of spin, estimated from Equation 2 are listed in Table III. Of particular note is the fact that the high overall spin concentration in GPF black is primarily due to conduction spins. Reviewing again the defect concentration data, we are tempted to suggest a closer correlation between *localized* spins, rather than total spins, and the structural defects.

An interesting feature of the carbon black results is the rough linearity observed between the line width ratio, $\Delta H_{\text{air}}/\Delta H_{\text{vac}}$, and the specific surface area of the black (Fig. 1). We envisage this ratio to be a measure of the interaction of these

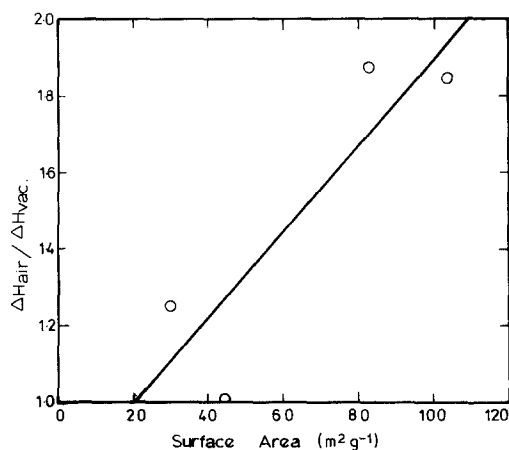


Figure 1 The dependence of carbon black surface area upon the ratio of the resonance line-width in air to the line-width *in vacuo*.

spins on the carbon black surface. The fact that the greatest change in line-width occurred for those blacks with the largest surface area highlights the surface character of at least some of the free spin species.

There was no obvious correlation between spin concentrations or line width and various physical properties of the blacks such as specific surface area, particle diameter or structure.

3.2. Filled polybutadiene

Incorporation of the carbon blacks into polybutadiene gives rise to two long-lived ESR resonances even up to room temperature (Fig. 2). The broad resonance is assigned to the carbon black, displaying as it does all the characteristics of the neat carbon black. There is superimposed on this resonance a narrow signal of width ~ 3 G and g value 2.0088, which is close to that for the free electron. This narrow signal is similar to the one reported by Sullivan and Wise [1] and Waldrup and Kraus [3] at cryogenic temperatures and ascribed by the latter to stabilized rubber radicals. There was no evidence, either at room temperature or below, of any signal similar to that observed in the unfilled polybutadiene. We recall that this resonance was traced to paramagnetic impurities in the unfilled material [12]. To establish if the narrow resonance in the filled sample was a modified version of the resonance observed in the unfilled polybutadiene, possibly exchange narrowed on incorporation of the black, a filled sample of the purified rubber (sample 2) was

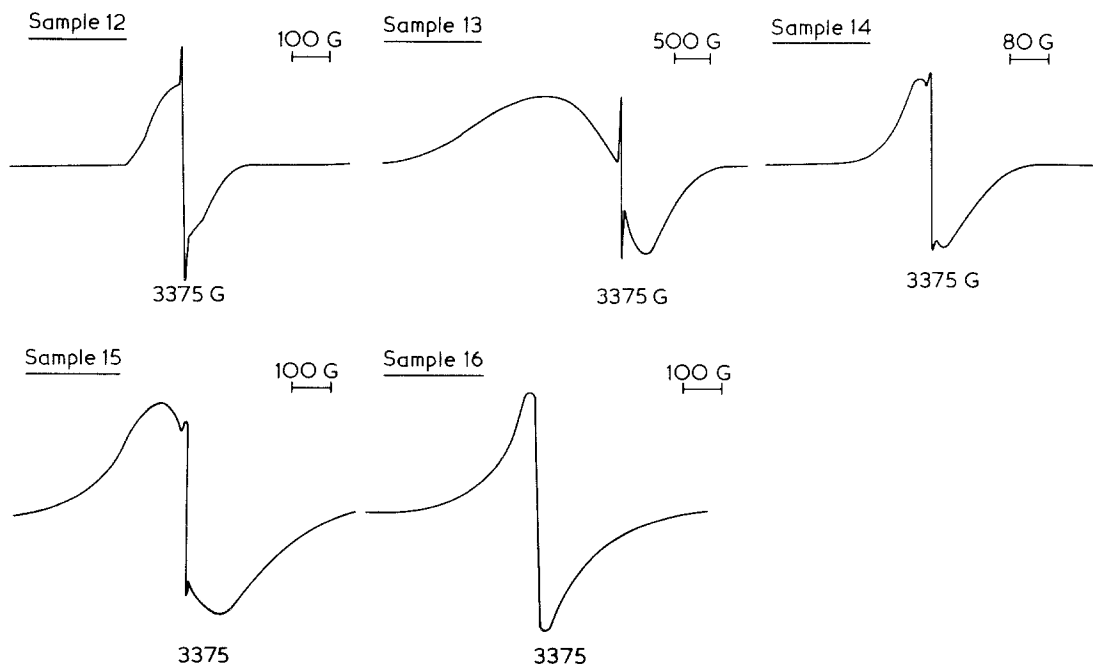


Figure 2 First derivative ESR spectra for a range of filled (50 phr) and milled (30 passes) rubber samples.

examined. No appreciable difference in the ESR response was observed, supporting the view that the narrow signal in the filled system was predominantly of different origin to the signal observed in the unfilled rubber.

3.3. Dependence on loading

As shown in Fig. 3 and Table V there is a linear increase in the rubber spin concentration (narrow signal) with loading. Spin concentrations per gram are of the order of 10^{16} . Such an increase is to be expected, since greater loading provides more surface area for rubber radical stabilization. Furthermore, the fact that bound rubber content increases linearly with loading leads to the linear variation of bound rubber content with rubber spin con-

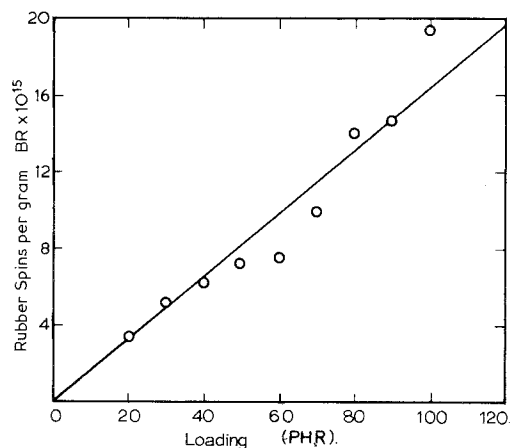


Figure 3 The dependence of rubber spin concentration per gram of rubber upon loading.

TABLE V

Sample	Loading	% bound rubber	Rubber spin conc. per gram R ($\times 10^{15}$)	Rubber spin per gram bound R ($\times 10^{16}$)	Rubber spin per gram CB ($\times 10^{15}$)	% total spins in bound rubber	Fraction total CB spins, conduction
3	100	23.7	19.9	10.1	19.9	100%	.75
4	90	16.4	14.8	8.3	16.4	92	—
5	80	12.1	14.2	12.0	17.8	100	—
6	70	13.3	10.0	5.9	14.4	78	—
7	60	11.1	8.6	8.5	14.3	100	—
8	50	7.9	8.3	10.6	16.6	100	.77
9	40	9.1	6.2	9.3	15.5	100	—
10	30	8.0	5.4	5.8	17.9	85	—
11	20	5.0	3.5	6.1	17.5	89	.83

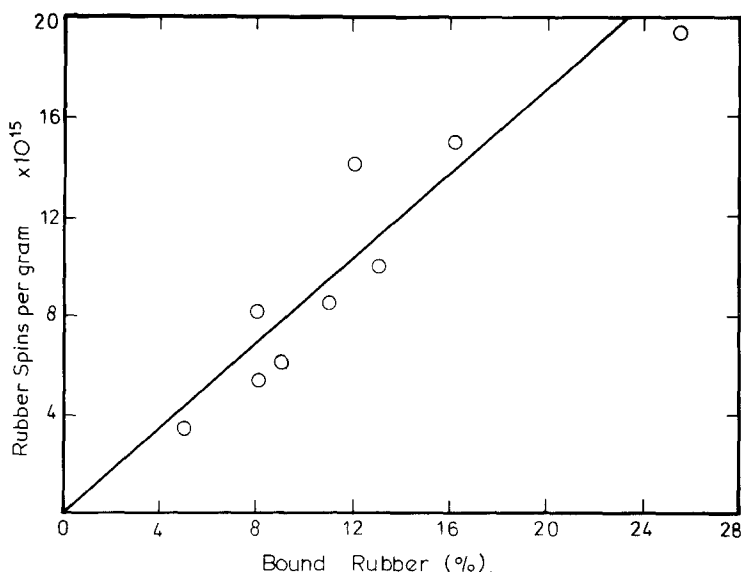


Figure 4 The dependence of rubber spin concentration per gram of rubber upon bound rubber content.

centration (Fig. 4). This result is significant for the extracted materials on the realization that almost all the rubber spins ($\sim 94\%$) are stabilized within the bound rubber region which constitutes only ~ 12 wt% of total rubber present. This result shows once again the primary role of the carbon black surface in the stabilization process.

In an earlier section we tentatively identified the localized spins in the carbon black with defect centres. If these centres play the dominant role in the free radical stabilization process then there should be a decrease in localized spin concentration with loading. The relative fractions of localized and conduction spins in the black have been determined (Table V) and it is observed that the localized spin concentrations do decrease with loading, in support of our proposals.

It is interesting to note from the data of Table V that the number of rubber spins per gram of carbon black is approximately constant at $\sim 16.7 \times 10^{15}$, and it is possible to obtain an estimate of the number of sites on the carbon black surface associated with stabilized free radicals. This crudely assumed a one-to-one relationship between such "acceptor" sites and the number of stabilized free radicals formed. The calculation also requires the carbon particle size, calculated from the e.m. particle diameter and the surface area exposed to the rubber, derived from BET(N_2 -absorption) measurements. Our data yields an estimated ~ 3 occupied acceptor sites per particle which corresponds to 5.7×10^{14} sites per m^2 .

The analysis presupposes, among other things, that the BET surface area is a suitable measure of

the amount of carbon black available to the rubber molecules. The validity of this criterion may be assessed by comparing this absorption surface area to the geometrical surface area based on the assumption of spherical particles. The ratio of these two area should reflect the particle "structure" parameter determined from DBP oil absorption measurements. On a scale where the ratio for HAF black is arbitrarily assigned a value 1 (which is, in fact, close to its DBP value) a ratio of 1.2 is observed for GPF black, which compares favourably with the DBP structure figure of ~ 1.3 (Table II). Thus the BET measure of available surface area appears to be a reasonable one.

In concluding this section, we note that there was no appreciable variation in g value or line-width of the narrow resonance with loading. A cursory analysis showed the line shape to be nearly Lorentzian.

3.4. Dependence on milling

The importance of rubber radical formation by means of homolytic bond fission during the mastication process, has been examined in some detail in the literature [2]. The normally short-lived rubber radicals [3] are stabilized because of the free radical affinity of the carbon black particles [40]. Since this process features prominently in the formation of bound rubber, it is appropriate to examine quantitatively the effects of milling.

Portions of the milled material were removed at different stages of the cold-rolling process to provide a series of samples as a function of the number of passes through the mill. The results for

TABLE VI

Millings	Rubber spin conc. per gram GPF ($\times 10^{16}$)	Rubber spin conc. per gram ISAF ($\times 10^{16}$)
0	—	0.76
1	—	1.8
3	1.2	2.0
5	1.5	2.6
7	—	2.4
10	1.6	2.4
15	1.6	2.8
20	2.2	3.0
25	—	3.2
30	2.2	2.8
40	2.3	3.0
50	2.2	2.8
60	2.5	2.4
70	2.5	—
80	—	3.0
100	—	2.4
120	—	2.2
140	—	2.8
160	—	2.6
180	—	2.6
200	—	2.0

two series of samples, each with a different black, are presented in Table VI and shown schematically in Fig. 5.

The two graphs, for GPF and ISAF black respectively, suggest a competitive process: initially, the spin concentration in the rubber increases rapidly with energy input (number of millings) up to an optimum of 20 to 30 passes. these results are consistent with earlier observations. This is reflected also in a sharply in-

creasing bound rubber development [3] which responds not only to the rubber radial buildup but also to an *in situ* structural breakdown of the carbon black [41, 42] leading to the generation of more radical trap sites. Beyond the critical point of about 30 passes, however, the rubber spin concentration, like the bound rubber, begins to decrease slowly. Thus it would appear that continued milling begins to destroy some of the bound rubber along with its associated stabilized free radical content. The reactivated free radicals so generated undergo some subsequent from of annihilation process the exact mechanism being unclear at this point. It is thought that a state of dynamic equilibrium exists in which the creation of newly formed bound rubber by chain cission is more than counterbalanced by disruption of existing bound rubber. *g* value and linewidth are invariant to the number of millings; only the spin concentrations vary. Thus the experiment allows one to determine an optimum number of millings for greatest bound rubber formation.

3.5. Dependence on carbon black type

Fig. 2 emphasises the different character of the ESR spectra from systems filled with different carbon blacks (samples 12 to 16). The pertinent data for this series are listed in Table VII. The results imply little specific correlation between the rubber spin concentration and surface area or particle diameter, attempts to obtain correlation between carbon black type and various nmr data met with a similar fate [12]. There is little doubt,

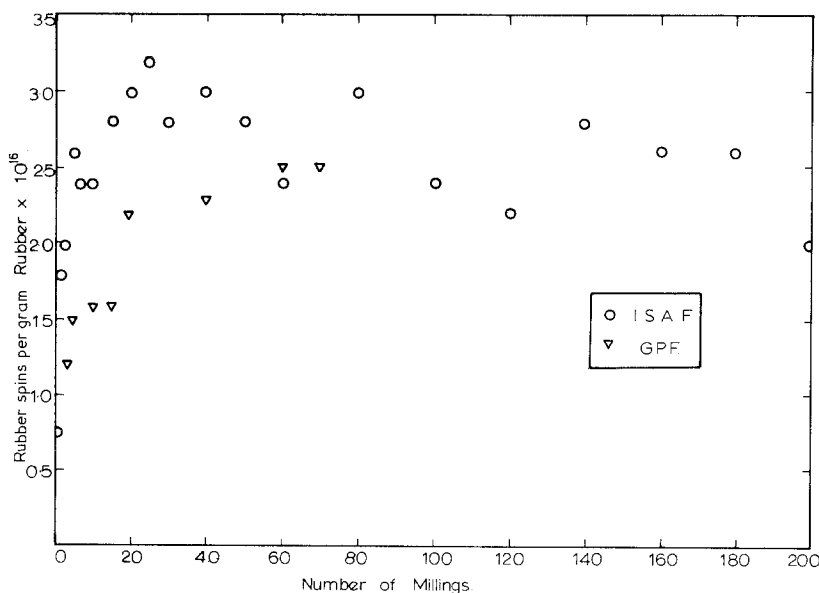


Figure 5 The dependence of rubber spin concentration per gram of rubber upon the number of millings.

TABLE VII

Sample	Carbon black	% bound rubber	ΔH_{BR} (G)	Rubber spin conc. per gram R ($\times 10^{16}$)	Rubber spin conc. per gram CB ($\times 10^{16}$)	Rubber spin conc. per gram bound R ($\times 10^{17}$)	% total spin in bound rubber	CB acceptor-site density sites m^{-2} ($\times 10^{14}$)	Fraction conduction spins
12	SRF	13.1	1.6	23.6	47.2	29	~100	156	—
13	GPF	7.9	2.25	0.8	1.6	1.1	~100	5.7	0.77
14	FEF	13.0	3.0	6.2	12.4	3.4	71	28.7	0.31
15	HAF	22.9	2.7	3.2	1.4	0.6	44	7.8	0.56
16	ISAF	18.0	2.8	2.5	5.0	1.8	~100	5.2	0.45
17	ISAF	15.4	2.4	2.8	5.6	1.4	61	5.2	0.45

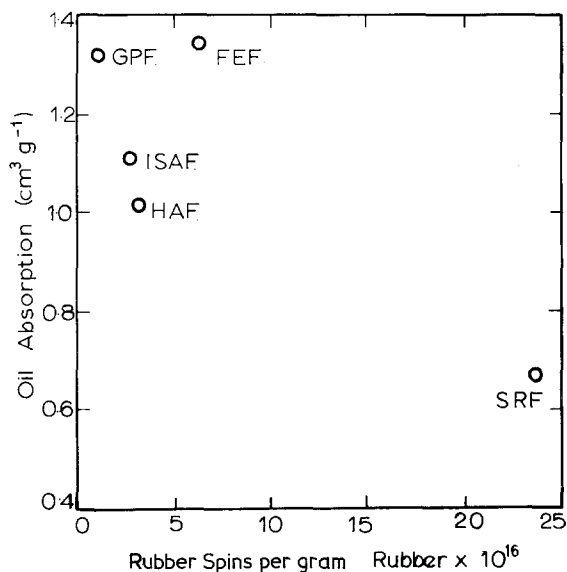


Figure 6 The dependence of oil absorption upon the number of rubber spins per gram of rubber.

however, that the structure of the blacks plays an important role [43, 44] and the graph of rubber spin concentration against structure, as determined by oil absorption, does reveal an interesting rough trend (Fig. 6) which is consistent with the nmr observations. In general, the amount of bound rubber formed, and therefore the rubber spin concentration, is lower than expected for the finer more highly structured carbon blacks. As interpreted earlier, this may be due to the limited availability of carbon black surface for interaction with the rubber. Also, the carbon black radical sites, normally used in the formation of the bound rubber, may well be involved directly in the primary agglomeration process which is increasingly important for the finer blacks.

A second correlation which emerges from the

data is that between the fraction of localized spins in the black and the rubber spin concentration (Fig. 7). This is further evidence in support of the primary role of the localized spins in the formation of stable free radicals in the bound rubber. Obviously the localized free spins are to be identified closely with the acceptor sites discussed earlier. These conclusions tend to favour the postulates of Donnet *et al.* with regard to the mechanism of stable free radical formation. They envisage the formation of quinone structures [45–48] which are converted to the inactive radicals responsible for the narrow rubber resonance.

4. Conclusions

The principal conclusions are as follows:

(i) There are two distinguishable free spin species in the carbon black: free spin carriers and localized free spins.

(ii) Defect concentrations, in the blacks calculated from X-ray data, correlate reasonably with the localized spin concentrations.

(iii) The estimated number of acceptor sites per carbon black particle associated with the stable free radicals observed in the bound rubber is ~ 3 , equivalent to $\sim 6 \times 10^{14}$ sites m^{-2} .

(iv) The bound rubber spin concentration increases with carbon black loading and bound rubber content. There is a decrease in carbon black localized spin concentration with loading. The number of bound rubber spins per gram of black is about constant, independent of loading.

(v) 20 to 30 millings will maximize the amount of bound rubber formed.

(vi) The interpretation of data, with carbon black type as the variable highlights the importance of including consideration of the "structure" parameter.

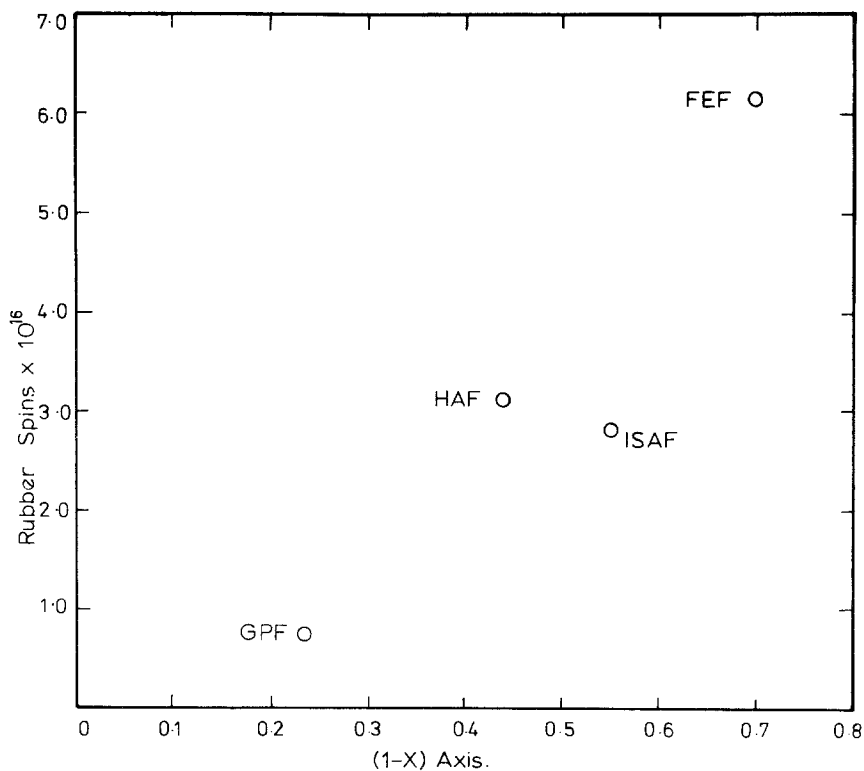


Figure 7 The dependence of rubber spin concentration upon the fraction of carbon black spins, $(1 - X)$ which are localized.

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