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Review

Characterization of dispersion state of filler and polymer–filler interactions in rubber–carbon black composites

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The physical properties of carbon black–filled rubbers are affected mainly by the distribution of filler, carbon black properties and polymer–filler interactions. A number of experimental methods and approaches for characterization of the dispersion state of filler in rubber–carbon black composites and an investigation of polymer–filler interactions are reviewed. The dispersion state characterization, electrical conductivity measurements, bound rubber evaluations, mechanical properties measurements, carbon black surface properties study, small angle X-ray scattering (SAXS) and nuclear magnetic resonance (NMR) spectroscopy are among the most important ones.

1. Introduction

In most of their industrial applications, elastomers are used as composite materials. The incorporation of carbon black into rubbery polymers imparts many interesting and useful properties to the particle–filled composite materials. It is well known that the properties mainly depend, among other things, on the dispersion condition of filler particles and their principal relevant properties (e.g. particle size, surface area, aggregate structure and surface activity) and on rubber–filler interactions [1, 2]. The uniform dispersion of carbon black throughout the polymer matrix is essential for rubber compounding to achieve optimum vulcanizate properties [3] and the degree of dispersion is a factor which ultimately controls the physical properties of the composite [4]. The importance of carbon black dispersion to the end use performance and economical aspects of rubber compounding has also been documented [5]. The characterization of the degree of filler dispersion in the polymer matrix and the polymer–filler interactions thus seems to be inevitably important. Several experimental techniques have been used for this characterization. The primary objective of this paper is to summarize recent advances in this field.

2. Experimental procedure

2.1. Dispersion state characterization

Dispersion can be defined as the distribution of filler particle size and interparticle distance in the matrix. A historical background of analytical procedures, including sample preparations, of the characterization of dispersions has been reviewed by Hess [6]. He and coworkers [7–10] directed their attention mainly to optical microscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-radiography and surface inspection measurements.

Ebell and Hemsley [11] developed a novel optical method for estimating the dispersion of carbon black in rubbers, which is based on a reflected light microscope set up for dark field observations. An attempt was also made to characterize the state of dispersion high abrasion furnace (of filler by a Fraunhofer diffraction of photographs of HAF) carbon black–filled styrene butadiene rubber (SBR) section by Oono [12]. He evaluated interparticle distances between carbon black aggregates in rubber matrix (800, 700 and 400 nm at filler concentrations of 20, 40 and 60 (parts per hundred parts of rubber (p.h.r.), respectively) and estimated carbon black aggregate size (an average diameter of 120 nm at 20 p.h.r.). An average number of primary particles in carbon black aggregate was found to be about 40. Nishi and coworkers [13, 14] tried to characterize the heterogenous structure of multicomponent polymer systems, using pattern recognition techniques.

The investigation of composite structure can be performed easily by image analysis. This rather broad subject is gaining more and more popularity. It deals mainly with the quantitative measurement and analysis of available information, such as the number, sizes or areas, etc., of features in an image. This task can be easily and quickly done by means of an image analyser [15]. Sumita and coworkers [16–18] have done extensive research to characterize the mode of dispersion of filler particles in carbon black–polymer composite materials. Sections of carbon black filled composite materials, prepared by breaking in liquid nitrogen,

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were observed by SEM. The state of dispersion of carbon black was characterized by the statistical processing of SEM photographs using the quadrate method and Morishita's I_δ value [19]. Morishita's I_δ index is one of the most useful quadrate methods, in which the total area of the SEM pattern is divided into small elementary parts with equal area and the number of the points in each element is calculated. The I_δ index, which plays an important role in the characterization of points dispersion, is given by [17]

$$I_\delta = q\delta \tag{1}$$

with

$$\delta = \frac{\sum_{i=1}^{q} n_i(n_i - 1)}{N(N-1)} \tag{2}$$

where q is the dividing number, n_i is the number of particles in the ith section and N is the total number of particles

$$N = \sum_{i=1}^{q} n_i \tag{3}$$

Fig. 1 shows schematically the dependence of I_δ on q for various distribution modes of particles. For Poisson's distribution all the δ are equal to q^{-1}, independently of the value of q, i.e. I_δ is always unity (Fig. 1a). For the regular mode of distribution, I_δ gradually decreases with increasing q value (Fig. 1b). For the aggregate mode, I_δ increases as the q value increases (Fig. 1c–f). The smaller the size of the aggregate, the larger the value of q at which I_δ becomes larger than unity (smaller size of aggregate: Fig. 1d, f; larger size of aggregate: Fig. 1c, e). Furthermore, when the particles are distributed in the regular mode in each aggregate, I_δ has a maximum peak at a certain value of q (Fig. 1e, f). For carbon black–SBR compounds, Shimizu *et al.* observed the change of distribution mode from aggregate mode to Poisson's with increasing load of filler (Fig. 2) [16].

Recently, Herzig and Baker [20] found an image analysis system coupled with electron microscopy to be a powerful tool in characterizing the morphology of polymer composites. They also tried to create computer simulations of cluster pattern images and compare them with image analysis results. Shih and Goldfinger [21] studied carbon black dispersion in a rubber matrix with an optical image analyser. They also investigated the dispersion of other additives in rubber compounds.

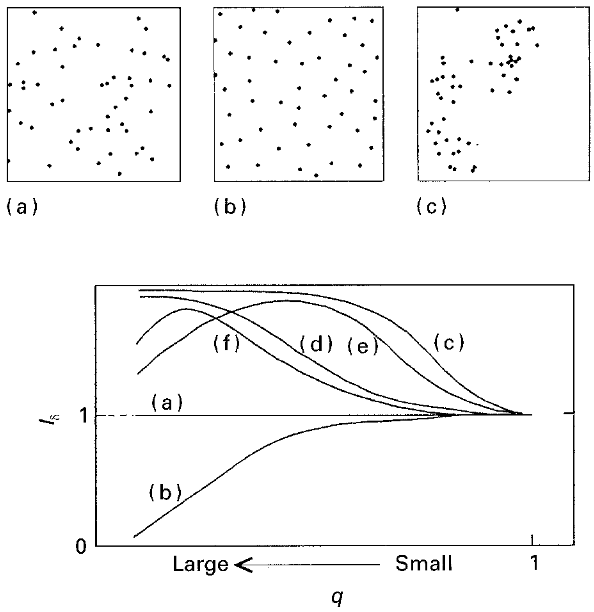

Figure 1 Schematic representation of the relationship between Morishita's index, I_δ, and quadrate number, q, for various distribution modes of particles: (a) Poisson's distribution, (b) regular distribution, (c) aggregate distribution in which the size of each aggregate is large and the particles are distributed in Poisson's mode in each aggregate, (d) aggregate distribution in which the size of each aggregate is small and the particles are distributed in Poisson's mode in each aggregate, (e) aggregate distribution in which the size of each aggregate is large and the particles are distributed in regular mode in each aggregate, (f) aggregate distribution in which the size of each aggregate is small and the particles are distributed in regular mode in each aggregate [16].

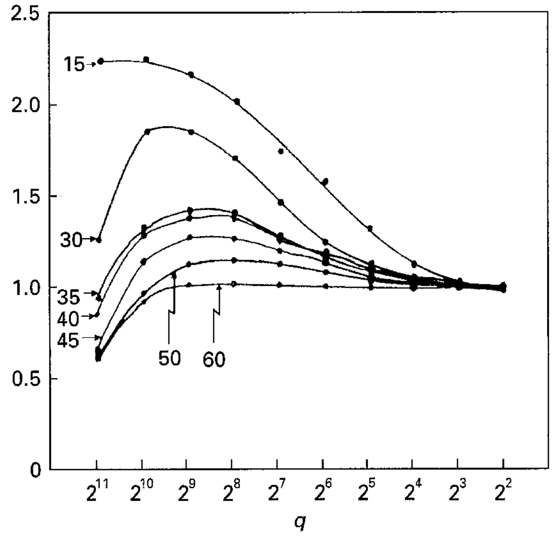

Figure 2 Morishita's I_δ index for carbon black filled SBR composite materials with various carbon black contents (p.h.r.) as a function of quadrat number, q, [16].

2.2. Electrical conductivity measurement

The electrical conductivity of rubber compounds is highly important to many manufacturers of rubber products and has been the subject of considerable interest and experimental study for many years [12, 22–32]. Electrically, the rubber–carbon black composite is an extremely heterogeneous one. Carbon black is a semiconductor ($\sigma \approx 10^5\ \Omega^{-1}\,\mathrm{m}^{-1}$), while unfilled rubbers have electrical conductivities that are characteristically very low, ($\sigma < 10^{-13}\ \Omega^{-1}\,\mathrm{m}^{-1}$), and in most electrical applications they are used as insulators. At low loading of carbon black, the conductivity of the composite is essentially that of a dielectric medium. The filler is distributed in the polymer matrix and there are no contacts between adjacent filler particles. As the loading is increased, agglomerates of the filler particle begin to form; a three-dimensional network of conducting phase is formed and an abrupt change in the conductivity is noted as a critical volume fraction of conductor is reached (so called percolation threshold). At high enough concentrations, a further increase in loading would not be expected to cause any significant increase in conductivity [33]. The dependence of electrical conductivity of carbon black–natural rubber (NR) composite on the volume fraction of filler is demonstrated in Fig. 3.

The level of conductivity depends upon the number of contacts or near contacts between conductive particles in the rubber matrix. Loading level and dispersion degree of filler are obviously major determinants in addition to polymer–filler interactions and physicochemical characteristics of the black. In the latter regard, the highly conductive grades are characterized by small particle size, high structure, high surface porosity and low volatile content [34]. The percolation threshold may also be influenced by the interaction between polymer and carbon black, especially with polymers of lower viscosity [31].

The transport of electron is considered to occur from one carbon black aggregate to another. In order for conduction to take place through the specimen, there must be pathways of sufficiently low resistivity which extend throughout the entire specimen. Aggregates which are isolated, or which are in clusters (agglomerates) which are themselves isolated from neighbouring aggregates or agglomerates by gaps of high resistivity, do not contribute to the conductance. So, if one adds conducting particles, such as carbon black aggregates, to a matrix one at a time, the particles will at first be isolated, then isolated clusters will be formed, and finally a through-going path will arise [33]. It appears that a comparatively small decrease in average distance between the aggregates could lead to an important conductivity increase [25]. Thus the electrical conductivity measurements, while most commonly being treated as an end use property of polymeric compounds, consequently reflect the dispersion state of carbon black–filled rubber compounds. This is demonstrated in Fig. 4 which compares the experimental results of SEM and electrical conductivity measurements under and above the percolation threshold [35] found for HAF carbon black in NR.

Verhelst *et al.* [24] studied the role of morphology and structure of carbon blacks in the electrical conductance of vulcanizates. Several authors investigated the influence of temperature on rubber compound electrical properties [25–28, 32]. Dynamic electrical and electromechanical properties of carbon black loaded rubber were also in the focus of interest [36, 37]. Sircar and Lamond [38] studied the effect of carbon black particle size distribution on electrical conductivity and found that wide distribution increased electrical conductivity of carbon black rubber compounds. An explanation was offered based on a higher probability of agglomeration for wider distribution blacks and therefore a lower average gap width between conducting particles [38].

Recently, models proposed to explain the electrical conductivity of mixtures made of conductive and insulating materials were reviewed [39]. The phenomenon of rubber–carbon black composite electrical properties

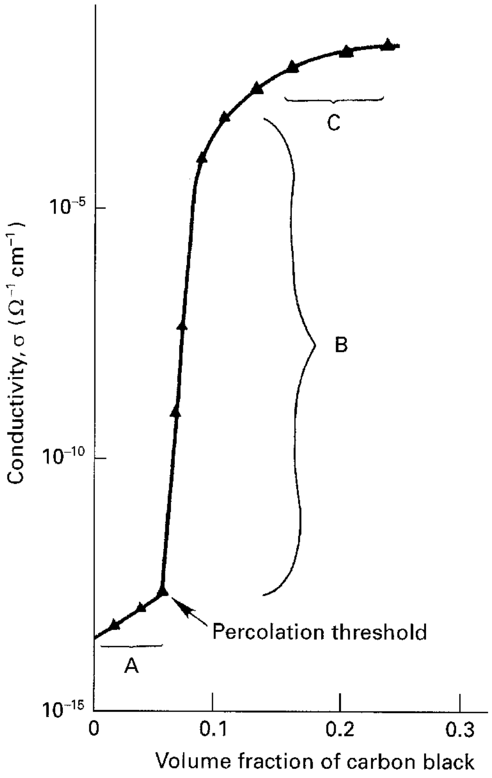

Figure 3 The dependence of electrical conductivity of carbon black–natural rubber compound on volume fraction of carbon black. Regions added as indicated: (A) insulating, (B) percolating, (C) limiting high conductivity [33].

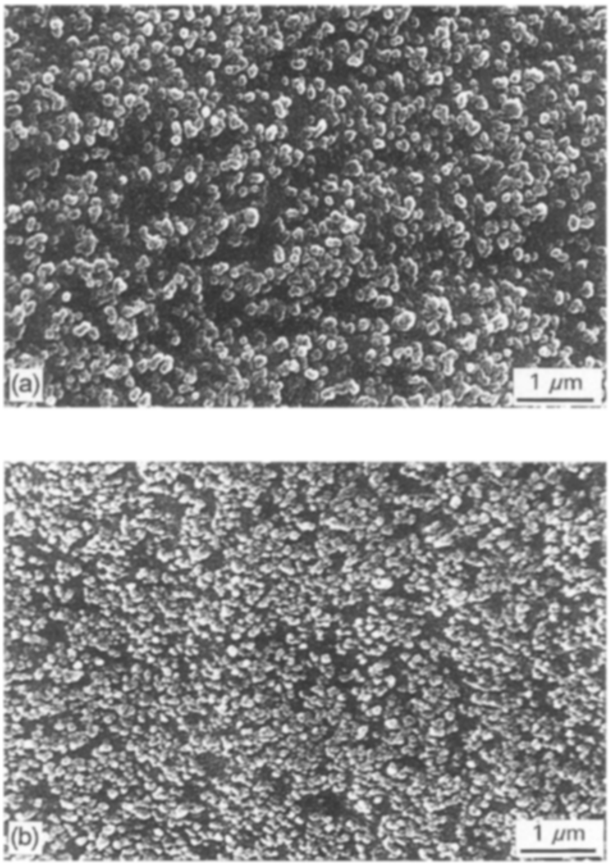

Figure 4 SEM photograph of (a) 20 p.h.r. HAF carbon black in NR, under percolation threshold, the conductivity is 5×10^{-15} S cm^{-1} (× 15000) ; and (b) 40 p.h.r. HAF carbon black in NR, above percolation threshold, the conductivity is 4×10^{-8} S cm^{-1} (× 15000) [35].

has been extensively studied, and there are a few comprehensive reviews [33, 34] on this subject.

2.3. Small angle X-ray scattering

Small angle X-ray scattering (SAXS) is a technique that is used widely to characterize multiphase systems which have structure on the 1–100 nm scale [40, 41]. The phases must have sufficient electron density differences in order for X-ray scattering to occur at small angles. It was demonstrated that SAXS can be used to characterize the filler particles *in situ* enabling the volume fraction, particle size and particle surface area to be determined for a filled polymer and factors such as aggregation to be examined [42–45]. SAXS technique is particularly useful because it can be used non-destructively to determine the above mentioned characteristics of filler incorporated into polymers.

Brown *et al.* [42] studied the surface areas of Aerosil silicas in air and dispersed in a silicone rubber. General agreement between the surface areas evaluated by the SAXS method and Brunauer–Emmett–Teller (BET) gas adsorption method was found. Young *et al.* [43] showed how SAXS can be used to characterize the size and the dispersion of individual filler particles both before and after incorporation in natural rubber. The structure of the carbon black was found to be significantly affected by incorporation into the rubber. The study of Deslandes *et al.* [45] showed that SAXS and TEM measurements produce similar results for the average agglomerate sizes of carbon black dispersions.

SAXS is a very important technique for studying the structure of fractals and other disordered systems on a scale of lengths from 1 to 200 nm [46, 47]. SAXS was also proven to be a useful technique for characterizing carbon black fractal dimensions, which quantifies the "structure"; the ruggedness of the material [48]. This fractal dimension of carbon black particles was determined using an adsorption technique [49], automated electron microscope image analyses (TEM–AIA) [50], and small angle neutron scattering (SANS) and TEM [51], too. In the last work, the fractal dimensions of the primary aggregates obtained by the two different techniques were in excellent agreement.

2.4. Rubber–filler compound properties versus carbon black morphology and surface properties

In several publications of Ayala *et al.* [52–54] the level of carbon black–elastomer interaction was studied by means of mechanical properties as a function of an interaction parameter, I, which is calculated from the static and dynamic modulus of vulcanized compounds. This parameter was derived as

$$I = \frac{\sigma}{\eta} \tag{4}$$

where σ is the slope of the stress–strain curve in a relatively linear region between 100 and 300% elongation, and η is a carbon–carbon networking factor based on the ratio of the dynamic elastic modulus, E', at 1 and 25% double strain amplitudes. It was found that the interaction parameter accentuates the contribution of strong carbon black–polymer interaction and reduces the influence of physical phenomena associated with carbon–carbon networking [53]. From Ayala *et al.* experimental data it is apparent that fineness and structure of carbon black remain among the most important parameters for carbon black reinforcement of rubber. However, at high strains the surface energy, i.e. surface activity, of the carbon black plays a substantial role in the performance of rubber compounds. Hydrogen content is considered to be the primary compositional factor relating to carbon black surface activity, while bound rubber and oxygen levels are specific measures of surface reactivity [52].

The investigators [54] derived an equation in which, within a given carbon black grade, the parameter I becomes a function of effective volume fraction, V_{eff}, and surface energy of carbon black. The equation was found to be in full agreement with experimental evidence (Fig. 5).

Ayala *et al.* applied a number of different techniques to measure carbon black surface reactivity and the level of carbon black–polymer interaction. Secondary ion mass spectroscopy (SIMS) analyses on the cut rubber compound surfaces showed overall variations in intensity which were proportional to the range and level of the bound rubber measurements. Also, heats of adsorption by inverse gas chromatography at infinite dilution were found to be useful as a measure of the carbon black surface energy related to rubber interactions [54].

Studies on adsorption energies of the low molecular weight analogs of elastomer [55] generally showed that the interactions between carbon blacks and rubbers depend not only on filler surface energies but also on the structure of the elastomers. Due to their polar functional groups, acrylonitrile butadiene rubber

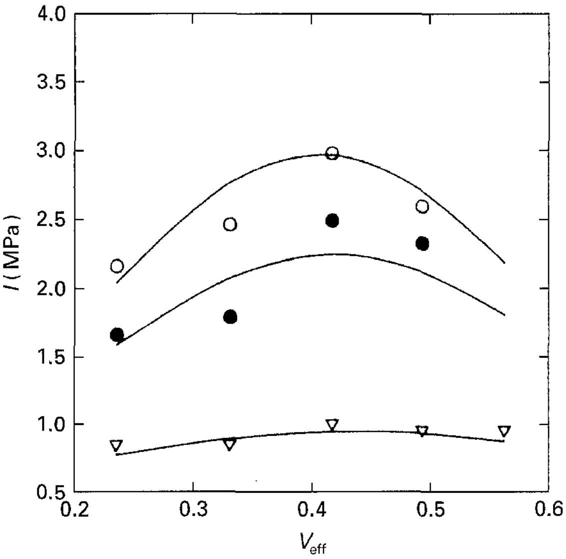

Figure 5 Interaction parameter, I, versus V_{eff} for N121 carbon black compounds (with different heat treatment). The lines were calculated from model equation, symbols represent I calculated from experimental data [54] : (○) N121 standard, (●) N121 G1100 °C, (▽) N121 G1500 °C.

(NBR) and SBR showed a stronger interaction with blacks than unsaturated rubbers. Among the rubbers simulated, butyl rubber (IIR) had the lowest interaction with the filler [55].

Investigations of rheological and mechanical properties of rubber compounds [56] showed that the surface energy of a filler plays a predominant role in rubber reinforcement and has a profound influence on the performance of rubber products.

Nakajima *et al.* [57–61] used tensile stress–strain, oscillatory shear and dynamic mechanical measurements for evaluation of the filler–rubber interactions in the uncrosslinked rubber–filler compounds.

2.5. Bound rubber studies

Generally, the incorporation of carbon black and other reinforcing fillers into (originally soluble) rubbery polymers results in a partial loss of polymer solubility. This filler-bound rubber is defined as a certain fraction of rubber strongly adsorbed on the surface of filler particles and is resistant to the desorptive action of the solvent. At higher filler concentration (and at higher fraction of bound rubber) the bound rubber forms a gel of filler particles held together in a three-dimensional lattice by longer interparticle polymer molecules. This bound rubber phenomenon has been extensively studied for many years, since it is considered as a factor in filler reinforcement of rubber, a measure of filler surface activity and polymer–filler interactions [62–71].

A number of authors have published theories which tried to predict this phenomenon [72–82]. Recently, Meissner [83] critically reviewed the existing theories and concluded that the most complete explanation of available experimental data is offered by a random adsorption model suggested by him [75, 76].

Bound rubber is measured by immersing small pieces of uncured rubber–filler mix in a large excess of a good solvent, such as toluene, for several days at room temperature [64]. When brought into contact with the solvent, the polymer–filler system generally becomes divided into three parts:

1. solvent–dispersed polymer chains (polymer solutions),
2. solvent–dispersed filler particles with polymer chains adsorbed on them, and
3. solvent–swollen coherent gel-like structure of filler particles connected through polymer chains [84–86].

The mass of polymer in any of these three parts, i.e. m_{pI}, m_{pII}, m_{pIII}, and also the mass of filler particles m_{fII}, m_{fIII} in parts II and III can in principle be determined experimentally [84]. For such measurements the following data can be obtained

1. $B = (m_{\mathrm{pII}} + m_{\mathrm{pIII}})\ /m_{\mathrm{p}}$, fraction of filler-bound polymer.
2. $G = m_{\mathrm{pIII}}/m_{\mathrm{p}}$, gel, fraction of polymer not dispersed by the solvent.

Where m_{p} is the total mass of the polymer. In the beginning (low filler concentration in rubber–filler compound), there is only adsorption of macromolecules on the solvent–dispersed filler particles, at higher concentrations of filler the gel starts to be created, and at high enough filler concentrations bound rubber exists completely in gel form. The dependence of gel on bound rubber fraction for fume silica–NR and fume silica–SBR systems is shown in Fig. 6. Points are experimentally measured data, curves are theoretically calculated fits from Meissner's theories [75, 76, 84].

The well known effect of preferential adsorption of longer polymer chains on filler found by many investigators [73, 75, 77, 87, 88] can be detected and quantitatively accounted for by the equation of the Meissner bound rubber theory, too [75]. The decrease of weight average molecular weight, M_{w}, and number average molecular weight, M_n, of extractable free (unbound) polymer from SBR–lamp carbon black compounds with increasing bound rubber content is shown in Fig. 7.

In general, bound rubber content increases with higher loading of filler. At a certain filler concentration, the filler particles with polymer chains adsorbed on them are not dispersed by the solvent, but form a coherent structure called polymer–filler gel. There are many factors influencing the bound rubber formation. In Table I they are classified according to filler variables, elastomer variables, effect of chemical additives, mixing variables and test methods [64]. As far as the filler is concerned, bound rubber is not only affected by the physicochemical characteristics of the filler surface, but also by filler morphology. With regard to the polymer, both the chemical structure of the molecules and their microstructure influence the level of bound rubber content [89]. Fig. 8 demonstrates the influence of polymer type and filler concentration on bound rubber content.

Wolff *et al.* [89] made a conclusion that the filler–polymer interaction leading to the formation of the bound rubber involves physical adsorption, chemisorption and mechanical interaction. Recently,

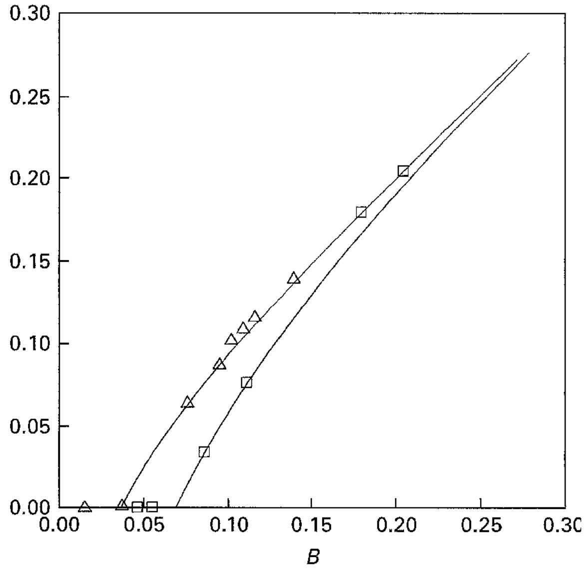

Figure 6 The dependence of polymer–filler gel, *G*, on bound rubber fraction, *B*, for two rubber–filler systems: points, experimental data; curves, theoretical fits of Meissner's theory [84] : (□) NR–fume silica, (△) SBR–fume silica.

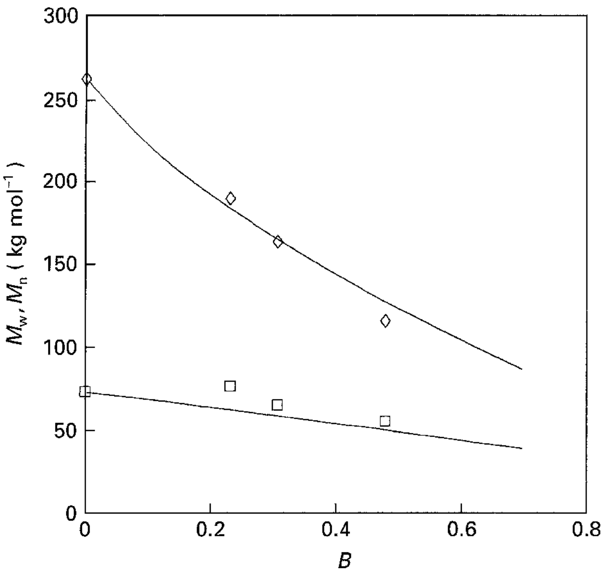

Figure 7 The dependence of (◇) weight average molecular weight, M_w, and (□) number average molecular weight, M_n, of extractable free (unbound) polymer from SBR–lamp carbon black compounds on bound rubber fraction, *B*: points, experimental data; curves, theoretical fits of Meissner's theory [85].

TABLE I Factors influencing bound rubber measurement [64]

- Filler
  - Concentration
  - Aggregate size (structure)
  - Surface area
  - Chemical composition
  - Surface activity
    - Free radical (aggregate breakdown)
    - Functional groups
    - Heat treatment (graphitization)
    - Surface treatments
      - Coupling agents
      - Hydrophobic agents
      - Surface active agents
- Elastomer
  - Chemical composition
  - Unsaturation
  - Stability
    - Thermal
    - Mechanochemical
    - Oxidative
- Chemical additives
  - Free radical terminators
  - Promoters
  - Coupling agents
  - Surface active agents
- Mixing variables
  - Bulk or solution
  - Mixing energy, time and temperature
- Test methods
  - Heat treatment of sample
  - Temperature of extraction

Roychoudhury and De [90] concluded that bound rubber formation is essentially a chemical process involving reactions between elastomer and carbon black.

2.6. NMR spectroscopy

The interaction of carbon black and rubber is a problem of considerable scientific interest. Knowledge of the structure and interactions in a rubber–carbon black mixture is important for understanding the mechanism of rubber reinforcement by active filler. NMR spectroscopy was found to be a very important tool for characterization of reinforced elastomers. Pulse NMR studies (proton spin–spin relaxation time, T_2, measurements) have produced important information on the structure of bound rubber phases and on changes of the mobility of rubber molecules in carbon black–filled rubber composites [91–104].

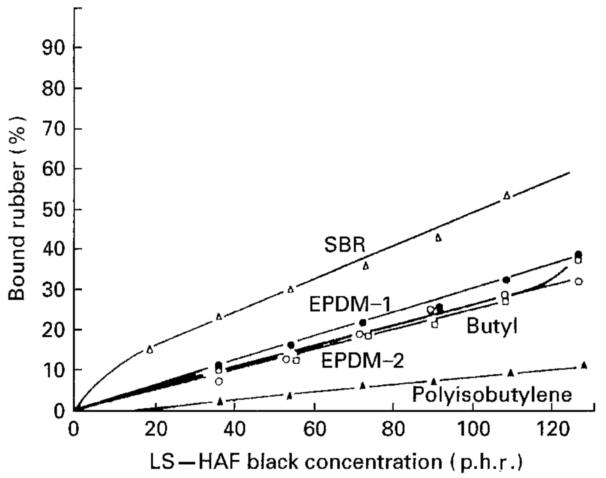

Figure 8 Effect of low structure (LS)–HAF carbon black concentration on bound rubber content of various rubbers (EPDM, ethylene propylene diene rubber) [65].

The NMR results showed three types of material distinguished by their characteristic molecular motions in the filled systems: a tightly bonded component presumably in the immediate vicinity of the filler particles, an outer region of loosely bound rubber, and a third component which exhibited motions essentially identical with those observed in the unfilled polymer [91]. The tightly bound rubber region (a core) and loosely bound rubber one (a shell) are schematically demonstrated in Fig. 9. The macromolecules in each region are supposed to have different segmental motion of chains and this was confirmed by spin–spin relaxation time measurements. This is shown in Fig. 10, where the spin–spin relaxation times of the pure rubber and the bound rubber components are compared.

The spin–spin relaxation time, T_2, and the fraction of each component were determined by fitting the solid echo signal to the Weibull function [96, 100]

$$h(t) = \sum_i h_{0i} \exp\left[-t/T_{2i}\right]^{E_i} \qquad (5)$$

where t is the time, E_i is the Weibull coefficient, h_{0i} is the signal intensity of the ith component at $t = 0$, $h(t)$ is the signal intensity at t, and T_{2i} is the spin–spin relaxation time of the ith component. The fraction of the jth component (f_j) is given by

$$f_j = h_{0i} / \sum_i h_{0i} \qquad (6)$$

The amount of loosely and tightly bound rubber, determined from T_2 component intensities, increases

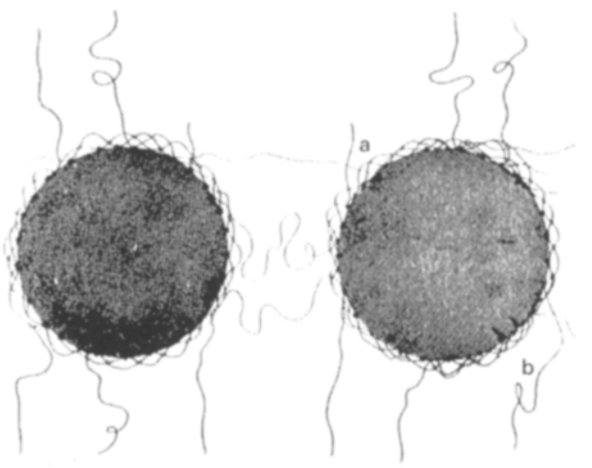

Figure 9 Schematical demonstration of (a) tightly and (b) loosely bound rubber regions [65].

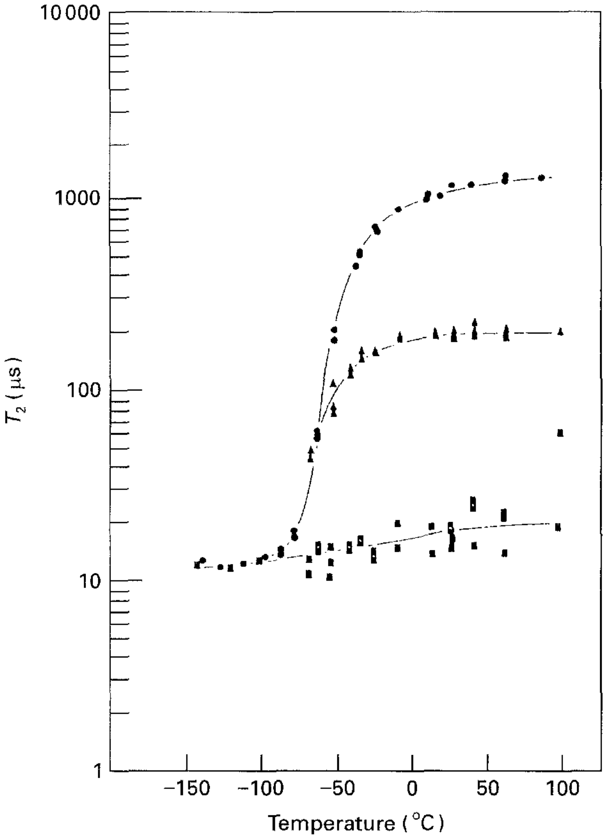

Figure 10 Temperature dependence of T_2 for (●) pure polybutadiene rubber, (▲) loosely bound rubber, and (■) tightly bound rubber [91].

with increasing loading and specific area of carbon black particles [94]. The average thickness of the bound rubber layer, ΔR_0, was computed using the Pliskin–Tokita expression [74]

$$B = \Delta R_0 f[(\phi \rho A)/(1 - \phi)] + G^i \qquad (7)$$

where B is the fraction of bound rubber, f is the fraction of total surface area exposed to the polymer (usually presumed equal to unity), ϕ is the volume fraction of carbon black in the composite, ρ and A are density and specific surface area of the carbon black particles, respectively, and G^i is the fraction of insoluble gel in the unfilled gum. The Pliskin–Tokita formula was found to be reasonably obeyed for the inner tightly bound layer as well as the total layer. The inner layer accounts for about one-fifth of the total layer thickness. The total bound rubber layer thickness was about 10 nm [92, 94].

The amounts and mobilities of tightly bound rubber and loosely bound rubber change with mixing time. The tightly bound rubber appears to be formed very quickly when the rubber segments become in contact with a new active surface of carbon black, followed by the rapid growth of the loosely bound rubber component around the surface of the preformed tightly bound rubber phase [95, 96]. The influence of carbon black surface modification by oxidation on molecular motion of bound rubber layer macromolecules was studied by Serizawa *et al.* [98, 99] and Asai *et al.* [100]. Both segmental mobility and bound rubber content in both bound rubber phases increased with carbon black surface treatment. The results can be explained as resulting from an increase in loop length of adsorbed macromolecules on the carbon black owing to the decrease in interaction between the treated carbon black and rubber.

3. Conclusions

The experimental methods and approaches of filler dispersion and polymer–filler interaction analysis have been reviewed in regard to their application to rubber systems.

There are a number of available dispersion analysis techniques which are summarized above. A combination of several of them seems to be the best way to obtain comprehensive information about the dispersion state of filler in the rubber matrix.

In order to achieve good properties of rubber vulcanizates, a uniform dispersion is necessary. Coran and Donnet [105–107] have studied the carbon black dispersion process, including the understanding of factors which affect the kinetics of dispersion.

Although there is no complete knowledge of the exact nature of rubber–filler interactions at present, the nature of segmental attachments of the polymer molecules to the filler surface appears to be both physical and chemical, depending upon filler surface activity and chemical functionality, and the chemical composition and the functionality of the elastomer [64]. Filler–filler networking plays an additional role in filler–rubber compounds. This "networking" component of filler dispersion was originally defined by Payne and Whittaker [108]. The term refers to the tendency for primary aggregates of carbon black to form a three-dimensional mesh-like configuration which is weakly held together by Van der Waals' bonding. It was found that the smaller the particle size of the black and the higher the loading, the more extensive the network.

Recently, Hall [109] wrote computer programs to place monosized unicell spherical particles in a three-dimensional space. Interparticle nearest-neighbour, surface–surface, average distance parameters can be calculated. These programs would be very useful in the area of particle filler–rubber compounds, even the author used them in graphic simulation of rubber modified materials, like high impact polystyrene.

In conclusion, a question can be asked. Why go through the time and trouble of measuring dispersion quality and polymer–filler interactions? There is a simple answer: the quality of rubber products containing reinforcing fillers is highly dependent on them.

Acknowledgements

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