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Gel-like behaviour of polybutadiene–carbon black compounds

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Recent experimental data of Cohen Addad and Frébourg on the adsorption of polybutadiene chains on the ISAF carbon black from bulk were compared with the polymer–filler gel formation theory. A very good agreement was obtained and the resulting parameter-values were similar to those recently determined for the SBR–ISAF black system. This lends support to the model upon which the theory is based: random adsorption of polymer segments, filler particles acting as a polyfunctional crosslinking agent. The Cohen Addad–Frébourg theoretical treatment of polybutadiene adsorption on carbon black (polymer chains bifunctional, dangling chains partially eliminated by the solvent) is critically reviewed. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In a recent paper of Cohen Addad and Frébourg[1] the phenomenon of polymer chain adsorption on the surface of carbon black from bulk has been studied experimentally using NMR, bound rubber and swelling measurements. Carbon black of the ISAF type with a specific surface area of $115 \, \text{m}^2 \, \text{g}^{-1}$ was mixed into polybutadiene rubber in concentrations c ranging from 0.1 to 0.4 (c is carbon black-to-polymer mass ratio). Three polybutadiene polymers were used with narrow molar mass distributions ($\bar{M}_w/\bar{M}_n = 1.05$) and number-average molar masses of 70, 120, 170 kg mol^{-1}, respectively. Extraction of the polymer–carbon black compounds was done by a good solvent of polybutadiene in order to extract free and loosely bound chains and to determine the fraction of bound rubber f_B. It has been found that f_B is a unique function of the product of filler concentration and polymer molar mass ($c\bar{M}_n$), the dependence extrapolating to the origin. An observation was made by the authors that the f_B *versus* ($c\bar{M}_n$) master curve is (slightly) curved upwards, in other words, that the specific amount of bound rubber f_B/c (mass of bound polymer per unit mass of filler) increases with c. They have concluded that adsorption of polybutadiene molecules on ISAF black is stabilized by increasing the filler concentration and that this result stands in contrast to the polydimethylsiloxane adsorption on silica where the specific amount of adsorbed polymer is lowered by increasing the silica concentration because more and more adsorbed chains are shared by filler aggregates. In order to give an interpretation to their f_B *versus* ($c\bar{M}_n$) master curve, the authors developed an adsorption model and on its basis derived a two-parameter equation which they showed to describe their experimental data well.

The present paper compares the underlying assumptions and results of the Cohen Addad and Frébourg (CAF) theory with those of the polymer–filler gel formation (PFGF) theory[2,3]. The latter is based on the assumption of filler particles acting as crosslinking points for polymer chains, the polymer–filler bonds formed being able to resist the desorptive action of the solvent. The PFGF theory predicts the existence of gel-point, preferential adsorption of longer chains, distinguishes between fraction G of gel polymer and fraction B of total filler bound polymer. In the present paper some of the aspects of the CAF theory are examined and it is shown that the experimental data of Cohen Addad and Frébourg can be very well described by the PFGF theory without using additional assumptions on the nature of polymer chains extraction which are included in the CAF theory.

THEORETICAL

The CAF theory

The CAF theory assumes the existence, on the carbon black surface, of sites of elementary interaction which can be established between any monomeric unit and the carbon black surface. It is further assumed that one polymer molecule can bridge two filler aggregates only. Therefore, each polymer molecule is considered as a bifunctional unit which can interact with the carbon black surface. The initial number of polymeric functions in mols per unit mass of carbon black is $(2/\bar{M}_n)/c$. The number of polymeric functions (mols per unit mass of filler) involved in the adsorption process is $2\mathcal{B}$ and the fraction of polymeric functions involved in the adsorption process is $\phi_p = c\bar{M}_n\mathcal{B}$. The fraction of chains which bridge two aggregates is ϕ_p^2, the fraction of dangling chains (those which are adsorbed only once) is $2\phi_p(1 - \phi_p)$ and the fraction of filler-bound polymer is

$$f_B = \phi_p^2 + 2\phi_p(1 - \phi_p) = 2\phi_p - \phi_p^2$$

After inserting for ϕ_p one obtains

$$f_B = 2c\bar{M}_n\mathcal{B} - (c\bar{M}_n\mathcal{B})^2 \tag{1}$$

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A one-parameter quadratic dependence of bound rubber fraction f_B on $(c\bar{M}_n)$ is obtained which is curved downwards. However, at this point the authors make an additional assumption: chains which are adsorbed at two points (bridging chains) are not eliminated by solvent extraction while chains which are adsorbed only once (dangling chains) are partially desorbed and extracted. The fraction of undesorbed dangling chains is β and the equation changes to:

$$f_B = 2c\bar{M}_n\beta\mathcal{B} + (1 - 2\beta)(c\bar{M}_n\mathcal{B})^2 \qquad (2)$$

Equation (2) has two adjustable parameters and acquires thus additional flexibility for data description. For $\beta > 0.5$ the dependence of f_B on $(c\bar{M}_n)$ is curved downwards and has a maximum above which f_B should decrease. For $\beta < 0.5$ it is curved upwards and for high values of $(c\bar{M}_n)$ it predicts an f_B higher than 1. From the comparison of equation (2) with their master curve the authors have obtained: $\beta = 0.35$, $\mathcal{B} = 4 \times 10^{-6}$ g^{-1} (the unit should be mol g^{-1}). They emphasize that equation (2) applies to all concentrations and to all molar masses, except for the lowest concentration of short chains ($c = 0.1$, $\bar{M}_n = 70$ kg mol^{-1}). For the polybutadiene–ISAF black system the $\mathcal{B}$-value was found to be independent of polymer molar mass while in the silica–polydimethylsiloxane system it depended on the square-root of chain length M. The authors suppose that before extraction the actual law of adsorption of polybutadiene on carbon black obeys Gaussian statistics where the number of contact points of one chain with the filler surface is expected[4] to be proportional to $\bar{M}_n^{1/2}$. However, due to a broad distribution of enthalpies of adsorption of butadiene monomeric units on carbon black the solvent extraction results in a partial elimination of adsorbed chains and this leads to a molar-mass independent $\mathcal{B}$.

The assumption that the solvent does not affect bridging chains while partially extracting chains which are adsorbed only once (dangling chains) does not seem to be well substantiated. It amounts to saying that the desorptive action of the solvent does not have a statistical character. In other words, according to the CAF theory, adsorption from bulk of reactive polymer functions on the filler surface proceeds at random and statistical reasoning is used to calculate equation (1), on the other hand the presence of solvent should bring about a selective (non-random) desorption at some points and this should lead to equation (2). However, how does an adsorbed monomeric unit know whether it belongs to a dangling chain or to a bridging chain? In the former case it should have a non-zero probability of desorption while in the latter case the probability of its desorption should be zero. This point should be clarified.

In the CAF paper[1] the swelling behaviour of polybutadiene–carbon black compounds was studied to obtain an experimental proof for the existence of a network structure. On the other hand, a proof based on theoretical reasoning was not attempted. Experimental results led the authors to the conclusion that the behaviour of systems with low values of $c\bar{M}_n$ corresponded to the formation of clusters rather than to the presence of gels. However, a theoretical calculation of the conditions leading to incipient gel formation is not given.

The assumption that each polymer chain—irrespective of its length—contains two reactive functions which can form bonds with the filler particle surface, has the consequence that the calculated bound rubber fraction becomes a unique function of the number average molar mass of the polymer. The type (width) of its molar mass distribution does not come into play and polymer chains of different length

adsorb on the filler surface irrespective of their molar mass in the same proportion they have in the initial distribution. In other words, the CAF theory predicts that there should be no preferential adsorption of longer chains. However, in a number of papers, including the early ones[5], evidence has been published to the contrary.

The PFGF theory

The PFGF theory is based on the following assumptions: there are active sites on the filler surface (concentration D, m^{-2}); polymer segments (monomeric units) interact with the filler surface and form bonds with its active sites at random; polymer–filler bonds are able to resist the desorptive action of the solvent; the number of reactive sites in a polymer chain increases with its length (it is taken equal to the polymerization degree); the fraction of filler adsorbed polymer segments is small; filler particle (aggregate) acts as a crosslinking point with a functionality f; a given polymer chain is allowed to adsorb on filler particles (aggregates) in a statistically random manner without imposing restrictions of the CAF type on the number of attachments. The Flory crosslinking theory[6] generalized for f-functional crosslinking gives means to calculate[2] the following properties of the polymer–filler system: the fraction B of total polymer bound to filler; the fraction G of polymer forming a three-dimensional gel-like structure with some $(G < B)$ or all $(G = B)$ filler particles; the existence of gel-point: for a given polymer there should be a critical filler concentration c_{gp} below which no gel is formed $(G = 0, B > 0)$ and above which gel starts to form with G approaching B at filler concentrations approximately $3c_{gp}$; the fraction w_{disp} of solvent-dispersed filler particles; the molar mass distribution of unbound polymer: preferential adsorption of longer chains is predicted as a consequence of the statistical nature of polymer segments adsorption. The PFGF theory was compared with experimental data on several elastomer–filler systems and a good description of the data was found[7]. The D-, f-values obtained had reasonable values. For SBR containing different grades of furnace blacks they were found to be rather insensitive to the filler particle size (specific surface area): D was ca. 1.5–1.8 10^{16} m^{-2}, f assumed values ca. 15–45.

An experimental testing of the PFGF theory requires the knowledge of the molar mass distribution of the polymer. For monodisperse chains the equation for G can be expressed in the following way:

$$\frac{cPMD}{N_A} = \frac{-\ln(1 - G)}{1 - (1 - G)^{f-1}} \qquad (3)$$

Here P is the specific surface area of the filler, M is the molar mass of the polymer, N_A is the Avogadro constant. The filler concentration c_{gp} for incipient gel formation is obtained from equation (3) by solving for $G = 0$:

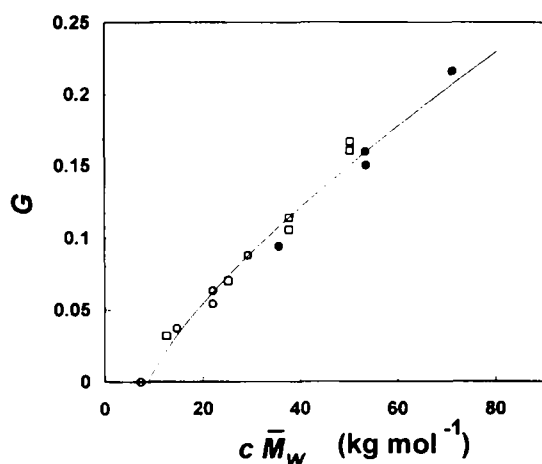$$c_{gp} = \frac{1}{f - 1}\frac{N_A}{PMD} \qquad (4)$$

For instance, if $D = 1.6 \times 10^{16}$ m^{-2}, $f = 35$, $M = 70$ kg/mol, $P = 1.15 \times 10^5$ m^2 kg^{-1}, then $c_{gp} = 0.137 = 13.7$ phr.

For values of f higher than ca. 30 and for G higher than ca. 0.2 the expression $(1 - G)^{f-1}$ becomes negligibly small and G approaches B, i.e. the total filler-bound polymer is in the gel form. The fraction of total filler-bound polymer B is given by:

$$\frac{cPMD}{N_A} = -\ln(1 - B) \qquad (5)$$
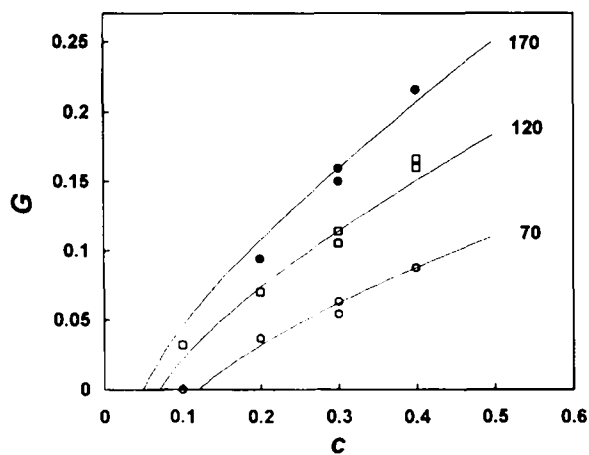
Figure 1 Dependence of G on ISAF black concentration c in polybutadienes with values of $(\bar{M}_n)$ (kg mol^{-1}) indicated on the curves. Points: experimental data of Cohen Addad and Frébourg [1]. Curves drawn using equation (3) with parameter values given in the text.

Figure 3 Region of *Figure 2* in the vicinity of the origin, enlarged. Curve B drawn with use of equation (5), curve G with use of equation (3).
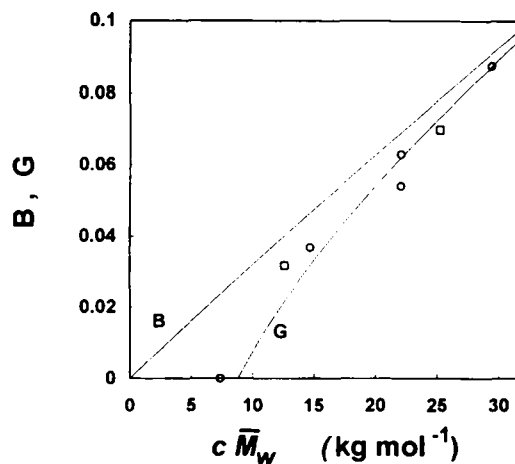

Figure 2 Dependence of G on $(c\bar{M}_w)$ for polybutadiene–ISAF black compounds (the same data as in *Figure 1*). $\bar{M}_w = \bar{M}_n \times 1.05$. Curve: theoretical, equation (3). Parameter values given in the text.

Figure 4 Dependence of G on $(c\bar{M}_w)$. (1) Curve and data (circles) from *Figure 2*, polybutadiene–ISAF black compounds. (2) Data on SBR–ISAF black [7] (full squares), curve calculated in the manner described in ref. [7] for parameter values given in the text.

In a good approximation, equations (3)–(5) may be used for narrow distribution polymers with as low polydispersity index as 1.05, if $\bar{M}_w$ is substituted for M.
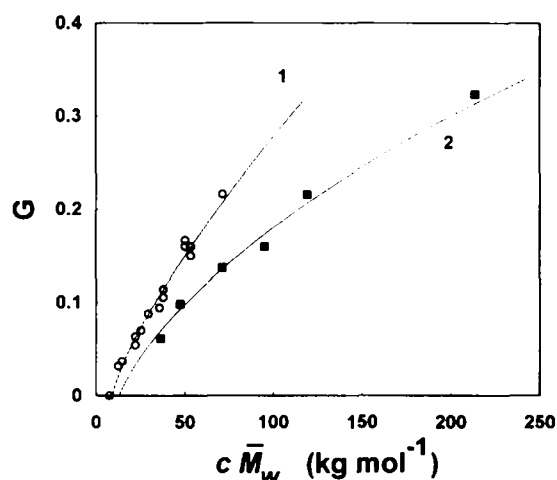
COMPARISON OF THE PFGF THEORY WITH THE CAF EXPERIMENTAL DATA

From the short description of their extraction experiments given by Cohen Addad and Frébourg[1] we have understood that the quantity f_B which they call fraction of bound polymer was determined by weighing and calculated from the mass of the unextracted and extracted sample. However, in the region of low $c\bar{M}_n$ some filler particles with polymer chains adsorbed on them may have become dispersed in the solvent. The remaining part of the compound is, in fact, the polymer–filler gel and its mass does not give information on the fraction B of total filler-bound polymer. To obtain B, all filler particles should be isolated (with help of centrifugation) and thermogravimetry gives then the amount of polymer adsorbed on them. The information obtained by weighing is closer to the value of G, the fraction of gel polymer. Therefore, the values of f_B given by CAF are treated here as gel fractions G.

From Cohen Addad and Frébourg's Fig. 1 we have

obtained the values of f_B and $(c\bar{M}_n)$ for nine polybutadiene–ISAF black compounds. One additional pair of values (for the compound with $\bar{M}_n = 170$ kg/mol and $c = 0.4$) was obtained from the text to the CAF Fig. 2. For the compound with $c = 0.1$, $\bar{M}_n = 170$ kg mol^{-1} the f_B-value is not given in the CAF paper. Four duplicate pairs of experimental values follow from texts to the CAF Figures 4 and 7. Based on this information the dependence of G on the filler concentration c is plotted in our *Figure 1*. It is seen that the experimental dependencies for the individual polybutadienes do not extrapolate to the origin. This is clearly visible especially for the low-molar mass polymer ($\bar{M}_n = 70$ kg/mol) where the zero value of G obtained by extrapolating the experimental data is attained somewhere in the vicinity of $c = 0.1$. The authors' comment that their equation (here equation (2)) does not apply for the lowest concentration of short chains is now understandable: there was no gel formed in the compound in question. Therefore, $G = 0$ is assumed here for $c = 0.1$ and $\bar{M}_n = 70$ kg/mol. Bound rubber fraction B of this compound is not zero but obviously it was not determined.

Theoretical curves calculated from equation (3) were fitted to the experimental data in *Figure 1* using the

following variable and parameter values: $M \equiv \bar{M}_w = \bar{M}_n \times$ 1.05, $P = 1.15 \times 10^5 \, \text{m}^2 \, \text{kg}^{-1}$, $D = 1.70 \times 10^{16} \, \text{m}^{-2}$, $f = 36$. The D-, f-values obtained here for the polybutadiene–ISAF black system are close to those obtained previously[7] for the SBR–ISAF black system ($D = 1.60 \times 10^{16} \, \text{m}^{-2}$, $f = 35$).

In *Figure 2* the gel fraction data of 11 compounds are plotted *versus* the product ($c\bar{M}_w$). The gel-point value $(c\bar{M}_w)_{gp} = 8.8 \, \text{kg mol}^{-1}$ can be calculated from equation (4). The measure of agreement between the theoretical curve and the experimental data may be characterized as good to excellent. The low-$(c\bar{M}_w)$ region of the graph is enlarged in *Figure 3* and the theoretical curve for B calculated with use of equation (5) is also drawn here. One can see that the bound rubber fraction for the $\bar{M}_w = 70 \, \text{kg mol}^{-1}$, $c = 0.1$ compound is predicted to be *ca.* 2.5%.

The dependence of G on $(c\bar{M}_w)$ for the polybutadiene–ISAF black system is compared in *Figure 4* with the analogous dependence obtained by us[7] for the SBR–ISAF black system ($P = 86.3 \times 10^3 \, \text{m}^2 \, \text{kg}^{-1}$, $\bar{M}_w = 235 \, \text{kg/mol}$, $D = 1.60 \times 10^{16} \, \text{m}^{-2}$, $f = 35$). The polydispersity index of the SBR polymer was rather high (3.36) and, consequently, dependence 2 is more curved downwards than dependence 1 for the narrow-distribution polymers.

CONCLUSION

The experimental data of the fraction of filler adsorbed polymer (in the gel form) obtained by Cohen Addad and Frébourg[1] using narrow distribution polybutadienes containing ISAF black can be described very well with use of the polymer–filler gel formation theory. The parameter-values obtained from the theory–experiment comparison are similar to those recently obtained by us for the SBR–ISAF black system[7]. This may serve as a support for the random crosslinking model upon which the PFGF theory is based. The CAF theory fails to predict the preferential adsorption of longer chains and the existence of gel-point and its assumption of non-random desorption of some chains during the solvent extraction does not seem to be substantiated.

ACKNOWLEDGEMENTS

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