Experimental Testing of the Polymer–Filler Gel Formation Theory. Part I

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SYNOPSIS

Experimental data were obtained on the concentration dependence of the fraction of total filler–bound polymer, fraction of polymer in a coherent polymer–filler gel, and fraction of solvent-dispersed filler particles in compounds of fume silica (Aerosil OX50) with natural rubber (NR) and styrene butadiene rubber (SBR). Predictions of the polymer–filler gel formation theory were tested and a good formal description of the data was obtained. The two adjustable parameters of the theory assume reasonable values. While A_0 is a characteristic of the filler interaction with polymer and has similar values in NR and SBR, the functionality f of the theoretically assumed filler particle acting as a polyfunctional crosslinker of polymer chains seems to depend on the polymer as well. Dimensions of the theoretical filler particle calculated from a comparison of experiment with theory are of the same order of magnitude but smaller than those of primary filler particles. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Adsorption of rubbery polymers on fine-particle fillers from bulk is known to result in a partial insolubilization of the polymer. The theories of this phenomenon, commonly known as bound rubber, have recently been critically examined.[1] The theory based on the random adsorption model[2] was found to satisfactorily describe the available experimental data. However, none of the existing theories of bound rubber has attempted a theoretical treatment of the observation that under most experimental conditions the filler particles with polymer chains adsorbed on them are not dispersed by the solvent but form a coherent structure called polymer–filler gel; in the case of carbon-black-filled compounds it is called carbon gel. Early explanations of the carbon gel structure suggested the possibility of filler particles being connected by longer polymer chains, and Kraus and Dugone[3] argued that a coherent gel can only be formed when the average interparticle surface-to-surface distance becomes commensurable with (or smaller than) the dimensions of the polymer chain coil.

Some time ago, one of the authors[4] published a theory of polymer–filler gel formation based on an assumption that in polymer–filler compounds the filler particles act as polyfunctional crosslinkers. The available (qualitative) observations on the gelation effect were found to be reasonably accounted for by the theory. In the present work the effect of gelation in polymer–filler compounds is studied experimentally in more detail and the results are compared with predictions of the polymer–filler gel formation theory.

THEORETICAL

A short review of the polymer–filler gel formation theory is given first since the journal where the original paper appeared may not be available to the reader.

Crosslinking with Polyfunctional Crosslinks

In the first step the Flory theory of crosslinking[5] was generalized to include the case of random crosslinking of linear chains by f-functional crosslinks. The fraction G of the gel is given by the relation[4]

$$G = 1 - \int_0^\infty w(y)\exp[-q_{cr}y(1 - S^{f-1})]\,dy \quad (1)$$

where y is the number of crosslinkable structural units in a primary chain, $w(y)\,dy$ is the mass fraction of chains having y in the range between y and $y + dy$, q_{cr} is the fraction of crosslinked structural units, S is the fraction of sol $(G + S = 1)$, and f is the number of crosslinked units per crosslink. The fraction $q_{cr,S}$ of crosslinked units in the sol is given by an (approximate) relation

$$q_{cr,S} = q_{cr}S^{f-1} \quad (2)$$

The chain-length distribution of primary polymer chains in the gel, $w(y)_G\,dy$, is given by the expression

$$w(y)_G\,dy$$
$$= \frac{w(y)}{G}\{1 - \exp[-q_{cr}y(1 - S^{f-1})]\}\,dy \quad (3)$$

from which the chain-length averages of primary chains in the gel (e.g., the number-average $\bar{y}_{n,G}$ or the mass-average $\bar{y}_{w,G}$) can be calculated. In the vicinity of the gel point $(S \to 1)$ the expression

$$\exp[-q_{cr}y(1 - S^{f-1})]$$

may be satisfactorily approximated by $1 - q_{cr}y(1 - S^{f-1})$, which, upon substitution into Eqs. (1) and (3), leads to the well-known relations:

$$\text{for } S \to 1: \quad q_{cr}\bar{y}_w = \frac{1}{f - 1}$$

$$\bar{y}_{w,G} = \bar{y}_z$$

$$\bar{y}_{n,G} = \bar{y}_w \quad (4)$$

where $\bar{y}_n$, $\bar{y}_w$, $\bar{y}_z$ are the number-average, mass-average, and z-average values of y in the primary distribution, respectively. Integration of Eq. (1) for the Schulz–Zimm distribution (SZD) gives[4]

$$\gamma_{cr} = \frac{1 - S^\epsilon}{\epsilon S^\epsilon(1 - S^{f-1})} \quad (5)$$

where

$$\gamma_{cr} = q_{cr}\bar{y}_w$$

ϵ is the dispersion parameter $(\epsilon = 1 - \bar{y}_n/\bar{y}_w)$, and γ_{cr} is the crosslinking index, i.e., the number of

crosslinked structural units per primary mass-average chain. For an experimental distribution Eq. (1) may be solved numerically.

As seen from Eqs. (1)–(5), the properties of the crosslinked system depend mainly on the fraction of crosslinked units q_{cr}, on the functionality f of the crosslinks, and on $\bar{M}_w$ of the primary polymer. The effect of the dispersion parameter of the polymer in not-too-wide distributions is less significant.

Polymer–Filler Gel Formation Theory

Equations (1)–(5) resulting from the theory of polyfunctional crosslinking were applied to the specific case of a polymer–filler system with the following assumptions:

1. Reactive sites exist on the surface of filler particles, the surface area per one reactive site being A_0; filler particles are of the same size; each filler particle contains f reactive sites on its surface. One polymer chain contains y structural units.
2. Each filler reactive site forms one bond with one polymer structural unit, i.e., a complete conversion of filler reactive sites is assumed. The polymer–filler bond is assumed to be strong enough to resist the desorptive action of the solvent.
3. One structural unit of the polymer is able to react with the filler surface only once.
4. The number of polymer structural units in the polymer–filler compound is much larger than that of filler reactive sites, i.e., the degree of conversion of polymer structural units q_{cr} is assumed to be small.
5. Crosslinking of polymer chains by filler particles is assumed to be random and exclusively intermolecular. The possibility of intramolecular loop formation is not taken into account.
6. When brought into contact with the solvent, the polymer–filler system generally becomes divided into three parts: (I) solvent-dispersed polymer chains (polymer solution), (II) solvent-dispersed filler particles with polymer chains adsorbed on them, and (III) solvent-swollen coherent gel-like structure of filler particles connected through polymer chains.

The mass of the polymer in any of these three parts (i.e., m_{p_I}, $m_{p_{II}}$, $m_{p_{III}}$), and also the mass of filler particles $m_{f_{II}}$, $m_{f_{III}}$ in parts II and III can in principle

be determined experimentally. From such measurements the following data can be obtained:

$U = m_{p_I}/m_p$, fraction of free (filler-unbound) polymer

$B = 1 - U = (m_{p_{II}} + m_{p_{III}})/m_p$, fraction of filler-bound polymer

$S = (m_{p_I} + m_{p_{II}})/m_p$, sol, fraction of solvent-dispersed polymer

$G = 1 - S = m_{p_{III}}/m_p$, gel, fraction of polymer not dispersed by the solvent

$w_{disp} = m_{f_{II}}/m_f$, fraction of solvent-dispersed filler particles

where m_p is the total mass of the polymer, m_f is the total mass of the filler, $c = m_f/m_p$ is the concentration of the filler (mass of filler per unit mass of polymer), B/c is the mass of the filler-bound polymer per unit mass of the total filler, $m_{p_{III}}/m_{f_{III}} = G/c(1 - w_{disp})$ is the mass of the polymer per unit mass of the filler in the gel.

Assumptions 2, 3, and 4 are identical with those used in the theory of bound rubber.[2] Also, the filler reactive sites and the polymer–filler bonds are of the same nature, and the definition of A_0 is identical with that of the bound rubber theory. On the assumption of exclusively intermolecular crosslinking the fraction of crosslinked units q_{cr} should be equal to that of adsorbed units q and should be related to A_0 by

$$q = q_{cr} = \frac{cPM_0}{A_0 N_A} \qquad (6)$$

where P is the specific surface area of the filler, M_0 is the molar mass of the polymer structural unit, and N_A is the Avogadro constant. Also, the crosslinking index $\gamma_{cr} = q_{cr}\bar{y}_w$ should be equal to the adsorption index of the bound rubber theory: $\gamma = q\bar{y}_w$. Inspection of Eq. (1) shows that above the gel point and for larger f values, S^{f-1} quickly decreases to zero with increasing q_{cr}. Under such conditions, the fraction G of the gel approaches the fraction B of bound rubber[2]

$$B = 1 - \int_0^\infty w(y)\exp(-qy)\,dy \qquad (7)$$

If f is larger than, say, 10, then gel point is reached at $\gamma_{cr} \leq 0.1$. Up to the gel point all the filler bound rubber is dispersed by the solvent. In the gel point the quantity $(B-G)$, i.e., the amount of the solvent-dispersed filler bound polymer, reaches a maximum. Above the gel point (i.e., with increasing c, P, $\bar{M}_w$), $(B-G)$ is predicted to decrease rapidly, G approaches

B and bound rubber then exists completely in the gel form.

It is also apparent that the bound rubber theory represents a special case of the polymer–filler gel formation theory, which is more general.

The fraction w_{disp} of solvent-dispersed filler particles is given by

$$w_{disp} = \frac{Sq_{cr,S}}{q_{cr}}$$

Using Eq. (2), the following relation for w_{disp} is obtained:

$$w_{disp} = S^f \qquad (8)$$

Again, above the gel point the fraction of solvent-dispersed filler particles is seen to decrease rapidly with increasing c, P, and $\bar{M}_w$.

Gel Point and Condition of Coherence

The fraction of bound rubber in the gel point, B_{gp}, depends on f and, in general, also on the molar mass distribution of the polymer. However, in the special case of the Schulz–Zimm distribution a simple expression for B_{gp} can be calculated. From the relation given previously [Ref. 1, Eq. (13)] and using $\gamma_{gp} = \gamma_{cr,gp} = 1/(f-1)$, we obtain

$$B_{gp} = 1 - \frac{1}{[1 + \epsilon/(f-1)]^{1/\epsilon}}$$

For $f > 11$, $\epsilon/(f-1)$ becomes small in comparison with unity. Expanding the binomial and taking the first terms, we obtain in the SZD:

$$B_{gp} \doteq 1/f \qquad (9)$$

According to this relation, the bound rubber fraction of SZD polymers in the gel point should be inversely proportional to f; for $f > 10$ it should be smaller than 10%.

The filler concentration in the gel point, c_{gp}, is obtained from Eqs. (4) and (6):

$$c_{gp} = \frac{A_0 N_A}{(f-1)P\bar{M}_w} \qquad (10)$$

If, for instance, in a given polymer–filler system (i.e., for P = const.), both A_0 and f are independent of $\bar{M}_w$, then c_{gp} is predicted to be inversely proportional to the first power of $\bar{M}_w$.

So far, gel point measurements in polymer–filler systems have attracted no attention in the literature. Rather, some interest was focused on the critical filler concentration for coherent carbon gel formation[3] (let us denote it by c_{coh}). The condition of coherence was defined as the inability of the solvent to wash filler particles out of the gel. For the sake of simplicity, we define coherent gel as a gel where $w_{disp} < 0.05$ (less than 5% filler particles are dispersed by the solvent, at least 95% filler particles form a coherent structure with part of the polymer). In the SZD the value of the crosslinking index $\gamma_{cr,coh}$ satisfying the condition $S^f = 0.05$ can be calculated for chosen values of f and ϵ from Eq. (5). It appears that for $f = 10 - 30$ and $\bar{M}_w/\bar{M}_n = 1.5 - 5$, $\gamma_{cr,coh}/\gamma_{cr,gp}$ assumes values between 3 and 3.5. Thus, the filler concentration c_{coh} producing bound rubber, which is almost completely in the form of a coherent gel, is equal to approximately three times the filler concentration c_{gp} necessary to produce the first infinitesimal amount of a three-dimensional gel-like structure.

EXPERIMENTAL

Materials

Natural Rubber (NR)

SMR 5 grade, masticated on a cold mill for 20 min. The limiting viscosity number (2.14 dL/g) was determined in toluene at 25°C. The Mark–Houwink equation with the Carter–Scott–Magat parameters[6] ($K = 5.02 \times 10^{-4}$, $a = 0.667$) gives $\bar{M}_v = 277$ kg/mol. The molar mass distribution of natural rubber with the given degree of mastication is often close to the most probable one.[7] In the latter distribution the above value of $\bar{M}_v$ leads to $\bar{M}_w = 300$ kg/mol, $\bar{M}_n = 150$ kg/mol.

Styrene Butadiene Rubber (SBR)

Kralex 1500, produced by the Kaučuk factory (Kralupy, Czech Republic). The masticated polymer (20 min on a cold mill) had a limiting viscosity number (toluene, 30°C) 1.78 dL/g. From the Homma–Fujita[8] [η]-M measurements we arrived at $K = 5.58 \times 10^{-4}$, $a = 0.675$ for the SBR–toluene system. These values yield $\bar{M}_v = 156$ kg/mol. The molar mass distribution of Kralex 1500 can be roughly described by the Wesslau function. In the latter distribution and assuming $\bar{M}_w/\bar{M}_n = 3$ we obtain from our $\bar{M}_v$: $\bar{M}_w = 175$ kg/mol, $\bar{M}_n = 58$ kg/mol.

Filler

Fume silica Aerosil OX 50 (Degussa, Germany). Producer specification: specific surface area (BET) $P = 50$ m²/g, average particle diameter 40 nm, moisture content (2 h, 105°C) less than 1.5%, ignition loss (2 h, 1000°C) less than 1%. Primary particles are fused to larger aggregates.

Compound Preparation

Polymer–filler compounds with varying filler concentration (see Tables I and II) were prepared in a 50-mL Brabender internal mixer using 25 rpm. The mixing temperature was controlled by 90°C circulating silicone oil. The exact filler concentration in each compound was calculated from the ignition loss of the compound (1000°C) and that of the filler with correction for the ash content of the polymer.

Bound Rubber and Gel Content Determination

After mixing, the compounds were sheeted-out on a two-roll mill, and the specimens were compression molded for 20 min at 100°C. This is a very mild heat treatment. Small samples of known mass (about 1 g) were placed in weighed pouches made of polyamide monofilament fabric and put into 200-cm³ bottles. The nongel part of the sample (i.e., m_{p_I}, $m_{p_{II}} + m_{f_{II}}$) was extracted by adding dry toluene (100 cm³). The solvent was changed three times during 5 days and the extract was collected for analysis. After extraction the pouch contained the coherent polymer–filler gel ($m_{p_{III}} + m_{f_{III}}$) swollen with toluene. It was dried and weighed and the mass of the polymer–filler gel was obtained by subtracting the mass of the dried pouch fabric. Thereafter the pouch with the dry polymer–filler gel was burnt in a laboratory furnace and the mass of the residue (silica filler) was recorded. From these data (taking into account the ash content of the fabric and that of the polymer and the ignition loss of the filler), $m_{p_{III}}$ and $m_{f_{III}}$ were

Table I Experimental Results for NR–Aerosil OX50 Compounds

c	B	G	w_{disp}
0.050	0.046	0	1.0
0.094	0.055	0	1.0
0.144	0.086	0.034	0.685
0.183	0.111	0.076	0.361
0.251	0.179	0.179	0
0.317	0.204	0.204	0

Table II Experimental Results for SBR–Aerosil OX50 Compounds

c	B	G	w_{disp}
0.046	0.015	0	1.0
0.111	0.037	0.001	0.917
0.145	0.076	0.064	0.082
0.198	0.095	0.087	0.030
0.243	0.109	0.109	0
0.313	0.102	0.102	0
0.365	0.116	0.116	0
0.402	0.139	0.139	0

obtained and $m_{f_{II}}$ could be estimated as $m_f - m_{f_{III}}$. The nongel part of bound rubber was isolated from the whole amount of toluene extract by centrifuging and also analyzed for the amount of polymer and filler. This gave estimates of $m_{p_{II}}$, $m_{f_{II}}$. With the known values of m_p, m_f, all the required data (B, G, w_{disp}) could be calculated.

RESULTS AND DISCUSSION

Equation (1) was tested experimentally using an obvious assumption [based on Eq. (6)] that the fraction of crosslinked units, q_{cr}, is proportional to the filler concentration c:

$$q_{cr} = kc \qquad (11)$$

Substitution of this relation into Eq. (1) yields the theoretical dependence of G on c, which contains two adjustable parameters: the functionality f of filler particles and the proportionality constant k. In principle, both can be obtained simultaneously from the G versus c dependence. Alternatively, it is possible to estimate each of these two parameters independently. With q equal to q_{cr}, the parameter k can be obtained from the B versus c dependence, which does not depend on f [Eq. (7), with the use of Eq. (6)]. This method has already been used when testing the bound rubber theory.[2] An independent estimate of the second parameter, f, can be obtained, e.g., from the G versus B correlation, which does not depend on k. As seen from Eqs. (1) and (7), at a given q_{cr} ($=q$) the values of G, B depend, in principle, only on f, while the possible effect of the molar mass distribution may be expected to be only marginal. A similar argument may be applied to the correlation with B of the fraction w_{disp} of solvent-dispersed filler particles and of the nongel part of bound rubber (B-G).

Experimental results are summarized in Tables I and II. The dependences of B on c found for both NR–Aerosil OX50 and SBR–Aerosil OX50 systems are compared with the bound rubber theory [Eq. (7)] in Figures 1 and 2, respectively. The proportionality constant k was adjusted to give the best description of experimental data, and the following values were obtained: $k = 1.72 \times 10^{-4}$ (NR–Aerosil OX50, the most probable distribution, $\bar{M}_w = 300$ kg/mol) and 1.68×10^{-4} (SBR–Aerosil OX50, the Wesslau distribution, $\bar{M}_w/\bar{M}_n = 3$, $\bar{M}_w = 175$ kg/mol). The k value being known, the filler surface area per one reactive site, A_0, is calculated from Eqs. (6) and (11):

$$A_0 = PM_0/kN_A$$

Practically the same values are obtained for both polymer–filler systems: 32 nm^2 for NR–Aerosil OX50 and 32.5 nm^2 for SBR–Aerosil OX50. This result indicates a similar degree of Aerosil OX50 interaction with NR and SBR and parallels that obtained previously[2] for furnace blacks in heat-treated compounds of NR and SBR.

From Tables I and II it is apparent that the gelation concentration c_{gp} is practically the same in both systems and is about 0.1. According to Eq. (10), with equal values of c_{gp} and A_0, a lower f should be obtained for a polymer with higher $\bar{M}_w$. This prediction is born out by experiment. In Figure 3 the G values are plotted versus the corresponding B values and the theoretical G versus B curves are drawn according to Eqs. (1) and (7) for the most probable distribution (NR) and for the Wesslau distribution (SBR, $\bar{M}_w/\bar{M}_n = 3$, lower $\bar{M}_w$ than that of NR). The
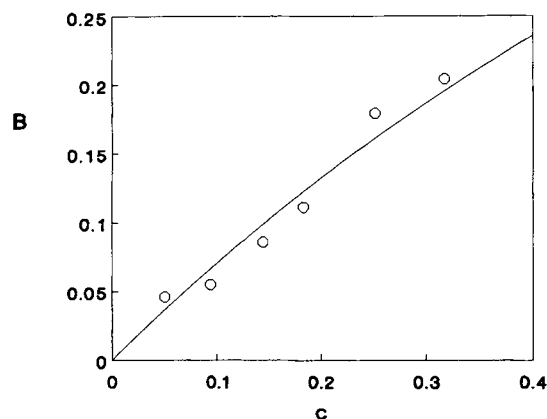

Figure 1 Dependence of bound rubber B on the filler concentration c for NR–Aerosil OX50. Points: experimental. Curve: theoretical [Eq. (7), the most probable distribution; $k = 1.72 \times 10^{-4}$].
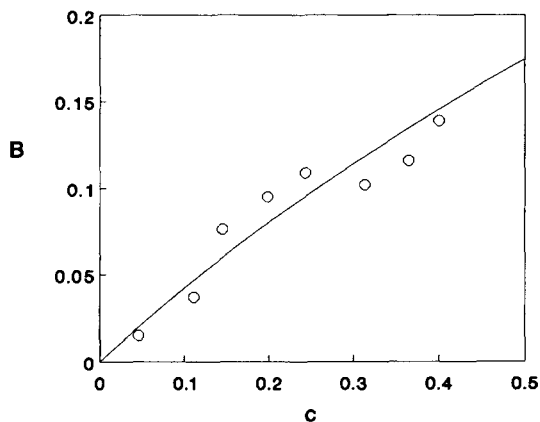
Figure 2 Dependence of bound rubber B on the filler concentration c for SBR–Aerosil OX50. Points: experimental. Curve: theoretical [eq. (7), the Wesslau distribution, $\bar{M}_w/\bar{M}_n = 3$; $k = 1.68 \times 10^{-4}$].

Figure 4 Nongel part of bound rubber $(B–G)$ as function of bound rubber B. Points: experimental (squares, SBR–Aerosil OX50; circles, NR–Aerosil OX50). Curves: theoretical. (1) SBR–Aerosil OX50, $f = 27$; (2) NR–Aerosil OX50, $f = 14.5$.

best fit to experimental data is obtained with f = 14.5 (NR–Aerosil OX50) and f = 27 (SBR–Aerosil OX50). The onset and course of gelation in the system is well seen and satisfactorily described by the theory. It should be mentioned that in the G versus B plot the scatter of data is partially eliminated and is less than that in the G versus c plot.

Complementary to Figure 3 is Figure 4, where the nongel part of bound rubber $(B–G)$ is plotted versus B and the data are described using the f values given above. The fraction of bound rubber in the gel point, B_{gp}, is lower in the SBR system (0.035) than in the NR system (0.067), in accordance with Eq. (9).

Experimental dependences of the fraction of solvent-dispersed filler particles on bound rubber are
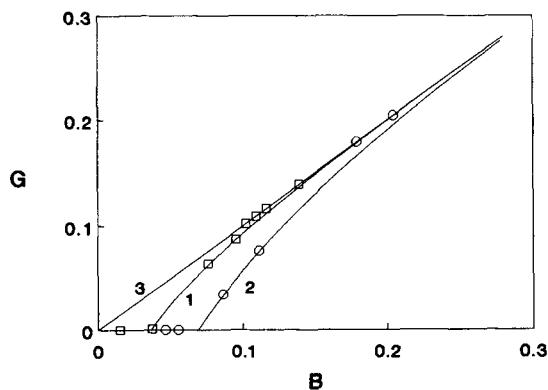
shown in Figure 5. Theoretical curves are drawn using Eqs. (1), (2) and (8) and the above f values. Again, predictions of the theory, i.e., a rapid decrease of w_{disp} to zero above the gel point, appear to be essentially correct. As expected, once the amount of bound rubber reaches about $2.5B_{gp}$ (or, when c increases to about $2.5c_{gp}$), practically all filler particles become part of a coherent polymer–filler gel and cannot be eluted by the solvent any more.

The finding that A_0 of Aerosil OX50 is practically the same both in NR and SBR is understandable and in accordance with previous experience. On the other hand, the fact that different values of the filler functionality were obtained in the two polydiene rubbers is less clear. The product of the two param-

Figure 3 Polymer–filler gel G as function of bound rubber B. Points: experimental (squares, SBR–Aerosil OX50; circles, NR–Aerosil OX50). Curves: theoretical. (1) SBR–Aerosil OX50, $f = 27$; (2) NR–Aerosil OX50, $f = 14.5$; (3) B vs. B line.
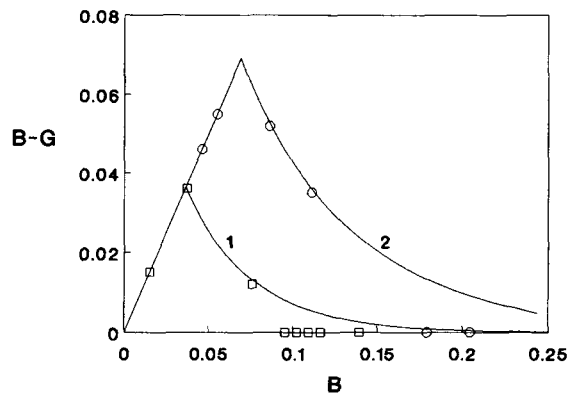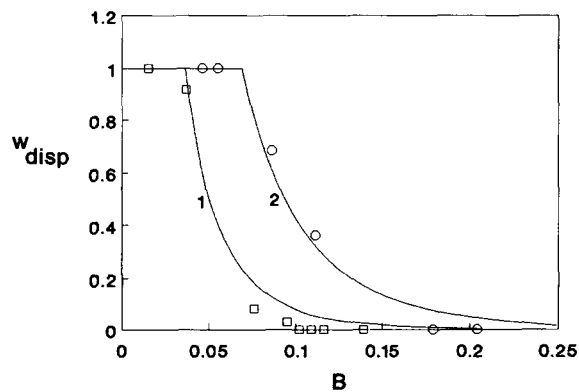

Figure 5 Fraction of solvent-dispersed filler particles w_{disp} as function of bound rubber B. Points: experimental (squares, SBR–Aerosil OX50; circles, NR–Aerosil OX50). Curves: theoretical, (1) SBR–Aerosil OX50, $f = 27$; (2) NR–Aerosil OX50, $f = 14.5$.

eters $(A_0 f)$, should give the surface area, SA_p, of the theoretically assumed particle, which acts as a crosslinker of polymer chains; its diameter d_p would be

$$SA_p = A_0 f$$

$$d_p = (SA_p/\pi)^{0.5}$$

In SBR the diameter d_p of the hypothetical cross-linking filler particle thus obtained is 17 nm, in NR it is 12 nm. This result might seem as a satisfactory order-of-magnitude agreement with the mean diameter of the primary particle of Aerosil OX50, which is 40 nm. However, it is probable that the actual particles participating in the formation of polymer–filler gel are in fact aggregates of the primary particles. In comparison with their dimensions, d_p of our crosslinking particle appears to be rather low.

One of the reasons of this discrepancy might be a possible occurrence of multiple segment adsorption of the same polymer chain on the same filler particle. From the point of view of the crosslinking model, such an effect is understood as intramolecular loop formation (wastage of crosslinking sites). It would leave the values of B (and A_0) unchanged, but the fraction of gel would be decreased. As a result, the value of f calculated from G would also be decreased, and if used to estimate the size of the theoretical crosslinking particle, it would lead to seemingly low values. Intramolecular loop formation may well be polymer-specific, and this could be the reason for the observed differences between NR and SBR.

Further experimental tests are in progress.

CONCLUSIONS

The polymer–filler gel formation theory predicts the existence of the critical filler concentration c_{gp} for incipient gel formation, an inverse proportionality (in the Schulz–Zimm distribution) between the amount of bound rubber in the gel point and the functionality f of the theoretical filler particles acting as polyfunctional crosslinkers, a rapid decrease, with increasing filler concentration c, of the fraction of solvent-dispersed filler particles that should drop practically to zero at concentrations greater than approximately $3c_{gp}$; above this concentration the filler-bound polymer should exist completely in the form of a coherent gel while at lower filler concentrations it should be partially (between c_{gp} and $3c_{gp}$) or totally (below c_{gp}) dispersible in the solvent. All these predictions of the theory are born out by experiments performed with use of fume silica filler and two polymers: NR and SBR. A reasonably good quantitative description of the data was obtained using the theoretical relations. This may be regarded as a good success of the theory that is based on a very simple model and contains only two adjustable parameters. An explanation for the rather low f values calculated from the comparison of theory with experiment was suggested.

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