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Thermomechanical properties of rubber/carbon black composites

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The peculiarities observed with the mechanical behaviour of rubber/carbon black composites, due to the formation of rigid structures of carbon black particles within the rubber matrix, were found to occur with their thermomechanical behaviour as well. Application of a model developed in order to cope with the mechanical behaviour led to suitable modification of prediction theories, not only to provide good agreement with experimental evidence, but also to yield satisfactory explanations for certain associated phenomena.

1. Introduction

Rubber/carbon black composites exhibit a peculiar mechanical behaviour including the following:

(i) Their mechanical moduli are much higher than those predicted by mechanical composite theories for the corresponding amount of filler.

(ii) The enormous increase in the values of the mechanical moduli depends very strongly on the size of the carbon black particles and less on their particular type.

(iii) When repeatedly strained above a certain level they exhibit stress softening, a phenomenon known as "Mullins effect".

(iv) When subjected to harmonic loading, their mechanical moduli exhibit intense frequency dependence, not explicable by means of the average size of the carbon black particles as compared to the respective wavelength.

This peculiar behaviour is generally explained in terms of a "structure" created by the filler particles, which are interconnected with strong high-energy bonds of rubber chains [1].

Various theories concerning the reinforcing mechanisms of rubber/carbon black composites have been proposed by different authors.

(a) "Hydrodynamic" theories, based on the classical work of Einstein, for compressible viscous fluids, were developed by Guth and Gold [2]. Van der Poel [3], Eilers and Van Dijck [4] and Brinkman [5].

(b) Strain amplification theory, developed by Mullins and Tobin [6].

(c) The theory of rubber network transformation mechanism was developed by Blanchard and Parkinson [7], who stressed the special role of carbon black particles in the linkages of rubber.

(d) The theory of interparticle chain breakage mechanism suggested by Bueche [8].

(e) The theory of molecular slippage mechanism suggested by Dannenberg [9] and others.

Based on the assumption that part of the soft matrix material is trapped or occluded within the rigid structure formed by the carbon black particles, thus acting as a reinforcing element, a more realistic approach was developed [1]. In fact, a "reinforcing factor", λ, was defined, such that

$$\lambda = v_s/v$$

where v is the actual volume fraction of active filler, i.e. of carbon black and v_s the volume fraction of non-active rigid filler required in order to produce the actual reinforcing effect. Determination of λ was obtained by using Van der Poel's theory [3], which was found sufficiently accurate for the kind of materials considered.

It was found that λ remains constant, while the volume fraction, v, of carbon black varies and it depends strongly on the active surface area of the latter. Clearly, λ is always > 1 and a typical example is a pure gum vulcanizate filled with a high-abrasion furnace black (HAF), for which $\lambda = 1.99$ and 1.44 for the low- and high-strain modulus, respectively.

A quantitative approach to the above situation can be obtained by a model consisting of the cubic arrangement of eight spherical particles (Fig. 1). The spherical inclusions are encapsulated by spherical shells of increased rigidity consisting of immobilized rubber, whose thickness a, depending on the particular type of rubber, is in reality of the order of 0.5 to5 nm. If r is the radius of the spherical particle, the volume of the cubical cell is equal to $V = [2(r + a)]^3$, the filler volume

$$V_f = 1/8(4\pi r^3/3) \times 8 = 4\pi r^3/3$$

and the volume fraction of the latter

$$V = V_f/V = (\pi/6)/(1 + a/r)^3$$

for which expression the reinforcing factor λ assumes the form

$$\lambda = v_s/v = 8(r + a)^3/(4\pi r^3/3)$$
$$= 1.909(1 + a/r)^3$$

leading to $\lambda = 1.909$ for contacting spheres ($a = 0$) and $\lambda = 2.541$ for $a/r = 0.1$, which are highly realistic values.

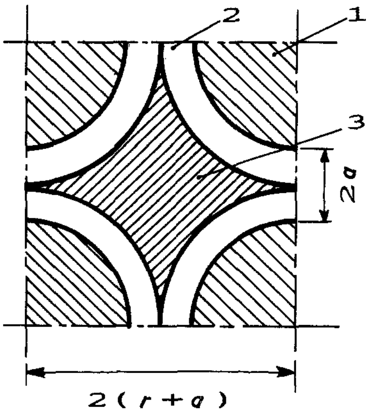


Figure 1 A model for the basic cell of the carbon black structure consisting of a cubic arrangement of eight identical spherical particles: 1, carbon black particle; 2, immobilized rubber; 3, occluded rubber.

In addition to the above phenomena, deviations between predicted and experimental values of thermal expansion coefficients were also observed with rubber/carbon black composites, which were attributed to strain-induced crystallization, occurring within the rubber phase. Therefore, it appeared an interesting task to investigate potential peculiarities in the thermomechanical behaviour of these materials in the light of the above approach, and this is the aim of the present work.

2. Prediction theories

A number of theories have been developed for the thermal expansion coefficients of particle composites, consisting of homogeneous and isotropic phases, and the corresponding expressions are given in the sequence. α and γ are the linear and cubical thermal expansion coefficients, respectively, E, G, k are Young's, shear and bulk modulus respectively, ν_m, ν_p, ν_c are Poisson's ratios for the respective material and v is the volume fraction of filler particles. Subscripts c, m and p are used for composite, matrix and particles, respectively. Theoretical predictions are grouped as follows [11–13].

(a) For spherical particle shape
Kerner:

$$\gamma_c = (1 - v)\gamma_m + \gamma_p - (\gamma_m - \gamma_p)v(1 - v)\Lambda \qquad (1)$$

where

$$\Lambda = [1/k_m - 1/k_p]/[v/k_m + (1 - v)/k_p + 0.75G_m]$$

Blackburn:

$$\gamma_c = \gamma_p + (\gamma_m - \gamma_p)A/B \qquad (2)$$

where

$$A = 3/2\,(1 - \nu_p)(1 - v)$$
$$B = 1/2\,(1 + \nu_p) + (1 - v)(1 - 2\nu_p) + (1 - 2\nu_m)\,v - E_p/E_m$$

Wang and Kwei:

$$\gamma_c = \gamma_m - (\gamma_m - \gamma_p)\,q \qquad (3)$$

where

$$q = [3\,(E_p/E_m)v]/[E_p/E_m\{2v(1 - 2\nu_m) + (1 + \nu_m)\} + 2(1 - v)(1 - 2\nu_p)]$$

Tummala and Friedberg:

$$\gamma_c = \gamma_m - v(\gamma_m - \gamma_p)W \qquad (4)$$

where

$$W = [(1 + \nu_m)/2E_m]/[(1 + \nu_m)/2E_m + (1 - 2\nu_p)/E_p]$$

(b) For any particle shape
Thomas:

$$\gamma_c^q = (1 - v)\gamma_m^q + v\gamma_p^q \qquad (5)$$

where q is an empirical parameter varying from + 1 to − 1.

Turner:

$$\gamma_c = [(1 - v)\gamma_m k_m + v\gamma_p k_p]/(1 - v)k_m + vk_p] \qquad (6)$$

Cribb:

$$\gamma_c = \theta_1\gamma_m + \theta_2\gamma_p \qquad (7)$$

where

$$\theta_1 = k_m(k_c - k_p)/k_c(k_m - k_p)$$
$$\theta_2 = k_p(k_m - k_c)/k_c(k_m - k_p)$$

Hobbs:

$$\gamma_c = A\gamma_m + B\gamma_p \qquad (8)$$

where

$$A = [k_H(k_m + 2k_p) - k_m k_p]/(k_H(k_m + k_p))]$$
$$B = [k_p(k_m - k_H)]/[k_H(k_m + k_p)]$$

and k_H is the bulk modulus of a composite containing cavities in the place of the filler particles [12].

3. Theoretical predictions for rubber/carbon black composites

Typical figures for the properties of rubber are [14]: $G_m = 0.7\,\mathrm{MPa}$, $E_m = 2.0\,\mathrm{MPa}$, $k_m = 1.0\,\mathrm{GPa}$, $\nu_m = 0.5$, $\varrho_m = 0.94 \times 10^3\,\mathrm{kg\,m^{-3}}$, $a_m = (20 \text{ to } 25) \times 10^{-5}\,{}^\circ\mathrm{C}^{-1}$, $\gamma_m = (60 \text{ to } 75) \times 10^{-5}\,{}^\circ\mathrm{C}^{-1}$. On the other hand, the mechanical moduli of carbon black, being of the order of several GPa, are much higher than those of rubber [1]. Therefore, the carbon black can be considered as rigid in the present consideration. Moreover, the linear thermal expansion coefficient of carbon black being of the order of $10^{-6}\,{}^\circ\mathrm{C}^{-1}$, is negligible in comparison to that of rubber [15] and can be admitted to be zero.

For these figures, the prediction equations already mentioned assume the following forms.

Kerner, Tummala/Friedberg:

$$\gamma_c/\gamma_m = 1 - v \qquad (9)$$

Blackburn:

$$\gamma_c/\gamma_m = 1.5(1 - v)/(1.5 - v) \qquad (10)$$

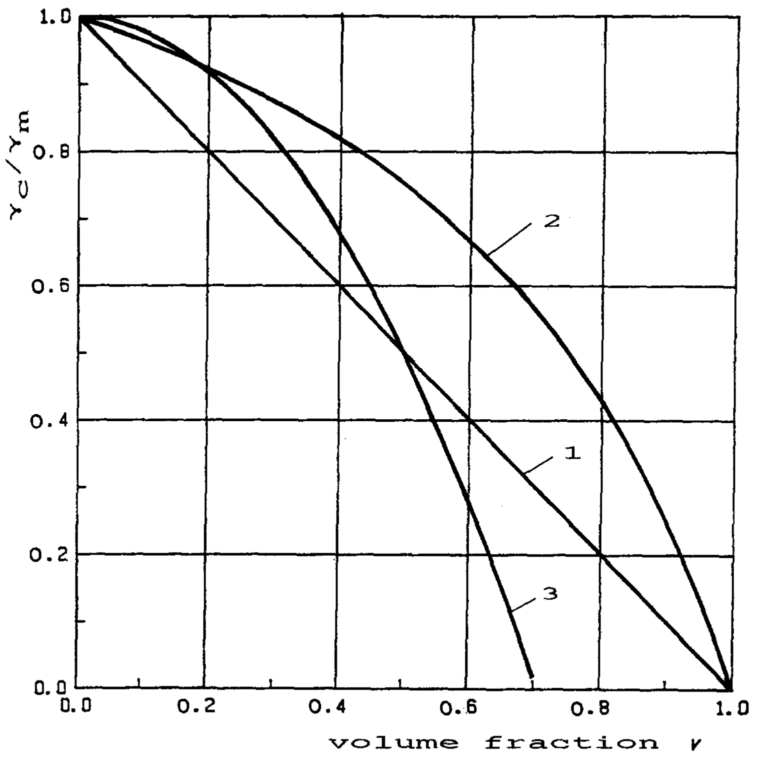


Figure 2 The ratio γ_m/γ_m plotted against volume fraction, v, of carbon black for three different predictions: 1, linear mixture equation; 2, Blackburn's equation; 3, Wang and Kwei's equation.

Wang and Kwei:

$$\gamma_c/\gamma_m = 1 - 2v^2 \qquad (11)$$

while the remaining ones are not applicable. Values of γ_c/γ_m as predicted by Equations 9 to 11 are plotted against volume fraction of filler in Fig. 2.

4. Comparison with experimental data

Experimental data selected from the literature [15], included two composites consisting of a styrene–butadiene–rubber (SBR) reinforced either with a HAF black (average particle diameter 24 to 28 nm, nitrogen surface area 80 m^2 g^{-1}) or an MT black (medium-thermal, average particle diameter 250 to 500 nm, nitrogen surface area 8 m^2 g^{-1}). Both the glassy and the rubbery states of the materials were considered. The glass transition temperature, T_g, of SBR, about $-16°$ C, was not substantially affected by the presence of carbon black. For both of the above materials, γ_c/γ_m plotted against v, is presented in Figs 3a and b for the glassy and the rubbery states. However, because at the rubbery state both materials appear to be characterized by identical curves (Fig. 3c), it is sufficient to use in the following, one of them, e.g. the one for SBR/HAF.

In fact, this latter experimental curve must be compared with the theoretical predictions of Equations 10 and 11. Equation 9, i.e. the linear rule of mixtures, is a very much simplified approach, which in general tends to underestimate the values of the respective parameters. The two predicted curves as well as the experimental one are presented in Fig. 4. Simple inspection confirms that the presence of carbon black affects thermal expansion in the rubbery state much stronger than predicted.

In order to follow the procedure adopted in [1] an "influence factor", λ_T, is defined, in analogy with the reinforcing factor, λ, used for the mechanical properties, in the following manner

$$\lambda_T = v_s/v$$

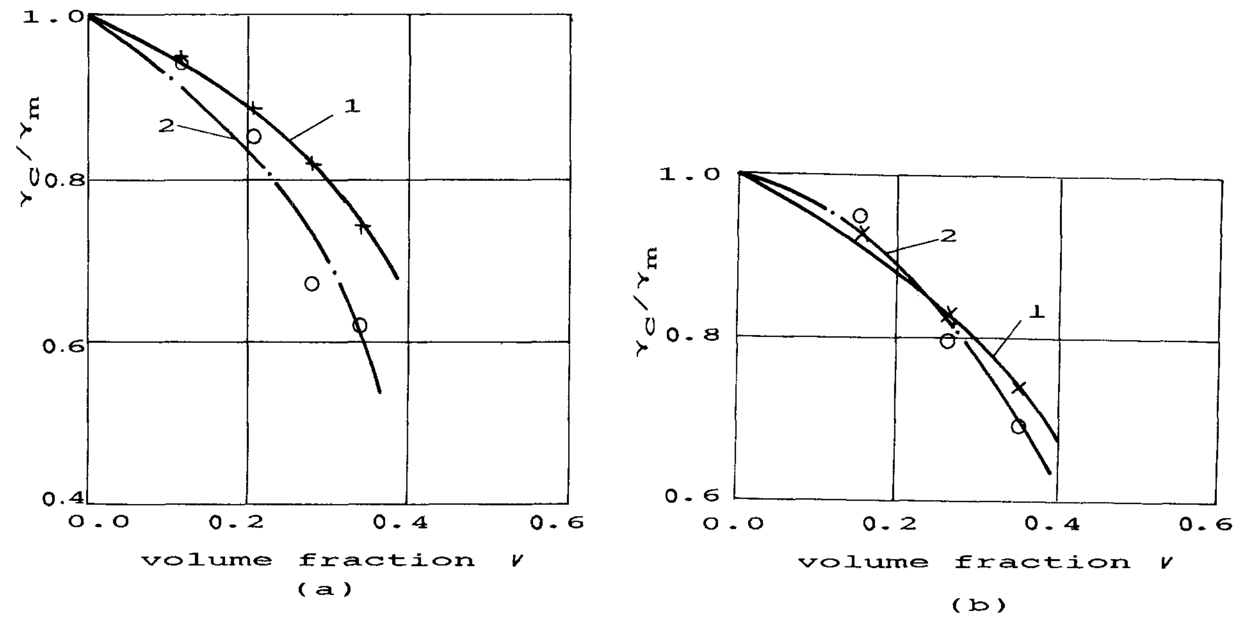
As there are two theoretical curves available, λ_T has to be determined on the basis of each one of them separately, with the procedure suggested in Fig. 4. For a given value of γ_c/γ_m, the actual volume fraction of filler v is derived from experiment, while the values of the latter, which would produce the corresponding predicted result are v_{s1} and v_{s2}, depending on the respective theoretical curve. Values for λ_{T1} and λ_{T2} plotted against v are presented in Figs 5a and b. Clearly, the theory of Wang and Kwei (curve 2, Fig. 4) provides a better approximation to reality with $\lambda_{T2} = 1.10$, against $\lambda_{T1} = 1.50$ derived from Blackburn's theory. However, in the former theory, an effective volume fraction of filler has been considered, taking into account the effect of mechanical stress fields developing because of temperature increases, resulting thus in a better approximation [16].

5. Discussion and conclusions

In order to apply the concept of immobilized and occluded rubber, the following reasoning should be applied.

The volume of a single spherical particle with radius r is equal to $4\pi r^3/3$. If an interphase of immobilized rubber of thickness a develops, this volume increases to $4\pi(r + a)^3/3$, and the ratio of the latter over the former is equal to $\lambda'_T = (1 + \alpha/r)^3$, expressing the effect of the influence factor, if only immobilized but not occluded rubber is involved. With $r/a = 6.0$, a very reasonable figure for furnace blacks, one has $\lambda'_T = 1.58$, which is very close to the figure experimentally obtained using Blackburn's theory, i.e. $\lambda_{T1} = 1.50$.

A micromechanical explanation for this particular phenomenon can be obtained by means of the basic cell model of Fig. 1. At this point, one should bear in mind that strain-softening or Mullins effect is due to breakage of interparticle chains and the subsequent



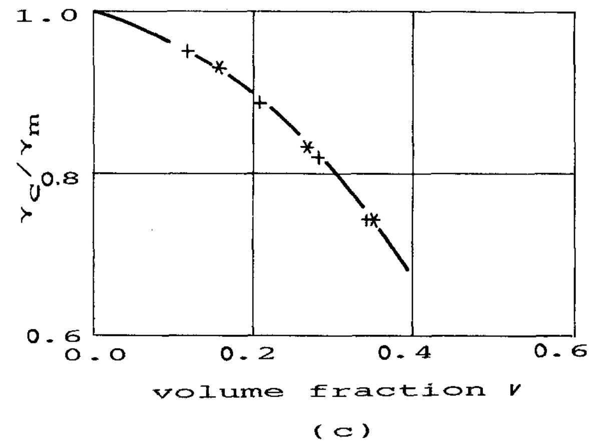


Figure 3 Experimental values of the ratio γ_c/γ_m plotted against volume fraction, v, of carbon black for a SBR rubber reinforced with (a) HAF carbon black in the rubbery (curve 1) and in the glassy (curve 2) state, (b) MT black in the rubbery (curve 1) and in the glassy (curve 2) state. (c) A common experimental curve for the rubbery state of both of the previous cases.

release of occluded rubber after repeated straining [1]. However, the same result can be effected by thermal straining. In fact, with increasing temperature, i.e. in the rubbery region of the matrix material, heat is flowing through the highly conductive structure of the carbon black particles into the nucleus of the basic cell, i.e. into the mass of occluded rubber. The latter, possessing a much higher thermal expansivity than the surrounding rigid structure, applies an increasing pressure on the latter until it breaks, thus releasing the occluded rubber.

The latter constitutes what could be termed the "thermal Mullins effect", and an impressive fact is that the reinforcing factor, corresponding to strain-softened material, assumes the value $\lambda_\infty = 1.44$ [1], i.e. remarkably close to the value $\lambda_T = 1.50$, obtained in the present work. The fact that the thermal expansion coefficient of these materials in their glassy state is much smaller than that in the rubbery state, in fact

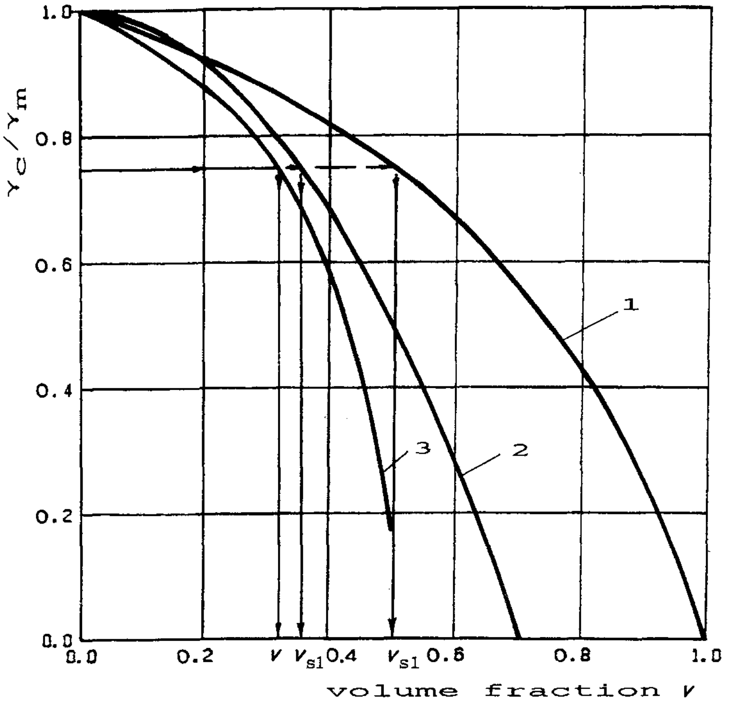


Figure 4 Theoretical predictions by Blackburn (curve 1) and by Wang and Kwei (curve 2) compared with experimental values (curve 3), and derivation of the respective effective volume fractions v_{s1} and v_{s2}.

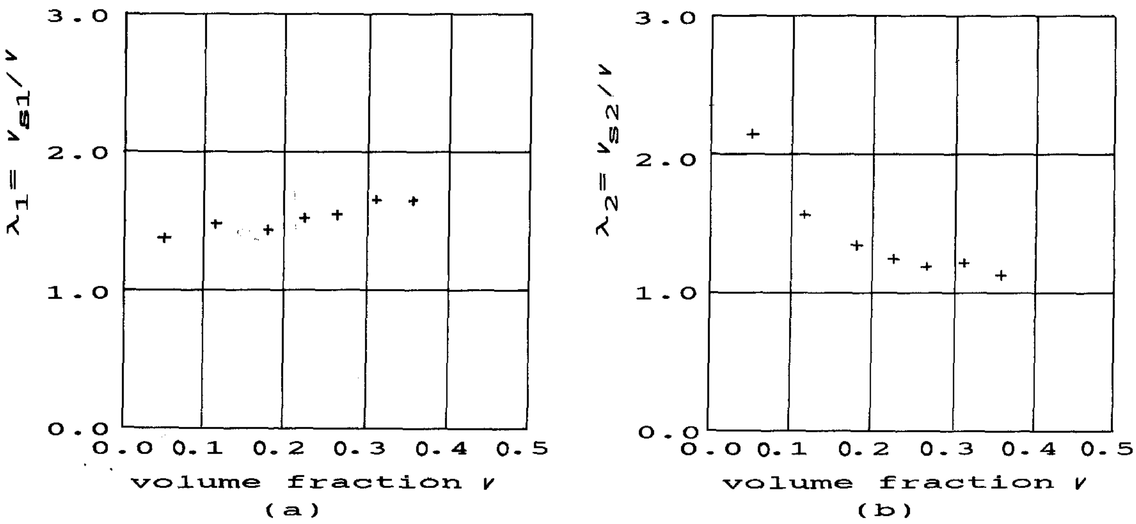


Figure 5 Variation of the influence factor, λ_T, with volume fraction, v, according to (a) Blackburn and (b) Wang and Kwei.

smaller than justified by the free volume reduction of the matrix [15], further confirms the above explanation.

In view of the above, the following conclusions can be drawn. Rubber/carbon black composites exhibit physical properties greatly different than predicted by the respective theories for composite materials consisting of non-active particles dispersed in a continuous matrix. In fact, not only the mechanical properties, but also the thermomechanical ones, notably the thermal expansion coefficients, seem to be drastically affected by the presence of carbon black in rubber. These peculiarities appear to be the result of "structuring" of the filler particles through immobilized rubber regions into rigid structures, in which soft rubber matrix is occluded and therefore compelled to act as reinforcing element.

The corresponding procedure applied in the investigation of mechanical properties elsewhere [1] was found to be applicable with the thermomechanical properties as well and provided a most satisfactory agreement between experimental and predicted figures. Furthermore, it was found that breakage of the immobilized rubber chains, which, when effected by repeated straining leads to strain-softening (a phenomenon known as Mullins effect), can also occur when the material is subjected to increased temperature, due to the high thermal expansion of the soft core of occluded rubber. The values of the respective parameters, providing quantitative estimates for the mechanical and thermal effects, were found in remarkable agreement.

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