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Study on the relationships between the structure of networks and mechanical properties of rubber vulcanizates

1. The theory of elasticity for rubber vulcanizates with carbon black fillers at large deformation

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Summary

Basing on that the fluctuations of chains and junctions in real vulcanizates with carbon black fillers are suppressed by the presence of three kinds of forces which are network, entanglement and carbon black-polymer interaction forces. A new molecular theory of rubber elasticity for vulcanizates with carbon blacks at large deformation was presented. It succeeds in relating the elastic state to molecular constitution by three important quantities (C_{100} , C_{020} and C_{200}). In which the severity of constraints by entanglements, crosslink and junctions of carbon blacks are characterized with four molecular parameters $\Phi_{\lambda c}$, $\Phi_{\lambda e}$, $\Phi_{\lambda' cf}$ and $\Phi_{\lambda' ef}$. The relationships of stress to strain for four types of deformation were derived from this theory.

Introduction

Carbon or graphite filled rubber vulcanizates are generally designed as particulate composites. Carbon blacks are widely used in SBR and NR vulcanizates and convey significant improvements in modulus, abrasion resistance, tensile strength and tear strength (1). They are uniquely efficient in these respects, but the phenomena are still not fully understood and the reason for this is still the subject of debate.

Many theories (2-3) and equations (4-5) have been put forth explaining the stress softing and relating modulus of composites to the volume fractions of fillers. But both of them are quite a few marked deficiencies: it shows a marked deviation from experiments at higher volume fractions of fillers, it can not predict the experimental fact that the modification of properties of the matrix by fillers may increase or decrease modulus of composites, and bound or occluded rubber, immobilization of polymer segments at the interface and secondary agglomeration are not taken into account. Therefore it is necessary to develop a complete theory of elasticity for rubber vulcanizates with carbon black fillers.

Theory of Elasticity

In previous papers (6) a new molecular theory of rubber elasticity with constraints of junctions and entanglements was proposed. It is based on these facts that the real networks differ from the phantom networks in that the chains are constrainted by two forces, one is the network forces between the chains direct connected to a crosslinked junction, the other one is the long range local entanglement forces between the trapped entanglement chains and it can shift along the chain contor, so that the extension of free fluctuations for chains and junctions in real networks will be generally suppressed as compared to the phantom networks; the structure of the real networks is not uniform, which consists of different length of chains.

Due to the presence of that two constraints the f_c crosslinked chains and 4 trapped entanglement chains respectively constitute a constituent chain of crosslinked and trapped entanglement networks. The two constituent chains are considered respectively as the statistically elementary unit of network assembly, in contradiction to that the classical theory of rubber elasticity considers the networks as a collection of Gaussian strants. Therefore we argue that the crosslinked and trapped entanglement networks are formed by the combination of two kinds of constituent chains with different dimensions of $\bar{\Lambda}_{ci}$ and $\bar{\Lambda}_{ej}$. Their probability distribution functions of end-to-end vector were respectively calculated by a developed method (6). Results show that the two distribution functions differ from the Gaussian function. Their expressions are given as follow:

$$F_c(r\bar{\Lambda}_{ci})d\bar{\Lambda}_{ci} = -\frac{f^2\beta_i^6}{2\pi^3} e^{-f\beta_{oi}(r^2+2\bar{\Lambda}_{ci}^2)} \frac{1}{\beta_{oi}^2\bar{\Lambda}_{ci}r} \sinh(2f\beta_{oi}^2\bar{\Lambda}_{ci}r)d\bar{\Lambda}_{ci} \tag{1}$$

and

$$F_e(r\Lambda_{ej})d\Lambda_{ej} = -2\,\frac{4^2\beta_j^6}{\pi^2}\,e^{-4\beta_{oj}^2(r^2+2\Lambda_{ej}^2)}\,\frac{\Lambda_{ej}}{\beta_{oj}^2 r}\sinh(8\beta_{oj}^2\Lambda_{ej}r)\,d\Lambda_{ej} \qquad (2)$$

Where f is functionality; Λ_{ci} and Λ_{ej} are the average dimensions of two kinds of constituent chains;

$\beta_o = 3/2\cdot\frac{1}{\langle r_o^2\rangle}$; $\beta_i = 3/2\cdot\frac{1}{\langle\Lambda_{ci}^2\rangle}$ and $\beta_j = 3/2\cdot\frac{1}{\langle\Lambda_{ej}^2\rangle}$

We have also proposed a mechanism of large deformation(6) that the two kinds of constituent chains in crosslinked and trapped entanglement networks are considered respectively as an independent elementary unit to take part in the macroscopic deformation and they are transformed affinely with strain by $\Lambda_{ij} = \alpha\Lambda_{ijo}$ (α is extension ratio), in contradiction to that the classical theory of rubber elasticity considers the individual chain as an independent elementary unit. So that it will show a marked nonaffineness effects at large deformation. But according to our proposed mechanism of large deformation the individual chain in the constituent chains only performed a small molecular cooperattive deformation through the topological rearrangement of the position of junction pairs. Therefore the three effects of the trapped entanglements, the nonaffineness in large deformation of chain vector and the non-Gaussian on the elasticity were taken into account at the same time in the proposed theory.

Basing on these distribution functions and the mechanism of large deformation the elastic free energy of deformation for crosslink-entanglement networks was calculated by the relation, $\Delta F_{TT} = kT\ln\Omega$, as the sum of two terms, one from the crosslinked networks ($\Delta F'_{cT}$), the other one from the trapped entanglement networks ($\Delta F'_{eT}$). Their approximate expressions are given by equation of (7). It succeeds in relating the elastic properties to molecular constitution by three molecular quanitties (C'_{100} , C'_{020} and C'_{200}), in which the severity of junction and entanglement constraints are characterized by two parameters ($\Phi_{\Lambda c} = \langle\langle\frac{\Lambda_{ci}^2}{\langle r_{oi}^2\rangle}\rangle\rangle$) and ($\Phi_{\Lambda e} = \langle\langle\frac{\Lambda_{ej}^2}{\langle r_{oj}^2\rangle}\rangle\rangle$). It can be seen from the equ. of (7) the free energy of deformation derived from the proposed theory differs the classical results by a term $(C'_{200c} + C'_{200e})\left[(\alpha_x^2 + \alpha_y^2 + \alpha_z^2)^2 - 9\right]$. The values of the difference increases with increasing deformation. It represents a pronounced upturn for high extensibilities due to non-Gaussian effects.

Theoretical stress to strain curves for five types of deformation derived from this theory are varified by experiments.(6) It shows that this theory can predict the rubber-like elasticity quantitatively at large deformation and explain the role of entanglements and the reduction of junction fluctuations on the functionality and the severity of constraints for the model PDMS networks.

In this paper the above theoretical method and procedure was extended to treat the rubber vulcanizates with carbon blacks and a new molecular theory of rubber elasticity with constraints of crosslink, trapped entanglements and carbon black junctions was presented. It is based on these facts that the structure of vulcanizates with carbon blacks is not uniform which consists of different length of chains and different size of carbon black aggregates; the extension of free fluctuations for chains and junctions in real vulcanizates with carbon blacks will be generally suppressed as compared to the phantom networks; and the large macroscopic deformation resulting from the external stress can only produce a small molecular deformation of network chain.

1). Model of Structure: The additions of fillers to the crosslink-entanglement networks give rise to the increase in the network chain density, since there are the physical and chemical ($f_{cf} + f_{ef}$) polymer chains to be juncted at a filler surface. Therefor we argued that the structure of rubber vulcanizates with carbon blacks are formed by the combination of three kinds of networks which are crosslink-entanglement networks, physical carbon black-polymer chain networks and chemical carbon black-polymer chain networks. Due to the constraints of the physical and chemical interaction forces the f_{cf} and f_{ef} polymer chains direct connected to a filler particle surface may be respectively considered as a constituent chain of physical and chemical carbon black-polymer chain networks with different dimensions of $\bar{\lambda}'_{cfi}$ and $\bar{\lambda}'_{efj}$. The crosslink-entanglement networks is formed by the combination of the other kinds of constituent chains with different dimensions of Λ_{ci} and Λ_{ej} (6).

2). Probability Distribution Function of End-to-End Vector: The probability distribution functions of end-to-end vectors (r') of two constituent chains with different dimensions of Λ'_{cfi} and Λ'_{efj} in carbon black-polymer chain networks were calculated by a developed method$^{(6)}$. They show that the probability distribution functions differ from the Gaussian function, and they are given by equations (3) and (4).

$$W(r'\Lambda'_{cfi}) = -\frac{f_{cf}^2}{2\pi^3}\beta_{ci}^6 e^{-f_{cf}\beta_{oci}^2(r'^2+2\Lambda'^2_{cfi})} \cdot \frac{1}{\beta_{oci}^2\Lambda'_{cfi}r'} \sinh(2f_{cf}\beta_{oci}^2\Lambda'_{cfi}r') \cdot d\Lambda'_{cfix}\, d\Lambda'_{cfiy}\, d\Lambda'_{cfiz} \tag{3}$$

and

$$W(r'\Lambda'_{efj}) = -2\frac{f_{ef}^2}{\pi^2}\beta_{ej}^6 e^{-f_{ef}\beta_{oej}^2(r'^2+2\Lambda'^2_{efj})} \cdot \frac{\Lambda'_{efj}}{\beta_{oej}^2 r'} \sinh(2f_{ef}\beta_{oej}^2\Lambda'_{efj}r') \cdot d\Lambda'_{efj} \tag{4}$$

where $\beta_{ocef}^2 = \frac{3}{2}[\langle(r'+a_{ij})^2\rangle]^{-1}$. The probability distribution functions of end-to-end vector for the other two constituent chains with different dimensions of Λ_{ci} and Λ_{ej} in crosslink-entanglement networks are given in the equs. of (1) and (2).

3). Mechanism of Large Deformation: The four kinds of constituent chains in the rubber vulcanizates with carbon black fillers are considered as an independent elementary unit to take part in the macroscopic deformation and they transformed affinely with the strain ($\Lambda'_{ij} = \alpha\Lambda'_{ij0}$), but the individual chains in the constituent chain can only performed a small molecular cooperative deformation through topological rearrangement of the position of junction pairs.

4). Elastic Free Energy of Deformation: With the above probability distribution functions and mechanism of large deformation, the elastic free energy of deformation was calculated by the following equation.

$$\Delta F = kT \ln \Omega \tag{5}$$

where Ω is the numbers of configuration.

A). Elastic Free Energy of Deformation for Carbon Black-Polymer Chain Networks: We have calculated the elastic free energy of deformation ($\Delta F'_{cefr}$) as the sum of two terms, one from the physical carbon black-polymer chain networks, and the other one from the chemical carbon black-polymer chain networks. It is given by equation of (6)

$$\Delta F'_{cefT}=\frac{1}{2}kT\{(\xi_{cf}B_{cf}+\xi_{ef}B_{ef})(\alpha_x^2+\alpha_y^2+\alpha_z^2-3)+(\xi_{cf}C_{cf}+\xi_{ef}C_{ef})[(\alpha_x^2+\alpha_y^2+\alpha_z^2)^2$$
$$-3^2]+\xi_{cf}D_{cf}\ln(\alpha_x\alpha_y\alpha_z)+\xi_{ef}D_{ef}\ln[\frac{1}{3}(\alpha_x^2+\alpha_y^2+\alpha_z^2)]\}$$
$$=(C_{100cf}+C_{100ef})(\alpha_x^2+\alpha_y^2+\alpha_z^2-3)+(C_{200cf}+C_{200ef})[(\alpha_x^2+\alpha_y^2+\alpha_z^2)^2-3^2]$$
$$+C_{020ef}\ln[\frac{1}{3}(\alpha_x^2+\alpha_y^2+\alpha_z^2)]+C_{001cf}\ln(\alpha_x\alpha_y\alpha_z) \qquad (6)$$

B). Elastic Free Energy of Deformation for Crosslink-Entanglement Networks: It is given by equation of (7) (6)

$$\Delta F'_{ceT}=\frac{1}{2}KT\{(\xi_cB_c+\xi_eB_e)(\alpha_x^2+\alpha_y^2+\alpha_z^2-3)+(\xi_cC_c+\xi_eC_e)[(\alpha_x^2+\alpha_y^2+\alpha_z^2)^2$$
$$-3^2]+\xi_cD_c\ln(\alpha_x\alpha_y\alpha_z)+\xi_eD_e\ln[\frac{1}{3}(\alpha_x^2+\alpha_y^2+\alpha_z^2)]\}$$
$$=(C'_{100c}+C'_{100e})(\alpha_x^2+\alpha_y^2+\alpha_z^2-3)+(C'_{200c}+C'_{200e})[(\alpha_x^2+\alpha_y^2+\alpha_z^2)^2-3^2]$$
$$+C'_{020e}\ln[\frac{1}{3}(\alpha_x^2+\alpha_y^2+\alpha_z^2)]+C'_{001c}\ln(\alpha_x\alpha_y\alpha_z) \qquad (7)$$

C). Elastic Free Energy of Deformation for Rubber Vulcanizates with Carbon Black Fillers: According to the model of structure the elastic free energy of deformation for rubber vulcanizates with carbon black fillers is equal to the summation of equations of (6) and (7). It is given by the following equation:

$$\Delta F_{TT}=\Delta F'_{cefT}+\Delta F'_{ceT}=\frac{1}{2}KT\{(\xi_cB_c+\xi_eB_e+\xi_{cf}B_{cf}+\xi_{ef}B_{ef})(\alpha_x^2+\alpha_y^2+\alpha_z^2-3)$$
$$+(\xi_cC_c+\xi_eC_e+\xi_{cf}C_{cf}+\xi_{ef}C_{ef})[(\alpha_x^2+\alpha_y^2+\alpha_z^2)^2-3^2]+(\xi_eD_e+\xi_{ef}D_{ef})$$
$$\ln[\frac{1}{3}(\alpha_x^2+\alpha_y^2+\alpha_z^2)]+(\xi_cD_c+\xi_{cf}D_{cf})\ln(\alpha_x\alpha_y\alpha_z)\}=(C_{100c}+C_{100e}+C_{100cf}$$
$$+C_{100ef})(\alpha_x^2+\alpha_y^2+\alpha_z^2-3)+(C_{200c}+C_{200e}+C_{200cf}+C_{200ef})[(\alpha_x^2+\alpha_y^2+\alpha_z^2)^2-3^2]$$
$$+(C_{020e}+C_{020ef})\ln[\frac{1}{3}(\alpha_x^2+\alpha_y^2+\alpha_z^2)]+(C_{001c}+C_{001cf})\ln(\alpha_x\alpha_y\alpha_z) \qquad (8)$$

where ξ_c, ξ_e, ξ_{cf} and ξ_{ef} are respectively the total number of elastically active chains in crosslinked, entangled, physical and chemical carbon black-polymer chain networks; ξ_cB_c, ξ_eB_e, $\xi_{cf}B_{cf}$ and $\xi_{ef}B_{ef}$ are respectively the number of elastically active long chains in crosslinked, entangled, physical and chemical carbon black-polymer chain networks; ξ_cC_c, ξ_eC_e, $\xi_{cf}C_{cf}$ and $\xi_{ef}C_{ef}$ are respectively the number of elastically active short chains in crosslinked, entangled, physical and chemical carbon black-polymer chain networks; ξ_cD_c and $\xi_{cf}D_{cf}$ are respectively the number of elastically active chains in connexion with changing volume; ξ_eD_e and $\xi_{ef}D_{ef}$ are respectively the number of elastically active chains in the entangled and physical carbon black-polymer chain networks; α_x, α_y and α_z are the deformation ratios in x, y, and z directions;

$$C_{100c}=\frac{1}{2}kT\xi_c B_c\ ;\ C_{100e}=\frac{1}{2}kT\xi_e B_e\ ;\ C_{100cf}=\frac{1}{2}kT\xi_{cf}B_{cf}\ ;\ C_{100ef}=\frac{1}{2}kT\xi_{ef}B_{ef}\ ;$$

$$C_{200c}=\frac{1}{2}kT\xi_c C_c\ ;\ C_{200e}=\frac{1}{2}kT\xi_e C_e\ ;\ C_{200cf}=\frac{1}{2}kT\xi_{cf}C_{cf}\ ;\ C_{200ef}=\frac{1}{2}kT\xi_{ef}C_{ef}\ ;$$

$$C_{020e}=\frac{1}{2}kT\xi_e D_e\ ;\ C_{020ef}=\frac{1}{2}kT\xi_{ef}D_{ef}\ ;\ C_{001c}=\frac{1}{2}kT\xi_c D_c$$

and $C_{001cf}=\frac{1}{2}kT\xi_{cf}D_{cf}$

These molecular quantities of $B_{c.e.f}$ 、 $C_{c.e.f}$ 、 $D_{c.e.f}$ are all functions of the parameters of constrainted severity ($\Phi_{\pi c}$ 、 $\Phi_{\pi e}$ 、 $\Phi_{\pi' ef}$ 、 $\Phi_{\pi' ef}$) and the functionalties (f_c 、 f_{cf} 、 f_{ef}). Their values are not only determined by the structure of carbon blacks but also by the crosslinked networks.

The Relationships of Stress to Strain

The relationships of stress to strain for four types of deformation at constant volume ($\alpha_x\alpha_y\alpha_z=1$) were derived from the equation of (8) by the relations of $\tau_i=(\frac{\partial\Delta F_{TT}}{\partial\alpha_i})$. They are given by the following equations:

1). Uniaxial Extension ($\tau_x=f/A_o$)

$$\tau=2(\alpha-\alpha^{-2})[C_1+C_2/(\alpha^2+2/\alpha)+2C_3(\alpha^2+2/\alpha)] \tag{9}$$

2). Equi-biaxial Extension

$$\tau=2(2+\alpha^3)(\alpha-\alpha^{-5})[C_1+C_2/(2\alpha^2+\alpha^{-4})+2C_3(2\alpha+\alpha^{-4})] \tag{10}$$

3). Unequi-biaxial Extension

$$t_x-t_y=2(\alpha_x^2-\alpha_y^2)[C_1+C_2/(\alpha_x^2+\alpha_y^2+\alpha_x^{-2}\alpha_y^{-2})+2C_3(\alpha_x^2+\alpha_y^2+\alpha_x^{-2}\alpha_y^{-2})] \tag{11}$$

4). Pure Shear

$$\tau=2(1+\alpha^2)(\alpha-\alpha^{-3})[C_1+C_2/(\alpha^2+\alpha^{-2}+1)+2C_3(\alpha^2+\alpha^{-2}+1)] \tag{12}$$

where $C_1=(C_{100c}+C_{100e}+C_{100cf}+C_{100ef})$; $C_2=(C_{020e}+C_{020ef})$;

$C_3=(C_{200c}+C_{200e}+C_{200cf}+C_{200ef})$

A new molecular theory of rubber elasticity for vulcanizates with carbon black fillers at large deformation was presented. It succeeds in relating the elastic state to molecular constitution by three important molecular quantities, in which the severity by entanglement, crosslink and junctions of carbon black constraints are characterized with four parameters $\Phi_{\pi e}$, $\Phi_{\pi c}$, $\Phi_{\pi' ef}$ and $\Phi_{\pi' cf}$. The relation— ships of stress to strain for four types of deformation were derived from this theory. The experimental verification of the proposed theory and the relationships of stress to strain will be reported in the next paper.

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