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

2. The reinforcement of elastomers by carbon blacks and it's characteristics

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Summary

A satisfactory account of reinforcement has been secured through the application of the theory of elasticity to rubber vulcanizates with carbon black fillers. A statistical theory of reinforcement by carbon blacks and it's characteristics were developed. Three methods for characterizating the reinforcement of carbon blacks by the difference of elastic free energy, retractive forces and modulus were derived from this theory. The influences of carbon blacks on mechanical properties of SBR and NR vulcanizates were studied by uniaxial equi-biaxial and unequi-biaxial extensions. These results show that an excellent agreement between the theory and experiments. A correlation between the structure parameters of C_{ijk} and the tensile strength for SBR vulcanizates filled by different grade of carbon blacks exists.

Introduction

Reinforcement of rubber by incorporation of carbon blacks is studied by many research workers. The degree of reinforcement provided by carbon blacks depends on a number of variables, such as the structure of networks, particle size and shape of fillers, interface characteristics and the nature of polymer-filler interaction at this interfaces. It is generally agreed that van der Waals forces are sufficient to give rise to reinforcing effects, but for superior reinforcement, high degree of adhesion between filler and polymer, produced chemical interaction and physical entrapement of free molecules are desirable [1-3]. Therefore bound and occluded rubber are frequently used as a criterion of polymer

-filler interaction of filler "activity" [4-6].

In previous paper [7] basing on this facts the theory of elasticity for rubber vulcanizates with carbon blacks was proposed. A satisfactory account of reinforcement has been secured through application of the theory of elasticity to rubber vulcanizates with carbon black fillers. A statistical theory of reinforcement by carbon blacks and it's characteristics were developed by us in this paper.

Statistical Theory of Reinforcement and It's Characteristics

1). Reinforcement of Elastomers by Carbon Blacks: The elastic free energy of deformation and the relationship of stress to strain for rubber vulcanizates with carbon black fillers and crosslink-entanglement networks are given by the following equations:

A). Elastic Free Energy of Deformation for Incompressible Rubber Vulcanizates with Carbon Blacks

$$\begin{aligned}\Delta F_{TT} = \tfrac{1}{2}kT\{&[\tfrac{\rho_p W}{\bar{d}_0}(f_{cf}\mu_{cf\xi'cf} + f_{ef}\mu_{ef1\xi'ef}) + \nu_{c\xi c} + \nu_{e\xi e}](\alpha_x^2+\alpha_y^2+\alpha_z^2-3) \\ &+ [\tfrac{\rho_p W}{\bar{d}_0}(f_{cf}\mu_{cfN\xi'cf} + f_{ef}\mu_{efN\xi'ef}) + \nu_{cN\xi c} + \nu_{eN\xi e}][(\alpha_x^2+\alpha_y^2+\alpha_z^2)^2-3^2] \\ &+ [\tfrac{\rho_p W}{\bar{d}_0} f_{ef}\mu_{ef2\xi'ef} + \nu_{e2\xi e}]\ln[\tfrac{1}{3}(\alpha_x^2+\alpha_y^2+\alpha_z^2]\} = c_1(\alpha_x^2+\alpha_y^2+\alpha_z^2-3) \\ &+ c_3[(\alpha_x^2+\alpha_y^2+\alpha_z^2)^2-3^2] + c_2\ln[\tfrac{1}{3}(\alpha_x^2+\alpha_y^2+\alpha_z^2)] \qquad (1)\end{aligned}$$

B). Elastic Free Energy of Deformation for Incompressible Crosslink-entanglement Networks

$$\begin{aligned}\Delta F'_{TT} = \tfrac{1}{2}kT\{&(\nu'_{c\xi c} + \nu'_{e\xi e})(\alpha_x^2+\alpha_y^2+\alpha_z^2-3) + (\nu'_{cN\xi c} + \nu'_{eN\xi e})[(\alpha_x^2+\alpha_y^2 \\ &+\alpha_z^2)^2-3^2] + \nu'_{e2\xi e}\ln[\tfrac{1}{3}(\alpha_x^2+\alpha_y^2+\alpha_z^2)]\} = c'_1(\alpha_x^2+\alpha_y^2+\alpha_z^2-3)] \\ &+ c'_3[(\alpha_x^2+\alpha_y^2+\alpha_z^2)^2-3^2] + c'_2\ln[\tfrac{1}{3}(\alpha_x^2+\alpha_y^2+\alpha_z^2)] \qquad (2)\end{aligned}$$

where k is Boltzamenn's constant; T is absolute temperature; ρ_p is the density of rubber vulcanizates with carbon blacks; W is weight fraction of fillers; $\bar{d}_0$ is the mass of a particulate filler; f_{cf} and f_{ef} are respectively the number of junction-points at a filler particle surface; $\mu_{cf\xi'cf}$ and $\mu_{ef\xi'ef}$ are respectively the number of the physical and chemical constituent chains per weight fraction in the carbon black-polymer long chain networks; $\mu_{cfN\xi'cf}$ and $\mu_{efN\xi'ef}$ are respectively the number of the physical and chemical constituent chains per weight fraction in the carbon black-polymer short chain networks; $\mu_{ef2\xi'ef}$ is the number of physical constituent chain per weight fraction in the carbon black-polymer chain networks; $\nu_{c\xi c}$, $\nu_{e\xi e}$, $\nu'_{c\xi c}$ and $\nu'_{e\xi e}$ are respectively the number of elastically active long chains in the crosslinked and entangled networks; $\nu_{cN\xi c}$, $\nu_{eN\xi c}$, $\nu'_{cN\xi c}$ and $\nu'_{eN\xi e}$ are the number of elastically active short chains in crosslinked and entangled networks; $\nu_{e2\xi e}$ and $\nu'_{e2\xi e}$ are respectively the number of elastically active chains in entangled networks; α_x , α_y and α_z are the deformation ratios in x, y, and z directions.

C). Relationships of Stress to Strain

(1) Uniaxial Extension

For rubber vulcanizates with carbon blacks,

$$\tau_1 = 2(\alpha-\alpha^{-2})[C_1 + C_2/(\alpha^2+2/\alpha) + 2C_3(\alpha^2+2/\alpha)] \qquad (3)$$

For crosslink-entanglement networks,

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

(2) Equi-biaxial Extension

$$\tau_2 = 2(2+\alpha^3)(\alpha-\alpha^{-5})[C_1 + C_2/(2\alpha^2+\alpha^{-4}) + 2C_3(2\alpha^2+\alpha^{-4})] \qquad (4)$$

(3) Unequi-biaxial Extension

$$(t_x - t_y) = 2(\alpha_x^2-\alpha_y^2)[C_1 + C_2/(\alpha_x^2+\alpha_y^2+\alpha_x^{-2}\alpha_y^{-2}) + 2C_3(\alpha_x^2+\alpha_y^2+\alpha_x^{-2}\alpha_y^{-2})] \qquad (5)$$

Method for Characterizating Reinforcement by Carbon Blacks

It is apparent that the elastic free energy of deformation (ΔF_{TT}), the retractive force (τ_1) and the values of modulus (C_1, C_2 and C_3) for rubber vulcanizates with carbon black fillers may be higher or lower than the corresponging values for rubber vulcanized under similar conditions without carbon blacks. Three methods for characterizating the reinforcement were derived from these relations, they are given by the following equations:

A). Method by the Difference of Elastic Free Energy of Deformation.

$$\Delta F_{ex} = \frac{1}{2}kT\{[\frac{\rho_f W}{d_0}(f_{cf}M_{cf\xi'cf} + f_{ef}M_{ef1\xi'ef}) - (\Delta\nu_{c\xi c} + \Delta\nu_{e\xi e})][\alpha_x^2+\alpha_y^2+\alpha_z^2-3]$$
$$+ [\frac{\rho_f W}{d_0} f_{ef}M_{ef2\xi'ef} - \Delta\nu_{e2\xi e}]\ln[\frac{1}{3}(\alpha_x^2+\alpha_y^2+\alpha_z^2)] + [\frac{\rho_f W}{d_0}(f_{cf}M_{cfN\xi'cf}$$
$$+ f_{ef}M_{efN\xi'ef}) - \Delta\nu_{cN\xi c} - \Delta\nu_{eN\xi e}][(\alpha_x^2+\alpha_y^2+\alpha_z^2)^2 - 3^2]\} \qquad (6)$$

B). Method by the Difference of Retractive Force.

$$\Delta\tau_1 = kT(\alpha-\alpha^{-2})\{[\frac{\rho_f W}{d_0}(f_{cf}M_{cf\xi'cf} + f_{ef}M_{ef1\xi'ef}) - (\Delta\nu_{c\xi c} + \Delta\nu_{e\xi e})]$$
$$+ [\frac{\rho_f W}{d_0} f_{ef}M_{ef2\xi'e} - \Delta\nu_{e2\xi e}](\alpha^2+2/\alpha)^{-1} + 2[\frac{\rho_f W}{d_0}(f_{cf}M_{cfN\xi'c}$$
$$+ f_{ef}M_{efN\xi'e}) - (\Delta\nu_{cN\xi c} + \Delta\nu_{eN\xi e})](\alpha^2+2/\alpha)\} \qquad (7)$$

where $\Delta V_{c\xi c}=(V_{c\xi c}-V'_{c\xi c})$, $\Delta V_{e\xi e}=(V_{e\xi e}-V'_{e\xi e})$; $\Delta V_{e2\xi e}=(V_{e2\xi e}-V'_{e2\xi e})$;

$\Delta V_{cN\xi c}=(V_{cN\xi c}-V'_{cN\xi c})$; $\Delta V_{eN\xi e}=(V_{eN\xi e}-V'_{eN\xi e})$

It is shown that when ΔF_{ex} and $\Delta \tau_1 > 0$, reinforcement is positive; when ΔF_{ex} and $\Delta \tau_1 < 0$, reinforcement is negative; when ΔF_{ex} and $\Delta \tau_1 = 0$, no reinforcement presents.

C). Method by the Difference of Modulus.

For eliminating the dependence of stress and strain the strength of reinforcement was proposed. The total strength of reinforcement may be divided into three parts, each of them is defined by it's fraction of mudulus. They are given as follow:

(1) Chemical Strength of Reingorcement

$$\left(\frac{\Delta C_1}{C_1'}\right)=\frac{P_\xi W}{d_0}\cdot\frac{f_{cf}M_{cf}\xi'_{cf}+f_{ef}M_{ef}\xi'_{ef}}{V'_{c\xi c}+V'_{e\xi e}}+(\Delta V_{c\xi c}+\Delta V_{e\xi e})/(V'_{c\xi c}+V'_{e\xi e}) \qquad (8)$$

(2) Physical Strength of Reinforcement

$$\left(\frac{\Delta C_2}{C_2'}\right)=\frac{P_\xi W}{d_0}\cdot\frac{f_{ef}M_{ef2}\xi'_{e}}{V'_{e2\xi e}}+\frac{\Delta V_{e2\xi e}}{V'_{e2\xi e}} \qquad (9)$$

(3) Short Chains Strength of Reinforcement

$$\left(\frac{\Delta C_3}{C_3'}\right)=\frac{P_\xi W}{d_0}\cdot\frac{f_{cf}M_{cfN}\xi'_{c}+f_{ef}M_{efN}\xi'_{e}}{V'_{cN\xi c}+V'_{eN\xi e}}+(\Delta V_{cN\xi c}+\Delta V_{eN\xi e})/(V'_{cN\xi c}+V'_{eN\xi e}) \qquad (10)$$

Comparison with Experiments

1) Experimental Results: The influences of carbon blacks on the mechanical properties of SBR and NR vulcanizates was studied by uniaxial, equi-biaxial and unequi-biaxial extension. The experimental stress-strain curves and tensile strength are given in Fig. 1 to 7.

2) Relationships of Stress to Strain:

The parameters of C_1, C_2 and C_3 for all samples are determined from the experiments by the methods of progressively linear approach (8) and linear regression. An example for determining the C_1, C_2 and C_3 from the uniaxial extension is given as follow:

Letting $x=\tau_1/2(\alpha-\alpha^{-2})$, $y=(\alpha^2+2/\alpha)^{-1}$ and $z=(\alpha^2+2/\alpha)$, the equation of (3) can be rewritten as a double-regression model in the form

$$x=C_1+C_2 y+2C_3 z \qquad (3'')$$

where y and z are a set of regressor, they can be obtained directly from the experimental observation. Therefore the coefficients of C_1 , C_2 and C_3 can be easily estimated by double regression method. The theoretical stress-strain curves for three types of deformation were calculated by the equations of (3) (4) and (5) with the given parameters, and the theoretical and experimental stress-strain curves are all given respectively in Fig. 1 to 4. An excellent agreement between the above experiments and the theoretical equations of (3), (4) and (5) derived from our proposed theory of elasticity was obtained. If the primary molecular weight of polymers is relatively large and the degree of crosslinking is relatively low, then this agreement between the experiments and theory can be obtained over a more large range of deformation ($\alpha \leqslant 5.0$). These results show that the most important feature of the proposed theory is that it predicts the rubber-like elasticity quantitatively even at higher strains.

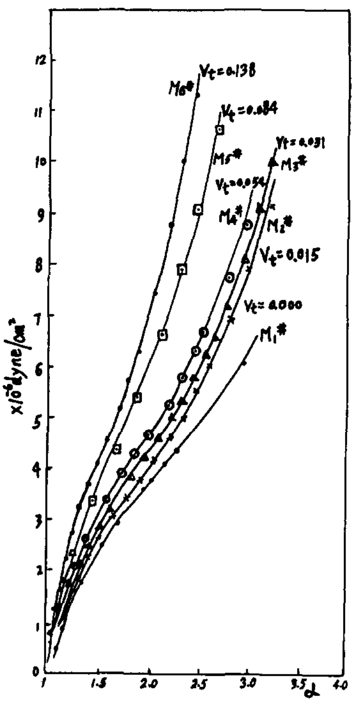

Fig. 1. Stress-strain curves of NR vulcanizates;[9]
. . . .experimental points;
———theoretical curves with Equ. (3).

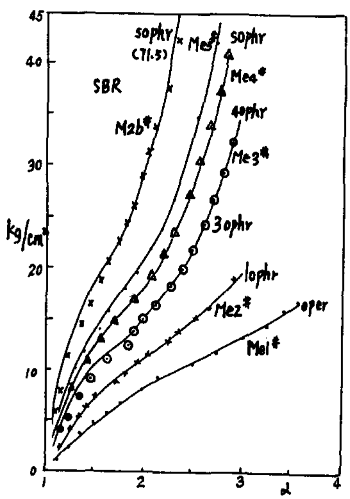

Fig.2.Stress-strain curves of SBR vulcanizates;[10]
. . . .experimental points;
———theoretical curves with Equ. (3).

3). Characteristics of Reinforcement: The excess elastic free energy of deformation and the excess retractive forces for filled SBR and NR vulcanizates were calculated by equations of (6) and (7). Their values are all larger than zero, it shows that carbon blacks convey significant improvement in modulus and tensile strength. For a given quantity of carbon blacks their values increase with increasing strain.

The strengths of reinforcement for filled SBR vulcanizates were calculated by equations of (8) and (9). It is found that the chemical and physical strengths of reinforcement linearly increase with increasing the weight fractions of carbon blacks. They are given in Fig. 5.

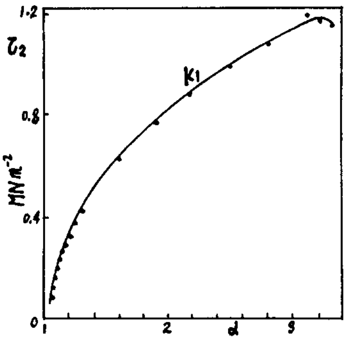

Fig.3.Stress-strain curves of NR vulcanizates; . . . .experimental points;(11) ———theoretical curves with Equ. (4).

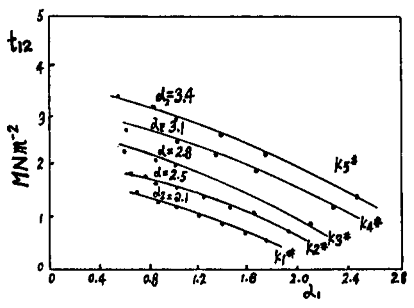

Fig.4.Stress-strain curves of NR vulcanizates; . . . .experimental points; (11) ———theoretical curves with Equ. (5).

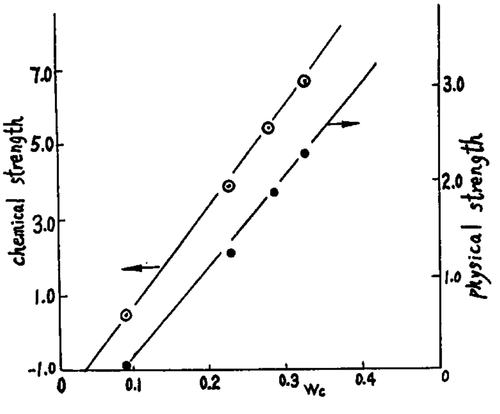

Fig.5. Dependences of chemical and physical strength on the fractions of carbon black.

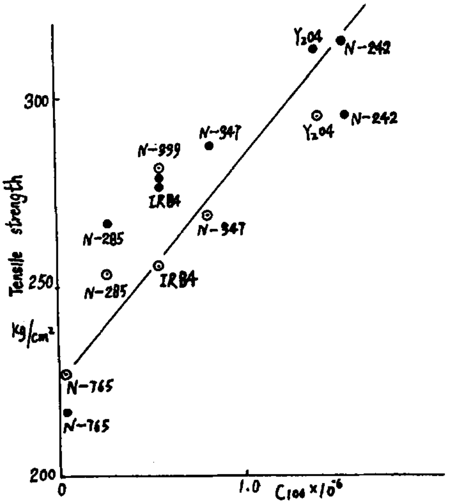

Fig.6.Dependence of tensile strength on the parameter of C_1.

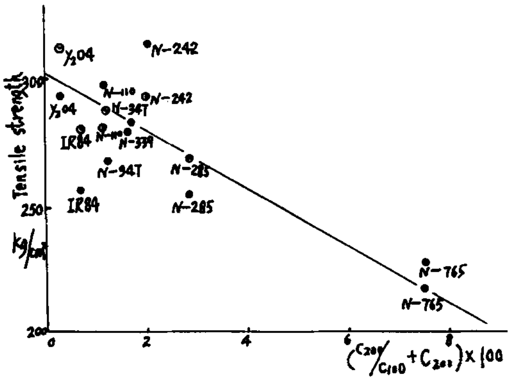

Fig.7.Dependence of tensile strength on the parameter of C_1.

4). Correlation between the Parameters of C and the Ultimate Strength: A correlation between the structure parameters of C and the tensile strength for SBR vulcanizates filled by different grade of carbon blacks was obtained. It shows that the tensile strength increases with increasing the values of parameters C_1 and decreases with increasing the values of ($\frac{C_3}{C_1 + C_3}$). They are given in Fig. 6 and 7. These symboles in each side of circule represent the kinds of carbon blacks. There are a correlation between the parameter of C_1 and the structure of carbon blacks for a given degree of crosslinking. It is shown that the C_1 increases with increasing the surface activity of carbon blacks and with decreasing the number average particle diameter.

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