

Hysteresis and Strain-Dependent Dynamic Mechanical Properties of Epoxidized Natural Rubber Filled with Surface-Oxidized Carbon Black

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Received 18 December 1996; accepted 31 May 1997

ABSTRACT: High-temperature molding of a mixture of epoxidized natural rubber (ENR) and intermediate super abrasion furnace (ISAF) carbon black results in strong rubber–filler interaction, the extent of which is greater in the case of the oxidized grade of the carbon black. It has been observed that ENR is bonded to the filler surface through the formation of primary bonds, such as ester and phenolic ether. An extensive filler–filler network formation takes place through the hydrogen bonding between the active groups of the rubber and filler surface. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 723–730, 1998

Key words: epoxidized natural rubber; surface-oxidized carbon black; hysteresis; dynamic mechanical properties

INTRODUCTION

It has been reported that surface oxidation of carbon black causes an increase in reinforcing potential of the filler in rubber, particularly in the case of polar rubbers.^{1–3} In an earlier article, the present authors reported evidence of formation of chemical bonds between epoxidized natural rubber (ENR) and the surface functional groups of intermediate super abrasion furnace (ISAF) carbon black during high-temperature molding of rubber–filler mixtures.⁴ Formation of rubber–filler bonds and their nature greatly affect the strain-dependent dynamic mechanical properties of filled rubbers.^{5–10}

The present article reports the results of studies on hysteresis and the effect of strain on the dynamic mechanical properties of ENR–carbon black mixture with special reference to the role of

surface oxidation of the filler surface in the formation of rubber–filler bonds.

EXPERIMENTAL

Details of the materials used are given in Table I, and the formulations of the different rubber mixes are given in Table II. Mixing of the filler with was done in a Brabender Plasticorder (model PLE-300) at 25°C and at a rotor speed of 60 rpm for 8 min. The equipment was fitted with a cam-type mixing head, and the mixing was done at a constant input of energy. The mixed compounds were passed through a laboratory size two-roll mill for making sheets.

The mixes were molded at 180°C for 90 min at a pressure of 10 MPa in a Moore hydraulic press. The molded samples were cooled to room temperature under 10 MPa pressure. The test pieces were cut from the molded sheets.

Dynamic mechanical analysis of the samples were carried out using a dynamic viscoelastometer rheovibron, DDV-III-EP (Orientec Corpora-

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Journal of Applied Polymer Science, Vol. 70, 723–730 (1998)

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CCC 0021-8995/98/040723-08

Table I Details of Materials Used

Materials	Characteristics	Sources
Epoxidized natural rubber (ENR)	50 mol % of double bonds are epoxidized; Mooney viscosity ML (1 + 4) at 120°C, 42; Molecular weight, \bar{M}_n , 4.7×10^5 ; \bar{M}_w/\bar{M}_n , 4.6.	Kumpulan Guthrie Berhad, Malaysia
Surface-oxidized intermediate super abrasion furnace black abbreviated as Ox-ISAF (trade name: Printex-550)	DBP, ^a 47 cm ³ /100 g; N ₂ SA, ^b 105 m ² /g; % O ₂ (by wt), 1.44; pH 2.8.	Degussa AG, Germany
Intermediate super abrasion furnace black, abbreviated as ISAF (trade name: Printex-55)	DBP, ^a 45; N ₂ SA, ^b 105 m ² /g; pH 9.5; % O ₂ (by wt), 0.90.	Degussa AG, Germany

^a Dibutyl phthalate absorption.

^b Nitrogen surface area.

tion, Japan) at a temperature of 25°C and at a frequency of 3.5 Hz. The sample dimension was $L \times 0.64 \times 0.2$ cm³, where L was varied from 1 to 6 cm and the strain amplitude varied from 0.0025 to 0.025 cm, and no prestretching force was applied on the samples. The variation in percentage double strain was within the range 0.083 to 5%. The double strain amplitude (DSA) is given as

$$\% \text{ DSA} = (2A/L) \times 100 \quad (1)$$

where A is the amplitude of vibration and L is the length of sample.

The hysteresis measurements were carried out with a dumbbell-shaped test specimen as per ASTM-D-412-80 in a Zwick Universal Testing machine (model 1445) at 50% elongation for 2 consecutive cycles.

Optical microscopic studies were carried out in Metallux-3 at a magnification of 500×, and the average particles size were measured.

RESULTS AND DISCUSSION

Figure 1 shows the hysteresis plots of ENR-carbon black mixtures. It is evident that surface

oxidation of filler causes an increase in hysteresis loss, and it increases with an increase in the filler loading. It is also apparent that as molding time increases, hysteresis loss increases. Formation of primary covalent bonds between the oxidized filler surface and rubber molecules, as reported earlier,⁴ would have caused a decrease in hysteresis loss in the case of the oxidized grade of the filler and particularly at a higher molding time.^{11,12} The observed increase in hysteresis loss in the present case indicates extensive formation of secondary bonds at the rubber-filler intersurface along with the formation of primary bonds. The results also indicate that formation of secondary bonds increases with an increase in molding time.

Figure 2(a) shows the variation of storage modulus as a function of filler loading. It is evident that the filler loading increases, $\Delta E'$ (that is, E'_0 minus E'_∞). This implies that on increasing the filler loading, the structure breakdown of filler increases, and the effect is more pronounced in the case of the oxidized grade of carbon black.

Figure 2(b) also shows the variation of storage modulus as a function of molding time at a fixed filler loading. It was observed that $\Delta E'$ increases with molding time, but the effect is more pro-

Table II Formulation of Mixes

Materials	Mix Designation								
	E	EI ₄	EI ₆	EI ₈	EI ₁₀	EO ₄	EO ₆	EO ₈	EO ₁₀
ENR	100	100	100	100	100	100	100	100	100
ISAF black	0	40	60	80	100	0	0	0	0
Ox-ISAF black	0	0	0	0	0	40	60	80	100

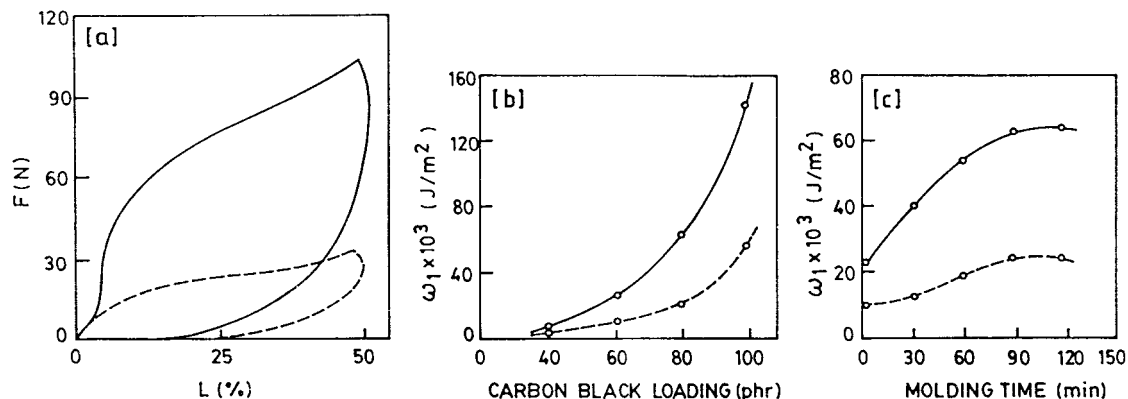


Figure 1 (a) Hysteresis loss of ENR-carbon black systems molded at 180°C for 90 min for 100 phr carbon black loading: (—) oxidized ISAF black; (---) ISAF black. (b) Hysteresis loss as a function of filler loading: (—○—) oxidized ISAF black; (---○---) ISAF black. (c) Hysteresis loss as a function of molding time at 80 phr of filler loading: (—○—) oxidized ISAF black; (---○---) ISAF black.

nounced in the case of the oxidized grade of carbon black. It has been reported that formation of primary bonds between rubber and the filler surface increases with an increase in molding time.¹⁰ However, the present results indicate formation of secondary bonds at the rubber-filler intersurface along with the primary bonds. It is the secondary bonds that are responsible for the increase in $\Delta E'$ at a higher molding time, particularly in the case of the oxidized grade of carbon black.

Results of hysteresis loss measurements are in conformity with the observations made on strain-

dependent dynamic mechanical properties. It is believed that the concentration of secondary bonds overshadows the primary bonds. While the primary bonds consist of phenolic ether and benzoate ester types of linkages (Fig. 3), secondary bonds are believed to be weak hydrogen-bonded structures (Figs. 4 and 5) and the weak rubber-filler bonds consisting of van der Waals types of forces. It is apparent that not all of the hydrogen-bonded structures are converted into primary bonds on prolonged molding. Accordingly, it is proposed that weak rubber-filler bonds facilitate

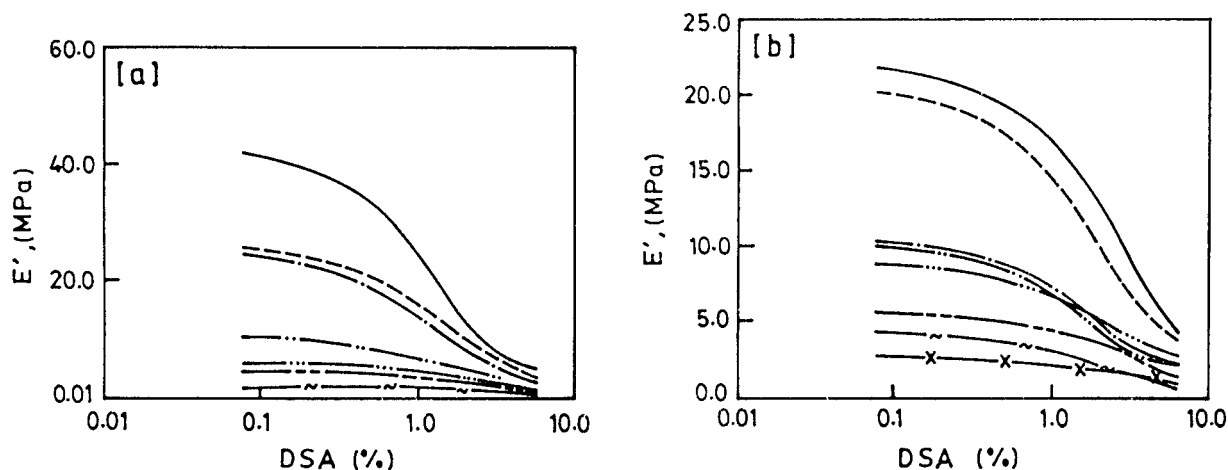


Figure 2 (a) Plots of storage modulus versus the percentage of DSA of different ENR-carbon black mixes: (—~—) E; (—) EO₁₀; (—·—) EO₈; (—··—) EO₆; (---) EI₁₀; (---·---) EI₈; (---·---) EI₆. (b) Plots of storage modulus versus the percentage DSA at 80 phr of carbon black loading for different molding times: (—) EO₈ (120 min); (---·---) EO₈ (90 min); (---··---) EO₈ (30 min); (---···---) EO₈ (2 min); (---) EI₈ (120 min); (---·---) EI₈ (90 min); (—~—) EI₈ (30 min); (—×—) EI₈ (2 min).

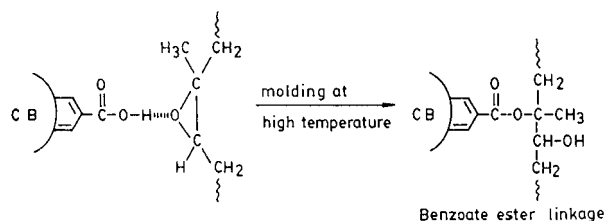


Figure 3 (a) Proposed mechanism for the formation of benzoate ester linkage between oxidized ISAF black and ENR.

formation of a agglomerate superstructure along with the sparsely populated rubber–filler covalent bonds (Fig. 5). Breakdown of the agglomerate superstructure under imposed strain is presumed to be responsible for the sharp fall of E' with DSA in the case of the oxidized grade of carbon black.

The proposed mechanism of the filler structure breakdown (Fig. 5) is supported from the optical microscopic studies on the samples EO_{10} and EI_{10} , before and after application of strain (Fig. 6). In the case of oxidized ISAF carbon black filled sample, it has been observed that the average particle size (agglomerated) is $30 \times 40 \mu\text{m}$, which decreases to $1 \times 1.5 \mu\text{m}$ on application of strain. But in the case of the nonoxidized grade of ISAF carbon black, the reduction in particle size on application of strain is from 20×30 to $3 \times 4 \mu\text{m}$. From Figure 6, it is also evident that oxidized black exists as discrete particles on the application of strain, whereas an agglomerate structure

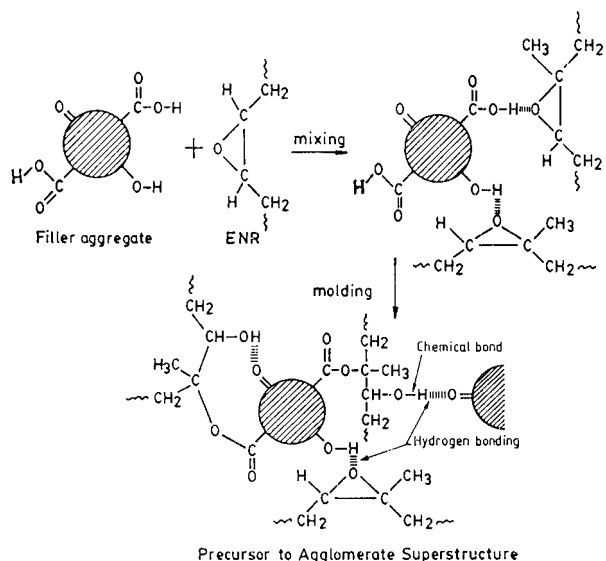


Figure 4 Plausible mechanism of formation of a network through secondary bonds (hydrogen bonding).

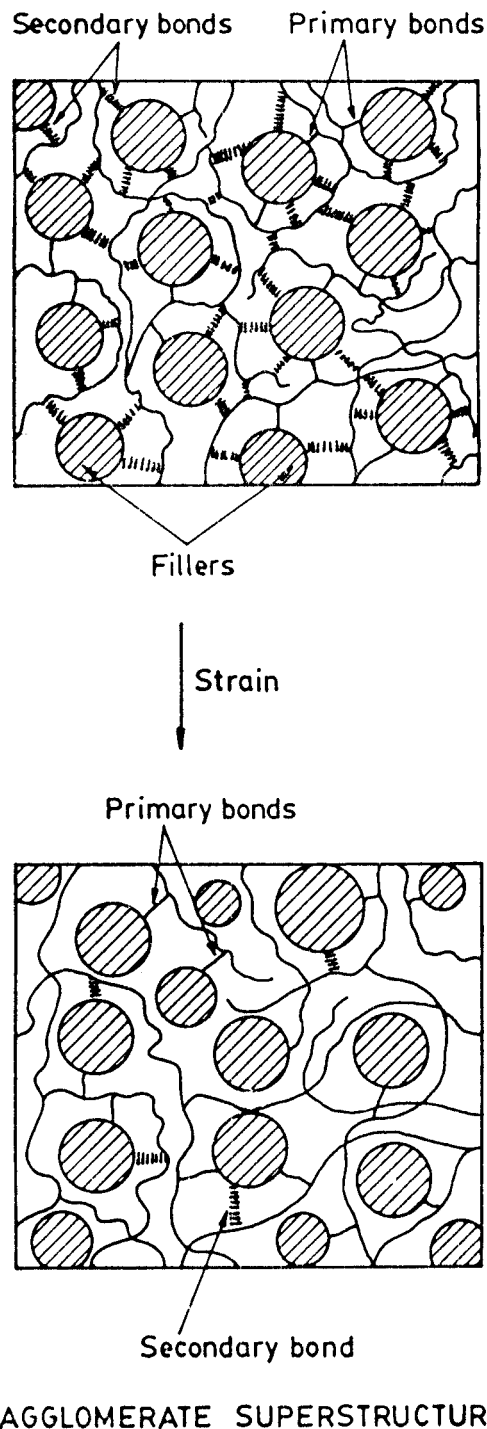


Figure 5 Breakdown of agglomerate super structures under an imposed strain.

is still observable in the case of the non-oxidized grade, even after application of strain.

The hydrodynamic interaction model for rubber reinforcement was developed by Guth and Gold.^{13,14} The model does not hold good for high

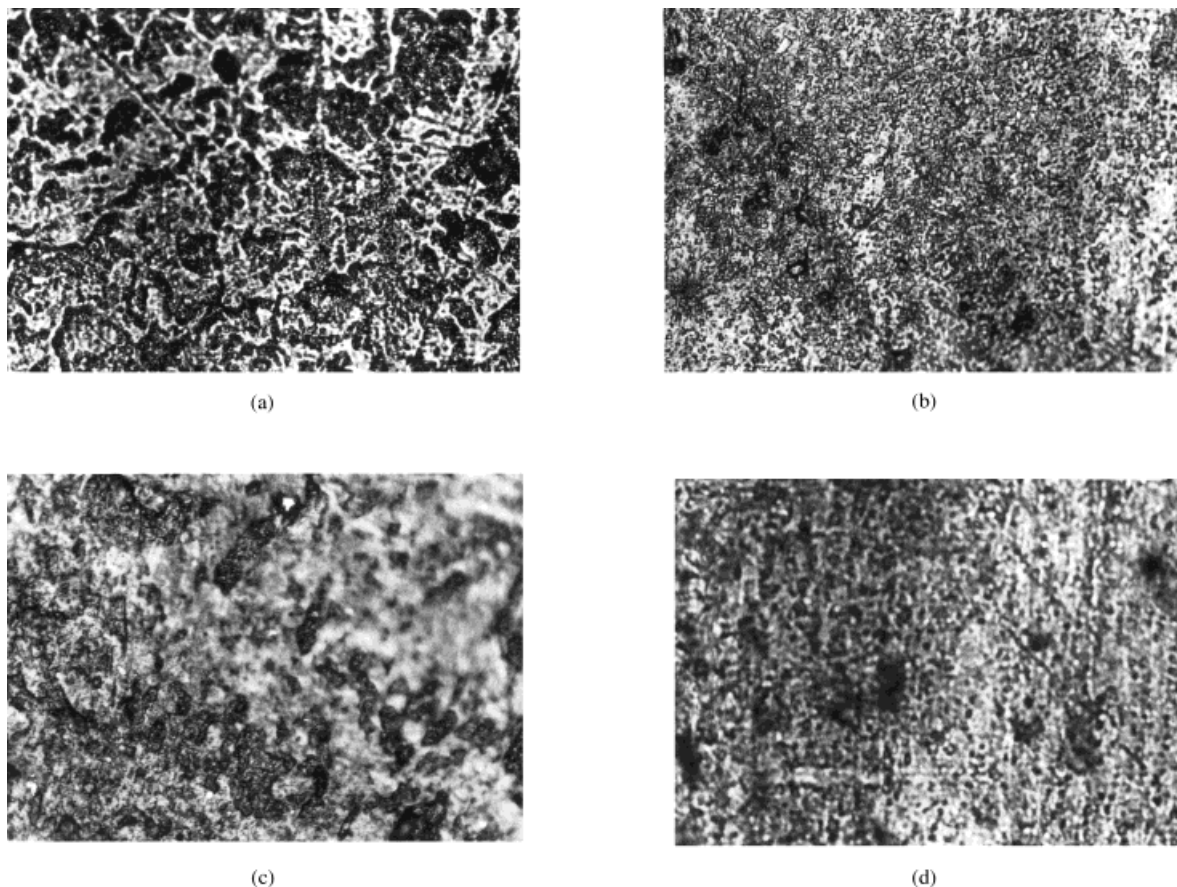


Figure 6 Results of optical microscopic studies: (a) EO₁₀ before application of strain; (b) EO₁₀ after application of strain; (c) EI₁₀ before application of strain; (d) EI₁₀ after application of strain.

structure carbon blacks, high filler loadings, and for cases having strong adsorption and chemical interaction between rubber and filler particles. The model is described by following equation:

$$E'_f = E'_0(1 + \alpha V_f + \beta V_f^2) \quad (2)$$

where E'_f and E'_0 are the storage moduli of the filled and the unfilled rubber, respectively, at high strain, and V_f is the volume fraction of filler. For Vander Walls types of interaction between rubber and the dispersed filler particles $\alpha = 2.5$ and $\beta = 14.1$.

Figure 7 shows the plots of E'_f/E'_0 versus volume fraction of filler (V_f). It was observed that in the case of the oxidized grade of carbon black, the modulus enhancement is much greater than the corresponding non-oxidized grade. It is well known that α increases with an increase in dispersion and β depends on molecular interaction.¹⁴

In the present case of ENR–carbon black systems, the following relations were obtained.

For ISAF carbon black,

$$E'_f = E'_0(1 + 1.7V_f + 85V_f^2) \quad (3)$$

For oxidized ISAF carbon black,

$$E'_f = E'_0(1 + 3.2V_f + 256V_f^2) \quad (4)$$

The increase in β in the case of oxidized grade of carbon black is ascribed to the strong interaction between the functional groups of the rubber and active sites on the filler surface. The high values of β have been reported previously by Mallick et al.¹⁰ in the case of carbon-black-filled ENR–polyacrylic acid blend system and by Bandyopadhyay et al. in the case of carboxylated nitrile rubber–carbon black system.¹⁵

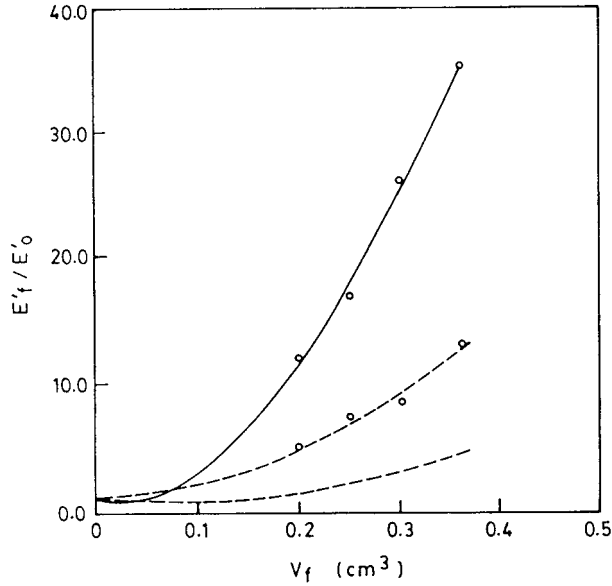


Figure 7 Variation of E'_f/E'_0 with V_f according to the Guth-Gold relation: (---) calculated plot; (—○—) oxidized ISAF black; (---○---) ISAF black.

Figure 8 shows the plots of loss modulus (E'') versus the percentage of DSA. For the unfilled ENR, there was no change in loss modulus with DSA, while for the filled ENR, the loss modulus increases with DSA, attains a peak, and then

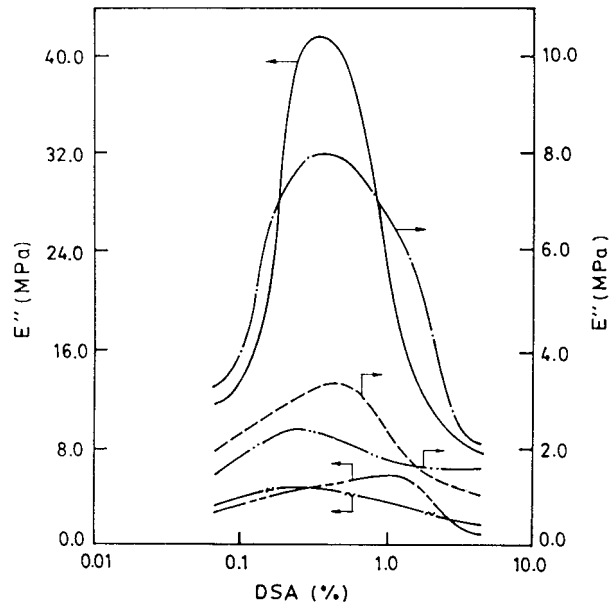


Figure 8 Plots of loss modulus (E'') versus the percentage of dynamic strain amplitude (% DSA): (—) EO_{10} ; (— · —) EO_8 ; (— · · —) EO_6 ; (---) EI_{10} ; (—) EI_8 ; (— ~ —) EI_6 .

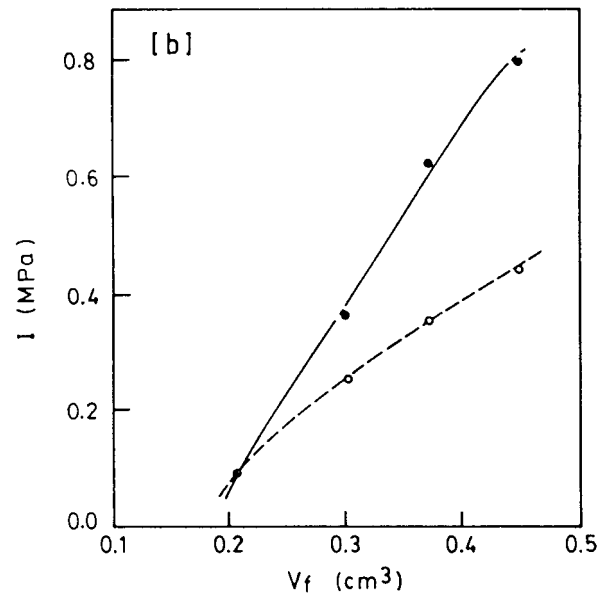
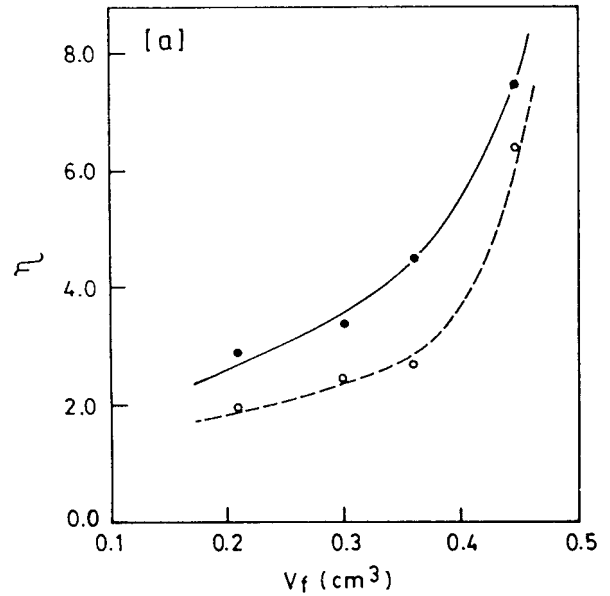


Figure 9 (a) Variation of η with V_f : (— · —) EO_8 ; (---○---) EI_8 . (b) Variation of I with V_f : (— · —) EO_8 ; (---○---) EI_8 .

decreases. Similar results have been explained earlier on the basis of secondary structures of the filler agglomerates.¹⁶⁻¹⁸ With the increase in strain, more filler particles are involved in this breakdown processes and, hence, E'' increases with DSA and passes through a maximum, where most of the agglomerates have been broken down. Beyond the maximum, the number of particles

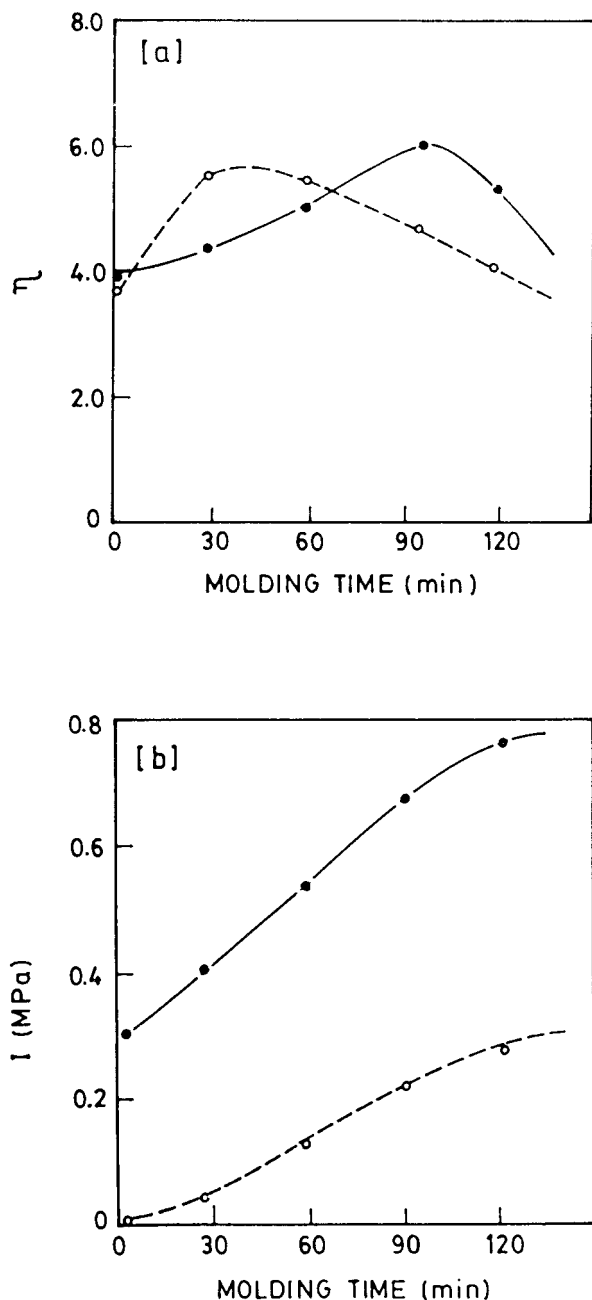


Figure 10 (a) Variation of η as a function of molding time: (—•—) EO₈; (---○---) EI₈. (b) Variation of I as a function of molding time: (—•—) EO₈, (---○---) EI₈.

involved in the breakdown process decreases, and, hence, E'' decreases. For rubber vulcanizates, typical peak values of E'' (that is, E''_{\max}) are reported to be 2–3 MPa.^{5,6,16} But in the present system (Fig. 8), a manifold increase in the E''_{\max} value was observed (42 MPa). In the case of super agglomerate structure formation in the carbon-black-filled polyacrylic acid–ENR system, E'' was found to be very high, that is, 256 MPa.¹⁰

Ayala et al.¹⁹ have proposed a rubber–filler interaction parameter, which is defined as

$$I = \sigma/\eta \quad (5)$$

where, σ is the slope of the stress–strain curve in the relatively linear region of low elongation, and η is the filler–filler networking factor, calculated from the ratio of storage modulus at low and high strain.

Figure 9 shows that rubber–filler interaction parameter (I) increases with an increase in filler loading in both grades of carbon black, but the value of I is greater in the case of the oxidized grade of carbon black. It is also apparent that the networking factor (η) increases with an increase in filler loading, but the rise in η is sharp at higher filler concentration, and this is true in both grades of carbon black.

Figure 10 shows the variation of both I and η with molding time. It is evident that both I and η increase with increase in molding time, and the effect is more prominent in the case of oxidized grade of ISAF carbon black. The results substantiate the findings that high-temperature molding of ENR–ISAF carbon black mixture causes formation of covalent bonds between the rubber and filler, resulting in an increase in I , while the secondary hydrogen-bonded rubber–carbon black structures result in an increase in η .

CONCLUSIONS

Functional groups on the carbon black surface interact with ENR to form both primary bonds as well as secondary hydrogen-bonded structures. The later, however, break down upon application of strain.

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