

Structure-Concentration Equivalence in Carbon Black Reinforcement of Elastomers. III. Application to Tensile Strength

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Synopsis

Using carbon blacks of constant specific surface area and surface chemical characteristics, but differing in degree of structure, it is shown that tensile strength, elongation at break and rupture energy are functions of the product av_2 , where v_2 is the volume concentration of carbon black and a is a structure dependent factor. Moreover, reductions of failure data to a common effective filler concentration are accomplished with the identical structure factors used earlier in modulus reductions. The values of the structure factors are linearly related to the dibutyl phthalate (DBP) absorption of carbon black, when care is taken to equalize the packing density prior to conducting the DBP test.

INTRODUCTION

The morphology of highly reinforcing carbon blacks is governed largely by the degree of interparticle fusion. The result of this fusion is primary aggregates, which in many ways resemble rigid, sometimes branched, random coils. The larger of these aggregates may contain as many as 100 or more individual particles. It is this morphology which is responsible for the so-called "structure" property of carbon black.^{1,2}

Recent studies by Medalia³ and the author^{4,5} have shown that polymer occluded within the internal void space of the primary structure aggregates is not free to share fully in the macroscopic deformation of a carbon black-filled rubber. Consequently, certain properties of black-reinforced rubbers become functions of an effective filler concentration, which includes the actual volume occupied by carbon plus a contribution from occluded polymer. The larger the internal void space of a carbon black ("high structure"), the greater the effective filler loading and its effects on such properties as modulus or extrusion die swell.

In the example of modulus, we may write, for carbon blacks *differing in structure alone*,

$$\sigma = \sigma(av_2, \epsilon), \quad (1)$$

where σ is the stress at extension ϵ of a vulcanizate containing a volume fraction v_2 of black and a is a function dependent on the degree of structure of the black. The stress depends, of course, also on the rubber, the de-

gree of crosslinking, temperature, strain rate, etc. The structure "shift factor" a shows excellent correlation with the standard dibutyl phthalate (DBP) absorption test for structure, but appears to be *linearly* related to the DBP value of carbon black following repeated static compression to 24000 psi, as recommended by Dollinger, Kallenberger, and Studebaker.⁶ Relative to an arbitrarily chosen reference black,

$$a = (24 + A)/(24 + A_0) \quad (2)$$

where A is the DBP value of the subject carbon black and A_0 is the corresponding value for the reference black, both determined by the precompression procedure.

In the present report, we show that the structure-concentration equivalence principle embodied in eq. (1) also holds for the tensile strength, σ_b , and energy input to break, U_b . For this to be possible it is necessary that the breaking elongation, ϵ_b , also follow structure-concentration equivalence, for only if

$$\epsilon_b = \epsilon_b(av_2) \quad (3)$$

will

$$\sigma_b = \sigma(av_2, \epsilon_b) \quad (4)$$

and

$$U_b = \int_0^{\epsilon_b} \sigma(av_2, \epsilon) d\epsilon = U(av_2, \epsilon_b) \quad (5)$$

be functions of the reduced variable av_2 alone.

EXPERIMENTAL

Four carbon blacks of nearly equal specific surface area, ca. 100 m²/g, but differing in their degree of fused chain structure were prepared specifically for this and related^{4,5} studies, as shown in Table I.

TABLE I
Characteristics of Four Carbon Blacks Used in This Study^a

	A	B	C	D
DBP absorption, cc/100 g				
as received	50	72	110	126
24M4	46	67	90	100
ASTM iodine number, mg/g	107	102	95	100
Combined hydrogen, %	0.28	0.28	0.28	0.28
Combined oxygen, %	0.8	0.9	1.1	1.0

^a Carbon black D meets the criteria of ASTM grade designation N285; the others have no commercial counterparts.

Recipe I (Tensile Strength Study). SBR 1500, 100; carbon black, variable; naphthenic processing oil, 10; zinc oxide, 3; stearic acid, 1; sulfur, 1.75; accelerator (CBS), 0.95; antioxidant, 1.

Recipe II (Tire Test). SBR 1712 rubber hydrocarbon, 70; *cis*-polybutadiene, 30; carbon black, variable; highly aromatic oil (total), 40; zinc oxide, 3; stearic acid, 2; sulfur, 2; accelerator (*t*BBS), 2; antioxidant, 1.

Tensile Test Procedure. Small rings (I.D. 2.4 cm, O.D. 2.7 cm, thickness 0.2 cm) were pulled at a cross-head rate of 10 in./min on an Instron tester. The energy density to break, U_b , was obtained by direct integration of the force over the cross-head travel and division by the volume of the ring. Because the maximum stress and strain in a ring specimen occur at the inside of the ring, the elongation at break, ϵ_b , was computed on the inside diameter. The stress at break, σ_b , was calculated by first computing the average stress based on the undeformed cross section, and the average strain over the cross section, at various extensions. This stress-strain curve was then extrapolated to ϵ_b , calculated as above, to obtain σ_b . The tensile strengths thus determined were somewhat larger than those observed in routine tensile testing employing strips. This was in part due to careful attention to experimental procedure (good filler dispersion, avoidance of surface flaws), but also to the small specimen size and the extrapolation method used for calculating σ_b . While the merits of the latter may be open to question, any systematic error introduced by it cannot possibly contribute to the success of the structure-concentration reduction.

Tire Test. Eight experimental compounds and a control containing 70 phr ISAF black were applied to unused 8.55×15 carcasses to form a nine-section tread. Four of the experimental sections contained blacks A to D at 70 phr. Blacks A and B were also tested at 79 and 76 phr, respectively. The remaining two sections contained blends of carbon blacks B and D (37 : G3) and A and C (59 : 41). Testing was done over routes of different severity as indicated by the actual miles/mil tread loss of the ISAF control section: low severity, 75 miles/mil; moderate severity, 55 miles/mil; high severity, 35 miles/mil.

RESULTS AND DISCUSSION

Figures 1 to 3 show ϵ_b , U_b , and σ_b for SBR-1500 reinforced with the four furnace carbon blacks A, B, C, and D, plotted against reduced black concentration. The identical reduction factors ($a = 0.60, 0.81, 1.00, \text{ and } 1.08$) were used in all three correlations; moreover, these are the same shift factors employed in the earlier modulus reductions^{4,5} and are given to within 0.01 unit by eq. (2). Carbon black C was used as the reference black.

Limitations^{4,5} of structure-concentration equivalence in regard to $\sigma(\epsilon)$ are threefold: (1) At small strains, σ is dominated by secondary agglomeration of the primary structure aggregates; (2) at very large strains failure of the filler-polymer bond will lead to stress relaxation; (3) any significant effect of the filler on the vulcanization reaction will upset the reduction. The first of these limitations will have no effect on σ_b and ϵ_b , for the effects of secondary agglomeration disappear already at small strains.⁷ Its effect on U_b

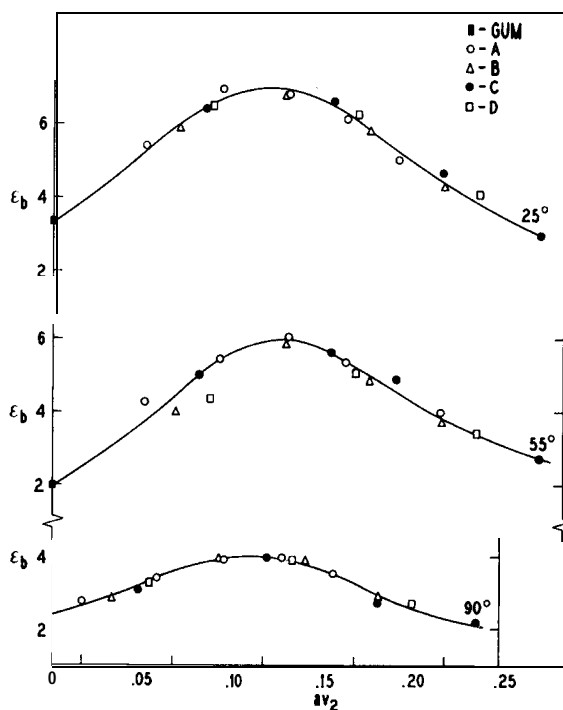


Fig. 1. Structure-concentration reduction of breaking strain.

will be small. Up to $\epsilon = 4$, "dewetting" of polymer from highly reinforcing blacks is insignificant.^{5,8} However, some failure of the polymer-filler bond would be expected to occur as the breaking elongation is approached. Evidently, the effect is not large in the present example and is submerged in the natural scatter of the stochastic variables plotted in Figures 1 to 3. Possible effects of the four carbon blacks of this study on vulcanization were previously shown to be small or constant.⁵

Because of the above limitations, structure-concentration equivalence will not apply generally to carbon blacks selected at random.⁵ The significance of the successful reductions shown here lies, therefore, primarily in their implications on the mechanism of carbon black reinforcement.

Harwood and Payne⁹ have demonstrated the applicability of the relationship

$$U_b = k(H_b \cdot \epsilon_b)^{1/2} \quad (6)$$

to carbon black-filled rubbers, where H_b is the hysteresis to break and k is a constant independent of filler type or loading. It is obvious that if U_b and ϵ_b are subject to structure-concentration equivalence, so must H_b . This prediction is supported by the fact, already reported,⁴ that structure-concentration reduction applies to stress softening, a major source of hysteresis in filled rubbers.

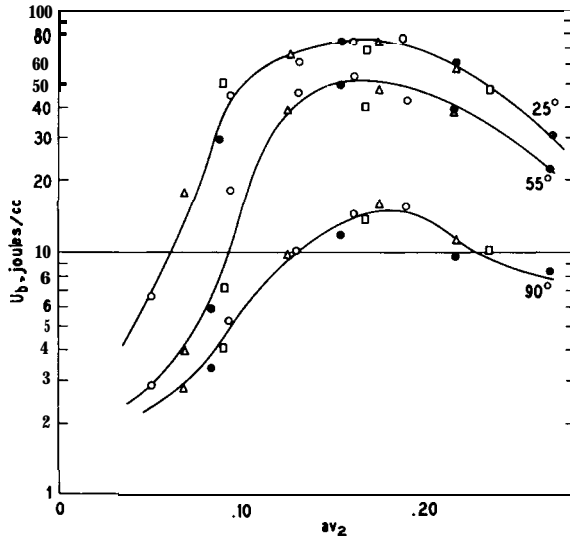


Fig. 2. Structure-concentration reduction of breaking energy.

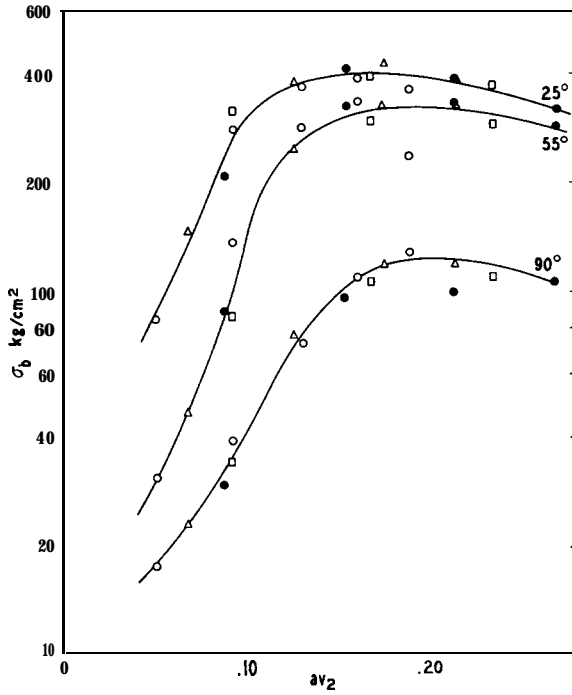


Fig. 3. Structure-concentration reduction of tensile strength.

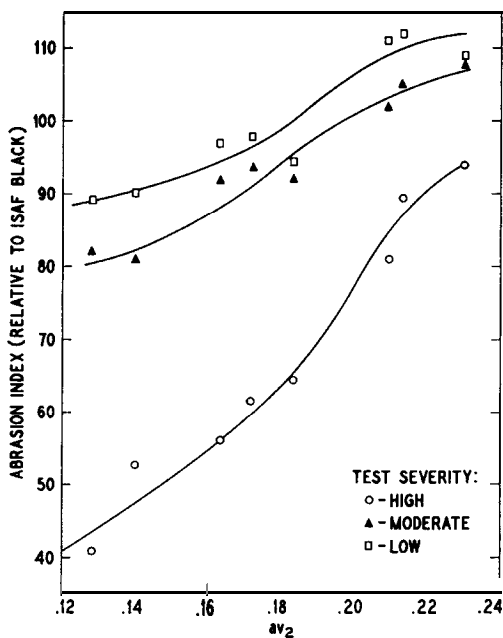


Fig. 4. Roadwear as a function of reduced black loading.

Another observation by Harwood and Payne⁹ applies to the relationship between U_b and ϵ_b :

$$U_b = k'(X\epsilon_b)^2. \quad (7)$$

The parameter X is assigned the role of a strain amplification factor and is a function of the filler concentration. Our results suggest that X should be based not on the actual, but on the effective, filler loading. The effect of this would be to generalize X with respect to structure variations and to change the concentration dependence of X .

Grosch and Schallamach¹⁰ have proposed an approximate relationship between U_b and abrasion loss A :

$$A = C\mu/U_b \quad (8)$$

where μ is the coefficient of friction and C is a constant. Since the coefficient of friction of black-filled vulcanizates is not particularly sensitive to carbon black structure, eq. (8) suggests that abrasion loss might be subject to structure-concentration reduction. Figure 4 shows roadwear data on the four blacks of the present study, plotted as functions of av_2 . One might expect the best correlation at high severity, where the mechanism of abrasion is predominantly bearing. Actually, the correlation is no worse at moderate and low severity of testing. While the data of Figure 4 are far too limited to prove the structure-concentration equivalence principle for roadwear under any condition, they also do not violate it in any way.

It is again emphasized that structure-concentration equivalence does not apply between carbon blacks differing significantly in primary particle size or specific surface area. Vulcanizates reinforced with large-particle carbon blacks have, of course, generally lower tensile strength than those containing small-particle blacks, even when αv_2 is the same. One reason for this is that the *individual* primary structure aggregates also become smaller and the interfacial area between rubber and carbon black becomes larger as the average particle size decreases. These features of the carbon black morphology are important in governing the strength of the rubber-filler bond and the hysteresis of the system, factors generally accepted to be fundamental to the reinforcement process.

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