The Effect of Type and Amount of Carbon Black on the Interaction between Polychloroprene Rubber and Motor Oil

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SYNOPSIS

The interaction constants between polychloroprene rubber, containing different amounts and types of carbon black, and a motor oil were experimentally determined. It was found that the interaction constant values are not affected by the type of carbon black as long as the mixes contain the same filler concentration and category, whereas mixes containing the same filler type but of different concentrations show different interaction constants.

INTRODUCTION

The volume fraction of rubber in the swollen network, v_r, is related to the molecular weight between crosslinks, M_c, and the molecular volume, V, by the well known Flory–Rhener equation;[1]

$$\ln(1 - v_r) + v_r + \mu v_r^2 = -\frac{\rho V}{M_c}\left(v_r^{1/3} - \frac{v_r}{2}\right) \quad (1)$$

where μ is the interaction constant and ρ is the density of rubber.

The kinetic theory of elasticity relates the M_c value to the force applied, F, to extend a test piece of cross-sectional area A_o to an extension ratio λ as

$$M_c = \frac{\lambda - \lambda^{-2}}{F} \rho R T A_o \quad (2)$$

where R is the gas constant and T is the absolute temperature.

The theory of elasticity was modified by Mooney[2] and Rivilin and Saunders[3] to fit some rubber compounds. However, in a previous article we showed that the kinetic theory of elasticity is applied in case of polychloroprene rubbers.[4]

The present work is undertaken with a view of studying the interaction constant between motor oil and polychloroprene rubber. Special emphasis is placed on the effect of carbon black (type and amount) on the interaction constant.

MATERIALS AND EXPERIMENTAL PROCEDURE RUBBER MIX FORMULATION

The mixes examined were based on Neoprene Elastomer, which is the generic name of chloroprene polymer (2-chloro-1,3-butadiene) supplied by E. I. DuPont de Nemors and Co. The grade used in this investigation is Neoprene WRT. The basic formulation is given in Table I.

Flectol H was used in the mix. It is a Monsanto product used for improving the flexing properties of rubber. The tetramethyl thiourea was used as a fast vulcanizing agent. Four types of carbon black were used: thermal medium (MT), semireinforcing furnace (SRF), high abrasion furnace (HAF), and superabrasion furnace (SAF). The HAF black was used at different concentrations 0, 10, 20, 40, and 60 phr. The three other blacks were used at only 40 phr. The characteristics of these blacks are given elsewhere.[5]

MIXING PROCEDURE AND TEST PIECE PREPARATION

Mastication and mixing were carried out using a water cooled two-roll mill (300 × 130 mm) operating at a friction ratio 5 : 4. Vulcanized sheets (from

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Table I Mix Formulation

	phr
Neoprene WRT	100
Flectol H (Monsanto)[a]	1.0
MgO	4.0
Stearic acid	0.75
Zinc oxide	5.0
TMTU[b]	0.75
Cabon black[c]	As indicated

[a] Acetone–aniline products.
[b] Tetramethyl thiourea.
[c] MT, SRF, HAF, and SAF blacks.

which the test pieces were cut) were produced by molding in an electrically heated platen press at 170°C. Rheometer (Monsanto type TM 100) tests at 170°C indicated that 90% crosslinking occurs at a cure time of 9 min. All samples were cured at this temperature and time.

RESULTS AND DISCUSSION

Restricted Volume Swelling

The swelling measurements of unfilled rubber mix expressed as, v_{r0}, and that of HAF filled rubber mix, v_{rf}, were performed at different carbon black concentrations; 0, 10, 20, 40, and 60 phr. The oil used in swelling was the commercial Misr HD Motor Oil 40.

Plotting the ratio v_{r0}/v_{rf} versus $\phi/(1-\phi)$ (where ϕ is the volume fraction of filler in the mix), a linear relationship is obtained, (cf. Fig. 1) which is in good agreement with the mathematical relation given by Kraus,[6]

$$v_{r0}/v_{rf} = 1 - [3C(1 - v_{r0}) + v_{r0} - 1]\phi/(1 - \phi)$$

in which C is a constant characterizing the filler.

The value of C was found to be 1.17 which is exactly the same value as that obtained by Kraus, although he used different polymers and solvents. These results signify (i) that Kraus' equation is important for filler adhesion and filler reinforcement to the swelling behaviour, (ii) that Kraus' equation can offer a useful method for detecting values of v_{r0} from v_{rf} or vice versa, and (iii) that the equation is valid for a particular black up to moderate loading of carbon black as far as the polymer, the swelling solvent, and the vulcanizing system are not interferring with the filler.

The restricted volume swelling could be interpreted in terms of adherence of rubber to aggregations of carbon black. Swelling is obviously restricted at the region around the filler aggregations but becomes normal at sufficient distance away from it.

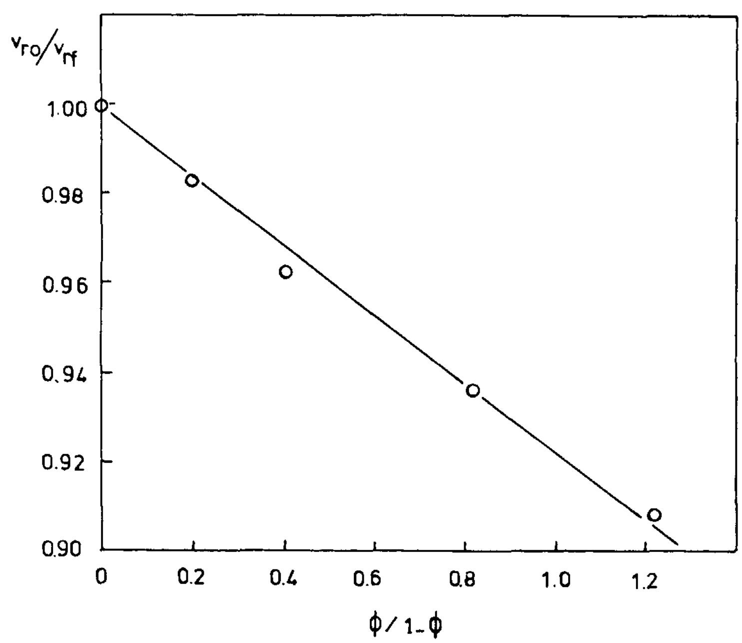

Figure 1 v_{r0}/v_{rf} vs. $\phi/(1-\phi)$ for samples containing different concentrations of HAF black.

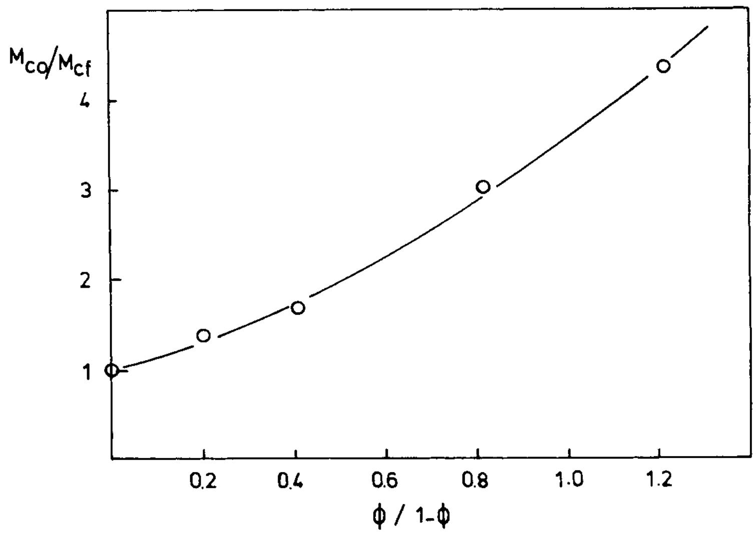

Figure 2 M_{c0}/M_{cf} vs. $\phi/(1-\phi)$ for samples containing different concentrations of HAF black.

The Relation between Carbon Black Concentration and Molecular Weight between Crosslinks (M_c)

The stress–strain measurements were carried out on samples filled with HAF black at different concentrations. The method used is given elsewhere.[5] From these measurements, M_{c0} and M_{cf} for unfilled and filled rubber mixes were calculated. Figure 2 illustrates the relation between M_{c0}/M_{cf} versus $\phi/(1-\phi)$. It can be seen that the number average molecular weights of the network M_c are reduced significantly with the increase of the filler concentration. This reduction can be explained on the basis of the increases in the shear forces imposed on the elastomer when it is masticated with the carbon black adhering filler.

Figure 3 shows a plot of v_{r0}/v_{rf} versus M_{c0}/M_{cf}. As is evident it is a useful relation to estimate one ratio by knowing the other, without additional experimental work.

Carbon Black Concentration and Interaction Constant

Using the M_c values obtained from the stress–strain measurements, and v_r values obtained from swelling measurements (correction was made to eliminate the volume fraction of carbon black in the mix),[7] the polymer solvent interaction constant was calculated, (see eq. (1)). On plotting $\phi/(1-\phi)$ versus the interaction constant (Fig. 4), one can notice the effect of carbon black loading on the interaction constant. Obviously this loading increases the carbon black aggregations and hence the reinforcement between rubber and carbon black. This reinforcement may affect the degree of physical crosslinking in the network structure of the rubber and in turn the μ values.

The Effect of Type of Carbon Black on the Polymer Solvent Interaction Constant

The aforementioned four types of carbon black were used. Forty parts by weight of each black was added to the mix (cf. Table I). The interaction constants between each mix and the oil used before were plotted against the corresponding M_c values (cf. Fig. 5). The latter includes also the interaction constant

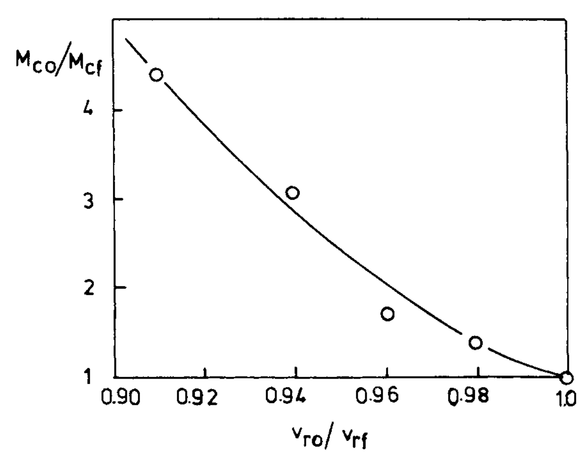

Figure 3 M_{c0}/M_{cf} vs. v_{r0}/v_{rf} for samples containing different concentrations of HAF black.

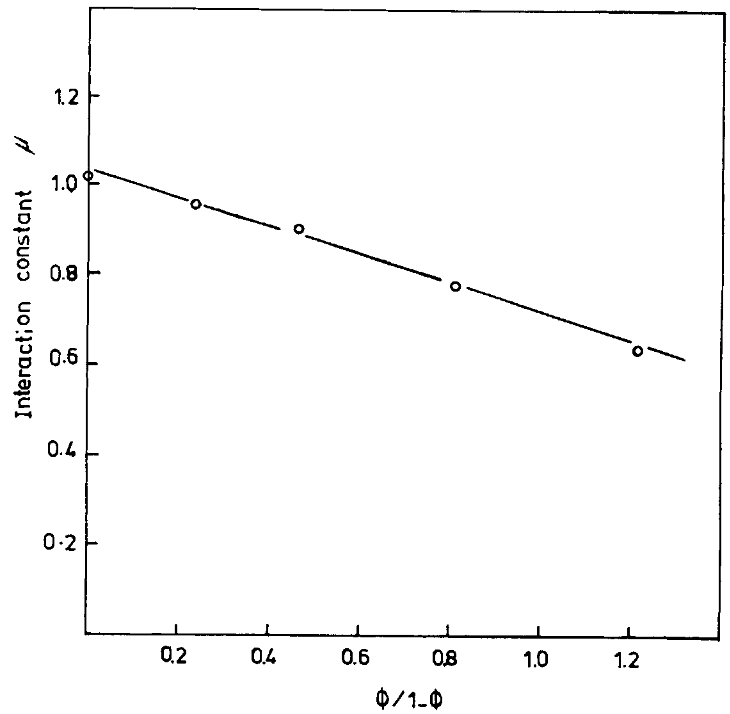

Figure 4 The interaction constants vs. $\phi/(1-\phi)$ for samples containing different concentrations of HAF black.

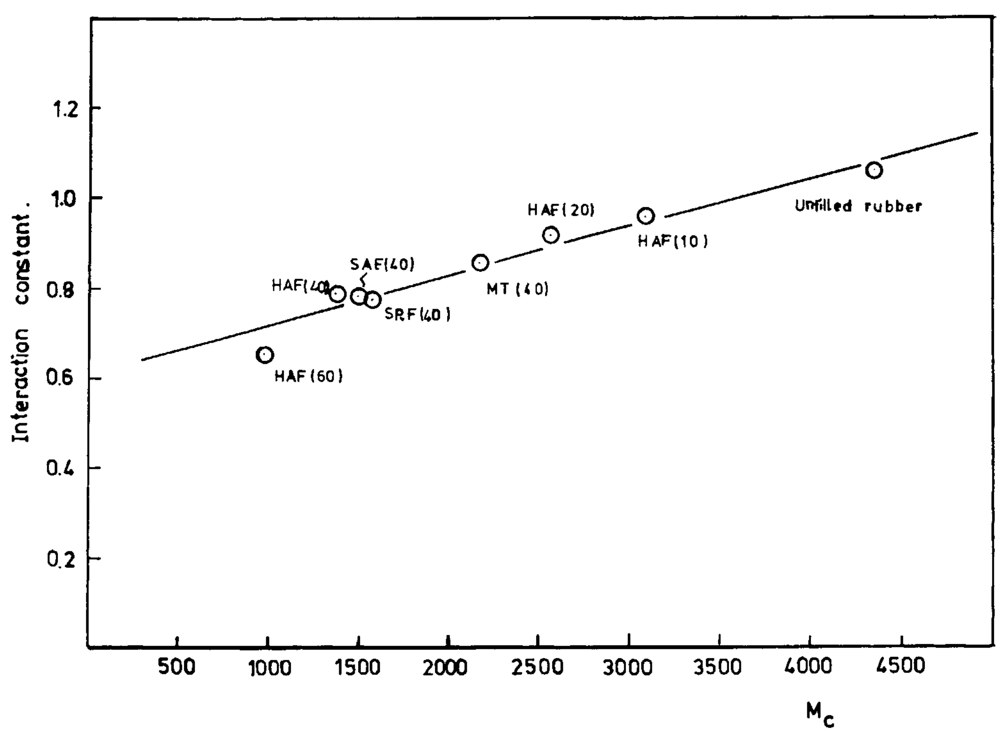

Figure 5 The interaction constants vs. M_c values for mixes containing different types and amount of carbon black (using one type of oil).

values of HAF black at the different concentrations. It is clear that the interaction constant values for mixes loaded with different types of carbon black at equal concentrations have nearly the same value. These values are very close in case of the three furnace blacks (SRF, HAF, and SAF) while in the case of thermal black (MT) it is slightly different.

This means that the interaction constant depends on the carbon black categories. The furnace black shows lower values of the interaction constant than that of the thermal black. The difference can be attributed to the fact that all furnace blacks are reinforcing fillers.

Generally, the interaction constant depends widely on the amount of filler in the rubber mix, categories of carbon black (thermal, furnace, etc.), while carbon black mixes of the same category and same amount of loading possess the same interaction constant value.

In conclusion, it is probably correct to say that the interaction constants are not affected by the type of carbon black as long as the mixes contain the same concentration of the filler. On the other hand fillers used are of the same categories (thermal, furnace, etc.), but of different concentrations show different interaction constants.

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