Dielectric Properties and Stress–Strain Measurements of Chloroprene Rubber Based on Different Carbon Black Fillers

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Synopsis

A systematic dielectric study of 1 kHz was carried out on chloroprene rubber, mixed with different types of carbon black and different concentrations. The measurements were carried out at room temperature (25°C). It was found that better dielectric properties cannot be achieved when the carbon black concentration exceeds 60% for MT, 40% for SRF, and 20% for both HAF and SAF. In addition, the relation between the dielectric constant ϵ' and the modulus of elasticity E for the different mixes were studied. From this study it was found that, up to certain carbon black volume concentration (depending on the filler type), the modulus equation $E_f = E_0\ (1 + 0.67\phi C + 1.62\phi C^2)$ can be used to relate the dielectric properties ϵ_f and ϵ_0 of carbon black filled and unfilled rubber compounds. The dielectric measurements were also related to the particle size and the structure of carbon black.

INTRODUCTION

The dielectric properties of a certain rubber depend widely on many factors: (i) the density of chain entanglements and chain ends, (ii) the crosslink density of the rubber, and (iii) the filler type and concentration. Many studies were carried out on the dielectric properties of natural and synthetic rubbers based on the different carbon black types and loading.[1–4]

Generally, it is known that the most important properties of carbon black are (i) the particle size, (ii) the structure, (iii) the physical nature of particle surface, (iv) the shape factor of carbon black aggregation in the rubber mix, and (v) the intermolecular and hydrodynamic adhesion between the polymer and carbon black which cause additional crosslinks to the polymer and effect directly the activation energy of the rubber.

It is more convenient to explain some of these carbon black properties and how they can be measured. The term structure refers to the joining together of carbon black forming the additional aggregates. This is normally measured by determining the total volume spaces between the aggregates per unit weight of black; the method was given by Gaton and Horn[5,6] or by X-ray diffraction.[7] The other term is the shape factor. This factor depends widely on the polymer chain and the way the carbon black particles aggregate inside the rubber mix. This aggregation is usually in the form of an elipse. The ratio between the major and minor axes of this elipse is known as the shape factor. This shape factor can be measured by using election microscope technique[8] or from stress–strain measurements.[9]

In this study the dielectric properties of chloroprene rubber based on four types of thermal and reinforcing carbon blacks (at different concentrations)

Journal of Applied Polymer Science, Vol. 31, 841–848 (1986)
 CCC 0021-8995/86/030841-08$04.00

will be investigated. The modulus of elasticity of all mixes will be obtained from stress–strain measurements. A trial will be made to relate the dielectric properties to that modulus.

MATERIALS AND EXPERIMENTAL PROCEDURE

Rubber Mix Formulation

The mixes used in this study are based on neoprene elastomer which is the generic name for chloroprene polymer (2-chloro-1, 3-butadiene) supplied by DuPont de Nemours and Co. The grade used in this study is neoprene WRT. The basic formulation is given in Table I. The flectol H that was used in this mix is a Monsanto product and is used to improve flexing properties of rubber. The tetramethyl thio urea (TMTU) is a very fast vulcanizing agent. Four types of carbon black were used: thermal medium (MT), semireinforcing furnace (SRF), hig abrasion furnace (HAF), and super abrasion furnace (SAF). The properties of these blacks[8] are given in Table II. The carbon black concentration was also studied as 0, 10, 20, 40, and 60 phr. These concentrations were used with each carbon black mentioned before.

Mixing Procedure and Test Piece Preparation

Mastication and mixing were carried out on a two-roll mill (300 × 130 mm) operating at a friction ratio of 1.25:1 with water cooling. Vulcanized sheets (from which test pieces were cut) were produced by molding in an electrically heated platen press at 170°C. Rheometer Monsanto type (NO TM100) tests at 170°C indicating that 90% crosslinking occurs at a cure time 9 min were given in all cases.

Stress–Strain and Modulus Measurements

For these measurements dumbbell test specimens of dimensions (20 × 4 × 1.5 mm) were used. Measurements were made at the center part, 2 cm in length. The center and width were measured accurately. Two clamps were designed to grip the sample; the downward clamp had a hook to hold a pan in which different weights were applied. The initial specimen length l_0 and the length l, corresponding to each force applied were measured accurately using an optical cathetometer. From these data, F/A_0 (force applied per unit original area) was plotted against $(l - l_0)/l_0$. The relation

TABLE I
Mix Formulation

Neoprene WRT	100
Flectol H (Monsanto)	1.0
Mg O	4.0
Stearic acid	0.75
Zinc oxide	5.0
TMTU	0.75
Carbon black	As indicated

TABLE II
Carbon Black Properties

Property	MT	SRF	HAF	SAF
	470	60	29	20
Structure ($cm^3/100$ g)	33	65	105	115

is almost linear; the slope of the lines obtained for the different samples between zero and 20% strain is taken as modulus. This modulus is denoted as E_0 and E for unfilled and filled carbon black rubbers, respectively.

Dielectric Measurements

For these measurements, samples of diameter 8 mm were cut off the same sheet used before in preparing the stress–strain samples. An automatic precision bridge type RLCB from Rohde and Schwarz was used to measure the capacitance component from which the dielectric constant ϵ' is obtained and also the loss factor tan δ. These measurements were carried out at 1 kHz and room temperature of about 25°C. The accuracy of capacitance measurements was $\pm$ 0.1% while for tan δ it was $\pm$ 5%.

RESULTS AND DISCUSSION

On studing the effect of carbon black concentration on the dielectric properties ϵ' and tan δ, it is noticed that both ϵ' and tan δ are increased with the increase of carbon concentration. This can be shown in Figure 1. It is also interesting to notice that, at certain concentrations of carbon black, ϵ' reaches extremely high values as a result of interfacial polarization between the carbon black particles and the polymer chain. Hence, the compound became conductive. This was reported before.[10]

This concentration shows an increase in the order MT > SRF > HFA > SAF. From these results it can be concluded that, to obtain better dielectric properties for rubber samples filled with carbon black, it is better not to increase the carbon black concentration to more than 60% for MT, 40% for SRF, and about 20% for both HAF and SAF.

As there is a close relation between the effect of carbon black type and its concentration on both the modulus and the dielectric properties of a filled rubber mix, the thoughts were directed to relate E_f/E_0, which is known by the modulus reinforcing factor; this can be obtained from stress-strain measurements to that of ϵ_f/ϵ_0, which we may call the dielectric reinforcing factor. The suffixes f and 0 are related to the filled and unfilled rubber vulcanizates. This relation can be shown in Figure 2. This relation seems to be interesting as it tends to be linear. The other interesting observation in this figure is that mixes which are far from this linearity cannot be accepted as good electric insulators. Meanwhile, those mixes which follow this linear relation are accepted both mechanically and electrically as insulators.

However, there is a well-known relation between E_f/E_0 and the carbon black volume concentration in a mix from which the shape factor can be

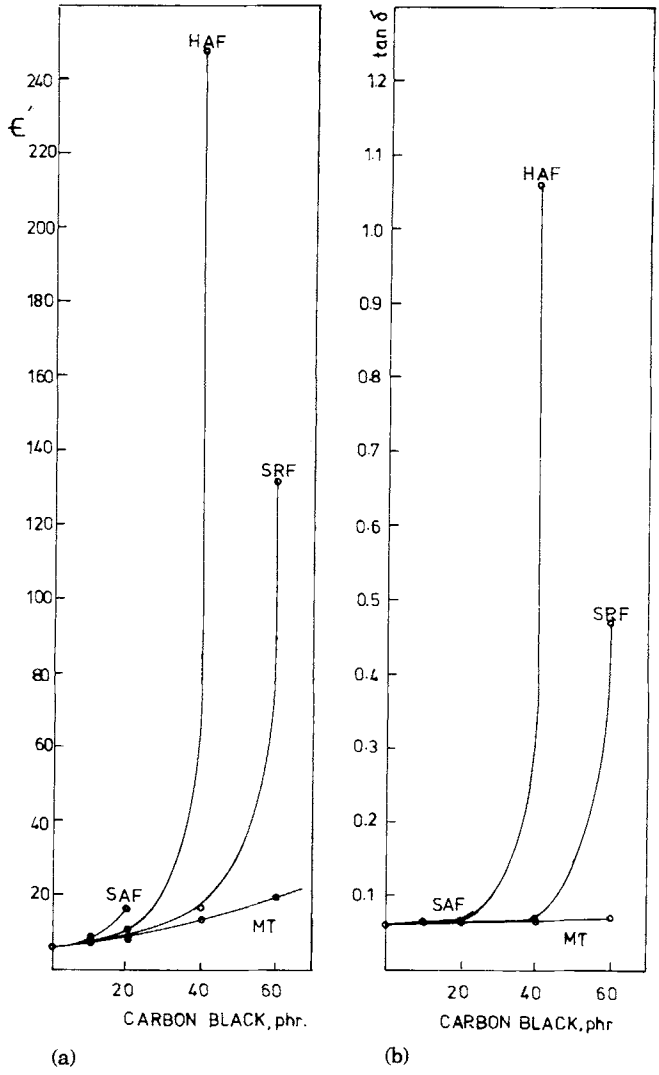

Fig. 1(a). Plot of dielectric constant ϵ' vs. carbon black concentration (phr).

Fig. 1(b). Plot of loss factor tan δ vs. carbon black concentration (phr).

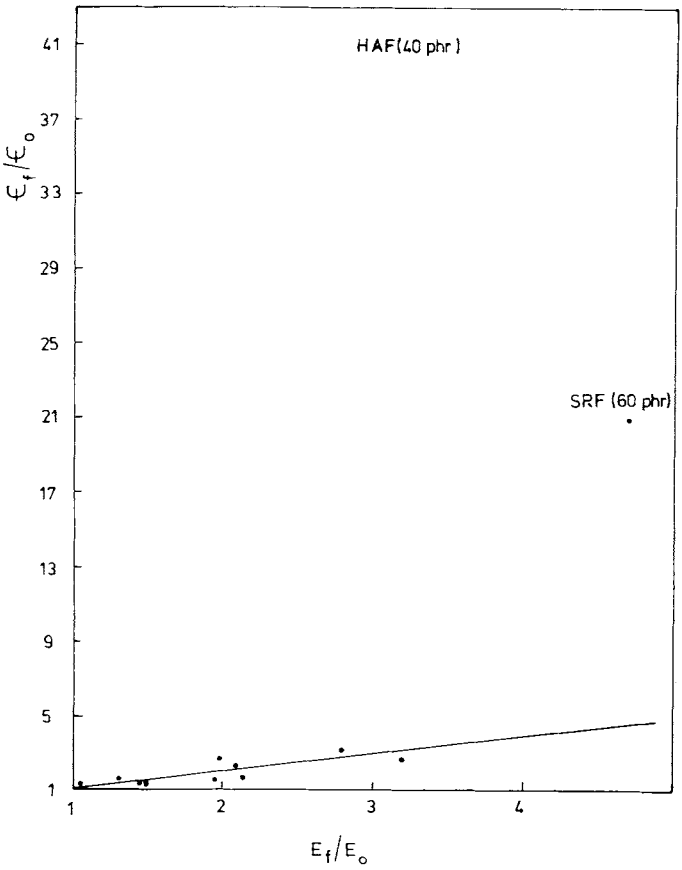

Fig. 2. Plot of ϵ_f/ϵ_0 vs. E_f/E_0.

obtained. These relations were given by Einstein, Guth Gold, and others by the equations[9]

$$E_f = E_0(1 + 2.5C) \tag{1}$$

$$E_f = E_0(1 + 2.5C + 14.1C^2) \tag{2}$$

and a modified equation for reinforcing rubber given as

$$E_f = E_0(1 + 0.67\phi C + 1.62\phi C^2) \tag{3}$$

where ϕ is the shape factor of the carbon black.

The close relation between modulus and dielectric properties ϵ' was shown here before; hence E_f/E_0 and ϵ_f/ϵ_0 were plotted against the carbon black volume concentration in Figure 3. It was found that for a certain type of carbon black the points representing these two ratios fit a certain equation calculated at a given shape factor ϕ. The shape factors of the different types of carbon black can be reported here as 3, 4, 5–6, and 6 for MT, SRF, HAF,

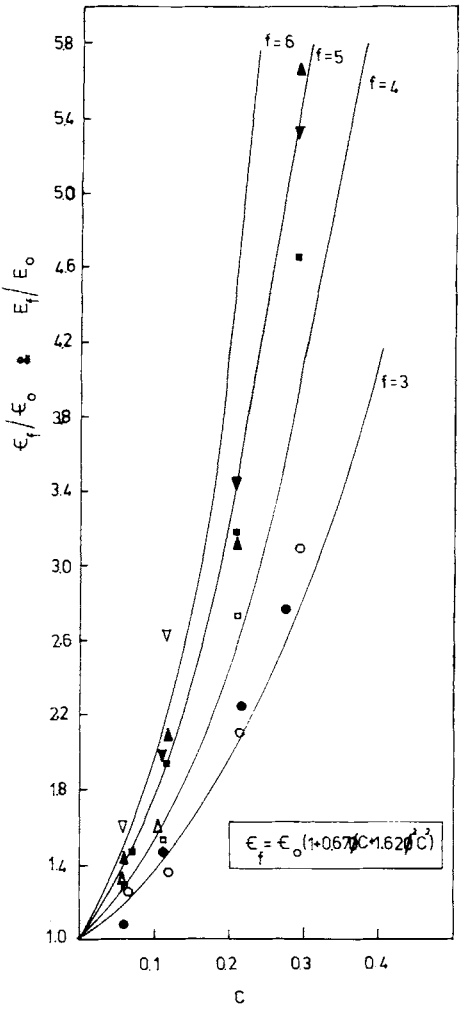

Fig. 3. Plot of ϵ_f/ϵ_0 and E_f/E_0 vs. the carbon black volume concentration C dielectric; (●,■,▲,▼) modulus; (●,○) MT; (■,□) SRF; (▲,△) HAF; (▼,▽) SAF.

and SAF, respectively. It may also be reported here that the modulus equation (3) can also be used for the dielectric reinforced measurements up to a certain carbon volume concentration depending on the filler type.

At low carbon black concentration (< 20 phr) the particle size has a little effect on the dielectric properties ϵ' but, at concentrations higher than 20 phr, there is a significant increase in ϵ' specially for the highly reinforced fillers HAF and SAF. This can be shown in Figure 4. In plotting the structure factor of carbon black against the ϵ' values, the relation shows results opposite to those given with the variation of particle size. This can be shown in Figure 5. The results given in Figures 4 and 5 may be attributed to the higher elasticity of the polymer at large particle size and higher structure

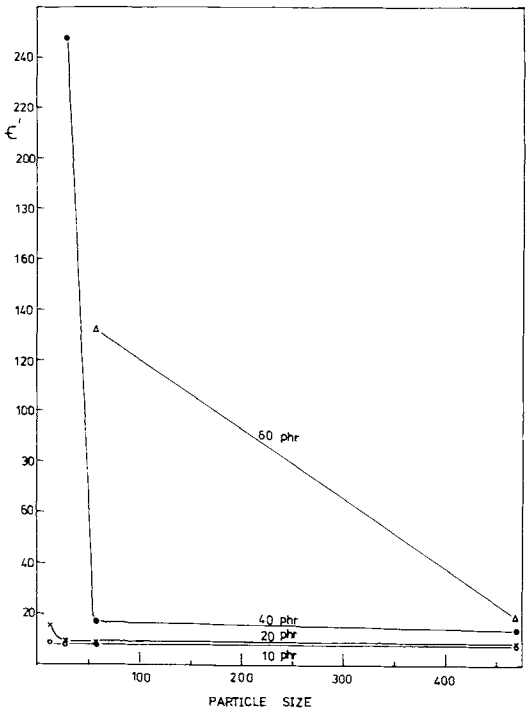

Fig. 4. Plot of ϵ vs. particle size of carbon black (nm).

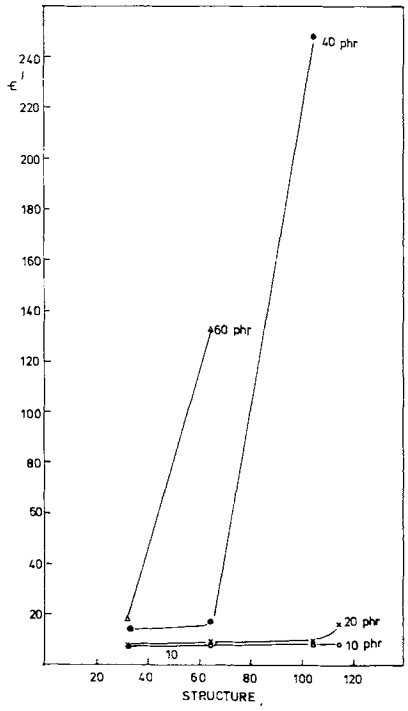

Fig. 5. Plot of ϵ' vs. the structure of carbon black ($cm^3/100$ g).

which cause a higher activation energy to the polymer than smaller particle size and structure.

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Received February 5, 1985
Accepted July 2, 1985