EFFECT OF CALCIUM CARBONATE, SILLITIN N85 AND CARBON BLACK FILLERS ON THE MECHANICAL AND ELECTRICAL PROPERTIES OF THE EPDM

A. A. El-Wakil and A. A. Abd El-Megeed
National Institute of Standards, El-Harm, Giza, Egypt
E-Mail: abdelaziz_elwakil@yahoo.com

ABSTRACT
The improvement of the service life of rubber is dependent on the behavior of the white and black fillers in rubber vulcanizates. The cross linking density of the EPDM vulcanizates, which contain sillitin N85, calcium carbonate, and SRF-black, was measured by using untrasonic technique, pulse echo technique. The aim of this work is to demonstrate the significance of the effect of the fillers on the mechanical and electrical properties of the EPDM. In order to demonstrate the significance of the effect of the fillers, we studied the effect of the aging on the EPDM vulcanizates, which contain sillitin N85, CaCO₃, and SRF. The cross linking density was determined by using the ultrasonic technique. It was found, the fillers improves the mechanical and electrical properties of the EPDM vulcanizates.

Keywords: ethylene propylene diene monomer, fillers, mechanical properties, electrical properties, thermal aging.

INTRODUCTION
Raw rubber, either polar or non polar, has poor physicomechanical properties. To improve these properties, some ingredients such as accelerators, activators, antioxidants, softeners, and white and black fillers were added to the rubber vulcanizates. The degree of reinforcement provided by filler depends on a number of variables, the most important of which is the development of a large polymer-filler interface. The most reinforcing fillers known are carbon blacks, silicas, clay, calcium carbonate, and mineral fillers. Thus, these fillers, or reinforcement aids are added to rubber formulations to optimize properties that meet a given service applications [1,2]. In polymer systems, fillers not only reduce the cost of the material but also reinforce the rubber and improve the properties of the rubber compounds [3-5].

This article deals with the study the effect of calcium carbonate, sillitin N85, and semi reinforcing furnace carbon black (SRF) on the mechanical and electrical properties of the ethylene propylene diene monomer. It is also aimed to study the effect of thermal aging on the mechanical and electrical properties of the EPDM formulations, which contain 30phr of the calcium carbonate sillitin N85, and SRF-black.

MATERIALS AND METHODS
The fillers that used in all the samples described in this study were sillitin N85 (SN85), calcium carbonate (CaCO₃), and semi-reinforcing furnace (SRF). Sillitin N85 is natural agglomerate of corpuscular quartz and lamellar kaolinite, supplied by Hoffmann mineral GmbH and Co. KG (Neuburg, Germany). The particle size of this sillitin N85 is 250 to 500 nm. Calcium carbonate supplied by Edwic (Cairo, Egypt). The particle size of this calcium carbonate is 2.5 µm. Semi-reinforcing furnace supplied by Transport and Engineering Co. (Alexandria, Egypt). The particle size of this SRF is 80-110 nm.

Preparation of EPDM mixes
A master batch of EPDM rubber was prepared and then loaded with calcium carbonate, sillitin N85 and SRF-black. Formulations for the EPDM mixes and final mixed compounds are given in Table-1. All rubber compounds were mixed according to the ASTM D 3182 operating at friction ratio 1.25:1. The vulcanization was carried out in an electrically heated platen press at 160°C to the optimum cure time that was determined by using the Oscillating Disc Rheometer, Alpha Technologies, Rheometer MDR 2000.

Aging study
Aging tests were performed in an air circulating oven fixed at 90°C for 2,4,6,8, and 10 days [6].

Tensile test
Tensile tests were performed according to ASTM D 412-98 test method by using dumbbell shaped test pieces, which were punched out from the molded sheets. The tests were carried out in a Zwick Universal Testing machine, model Z010 at 23 ± 2°C and a cross head speed of 500 mm/min. The results reported here are averages of three samples.

Cross linking density measurement
The cross linking density of the EPDM vulcanizates, which contain sillitin N85, calcium carbonate, and SRF-black, was measured by using untrasonic technique, pulse echo technique. The ultrasound measurements in this study were performed using the following equipments: Oscilloscope (54615B hp) had used to obtain the time traveling through specimen, Flaw detector (USIP 20 Krautkramer) had used to display echo, Step block, VI and VII blocks had used as reference steel blocks (having known thickness and velocity), and Transducer (Krautkramer) having 2 MHz frequency [7].
\[ \mu = 0.93 \, C_L^2 \]
\[ \lambda = 0.93 \left( (C_L^2) - 2(C_T^2) \right) \]

\( \mu \) and \( \lambda \) are Lamé' constants

\( C_L \) is the longitudinal velocity

\( C_T \) is the shear velocity

\[ \sigma = \lambda / (2(\lambda + \mu)) \]

\( \sigma \) = Poisson's ratio

\[ \sigma = 1 / \rho \]

\( \sigma \) is the conductivity

\[ \varepsilon' = \frac{C_x}{C_A} \]

\( \varepsilon' \) is the dielectric constant

\( C_x \) is the capacitance of the specimen

\( C_A \) is the capacitance of the electrodes

**Electrical properties measurement**

The capacitance and dissipation factor of the various EPDM vulcanizates were measured using the General Radio Capacitance Measuring System, Type 1615-A. This bridge is a transformer ratio arms designed to measure the capacitance and dissipation factor with high accuracy up to 0.01% [8].

\[ \rho = \frac{(D/2\pi f \, C)}{(A/t)} \]

Where

\( \rho \) is the resistivity

\( D \) is the dissipation factor

\( f \) is the frequency

\( C \) is the capacitance

\( A \) is the cross section of the specimen

\( t \) is the specimen thickness

**RESULTS AND DISCUSSIONS**

The most reinforcing fillers known are carbon blacks, sillitin N85, and calcium carbonate. Carbon blacks represent the preeminent class of reinforcing fillers, both in tonnage and in variety of properties, so we direct our attention primarily to them. Rubber filler clays are classified as either “hard” or “soft” in relation to their particle size and stiffening effect in rubber. A hard clay will have median particle size of approximately 250 to 500 nm, and will impart high modulus, high tensile strength, stiffness, and good abrasion resistance to rubber compounds. It will substitute for a portion of the more expensive carbon black in certain compounds without sacrificing physical properties.

**Mechanical properties**

The relation between the retained tensile strength values of EPDM vulcanizates, which contain sillitin N85, calcium carbonate and semi-reinforcement furnace, and the aging time, are shown in Figure-1.

**Table-1.** EPDM mix formulations.

<table>
<thead>
<tr>
<th>Mix ingredients</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene propylene diene monomer (EPDM)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Activator</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1- Zinc oxide</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>2- Stearic acid</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Processing oil (Naphthenic oil)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>sulfur</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Accelerators 1- Mercaptobenzthiazole</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>(MBT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2- Tetramethylthiuram disulphide (TMTD)</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>Antioxidant</td>
<td></td>
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</tr>
<tr>
<td>(N-phenyl-N-(1,3-dimethylbutyl)-p-</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>phenylenediamine, 6PPD)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sillitin N85</td>
<td>-</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>Semi reinforcing furnace carbon black</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30</td>
</tr>
</tbody>
</table>

Where

\( \varepsilon' \) is the dielectric constant

\( C_x \) is the capacitance of the specimen

\( C_A \) is the capacitance of the electrodes
Figure-1 indicates the added fillers sillitin N85, calcium carbonate, and the SRF enhances the mechanical properties the EPDM vulcanizates. The tensile strength of EPDM vulcanizates, which contain SRF and sillitin N85 respectively increased with aging time at 2 days then it decreased with increasing aging time up to 10 days. Because the crosslink density between EPDM chains increased at aging time 2 days then slightly decreased with increasing aging time up to 10 days as shown in Figure-2. The mechanical properties of EPDM mixes containing calcium carbonate and the control mix decreased with increasing aging time from 2 days to 10 days.

The relation between the crosslinking density of EPDM vulcanizates, which contain sillitin N85, calcium carbonate and semi-reinforcement furnace and the aging time are shown in Figure-2.
From Figure-2 it can note that the cross linking density within the EPDM vulcanizates, which contain SRF and SN85, increased at aging time 2 days then decreased with increasing aging time up to 10 days. Because at 2 days aging time, the vulcanization process was completed then the aging caused the degradation for the crosslink between EPDM vulcanizates with increase aging time from 2 days up to 10 days [9]. In case of EPDM vulcanizates, which contain calcium carbonate, and the control mix, the crosslink density decreased with increasing aging time up to 10 days. Because at the initiate of aging process, the aging causes degradation of the crosslink density between EPDM chains.

The effect of SN85, CaCO$_3$, SRF on elongation at break values, % of the EPDM vulcanizates are shown in Figure-3.

![Image](image_url)

**Figure (3) Relation between retained elongation at break, % and aging time, days.**

It is obvious that the EPDM vulcanizate, which contain SRF, has higher elongation at break values than the EPDM vulcanizates, which contain sillitin N85 and calcium carbonate, and the control mix. Because the particle size of SRF is lower than that of SN85, and CaCO$_3$. When the fillers are mixed into rubber in conventional equipment, the first step (incorporation) is penetration of the fillers into the void space, replacing the trapped air. If at this stage considerable rubber - filler interaction occurs, subsequent dispersion is rendered more difficult as bound rubber cements many primary aggregates together loose filler. This occurs before the filler is randomly dispersed. For this reason the particle size of the fillers play the important role in the reinforcement process. Because, when the filler has small particle size, the filler has more ability to disperse within the rubber. At the same time SRF is quite rapidly incorporated within the EPDM vulcanizates [10].

**Electrical properties**

In many industrial applications, rubber articles are used as electrical insulators since rubbers in general are one of the families that have better dielectric properties. The study of these properties would provide useful information about the behaviour of molecules when they are under the influence of an electric field. The various EPDM vulcanizates loaded with CaCO$_3$, SN85, and SRF were aged at 90$^\circ$C for 2, 4, 6, 8, and 10 days then measured electrically. The values of conductivity and dielectric constant were calculated and plotted versus aging time as shown in Figures 4 and 5, respectively.
From Figure-4, it is clear that the conductivity values are nearly unaffected along the entire range of aging. Meanwhile these values are dependent on the type of filler that used where the conductivity of the EPDM vulcanizate, which contain the sillitin N85 is more than that of the control mix and the EPDM vulcanizates, which contain the CaCO$_3$ and the SRF. Because this high conductivity is basically attributed to the mobility of the free electrons taken place through the interaction between functional filler, sillitin N85, and the EPDM vulcanizate. Therefore the charge carriers hopping movements between filler aggregates and increase conductivity of the EPDM vulcanizate [11].
From Figure-5 it is observed that the dielectric constant slightly decreased with increasing the aging time. It is clear from Figure-5 that, the white filler, sillitin N85 and calcium carbonate decrease the dielectric constant values of the EPDM vulcanizates. EPDM vulcanizate, which contain SRF, has higher dielectric constant value. This could be attributed to the hindrance of the free charge and electron mobility raised by the created extra crosslinks, as shown in Figure-2, within the EPDM vulcanizate, which contain SRF [12].

CONCLUSIONS

a) The crosslinking density within the EPDM vulcanizate increased by using the semi-reinforcing furnace as filler. Accordingly, SRF enhance the mechanical properties of the EPDM vulcanizate;

b) The EPDM vulcanizate, which contain sillitin N85, has higher conductivity value than other EPDM vulcanizates; and

c) The semi-reinforcing furnace enhances the dielectric constant for the Ethylene propylene diene monomer vulcanizate.

REFERENCES


