

Effect of Biaxial Stress on Mechanical and Electrical Properties of Some Rubber Nanocomposites

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Abstract: The stress strain behavior of nanostructure carbon reinforced rubber composites was studied. The effect of both uniaxial and biaxial tensile stress on electrical conductivity of our samples was investigated. We have noticed that electrical conductivity decreased on applying uniaxial loading and increased with increasing biaxial tensile ones. Both elastic modulus and yield points in uniaxial and biaxial mode of stress were obtained and compared with increasing the concentration of nano-filler. Calculated values of the knee point strains have been obtained, and we made a fitting for our experimental results.

Keywords: Biaxial tension, Equivalent stress, Electrical conductivity

I. INTRODUCTION

Study of mechanics of rubbers under uniaxial and biaxial static loadings is of a great interest since the use of such materials has been widespread in many industrial applications. The mechanical behavior of rubber (polymers) is affected by many external and internal factors [1]. The mechanical tests frequently performed on rubbers are of two types: compression and tension. Tension can be applied in a uniaxial, planar or equibiaxial states [2,3]. Reinforcement of elastomers by active, nanostructured fillers such as carbon black or silica is one of the most important factors for producing high performance rubber products [4-7]. The tensile stress – strain is one of the basic characteristics for rubbers. A relevant test method is standardized [8] and is widely used to determine deformation and stress at the breakdown point. Conductive polymer composites are usually produced by incorporating conducting filler such as carbon black (CB) in an insulating matrix [9].

II. MATERIALS AND EXPERIMENTAL WORK

Materials

The materials used in this study is elaborated on purpose, in order to have two main components i.e. natural rubber and nanostructure (50 nanometer particle size) carbon black which is named Fast Extrusion Furnace (FEF) (materials were from Alexandria Company for carbon – Alexandria – Egypt), and a small number of additives like sulfur, accelerator and lubricants. The composition for 100 gram of natural rubber is the following one: stearic acid 2.0 gram, ZnO 5.0 gram, sulphur 1.5 gram, accelerator CBS 2.5 gram and FEF carbon black is variable from zero to 90 Phr (Part per hundred Part).

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Preparation of the Rubber Compounds and Vulcanizates

The prepared compounded rubber was left for at least 24 hours before vulcanization. The vulcanization process conducted at 140°C under a pressure of 40 kg/cm² for 20 minute. For reasonable stability and reproducibility of parameter, samples were subjected to thermal aging at 343 K for 25 days in an electric oven [10] before measurements.

Characterization and Testing

Mechanical testing:

Static tensile mechanical properties were carried out to determine the mechanical behavior of natural rubber nanocomposite samples using simple tensile apparatus. Rectangular – shaped samples were cut from molded sheets. Tensile tests were performed at room temperature (300 K).

Uniaxial tensile test:

In uniaxial stress-strain measurements, the samples were stretched with different loads. The corresponding elongation has been recorded continuously with constant stress rate throughout the extension until rupture of the samples took place. The rubber specimens used were in the form of Rectangle shape (2.5 cm in length and 0.5 cm in width) with different thicknesses for different samples. Using the dimensions of samples, stresses and strains were calculated.

Biaxial tensile test:

For experimental measurements, the specimen was clamped with biaxial square shaped sample holder. The rubber specimens used were in the form of square shaped samples. Only pure natural rubber and 10, 20 and 40 Phr FEF nanostructure carbon black loaded natural rubber samples were tested due to limitation of our biaxial tensile machine.

DC electrical conductivity measurements:

The DC Current voltage measurements of our samples were carried out using a digital electrometer type (KEITHLEY 485 auto ranging picoammeter), and a smoothly variable power supply. The DC-electrical conductivity σ was then calculated.

III. RESULTS AND DISCUSSION

Comparison Between Uniaxial and Biaxial Tensile Mechanical Properties

Stress stain curves are one of the most important characteristics for rubbers, which are used to evaluate the mechanical properties of materials. A relevant test method is standardized [8] and is widely used to determine deformation and stress at the breakdown point. However, stress strain curve contains additional information about rubber properties which is currently not being used. There is also an increasing interest in biaxial tensile loading as it allows consideration of the biaxial stress conditions that exist in rubber applications. However, the advantages of biaxial tests over uniaxial tests have not been clearly demonstrated [11].

Square shaped specimens (2.4 cm in Length) were tested on a homemade biaxial testing machine at a constant temperature 300 K. Square specimens were stretched up to failure.

Experimental results for pure natural rubber and those loaded with 10, 20 and 40 phr of nanostructure FEF carbon black are shown in Fig. 1. It was not possible to measure more than 40% of engineering strain before failure of the specimen in case of an equibiaxial test. This limitation is due to the testing machine limitation. The central part is under biaxial stress while the arms are under uniaxial stress.

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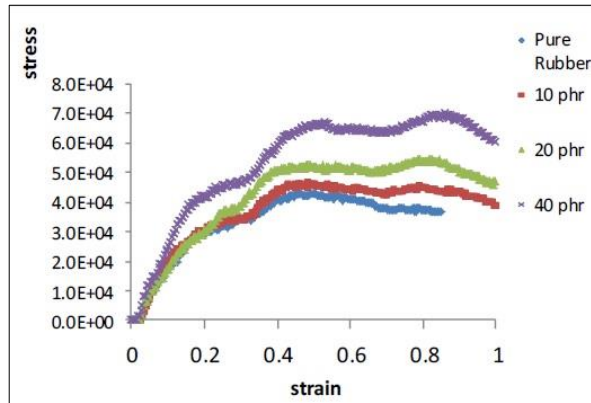


Fig. 1. Biaxial tensile stress – strain curve for pure natural rubber NR, and samples loaded with 10, 20 and 40 Phr of nanostructure FEF carbon black.

In order to compare uniaxial and biaxial test results, the equivalent stress and equivalent strain must be calculated for the biaxial test based on Von Mises equations. For a biaxial loading without shear these equations are:

$$\sigma_{eq} = \left[\sigma_x^2 + \sigma_y^2 - \sigma_x \sigma_y \right]^{1/2} \quad (1)$$

$$\varepsilon_{eq} = \left(\frac{1}{1+\nu} \right) \left[1/2 (\varepsilon_x + \varepsilon_y)^2 + (\varepsilon_y - \varepsilon_z)^2 - (\varepsilon_z - \varepsilon_x)^2 \right]^{1/2} \quad (2)$$

Moreover, because large strains occurs in the sample, the true stress and true strains must be used and calculated from the equations:

For Uniaxial Tests

$$\varepsilon_{eq} = \ln(1 + \varepsilon_x) \quad (3)$$

The true stress σ_x must take into account that the variation of the sample cross section during the loading and this is equal to:

$$\sigma_x = \frac{S_x}{(1 + e_y)(1 + e_z)} = \frac{S_x}{\exp^{(e_y + e_z)}} \quad (4)$$

Where $\varepsilon_x, \varepsilon_y, \varepsilon_z$ are the engineering strains in the x, y and z directions respectively and σ_x is the engineering stress.

For uniaxial test, the true strains in the through thickness and transverse directions are equal and related to longitudinal true strain by the Poisson's ratio:

$$\varepsilon_y = \varepsilon_z = -\nu \varepsilon_x \quad (5)$$

Therefore, the true stress can be calculated by:

$$\sigma_x = \frac{S_x}{\exp^{(-2\nu \varepsilon_x)}} \quad (6)$$

Similarly, it is possible to define true strains and true stresses for a biaxial test based on the engineering strain and engineering stresses that is shown in Fig. 2.

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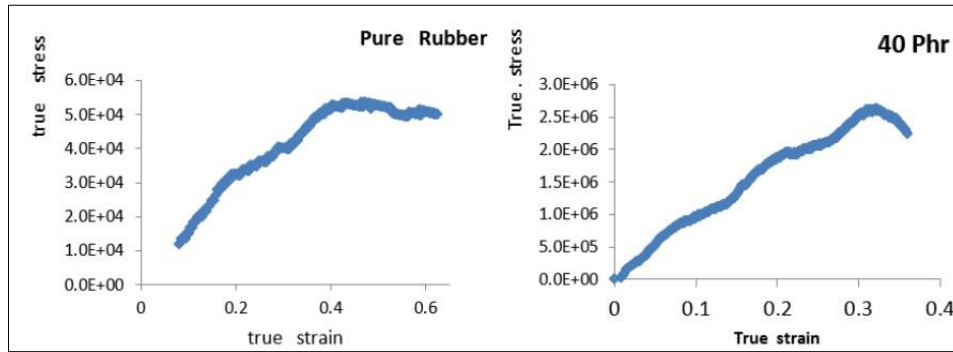


Fig. 2. True stress – strain of the tested samples pure natural rubber and (40 Phr) FEF loaded composites as examples (biaxially).

Biaxial Test

The true strains are defined by:

$$\varepsilon_x = \ln(1 + e_x), \quad \varepsilon_y = \ln(1 + e_y) \quad (7)$$

And the true stress given by:

$$\sigma_x = \frac{S_x}{\exp(\varepsilon_y + \varepsilon_z)}, \quad \sigma_y = \frac{S_x}{\exp(\varepsilon_x + \varepsilon_z)} \quad (8)$$

Where the through – thickness true strain is given by:

$$\varepsilon_z = \frac{\nu}{\nu - 1} (\varepsilon_x + \varepsilon_y) \quad (9)$$

As a result, using equivalent true stress and equivalent true strain representation, one obtains the description of the material behavior independently of the sample geometry and stress rate. The corresponding curves are shown in Figs. 3 and 4 for uniaxial and biaxial test for samples natural rubber and samples loaded with 10, 20 and 40 phr of FEF carbon black.

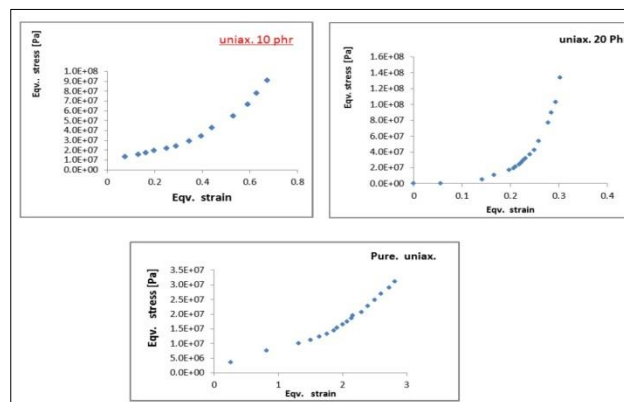


Fig. 3. Equivalent stress strain curve (uniaxially) for pure NR loaded with 10, 20 and 40 phr of FEF black.

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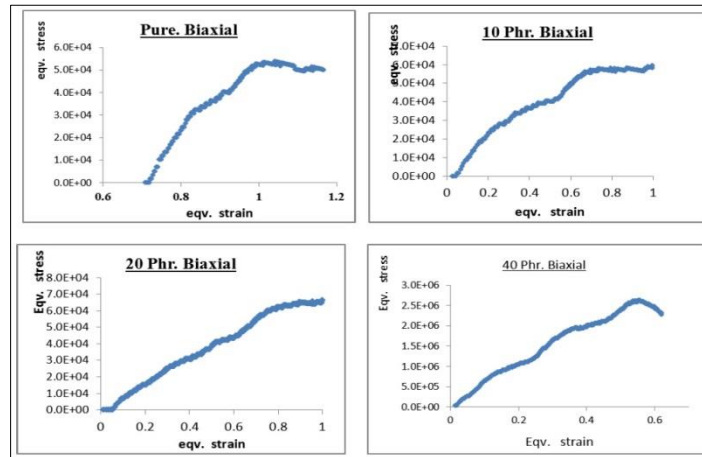


Fig. 4. Equivalent stress strain curve (biaxially) for pure NR loaded with 10, 20 and 40 phr of FEF Black.

The elastic modulus and the yield stress were calculated for each tested sample both in uniaxial and biaxial tests. The yield (first yield) stress was estimated by the intersection of two tangent lines [12,13]. The first line is the extension of the linear elastic part while the second is the tangent of the curve between first and second yield points. Results are tabulated in Tables 1 and 2.

Table 1. The elastic modulus and the yield stress (uniaxially).

Sample [uniaxial] [Phr]	1st yield	Elastic Modulus [Y, MPa] [uniaxial]
Pure	1.5×10^7	1.5
10	2.5×10^7	20
20	2.5×10^7	23
40	3.0×10^7	30
50	3.5×10^7	34.5
70	4.2×10^7	44.6
80	8×10^7	52
90	4×10^8	70

Table 2. The elastic modulus and yield stress (Biaxially).

Sample [Biaxial]	1st yield	2nd yield	Elastic Modulus [Pa] Biaxially
Pure	3.2×10^4	4.0×10^4	1.5×10^5
10 Phr	2.7×10^4	4.2×10^4	1.7×10^5
20 Phr	2.5×10^4	4.2×10^4	1.75×10^5
40 Phr	5.7×10^5	1.9×10^6	5.8×10^6

Following Kucherskii [14] method to find the knee – point strain, sample of unloaded NR and loaded with 10, 20 and 40 phr of FEF black were subjected to repeated measurements to study the effect of biaxial tests on the knee point strains. Fig. 5 shows $d\sigma/d\lambda$ versus λ (extension ratio) that we call knee Point Curve (Fig. 5a) typical fitting tensile biaxial – stress strain curve (sample 10 Phr FEF nanostructure carbon black as an example). Table 3 represents the

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values of the knee point in biaxial tests mode. It can be seen that knee point stains also decreases as filler content increases.

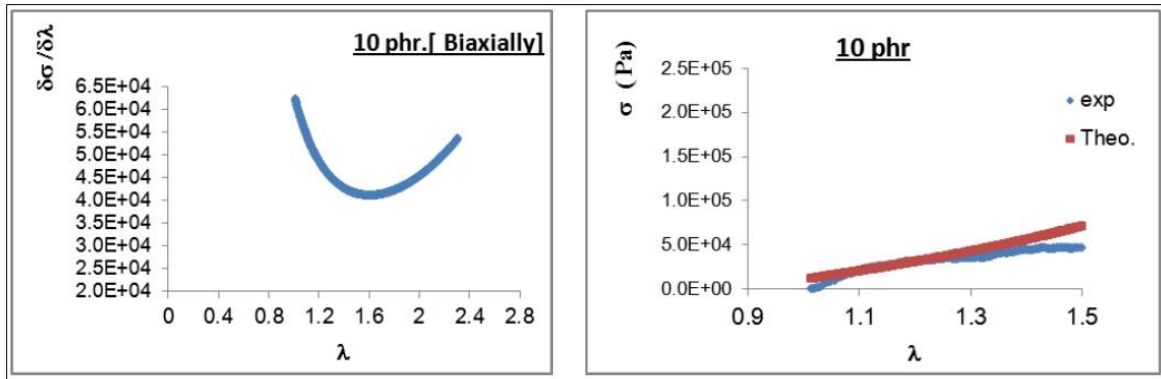


Fig. 5. (a) $(d\sigma/d\lambda)$ versus λ (extension ratio) and (b) Typical fitting tensile biaxial – stress strain curve.

Table 3. Represents the variation of the knee point values with biaxial extension.

Sample	Knee Point [Biaxially]
Pure	1.6
10 Phr	1.58
20 Phr	1.48

Effect of Uniaxial and Biaxial Stresses on the Electrical Conductivity of FEF / Natural Rubber Vulcanizates

There are two basic factors causing changes in structure as a result of strain, namely softening and molecular orientation:

i) Softening would occur by the virtue of two reasons. First, rupture of weak polymer filler bonds [15,16] which is manifested by a decrease in the elasticity modules [17] and, second hardness of the system [18,19] as the strain is increased . It is also judged by the fact that the polymer cannot attain equilibrium after the release of the strain, so that, it displays less resistance to repeated deformation. It is considered that, the second of these effects is not dependent on the presence if the filler [20,21]. ii) Molecular orientation develops vigorously upon stretching alongside softening and can be assisted by it [22]. The process is aided by the presence of an active filler [15,21] and in state of a complex stresses it is usually hindered. The variation of mechanical properties with time is generally an important problem [23]. It seemed interesting, therefore, to leave the specimen for a time interval (24 hours) under each specified value of uniaxial and biaxial extension. There was a noticeable current creep during this duration which was associated with the processes of regrouping of macromolecules within aggregates. Such process had to take place until equilibrium was established. When the current through the sample reached constant value, the effect of uniaxial and biaxial extension on the electrical conductivity of FEF / natural rubber samples were studied using just two samples in close contact to the percolation threshold (50 and 70 Phr of FEF loaded/ natural rubber composites). Fig. 5. represent the dependence of the σ_{dc} on the uniaxial and biaxial extension, for 50 and 70 Phr FEF loaded / natural rubber samples respectively. The σ_{dc} detected in uniaxial extension is measured in the direction of uni-extension (longitudinal conductivity), meanwhile σ_{dc} was detected in a direction perpendicular to the biaxial extension (transverse direction).

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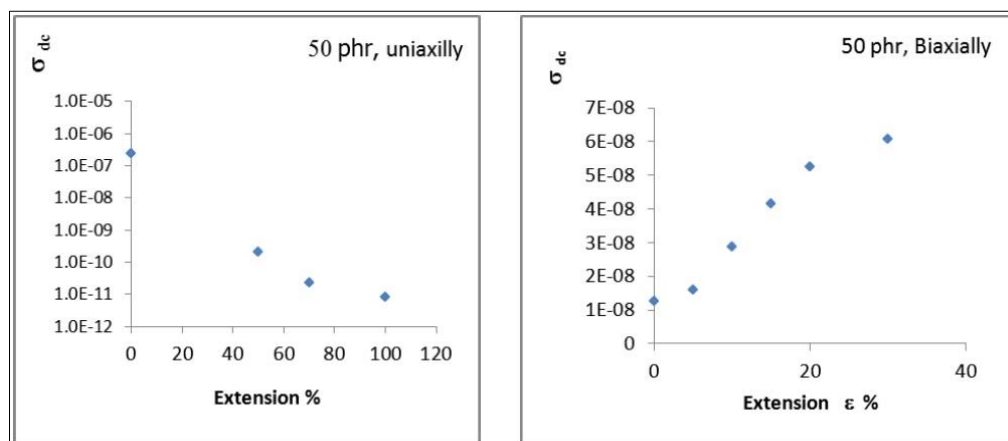


Fig. 6. (a) Sample of 50 Phr for uniaxial test. (b) Sample of 70 Phr for biaxial test.

It is obvious from Fig. 6 that σ_{dc} long decrease appreciably (for the two samples) with uniaxial extension, since carbon particles are force into spread from each other by extension after reaching a certain uni-axial extension value depending on the carbon black concentration (50% and 70% for samples loaded with 50 and 70 phr respectively), the change in σ_{dc} long. begins to increase. The bi-axial extension elucidate a reverse behavior of the σ_{dc} trans. on the value of the biaxial extension which suggests that upon biaxial extension carbon particles are forced into closer contact by the applied biaxial extension in the transverse which causes σ_{dc} trans. to increase.

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