Effect of $BaTiO_3$ on the Mechanical Properties of Nitrile-Butadiene Rubber (NBR) Vulcanizates.

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The effect of $BaTio_3$ content on the elastic behaviour of Nitrrile-Butadiene Rubber (NBR) vulcanizates loaded with 65 phr of Super Reinforced Furnace (SRF) black has been studied by carrying out equilibrium stress-strain measurements at 300K. Young's modulus (E) and the number of effective chains per unit volume (ν) as a function of $BaTiO_3$ content were calculated. A small increase at low contents was detected followed with a large decrease at high concentrations. The average molecular weight (M_e) was found to have an opposite behaviour of (ν). The maximum change in entropy (ΔS_{max}) and the work done (W) on rubber chains during extension were found to decrease slightly at low loading followed with a high increase at high $BaTiO_3$ loadings. Stress-strain cycling was also carried out and hysteresis was found. The energy density loss and the remnant strain after each cycle were also studied.

1. Introduction:

Fillers and their effect on the mechanical properties of elastomers are of great interest and they can be used very efficiently to enhance the physical properties. The mechanical properties of elastomers filled with fillers are influenced by factors such as type and volume fraction of filler as well as processing conditions [1]. The elastic behaviour of vulcanized rubber may be taken as a quantitative basis for understanding the effect of fillers on stiffness and strength [2]. The following theoretical expression relating the elastic modulus "E" of the filled rubber to the modulus "E_o" of the matrix has been suggested [3] as:

$$E = E_o (1 + 0.67 \, f \, C + 1.62 \, f^2 C^2) \qquad (1)$$

where "C" is the volume fraction of filler and "f" is a factor describing the asymmetric nature of the aggregated clusters that is expressed by the ratio of their length to width.

The change in entropy "ΔS" of the chains in a rubber matrix when deformed under tension is [4]

$$\Delta S = -\frac{1}{2} k \, \nu \, V \, (\lambda^2 + \frac{2}{\lambda} - 3) \tag{2}$$

where "k" is Boltzmann's constant, "ν" is the number of effective plastic chains per unit volume, "V" is the volume of the matrix and "λ" is the extension ratio = L/L_o, (L_o and L are the lengths before and after extension). The work done on the rubber is [4]

$$W = -\frac{1}{2} k \, T \, \nu \, V \, (\lambda^2 + \frac{2}{\lambda} - 3) \tag{3}$$

with T is the absolute temperature. Moreover, since $W = -\int F \, dL$, one can get the relation of the classical theory [5-6] of rubber elasticity as:

$$F = A\nu kT(\lambda^2 - \lambda^{-1}) \tag{4}$$

where "F" is the force acting and "A" is the area which depends on the considered model.

In a real rubber, there is local interaction between segments [7-9], and this may give rise to another contribution to the stress, which is neglected by the kinetic theory. The continuum mechanics of an incompressible elastic body leads to the well known expression for stress (σ) in case of simple extension [10,11].

$$\sigma = 2(C_1 + \frac{C_2}{\lambda}) \, (\lambda - \lambda^{-2}) \tag{5}$$

where C_1 and C_2 are constants. Many studies have been conducted to investigate Eqn. (5) [12-17].

On the other hand, stress-strain cycling of real rubbers is accompanied by hysteresis. It was thought that, the study of hysteresis measurements of composites would be interesting in order to know their behaviour in service [18]. Hysteresis is a measure of energy density dissipated by a material during cyclic deformation. Fillers are known to cause an increase in hysteresis loss in rubbers, and hysteresis measurements can be used to estimate the reinforcing ability of fillers [18]. Hysteresis arises due to the wetting between the filler particles and the matrix [18, 19].

As a continuation of a previous work [17], the present one deals with the effect of adding $BaTiO_3$ powder on the elastic behaviour of Nitrrile-Butadiene Rubber (NBR) vulcanizates loaded with 65 phr of SRF carbon black. This was done by applying the Zang et al relation [15]. Moreover, the effect of $BaTiO_3$ on the hysteresis loss has also been elucidated.

2. Experimental:

A master patch of Nitrile-Butadiene Rubber (NBR) loaded with 65 phr (parts per hundred parts of rubber by weight) of Super-Reinforcement Furnace (SRF) carbon black was prepared. Different concentrations of $BaTiO_3$ powder were then added. All samples were prepared according to the recipes presented in Table (1).

Table(1): Mix formation of 65SRF/NBR composites loaded with different concentrations of $BaTiO_3$.

Ingredients	Quantity (phr)
NBR	100
SRF	65
Processing oil	10
Stearic acid	2
MBTS[a]	2
PBN[b]	1
Zinc Oxide	2
Sulfur	2
$BaTiO_3$	0,10,20,30,40,60 and 80

[a] Dibenthiazole disulphide.
[b] Poly 2,2,4, Trimethyl-1,2 Dihydroguinoline.

All rubber mixtures were prepared on a two-roll mill 170 mm in diameter, with a working distance of 300 mm. The speed of the slow roll was 24 revolutions per minute and the gear ratio is 1.4. Vulcanization of all samples was conducted at 152 $\pm$ 2 ^{o}C under a pressure of 40 kg/cm^2 for 20 minutes. The stress-strain measurements were carried out at 300 K using a locally manufactured tester [16]. The tensile strain was measured with a strain gauge (sensitivity 10^{-3} cm) after 5 minutes each application of load.

3. Results and Discussions:

3.1. Stress-Strain Behaviour

Stress-strain curves obtained for 65 SRF/NBR vulcanizates loaded with different concentrations of $BaTiO_3$ are shown in Fig. (1). The curves show a linear portion from the origin up to strains of about 10%. At higher strains the curves show the segmoid shape characteristic of rubber like materials. The linear portions at low extensions are used to determine Young's modulus "E" of the studied vulcanizates and is plotted in Fig. (2) as a function of the concentration of $BaTiO_3$. The Figure shows a maximum value of Young's modulus at 20 phr of $BaTiO_3$.

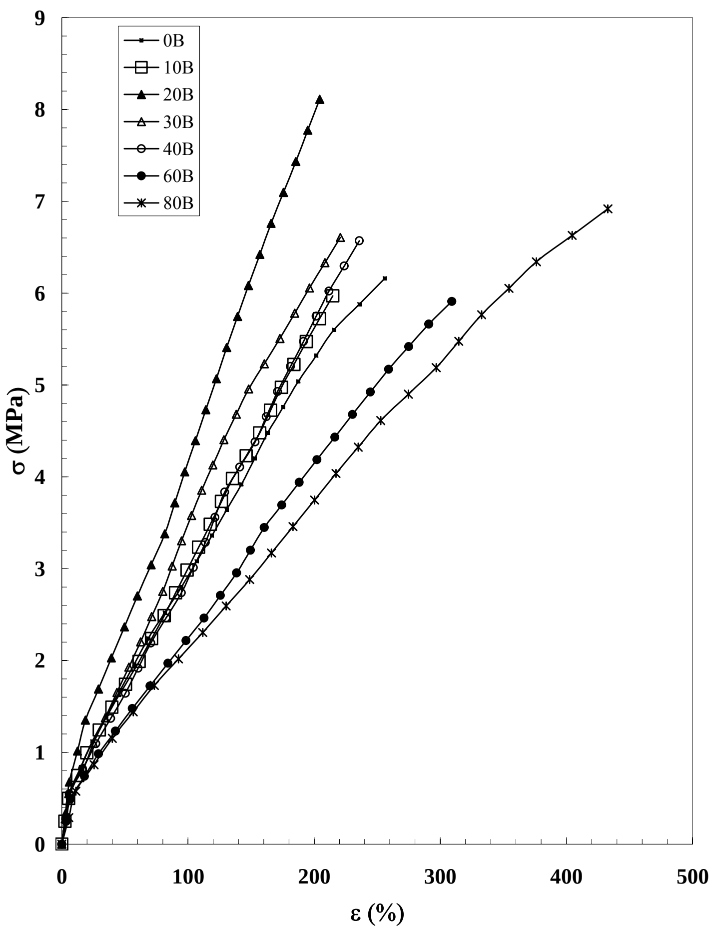

Fig. (1): The stress-strain curves for 65 SRF/NBR vulcanizates loaded with different concentrations of $BaTiO_3$.

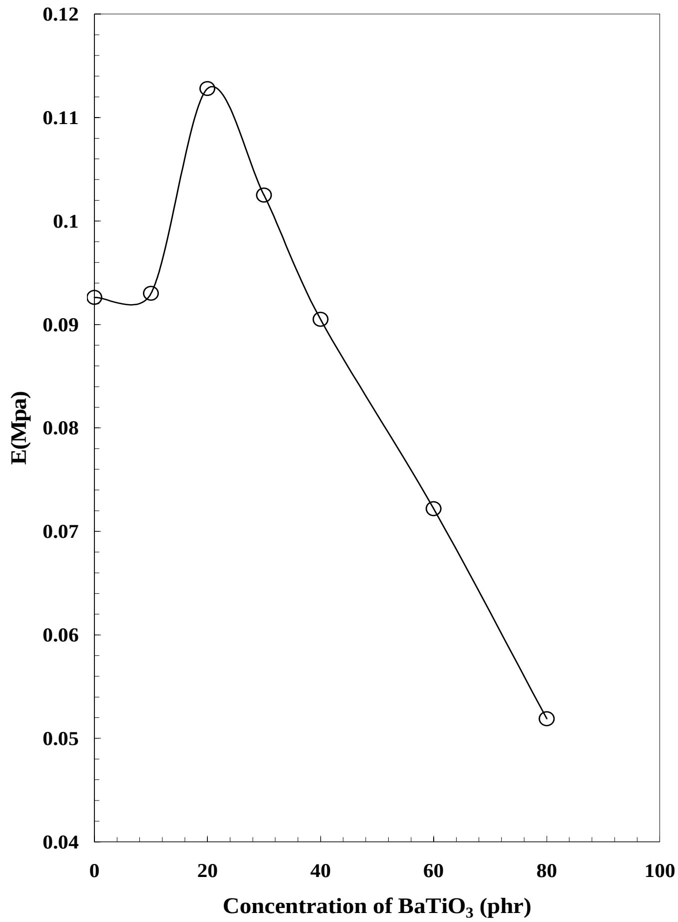

Fig. (2): The dependence of Young's modulus on the concentration of $BaTiO_3$.

3.2. Entropy and Work done

The data in Fig. (1) was re-plotted again between "σ" and ($\lambda^2 - \lambda^{-1}$) as shown in Fig. (3). One gets a group of straight lines according to the equation [16].

$$\sigma = \sigma o + G\,(\lambda^2 - \lambda^{-1}) \quad (6)$$

with slope "G" and intersection "σ_o" at $\lambda^2 - \lambda^{-1} = 0$. The value of "$\sigma_o$" is 1.18 Mpa and it depends only on the chemical nature of the gum rubber matrix [14,17]. The values of "G" that depend on the degree of crosslinking [14,17] are listed in Table (2) and were found to have a maximum for samples containing 20 phr of $BaTiO_3$.

The average molecular weight "M_e" between crosslinks and the number of effective plastic chains per unit volume "ν" have been calculated from the values of "G" according to [14,17].

$$G = A\nu kT = \frac{A\rho RT}{M_e} \tag{7}$$

where "ρ" is the density of the rubber matrix and "R" is the universal gas constant. The calculated values of both "M_e" and "ν" are listed in Table(2); the maximum value of "ν" and the minimum value of "M_e" take place at a concentration of 20 phr of $BaTiO_3$.

Table (2): The calculated values of "G", "M_e" and "ν" for all vulcanizates.

phr of $BaTiO_3$	G (MPa)	M_e x10^5	ν (x10^{20}cm^{-3})
0	0.48	4.97	1.17
10	0.46	5.29	1.10
20	0.84	2.85	2.04
30	0.63	3.79	1.53
40	0.53	4.55	1.28
60	0.33	7.28	0.80
80	0.29	8.41	0.69

The calculated values of "ν" are used in Eqns. (2) and (3) to get the change in entropy "ΔS" and the work done "W". Fig. (4) illustrates the dependence of the change in entropy on strain for all samples. The Figure shows an increase in "ΔS" as the strain increases for all composites. This may show high disorder in the matrix at small strains and the matrix becomes less disordered at high strains. Fig. (5) shows the variation of the maximum change in entropy "ΔS_{max}" and the work done on rubber chains during extension as a function of the $BaTiO_3$ content. The figure records maximum change in entropy for 80 phr $BaTiO_3$ content and minimum for 10 and 20 phr and this means that addition of these loadings of $BaTiO_3$ makes the matrix more ordered than other higher concentrations.

From the last discussions it is apparent that addition of 20 phr of $BaTiO_3$ may make additional physical bonds leading to the noticeable increase in the values of "E" and "ν".

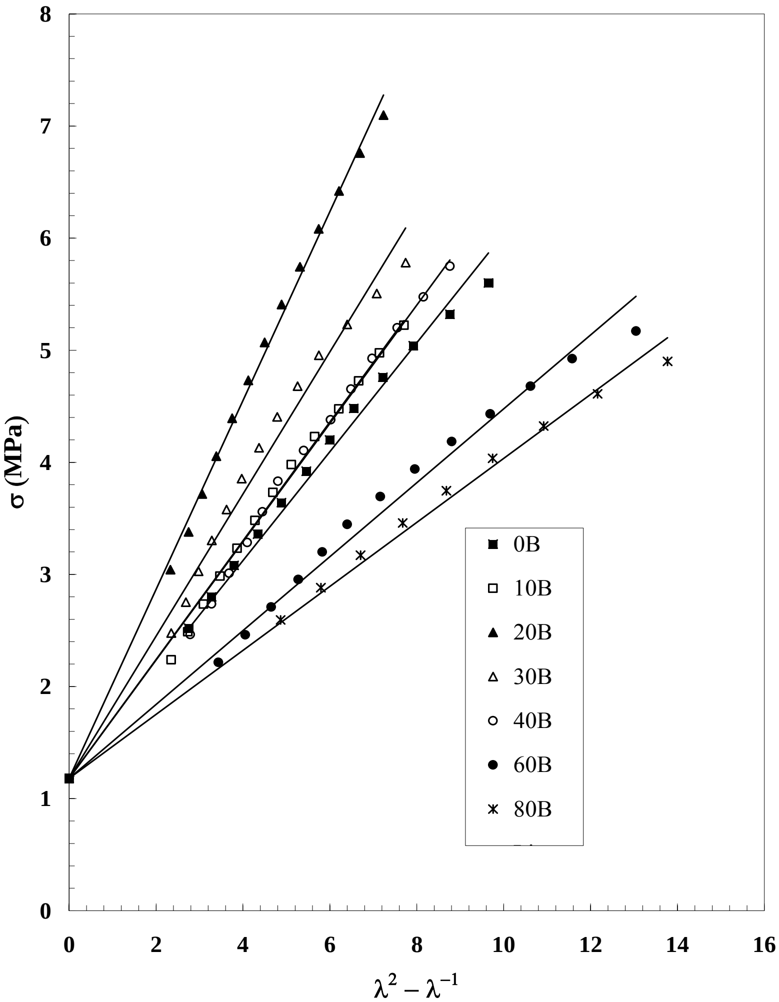

Fig. (3): The dependence of the true stress on ($\lambda^2 - \lambda^{-1}$) for all vulcanizates.

3.3. Hysteresis Loss

Some of the sources for supplying energy to a sample are; (1) stored strain energy and (2) energy supplied directly by the testing machine [20]. In turn, the energy that is supplied can be expended in three ways [20]; (1) by breaking of bonds that were present by force crack propagation, (2) via hysteresis loss due to irreversible deformation process and (3) by straining material that became newly deformed as a result of crack propagation.

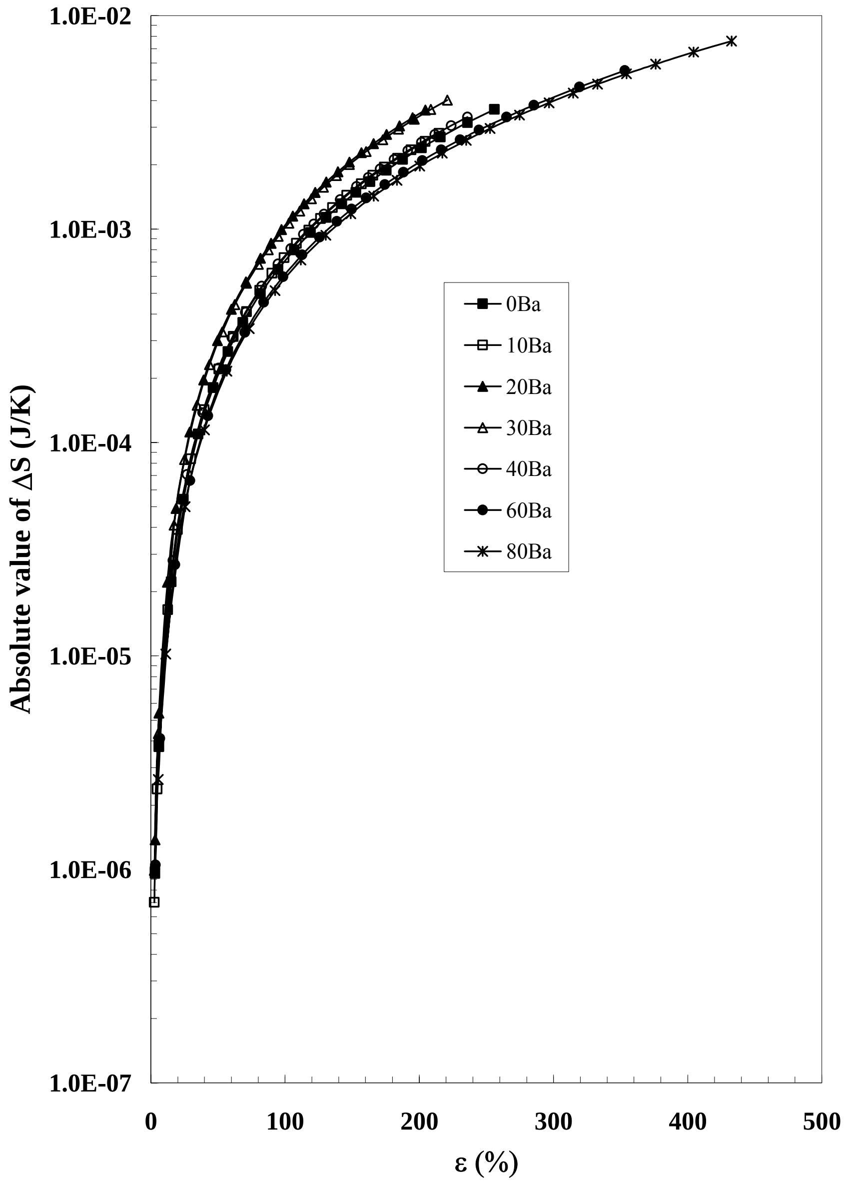

Fig. (4): The dependence of the absolute change in entropy on the strain for all composites.

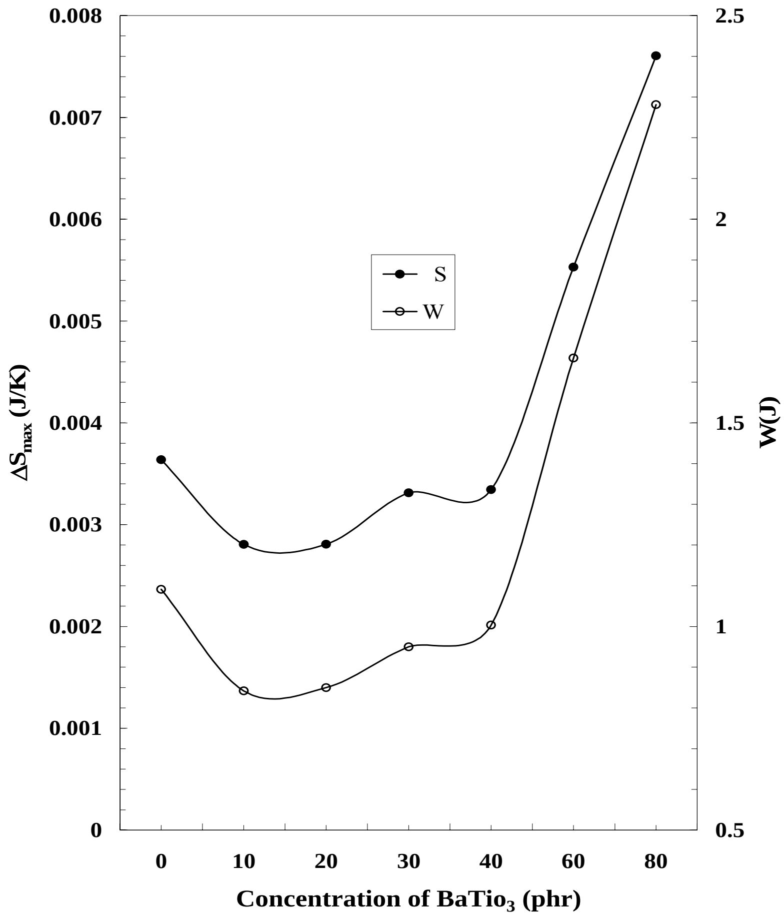

Fig. (5): The dependence of both maximum absolute change in entropy and work done on the concentration of $BaTiO_3$.

Figure (6) shows the stress-strain hysteresis for 65SRF/NBR loaded with different concentrations of $BaTiO_3$. The energy density lost for each cycle (calculated from the area enclosed by the loop) for the different concentrations of $BaTiO_3$ is shown in Fig. (7-a). It is noticed that the addition of $BaTiO_3$ to the vulcanizates increased the energy density lost beyond a concentration of 40phr. At multiple cycles, the energy density loss decreased and became reasonably constant from the third cycle. This is because the rubber segments which were partially strained by the previous deformation were stretched again [18]. Fig. (7-b) shows the remnant strain after each cycle for all composites. It is noticed that samples containing high concentrations of $BaTiO_3$ have high remnant strain as well as energy density loss. Figures (6) and (7) show also that samples containing 10 to 40 phr of $BaTiO_3$ have the smallest remnant strain, low energy density loss and the highest stress needed to produce small strain among the four cycles. This may be due to the formation of additional physical bonds for such content as discussed in the last section.

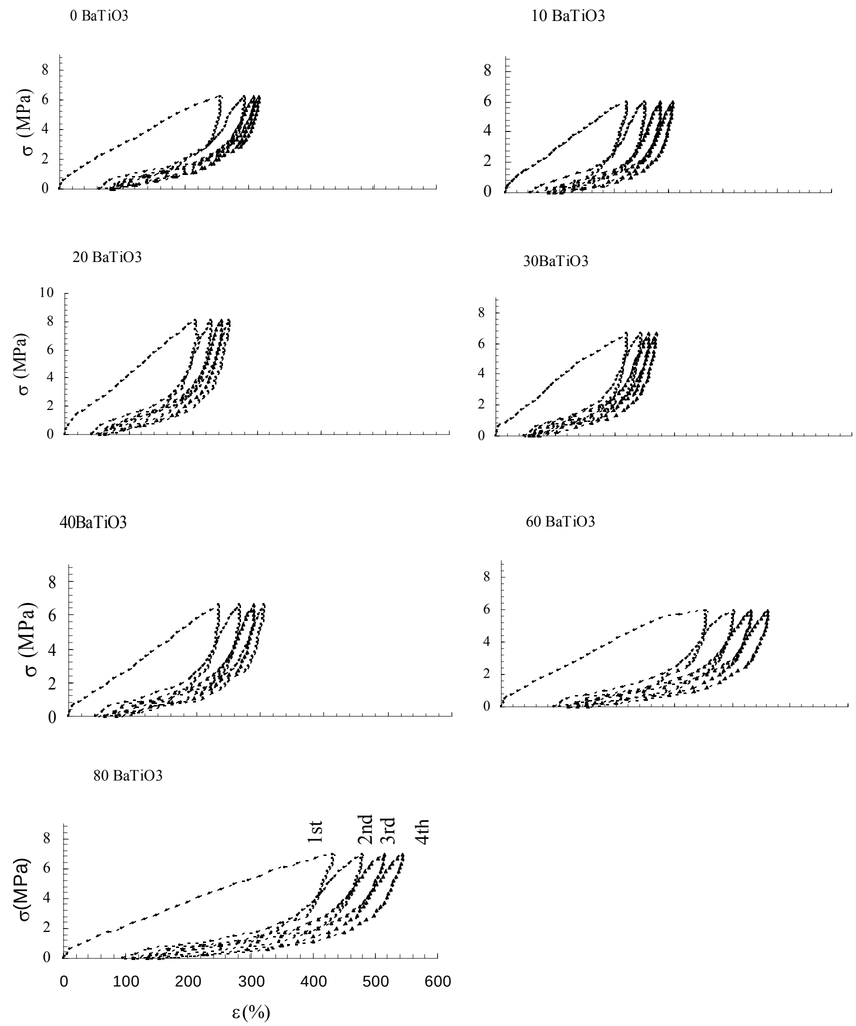

Fig. (6): Hysteresis plots for all composites.

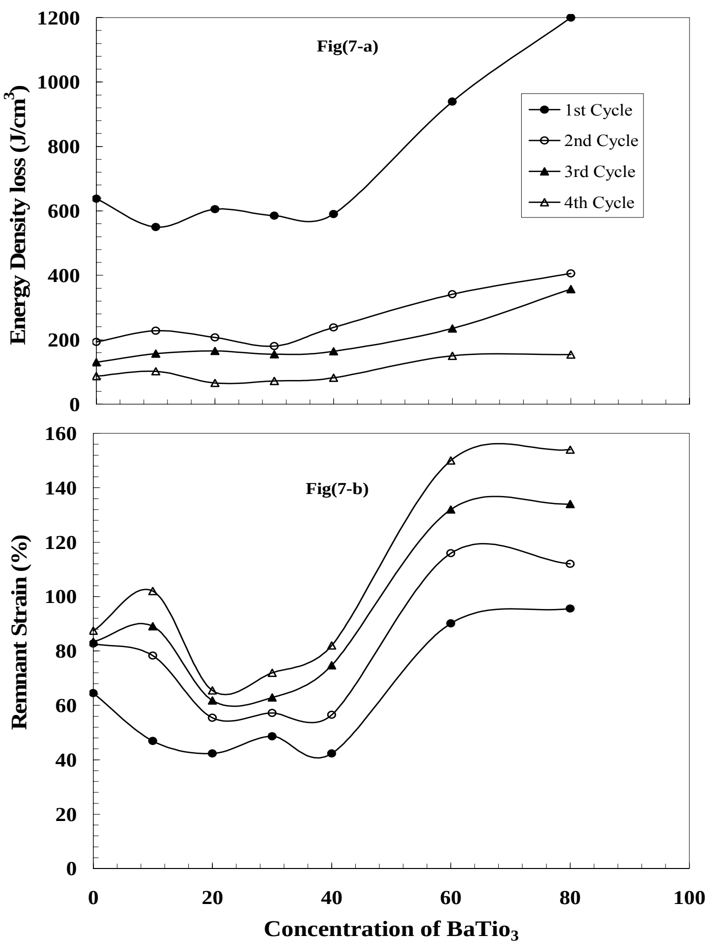

Fig. (7): The dependence of both energy density loss [Fig.(7-a)] and remnant strain [Fig.(7-b)] on the concentration of $BaTiO_3$ for different stress-strain cycles.

4. Conclusion:

Addition of barium titanate ceramic powder has clear effects on the mechanical behavior of rubber vulcanizates. A relatively small percentage of Barium titanate (~ 20phr) results in an increase in Young's modulus and the number of effective chains per unit volume while it decreases the average molecular weight between crosslinks. It also results in a minimum value of remnant strain.

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