

Static Deformation of Low Structure HAF Black-Loaded (SBR+NR) Rubber Blend

A.M.Y. El-Lawindy

Department of Physics, Faculty of Science, Suez Canal University. Ismailia, Egypt

The stress-strain behavior of different concentrations of low-structure high abrasion furnace black (HAF-LS)- loaded rubber blend of styrene butadiene rubber and natural rubber (SBR+NR) of equal parts was measured. Moduli of elasticity and the n- measure of such blends were calculated using different approaches. An anomaly, of modulus of elasticity, found at 50 phr may be attributed either to what is called compact structure and/or to the early crystallization of natural rubber (NR) in the blend. These assumptions are confirmed through the measurement of the swelling factor as a function of time of swelling in kerosene.

Introduction:

It is known that NR crystallizes under stretching, so that it resists deformation and enhances its strength while SBR does not crystallize. Mixtures of NR and SBR are quite often used in order to get desired technological properties.

Our previous work [1] used the equation for the true stress- true strain at simple tension suggested in the Blatz et al. [2],

$$\bar{\sigma} = \frac{2G_0}{n} (\lambda^n - \lambda^{-n/2}) \quad (1)$$

where σ is the true stress and G is the shear modulus at the origin, $\lambda = 1$, and λ is the extension ratio, to ascertain experimental data of different rubber affected by different types of carbon black. It was found that, the n measure was always a material constant of the host rubber. The values for SBR and NR were 3.5 ± 0.4 and 2.3 ± 0.2 , respectively and the modulus of elasticity, at simple tension, was found non-linear as a function of carbon black concentration.

In the present work, HAF-LS, of different concentration, was compounded with a blend of equal parts of SBR and NR, with the aim of studying the behavior of the n - measure and the elasticity modulus of such new composite.

On the other hand, the swelling in kerosene, as a function of time, test was performed on all samples to elucidate the internal structure of the new composites. One useful parameter such as, the swelling factor was calculated and used to assist in the explanation of the stress-strain data.

Experimental Technique:

The samples investigated in this study, were mixtures of equal parts of NR and SBR-1502 as a host rubber compounded with different concentrations of I-IAF-LS ($85 \text{ m}^2/\text{g}$ surface area and 255 \AA particle diameter), according to the recipe shown in Table 1.

Table 1: The recipe of the samples used.

Ingredient	Quantity (phr)	Sample name									
		L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
NR	50										
SBR-1502	0										
Zinc Oxide	5										
Stearic acid	12										
HAF-LS	Variable										
Processing oil	10	10	20	30	40	50	60	70	80	90	100
MBTS	2										
PBN	1										
Sulfur	2										

(phr is part per hundred parts of rubber by weight, MBTS is Dibenzthiazyl disulphide, and PBN is Phenyl- a possible carcinogenic compound.)

Ingredients of the rubber blend were mixed on a 2-roll laboratory mill of 170-mm diameter, 300-mm length, the speed of slow roll being 18 rpm and gear ratio 1.4. The ingredients were added in the order as shown in Table 1. The compounded rubber was left for 24 hours before vulcanization. The vulcanization process was performed at 143°C under a pressure of 4 Kg/cm² for 30 minutes. To insure reproducibility, the samples were conditioned at 7°C for 50 days [3].

The test samples were strips of 2 cm working length and of ~4mm² cross-sectional area.

Stress-strain measurements were performed using a tensile test machine (AMETEK, USA). A digital force gauge (Hunter Spring ACCU Force II, 0.01 N resolution, USA) connected to a microprocessor was used to measure extension force. A home made motor attachment was used to control the strain rate through a gearbox. The strain rate was preset using a variable DC power supply, and was measured using a micro-switch attached to the apparatus wheel. The accuracy of strain measurement was about 0.1 mm. The strain rate throughout the experiment was fixed at 1 mm/sec.

Results and Discussion:

Figure 1 shows the stress-strain behavior of rubber blends. In Table 2 the obtained mechanical parameters which are modulus of elasticity Y (N/m²) true stress at break, σ_b (N/m²) and strain at break, C_b , are listed. Y (N/m²) was calculated as the slope of true stress-extension ratio curves up to $\lambda = 2$.

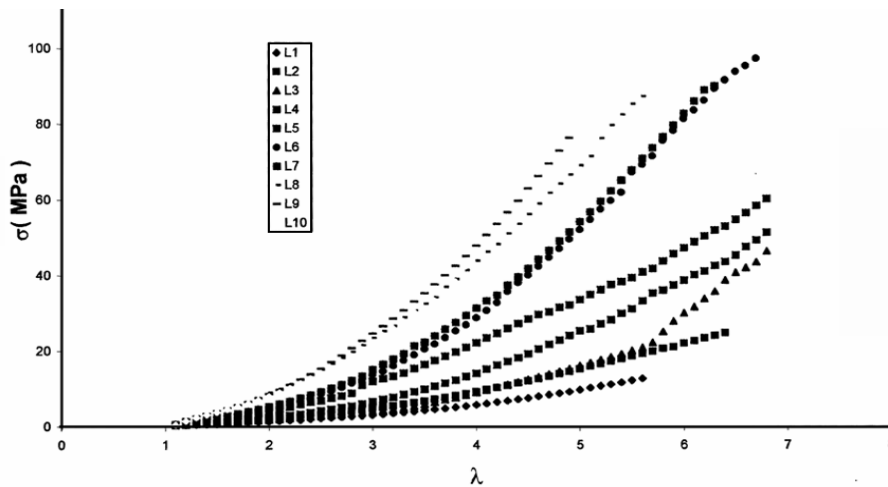


Fig. (1): The true stress-true strain behavior for all samples.

Table (2): A list of resulted mechanical parameters obtained from true stress-strain characteristics (Figure 1).

Sample	Y (MPa)	σ_b (MPa)	ϵ_b
L1	1.17	21.6	6.1
L2	1.57	29.4	6.1
L3	1.55	3.7	6.2
L4	2.29	62.0	6.3
L5	3.94	76.0	6.6
L6	4.05	95.4	5.6
L7	4.98	90.1	5/3
L8	8.85	87.3	4.6
L9	8.08	88.3	4.1
L10	7.98	54.4	3.3

The stress-strain, equation 1, is approximated by Malkin et al. [4], to

$$\log \frac{2\sigma}{3E_0} = n \log \lambda - \log n, \quad (2)$$

where E_0 is the initial value of the elastic modulus in un-axial tension, and suggested a graphical method for the determination of the constants n and E by constructing a plot of $\log \sigma$ versus $\log \lambda$, (Figure 2). These data, were fitted using linear least square method. The correlation coefficients, R^2 were found not less than 0.9. The n -measure was obtained from the slopes, whereas E was obtained from the intercept of the fitted curves.

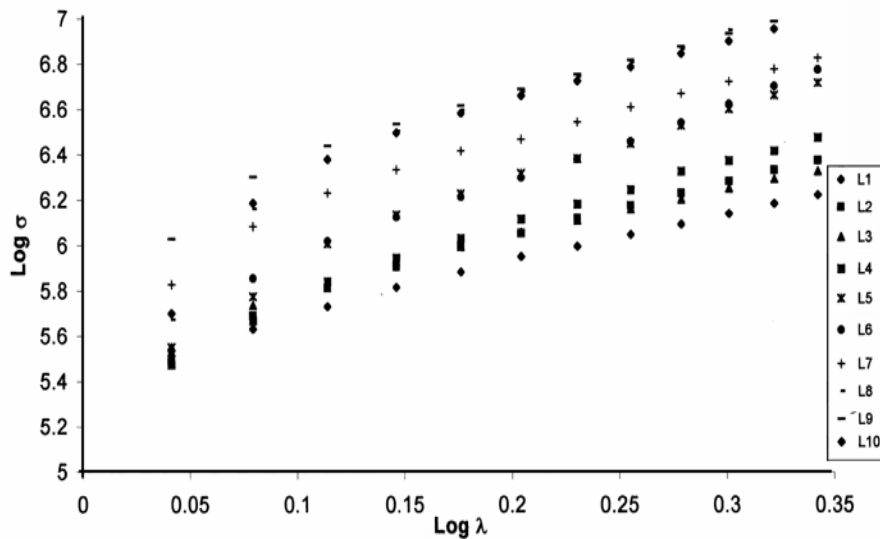


Fig. 2: The behavior of Log versus log λ .

An average value of $n = 2.54 \pm 0.21$, was obtained. Considering that the blend contains the same parts from both types of rubber, it is interesting to note that this n value approximately equals the average value of both individual $NR = 2.30 \pm 0.23$ and $SBR = 3.50 \pm 0.35$ rubber respectively [1]. This result raises a question about the value of n if blending rubber of different concentration is considered.

On the other hand, the rubbery modulus has been calculated from different approaches of stress-strain data at simple tension, $\lambda = 2$.

According to kinetic theory [5-7] of rubber elasticity, the stress-strain takes the form

$$\bar{\sigma} = G_1 (\lambda^2 - \lambda^{-1}) \quad (3)$$

where G_1 represents the rubbery modulus and $\bar{\sigma}$ represents the true stress. Zang et al. [8] used an equation of the form;

$$\bar{\sigma} = \sigma_0 + G_2 (\lambda^2 - \lambda^{-1}) \quad (4)$$

where σ_0 was found to depend only on the chemical nature of rubber and may be ascribed to local interaction of the segments of rubber. G_2 was found to depend only on the degree of cross-linking and seems to represent the rubbery modulus of the kinetic theory

Figure 3 shows the relation between true stress, σ (N/m^2) and $(\lambda^2 - \lambda^{-1})$, up to $\lambda = 2$. The parameter G_1 was obtained from linear least squares fitting at intercept equals zero, equation 3, whereas G_2 was obtained at intercept equals to σ_0 , equation 4. The values of σ_0 were found negative except at 100 phr loading. The fitting correlation coefficient, R of the linear least squares fitting, for both equations, were rarely less than 0.98. Figure 4 shows the behavior of $G = Y/3$, $G_0 = E_0/3$. G_1 and G_2 as a function of black concentration. It is seen that their behavior with concentration is similar in the four cases. Also, one may consider that G_1 and G_2 represent shear modulus in the simple kinetic theory, equation 3.

The anomaly at 50 phr HAF-LS concentration may be attributed either to the formation of what is called compact structure of carbon black at 50 phr or to an early crystallization of NR rubber inside the composites. Since NR tends to crystallize at small extension, one may expect an increase in the modulus of elasticity. As the concentration increases, the interaction between rubber chains atoms and surrounding medium increase. Rotational angle motion may then be suppressed during deformation and large amounts of energy are stored in backbone angles and bond length deformation. At higher concentration, the effect of reinforcement of SBR may predominate up to certain concentration, 90

phr of HAF-LS. Above such concentration, the sample starts to become tougher. This decrease of G with increasing carbon concentration above 90 phr may be attributed to the weak interaction between carbon particles upon the formation of carbon agglomerates.

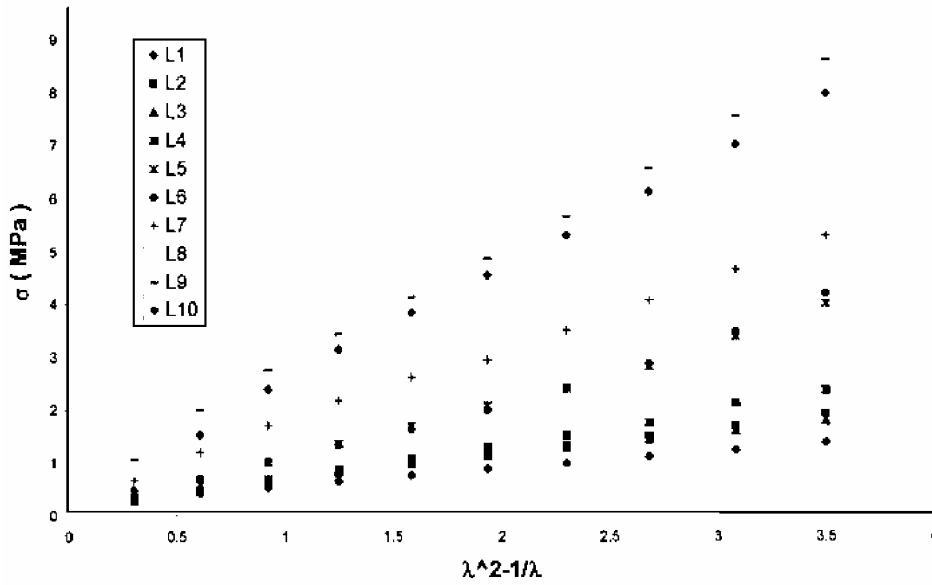


Fig. (3): The relation between true stress, (N/m^2) and $(\lambda^2 - \lambda^{-1})$ up to $\lambda = 2$

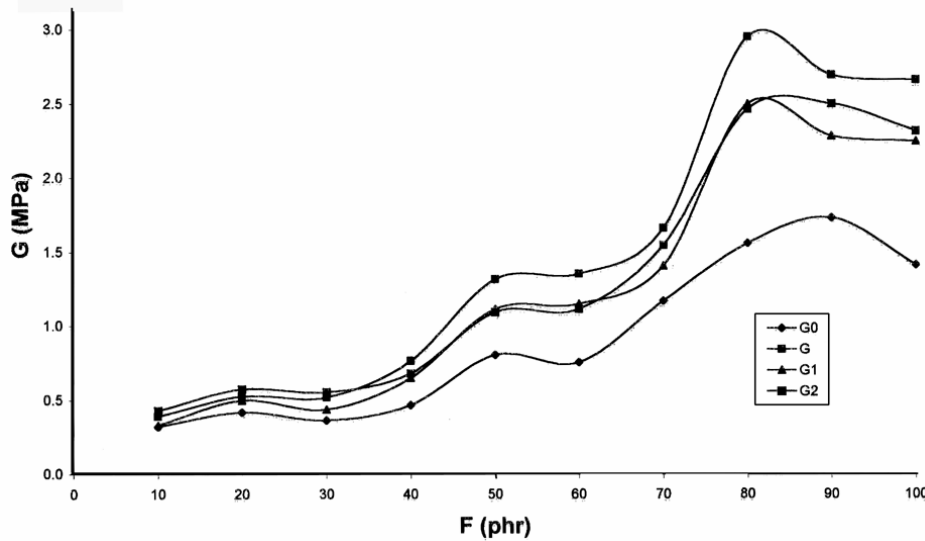


Fig. (4): The behavior of the modulus of elasticity, G , G_0 , G_1 and G_2 , as functions of carbon black concentration.

To confirm these assumptions, swelling in kerosene as a function of time was performed. In this experiment, the swelling factor, $Q(t)\%$ was obtained as a function of time, (Figure 5).

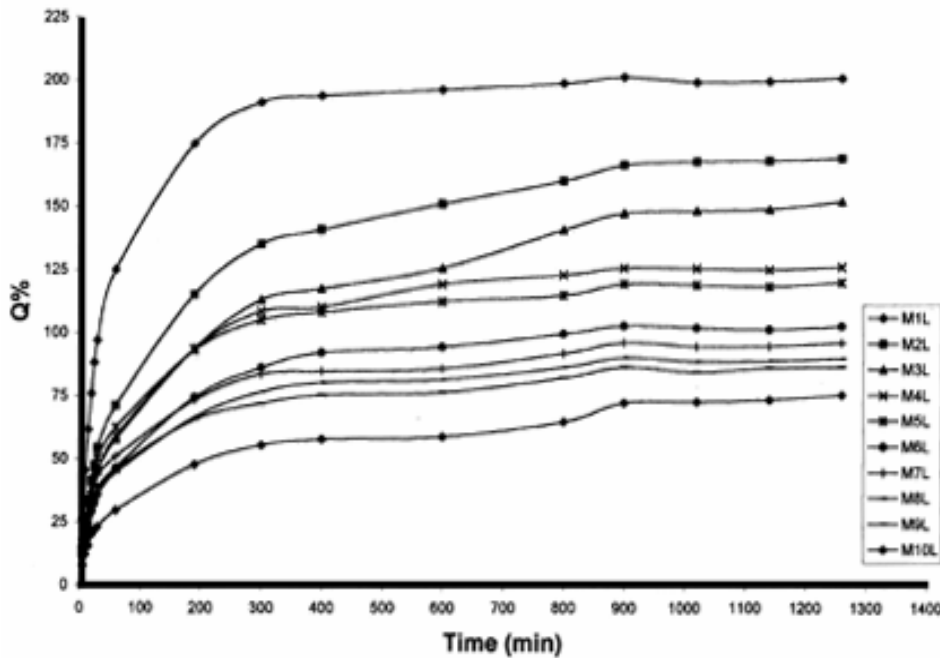


Fig. (5): The swelling factor, $Q(t)\%$, as a function of swelling time $t(\text{min})$ in kerosene.

It is known that carbon black does not dissolve in kerosene, and the host rubber may swell in kerosene. This means that the distance between carbon aggregates may be changed during swelling. Figure 6, represents the change in the average values of maximum swelling factor, $Q_m\%$, as a function of carbon blacks concentration. One can observe that the $Q_m\%$, in general, decreases by increasing carbon black concentration, denoting an open aggregate carbon structure, which has a high bulk. But at 50-phr concentration Q is slightly different from that at 40 phr, which means that there is a slight change in the distance between carbon black particle [9]. This may indicate clustered aggregates, which are more compacts and/or increased interactions inside the rubber composite. Also, the modulus of elasticity of samples containing 50 phr and 60 phr are nearly the same, (Table 2), whereas the value of the sample containing 40 phr is lower than their value,. This may explain the anomaly, at 50-phr carbon black concentration, observed in Figure 4.

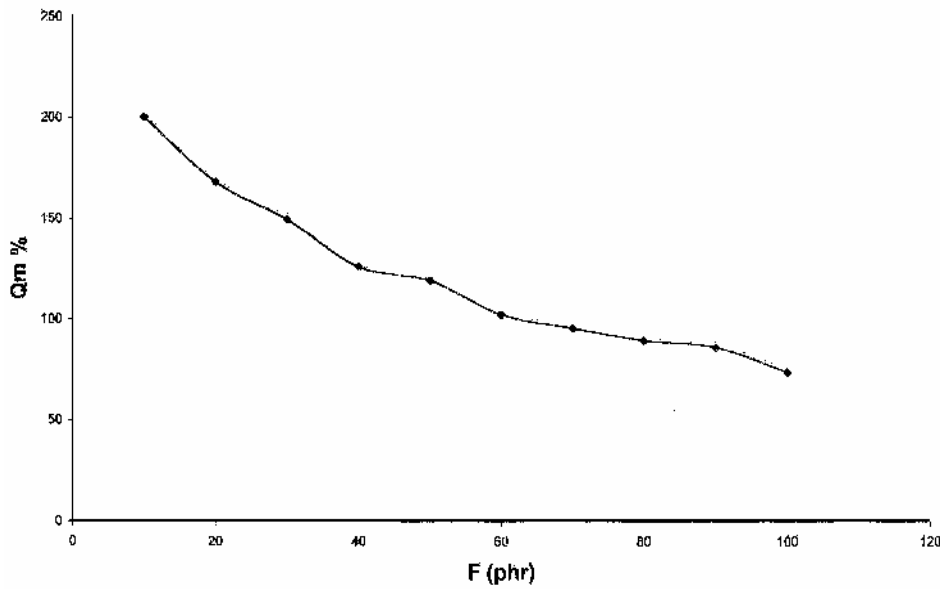


Fig. (6): The behavior of the average value of the maximum swelling factor $Q_m\%$ as a function of carbon black concentration, $F(\text{phr})$

This behavior was observed [1] for fast extruding furnace black FEF/SBR composite, which are loaded with different concentrations of FEF carbon black.

The anomaly at 80 phr concentration is attributed to the sample brittleness at such high filler concentration.

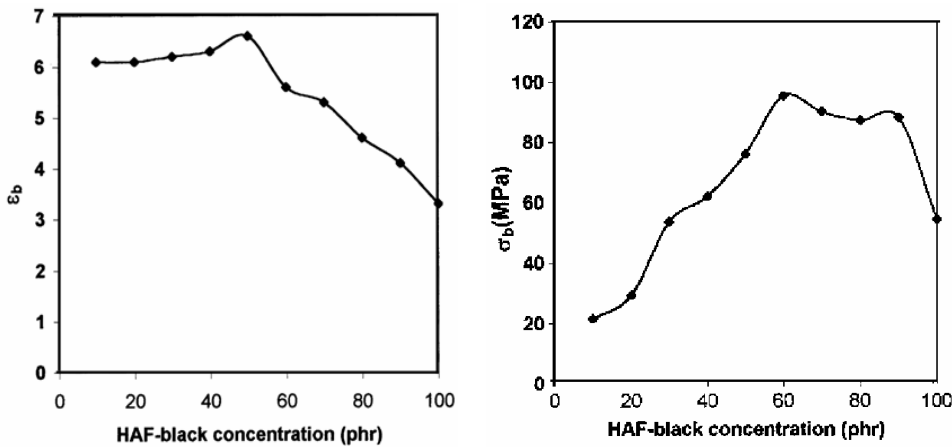


Fig. (7): The behavior of the true stress at break, σ_b (N/m^2) and strain at break, ϵ_b , as functions of carbon black concentration

The mechanical parameters, σ_f and ϵ_b are shown in Fig. 7. This figure shows an optimum strength at 60 phr of HAF-LS carbon black, after which a decrease is obtained. This behaviour may be attributed to a percolation concentration for such carbon black in the blend and/or to the crystallinity under stretching of NR in the blend. Above this concentration, the dilution effect of carbon black may take place. This may explain the gradual decrease of ϵ_b .

Conclusion:

One may conclude that the n-measure is still a material parameter, even the host rubber is a mixture of two types of rubber. The n-measure was found to have the average value for that of SBR and NR individually. Future work should endeavour to find out the value of n at different concentration of both types of rubber in the blend.

The anomaly of modulus of elasticity at 50-phr HAF-LS carbon black concentration is attributed to a compact structure and/or early crystallization of NR rubber inside the matrix at such concentration. This conclusion was confirmed through the measurement of the swelling factor as a function of time.

References:

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