Effect of pre-extension on the Electrical Conductivity of Styrene Butadiene Rubber loaded with HAF and GPF Carbon Black.

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Abstract :

The effect of pre-extension on the electrical conductivity of the HAF / SBR and GPF/SBR composites with carbon black concentrations of 50, 75 and 100 phr (part per hundred parts of rubber by weight) have been studied. The mechanisms controlling the electrical conduction in the unextended and pre-extended sample have been found to be hopping , tunneling and ohmic conduction mechanisms, respectively.

The X-ray integral intensity of the halo (I) increases with increasing the extension ratio. Moreover, the peak of the integral intensity (I) is grown and shifted towards larger scattering angles with increasing the extension ratio. These observations indicate that the polymeric chain segments under extension are stretched and oriented in the direction of extension and more packed side by side.

A decrease in the X-ray intensity at high carbon concentrations is thought to be due to a decrease in the dispersion of carbon black as a result of overlapping process of carbon aggregates to form large agglomerates.

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INTRODUCTION

The wide usage of rubber material is largely due to their valuable mechanical , electrical properties and especially to their high strength . The contribution of the addition of carbon black filler to the Styrene-Butadiene rubber (SBR) changes the structural and electrical properties.

The electrical and structural problems arising from the interaction of elastomer SBR with different types of carbon black filler has been studied to reveal some aspects to the wide usage of the rubber at various temperatures.

The behaviour of the amorphous chain segments in the volcanized HAF / SBR and GPF /SBR and extension is studied by a wide angle X-ray scattering (WAXS)

EXPERIMENTAL TECHNIQUE

Styrene-Butadiene rubber with 50,75,and 100(phr) of high abrasion furnace (HAF) and general purpose furnace (GPF) carbon black was prepared according to the recipe mentioned in (Table (1)) .

The test samples were shaped during volcanization process into sheets of 2.5 cm long, 0.3 cm wide and 0.16 cm thick. The rubber volcanization was conducted at 143C° under a pressure of 40 Kg. F/ cm^2 for 30 minutes. A simple device was used to carry out measurement of electrical conductivity of pre-extended samples as was described in previous work (1).

To ensure a good contact the two ends of the rubber samples were coated with silver paste before clamping.

For X-ray measurements, an X-ray (philips) diffractometer was used with Cu k_α (λ=1.54A°).The apparatus works at 15mA and 35 kV. Samples of concentrations (0, 25, 50, 75 and 100 phr) and /or types of carbon black (HAF ,GPF) have been studied at room temperature (303 K).

Table (1)

	(phr) [a]
Styrene - Butadiene rubber (SBR)	100.0
Zinc oxide	5.0
Stearic acid	2.0
Processing oil	5.0
HAF or GPF	0, 25, 50, 75 and 100
(MBTS)[b]	1.5
(Anox H.B)[c]	1.0
(6PPD)[d]	1.0
Sulpher	2.0

a Part per hundred parts of rubber by weight

b Debenzthiazole disulphide

c Poly 2, 4, 6 trimethyl - 1, 2 dihydroyuinoline

d N - (1,3 Dimethyl butyle) - N - phenyl = P - phenylenediamine

EXPERIMENTAL RESULTS

The effect of tensile deformation ?= $\frac{\Delta L}{L}$ on the J-E characteristics of HAF/SBR and GPF/SBR samples of carbon concentrations 50,75 and 100 phr has been investigated (see Fig.1). It has been noticed that these relations are sensitive to the type and concentration of carbon black and the value of tensile deformation.Besides,the J-E characteristics of both groups of HAF/SBR and GPF/SBR samples are linear relations.

DC Electrical conductivity Under Different Tensile Deformation:

The variation of the electrical conductivity σ_e with different tensile deformations of HAF/SBR and GPF/SBR samples of different concentrations of carbon black are investigated(see Fig 2). It has been noticed that the electrical conductivity of the two groups of samples increases by increasing the concentration of carbon black and the value of tensile deformation. Besides, the electrical conductivity of HAF/SBR has been found to be higher than that of GPF/SBR samples of the same concentration of carbon black and the same value of tensile deformation. Also it has been found that the dependence of the equilibrium conductivity upon tensile deformation obeys a quadratic relationship on the form of

$$\sigma_c = A + B? + C?^2$$

where ? is the tensile deformation A , B ,and C are constants have been calculated.

The wide angle X-ray scattering (WAXS) techniques is used to obtain the diffraction patterns of different concentrations of HAF/SBR and GPF/SBR samples and under different extension ratios for 25 HAF/SBR and 25 GPF/SBR are shown in figs.(3,4).The extension ratio $\lambda = \frac{L}{Lo}$ where L, Lo are the extended and unextended lengths of the test samples, respectively. From these diffraction patterns the following parameters are calculated:

1) the integral intensity of the halo (I)

2) the half height width of the halo (?W)

The dependence of (I) and (?W) on the concentration and type of carbon black and the relation between (I) and the extension ratio (λ) are plotted in fig .(5) .

From this figure it has been noticed that (I) increases with the concentration of carbon black to a certain concentration after which it decreases.

This concentration depends on the type of carbon black where it is 50 phr and 75 phr for HAF and GPF composites respectively. The half height width of the halo (?W) has been found to increase with the increasing of carbon black concentration for both types of carbon black. Under pre-extension the halo becomes stronger and the maximum of this halo is shifted towards the larger scattering angle(2?) where(2?=20°) for the unextended sample while for extended one (2? = 20.8°).

DISCUSSION

The electrical conductivity of the unextended and pre-extended HAF/SBR and GPF/SBR samples have been investigated (see Figs 1,2). It has been found to depend significantly on the degree of pre-extension, the type and concentration of carbon black. It has been found to increase with increasing the concentration of carbon black of both types.

Besides, the value of (σ_e) of HAF/SBR is higher than that of GPF/SBR composites of the same concentration. The increase in the electrical conductivity with increasing the concentration of carbon black may be attributed to the fact that as the carbon black concentration is increased. the interaction between the polymer and the carbon aggregates is increased. This leads to the decrease in the hopping and tunneling paths between the aggregates and the SBR, consequently the electrical conductivity is increased.

Moreover, the HAF/carbon black (of 29nm particle size) has more probability of interaction than with the polymer and has shorter hopping and tunneling paths between the aggregates and SBR than with the GPF carbon black(of 50nm particle size). This may interpret the higher values of the electrical conductivity of HAF/SBR than those of the GPF/SBR composites of the same concentration of carbon black.

The electrical conductivity of the tested samples has been affected by the degree of pre-extension. The conduction mechanism of the unextended samples might be attributed to the tunneling or hopping mechanism(1). The initial values of pre-- extension cause a decrease in the electrical conductivity reaching a minimum value at ?=10% (Mullins effect)(2), then it increases by further increasing of the degree of pre-extension.

In the first region of pre-extension (for ? less than 10%)the decrease in σ_e with increasing of ? might be due to a breakdown in the carbon structure or a destruction process might occur. By further increasing the degree of pre-extension (from 10% to 20%) the breakdown of carbon structure stops as the destruction and construction processes might become equally probable which may produce the stable character of (σ_e) [3].

At relatively higher pre-extension from 20% to 100% the reformation processes of carbon black network, to reform aggregates to be agglomerates are more probable than the destruction processes which are accompanied by the reformation of a certain degree of packing. These two processes may be responsible for the observed increase in (σ_e) due to the decrease in the hopping and tunneling height and paths between the SBR barriers and carbon black by more reformation of carbon structure. In this case a new process starts which is the realignment of polymeric chains in the direction of stretching [4].

The loaded SBR with 100 phr of carbon black of both types shows a metal like conductivity. The conduction mechanism in this case is due to the direct contacts between carbon particles and aggregates to form stacking carbon faults and paths.

Moreover, the linear dependence betweenlo g I and logE (see Fig .1) indicates that the obtained results could be expressed mathematically by an equation of the form

$$J = BE^{n}$$

where B and n are constants, the value of the field exponent (n) has been calculated and found to be nearly equal to unity for all curves. This observation indicates that the Ohmic conduction [5] is the dominating conduction mechanism in tested samples under the present experimental conditions.

Microstructural properties

In order to study the effect of pre-extension on the degree of packing of the HAF/SBR and the GPF/SBR composites, X-ray diffraction diagrams of both unextended and pre-extended samples were recorded.

From Figs.(3,4 and 5) the X-ray integral intensity (I) and the width of the half height of the halo (?W) for the HAF/SBR and GPF/SBR samples have been found to increase with increasing the concentration of carbon black of both types .In the present case the non-crystalline HAF/SBR and GPF/SBR composites which were pre-extended (λ=2,3) the chain segments were forced to pack side by side as a short degree of packing or clustering. The parameter(I) for the tested samples exhibited peak values at carbon concentrations 50 phr for the HAF/ and 75phr for the GPF. After the concentrations 50phr and 75phr for the HAF and GPF composites respectively the integral intensity of the halo gradually decreases showing the tendency towards the perfect amorphous state which is evident from the reduction in height and the increase in width of the half height of the halo (?W). Besides, the integral intensity (I) of the pre-extended 25phr HAF/SBR and 25phr GPF/SBR samples have been found to increase with increasing the extension ratio (λ). These observations indicate that the dispersion of carbon black particles with increasing the carbon black concentration has reached the optimum dispersion conditions at carbon concentrations 50phr and 75phr for the HAF and the GPF composites respectively. By further increasing the carbon black concentrations the dispersion process decreases due to the agglomeration of the particles and aggregates of carbon black.

It is also noticed that the peak of the halo of the pre-extended 25phr HAF/SBR and 25phr GPF/SBR samples is grown and shifted towards larger scattering angle as the pre-extension ratio is increased. This observation indicates that the periodicity of the stretched polymeric chain segments under pre-extension are increased and oriented in the direction of extension and are more packed side by side. This result agrees well with previous one obtained by N. Miyadera et. al [6]

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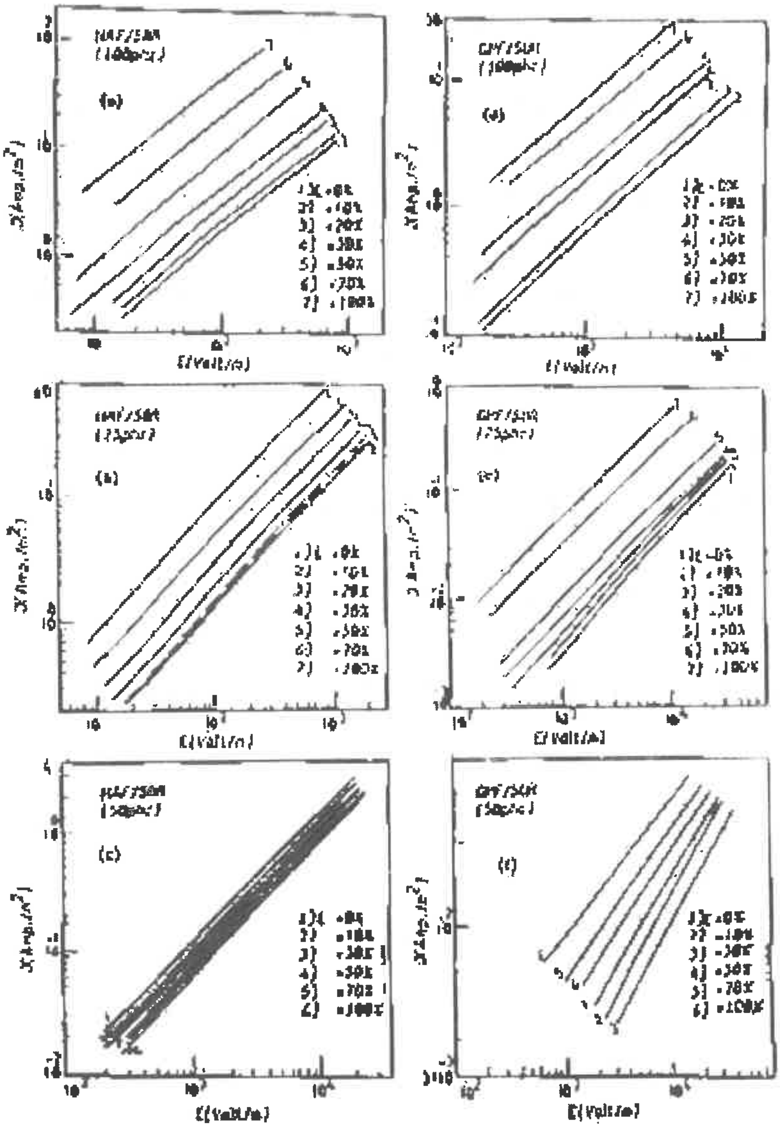

Fig. (1) : J-E characteristics at different strain , ε (%) for different concentrations of HAF(a-c) & GPF (d-f) at T=303K

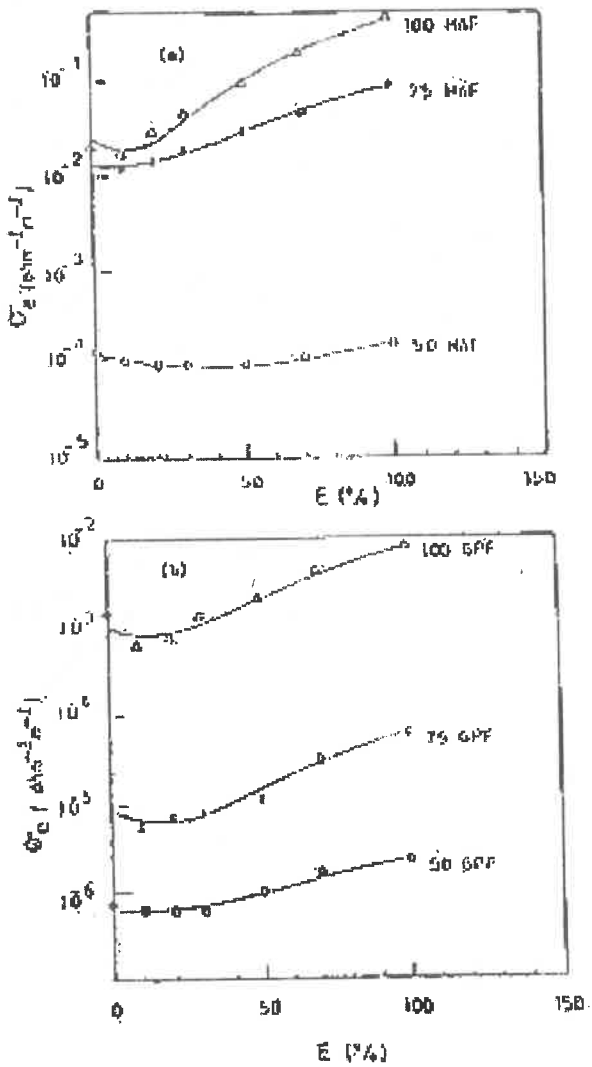

Fig. (2) : The variation of σ_e (Ohm^{-1}m^{-1}) with strain, ε(%) for different concentrations of (a) HAF & (b) GPF at T=303K

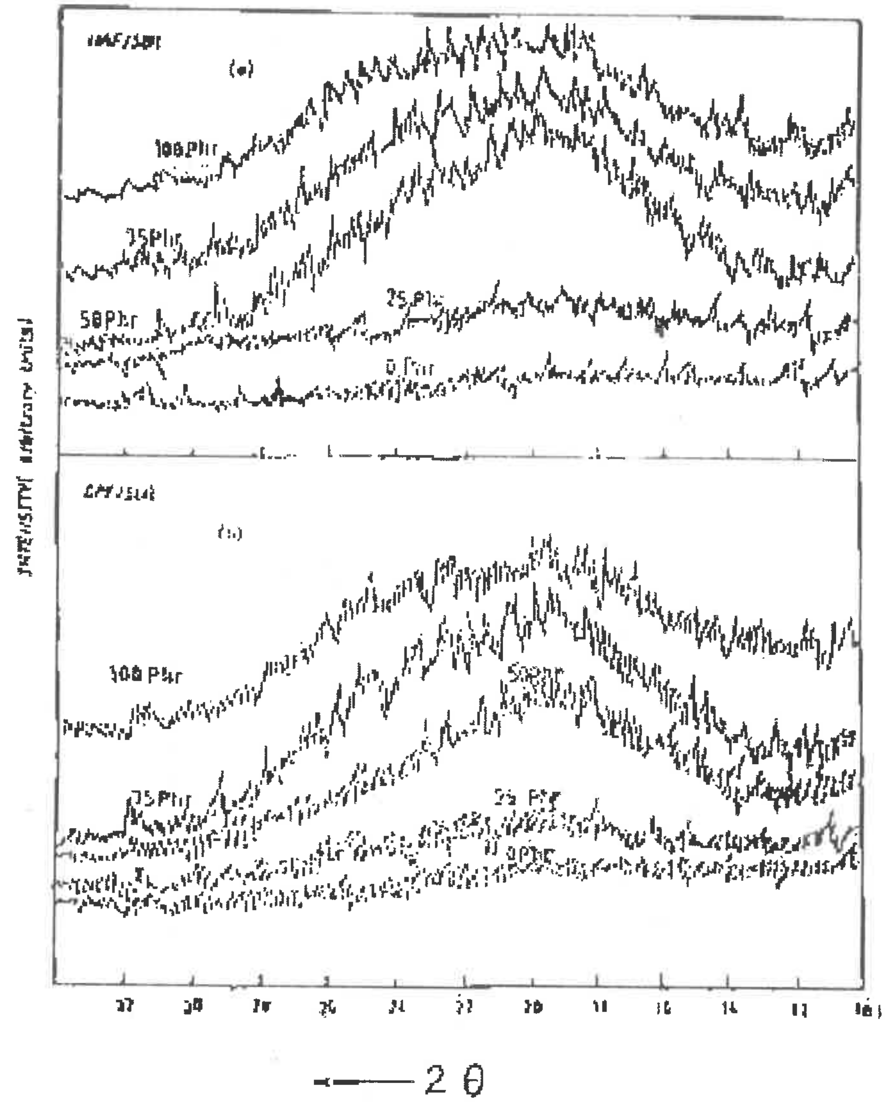

Fig. (3) : X-ray diffraction diagram of both filled and unfilled samples for (a) HAF/SBR & (b) GPF/SBR composites at T=303K, extension ratio, 1=1

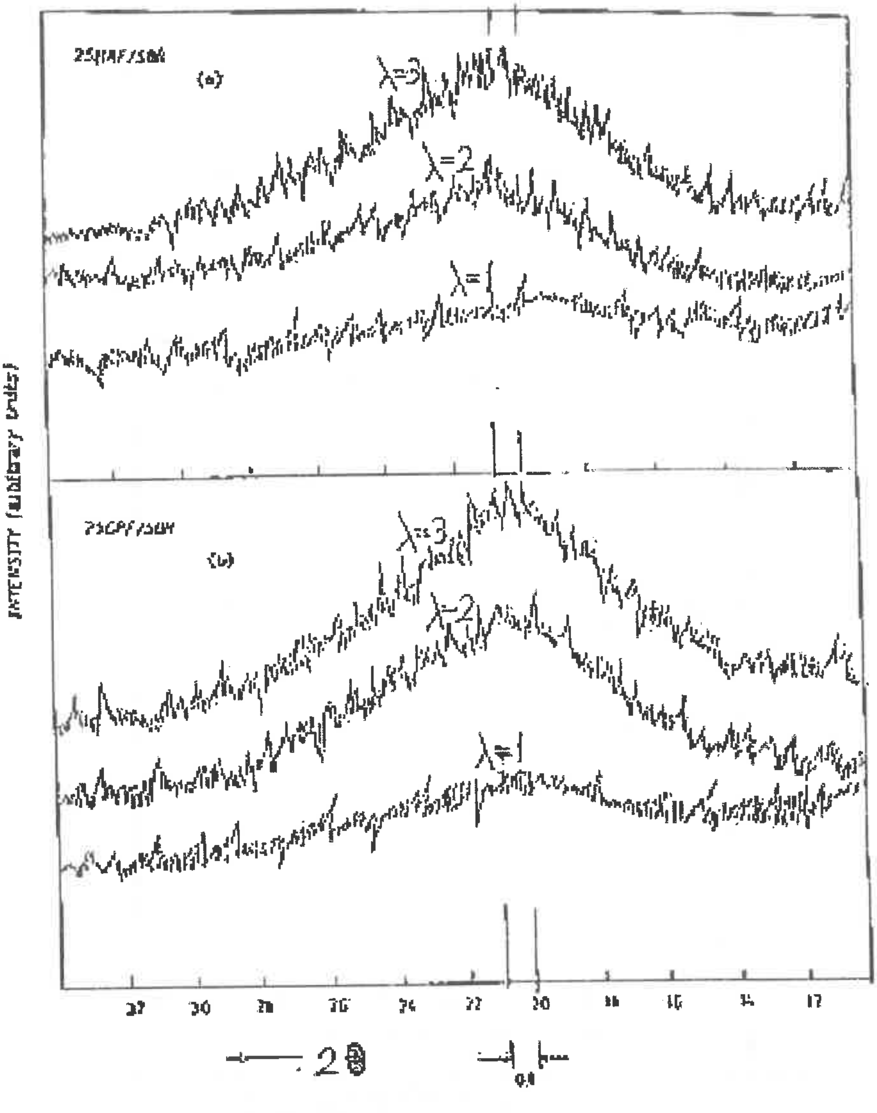

Fig. (4) : X-ray diffraction diagram under different extension ratio, λ = 1,2 and 3 for (a) 25HAF/SBR and (b)GPF/SBR composites

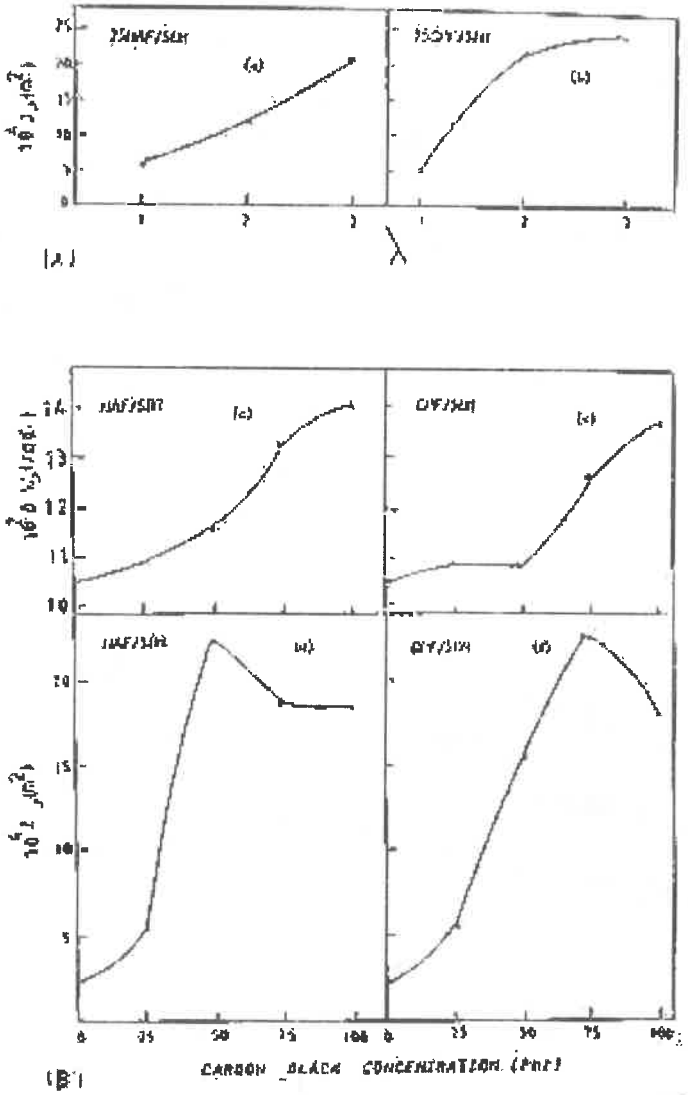

Fig. (5) : A) The variation of X-ray integral intensity, I of the halo with the extension ratio, λ for (a) 25HAF/SBR and (b)GPF/SBR composites

B) The variation of X-ray integral intensity, I and the half height width, ΔW of the halo for HAF/SBR (c-d) & GPF/SBR (e-f) composites at T =303K

دراسة تأثير الشد الإبتدائي على التوصيل الكهربي لمادتي مطاط ستيرين / بيوتادين المحملة بالكربون الأسود

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خلاصــــة :

تمت دراسة تأثير الشد على التوصيل الكهربائي لمادة الإستيرين بيوتادين المحمل بالكاربون الأســود مــن النوع HAF والنوع GPF بتركيزات 50 ، 75 و 100 جزء لكل مائة جزء وزني مــن المطــاط . وقــد وجــد أن ميكانيكية التوصيل لعينات البحث هي التوصيل القفزي والتوصيل النفقي والتوصيل الأومي .

وتم إستخدام الأشعة السينية لفحص التركيب الدقيق للعينات ووجد أن شدة حيود الأشــعة الســينية (I) تزداد بزيادة نسبة شد العينة ويزداد كذلك عرض الهدبة (W½) بزيادة نسبة تركيز الكاربون . كما أن القيمة العظمــى لشدة الأشعة (I) تزداد وتتزاوح باتجاه زوايا التشتت الكبيرة مع زيادة نسبة الشد .

هذه الملاحظات تبين أن قطع سلاسل البوليمر تستطيل وتتجه باتجاه الشد وتتقارب جنبا إلى جنب .

ويعتقد أن نقصان شدة الأشعة السينية عند التركيزات الكبيرة للكاربون هــو نتيجــة عمليــات تقــارب لمجموعات الكاربون لتكوين مجموعات كبيرة بفعل الشد .

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