Strain Effect on the Electrical Conductivity of CB/SEBS and GP/SEBS Composites

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Summary: Carbon black (CB) and Graphite (GP) were embedded in poly(styrene–ethylene/butylene–styrene) (SEBS) to form CB/SEBS and GP/SEBS composites. The electrical resistance was monitored in situ during tensile, compressive and dynamic mechanical tests, obtaining a correlation between the electrical response and strain. In the dynamic test the conductivity of the composites showed almost the same behavior than the elastic modulus, decreasing at deformations higher than 1%.

Keywords: Payne effect; Piezoresistive effect; SEBS

Introduction

Conductive polymer composites can be obtained by adding conductive particles, such as carbon black, to an insulating matrix. Several applications have been found for these materials, such as electromagnetic shielding materials, self-regulating heaters, current protection devices, stress sensor and strain sensor.[1–3] Because of their good mechanical properties, like flexibility and capacity to absorb mechanical vibrations, and their low costs elastomers composites have gained attention in the last years.[4,5] The electrical behavior of this conductive composite follows the percolation theory that states that resistivity decreases dramatically when a critical volume fraction is reached, named percolation threshold; above this value the composite behaves like a conductor.[6] When external stimulus, mechanical, thermal, magnetic or chemical, are applied to a composite with a concentration of particles around the percolation value an appreciable variation in the resistivity can be observed.

Among this stimulus, the effect of strain, named piezoresistance, has been mostly studied in compressive and in tensile strain,[3,7–10] under one of two conditions: a) fixed values of strain are applied or b) the composite is subjected to a continuous strain while electric resistance is read. However, no work has been found on the effect of dynamic strain under flexion, during a DMA measurement.

In this work composites of SEBS with CB and GP were compounded at different volume fractions to study the piezoresistive behavior during a DMA measurement in flexion mode. Samples above the critical concentration of both particles were selected.

Experimental Part

SEBS was used as the polymer matrix and as reinforcing fillers were used Carbon Black (CB) and Graphite (GP). The composites were prepared by melt-compounding in an internal mixer (Brabender PLASTI-CORDER). The mixer was operated at 235 °C and at a speed of 30 rpm. Two kind of samples were obtain by compression molded, a) disc-shaped samples of 19 mm diameter with 10 mm of thickness for compression measurements and b) rectangular-shaped of 63 × 12 mm and 3 mm thick for others tests. Materials used in this study are listed in Table 1.

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Table 1.
Description of materials.

Materials	Technical information	Supplier
Polymer matrix	*Poly(Styrene-etylene/butylenes–styrene) block copolymer* Kraton G 1652 Molecular weight = 80000 g/mol Styrene content = 33 wt% MFI = 1.6 g/10 min	Shell Chemical
Reinforcing fillers	*Black carbon* Vulcan XC-72 Superficial area = 254 m^2/g Average diameter of primary particles = 30 nm Purity = 98%	Cabot Co.
	Graphite "O" type Carbon = 98% Average size = 250 μrn	Grafitos de México Co.

The electrical conductivity was measured as a function of electric resistance, by the two-probe method at ambient conditions to characterize electrical percolation threshold using an electrometer 6517A (Keythley). Measurements were taken when a steady state value was reached, in 1 minute intervals. In order to check the reproducibility, five measurements were conducted for different samples. To assure good electrical contact the samples ends were coated with silver paint. The electrical conductivity of the sample, σ, was determined according to the equation:

$$\sigma = (L)/(A * R)$$

where R is the electric resistance of the sample, L the length between electrodes and A the sample area.

For compression and tensile tests an Instron machine, 4301, was used. The displacement between electrodes did not exceed 1.5 mm, subjecting the composites to small strains. A constant cross head speed of 0.5 mm/min was used for both tests. In the other hand, the dynamic mechanical analysis (DMA) measurements were performed at the RSA III (TA Instruments) with a clamped three-point bending tool. The conditions for strain sweep test was a frequency of 1 Hz, temperature of 25 °C and a interval of deformation from $1.0e^{-4}$ to 3%. To verify the material behavior, the experimental steps aforementioned were done twice per concentration, but just one is showed.

For in situ correlation between electrical resistance and strain, the electric resistance was simultaneously read on the multimeter 344014 (Hewlett Packard). Figure 1 shows the different systems used for measurements of electric resistance (R) while the composites were submitted under strain. The electrical resistance was measured at intervals of 1 seg. Electrical and mechanical data were recorded in a computer as a function of time.

Results and Discussion

To determine the percolation threshold, electric measurements were carried out at room temperature for different loading concentration. Figure 2 plots the electrical conductivity versus concentration for CB and GP composites. Samples with volume fraction of 0.032 CB and 0.051 GP appeared to be within the percolation threshold. Composites with CB showed higher values of electric conductivity than those with GP. For example, samples with practically same conductor behavior differ around 7%, between 5.3 vol. % of CB to 12 vol. % of GP. This is due to the high tendency of CB to establish continuous conductive paths through the composite. To examine the electric behavior of the conducting compo-

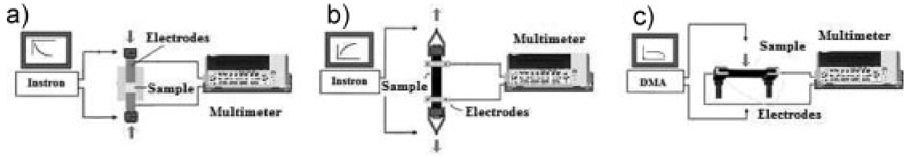

Figure 1.
Systems used for characterizing the electric behavior during a) compression, b) tension, and c) DMA flexion test.

sites when a deformation is applied a high conductive composite were selected, especially CB composites. In order to understand the piezoresistive behavior in DMA probe, using the dual cantilever geometry, compression in tensile test was performed. During DMA test with this geometry, the sample is subjected to tension and compression at the same time.

To compared the piezoresistance of the samples it was used the relative resistance $(R\text{-}R_O / R_O)$, where R is the instantaneous resistance and R_O is the value measured at none compressive strain. To avoid deformation perpendicular to the applied stress the sample was confined in an insulating cylinder. Figure 3 shows the dependence of relative resistance on compressive strain for CB and GP composites. The decreased observed in relative resistance, as strain increases, can be explained as a change in distance among conductive particles. As the sample is constrained in the cylinder, the increase of compressive strain decreases the interparticle separation, leading to a reformation of conductive channels by means of the contact effect and tunneling effect; getting a more conductive composite than a zero deformation composite. However, at values of ε larger than 3%, no changes in the relative resistance were observed, due to the saturation of conductive channels.

The correlation between relative resistance and tensile strain it is showed in Figure 4, again, the GP behavior is showed

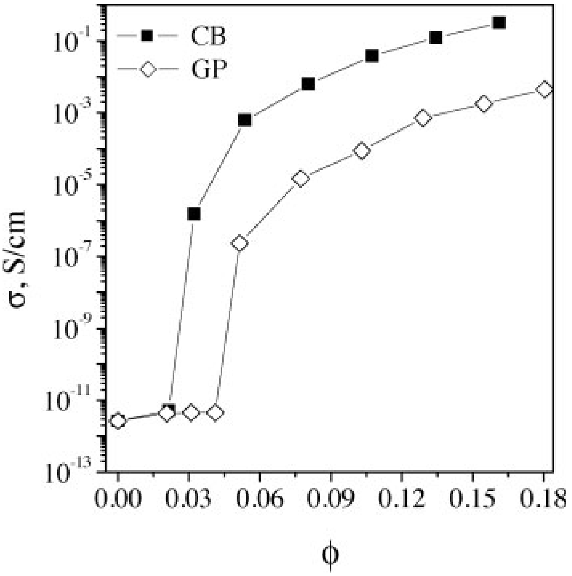

Figure 2.
Electrical conductivity as a function of volume fraction particles weight concentration for CB and GP composites.

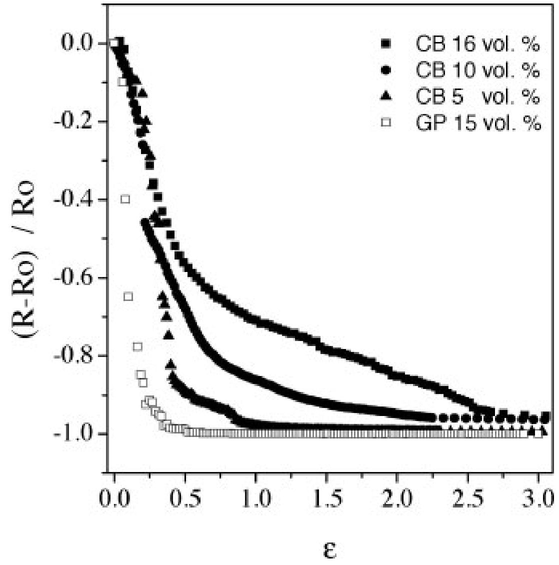

Figure 3.
Relative resistance of CB and GP composites as a function of compressive strain.

as function of one sample. The values of deformation for these static tests are in the linear region of the composites studied. Contrary to results on compression tests, an increase in the relative resistance is observed, as deformation reached 2%. Then a steady value is obtained. When the sample is stretched, the conductive particles are dragged with the polymer chains and pulled apart; resulting in an increase of interparticle distance, increasing relative resistance of the sample.

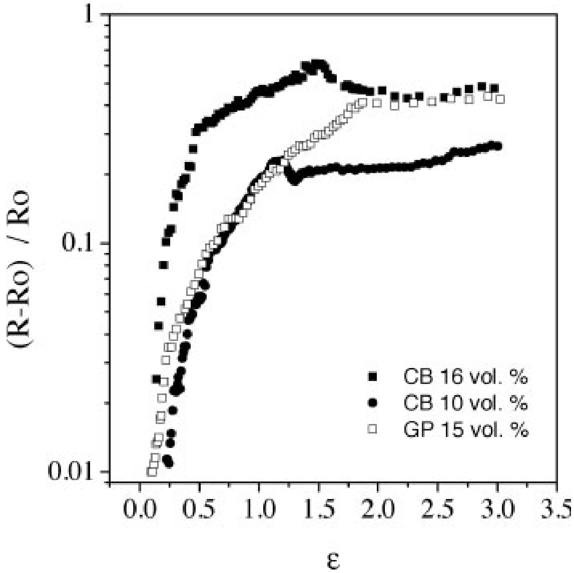

Figure 4.
Relative resistance of CB and GP composites as a function of tensile strain.

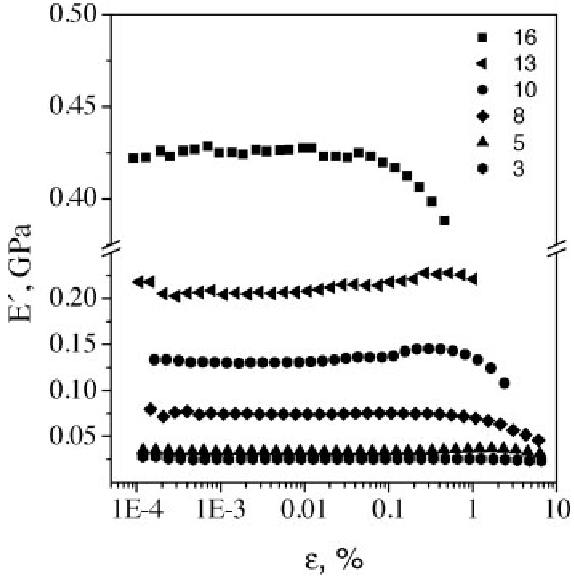

Figure 5.
Dynamic strain dependence of elastic modulus for SEBS compounds at different concentrations of CB.

Besides the improvement of electrical properties, the addition of CB and GP to an elastomer reinforces its mechanical and viscoelastic behavior. The DMA, in flexion mode, was used to measure the piezoresistive phenomenon of the composites in a dynamic test. In Figures 5 and 6 can be seen the influence of fillers on the dynamic elastic modulus. An increment of the value of low strain modulus by adding filler is observed, especially in CB composites. This increment is related to the formation of filler-filler

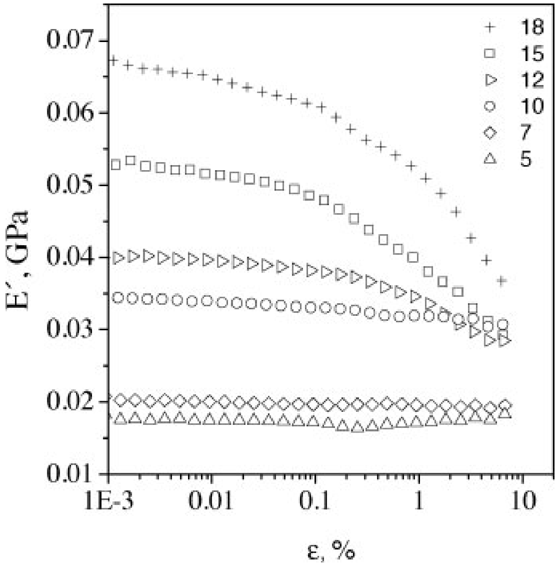

Figure 6.
Dynamic strain dependence of elastic modulus for SEBS compounds at different concentrations of GP.

interactions as loading rises, forming a network called secondary structure. This structure results from the tendency of particles to agglomerate.[11] For a given sample, when increasing dynamic strain a non-linearity is observed, high strain modulus has a decrement, by means of breakdown of the secondary structure. CB composites showed a higher fall on the high strain modulus than GP composites. Instead, composites with GP obtain a lower value of deformation in which the elastic modulus begins to drop, falling since a 0.01% of deformation was reached. It is worth mentioning that the limit force of the equipment was reached with values showed and it was not possible to obtain higher deformation.

As this non-linearity observed, known as Payne effect,[12] is mainly caused by the secondary structure, formed by agglomerated particles, it could be reflected in the electric properties of the composite. For measurements of electric resistance of CB and GP composites as a function of the dynamic strain amplitude, special home-made copper clamps were used to guarantee a well fastened sample and good electric contact. We can see in Figure 7 that electrical conductivity reproduces fairly well the pattern observed in Figures 5 and 6 for elastic modulus. The initial value of conductivity stays stable until it shows a deformation of 0.01% and 1%, for CB and GP composite, respectively. Above this value a decrement is observed. This change is related with the destruction of the conductive network in the composite as deformation increases, destroying and separating the agglomerates of particles.

In a three point-flexion test the sample is subjected to compressive and tensile strains at the same time. As seen before, compression, with the perpendicular deformation restricted, and tension tests produce contrary effects on electric resistance of composites; an increase of electric resistance, decrease of electric conductivity, was observed in the tension test caused by the separation of conductive particles as deformation was applied. We can assume that the same phenomenon, separation of conductive particles, dominates the electric response in the DMA test. The electric behavior in real time during the DMA test is plotted in Figure 8 for a sample of 10.7 vol% CB. We can see that both tension and DMA tests increases the electric response at times larger than 200s.

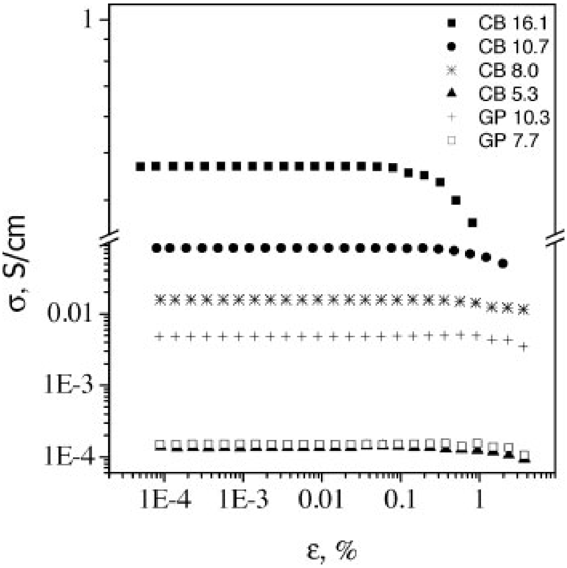

Figure 7.
Dynamic strain dependence of electric conductivity for CB and GP composites during a DMA test.

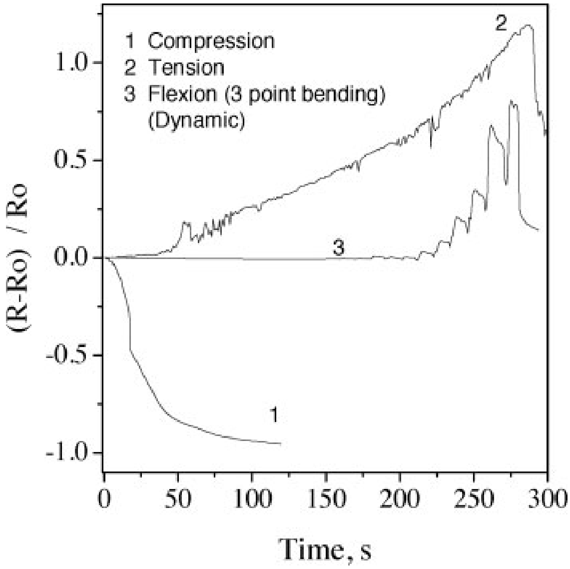

Figure 8.
Relative resistance of SEBS composites with 10.7 vol % of CB as a function of time for different mechanical test.

In a dynamic mechanic strain sweep test successive measurements are taken from the sample at selected strains. During a single measurement the equipment determines an average of measurements for a given strain. In Figure 8 we can see this single measurement like steps, especially above a time of 200 s, for relative resistance. There is a lack of response between the measurements of each step, reflected as a relaxation in resistance. In this way the electric behavior of the material follows quite well the mechanical behavior of the test.

The conductive composites showed the Payne effect, a decrease in elastic modulus upon increasing strain amplitude, during dynamic strain sweep. The piezoresistive behavior during this test showed a drop in the initial value of electrical conductivity at deformations higher than 1%. An explanation for this decrement can be related to the separation of conductive particles that form the secondary structure.

Conclusions

The piezoresistive effects on CB/SEBS and GP/SEBS composites were examined above the percolation threshold, 3.2 and 5.1 vol. % respectively. Relative resistance for the composites changed up one order of magnitude at stretching 1% and a decrease up one order upon 0.5% of compressive strain, as particles approached each other because the perpendicular deformation is restricted. A better response to strain was obtained in CB composites.

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