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# DMA ANALYSIS OF CONDUCTIVE BR/EPDM/CB BLENDS

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## Abstract

In the present work, Dynamical Mechanical Analysis was employed in order to evaluate viscoelastic properties of polybutadiene (BR)/EPDM/Carbon black (CB) blends as a function of the strain amplitude. As expected, storage modulus, G', of conductive samples presented a strong dependence on strain amplitude as describe by the Payne effect. This effect appears in compounds at the electrical percolation threshold and is stronger as CB content is rinsed. However, linear viscoelastic region (LVR), a characteristic section of the curve which has had little attention in this type of studies, presented also a great dependence on CB concentration, i.e. LVR is shorter as carbon black content and, hence, the conductivity of samples, increases. Respect to the influence of the elastomeric ratio BR/EPDM, EPDM alone (ratio 0/100), which had the highest viscosity, was the only formulation without a significant G' dependence on strain at 15 % w/w of CB. Also, conductivity was measured before and after the deformation cycle, in such a way that these data were useful as an indication of the structure recovery. As electrical end mechanical hysteresis is related to the state of (CB) distribution these results are envisaged to balance mechanical and electrical stability.

## Introduction

Viscoelastic properties of polymeric carbon black compounds are sensitive to the filler distribution, i.e. storage and loss modulus are well known to be dependent on the strain because of the Payne effect[1, 2] which describes the decrease of the storage modulus with strain. One interpretation of this effect is a modification of the composite microstructure. Based on this argument, since electrical properties are also dependent on filler dispersion and distribution, morphology of conductive composites might be inferred from DMA measurements.

At high amplitudes of cyclic deformation, the carbon black network is broken down, regardless of the loading or interaggregate bond strength, causing a drop in the elastic modulus, G', which is then governed only by the individual carbon black aggregates. Certainly, it is important to say that, according to Wang[4], even a carbon black network is probably a network of carbon black aggregates connected by thin layers of adsorbed polymer molecules. In a well-dispersed compound at low loadings, where the individual aggregates are well separated, the amplitude effect is very small[3].

Establishing an analogy with the measurement of electrical conductivity, when the network structure is broken down, the conductivity drops in a significant way, just as G' does; also, in a well dispersed system, the conductivity is not affected by any strain. In this manner it is possible to recognize the electrical percolation region when a significant dependence of G' as a function of amplitude can be observed.

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## Experimental

Oil extended polybutadiene (BR) from Tecnopol and EPDM from Du Pont were used as elastomeric matrix blend. Conductive carbon black was supplied by Cabot Corp. Samples were prepared in a Brabender internal mixer at 120 °C and 63 rpm. Elastomers were mixed for a minute before the addition of the filler. After that, carbon black was added and mixed for 2 minutes. Next, the material was compression molded by a PHI hydraulic press at 160 °C and pressure of 883 KPa during 10 minutes. Conductivity was determined by a Siemens conduct meter L-300 in samples of 5 cm x 1.2 cm x 0.3 cm. Dynamic measurements were carried out in a Universal Dynamic Spectrometer Paar Physica UDS 200 in torsion mode at fixed frequency of 1 Hz and an a strain range of 0 – 30 %, at room temperature.

## Results and Discussion

According to Figures 1 to 3, a stronger dependence of G' respect to the strain appears as carbon black content is increased. As a matter of fact, at 15 % (w/w) of carbon black content, when G' start to decrease in Fig. 1 and 2, the system enters the percolation region in the curve conductivity–CB content of the Fig. 5. This fact shows that conductivity and modulus are related trough the formation of network structures.

As mentioned early, the agglomerated structure is very sensitive to dynamic strain, in such a way that dynamic measurements can assess the existence of continuous structures of carbon black just as conductivity measurements do[4].

Carbon black network is responsible for the stiffness of the compound. As strain amplitude is increased, this network is disrupted and the storage modulus decreases. In addition, under conditions of agglomeration there is a portion of rubber which is trapped or caged in the filler network. These rubber molecules raise the effective volume of filler as they are immobilized or rigid in the interstices between agglomerates and aggregates. The breakdown of the filler network by increasing strain amplitude would release the trapped rubber so that the effective filler volume fraction and hence the modulus will decrease[5].

Unlikely Figs. 1 and 2, Fig. 3 shows that G' dependence is observed until 20 % CB for the EPDM alone, which represents, actually, the percolation concentration in Fig. 5. This result agrees with a previous study[5], in which, the dispersion of CB in EPDM was found to be greater than that in BR because of the higher viscosity.

A more defined and shorter LVR in samples with the highest CB concentration implies that the system is less capable of absorb the stress imposed because of the increasing portion of rigid material, which causes a higher internal friction as agglomerates get more packed. This situation establishes that as conductivity increases, lower deformations are allowed in order to preserve the good performance of the material in a conductive application, i.e. touch sensors.

Even tough thixotropic nature of CB elastomeric compounds has been mentioned by Payne[1,2], the present study was also intended, so far, to evaluate this effect as function of CB concentration and, more important, the relation to conductivity loss (Table III). Fig. 5 shows how at 10 % of CB a hysteresis loop appears, evidencing an important agglomeration previous to enter the electric percolation region. It is important to point out that 15 % CB represents the superior limit of the percolation region. At this concentration, the hysteresis is considerably larger. At higher CB concentrations, a greater area of hysteresis is expected; however, the limit of strain had to be different because of the major damage suffered by the samples with higher CB concentrations at large strains.

According to Table III, the composites present certain mechanical and electrical losses after the cycle. These are larger in the case of conductivity. However, in spite of the different hysteresis magnitudes, conductive samples in general present relatively small values for mechanical and electrical losses, suggesting a high recovery of the carbon black network. In the other hand, a not well defined trend in the values of Table III could confirm that conductive network is not really formed by direct contact between aggregates, but connected by adsorbed polymer layers or gaps which depend on a not easy controlled filler distribution.

These results provide an excellent support when it comes with the performance of electric sensors or devices employing this type of materials. Furthermore, Fig. 6 shows that hysteresis of G'related to frequency effect is just a little larger as this increases from 0.1 to 1 Hz. A dramatic change occurs at still higher magnitude order of frequency, when G' present a very high initial modulus and actually appears to increase with strain.

## Conclusions

Even tough a more complete series of analysis are to be made, present results states that a mechanical and electrical percolation are stretchy related trough the existence of continuous paths which induces the composite to respond in a particular manner (Payne effect and electric percolation) to mechanical and electric stimuli.

Composites of high conductivity are allowed to suffer only small instantaneous deformations before CB structure loss a proper arrangement related to electric performance. In spite of the above, conductive composites are capable of going trough relatively large deformations (5 -20 %) with relatively small losses after recovery. High mechanical hysteresis is presented by these materials above the percolation threshold.

In the other hand, frequency has an important effect in the dynamic behavior of these materials as a function of strain.

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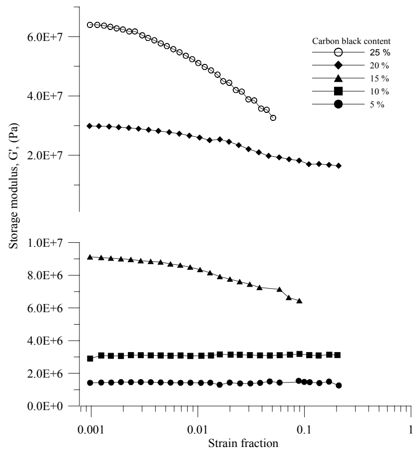


Fig. 1. Storage Modulus, G', as a function of the strain fraction for a 100/0 (w/w) BR/EPDM blend at different CB concentration.

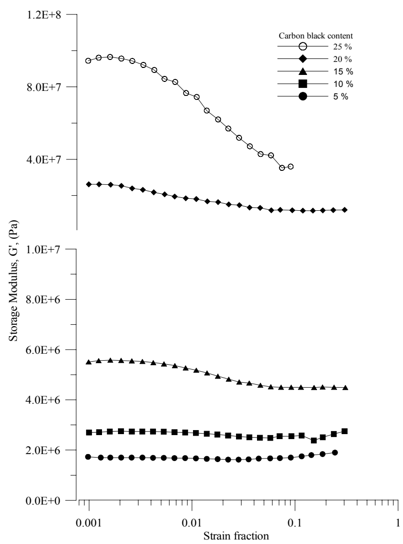


Fig. 2. Storage modulus, G', as a function of the strain fraction for a 50/50 (w/w) BR/EPDM blend at different CB concentrations.

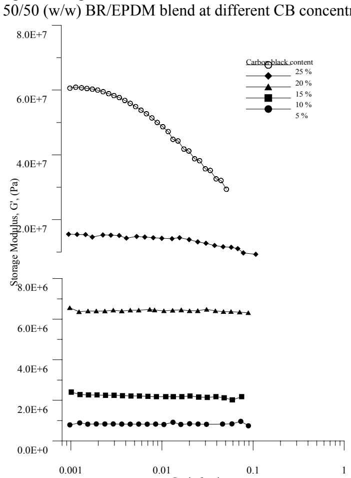


Fig. 3. Storage modulus, G', as a function of the strain fraction for a 0/100 (w/w) BR/EPDM blend at different CB concentrations.

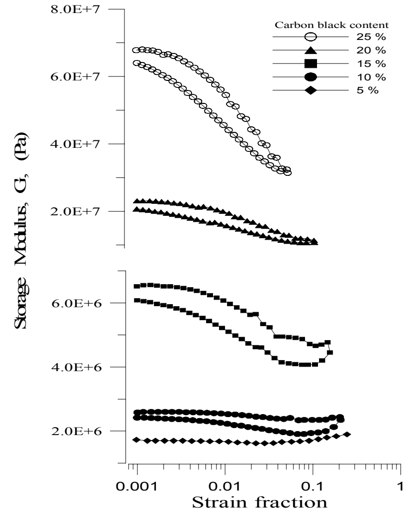


Fig. 4. Recovery of storage modulus for a 50/50 (w/w) BR/EPDM blend at different CB concentrations.

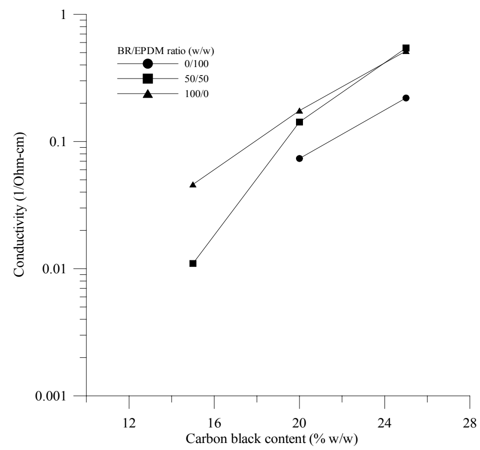


Fig. 5. Conductivity as a function of carbon black content for different BR/EPDM ratio.

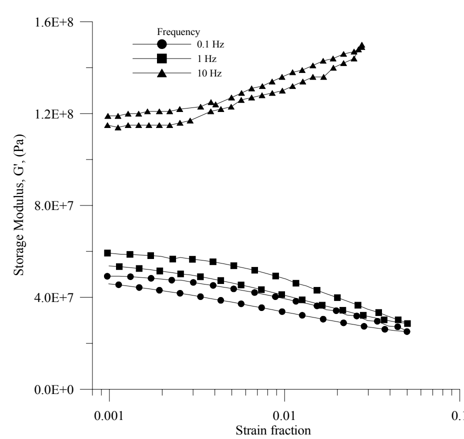


Fig. 6. Hysteresis Cycle at different frequencies for a 0/100 BR/EPDM blend at 25 % of CB.