AGING AND DIELECTRIC RELAXATION OF CARBON BLACK/POLYMER NANOCOMPOSITES

C. Brosseau and A. Mdarhri

Lab-STICC, Université Européenne de Bretagne, CS 93837, 6 avenue Le Gorgeu, 29238 Brest Cedex 3, France.

Introduction

Carbon black (CB) filled semi-crystalline ethylene butylacrylate (EBA) copolymer networks are investigated to search for the time dependence of the microwave effective complex permittivity of samples which are submitted to a uniaxial tension. With respect to this purpose, we argue that the phenomenology for physical aging in these materials is related to the change of the mesostructure, formed by the heterogeneous three-dimensional interconnected network of polymer and of aggregates (or agglomerates) of CB particles, as the composite is stretched. Examination of the surface and volume morphological evolutions of these materials under the action of a mechanical stress at the microscale by scanning electron microscopy and atomic force microscopy indicates that aging during a few hundreds of hours, even at a moderate strain, generates voids and cracks which are aligned along the stretching direction.

Experimental

In the present contribution, we used an EBA copolymer filled by acetylene CB (Denka Black). The glass temperature transition of the neat polymer matrix is T_g=198 K, and the crystallinity, determined by differential scanning calorimetry is $w_c \approx 20$ vol%. We refer to Ref. [1] for experimental details of the sample preparation procedure. The motivation for this choice of materials is that the investigated samples were previously characterized by conductivity measurement (two-probe dc, for the high resistivity samples, and four-probe ac (that eliminates the influence of contact resistance) using an Agilent 4294A precision impedance analyzer, for the low resistivity samples, electrical transport measurements) [1]. The conductivity data evidence a percolation transition at $\phi_c = 8$ vol%. We obtained the microwave effective complex (relative) permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ from the measurement of the scattering parameters (S parameters) using a Agilent H8753ES vector network analyzer. Our procedure for measuring the microwave effective permittivity of soft materials during an uniaxial stress is reminiscent of the innovative technique described in Ref. [1]. For the electromagnetic analysis, a typical rectangular parallelipipedic sample with initial thickness $d_0 = 1.85$ mm, width $w_0 = 5$ mm, and length $\ell_0 = 70$ mm was employed. Our experimental setup allows us to measure the effective complex permittivity in the frequency range 300 MHz $\leq F \leq 5$ GHz. All measurements were carried out under ambient laboratory conditions ($T \approx T_g + 100$ K). To understand the relation between properties and details of the microstructure, the electromagnetic measurements have been complemented by scanning electron microscope (SEM) (Hitachi S-3200 N) imaging of gold-coated samples at an acceleration voltage of 10 kV. Samples were also characterized with atomic force microscope (AFM) (Veeco Nanoscope Multimode V) in tapping mode using silicon probes (TAP150, Veeco) under ambient conditions at scan speeds of 10-50 μms^{-1}.

Results and Discussion

We have used gigahertz frequency-domain spectroscopy (GHz-FDS) to monitor physical aging in a series CB filled polymer samples under uniaxial strain over times ranging from hours to weeks. While our results are on quite small values of the initial extension ratio λ_0 presently, they shed light on the aging behavior of these materials. Our main findings are as follows. First, by choosing CB volume fractions below and above the percolation threshold, we found that the ε' and ε'' spectra in the frequency range of interest display important generic features depending on the CB content and stretching ratios. We find that, for samples containing a CB volume fraction close and away from the percolation threshold ε' and ε'', at a given frequency and for a specific value of λ_0, are found to be constant over the aging time (Fig.1). For the sample above the percolation threshold and low strain, the effective permittivity follows a logarithm of time variation, while at sufficiently high strain ε remains constant. Another generic feature of these significant experimental observations is that the different permittivity behaviors above and below percolation threshold are the result of different aging mechanisms. More precisely, they can be qualitatively explained as follows: on the one hand, the aging mechanism is predominantly entropic and is mainly driven by the elasticity network of the polymer chains, and hence we do not expect there to be a strong temporal dependence of permittivity; on the other hand, at CB volume fraction higher than the

percolation threshold and low stress, the percolating network evidences serious damage under local stress. Central to this phenomenological scenario is that physical aging, as seen by the change of the electromagnetic properties, is related to the change of the mesostructure, formed by the heterogeneous three-dimensional interconnected network of polymer and of aggregates (or agglomerates) of CB particles, as the composite is stretched [2-3]. In this way, SEM and AFM observations (Fig. 2) bring useful morphological information on voids and cracks which show an anisotropic distribution in the direction of the applied strain.

Fig. 2 : Tapping mode AFM images (scanning speed=20 μms^{-1}) of representative areas from an extension plane parallel to the stretching direction, of the sample containing 8.42 vol% CB aged during 192 h at λ_0=1.12: (a) topography image, (1) and (2) denote two particular cracks. The line scan is taken along the line in the corresponding image; (b) corresponding depth profile of image (a), and (c) high resolution surface height map showing the detail of cracks in a 500 nm scan.

Conclusion

Our experimental study opens up some new perspectives by using GHz-FDS to probe the electromagnetic properties at continuum length scales for soft composites subjected to a uniaxial tension during a long time t of application. The identification of the aging behavior is of great experimental interest because this should help design new means of controlling the kinetics of aging. Technological implications abound within the automobile tire industry, wearable and stretchable electronics, functionalized artificial skin and muscles for robotics.

References

[1] A. Mdarhri, C. Brosseau, and F. Carmona, J. Appl. Phys. **101**, 084111 (2007).
[2] C. Brosseau, A. Mdarhri, and A. Vidal, J. Appl. Phys. **104** 074105 (2008).
[3] A. Mdarhri, P. Elies, and C. Brosseau, J. Appl. Phys. **104**, 123518 (2008).

Fig. 1: The variations of the real and imaginary parts of the effective (relative) permittivity for a composite sample containing 8.42 vol% CB as a function of the time t of strain application at an initial extension ratio λ_0. (a) $\lambda_0 = 1.04$, (b) $\lambda_0 = 1.08$, and (c) $\lambda_0 = 1.12$. Open (resp. filled) squares correspond to $\varepsilon^{''}$ (resp. $\varepsilon^{'}$). Open (resp. filled) triangles correspond to $\varepsilon^{''}$ (resp. $\varepsilon^{'}$) of the unaged samples. Room temperature. The vertical bars represent the estimate of uncertainties in measuring $\varepsilon^{'}$ and $\varepsilon^{''}$. The dashed lines are guides for the eye.