Composites Science and Technology 142 (2017) 91–97

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Understanding the strain-dependent dielectric behavior of carbon black reinforced natural rubber – An interfacial or bulk phenomenon?

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A R T I C L E I N F O

Article history:
Received 13 October 2016
Received in revised form
27 January 2017
Accepted 1 February 2017
Available online 3 February 2017

A B S T R A C T

Filler-polymer interactions are one of the keys to understanding the physical properties of polymer composites. These interactions give rise to an interface with specific properties that may have a nontrivial effect on the macroscopic properties of composites. Direct measurement of the interface properties at nanometer scale is usually unavailable. Thus, interface properties are often back calculated from the bulk response using a computational model. However, if the model does not take into account the morphology of the filler dispersion, the results can be misleading. Recently it has been found that the dielectric response of a carbon black filled natural rubber film can change dramatically upon stretching [M. Huang, *Macromolecules* **49**, 2339 (2016)]. In this paper, we will show that this phenomenon can be largely explained by changes in filler cluster connectivity due to strain and is probably not caused by changes in the interfacial interactions. To support the argument, the polarization mechanism of the composites in the measured frequency range is analyzed and numerical models are developed to virtually reproduce the physical phenomenon as a function of strain. A power-law dependence of dielectric permittivity with strain is derived, which matches closely with the experimental results.

1. Introduction

Polymers are often reinforced with nanoparticles to improve the electrical and mechanical properties and it has been a heated research topic these years to optimize the material performance [1–6]. For a heterogeneous system, the properties of the filler/matrix interface, and the filler geometry and dispersion morphology are major factors that affect the composite ultimate properties [7–10]. The interface includes a 2D interfacial area and a 3D interfacial region that accounts for the effects extending into the matrix. The properties of the interface depend on the physical and chemical interactions between the two phases and are independent of filler or aggregate geometry and dispersion [8,11–13]. Filler geometry and dispersion impact properties because they not only determine the volume of the interfacial region, but also influence how mechanical or electrical stress are distributed, at what volume fraction percolation occurs, etc. [14,15] Directly probing the local interfacial behavior can be difficult due to the small scale and thus, the interface properties are often determined using a computational model that includes the interface and then back calculating the interfacial response from the bulk properties. However, the pitfall of this method is that the change in properties due to the addition of nanofillers is often a combination of interfacial and filler geometry/dispersion/morphology effects. The result can be largely biased if the latter is not accounted for accurately. This is especially true for fillers with fractal geometry or large aspect ratios. To address this issue, finite element based numerical simulations have been developed to include the geometric information derived from the real microscopic images [15–18].

M. Huang et al. recently found that the dielectric response of a carbon black filled natural rubber film can change dramatically upon stretching and it was implied that this is a result of changes in the interfacial properties due to strain [1]. In this paper, we demonstrate that the bulk response can be explained primarily from changes in filler morphology due to strain, which excludes the interfacial properties changes as the necessary cause of the phenomenon. This paper starts with a brief review of Maxwell-Wagner-Sillars (MWS) polarization, which is believed to dominate the dielectric response of the composite in this case. The impact of filler dispersion on the dielectric permittivity is then discussed. Finite element simulations are used to explicitly model the changes in filler dispersion morphology due to strain and the

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http://dx.doi.org/10.1016/j.compscitech.2017.02.003

resulting change in dielectric responses. The change in filler network morphology is analyzed and its effect on the electric field distribution and dielectric polarization is thoroughly discussed.

2. Theoretical considerations

2.1. Maxwell-Wagner-Sillars (MWS) polarization

Fig. 1 shows the measured dielectric spectra of a carbon black filled natural rubber at the volume fraction of 0.13 at different mixing times. The results are taken from [M. Huang *Macromolecules* **49**, 2339 (2016)], where a N330 carbon black used and the rubber to dicumyl peroxide w/w ratio is 50:1 [1]. In all cases, the real permittivity shows a gradual step-increase from 10^7 Hz to 100 Hz, while the imaginary part exhibits a peak around 10^6 Hz, and a large increase at 1 kHz and below. The peak in the imaginary permittivity and the step-increase in the real part at high frequency is due to the onset of the Maxwell-Wagner-Sillars (MWS) polarization [19,20]. The sharp rise of imaginary permittivity at low frequency ($f < 1$ kHz) is caused by dc leakage current, which increases the imaginary permittivity with frequency in a manner of $\varepsilon'' = \sigma_{dc}/\omega$, with σ_{dc} being the dc conductivity [21]. But dc conduction has no effect on the real permittivity, as it does not store energy. The electrode polarization can be excluded as no simultaneous increase of real and imaginary permittivity with decreasing frequency is observed [22].

It is well known that for composites containing conductive fillers in insulating polymers, the dielectric response at radio frequency and below ($f < 100$ MHz) is largely affected by Maxwell-Wagner-Sillars (MWS) polarization [19,20]. MWS polarization arises from the accumulation of charges at phase boundaries due to the limited conductivity in the polymer matrix. This concentrates the field in the polymer, and thus increases the polarization [21]. At short times, the field partition between two phases is primarily determined by the fast polarization of bound charges, which determines the real permittivity in the high frequency limit, denoted as ε_∞, and

$$\frac{E_f}{E_m} \sim \frac{\varepsilon_{\infty,m}}{\varepsilon_{\infty,f}}, \qquad t < \tau \tag{1}$$

The subscripts *f* and *m* denote the filler and matrix, respectively, and τ is the time constant of MWS polarization. At long times, free charges (free electron in the case of carbon black) start to flow and will accumulate at phase boundaries with time because of the conductivity difference between the two phases. The field partition is being shifted as a result of charge accumulation until the current density in the two phases equilibrates, and from Ohm's law, the equilibrium field partition at long times is primarily determined by the dc conductivity of each phase,

$$\frac{E_f}{E_m} \sim \frac{\sigma_m}{\sigma_f}, \qquad t > \tau \tag{2}$$

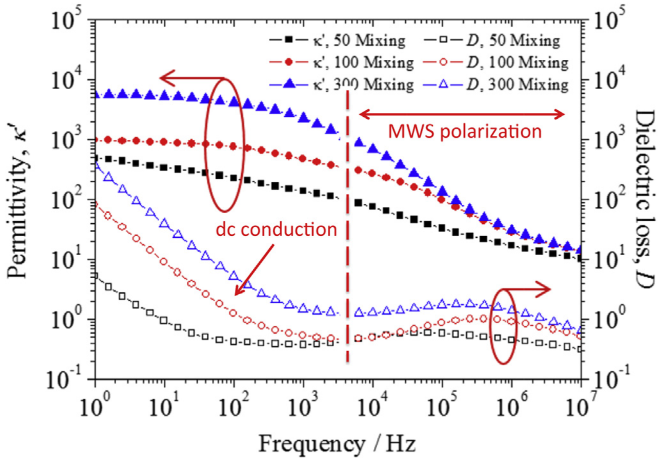

Fig. 1. The dielectric spectroscopy of rubber filled with 13 vol% carbon black with different mixing times (i.e. 50, 100, 300) measured at room temperature. Results are taken from [M. Huang *Macromolecules* **49**, 2339 (2016)]. Figure is adapted with permission. Copyright ACS, 2016.

with σ being the conductivity. Due to abundant free electrons in carbon black,

$$\frac{\sigma_f}{\sigma_m} >> \frac{\varepsilon_{\infty,f}}{\varepsilon_{\infty,m}} \tag{3}$$

which means that giant MWS polarization will be induced as the frequency decreases and the field partition changes dramatically. Fig. 2 elucidates this effect by mapping out the field distribution at 10 MHz and 1 kHz respectively for an arbitrary 2D composite containing conductive fillers. It shows that due to the rise of MWS polarization, the field intensification in the polymer matrix increases significantly at the lower frequency.

MWS polarization is a natural result of solving Maxwell's equations in the frequency domain. The polarization has the same form of an ideal Debye dipole relaxation across the spectrum, characterized with a step increase in the real permittivity and a peak in the imaginary part,

$$\varepsilon = \frac{\Delta\varepsilon}{1 + i\omega\tau} + \varepsilon_\infty \tag{4}$$

The relaxation intensity of MWS polarization, $\Delta\varepsilon$, depends on the difference between σ_f/σ_m and $\varepsilon_{\infty,f}/\varepsilon_{\infty,m}$. The time constant depends on the ratio of the high frequency real permittivity to the dc conductivity, and for a simple stacking two-layer geometry, the time constant is given by

$$\tau = \frac{\varepsilon_{\infty,1}f_1 + \varepsilon_{\infty,2}f_2}{\sigma_1 f_2 + \sigma_2 f_1} \tag{5}$$

Where ε, σ, f are the high frequency real permittivity, dc conductivity and volume fraction of each phase respectively. The actual composite has more than one time constant due to the complexity of the filler morphology, so the loss peak is usually broader than predicted by (4). Fig. 1 shows a loss peak around $10^5 \sim 10^6$ Hz, corresponding to a time constant of $10^{-5} \sim 10^{-6}$ s, which is expected due to the high conductivity of carbon black. Therefore the MWS polarization in this case starts at a high frequency, with its effect extending into the entire low frequency region. It accounts for the large step-increase in the real permittivity shown in Fig. 1.

Though the MWS polarization is also termed “interfacial polarization”, it has nothing to do with the interfacial interactions between the polymer and filler and thus does not explicitly depend on the interfacial area, which distinguishes it from other interfacial effects. This can be most clearly seen from the space charge distribution shown in Fig. 2c that the accumulated charges are not uniformly distributed along the interface but mostly concentrated at the upper and lower edges of the connected clusters with opposite signs, forming a large dipole across the entire filler phase. The polarization density is calculated by normalizing the dipole moment to the cluster volume instead of the surface area, the same way as calculating the polarization density induced by bound charges. This further confirms MWS polarization as a bulk effect.