SPE
SOCIETY OF PLASTICS ENGINEERS
Plastics Research Online
10.2417/spepro.006998

Influence of temperature on the electrical properties of conductive polymer composites

Michael Jones Silva, Paulo Vinicius Rebeque, Alex Otávio Sanches, José Antônio Malmonge, Haroldo Naoyuki Nagashima, and Darcy Hiroe Fujii Kanda

Incorporation of carbon black nanofillers into castor oil polyurethane improves the electrical conductivity of the materials, through a thermally activated process.

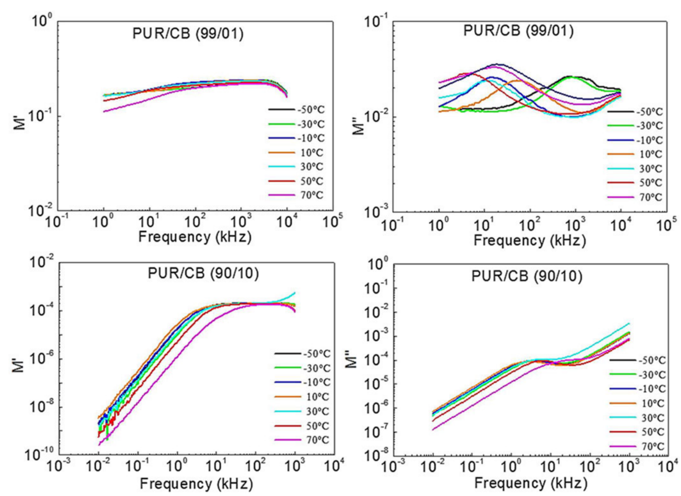

Figure 1. *The real (M') and imaginary (M'') parts of the electric modulus, shown as a function of frequency for different temperatures (between −50 and 70°C). Results are shown for the castor oil polyurethane/carbon black (PUR/CB) nanocomposite samples containing (top) 1% and (bottom) 10% CB (by mass), i.e., the 99/01 and 99/10 films, respectively.*

Conventional polymers are generally considered to be electrically insulating materials because they contain a low concentration of free charge carriers. Conductive polymer composites (CPCs)—conventional polymers that contain conductive fillers—have thus been developed to combine the excellent mechanical properties, lightness, flexibility, and processability of polymers with the electrical properties of conductive solids.[1–3] Furthermore, CPCs prepared from natural polymer matrices—including natural rubber, cellulose nanowhiskers, and castor oil polyurethane (PUR)—have attracted much attention in the last few decades because they can be obtained from renewable and natural sources.[4–6] CPCs can be used in a wide range of applications, e.g., electrostatic dissipating devices, antistatic flooring, sensors, and conductive adhesives.[7] It is therefore important to understand the specific electrical conduction mechanisms that occur in the materials, for each of their applications.

In previous work, it has been demonstrated that the electrical conductivity of CPCs is strongly influenced by factors such as the preparation method, quantity, and distribution of the conductive filler material within the polymeric matrix, as well as by the volume fraction and conductivity of the constituent phases.[8] In addition, charge transport in CPCs can be determined by two main mechanisms: a percolation model for hopping conduction and the tunneling effect between isolated conducting particles.[6,9] Electrical conductivity is also strongly influenced by variations in temperature that the CPC is subjected to. That is, as the temperature increases in the composites, the activity energy of charge carriers also increases. This makes the hop between localized states more favorable and the material more conductive.[10] Although several previous studies have illustrated the potential of carbon-based fillers to improve the electrical properties of insulating polymer matrices, little research so far has focused on the electrical properties of biopolymer-based CPCs that contain carbon fillers.

In this work,[11] we have therefore evaluated how temperature affects the electrical and dielectric properties of thick films of nanocomposites that contain a biopolymer (PUR) matrix and carbon black (CB) nanoparticles. We used the casting method to prepare our PUR/CB nanocomposites, which contained between 1 and 10% (by mass) CB. We then performed direct current electrical conductivity and impedance spectroscopy measurements to assess the electrical properties of the samples. In particular, we used an impedance analyzer (Hewlett

Continued on next page

SPE Plastics Research Online
10.2417/spepro.006998 Page 2/3

Packard, Model 4192A), in the 10^2–10^6Hz frequency range, to measure the AC conductivity of the PUR/CB films at different temperatures.

We analyzed the electrical response of our material by using the complex electric modulus formalism, which is based on polarization analysis. This is possible because interfacial polarization is almost always present in CPCs (due to the fillers that are dispersed in the systems). This interfacial polarization, however, is masked by the electrical conductivity, and the dielectric permittivity can be very high at low frequencies. Nonetheless, this problem can be overcome by formulating a complex electric modulus, which is calculated from the complex impedance data.[12]

We show the real and imaginary parts of this complex electric modulus for our samples that contain CB concentrations above and below the percolation threshold, for a wide frequency range and different temperatures, in Figure 1. We find that the modulus peaks shift toward higher frequencies with increasing temperature. This is evidence of temperature-dependent behavior that can be described by an Arrhenius equation. In addition, we observe an asymmetric enlargement of the peak. This indicates propagation of relaxation that involves different time constants and that exhibits non-Debye-type behavior.

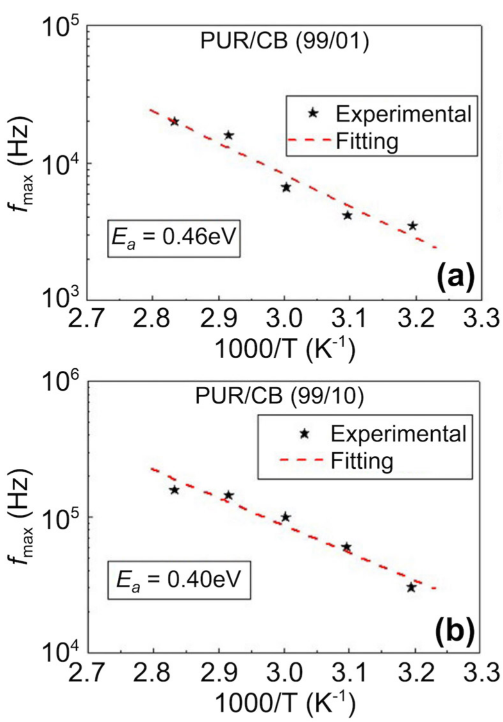

Figure 2. *The maximum peak frequency (f_{max}), as a function of the inverse of temperature (T), for the (a) 99/01 and (b) 99/10 PUR/CB samples. E_a: Activation energy.*

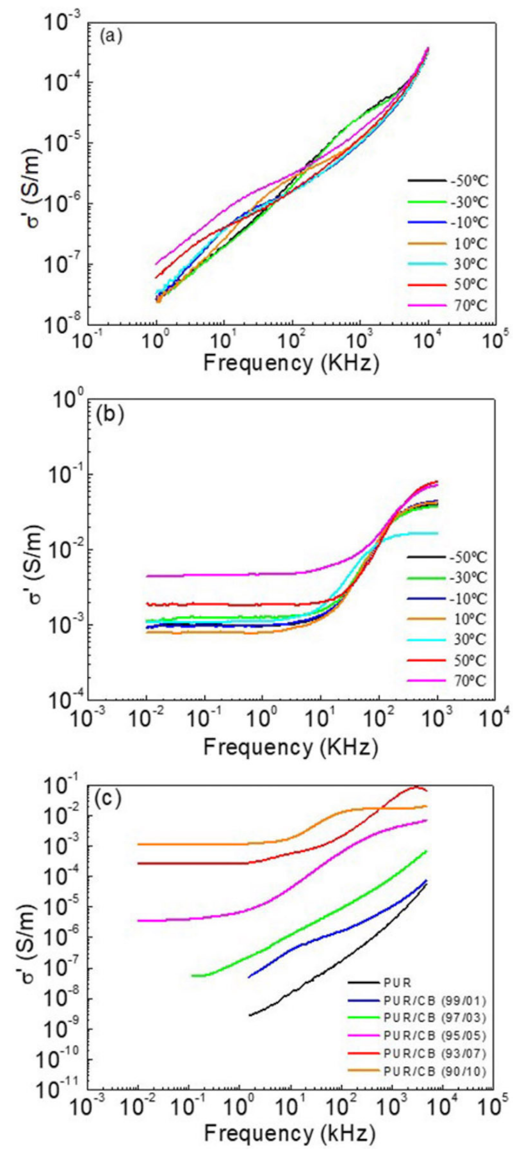

Figure 3. *The real component of electrical conductivity (σ') as a function of frequency for the (a) 99/01 and (b) 99/10 PUR/CB samples at different temperatures. (c) The real component of electrical conductivity as a function of frequency for PUR and PUR/CB nanocomposites (containing 1, 3, 5, 7, and 10% CB by mass) at ambient temperature.*

Using the Arrhenius equation, we can then determine the activation energy of the charge carriers in the samples from the slope of semi-logarithmic graphs of the maximum peak frequency as a function of the inverse of the temperature (see Figure 2). Our results indicate that the activation energy decreases with an increase in the amount of CB

Continued on next page

contained within the polymer matrix of our samples. This behavior arises because of the large size of the conductive region, and is in agreement with previous reports for polymethylmethacrylate/CB composites.[13]

We also show the real part of the electrical conductivity, as a function of frequency and at different temperatures, for the same two PUR/CB samples in Figure 3. We observe frequency-dependent behavior for samples with CB concentrations below the percolation threshold. For the samples above this threshold, however, our results indicate two well-defined regions in the electrical conductivity curve: a frequency-dependent region and a frequency-independent region. In the frequency-independent region, the charge carriers traverse a large distance by virtue of the tunneling effect. This involves isolated conductors even before the direction of the electric field is reversed.[11] In contrast, the conduction of charge carriers in the frequency-dependent region occurs via hopping between the localized states, which is why an almost linear increase in electrical conductivity is observed. Finally, our measurements also illustrate the influence of temperature on the conductivity of the composites. That is, our results demonstrate that the conduction process is thermally activated.[11]

In summary, we have investigated the electrical properties of conductive polymer composite films that contain a PUR matrix and CB nanofillers. We have used both experimental and theoretical approaches to assess the electrical properties. We find that the samples exhibit excellent electrical and mechanical characteristics, caused by the incorporation of CB into the PUR matrix. In our future work, we intend to use other conductive fillers (e.g., carbon nanotubes, graphene nanoplatelets, and conductive polymers) to improve the electrical and mechanical properties of additional natural polymers (such as natural rubber), with the aim of making them suitable for application as electrostatic dissipating devices, and as antistatic flooring and coating materials.

Author Information

Michael Jones Silva
Universidade Estadual Paulista (Unesp)
Rosana, Brazil

Michael Jones Silva obtained his PhD in materials science from Unesp and is now a professor. His work is focused on the development of conductive polymer composites and nanocomposites for applications as smart materials.

Paulo Vinicius Rebeque
Instituto Federal do Rio Grande do Sul
Bento Gonçalves, Brazil

Alex Otávio Sanches, José Antônio Malmonge, Haroldo Naoyuki Nagashima, and Darcy Hiroe Fujii Kanda
Department of Physics and Chemistry
Unesp
Ilha Solteira, Brazil

References

1. P. Marin-Franch, D. L. Tunnicliffe, and D. K. Das-Gupta, *Dielectric properties and spatial distribution of polarization of ceramic + polymer composite sensors*, **Mater. Res. Innov. 4**, pp. 334–339, 2001.
2. W. K. Sakamoto, P. Marin-Franch, and D. K. Gupta, *Characterization and application of PZT/PU and graphite doped PZT/PU composite*, **Sensors Actuat. A 100**, pp. 165–174, 2002.
3. F. Li, L. Qi, J. Yang, M. Xu, X. Luo, and D. Ma, *Polyurethane/conducting carbon black composites: structure, electric conductivity, strain recovery behavior, and their relationships*, **J. App. Polym. Sci. 75**, pp. 68–77, 2000.
4. M. J. da Silva, A. O. Sanches, L. F. Malmonge, and J. A. Malmonge, *Electrical, mechanical, and thermal analysis of natural rubber/polyaniline-Dbsa composite*, **Mater. Res. 17**, pp. 59–63, 2014.
5. M. J. Silva, A. O. Sanches, L. F. Malmonge, E. S. Medeiros, M. F. Rosa, C. M. McMahan, and J. A. Malmonge, *Conductive nanocomposites based on cellulose nanofibrils coated with polyaniline-DBSA via in situ polymerization*, **Macromolec. Symp. 319**, pp. 196–202, 2012.
6. M. J. da Silva, D. H. F. Kanda, and H. N. Nagashima, *Mechanism of charge transport in castor oil-based polyurethane/carbon black composite (PU/CB)*, **J. Non-Crys. Solids 358**, pp. 270–275, 2012.
7. I. Novák, I. Krupa, and I. Chodák, *Relation between electrical and mechanical properties in polyurethane/carbon black adhesives*, **J. Mater. Sci. Lett. 21**, pp. 1039–1041, 2002.
8. R. Strümpler and J. Glatz-Reichenbach, *Conducting polymer composites*, **J. Electroceram. 3**, pp. 329–346, 1999.
9. V. N. Prigodin and A. J. Epstein, *Nature of insulator-metal transition and novel mechanism of charge transport in the metallic state of highly doped electronic polymers*, **Synthetic Metals 125**, pp. 43–53, 2001.
10. N. F. Mott, **Metal-Insulator Transitions**, CRC Press, 1990.
11. P. V. Rebeque, M. J. Silva, C. R. Cena, H. N. Nagashima, J. A. Malmonge, and D. H. F. Kanda, *Analysis of the electrical conduction in percolative nanocomposites based on castor-oil polyurethane with carbon black and activated carbon nanopowder*, **Polym. Compos.**, 2017. doi:10.1002/pc.24588
12. M. D. Migahed, M. Ishra, T. Fahmy, and A. Barakat, *Electric modulus and AC conductivity studies in conducting PPy composite films at low temperature*, **J. Phys. Chem. Solids 65**, pp. 1121–1125, 2004.
13. Z. M. Eliamat, A. M. Zihlif, and G. Ragosta, *DC electrical conductivity of poly(methyl methacrylate)/carbon black composites at low temperatures*, **J. Mater. Sci. Mater. Electron. 19**, pp. 1035–1038, 2008.