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Thickness effect on electric resistivity on polystyrene and carbon black-based composites

S. Hernández-López¹, E. Viguera-Santiago¹, M. Mayorga -Rojas², D. Reyes-Contreras²

¹Laboratorio de Investigación y Desarrollo de Materiales Avanzados (LIDMA) Facultad de Química, Paseo Colón Esquina con Paseo Tollocan, s/n, CP 50000, Toluca estado de México.

²Facultad de Ciencias, Universidad Autónoma del Estado de México. Av. Instituto Literario 100 Ote. C. P. 50000, Toluca, Estado de México, México.

E-mail: evig uerass@uaemex.mx

Abstract. Changes on electrical resistivity were experimentally studied for polystyrene and carbon black-based composites respect to the temperature. 22% w/w carbon black composite films at 30 μm , 2mm y 1cm thick were submitted to thermal heating-cooling cycles from room temperature to 100°C, slightly up to T_g of the composite. For each cycle changes on electrical resistivity constituent a hysteresis loop that depends on the sample thickness. The changes during the heating stage could be explained as a consequence of the thermal expansion and mobility of the polymer chains at T_g , producing a disconnecting of the electrical contacts among carbon black particles and an important increasing (200%) of the electrical resistivity. For each cycle, the hysteresis loop was observed in thicker samples, whereas for 30 μm thickness sample the hysteresis loop was lost after four cycles.

1. Introduction

Is well know that in conductive polymer composites with carbon black (CB) the conductive to dielectric transition could carried out in two ways: one is modifying the CB particles concentration [1] and the other is by heating until some polymer transition is achieved as melting (T_m) or glass transition (T_g) temperatures in crystalline/semicrystalline and amorphous polymers, respectively [2]. The existence of these resistivity modifiers mechanisms has allowed the use of those type of composites materials in a broad gamma of practical applications [3]. Preparation, optimization and modification of the electrical properties in polymer composites are dependent of the couple polymer - carbon particles. This includes the physical and chemical properties of the polymer matrix; the geometry, size and morphology of the CB particles as essential factors for the final characteristics of the polymer composites [1-3]. The dependence of the resistivity with temperature could be metallic type as semiconductor one [4,5] and some polymer composites show it as the well known positive temperature coefficient (PTC). This PTC response consists in an increasing of the resistivity in some

magnitude orders when the composite is heated until T_m or T_g [2,6]. Significant attention has been paid to this effect in polymer composites based on semicrystalline thermoplastic polymers and epoxy resins or thermoset matrixes [7]. Temperature dependence of electrical conductivity in polymer composites are a function of the heating and cooling rate [7], of the number of heating-cooling cycles [8], the polymer-filler composite pair and their proportions [1-11]. Many are the factors involved in that behavior, however there are a few studies related with the sample thickness [9] as another variant which could be involve in the temperature response. Is worthy note that important information about mechanical and electrical stability, reversibility and electrical reproducibility of the systems trough these studies represent possible application such a thermal switches on temperature control, among others technological applications.

The basic mechanism of electro-thermal behavior is still understood because of the complex nature of the composites. However an accepted way for explaining the resistivity changes as a function of temperature considers the polymer matrix expansion during the heating process where the CB particles separates increasing the distance among them and diminishing the electrical contacts (conductive networks) [10].

In this work the electro-thermal behavior of polymer composites based on atactic (amorphous) polystyrene polymer and Vulcan XC72 -CB was studied. We show that the conductive composite thickness plays an important roll on electro-thermal behavior in these kinds of composites during heating-cooling cycles at their T_g . An electro-thermal open hysteresis loop was observed in all samples for the first cycles. At the end of the fourth cycle, the resistivity vs temperature curve was reversible for the thinnest sample and a close hysteresis loop was observed for thicker samples.

2. Experimental

Polystyrene (PS) 10,000 Mw, analytic grade tetrahydrofurane (THF) were purchased from Sigma-Aldrich, Co. Carbon black (CB) Vulcan XC72 was donated by Cabot Co. and they were used without any other treatment. Glass transition (T_g) of 22% PS+CB composite was 98°C as determined by calorimetry in a SDT Q600 Modulus, under nitrogen atmosphere and a heating rate of 10°C/min. Composite was obtained by ultrasonic mixing using THF as solvent [12]. Films of 30 μm thickness were deposited on glass substrates by spin coating using that solution. Then the solvent was evaporated from the remaining solution and cylinders of 2 mm and 1 cm heights and 4.5 mm radius were obtained by compressing moulding at 120 °C [12]. For films, electrical contacts were painted as parallel lines on the same face. For bulk samples both faces were full covered with conductive silver paste [12]. All samples were submitted to six heating-cooling cycles into a home made oven. During the heating samples were heated from room temperature (25°C) to 100°C (T_g of the composite) at a rate of 1.5°C/min. The cooling stage was from 100 to 25°C at 0.2°/min. Electrical resistance and temperature were measured simultaneously at intervals of one second using digital multimeters coupled to a computer.

3. Results and discussion

The effect of the composite thickness was relevant from the initial resistivity. There was a difference of three magnitude orders at least between the thinnest (30 μm) and the thicker films (Figure 1). The changes on electrical resistivity during the thermal treatments evidenced significantly variation according to the sample thickness too. They also showed a common behaviour which consisted on the different resistivity value between the initial (before the thermal treatment) and the end of the first cycle (Figure 1). This difference was really important for the thin layer (30 μm) for about one magnitude order higher. For thick samples that difference was depreciable (Figure 1).

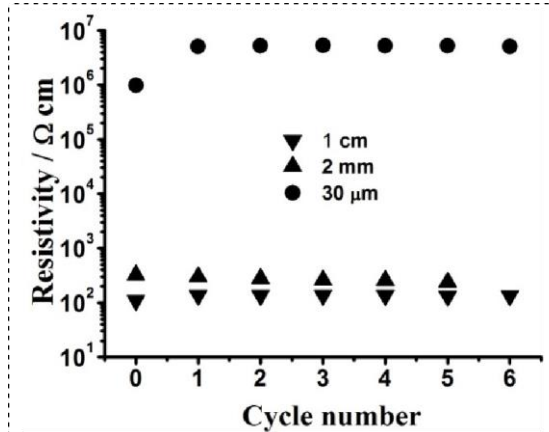


Figure 1. Resistivity values after each cycle number

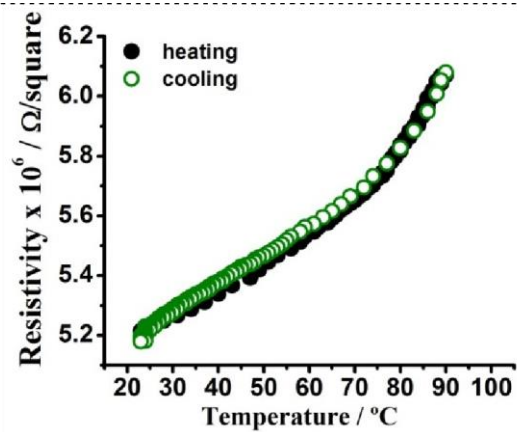


Figure 2. Resistivity behavior for the 30 μm film at fourth thermal cycle

With the increasing of the cycle's number, all samples tended to a stable resistivity value. This asymptotic behaviour was reached after the fourth cycle for 30 μm and 2 mm thickness samples (squares and triangles curves in Figure 1). For 30 μm film the resistivity changes were reversible (Figure 2) through the all trajectory whereas the resistivity for thick samples builds a close hysteresis loop after the fourth cycle (Figures 3 and 4). An explanation of those behaviours is related with a redistribution of the CB particles: during the heating, the thermal polymer expansion and the consequent increasing in the molecular movement lets a redistribution of them, a disconnection-reconnection of the conductive networks allowing a new conductive configuration.

This effect was more evident in the thinnest film due to the electro thermal response follow a reversible behaviour of the resistivity during the heating -cooling treatments meaning that a conductive network in equilibrium is accomplished. For thicker samples this equilibrium configuration was not reached even after 6 cycles following a close hysteresis loop. In this case there are continuous contact configuration changes of the carbon particles during the heating and cooling process, however the average of all of them predominate and render the same final resistivity value.

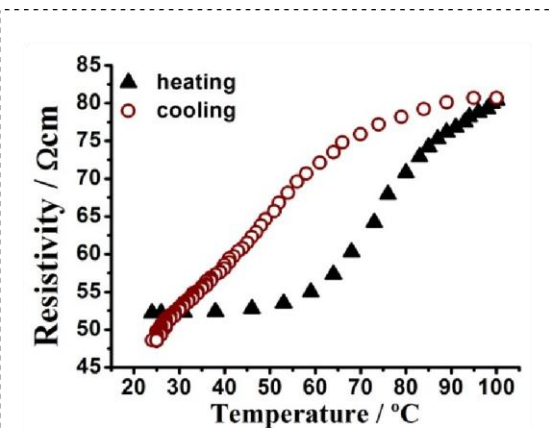


Figure 3. Open hysteresis loop for the resistivity as a function of temperature showed by the 2 mm sample at the third cycle.

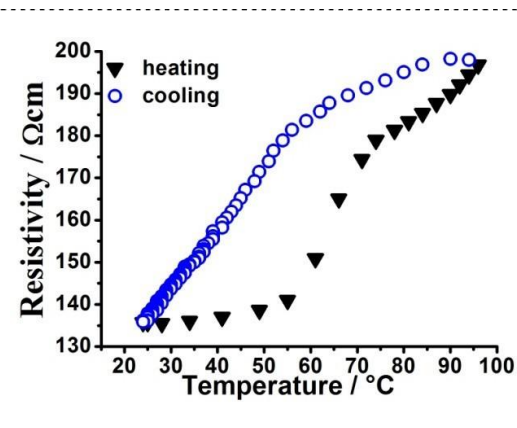


Figure 4. Close hysteresis loop for the 1 cm sample at the fourth cycle.

This redistribution explained in terms of the polymer movement has an important dependence of the thickness. As the thickness diminishes the contact's number among the conductive particles also diminishes in the same direction as the thickness do, according to the description in [13]. As a consequence the redistribution and probability of conductive particles to acquire the same conductive configuration is high for thin films, attributing them the observed reversibility.

4. Conclusions

Electrical resistivity of PS + CB composites reaches a stable final value after several heating -cooling cycles dependently of the sample thickness. For a thin composite film (30 μm) the hysteresis loop was lost after four cycles. For thicker samples the resistivity as temperature dependent showed a close hysteresis loop after being submitted to six treatments. We consider that those behaviours are associated to a change in spatial configuration and original distribution of the CB particles due to an increasing of the polymer chains motion as the temperature reaches its T_g . The number of CB-electrical contacts was clearly modified for the thin film during the first four cycles until it reached equilibrium. However for thicker samples the resistivity changed during the heating and cooling steps but at the end of the cycles that value was practically the same, meaning that total average of CB contacts was no modified.

5. Acknowledgments

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