

Changes in the Electrical Resistivity of Thin-Films for Polymer Composites Induced by Heating-Cooling Cycles

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Abstract: This paper is focus on the analysis of the electrical resistivity of polymer composites respect to the temperature when samples are under heating-cooling cycles in two type of experiments namely: (1) at three different heating rates and (2) an isothermic one. Three different films S1, S2 and S3 of Polystyrene + 22 wt% CB were submitted to several heating-cooling cycles until a reversing process of the resistivity behavior was reached for each film. The heating was performed from room temperature, RT (24 °C) to 120 °C at rates of 1, 2 and 5 °C/min, respectively. A fourth film S4 was exposed to isothermic-heating-cooling cycles, consisting on heat from RT to 120 °C (at 2 °C/min) and keep the film at 120 °C for 2.5 hours. The cooling rate was 0.2 °C/min for all samples. Results show that the cycle's number for reaching the electrical stability of films were strongly dependent on the heating rate more than the kind of process (continuous or isothermic). Main analysis shows that as a lower the heating rate (1 °C/min) the number of heating-cooling cycles for reaching the reversibility (electrical stability) are less (6 cycles in our case) than those for higher heating rates (9 and 12 cycles). Results are explained in terms of the redistribution of carbon black particles due to the composite's structural and thermal relaxation; in other words the dynamic polymer chain mobility during the heating process and the chain relaxation process during the cooling one.

Key words: Conductive polymer composites, PTC effect, thermostability.

Nomenclature

<i>PS:</i>	Polystyrene
<i>CB:</i>	Carbon black
<i>RT:</i>	Room temperature
<i>K:</i>	Kilo
<i>M:</i>	Mega
<i>CPC's:</i>	Conductive polymer composites
<i>T_g:</i>	Glass transition temperature
<i>T_m:</i>	Melting temperature
<i>PTC:</i>	Positive coefficient temperature
<i>rpm:</i>	Revolutions per minute
<i>I_R:</i>	Response intensity
<i>I_{PTC}:</i>	Response intensity of PTC

Greek letters

μ :	Micrometer
r :	Resistivity
r_T :	Resistivity at set temperature
r_{RT} :	Resistivity at room temperature
Ω :	Ohm

1. Introduction

The electrical conduction mechanism on polymer composites is based on the principle of formation of conducting paths due to electrical contact between conductive particles [1-9]. Conductive polymer composites exhibit stimulus-sensitive behavior that leads to the conductive particles to undergoing conformational changes in response to different external

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variables such as mechanical stresses or strain [10-13], when they are exposed for instance to natural and organic solvents or vapors [14-20], to changes in pressure [11, 21-24], electrical fields [25-28], or temperature. One of the thermal characteristics of conductive polymer composites (CPC's), is a sharp increase in resistivity while the temperature increases near to melting or glassy temperatures, T_m or T_g respectively, which is known as the positive temperature coefficient (PTC) effect [29-42]. PTC plays a relevant role in several practical applications such as thermal switches, on temperature control, self-regulating heaters, among others. However, polymer composites do not show reliable reproducibility in resistivity for long periods of exposition or when they undergo several thermal cycles. The basic mechanism of electro-thermal behavior is still not well understood because of the complex nature of the composites. However, an accepted explanation deduced from several mechanisms and models proposed for some authors [43-45] is that changes in resistivity as a function of temperature consider that conductive paths are broken due to the expansion of the polymer matrix (thermoplasticity effect) during the heating process: the interparticle distance increases significantly and decreases the number of conducting paths. According to the tunneling theory, the tunneling probability of an electron is related to the interparticle distance. Therefore, the probability of interparticle distance greater than 10 nm [41]. On the other hand, amorphous polystyrene is one of the most used polymers as an engineered material in which carbon particles could be dispersed. These composite materials have been studied as conductive, mechanically reinforced, gas sensors, and thermoelectric control in blends and several copolymers. Its thermoelectric response has been a few studied due to its amorphous nature. Their temperature response is not so high as in semicrystalline polymers as *st*-Polystyrene [45], polyethylene [44-46], polybutadiene [39],

polypropylene, polyesters [35, 40, 47], or polyamides (Ref. [48]), in which the volume thermal expansion is abrupt near to melting temperature T_m , observing changes in resistivity of many orders of magnitude, as well as in some crosslinked systems as epoxy resins and polyurethanes [29, 30]. However, the chain polymer movements achieved at its T_g is enough in order to get a stable electrical state and a moderate PTC. From all those studies, it has been evidenced that the PTC in CPCs greatly depends on the properties of polymer matrices [30, 46, 49], on the type and quantity of conducting fillers [30, 38, 41, 45, 49], on the processing condition [49], on the heating rate [29], on the range of heating (cooling) temperature (peak temperature) [36, 45, 47], on the isothermal treatments and on the number of treatments [36, 40, 50]. However, electrical stability with time, reversibility and electrical reproducibility of composite materials are very important parameters that are taken into account in the abovementioned applications and they have been seldom studied [36, 41, 47] along the entire heating-cooling process. Authors of the present paper have shown in a previous work that the thermo-electric behavior of this material also has a dependence with the thickness when samples undergo thermal cycles [42]. It was evaluated a polystyrene composite with carbon black, concluding that as thinner the sample, fewer cycle treatments needed the composite to reach the thermoelectrical stability.

In the present work, the electro-thermal behavior of around 100 μm films of a polymer composite based on polystyrene (PS) and carbon black (CB) Vulcan XC72 is studied during continuous heating-cooling cycles (from 24 to above T_g) respect to the heating rate and to the isothermic cycles. It is observed that the electrical resistivity increases during the heating process (PTC effect), decreases in the cooling step and after several continuous or isothermal cycles, electrical resistivity of the samples tends to stabilize at a definite value in a reversible process, and negative temperature coefficient (NTC) was not observed. The number of

cycles related with the ability to reach the stability, depends on the heating rate more than the type of the process (continuous or isothermic). We demonstrate that experiments on heating-cooling on thin films of PS + CB are a good technique to obtain composites with stable electrical resistivity. As we abovementioned, the reproducibility and time stability of the resistivity after the heating-cooling cycles are key parameters for their possible applications. Thin films reported in this paper displayed out good thermal stability due to their resistivity returns to the initial value after the overall cycle, independently of the type of thermal treatment, opening the possibility to use these as thermal actuators or another kind of thermometer depending on the final temperature of work, magnitude in resistivity change, the initial resistance, the rate of the response, etc [48, 49]. The difference of other reports on heating-cooling experiments with our work is that they not report the cooling process and they use some more sophisticated alternatives as chemical or irradiative crosslinking [51-53] and/or the use of organic [54] or inorganic additives [51, 55, 56] in order to reach stability and no to have NTC effect. Authors consider that during each cooling the polymeric chains relaxation leads to the CB nanoparticles was trapped going to a new spatial configuration which is must stable that the previous one until they reach a maximal and optimal configuration which do not change any more with further thermal cycles.

2. Materials and Experiments

Carbon Black (CB) as conductor material was donated by Cabot Co. polystyrene (PS) and tetrahydrofuran (THF) in analytic grade was purchased by Sigma-Aldrich Co., materials were used as received. 3 g of polymer composite (22 wt% CB) was obtained using the dissolution method in 300 mL of THF as solvent and an ultrasonic bath for dispersing the CB particles (20 °C and 12 hr of shakeup). Films of 100-130 μm in thickness were deposited on clean glass substrates (2 \times 2 cm) by spin coating (1,200 rpm) that

solution. Films were well dried under vacuum for 24 hr and then silver contacts were painted as parallel lines (of 3 mm width and separated 1 cm) on the same film face. From the remaining composite dissolution THF was removed by distillation in order to characterize the T_g of the composite. T_g was measured in a TA-Instruments SDT Q 600 modulus from 60 to 110 °C at a heating rate of 1, 2 and 5 °C/min and under nitrogen gas (100 mL/min). It was detected as the half of the step change in the line base from the second run, giving a value of 97, 100 and 103 °C, respectively.

Three films, *S1*, *S2* and *S3*, with initial resistivities of 0.98, 0.35 and 0.16 M/square, had to be submitted to six, nine and twelve heating-cooling cycles, respectively on a made-oven in order to reach the electrical stability established by a reversible behavior of the resistivity during the heating and cooling process. The samples were heated at rate of 1, 2 and 5 °C/min respectively, from room temperature (24 °C) to 120 °C. A fourth sample *S4* (0.17 M/square) had to be exposed to six heating-cooling isothermal-cycles from room temperature to 120 degrees holding the sample at this temperature for 2.5 hr, and then allowed the cooling. The cooling process was carried out at a rate of 0.2 °C/min for all samples. Electrical resistance and temperature were simultaneously measured at intervals of one minute using digital multimeters coupled to a computer.

3. Experimental Results

The graphics show the first, second and the last heating-cooling cycles for each sample. The respective curves describe the evolution of electrical resistivity as a function of temperature at a given heating rate.

Fig. 1 shows the electro-thermal behavior for the sample *S1*, which was under thermal heating-cooling cycles at a heating rate of 1 °C/min. Circles represent the electrical resistivity data for the heating process and hollow triangles the same parameter but for cooling step. Initial electrical resistivity for *S1* before to start the first thermal cycle was 0.97 M Ω /square, a value

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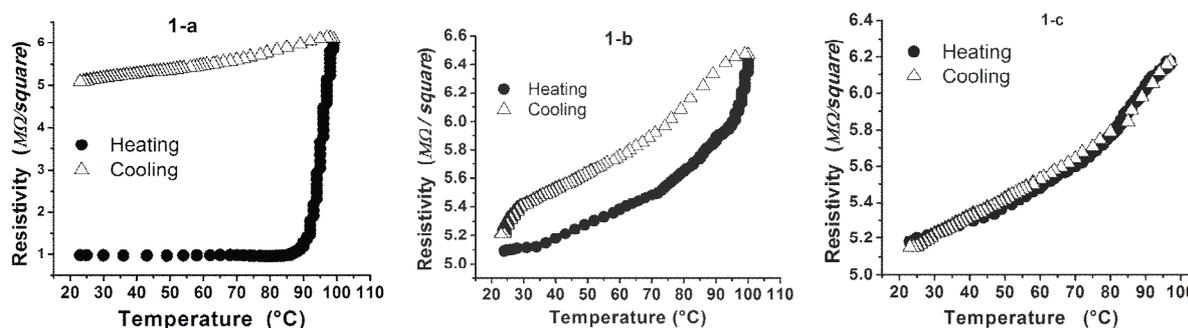


Fig. 1 Electro-thermal behavior for the sample *S1* (heating rate at 1 °C/min). Heating and cooling curves for (a) the first cycle, (b) second cycle and (c) Sixth cycle.

that is constant until 90 °C, very close to its T_g , and at this point the trajectory becomes exponential and the resistivity increases sharply until it reaches its maximal resistivity, 6.10 MΩ/square. At this moment the resistivity change, Δr is 5.10 MΩ/square and the intensity of the resistivity response, $I_R = \log(r_T/r_{RT})$, is 0.79.

During the cooling process the resistivity decreases as shown in Fig. 1-a. However, at the end of the first cooling step the resistivity does not return to its initial value, then another room-temperature resistivity was obtained, and this resistivity is the initial point for next cycle. The value at this point was 5.10 MΩ/square, showing an increase of 4.10 MΩ/square with respect to its initial value. For the second thermal-cycle, the electrical behavior of the sample *S1* was a quite different to the first (Fig. 1b). It started at 5.10 MΩ/square and it could be observed (Fig. 1b) that resistivity increases from the beginning of the heating step, it is almost linear until the final temperature, reaching a maximal resistivity (6.50 MΩ/square), but

giving a lower $\Delta r = 1.40$ and $I_R = 0.11$ than those for the first cycle.

In the same way as the first cycle, during cooling process the resistivity decreases (at 5.20 MΩ/square), but it does not reach the same value as the initial for this second cycle, however there is a difference of only 0.10 MΩ/square. From the second to the fifth cycle, the thermo electrical behavior is very similar; the only difference is that the hysteresis loop gets closer. For sample *S1* were enough six heating-cooling cycles in order to obtain a reversible process of the electrical behavior. At the sixth and further cycles the hysteresis loop converted in almost a perfect one reversible way for resistivity (Fig. 1c).

Figs. 2 and 3 describe the electrical behavior of the sample *S2* and *S3*, which were heated at 2 and 5 °C/min all the heating steps, respectively. The observed behavior for both samples was very similar to *S1* in the sense of an increasing in resistivity during the heating process, a decreasing of it during the cooling steps, the hysteresis loop which gets closer as the cycle

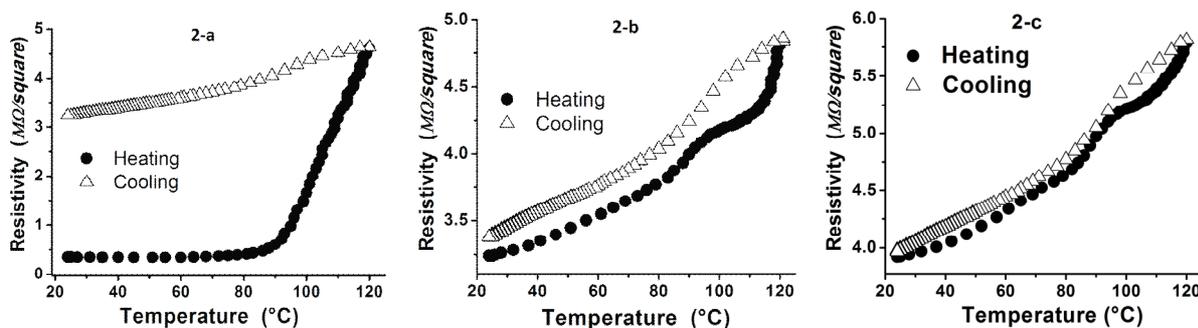


Fig. 2 Electro-thermal behavior for the sample *S2* (heating rate at 2 °C/min). Heating and cooling curves for (a) the first cycle, (b) second cycle and (c) Ninth cycle.

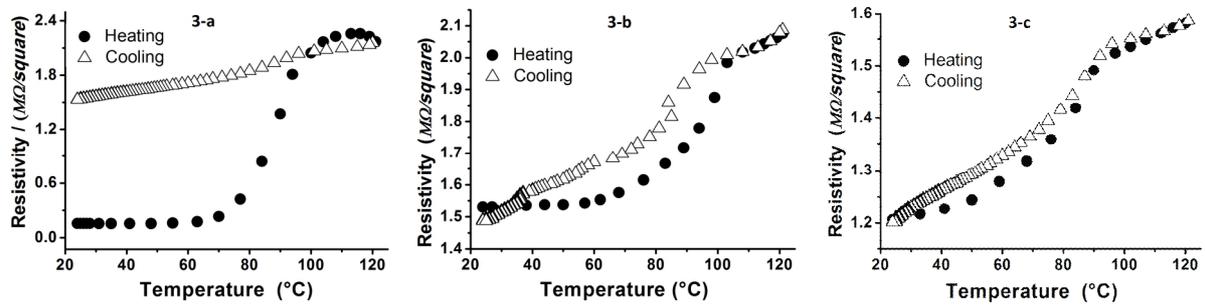


Fig. 3 Electro-thermal behavior for the sample S3 (heating rate at 5 °C/min). Heating and cooling curves for (a) the first cycle, (b) second cycle and (c) twelfth cycle.

Table 1 % $\Delta\rho$ in first, second and the last cycle for the four samples, as well as the intensity of the PTC response, I_R for the last heating treatment.

Number of cycle	$\Delta\rho\%/I_R$			
	S1	S2	S3	S4
First	423/0.80	825/0.12	838/1.14	1330/1.2
Second	1.90/0.11	4.0/0.18	2.0/0.14	13.70/0.15
Last	(6th) 0.56/0.08	(9th)* -1.10/ 0.16	(12th) 0.40/0.12	(7th) 0.90/0.12

* The negative sign is due to the resistivity at the end of the last cooling rate was minor than the initial heating rate in that last cycle.

numbers increases and finally it disappears and become in a reversible process.

Table 1 summarizes the $\Delta\rho$ percentage between the initial, second and final resistivity of the samples and the intensity of the resistivity response for the last heating process that could be attributable to the PTC response of the stabilized films.

Thinking that isothermic treatments at 120 °C could accelerate the equilibrium (reversibility) of the resistivity behavior, the sample S4 was exposed to seven isothermal-cycles. The results were similar to the discussed before but, at difference of the sample S3 in which was used the same heating rate and needed 12 thermal cycles, the sample S4 reached the stability before, at the seventh cycle. It seems to be an advantage however these experiments were very long and it does not deserve the inverted time. Fig. 4 shows only the heating and isothermic behavior for each cycle and it illustrates that once the sample reaches 120 °C which takes around 48 min (2 °C/min) and is distinguished by the sharply increasing in resistivity in all curves of Fig. 4 the resistivity practically does not change during the isothermic treatment, it only fluctuates around ± 0.15 MΩ/square. The resistivity in

the first heating until 120 °C increases from 0.17 to 2.43 MΩ/square and during the isothermic process it reaches as maximal value 3.0 MΩ/square ($\Delta\rho = 2.80$ MΩ/square, $I_R = 1.20$). The electrical resistivity at the end of the cooling process, similar to previous samples does not return to the initial value, it reaches 2.43 MΩ/square. This behavior is observed for further cycles until resistance converges at the sixth and seventh cycles as it can seen in Fig. 4, being it the moment considered as the sample has reached it stability. At the end of the seventh cooling the resistivity has reached 3.24 MΩ/square which is the

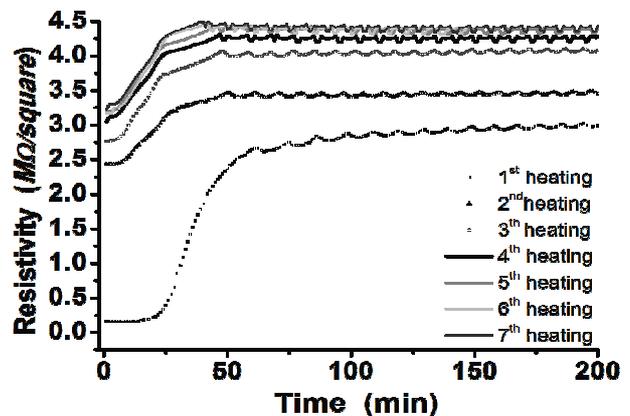


Fig. 4 Electro-thermal behaviors to sample S4 as temperature function in isothermal-cycles.

same value at the sixth cycle.

4. Discussion

Experimental results showed very interesting behavior of electrical resistivity as a function of the heating rate in the polymeric compound studied. The electrical resistivity during the heating process increased to a maximum value and decreases during the cooling process without returning to its original value in all samples, tracing a hysteresis loop in resistivity. However, after several thermal and isothermal cycles, electrical resistivity stabilizes and forms one way in the full cycle, showing that the thermo-electric process becomes almost perfectly reversible. As it can be seen in Table 1, there is a $\Delta\rho$ of less than 1% at the stabilized process which is trivial but reliable in comparison with the first three of four cycles.

It is evident that the variation percentage of electrical resistivity in the first heat cycle is very large in comparison with the second and last treatment in all four samples. This electrical response is the same regardless of experimental conditions at least for this compound. The changes of resistivity at the end of the first cycle are very sharply due the mechanical history (spin-coating) which is erased by heating-cooling process. During the production of the thin films, the carbon black particles and polymeric networks are stressed in some way when simultaneously the solvent is evaporated and the chains are submitted to centrifuge force. The resistivity increasing during the heating is associated more than to a thermal expansion of the composite, specifically of the polymer matrix, to a movement of the polymer chains. From the glassy to the rubber state the polymer chains start to get a coordinated segmental motion as they reach the T_g . The effect of thermal expansion and chain movements is directly associated with the physical disconnection (separation) and reconnection of the CB particles but the equilibrium could be slower or faster depending on the heating rate. When the heating rate is slow ($1\text{ }^\circ\text{C}/\text{min}$), even the disconnection is evident near to T_g ,

the softly movements of polymer chains their kinetic energy increases slowly permit to release the tension faster giving to the carbon blacks particles and chains more time to found together another more stable configuration in each cycle.

During the cooling process the mobility of chains polymer is also reduced as a result of thermal relaxation and the CB particles are reconnected again until the temperature is enough below T_g that chains do not have more movements (only vibrations) “freezing” the new configurations, and decreasing the resistivity. These new contacts could be evidenced by the different hysteresis loop shown after the first cycles. The irreversibility of resistivity during the complete cycle is the result of the redistribution. As the cycles number increases, the electrical resistivity returns almost exactly by the same path. At this point the spatial configuration of polymer chains and CB particles has reached its most stable conformation, which does not change by subsequent thermal cycles at the same experimental conditions.

The isothermal treatments done to the sample *S4* have the same behavior as previous samples during the heating ($24\text{-}120\text{ }^\circ\text{C}$) and cooling processes, increasing and decreasing in each case. Resistivity fluctuations in the isothermal process are associated with little changes in temperature, which induces a weak disconnection-reconnection of the carbon black particles. Fig. 4 indicates that the thermoelectric performance of the polymeric compound studied is very similar when it is subjected to thermal treatments under different experimental conditions. In this study we choice a long time thinking the equilibrium could be reached with only one or two cycles due to the relative long time to reorganize the chain polymers and the conductive particles in a better geometry and more stable conductive networks. However, it could be interesting explore other isothermic times longer and shorter than the considered in this work. As observed in another work [40] made on semicrystalline matrix with carbon black, samples were submitted to different

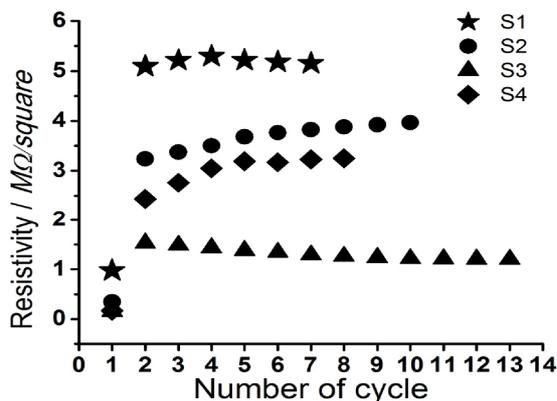


Fig. 5 Resistivity of the four samples after each cycle.

isothermic times resulting important in the PTC response unfortunately they don't make stability experiments under those conditions.

Fig. 5 summarizes the resistivity of the studied samples after each full heating-cooling cycle. It could be clearly appreciated that the resistivity tends to stabilize at a fixed value in all cases. This effect is associated with the fact that both polymer chains and conductive fillers equilibrate into a more stable spatial configuration reaching it faster as the heating rate is low.

Finally, as is exhibit in Table 1, the results of the response intensity (IR) of the films during the first, second and last heating are really important. As we analyze once the samples have reached the stability (last heating) show similar values of IR (around 0.12) which could be considered as the real IPTC. They were much smaller than corresponding to the first cycle, but independent of the heating rate treatment. These results are opposite to those obtained by Hirano, et al. [29]. They analyze the PTC response in epoxy resins as a function of the heating rate, concluded that the IPTC becomes important as the heating rate increases. At low heating rates (less than 0.3 min) the PTC intensity response (IPTC) is almost imperceptible compared with those obtained at higher heating rates. They explain their results in terms of at higher rates the conductive particles move quickly with the abrupt polymer expansion.

In this case the same response was not observed and

it could be due to the dissimilar polymer composite system under study, the different explored heating rates, but also that they considered as real PTC the first heating treatment. In our case, once equilibrated the samples, the real I_{PTC} as expected, was very small but independent of the heating. Considering that films with similar thickness were prepared from the same mix solution, it is logic that after any kind of thermal treatment and started resistivity, the composite reaches the stability in which the same PTC response intensity is achieved.

5. Conclusions

Films of PS + NC-based composite shown different thermoelectric behavior directly associated with the heating rate in heating-cooling cycles and in turn with the slow or fast mobility when the polymer chains reach the T_g . Polymer chains movements and the polymer expansion during the heating step induce the separation and reorganization of conductive particles in such a way that the hysteresis loop in resistivity as a function of the number of heating-cooling cycles gets closer until it becomes in a one reversible way. At this moment, it is considered that films acquire a thermal equilibrium in which polymer chains and carbon black particles have achieve the most stable geometry. In this status the resistivity stabilizes at specific values at each exposed temperature during heating or cooling steps. The isothermic experiment analyzed has no an important influence in to reach faster the stability of the sample. Finally, the intensity response for the last heating process in each sample was calculated in order to compare the real PTC intensity for a stabilized sample respect to the first or second cycles which usually are considered in other works as the valid PTC response. In this work was demonstrate the relevance in to stabilize first the thermoelectric response of a sample independent of the thermal treatment and initial electrical properties, in order to have properties in this case a PTC response, reliable and reproducible which are very important parameters taken in account at the

moment of thinking in a practical application.

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