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Study of the Thermally Stimulated Depolarization Current (TSDC) for composites of Acrylonitrile Butadiene Rubber (NBR) loaded with HAF

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Abstract

The thermally stimulated discharge (TSDC) current is studied for acrylonitrile butadiene rubber (NBR) loaded with different high abrasion furnace carbon black (HAF). TSDC peak appears only for higher HAF contents > 60phr (70 and 80phr of HAF contents), the TSDC spectra consist of a sharp peak corresponding to a peak temperature T_m which is slightly shifted to higher temperature for 70phr loaded NBR samples and to lower temperature for 80phr loaded NBR sample, with poling field (10V/cm to 50V/cm). The activation energy U and relaxation time τ for TSDC peak were calculated using the initial rise method. The calculated values of U are nearly constant for sample 70phr and slightly increase for sample 80phr with increasing poling field E_p. The calculated values of τ at peak temperature T_m are nearly constant for two samples (70phr & 80phr) with different poling field, whereas the calculated values of relaxation time τ at T_o = 300K increased with increase of poling field.

Keywords*:* Conductive elastomers TSDC; acrylonitrile butadiene rubber (NBR); HAF

1. Introduction

Conductive elastomers (CEs) have been used for many years in switches in automobile horns and door open sensors, and automobile ignition wires are made of this material. CEs have found wide use in applications involving dissipation of static electricity. This includes many applications in hospital operating rooms where a spark could ignite highly explosive anesthetics. Automobile and truck tires, especially for vehicles carrying explosives, are made conductive to eliminate sparking. Many integrated circuit chips can be destroyed by static discharge. To prevent this, CE devices are used to electrically connect the chip leads during shipping and also ground those handling the chips. CEs have been used extensively in electromagnetic shielding gaskets in military and nonmilitary applications [1].

Conductive rubber composites are widely used for different applications such as electrostatic charge dissipation, touch control switches and electromagnetic interference (EMI) shielding, and surface heaters. These materials need the desired electrical properties as well as sound mechanical properties. Various rubbers are being widely used for preparation of such composites, e.g., silicone, nitrile, butyl, natural rubber, ethylene-propylene rubber (EPR) and ethylene-propylene-diene monomer (EPDM), rubber (*c.f.* [2] and related references cited therein).

Acrylonitrile butadiene rubber (NBR) is a synthetic rubber and is one of the most widely used commercialized and mass productive elastomers. However, its mechanical properties like tensile and tear strength are poor. Such properties can be improved by adding fine particle fillers during the vulcanization process of NBR [3-7]. Among the available fillers, carbon black is one of the most suitable fillers because it is not only improving the mechanical, but also the electrical properties besides being a low cost filler. There are different types of carbon black and each type has specific properties such as surface area, particle size, structure and its tendency to aggregate. One of the most widely used types is high abrasion furnace (HAF) due to its small particle size and giving a good abrasion resistance and tensile strength [8].

The thermally stimulated depolarization current (TSDC) technique was introduced three decades ago for investigating the dielectric properties of alkali halides. The TSDC is considered as a basic tool for the identification and evaluation of dipole

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orientation processes and of trapping and recombination levels. The reason that TSDC, a thermal analysis technique, is being used increasingly relates to two factors: high sensitivity and high resolution. The sensitivity arises because electrical techniques can yield signals derived from exceedingly subtle effects [9].

This study focused on TSDC of NBR loaded with different concentration of HAF black. The effect of HAF-black contents on the TSDC spectrum will also be investigated. In addition, we restrict our attention to investigating the relaxation process in NBR/HAF composites via (TSDC) technique. Evaluation of peak parameters, such as activation energy and relaxation time has been carried out.

2. Experimental details

The properties of the rubber composites depend largely on the preparation method [10], such as the order of adding the ingredients, time of mixing and processing. So it is very important that all samples have the same circumstances and pass through the same procedure. The rubber composites were prepared by using a two roll mill of 300 mm length, 170mm diameter with speed of slow roll 18 rev /min and gear ratio 1.4 [11]. The prepared compounded rubber was left for at least 24 hours before vulcanization. The vulcanization process was conducted at 140°C under a pressure of 40Kg/cm^2 for 30 min inside a stainless steel mold and separated from its surface using sheets of polyethylene terephthalte (PET) to avoid adhesion after vulcanization process. For reasonable stability and reproducibility of parameter, samples were subjected to thermal aging at 343K for 25 days in an electrical oven before measurements were made [12, 13]. The obtained films were in the form of sheets with a thickness of 0.5 cm. The samples have the compositions shown in Table (1). They were prepared from commercial ingredients according to standard techniques [14].

The samples used in TSDC-measurements were cut in desk shape with diameter 1cm. The sample holder consists of two parallel plates of brass electrodes, which were isolated from each other using Teflon. In thermally stimulated depolarization (TSD) experiment the sample is exposed to static field E_p for time t_p, at a fixed temperature T_p; the temperature should be enough to allow the complete orientation of all the dipoles, and not too high, in order to avoid heavy space-charge contributions in depolarization process [15]. Moreover, to reduce this kind of electric relaxation, space charge, after the field is switched off, the electrodes are short-circuited for a certain amount of time to remove stray charges. This is followed by quenching to lower temperature and the depolarization current is measured during a slow heating to higher temperature again.

Table 1. Composition of NBR samples containing different concentrations of HAF carbon black

Ingredient (phr)*	**Samples**										
NBR	100	100	100	100	100	100	100	100	100	100	100
HAF(N-330)	0	10	20	30	40	50	60	70	80	90	100
Processing oil	10	10	10	10	10	10	10	10	10	10	10
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBTS	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
PBN	1	1	1	1	1	1	1	1	1	1	1
Zinc	5	5	5	5	5	5	5	5	5	5	5
Sulfur	2	2	2	2	2	2	2	2	2	2	2

*Parts per hundred parts of rubber by weight

In order to investigate the behavior of TSDC on heating, all samples were poled after preparation in order to investigate the TSDC properties. The poling conditions were the same for all samples (t_p=60 min, T_p=100°C) except the poling field which is altered and takes the values in range (10 V/cm–3×10^3 V/cm). The samples were subsequently warmed up at a constant rate 1°C/min, and the discharge current was registered as a function of temperature using digital electrometer type (Keithley 616), with a range varying from 10^{-13} to 10^{-1}A. The sensitivity of temperature reading is 0.1°C using thermometer (PHYWE GTH 1160).

3. Result and Discussion

Figures 1 and 2 show the effect of poling field for pure NBR and loaded with low HAF content ≤30phr samples on the TSDC – temperature. It may be concluded from this figure that the TSDC shows a good stability with no decay (for all pure and / NBR samples loaded with low HAF content ≤30phr), where above it the TSDC spectrum (for all loaded NBR samples) shows a reduction of space charge in the NBR matrix upon increasing the value of E_p (1×10^3 – 3×10^3 V/cm). Furthermore, Van Turnhout [16] indicated that the space charge may be released at temperatures greater than the dipolar relaxation maxima.

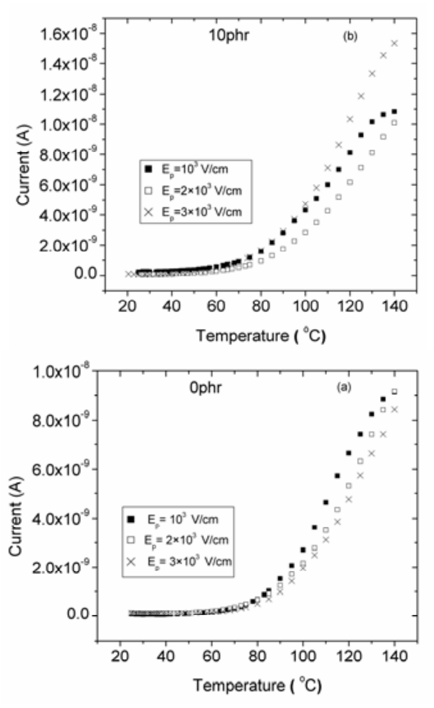


Fig. 1. The effect of poling field on the TSDC-temperature curves for 0phr10phr samples respectively.

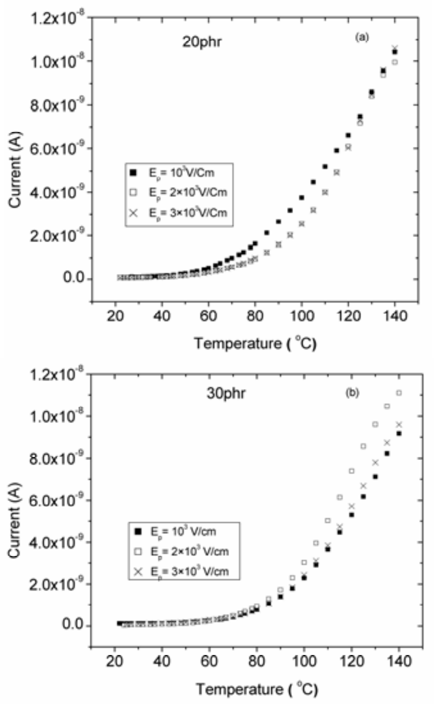


Fig. 2. The effect of poling field on the TSDC-temperature curves for 20phr 30phr samples respectively

For moderate HAF contents (40 & 60phr) in the NBR matrix (Figs. 3, 4) a small kink around 130°C was detected (that vanishes with higher poling field). This means that, such concentrations of HAF (40 and 60phr) are sufficient to induce appreciable change in the morphological behavior of NBR in the composite. The increase of values of TSDC with HAF contents is once more understood on the basis of the high polarizability of HAF particles and their role in TSDC and in orienting the dipoles [8, 17].

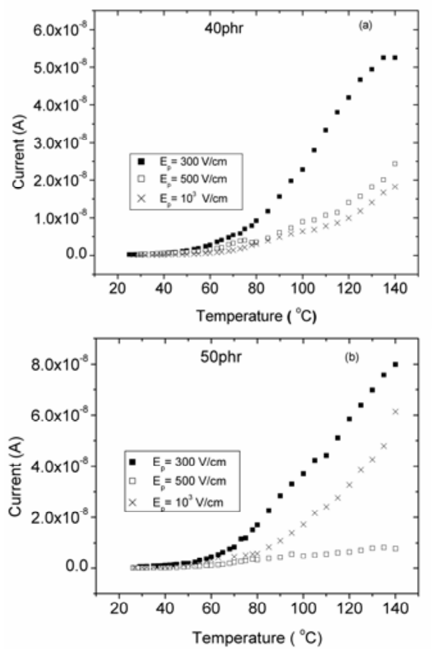


Fig. 3. The effect of poling field on the TSDC-temperature curves for 40phr 50phr samples respectively

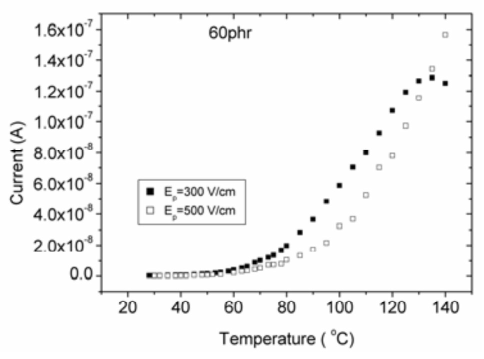


Fig. 4. The effect of poling field on the TSDC-temperature curves for 60phr sample

For higher HAF contents > 60phr (70 and 80phr of HAF contents) shown in Figs. 5 and 6, the TSDC spectra consists of a sharp peak corresponding to a peak temperature T_m which is slightly shifted-to higher temperature for 70phr loaded NBR samples and to lower temperature for 80phr loaded NBR sample-with poling fields ranging from 10V/cm to

50V/cm. The peak current I_m is plotted as a function of the polarizing field as shown in Fig. 7 for 70 and 80phr loaded samples. This peak current is inversely proportional to the polarizing field within the experimental range.

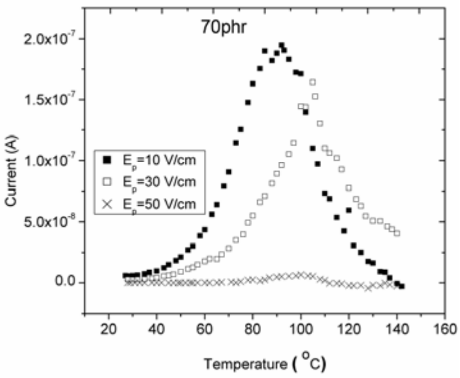


Fig. 5. The effect of poling field on the TSDC-temperature curve for 70phr sample

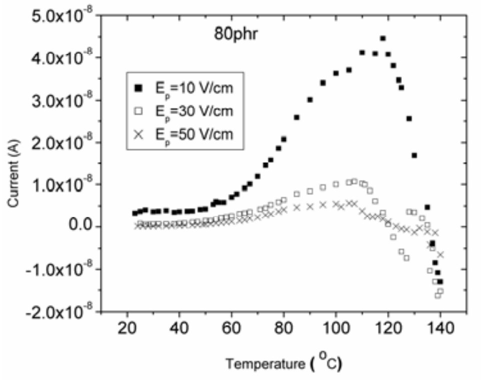


Fig. 6. The effect of poling field on the TSDC-temperature curve for 80ph sample

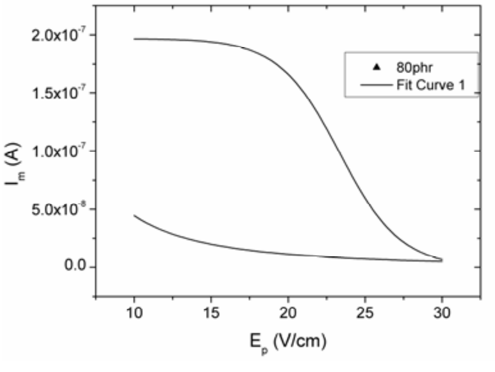


Fig. 7. The peak current I_m as a function of polarizing field for 70 and 80 phr loaded NBR samples

In the considered temperature range, the proposed relaxation mechanisms are uniform (for samples 70 and 80 HAF/NBR), and may be due to dipole relaxation or to migration of ionic and electronic charge carriers. If a non-distributed relaxation process is assumed, both relaxation processes can be described by similar equations for the depolarization current density. The equation which was introduced by Bucci et al [18, 19], who called their method ionic thermocurrent (ITC), is:-

$$J(T) = A\exp\left[-\frac{U}{KT} - \frac{\upsilon^{-1}}{\tau_0}\int_{T_0}^{T}\exp\left(-\frac{U}{KT'}\right)dT'\right] \qquad (1)$$

where U is the activation energy, K the Boltzmann constant, υ is the heating rate (1°C/min), T is a temperature well above the temperature of the maximum of the TSDC peak and T_o (the so called freezing temperature) is the initial temperature of the TSDC discharge. In the case of the dipole relaxation the constants A and B are:

$$A = \frac{P_0}{\tau_0} = \frac{N\mu^2 E_p}{3KT_p\tau_0} \qquad (2)$$

$$B = \tau_0^{-1} \qquad (3)$$

where τ_0 is the pre-exponential factor in an Arrhenius type relaxation time and P_o is the total polarization achieved, which can be expressed in terms of the number of dipole per unit volume N, their dipolar moment μ, the applied field E_p and the polarization temperature T_p by means of the Langevin law with the approximation $\mu E_p \ll KT$. In the case of ionic charge relaxation these constants are:

$$A = \frac{\sigma_0 Q_0}{\varepsilon_r \varepsilon_0} \qquad (4)$$

$$B = \frac{\sigma_0}{\varepsilon_r \varepsilon_0} \qquad (5)$$

where Q_o is the image charge induced on the sample electrode, σ_o is the pre-exponential factor in an Arrhenius type conductivity, and ε_o and ε_r are the vacuum and relative permittivity respectively.

On differentiating equation (1), the relation between the temperature T_m at which the maximum current and τ_0 flows can be written as:

$$\tau_0 = (KT_m^2)/[\upsilon U\exp(U/KT_m)] \qquad (6)$$

where υ is the heating rate. The low temperature tail of equation (1) may be written as:

$$\ln J(T) = \text{constant} - U/KT \qquad (7)$$

U may be determined from a semi-log plot of J(T) versus 1/T, the "initial rise method" of Garlick and Gibson [20]. Using this value of U and equation (6) and equation:

$$\tau = \tau_0 \exp(\frac{U}{KT}) \quad (8)$$

the value of τ at T_m and room temperature, say 300K, may be calculated.

For the determination of activation energy U and relaxation time using the initial rise method [20], ln J(T) versus 1/T is plotted in Figs. 8 and 9. The activation energy is calculated making use of equation (7). The relaxation time at T_m and 300K is calculated using equation (8) (cf Table 2). The values of calculated activation energy U from initial rising method are nearly constant for sample 70phr and slightly increase for sample 80phr with increasing poling field E_p. The calculated values of relaxation time τ at peak temperature T_m are nearly constant for two samples (70phr & 80phr) with different poling field, whereas the calculated values of relaxation time τ at T_o = 300K increased with increasing poling field.

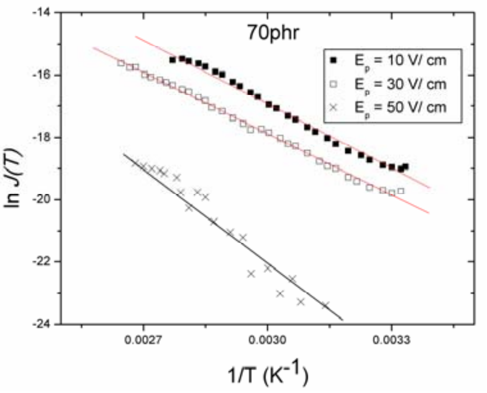


Fig. 8. ln J(T) versus 1/T for 70phr sample at different values of poling field E_p

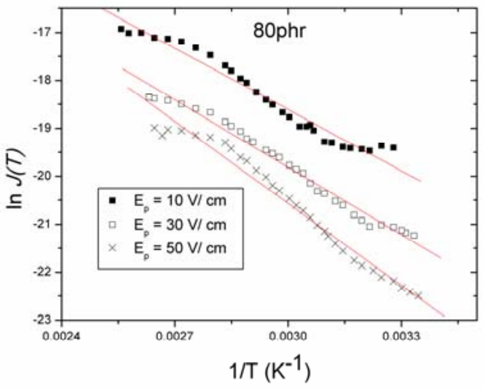
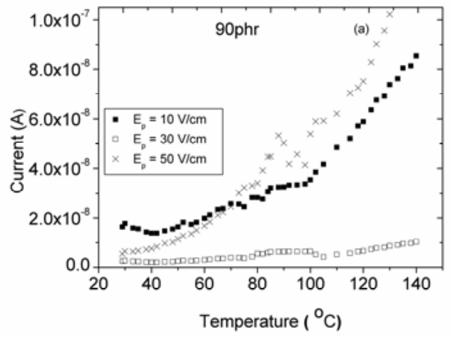


Fig. 9. ln J(T) versus 1/T for 80phr sample at different values of poling field E_p.

Table 2. The values of the calculated activation energies and relaxation times for 70phr and 80phr samples at different poling fields

HAF contents (phr)	E_p(V/cm)	U (Activation Energy)(ev)	τ (hr) at T_m	τ (hr) at 300K
70	10	0.59	0.33	18.8
	30	0.57	0.36	31
	50	0.6	0.35	52.8
80	10	0.37	0.55	11.7
	30	0.4	0.5	13.6
	50	0.49	0.42	20

For samples 90phr and 100phr as shown in Fig. 10, small peaks exist nearly at the same T_m as in 70phr and 80phr. These small peaks may be due to high aggregation of carbon black particles in these HAF contents (90phr and 100phr) which reduces the density of trapping centers [21].



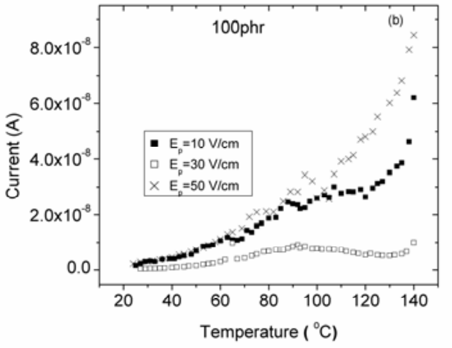


Fig. 10. The effect of poling field on the TSDC-temperature curve for samples 90phr and100phr respectively

4. Conclusion

TSDC for low loaded NBR composite with HAF shows a good stability with no decay. For higher concentration of carbon black, the TSDC spectrum for all loaded NBR samples shows a reduction of space charge in the NBR matrix upon increasing the value of E_p from 1×10^3 V/cm to 3×10^3 V/cm. Meanwhile, for moderate HAF contents (40 & 60phr) in the NBR matrix a small kink around 130°C was detected, the kink vanished with higher poling field. This means that, this concentration of HAF (40 and 60phr) is sufficient to induce appreciable change in the morphological behavior for NBR in the composite. Bond heterogeneity polarization, detrapping of charge carriers from trapping sites of various types, and conductive filler in the NBR matrix are among the important factors to be considered in accounting for the proposed mechanisms responsible for the TSDC in HAF/NBR composites.

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