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TSDC spectra in negatively corona charged ABS electrets

M. D. Migahed*, A. M. Shaban, A. EL-Khodary, and H. R. Hafiz

Department of Physics, Faculty of Science, Mansoura University, Mansoura, Egypt

SUMMARY

Corona charging technique has been used during polymer electret formation.Investigations of the thermally stimulated depolarization current (TSDC) in the electrets formed from Acrylonitrile-Butadiene-Styrene (ABS) terpolymer films were carried out. The optimum conditions for negatively corona-charged ABS films were determined. With the aid of partial heating technique, a single peak was obtained at $T=381\pm2$ K. This peak is associated with the temperature which was attributed to the motion of the bulk detrapping electrons arising from the thermal agitation as well as from erosion of the traps by the molecular motion. The activation energy of the process has been calculated. The electret property can be described in terms of dipolar relaxation process .

I . INTRODUCTION

Many polymers can be considered as electrically insulating and poor conductors of charges .. However, these materials can be transfered into an electret by corona charging (1,2). Charging processes consist in the deposition of real charges either on the surface or in the bulk material at room or elevated temperatures . The charged materials can be characterized by measuring the discharge currents under isothermal conditions as a function of the poling conditions . The TSDC technique has widely been used to investigate electret properties and their dependence on molecular relaxation processes taking place in the polymer (3-6). By thermally depolarization of the polymer electrets in a wide range of temperatures, various molecular motions including those related to the glass-rubber transtion are revealed (7). ABS has a special interest because of its widely practical applications in electrothermography . Studies on the ABS thermoelectret have been previously performed (8-10). The use of a corona discharges are now extensively used (11). Hence, the influence of some corona charging parameters on the ABS electret properties will be discussed in this work . It is aimed to gain a basic knowledge on the relationships between the total spectrum of molecular motions of the polymer chains which depends on chargig condition and electret properties to determine trapping parameters and hopefully the nature of the trapping sites .

II. MATERIAL AND EXPERIMENTAL TECHNIQUES

Acrylonitrile - Butadiene - Styrene copolymer is Novodur ABS - PH-AT of Bayer AG , West Germany . It consists of Acrylonitrile (A) Styrene (S)

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*To whom offprint requests should be sent copolymer grafted on polybutadiene (B). The relative compositions of the copolymer are A : 24 % , B : 14 % and S : 62 % . I R studies were done with Infrared Spectrometer Perkin Elmer 1430 . The I R spectrum of ABS films proved the presence of functional group such as the nitrile group which in turn did not affected by the heat treatment (12).

Differential scanning calorimetry (DSC) studies in the present work (12) show that ABS does not have a well-defined glass-transition temperature T_m . A weak transition-temperature was observed at about 393 K .

Films of thickness 40 - 110 µ m were prepared using Carver Laboratory hot press model M 2114 Freds supplied by Carver Fountain U.S.A. . The optimum condition of temperature and pressure were 430 K and 2.575 k bar respectively . The time allowed for the complete process was 20 min. .

The sample temperature was measured using Beckman industrial temperature /voltage converter thermocouple (TP 850). Current was recoreded using a Keithly electrometer type 610 C .

The corona charging method can be achieved by applying the threshold voltage for the avalanche process in which the corona region exists . The negative corona electrode which is a brush of very smooth graphite fibre of diameter 10 µ m is connected with the negative terminal of the high voltage biasing power supply . The counter electrode is a spring sheet connected with the ground and 1.0 mm spaced (by air at atmospheric pressure)from the corona electrode (Ag-paste). The Keithly electrometer is connected in series between the counter electrode and ground . By increasing the applied votage , the current through the electrometer increases and at a certain voltage the current begins to increase rapidly (avalanche) which is an evidence for the corona begining .

Partial heating (PH) technique is used for resolving the TSDC spectrum . This technique consists of preconditioning the sample at 413 K for 15 min. in a short circuit configuration to remove any induced charges. Then the sample is formed into thermoelectret by polarising it at 383 K by an electric field of about $5x10^6$ v/m for one hour and finally quenched to the room temperature with the field still applied . The sample is then partially depolarized by partial heating (separated by cooling) up to 400 K with a rate of heating b = 3 K/min. . In each temperature interval the depolarization current was recorded through the external circuit .

III. RESULTS AND DISCUSSION

III.a.Factor Influencing TSDC

The experimental results of the present work showed that the charging time,film thickness, poling voltage and ageing are factors that influencing the discharge current spectrum behaviour .

Fig. (1-a) represents the over-all thermal current obtained from negatively charged ABS using a silver - paste electrode on the charged surface at different charging time . As the figure shows ,the thermal current level increases as the charging time increases at a fixed film thickness. Further, the complexity of the spectra, with the presence of several overlapping peaks is apparent. The uppermost peak occurs at 353 K and the height of its shoulder on the lower temperature scale increases as the charging time increases. The shift in this peak position with time indicates that it is due to space charge polarization.

Fig. (1-b) shows the TSDC thermogram of negatively corona charged of different film thickness at constant charging time. As it is clear , a forward shift in the temperature at which the uppermost peak occurs , is observable as the film thickness decreases . Investigation of the spectra in figures (1 - a and b) reveals that as the charging time increases and the film thickness decreases, the injected charges from the corona electrode to the sample surface increases , thus the net surface charge increases. Moreover, the charges with high energy are capable to penetrate to a slight depth from the surface (6). It is assumed that, as the sample thickness decreases , the penetration depth approaches the opposite surface . Therefore , we observe in the figures as a result of the deposition of the real charges , both the surface charges (up to 363 K) and the bulk material charges (from 363 up to 403 K). The bulk materials charges, as measured by current peak at ca 381 K is associated with the glass-transition temperature .

Detailed studies (12) revealed that the most proper condition for preparing the negatively charged corona ABS electrets are poling time (or corona time) t = 2 min. , air gap = 1 mm and either poling voltage - 5 kv and thickness = 30 µm or poling voltage - 6 kv and thickness = 40 µm.

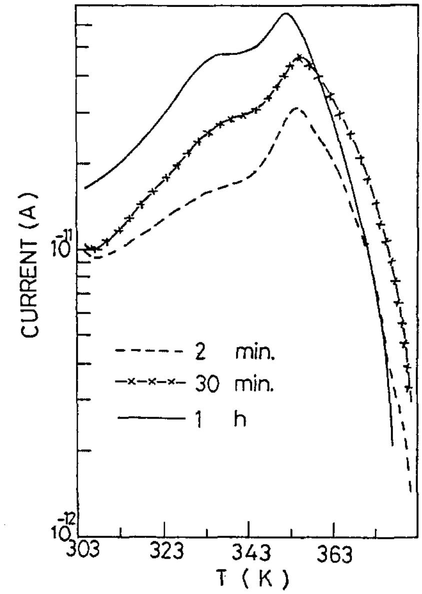

Fig. 1-a Thermal current spectra from a negatively corona-charged ABS (64 µm), Vc = -5 kV , T=303K at different charging times. b = 3 K/min. Ag-paste as electrode .

Charging process results in , as seen before , two types of charges namely surface and bulk material charges . To confirm this argument the electrets were stored for different time intervals . Comparison of spectra taken a few seconds after charging with spectra taken days later shows as in figure (1- c) a reduction in the relative magnitude of the lower temperature peaks indicating the presence of some rapid discharge process . Hence, the reduction in the lower temperature current may be attributed to the elimination of charges trapped on the sample surface as a result of neutralization with other opposite charges present in atmospheric air . Furthermore , it is to be seen that the height of the heigh temperature peak decreases on storage. This result inserts an evidence for the storage effect which in turn may be attributed to the neutralization of some free charges with their image charges inside the polymeric matrix .

Hence, we could conclude that the appearance of the high temperature peak near the glass-transition temperature indicates that traps are closely linked or form part of the native polymer structure. Hence, the charges, so to speak, are shaken out of their traps by strong internal molecular motion. In other words, the detrapping is a dual process arising from the thermal agitation of the electrons in the traps as well as from erosion of the traps by the molecular motion.

III.b. Partial Heating Technique

Fig. (2) illustrates a series of partial heatings of ABS sample to 303,313,323,...,403 K, each seperated by rapid cooling to room temperature. Root mean square plots through the ln I vs 1/T [first rise method (13)] data are shown . In some cases a single straight line fits all of the data but in many cases curvature is apparent and two lines are required. In general, there is a gradual increase in the slope of the lines, indicating an increase in the apparent activation energy. It must be mentioned that a clean peak could be obtained at $T_m = 381 \pm 2$ K .

Fig. (3) represents the plot of the activation energy against partial heating temperature ($T_{P.H}$). It seems that there is a three flat spots on the curve corresponding to 0.12, 0.49 and 1.68 eV. This result is in good agreement of Duke and Fabish (14) argument that trapping sites associated with chemical groups attached to the polymers backbone will not, because of different spatial configurations, have a unique energy. Rather in a polymeric matrix ,the energy of traps associated with side groups may be distributed.

Jonscher (15) believes that activation energies as high as 1.6 eV are usually (but not always) associated with ionic traps in amorphous materials. Other authors (16)using negative corona as a source of charge have also successfully interpreted their results in terms of electron trapping. The experiment of Shahin (17), which is similar to our experiments revealed that the

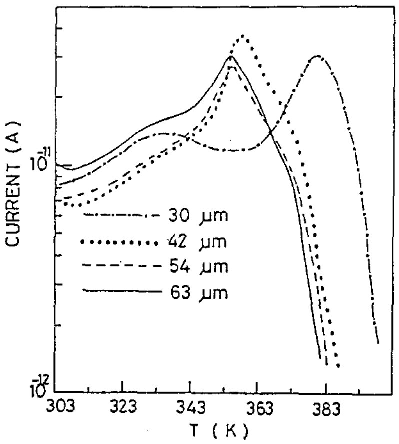

Fig. 1-b Thermal current spectra from a negatively corona-charged with Vc = - 5 k V for 2 min, at different film thicknesses. b= 3 K / min. Ag-past as electrode.

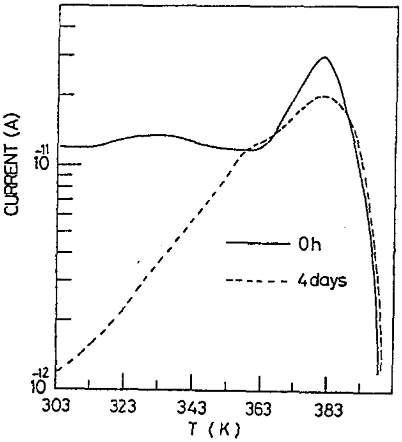

Fig. 1-c Storge effect on the thermal current spectrum from negatively corona-charging of 40 um thick sample, Vc = - 6 kV, Tc = 2 min. and b = 3 K / min .

dominant charge carrier in negative corona in air at atmospheric pressure were CO_3^- ions. These ions may dissociate on landing on the polymer to yield electrons or may be trapped. It seems that the distinction between electronic and ionic traps is a difficult problem. The high temperature peak cannot be interpreted as a distribution of ionic traps, either, since on changing the film thickness or the charging voltage using gaps of 1.2 and 3 m m, the same value of activation energy (1.6 e V) was obtained and the temperature of maximum current remained constant at 381 K. Because of the electron withdrawing property of both the benzene ring and the - C ≡ N groups, these may be considered as the trapping centers in the molecule. Hence, one could conclude that the high temperature peak may be due to electronic detrapping process and the electret property can be described in terms of dipolar relaxation frequency.

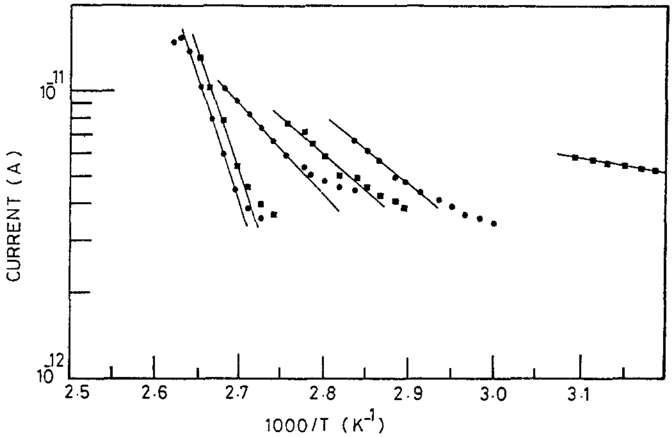

Fig. 2 Arrhenius plots obtained from initial rise in partial heating series .

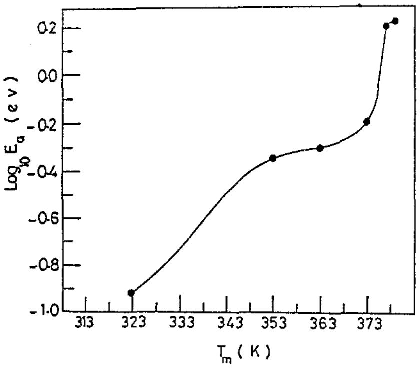

Fig. 3 Change in the apparent activation energy (E_a) with increasing the maximum T_m of the partial heating .

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