Journal of Advances in Science and Technology
Vol. 12, Issue No. 24, November-2016, ISSN 2230-9659

A Research about Current Techniques of Thermally Stimulated Depolarization Currents (TSDC)

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Abstract – Thermally Stimulated Depolarization Currents (TSDC) technique has been applied to investigate the hydration structure of six proteins with different structural motifs: pepsin, β-lactoglobulin, α-chymotrypsin, bovine serum albumin, human serum albumin and myoglobin, at very low hydration level (water vapor activity aw ≈ 0.80) both in the native state and after treatment in trifluoroethanol/water mixture 80% (v/v). A combined approach based on the use of the TSDC technique, able to distinguish H2O dipoles belonging to the solvation shell in terms of their order degree and mobility, and of FTIR and CD spectroscopies has allowed us to reexamine the problem of conformational stability of macromolecules as a function of their hydration.

Two modifications of the Thermally Stimulated Depolarization Current method are proposed to improve resolution and sensitivity of the method by connecting either a real capacitor, or an additional resistor in series with the sample. It is shown experimentally that high sensitivity of the TSDC method with an air gap can be obtained, if the gap is substituted by the capacitor, while all advantages of the method remain in force. It has been found that in one experiment it is possible not only to measure the TSD current, but also to obtain data on the Thermally Stimulated Conductivity, if the properly selected additional resistor is periodically switched on and off.

A simplified theory of thermally stimulated depolarization current of a parallel-plate condenser filled with heterogeneous solid consisting of two dielectrics is presented. It is assumed that the particles (with different shapes and dimensions) of one dielectric are sparsely distributed in another dielectric. A second basic assumption is that the average field in the solid is equal to the external electric field.

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INTRODUCTION

The Thermally stimulated depolarization current (TSDC) technique is ideal for the investigation of the structure of polymers, semi-crystalline polymers and co-polymers because it is a more sensitive alternative than other thermal analysis techniques for detecting the transitions that depend on changes in mobility of molecular scale structural units. TSDC is a general method for investigating the electrical properties of high solids via the study of thermal relaxation effects and as such offers an alternative scheme to the conventional bridge methods or current voltage temperature measurements.

Thermally stimulated depolarization current (TSDC) is a conventional technique for investigation of charge storage and transport processes in high resistivity materials and polymers. For many applications of polymers and doped polymers, it is necessary to know the dielectric properties of material (e.g. insulators and packaging substrates). Polymer films, which can be polarized in an external electrical field, find applications as sensors sensitive to mechanical vibrations, temperature changes or moisture. Further application of doped materials is polymer based field effect transistor sensors. For the standard TSD experiment, which is comparable to a dielectric loss measurement, the low equivalent frequency and high sensitivity (ability to detect dipole concentration of 10^{15} dipoles per cm^3) make TSD quite useful for the study of amorphous relaxations in polymers and their crystallizable blends. Furthermore, by using the thermal sampling method, the rather broad and diffuse glass transitions in polymers and the semi crystalline blends can be readily quantified.

The basic principle of the technique and the evolution of the various experimental parameters of polarization and depolarization steps are schematically illustrated in this paper. The thermal cycle of polarization and depolarization consist essentially of the following steps:-

(a) Placing the sample between short-circuited electrodes in an oven and heating up to a temperature T_p higher than the glass transition temperature T_g of the polymer to eliminate the surface and volume charges.

(b) Application of a DC electric field E_p at the temperature T_p for a time t_p longer than the expected relaxation time for the reorientation of dipoles.

(c) Rapid cooling of the sample in the field to a temperature T0, $T_0 \leq T_p$, where all the dipole/ionic motion is completely hindered.

(d) The sample is subsequently short circuited for a few minute to remove stray charges.

(e) The sample is connected to an electrometer (lowest detectable range $\approx 10^{-15}$).

(f) The sample is heated at a linear rate r (1 to 3^0C per min) and depolarization current is measured as a function of temperature.

The resulting TSDC spectrum shows maximas corresponding to various decay processes. The special advantages of interest of this technique are:

(a) Conductivity does not influence the measurements.

(b) The motion of small chain segments having very low losses are perceptible and can be measured.

(c) The phenomenon varying with time/temperature can be analyzed.

(d) Low frequency pattern of the dielectrics can be elucidated simple and effective way.

Thermally stimulated depolarization current measurement is one of the most important methods for identifying and characterizing relaxation processes, charge-storage, and charge-decay processes in electrified dielectrics and electrets. The charge of electrets may be generated by various mechanisms: orientation of permanent dipoles (in polar materials), trapping of charges by structural defects and impurity centers, and build-up of charges near heterogeneities such as the amorphous-crystalline interfaces in semi-crystalline polymers, and the grain boundaries in polycrystalline materials.

To study the charge decay and contribution of electrets under constant heating rate, TSDC technique was introduced. The decay processes are thus investigated as a function of temperature instead of time. At room temperature, charge decay measurements are rather time consuming, because at such low temperatures the dipoles and charges remain virtually immobile. However, when the environment around the electret becomes mobile, the dipoles and charges quickly regain their freedom of motion. Thermal stimulation of the discharge therefore shortens the measurement considerably. During such heat-stimulated discharge, a metal connection between two electrodes generates a weak current that shows a number of peaks when recorded as a function of temperature. The shape and location of these peaks are characteristic of the electrets' charges storage mechanisms. Analysis of the peaks yields detailed information on the permanent dipoles (density, relaxation time, activation energy) and trapping parameters (energies, concentration, and capture cross section of traps).

Although TSDC has a relatively short history, it has already evolved into a basic tool for the identification and evaluation of dipole reorientation processes and of trapping and recombination levels. Its rapid growth has been spurred on by the fact that charge-trapping and charge-transport phenomena are not only of vital importance for electrets, but also for materials used in thin films, photoconductors, electro-optical devices, etc.

MECHANISMS INVOLVED IN TSDC

Persistent polarization (electrets effect) in polymer may arise due to various mechanisms namely:

(a) Orientation of permanent dipoles (in polar material),

(b) Trapping of charges by structural defects and impurity centers, and

(c) Build up of charges near heterogeneties such as (i) the amorphous-crystalline interfaces in semi-crystalline polymers, and (ii) the grain boundaries in polycrystalline materials.

Depending upon the nature of polarized polymer (electret) anyone or even more than two of the above process may take place during discharge. Thus, the net charge of an electret is, generally, due to the aligned dipoles and space charges. The latter are excess charges which cause the electret to be not locally neutral. However, prior to the formation of the electret, the neutral polymer initially contains free charges. When an external field is applied they exhibit themselves in conduction current. Hence, it is obvious that in addition to the excess charges equilibrium charge must also exist in the electret. These inherent charges do not contribute to its net charge, but are responsible for its intrinsic ohmic conductivity that varies linearly with the field. In contrast, the TSDC due to the conductional motion of the space charges will vary non- linearly.

In electret made from polar materials the disorientation of dipoles plays a prominent role. However, discharge by dipole disorientation is

thermally activated and thus can be speeded up by heating. Often, the disorientation energy or the so called activation energy is not the same for all the dipoles. Therefore, if the differences in the various disorientation energies are not large, we can safely assume a continuous distribution of activation energies for which all individual peaks overlap and merge into a broad peak. As a result of disorientation of polar side groups in polymers at low temperatures such broad peaks are clearly identified.

The appearance of these broad peaks may also possibly be due to a difference in the rotational mass of the dipoles. These differences may occur in a polymer when heated to its softening temperature at which the dipoles are disoriented by the mobility of the main chain segments. This disorientation is responsible for the $\alpha\alpha$ peaks located at the glass rubber transition temperature (T_g) of the polymer.

TSDC SYSTEM INSTRUMENTATION DESIGN

This TSDC system is composed of TSDC cell, main chamber, heating unit, cooling unit, electrical unit, vacuum unit, and data acquisition unit. The heating and cooling units provide a wide temperature range from -200° C to 300° C. A Keithley 6517B Multi-meter can supply up to 1000V DC voltage to sample, and can measure DC current from 10aA to 21mA. The vacuum unit creates vacuum environment inside of main chamber, which is aim to avoid external factor's effect. All experimental data is converted to digital signal and recorded by LabView software. The TSDC curve will be plotted automatically by Labview. Figure 1 presents the overview of the whole TSDC system.

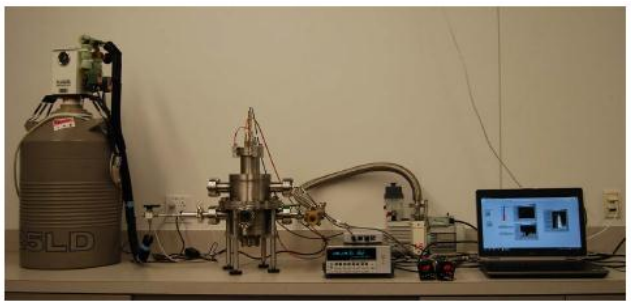

Figure 1: Overview of whole TSDC system.

The TSDC Cell was designed by Novocontrol Company, which is a German manufacturer of high-tech measuring and automation systems for industrial control and scientific research. This sample cell has been designed for measurements of thermally stimulated depolarization current (TSDC) of solid samples. It has a massive stainless steel construction and gold-plated electrodes with reliable electrical insulation. Integrated interlock switch enables high voltage application only if the cell is mounted into the temperature chamber. The connection on the top flange includes a high voltage connector for the high DC-polarization and two BNC connectors for the electrometer input. Up to 1000V DC voltage can be supplied and 10aA current can be measured. It has a wide temperature range from -200° C to 300° C. PT100 temperature sensor is integrated to bottom electrode which makes the system to be able to determine sample's temperature accurately.

The main chamber is the main structure of the system. It plays the roles of supporting TSDC cell, providing enclosed environment for experiment, and connecting to other component of system. The main chamber is made by 304 stainless steel, which makes the main chamber have uniform geometry shape under extreme low and high temperature environment. 3D model of chamber designed by Pro/Engineering software and real chamber view. There are totally seven ports on the chamber. This section shows the function for each port. All the ports of main chamber are designed to standard 2-3/4"UHV flange. By using standard flange adapter from Lesker Company: 2-3/4"UHV FLANGE TO QF25, every function units can be easily connected to main chamber.

The heating function of the TSDC system is achieved by hot-nitrogen gas. Gas heater from Omega Company is used to heat up compressed air. Hot gas is injected to sample directly by a gas feeedthrough and nozzle which are connected to the main chamber. To make the main chamber have satisfied thermal insulation performance, clay thermal insulation is attached to the inner surface of the main chamber. By using hot-gas heating unit, sample could be heated up to 300° C. The TSDC experiment not only requires system to heat up sample as fast as possible, but also requires a controllable slow heating. For quick heating, hot-gas is able to heat up sample to 300° C in 3 minutes. For slow heating, the temperature controller of the unit can output a constant heating rate; usually 4° C/minutes to 8° C/minutes is used during experiment.

The TSDC system use liquid nitrogen to cool down sample. A tremendous amount of energy can be taken away when liquid nitrogen is rapidly vaporized. This is the basic principle of liquid nitrogen cooling. The TSDC system uses a nitrogen container from PLANER Company. The Container has a 25 liter capacity. One solenoid valve is used to turn On/Off of the container. On the top of container, there is one air-pressure meter designed to indicate the pressure of container. The pipe of liquid nitrogen was connected to main chamber by a specific liquid nitrogen feedthrough from Lesker Company. One additional 3-way valve was connected between container pipe and feedthrough. The purpose of 3-way valve is to improve system cooling performance. After turning on the solenoid valve, the temperature of liquid gas comes out from container is not that low.

It is because the container and pipe themselves need to be cooled down first. However, TSDC experiment requires cooling down as quickly as possible. Therefore, liquid gas should not be injected to main chamber at the beginning of cooling process. Liquid gas can be injected to outer of chamber by operate 3-way. When temperature of liquid gas goes down to extreme low, turn 3-way valve to main chamber direction, the low nitrogen gas was injected to sample directly at this time. TSDC sample can be cool down to – 150° C in two minutes.

TSDC: A SENSITIVE TECHNIQUE FOR ANALYZING PROTEIN STRUCTURE

It is well known that proteins exist and act in a predominantly aqueous solvent environment. In fact, water controls and affects many features of structure and function of biological macromolecules. The accepted model of protein hydration assumes the existence of discrete water-binding sites both within clefts and cavities and on the polypeptide surface. TSDC is a dielectric technique which was proved to be a powerful tool for studying hydration water in biological macromolecules being able to distinguish water dipoles with different mobility in the temperature domain. It is based on the water microdynamics which depends on the surrounding: as a consequence, families of water can be distinguished by different dielectric relaxation times and different statistical weights. The method is characterized by high sensitivity and resolving power: dipole concentration as low as 0.1 ppm can be accurately measured.

The typical TSDC spectrum (a plot of the depolarization current as a function of the temperature) for a protein consists, as a rule, of two main peaks, generally called Low Temperature (LT) and High Temperature (HT) peak, respectively, the former being related to water molecules located in the grooves of the folded structure and the latter to the external ones, layered on the polypeptide surface. A recent TSDC study, performed on poly-L-lysine in different conformational states, has suggested that the solvent arrangement around the polypeptide structure depends almost exclusively on the protein surface geometry and on the hydrogen bonding capability. On these bases, TSDC measurements were carried out on lysozyme to explore the conformational changes accompanying the transition of the protein into the amyloid form. The results showed large differences between the TSDC spectra related to the two different protein conformations, for what concerns the number and position of the main peaks. In fact, the native form displayed two peaks, at TM = 175 K and at TM = 297 K, while the amyloid one exhibited only a peak at intermediate temperature (TM = 235 K).

With the aim to investigate how the molecular geometry and the hydration are related by analyzing the TSDC spectra dependence on the protein conformational structure, six proteins of different conformational types were considered in the present work: pepsin, β-lactoglobulin, α-chymotrypsin (mainly-beta proteins), bovine serum albumin (BSA), human serum albumin (HSA) and myoglobin (mainly-alpha proteins). They were studied in the native form and after treatment in 2,2,2 – trifluorethanol (TFE)/water mixture 80% (v/v). This organic solvent has been shown to promote α-helical secondary structure formation by replacing the hydration shell with fluoroalchohol molecules, a process inducing protein dehydration.

TSDC FOR COMPOSITES OF ACRYLONITRILE BUTADIENE RUBBER

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.

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. 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. 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.

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 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.

EXPERIMENTAL PROCEDURE

Circular pure and biocomposite samples were obtained from the solution grown PVA and Palm Leaf powder based biocomposite polymers of various weight% 100:00; 95:05; 90:10, 85:15 and 80:20. Pressed Aluminum foil electrodes were used for TSDC measurements. The samples were sandwiched between two electrodes of the sample holder which was placed in a temperature controlled oven. The upper electrode was given a positive potential through a high voltage power supply while the lower electrode was grounded.

The temperature of the specimen was raised to the desired value (Tp) and the temperature was maintained for half an hour. After this the power supply was turned on and the desired polarizing voltage (Vp) was applied. The sample was kept in the polarizing field at the polarizing temperature for 30 minutes. It was then allowed to attain room temperature with applied polarizing field. The rate of cooling was adjusted in such a way that the thermostat could reach the room temperature within 30 minutes. The total time of polarization was thus adjusted to be 90 minutes in each case. The field was then removed and the thermoelectret was then short circuited at room temperature for 5 minutes to remove the frictional and stray surface charges.

For TSDC measurement, the sample was short circuited through an electrometer and was reheated at a linear heating rate of 3oC/min. The depolarization current was recorded at regular temperature intervals using Electrometer Amplifier Model EA 815, Electronics Corporation of India Limited.

For the present investigation thermo electrets were prepared at the polarization temperatures of 50, 70, 90 and 110 °C with polarizing fields of 10, 15, 20 and 25kV/cm. For each measurement a fresh sample was taken and the TSDC was recorded.

CONCLUSION

By the comparison between different techniques, TSDC technique is more sensitive in resolving polymer glass transition analysis. By window polarization test, each individual particle's behavior can be determined accurately. Meanwhile a range of activation energy can be determined. What is more, the frequency requirement for distinguishing these multiple transition is very low, since TSDC is a low frequency technique; therefore, TSDC is ideal in resolution of weak transition in polymer materials.

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 Ep from 1□103 V/cm to 3□103 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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