THE STUDY OF MECHANISMS AND CHARACTER OF CONDUCTION IN POLYMERS

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Abstract- ***The study of mechanisms and character of conduction in polymeric materials has become an increasingly interesting area of research because they have good potential for various devices. The elucidation of the charge injection and carrier migration processes becomes essential for future use of these materials. The study of conduction is of considerable significance from two major points of view- firstly, for its own sake, because charge transfer characteristics are of fundamental interest and secondly for the information, studies can provide on the nature of electrical contacts, which may have a great influence on the measured electrical properties. The charge storage properties of polymers can be considerably modified with the help of suitable dopant . In the present paper a theoretical approach has been made to discuss the introduction of polymer, preparation techniques of foil samples. For their proper characterization a brief knowledge is also presented about the various studies like thermally stimulated discharge current , transient current measurement , electrical conduction ,infrared ,ultra-voilet, X-ray diffraction, field emission scanning electron microscopy and atomic force microscopy .***

Key words- Polymer, Charge injection and carrier migration ,thermally stimulated discharge current , transient current measurement , electrical conduction ,infrared ,ultra-voilet, X-ray diffraction, field emission scanning electron microscopy and atomic force microscopy .

1. INTRODUCTION

From the age of stones and metals, we have come to the age of nuclear energy and polymers. Indeed, we live in the world of polymers. That is why Scientists, technologists and engineers have termed this era as the 'Polymeric age'. Our daily life can be scarcely envisioned without the polymers, as nearly all products that we use contain polymers in some form (1,2).

A polymer is made up of many small molecules which combine to form a single long or large molecule .The individual small molecules from which a polymer is formed are known as monomer molecule and are linked to form a big polymer molecule the process being known as 'Polymerization' (3).Studies on polymer have attracted a particular attention due to their useful, mechanical properties, unique disordered structure and their potential application in many technological and engineering areas. The minturization of solid state devises has opened up yet another field for use of polymer, which is very vast fascinating and promising (4,5).

Polymers show extremely good charge storage capabilities and are available as flexible thin films. The non-polar polymers with low dielectric constant have important role in biology and medical field ;but their charge capacity and storage stability are nor favorable . On the contrary, the polar polymers possess very good electret properties but their cost is too high for wide spread application. The polarization is attributed to charge in their order electrically charged particles of a dielectric in space. The process causes the formation of an electric moment in each polarizing entity (atom, ion and /or molecule), and therefore in the entire volume of the dielectric. As far as electrets which can create an external electric field are concerned, large scale applications have been developed; the main ones being in the field of condenser microphones. Various types of sensors are also being studied out of the acoustical frequency range, for instance to produce or detect ultrasonic waves. Choice of the polymeric dielectric for each concrete use depends on its dielectric and other physical properties over a wide range of temperature and electric field frequencies. Polymers have also found wide application in bioengineering for understanding of biological memory in regeneration, electrical mediation on tissue growth and other phenomenon (6-8).

In 1962, microphones with thin flexible polymer electrets were introduced which upon proper choice of electret material and other improvements gained widespread commercial acceptance. More recently introduced electret devices include GAS filters, motors, and relays switches optical display system and radiation dosimeters. In radiation dosimeter the decay of previously stored charge or the generation of radiation-induced conductivity is employed to measure radiation doses. The relay type switches utilizes the external field of electrets to open or close contacts. Another group of applications namely those relation to Biophysics. A number of new electret applications are based on the pyro and piezoelectric effects in polarized polymer material. Of all commercial application of electret transducers, the high fidelity electret microphones for amateur, professional, studio and tape recorder use is most prominent. Other use of electret microphones are in sound level meters, noise dosimeters and movie cameras. The success of the electret microphones in theses application is primarily due to its excellent acoustic quality and low cost. In the US and Canadian telephone system, foil electret microphones are being used in speaker phones. The demand for high efficiency filters which remove submicron particles from pulled gases has led to the developed of electret filters consisting of charge polymer fibers. The electret filters are made from polypropylene film, which is first stretched to increase its mechanical strength and then changed by application of a corona discharge. Electret motors and generators have been suggested for use in power engineering(9-11).

The carrier mobility can be greatly affected by impregnating the polymer with suitable dopants. Considerable attention should be devoted to the problems of the change in electrical properties of polymer due to intentional doping with low molecular weight compounds, Depending on their chemical structure and way in which they react with the macromolecular matrix, doping substances decrease the resistivity of the polymer to different degrees. Dopant molecules generally occupy the interstitial positions between the polymer chains and link them with some types of bonds due to charge transfer process. This reduces the interstitial barriers and increases the transition probability of hopping electrons across these barriers, thus increasing the carrier mobility (12,13).

Organic /Inorganic materials are introduced into the polymers to decrease the effectiveness of inter-molecular (inter chain) interaction. The microscopic effect of plasticizing usually manifests itself in a reduction of the glass transition temperature. Both low and high molecular substances are used as plasticizers. The plasticizing action depends on the chemical structure, size and shape of plasticizer molecules. The effectiveness of the plasticizer depends to a considerable extent on the confirmation set of its molecule. Plasticizers whose molecule can take on a greater number of confirmations lower the glass transition temperatures of a polymer to a great extent. The conductivity of polymers can be greatly affected by doping them with suitable impurities. Both inorganic and organic impurities can be used to modify the electrical conductivity of polymers. Inorganic impurities have more profound effects than organic impurities (14,15).

2. PREPARATION OF SAMPLE AND STUDIES FOR THE CHARACTERIZATION

The isothermal immersion technique will be utilized for preparing samples in foil form. The solution will be prepared in a glass beaker by dissolving known amount of in chemically pure solvent the solution will be kept for 24 hours to get a homogeneous and transparent solution. The solution thus prepared will then poured onto an optically plane cleaned glass plate floating on mercury. The solvent will be allowed to evaporate in an oven at high temperature for 24 hours to yield the desired samples. This will be followed by room temperature out gassing at 10^{-5} torr for a further period of 12 hours to remove any residual solvent. The plate will be then drawn slowly out of the solution, leaving a uniform film on the plate. Samples thus obtained will be uniformly smooth and can be easily peeled from the glass surface. The prepared samples were then sandwiched between the metallic electrodes inside in an oven and heated to pre- determined polarization temperature .The polarization may be carried out by connecting a DC power supply in series with the sample and with an Electrometer (carefully shielded and earthed to avoid earthing loops and extraneous electric noise). Hence a humble attempt can be made to characterize the pure and doped foil samples by studying electrical properties using thermally stimulated discharge current(TSDC), transient currents in charging and discharging modes, electrical conduction, dielectric and spectroscopic studies i.e. IR,UV, XRD ,FE-SEM and AFM.

(a) Thermally Stimulated Discharge Current (TSDC)

Polymers are generally good dielectrics which are capable of storing charge in them permanently, when subjected to field-temperature treatment and are known as thermoelectrets. When such thermoelectrets are subjected to a programmed heat treatment, they give rise to a current in the external circuit which is known as thermally stimulated discharge current (TSDC). TSDC is an accurate, sensitive and convenient method for studying the charging and discharging processes in dielectrics. These currents are due to the dielectric relaxation behavior and motion of free charges in the polymers. Hence, TSDC technique can be used to understand the low frequency dielectric behavior and relaxation processes on the atomic scale. Because of the high sensitivity of the technique, it is also used to investigate the low concentration of the dipolar impurities, formation and aggregation of impurity-vacancy complexes, phase transitions, photographic response of silver halide, etc. This technique is a powerful method to gain an insight into the mechanisms of charge migration and dipolar motions (16,17). The process of TSDC measurement involves the poling of the polymer film for certain values of poling parameters such as poling field (E_p), poling temperature (T_P) and poling time (t_P) and its heating in a specially designed cell, with a constant heating rate.

The analysis of the resulting thermogram of TSDC will help to obtain various material parameters, such as energetic and spatial trap depths, trap densities , trap structure, rate parameters etc. and hence will enable to arrive at various conclusions including those about energetic and spatial distribution of traps and the effect of changing conditions on charge storage and transport processes in the polymer. TSDC reveals the nature of various decay processes quickly and precisely which confirms it as an attractive tool for determining the electret behavior.

(b) Transient Current and Electrical Conduction Current

The nature of transient charging and discharging currents differ from material to material depending upon the mechanisms involved. The discharging current is usually mirror image of charging current, provided that a steady state current does not occur. Hence discharging currents can yield information about charging processes even when the corresponding charging current is masked by conduction current at charging (18,19).

Transient current in dielectrics, observed upon the application or removal of step voltage, have been studied extensively to throw light on the polarization process in these materials, the important in which are dipolar orientation, space charge formation, trapping in the bulk, tunneling of charge carrier from an localized state to another etc. By knowing these currents, it becomes necessary to discover the actual conductivity of the material (20,21).

The electrical conductivity (σ) of a solid is defined as the ratio of current density (J) to the electric field (F).The conventional measuring technique consists of applying a known voltage across a sample of known dimensions and determining the current in the external circuit. The electrical conductivity of polymers must be understood in order to improve their performance as electrical insulators. At the present time, there is a need to produce material with lower conductivity than is currently available without compromising the desirable mechanical and electrical properties in order to satisfy the continuing demand for high-quality communications cables and optical fibers and low-loss conventional power apparatus and cables. A further requirement will be for better standoffs for superconducting power cables (22,23).

The electrical conduction in polymer film has much importance due to the discovery of the memory phenomenon in thin film devises. In recent years, because of need for electrostatic charge dissipation, electromagnetic shielding, new polymers with electrical conductivity have been formulated. This led to new discoveries in the area of conducting polymers, which has now become one of the important topics of research (24-26).

(c) Dielectric Measurement

The dielectric behavior of polymeric films is of direct interest to both the basic studies of electrical conduction through such films and their application in capacitors for microelectronics. To obtain high values of capacitance the dielectric constant should be high and the thickness be small. Due to the difficulty of obtaining structurally continuous and stable ultrathin films, capacitor applications are generally limited to thick films. The evaluation of the dielectric properties of insulator films is carried out by measuring simultaneously the capacitance and the dissipation factor over a wide range of frequencies and temperature. The most important property of dielectrics is their ability to be polarized under the action of an external electric field(27,28).

A suitable combination of time, temperature and field dependence of current response measured as a function of time after application to or removal from the samples of a dc- voltage will help to have the deeper understanding of charge injection mechanisms and the amount of trapping

taking place in the material. The results will be used to derive various information valuable to understand the storage and transport mechanisms of charge(29,30).

(d) Spectroscopic studies- IR, UV, XRD,FE-SEM and AFM

The word spectroscopy is used as collective term for all the analytical techniques based on the interaction of light and matter. The spectroscopic methods are the most direct and most powerful means of obtaining information on the electronic structure of materials (31). Spectroscopy is the study of interaction of electromagnetic radiation with a chemical substance when energy in the form of electromagnet radiation (or photons) interacts with a material, the absorption and re-emission processes that occur depend largely on the electronic structure of the material (32). The different types of spectroscopy depend chiefly on the energy range used and the nature of the interaction involved. Properties of a polymer are party dependent on their physical as well as chemical structure. Chemical structure of polymers may be modified by doping, copolymerization, substitution and blend formation etc. These processes affect the electrical behavior to various extents (33).

The structural information and effects of structural modification in polymers can be investigated by using a number of techniques viz. infrared (IR) (34), ultraviolet(UV) (35), X-Ray diffraction (XRD) (36), field emission scanning electron microscopy (FE-SEM) (37) and atomic force microscope (AFM) (38). In case of polymer, these techniques are used to analyze the relation between microstructure and electrical or mechanical properties. The nature of the interaction depends upon the properties of the substance. Infra-red (I.R) study of polymers is useful in studying structural modifications occurring during electrets formations, or on sensitizing with impurities. Also it provides information about (i) the chemical bonding or molecular structure of materials, whether organic or inorganic (ii) gives information about the functional groups of an Organic molecule and

(iii) is used to identify unknown materials and materials phases present in a specimen. Ultra violet absorption (U.V) spectra investigate the promotion of electrons from lower state to the higher energy state in UV and visible region .The X-Ray diffraction (XRD) is one of the most important nondestructive tool used to analyze all kinds of matter ranging from fluids, to powder, films and crystals. The XRD spectra described the change in crystalline and average intermolecular spacing after introducing the sensitizer in polymer matrix.

The Scanning Electron Microscope (SEM) is a type of electron microscope that uses high-energy beam of electrons to scan the sample surface in a raster pattern to obtain image. The SEM produce images of high resolution, which means that closely spaced features can be examined at a high magnification and large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. SEM is most widely used for revealing information about the microstructures and orientation of the samples. In the early 1950's scanning electron microscopes have developed new areas of study in the medical and physical science communities .All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope one of the most useful instrument in research today.SEM is most widely used for revealing information about the microstructures and orientation of the samples.

The Atomic Force Microscope (AFM) is a very high-resolution type of scanning probe microscope. Unlike traditional microscopes, the AFM does not rely on electromagnetic radiation such as photon or electron beams to create an image but is based on the interactive forces called the Vander Waals force between the sample and the tip. It does not require vacuum environment or any special sample preparation, and can be used in either an ambient or liquid environment. For most applications, the AFM is operated in one of the following three modes (a)Contact mode (b) Non-Contact mode and (c) Semi contact mode or Intermittent mode or Tapping mode .The AFM is one of the foremost tool for imaging measuring and manipulating matter at the nanoscale. The information is gathered by "feeling" the surface with a mechanical probe .Piezoelectric element that facilitate tiny but accurate and precise movements on command enable the very precise scanning .

3. CONCLUSION

On the basis of the useful information obtained from the various measurements as discussed above one can try to develop a correlation and consistent comprehensive interpretation for charge storage and transport behavior , and to get an overall view of various aspects of polarization and relaxation phenomenon in pure and doped thermoelectrets . The knowledge so obtained will help in understanding the complexity of conduction behavior of mixed system and the modification in trap behavior brought about by doping. In order to get a clear picture of variation of structure in pure and doped samples and to arrive at unambiguous interpretation of the results of thermally stimulated discharge current, and transient currents, dark conduction currents it is necessary to carry out IR,UV ,XRD spectra , FE-SEM and AFM studies . In addition to the academic importance, the work summarized above may be of considerable technical and industrial applications and will be a step towards finding the suitable conditions for most stable electrets.

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