

## STUDY OF DIELECTRIC BEHAVIOR OF NANOPOROUS POLYCARBONATE MEMBRANE FOR FUTURE NANO-ELECTRET APPLICATIONS

RAJESH KALIA, SUNIL KUMAR\*, H. S. BHATTI<sup>a</sup>, J. K. SHARMA

*Department of Physics, Maharishi Markandeshwar University, Mullana(Ambala)-133 230, Haryana, India*

*<sup>a</sup>Department of Physics, Punjabi University, Patiala-147 002, Punjab, India*

In this paper capacitance measurements of a nanoporous polycarbonate membrane are undertaken to study the dielectric behaviour. The recent interest in research on electret is the study of electret phenomenon in polymers, their blends, polymer-ceramic composites and hybrid piezoelectric polymer films on micro and nano-machined silicon dioxide layers. The activation energy and charge released can be studied with the variation of poling field, poling temperature, and poling time on the basis of peaks obtained. The disorientation of dipoles destroys the persistent dipole polarization by redistributing all the dipoles. For disorientation of dipoles certain amount of energy i.e. activation energy is required which will rotate the coupled pair of charges. The properties mentioned above also change drastically at nanoscale. The studies mentioned in the paper is done at variable temperature. The temperature range selected is from room temperature to 200 degree celsius. Time resolved laser induced Photoluminescence studies (TRLIP) are also conducted to confirm the existence of energy levels in polycarbonate NTFs, which is very important from Electret point of view.

(Received October 25, 2008; accepted October 30, 2008)

*Keywords:* Polycarbonate, Electret, Dielectric, Capacitance

### 1. Introduction

The word Electret was derived by Heaviside (1892) to describe a permanently polarized dielectric, which is equivalent to a permanent magnet. A Japanese Physicist, Eguchi, prepared the first Electret in 1919 from carnauba wax [1]. The Electret research was pursued with two main objectives: development of human resources and search for new advanced materials. The Electret effect first discovered in Carnauba wax obtained from a palm tree of Brazil has come a long way with the introduction of polymers. The study of Electret phenomenon in polymers, their blends, polymer-Ceramic composites and hybrid piezoelectric polymer films on micro-machined silicon dioxide layers have generated much interest and research activity in past few years.

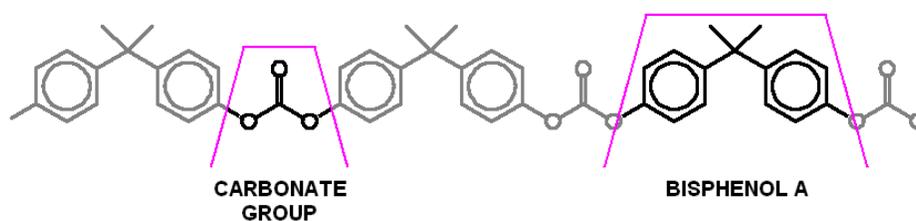
Thermally stimulated discharge (TSD) is a technique that has contributed significantly to the current understanding of charge decay and charge storage processes in Electret. TSD is the study of charge decay by heating the Electret at constant rate. These decay processes are investigated as a function of temperature. At room temperature the charge decay measurements are time consuming. The TSD technique shortens the time for measurements. So it is playing a vital role in Electret research. TSD of polymer has become a widely used experimental technique for the investigation of various material parameters such as charge storage properties, determination of mean depth of the internal charge, activation energies of traps and trap structure of the material. The thermally stimulated discharge conductivity is induced by thermal release of dipoles, ions and trapped electrons [2]. The thermally stimulated conductivity is applied to dielectrics in which a store of non-equilibrium carriers can be performed by nuclear radiations. In electrets made from polar materials the disorientation of dipoles plays a prominent role. This disorientation tends to

destroy the persistent dipole polarization by redistribution of all the dipoles at random. The disorientation of dipoles involves the rotation of coupled pair of positive or negative charges and requires certain activation energy per dipole. The activation energy is not same for all the dipoles. The current-temperature plot will then consist of several peaks, because the dipoles with low activation energy will disorient at low temperatures, while those with high activation energy will only respond at higher temperatures. So, the activation energy is a great factor to study depolarization effect and also the conduction. The considerable amount of work has been reported on steady state electrical conduction in insulating polymeric films and polymer composite thin films. Fridkin and Zheludev [3], Gross [4] and Latour [5] extensively reviewed the methods of formation of thermoelectrets. Turnhout [6] reported the thermally stimulated discharge of polymer electrets. The study of resistivity and thermal noise of amorphous polymers (polystyrene, polymethyl methacrylate, polyvinylchloride) containing a small percentage of carbon-black was reported by Klason and Kubat [7]. Time dependent resistivity was recorded in glass transition ( $T_g$ ) and melting temperature ( $T_m$ ) region. The conductivity of Polystyrene (PS) was studied [8] at constant polarizing field but at different polarizing temperature. It is only in recent years that the possibility of technological application of electrification of polymer due to its contact with metal has been discovered [9]. Pissis *et al* [10] reported the electric and dielectric measurements of several conducting (polyethylene oxide) PEO-based electrolytes, by using thermally stimulated depolarization current (TSDC) and thermally stimulated polarization currents (TSPC). Negau and Negau [11] obtained results in thermally stimulated discharge current (TSDC) peak above room temperature. Sangawar and Adgaonkar [12] reported that conductivity of Polystyrene (PS) increases with the concentration of benzoic acid. The electrical conductivity study of PS and polymethyl methacrylate (PMMA) iodine doped electrets was reported by Sangawar [13]. Sawarkar *et al* [14] studied the depolarization currents in semiconducting 50PbO–50B<sub>2</sub>O<sub>3</sub> glasses and evaluated the various parameters such as trap depth, trap density, activation energy etc. Ghosh [15] reported the use of inherently conducting polymers intimately with or dispersed in a second polymer matrix (i.e. insulating in character) during or subsequent to synthesis. Measurement of thermally stimulated discharge conductivity was reported by Belsare and Deogaonkar [16]. Khare *et al* [17] measured the thermally stimulated discharge current (TSDC) and electrical conductivity in metal (1) and ethyl cellulose–metal (1)/(2) systems. Quamara JK *et al* [18] reported the study of dielectric relaxation processes in poly (*p*-phenylene sulfide) using a thermally stimulated discharge current technique. Polymer composites based on charge transfer complex of phenothiazine and iodine with polystyrene prepared in different weight ratios have been characterized by FTIR, XRD, mechanical microstructure and electrical properties (d.c. as well as a.c.) by Singh *et al* [19]. The study of thermally stimulated discharge current and dielectric constant of semiconducting glasses was reported by Burghate D K [20]. Garg Maneesha and Quamara JK [21] reported the multiple relaxation processes in high-energy ion irradiated kapton-H polyimide. The TSD conductivity study of activated charcoal-polyvinyl chloride (PVC) thin film thermostat was reported by Sangawar *et al* [22]. The method used for measurement of conductivity was same as reported earlier by [23]. The electrical conductivity of naphthalene doped polystyrene (PS) films (nearly 61.58  $\mu\text{m}$  thick) was studied as a function of dopant concentration and temperature [24]. The method for measurement of conductivity was the same as reported by Belsare and Deogaonkar [15]. At the nanoscale the above mentioned properties are bound to change. That is why in this paper, we have tried to see the effect of temperature on the capacitance generated in nanoporous polycarbonate membranes for future nano-electret application. TRLIP studies are also conducted to support dielectric studies.

## 2. Experimental

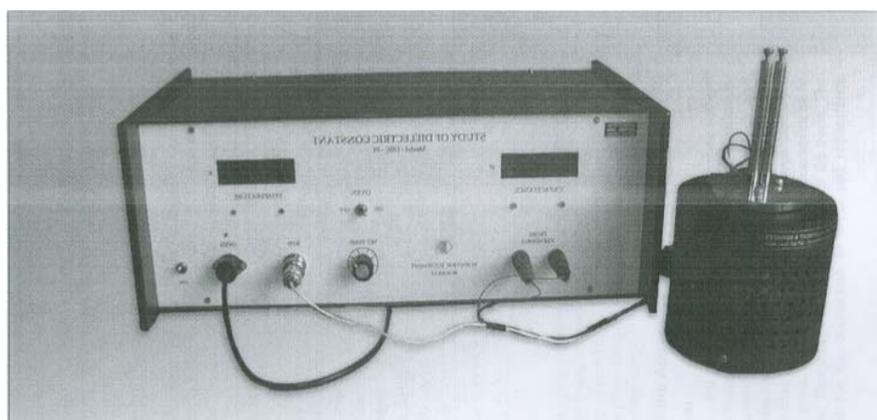
Track etched Polycarbonate nanoporous membranes having a pore-size of 100nm have been procured from Nuclepore, USA. Microporous and nanoporous polymer membranes are commercially available filters, which are prepared by the track-etch method. This method entails bombarding a sheet of the desired material with nuclear fission fragments to create damaged tracks in this material, and then chemically etching these tracks to get micro and nano-pores. A broad

range of pores diameters (down to 10nm) is available, and pore densities approaching  $10^9$  pores  $\text{cm}^{-2}$  can be obtained. The pores in these membranes are randomly distributed across the membrane surfaces with uniform diameters. However, due to the random nature of the pore-production process, the pores have tilt with respect to the surface normal, and a number of pores may actually intersect with in the membrane. The term Polycarbonate describes a polymer which is composed of units of bis-phenol A, connected by carbonate-linkages in its backbone chain. Chemically, a carbonate group is a di-ester of carbonic acid. The result is a polymeric chain as can be seen in Fig. 1



*Fig. 1 Structure of the Polycarbonate Chain.*

Dielectric setup used for capacitance measurements of nanoporous polycarbonate membrane is shown in Fig-2. The sample chamber and the contacts are shown in Fig-3.



*Fig. 2. Dielectric Setup for capacitance measurements*

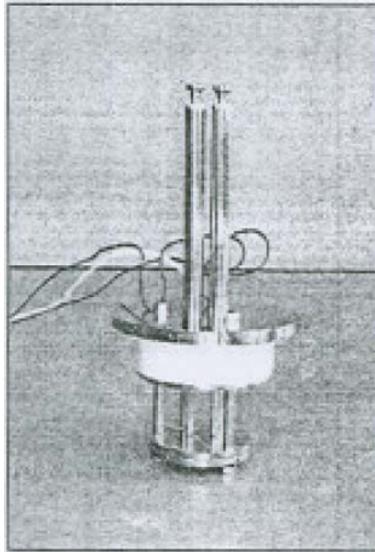


Fig. 3. Two Probe setup.

### TRLIP Studies

Laser induced pulse excitation method(Fig-4) is used to study the PL spectra and to correlate it with the dielectric behaviour of polycarbonate membranes. Nitrogen laser is the most suitable excitation source (337.1 nm) to irradiate the polycarbonate having pulse-width of 5-7ns and average power of 10 kW and peak power of 1MW. High photon flux density of the Nitrogen laser is extremely useful to excite the short-lived shallow trapping states in any type of material. The photoluminescence from the sample at an angle of  $90^\circ$  to the incident beam was collected by a fast photo-multiplier tube through an assembly of monochromator.

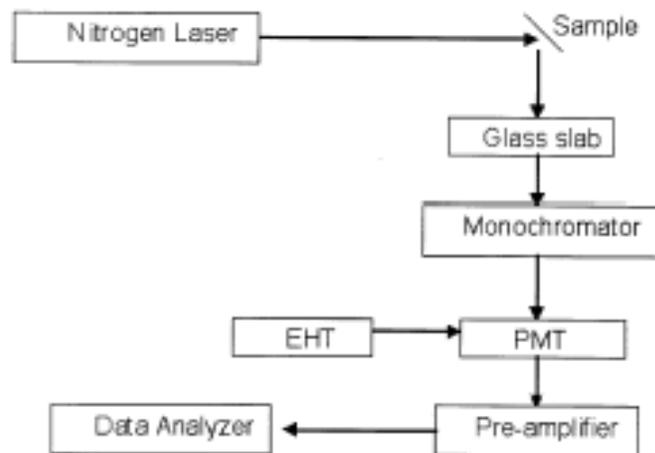


Fig. 4. Photoluminescence setup

### 3. Results and Discussion

Initially the focus of Electret/Polymers research was charge production and stability of polymers/electrets. Polymers as insulating medium in plastic and resins have attracted maximum attention of researchers. During Thermally stimulated discharge an nanoporous polycarbonate

membrane connected to two electrodes generates a graph(Fig-5) that shows a number of peaks when recorded as a function of temperature. The location and shape of these peaks are characteristics of mechanisms by which the polycarbonate membrane store their charges. The analysis of these peaks give the detailed information on permanent dipoles (density, relaxation time, activation energy) and trapping parameters (energies, concentration, cross-section of traps). Table-1 shows the tabular form of the data recorded between temperature and capacitance.

The laser induced photoluminescence of polycarbonate NTFs confirms the creation of new energy traps from irradiation of the nascent polycarbonate samples. The decay signal(Fig-6) from the polycarbonate NTF was recorded by digital storage oscilloscope(TDS-1012). Polycarbonate NTFs emits weak fluorescence in the wavelength range of 400-500 nm under laser irradiation having a peak wavelength at 440nm. The visible emission shows that during the creation of NTFs after irradiating nascent polycarbonate samples, energy levels are formed in the host polycarbonate membrane.

*Table-1*

S.No	Temperature(°C)	Capacitance(pF)
1.	35.9	2210
2.	37.6	2821
3.	43.3	2780
4.	60	1460
5.	63.8	2200
6.	71.2	2403
7.	77.4	2040
8.	83.4	2230
9.	103.6	1730
10.	105	2050
11.	115.9	2760
12.	127.6	2150
13.	132.1	1500
14.	135	2100
15.	139.9	1450
16.	141	2050
17.	148.4	2250
18.	152	2500
19.	154	2180
20.	160	2320
21.	163	2304
22.	170	2410
23.	176	2270
24.	180	2420
25.	187	2710
26.	189.4	2800
27.	191	2820
28.	192	2500
29.	195.8	2400
30.	198	2700

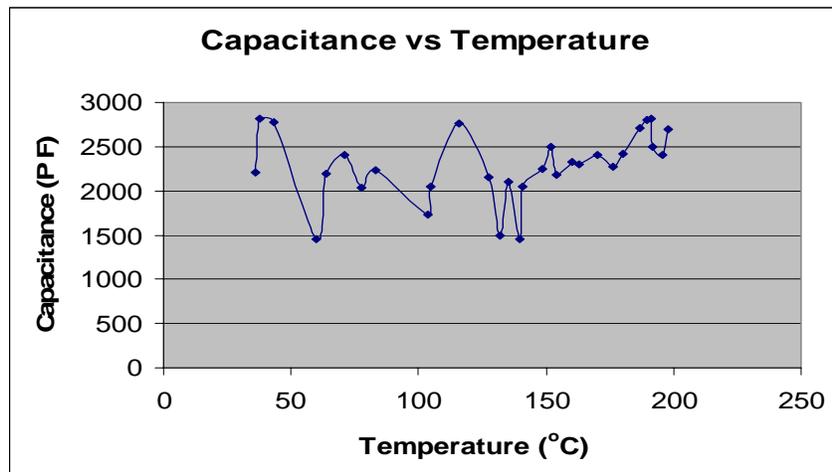


Fig. 5. Capacitance vs Temperature curve of nano-porous polycarbonate NTFs

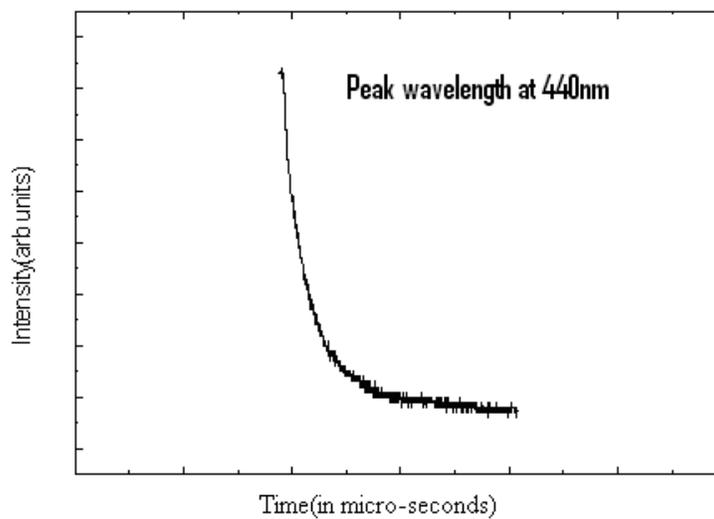


Fig. 6. TRLIP spectra of nano-porous polycarbonate NTFs.

#### 4. Conclusions

In this paper dielectric behavior in terms of capacitance of nanoporous polycarbonate membrane is studied. The charging and discharging mechanism with respect to temperature shows that nanoporous polycarbonate NTFs can be used as future electret applications. The TRLIP studies supports the electret behaviour in polycarbonate NTFs. The research on mechanism of electret formation in nanoporous polycarbonate and characterization aspects is going on and in future it will play a major role. There are large applications of electret technology in energy and health sensors.

## References

- [1] Eguchi M, Proc. Phys. Math. Soc. Jpn **1**, 326, (1919).
- [2] Sangawar V S and Adgaonkar C S, J. Polym. Mater. **12**, 11, (1995).
- [3] Fridkin V M and Zheludev I S, Photoelectrets and electrographic process (NY: Consultants Bureau), (1961).
- [4] Gross B, Charge storage in solid dielectrics (Amsterdam: Elsevier), (1964).
- [5] Latour M., Appl. Phys. (Paris) **7**, 115, (1972).
- [6] Turnhout J Van, Thermally stimulated discharge of polymer electret (Amsterdam: Elsevier) p. 25, (1975).
- [7] Klason Carl and Kubat Josef, J. Appl. Polym. Sci., **19**,831 (1975).
- [8] Ranjit Singh and Datt S C, Indian J. Pure & Appl. Phys., **18**, 839 (1980).
- [9] Srivastava S K, Ranade J D and Srivastava A P, Polymer, **22**, 1645 (1981).
- [10] Pissis P, Laudat J, Thonas C, Apekis L and Kyritsis A , Proc. ISE, **8**, 392 ( 1994).
- [11] Negau E and Negau R , Proc. ISE, **8**, 528( 1994).
- [12] Sangawar V S and Adgaonkar C S, J. Polym. Mater., **12**, 11( 1995).
- [13] Sangawar V S, D.C. electrical conductivity study of polystyrene and polymethyl methacrylate iodine doped thermoelectrets, Ph.D. Thesis, Amravati University, Amravati (1996).
- [14] Sawarkar S B, Deogaonkar V S, Pakade S V, Yawale S P, Indian J. Pure Appl. Phys., **35**, 281 (1997).
- [15] Ghosh P, J. Polym. Mater., **14**, 193 ( 1997).
- [16] Belsare N G and Deogaonkar V S, J. Polym. Mater., **15**, 157,( 1998).
- [17] Khare P K, Verma A and Paliwal S K, Bull. Mater. Sci., **21**, 207 (1998).
- [18] Quamara JK et al, Macromol Chem Phys, **202**, 1955-1960 ( 2001).
- [19] Singh R A et al, Bull. Mater. Sci., **28**, 423 ( 2005).
- [20] Burghate D K, Deogaonkar V S, Sawarkar S B and Yawale S P, Bull. Mater. Sci., **26**, 267 (2003).
- [21] Garg Maneesha and Quamara JK, multiple relaxation processes in high-energy ion irradiated kapton-H polyimide: Thermally stimulated depolarization current study(2006)
- [22] Sangawar V S et al, Bull. Mater. Sci., **29**, 413 (2006).
- [23] Kher V G and Adgaonkar C S, Indian J. Pure & Appl. Phys., **10**, 902 (1972).
- [24] Sangawar V S et al, Bull. Mater. Sci. **30**(2), 163 (2007).