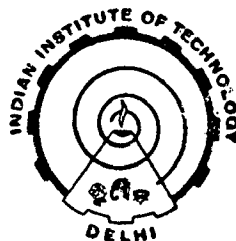


**STUDIES ON THE ELECTRONIC AND PYROELECTRIC PROPERTIES
IN POLYMERS
WITH SPECIAL REFERENCE TO POLY (VINYLIDENE FLUORIDE)**

By
TARA KAURA
PHYSICS DEPARTMENT

SUBMITTED
IN FULFILMENT OF
THE REQUIREMENTS OF THE DEGREE
DOCTOR OF PHILOSOPHY



to the
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
August, 1983

CERTIFICATE

I am satisfied that the thesis entitled "Studies on the Electronic and Pyroelectric Properties in Polymers with Special Reference to Poly(vinylidene Fluoride) by Tara Kaura is worthy of consideration for the award of the Degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by her under my guidance and supervision. The results in it have not been submitted in part or full to any other university or institute for award of any Degree/Diploma



Professor P.K.C. Pillai
(Research Supervisor)
Head of the Physics Department,
Indian Institute of Technology, Delhi,
New Delhi 110 016
INDIA

ACKNOWLEDGEMENTS

I take this opportunity to express my deep sense of gratitude to my supervisor Professor P.K.C. Pillai, Head of the Department of Physics, I.I.T. Delhi for his valuable guidance, untiring supervision and encouraging discussions during the course of my research work. I am also thankful to Dr. V.K. Srivastava and others in the Physics Department, University of Roorkee for their help and support in completing a part of this work at Roorkee.

I am extremely grateful to Dr. A.R. Verma, former Director, N.P.L. and his colleagues for their help in carrying out some X-ray diffraction experiments at N.P.L.

I gratefully acknowledge the assistance received from my friends at I.I.T. Delhi specially that from Dr. (Miss) Rashmi.

Mr. S.L. Aneja deserves special thanks for typing the present thesis in a record time at a very short notice.

The financial assistance from I.I.T. Delhi and C.S.I.R. India in the form of Fellowship is gratefully acknowledged.

Tara Kaura

(TARA KAURA)

PREFACE

The last two/three decades have seen a phenomenal growth of the science of materials and it is still continuing with more and more involvement in terms of both the scientific manpower and financial commitments. Basically the attempt has been to invent new materials to find new technological applications of the existing ones. Synthetic polymers belong to such a class of important materials with their remarkable diversity of properties. There are well known electrical applications of polymers in the form of devices but basically the role of the polymers is to resist electrical conduction. They have gained special status because of the need for large area electronic devices and low cost of fabrication.

Among the class of polymers the PVDF has emerged as one of the most promising material for variety of reasons. It is suitable for various technological applications such as IR detectors, ultrasonic transducers, optical and electronic devices etc. However, the details of structural properties in relation to its chemical and pyroelectric behaviour are not well understood. The field therefore remains an area of certain amount of controversy and contention.

The attempt through the investigations contained in this thesis has been to understand the correlation between the electrical and the structural properties of PVDF. It has also been possible to establish how these structural

properties depend on variations of temperature or stresses applied and thereby showing stability of PVDF when used in the form of devices. A short account of the work chapter-wise is presented below.

Chapter I of the thesis is devoted to an overall view of the present status of the understanding of the electronic and pyroelectric properties of polymers together with the actual and possible technological applications. In addition this chapter also contains an outline of the scope of present investigations and motivation for carrying out the same.

Chapter II deals with the details of the sample preparation and the various measurement techniques employed in the present studies. The results of the measurements of the optical and structural properties of PVDF are also described in this chapter.

The third Chapter contains the results of measurements of the effect of field and temperature on absorption currents in PVDF. The low frequency dielectric loss has also been evaluated using Hamon's approximation. The analysis of the observed experimental results enable us to identify the mechanism responsible for electrical conduction in PVDF.

In Chapter IV carrier mobility has been determined using a step field excitation technique. The results have been analysed with an aim to understand the conduction process in PVDF.

Chapter V deals with the results of the study of surface potential decay characteristics of solvent-cast pure and iodine doped and commercial unstretched and stretched PVDF films. An attempt is made to understand the processes involved in the corona poling of PVDF .

In Chapter VI a new model is proposed for pyroelectric effect taking into account the hopping of trapped charge carriers over the potential barrier and the existence of trapped charge gradient. The theory has been tested using some of the experimental results on solvent cast PVDF films.

Chapter VII contains the results and analysis of TSC investigations carried out in a series of experiments involving different poling conditions. These studies have enabled the evaluation of the trap depth , trap density, capture cross-section and attempt to escape frequency associated with prominent trapping centers.

A summary of the results and conclusions of the various studies on the electronic and pyroelectric properties in PVDF is presented in Chapter VIII.

Part of the results presented in the thesis have also resulted in the following research papers.

1. Proposed Model for Pyroelectric Effect in Poly(vinylidene Fluoride), J. Appl. Polym. Sci., 25,703-710(1980).

2. Drift Mobility Determination Using Surface Charge Decay Technique in Polyvinylidene Fluoride (PVDF), Polymer, 80, 232 (1981).
3. Step Voltage Transient Currents in Polyvinylidene Fluoride, J. Appl. Phys., July 1983
4. Pyroelectric Current in Cellulose-Acetate Films, Presented in the Conference on Ferroelectrics, 1980, IIT Delhi, India.
5. Absorption Current Studies in Polyvinylidene Fluoride (to be published).
6. Thermally Stimulated Currents in I_2 and Chloranil Doped PVDF (communicated).
7. Surface Potential Decay in PVDF in Stretched and Unstretched PVDF Films (communicated).

CONTENTS

	Page
CHAPTER I INTRODUCTION ..	1
1.1 Introduction ..	1
1.2 Conduction in Polymers ..	2
1.2.1 Ohmic and Non-ohmic Contacts ..	4
1.2.3 Space-Charge-Limited Currents (SCLC) ..	6
1.2.4 Ionic Conduction ..	9
1.2.5 Results in Polymers ..	11
1.3 Carrier Transport in Polymers ..	12
1.3.1 Transport Models for Polymers ..	13
1.3.2 Trapping States in Polymers ..	15
1.3.3 Carrier Mobility in Polymers ..	16
1.4 Doping in Polymers ..	17
1.4.1 Structure of Polymers ..	19
1.4.2 Optical Studies in Polymers ..	20
1.5 Charge Storage Properties of Polymers ..	22
1.5.1 Thermally Stimulated Discharge Currents (TSDC) ..	23
1.5.2 Transient Charging Currents in Polymers ..	25
1.6 Piezo- and Pyroelectricity in Polymers ..	27
1.6.1 Physical, Chemical and Morphological Properties of PVDF ..	28
1.6.2 Pyroelectric Coefficient and Applications ..	30
1.7 Surface Charging of Polymers ..	32
1.8 Scope of the Present Work ..	33
References ..	35

	Page
CHAPTER II	
EXPERIMENTAL: MEASUREMENTS AND INSTRUMENTATION AND STRUCTURAL INVESTIGATIONS	.. 50
2.1 Materials Used and Their Specifications	.. 50
2.2 Sample Preparation	.. 52
2.2.1 Solvent-Cast Films	.. 52
2.2.2 Electrodes	.. 53
2.3 Measurement Techniques and Instrumentation	.. 53
2.3.1 Measurement Cell	.. 53
2.3.2 Transient and Conduction Current Measurements	.. 54
2.3.3 Non-isothermal Current Measurements: Pyroelectric Current Measurements	.. 55
2.3.4 Surface Potential Decay Measurements	.. 57
2.3.5 Structural and Optical Studies	.. 59
References	.. 62
CHAPTER III	
THE STUDY OF ABSORPTION CURRENTS IN PVDF	.. 64
3.1 Introduction	.. 64
3.2 Experimental Results	.. 65
3.2.1 General Features of Charging Currents	.. 65
3.2.2 Field Dependence and the Quasi-Steady State Conduction	.. 67
3.2.3 Discharge Currents	.. 68
3.2.4 Low Frequency Dielectric Loss and Hamon Approxi- mation	.. 69

	Page
3.3 Discussion	72
3.4 Conclusions	76
References	77
 CHAPTER IV	
DETERMINATION OF CARRIER MOBILITY IN PVDF USING A STEP FIELD EXCITATION TECHNIQUE	79
4.1 Introduction	79
4.2 Effect of Contact on Transient Response to Step Field Excitation	80
4.3 Experimental Results	82
4.3.1 Voltage Dependence of Current Transients	82
4.3.2 Evaluation of Mobility	84
4.4 Discussion	86
4.5 Conclusions	89
References	91
 CHAPTER V	
STUDY OF THE SURFACE POTENTIAL DECAY CHARACTERISTICS OF PVDF FILMS	94
5.1 Introduction	94
5.2 Corona Injection Process	94
5.3 Results and Discussion	97
5.3.1 Isothermal Surface Potential Decay in Commercial PVDF Films	97
5.3.2 Surface Potential Decay in Solvent-Cast PVDF and PVDF:I ₂ Films	102
5.4 Conclusions	104
References	106

	Page
CHAPTER VI	
PROPOSED MODEL FOR PYROELECTRIC EFFECT IN PVDF	.. 108
6.1 Introduction	.. 108
6.2 Experimental Results	.. 109
6.3 Proposed Model and Discussion of Results	.. 111
6.4 Conclusions	.. 118
References	.. 119
CHAPTER VII	
THERMALLY STIMULATED CURRENTS IN PURE AND DOPED PVDF FILMS	.. 121
7.1 Introduction	.. 121
7.2 Background of TSC Analysis	.. 122
7.3 Results	.. 124
7.3.1 Field and Temperature Dependence of TSC for Commercial PVDF Films	.. 124
7.3.2 TSC Results for Solvent-Cast Pure and Doped PVDF Films	.. 125
7.3.3 Determination of Trapping Parameters from TSC	.. 128
7.4 Discussion	.. 128
7.5 Conclusions	.. 132
References	.. 134
CHAPTER VIII	
SUMMARY AND CONCLUSIONS	.. 136
8.1 Structural and Optical Properties	.. 136
8.2 Absorption Currents	.. 137
8.3 Carrier Mobility	.. 138
8.4 Surface Potential Decay Investigations	.. 139
8.5 Pyroelectricity and the Proposed Model	.. 141
Bio-Data	.. 145
List of Tables	.. 146