

**POSITRON ANNIHILATION SPECTROSCOPIC
STUDY OF POLY(CHLOROTRIFLUOROETHYLENE)
UNDER THE INFLUENCE OF COMPRESSION,
ELONGATION AND AGING**

THESIS

*SUBMITTED TO THE UNIVERSITY OF MYSORE
FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY
IN PHYSICS*

By

P. RAMACHANDRA

Supervisor

Dr. C. Ranganathaiah



**DEPARTMENT OF STUDIES IN PHYSICS
UNIVERSITY OF MYSORE
MANASAGANGOTRI, MYSORE-570 006
INDIA
1997.**

**POSITRON ANNIHILATION SPECTROSCOPIC
STUDY OF POLY(CHLOROTRIFLUOROETHYLENE)
UNDER THE INFLUENCE OF COMPRESSION,
ELONGATION AND AGING**

THESIS

*SUBMITTED TO THE UNIVERSITY OF MYSORE
FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY
IN PHYSICS*

By

P. RAMACHANDRA

Supervisor

Dr. C. Ranganathaiah



**DEPARTMENT OF STUDIES IN PHYSICS
UNIVERSITY OF MYSORE
MANASAGANGOTRI, MYSORE-570 006
INDIA
1997.**

IN FOND MEMORY OF

Late Smt. PUTTARANGAMMA

and

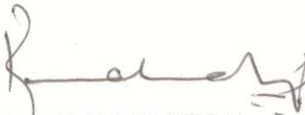
Late Smt. MAHADEVAMMA

DECLARATION

I hereby state that this thesis entitled "POSITRON ANNIHILATION SPECTROSCOPIC STUDY OF POLY (CHLOROTRIFLUOROETHYLENE) UNDER THE INFLUENCE OF COMPRESSION, ELONGATION AND AGING" has been revised by myself under the guidance of Prof C.Ranganathaiah incorporating the suggestions of the Indian examiner. The thesis in its present form is in conformity with the recommended suggestions of the examiner.

Mysore

20 August, 1998



(P. RAMACHANDRA)

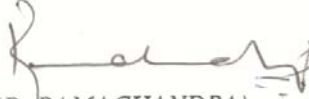
DECLARATION

I hereby state that this thesis entitled "POSITRON ANNIHILATION SPECTROSCOPIC STUDY OF POLY(CHLOROTRIFLUORO-ETHYLENE) UNDER THE INFLUENCE OF COMPRESSION, ELONGATION AND AGING" has been composed by myself and comprises the results of my investigations carried out in the Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore under the supervision of Dr. C. Ranganathaiah, Reader in Physics.

I also state that this thesis or any part of it has not been previously formed the basis for the award of any Degree, Diploma or other similar title.

Mysore,

15 September, 1977




(P. RAMACHANDRA)

CERTIFICATE

I certify that Mr. P. Ramachandra has revised the thesis independently incorporating the suggestions of the Indian examiner under my supervision. Now the thesis is suitable for reevaluation.


*Mysore
August, 1998*


Dr. C. RANGANATHAIAH - 20/8/98
Professor
Department of Studies in Physics
University of Mysore
Manasagangotri, Mysore - 570 006.

CERTIFICATE

I certify that this thesis comprises of the bonafide research work done by Mr. P. Ramachandra independently under my guidance and supervision.

*Mysore
September, 1997*

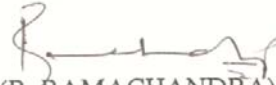

Dr. C. RANGANATHAIAH 22/9/97
Reader
Department of Studies in Physics
University of Mysore
Manasagangotri, Mysore - 570 006.

PREFACE

The conventional inorganic materials such as metals fail under adverse environmental conditions. Because of the excellent barrier properties, the organic materials such as polymers soon replaced the conventional materials. In order to use these materials effectively under various conditions, basic understanding of the defect nature of these materials is highly essential. Eversince the existence of free volume was postulated, this has become an interesting topic in polymer research. There has been a constant effort to understand the polymer properties in terms of free volume. Since, the dimensions of free volume holes are of sub-microscopic level, only few experimental techniques are available to characterize them. One among them is the Positron Annihilation Lifetime technique which has proved to be a novel technique to characterize the defects in condensed media. This is because of the fact that positrons and positronium preferentially scan the defects/ open volumes like free volumes. Since the annihilation characteristics can be measured accurately, the information on defects/ free volumes can be derived from positron annihilation parameters.

This thesis is divided into seven chapters. Chapter I gives an introduction to polymers and to the theory of positron annihilation technique. A brief description of Positron Lifetime Spectrometer and functioning of various components is provided in chapter II. Chapter III gives the author's investigation on Poly(chlorotrifluoroethylene)-PCTFE with different concentration of VF₂ comonomer viz., 22A, TVS and HP when subjected to elongation and compression. Chapter IV provides a brief theory on physical aging process in polymers and aging results on 22A and HP. Chapter V provides the author's investigation on the annealing behavior of 22A, TVS and HP. The results on the annealing behavior of strained HP and compressed 22A are given in chapter VI. Finally, the salient features of the thesis are provided in chapter VII.

Mysore



(P. RAMACHANDRA)

September 1977

ACKNOWLEDGEMENTS

*I deem it a proud privilege to be the student of my revered Research Supervisor **Dr. C. Ranganathaiah**, Reader, Department of Physics, University of Mysore, Manasagangotri, Mysore. I am extremely grateful and indebted to him for his excellent, inspiring and valuable suggestions, criticisms and constant encouragement throughout the research work. I am fortunate enough to be associated with such an experienced guide.*

*I am highly thankful to **Dr. S. Gopal**, Vice-Chancellor, Mangalore University, Mangalore and former Chairman, Department of Physics, University of Mysore, Manasagangotri, Mysore for his encouragement and support during the initial stages of this research work.*

*I express my deep sense of gratitude to my brother-in-law **Dr. N.S. Murthy**, AlliedSignal Inc., NJ, USA for his encouragement to take up this research work and helped me in supplying polymer samples. I am also thankful to my another brother-in-law **Mr. Aswathanarayana Swamy**, Giri Electronics, Mandi Mohalla, Mysore for his constant help and encouragement throughout this work.*

*I would have not come to this position today, without the service and sacrifice of my brother **Mr. P. Sannappaiah**, Senior Labour Inspector, Bangalore, India and his family. I shall be ever grateful and thankful to them.*

*I am grateful to **Prof. G.H. Sawkar**, former Principal of K. G. F. First Grade College and present Director of College Development Council, Bangalore University, Bangalore and to **Dr. V. Sreeramalu**, H.O.D. of Physics, K.G.F. First Grade College, Oorgaum, Kolar Gold Fields, India who has inspired and helped me to take up and to complete this work. My thanks are also due to my learned colleague **Mr. T.S.G. Ravichandran**, for his support during the course of this investigation.*

No words are sufficient to express my gratitude to my learned colleague **Dr. R. 'Ramani**, Research Associate, Department of Physics, Manasagangotri, Mysore for his help and whole hearted co-operation extended to me to complete this work.

It is my pleasant duty to acknowledge warmly the generous help and co-operation extended to me by my colleagues, **Mr.G. Rangopal, Mr. Gani Shariff, Mr. M.C. Thimme Gowda and Mr. P.M. Sathyanarayana**.

I am grateful to **Dr. B. Viswanathan**, Head, Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, India who taught us basic principles and for his encouragement during the budding stages of this work.

I am very much thankful to the Director and to **Dr. G.M. Nagaraja Rao**, National Institute of Rock Mechanics (NIRM), Kolar Gold Fields, India for his help to compress the polymer samples in their laboratory. I am also thankful to the Managing Director and to **Mr. T. V. Shetty and Mr. R.B. Ranganatha**, E.M. Division Lab, Bharaths Earth Movers Limited (BEML), Kolar Gold Fields, India for their help to elongate the polymer samples.

I am extremely grateful to **Dr. M. Eldrup**, Department of Chemistry, Rison National Laboratory, Denmark for providing the computer program PATFIT-88

I am very much thankful to **The University of Mysore**, Mysore for providing facilities to carry out the research work in the Department of Studies in Physics, Manasagangotri, Mysore on Part-time basis.

I offer my sincere thanks to **Prof. M.S. Madhava**, Chairman, Department of Physics, University of Mysore, Manasagangotri, Mysore for his encouragement and support during the course of this work. My sincere thanks are also due to **Profs. J. Shashidhara Prasad, K. Gopala and Ramakrishna Gowda**, Department Physics, University of Mysore, Manasagangotri, Mysore for their encouragement.

*I express my special gratitude to **Smt. Nirmalambha Ranganathaiah** for her affection and encouragement during the course of this research work.*

*I wish to record my profound thanks to my beloved wife, **Mrs. Geetha Ramachandra** for her affection and encouragement which enabled me to complete this work. My very special thanks to my children **Mr. Honnesh** and **Miss. Puneetha** for their patience during my frequent absence from home.*

*I wish to express my sincere thanks to my father **M. Pettigappa**, and to my brothers and sisters for their affection and inspiration which enabled me to complete this research work.*

It is a pleasure to record my sincere thanks to all the members of the teaching faculty and all the Research Fellows of the Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore for their co-operation and encouragement during the course of this work. I wish to thank all the non-teaching staff of the Department of Studies in Physics, University of Mysore, Mysore for their help received directly or indirectly.

Finally, I wish to thank all the persons who have helped me directly or indirectly during my research work.

*Mysore
September 1997*



(P. RAMACHANDRA)

CONTENTS

CHAPTER I	:	Introduction	1
CHAPTER II	:	Experimental technique and data processing	41
CHAPTER III	:	Effect of stress on the microstructure of Poly(chlorotrifluoroethylene)	69
		(a) Tensile behavior of uniaxially drawn Poly(chlorotrifluoroethylene)	
		(b) Compressibility of Poly(chlorotrifluoroethylene)	
CHAPTER IV	:	Physical aging of Poly(chlorotrifluoroethylene)	92
CHAPTER V	:	Influence of Vinylidene fluoride on the annealing behavior of Poly(chlorotrifluoroethylene)	113
CHAPTER VI	:	Effect of pressure on the annealing behavior of Poly(chlorotrifluoroethylene)	127
		(a) Annealing behavior of strained (elongated) Poly(chlorotrifluoroethylene)	
		(b) Annealing behavior of compressed Poly(chlorotrifluoroethylene)	
CHAPTER VII	:	Summary	143
		List of author's publications	146