STUDIES ON THE DIELECTRIC AND ELECTRONIC PROCESSES IN POLYMERS

WITH SPECIAL REFERENCE TO

POLY VINYL CINNAMATE AND POLY VINYL CARBAZOLE

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PREFACE

Polymers have found applications in almost all walks of life. In the field of electrical and electronic industries, polymers have considerably improved their status in recent years. In addition to their conventional role as electrical insulators, they now feature as sensitive elements - sensitive to temperature, radiation and electric stress. The furthering of these newer vistas demands an understanding of the underlying dielectric and electronic processes in polymers. And this forms the topic of the present thesis.

Coming to think of the 'dielectric and electronic processes in polymers', one is reminded of Ecclesiastes (Chapt. 9, Verse 11):

> "The race is not to the swift, nor the battle to the strong -
> But time and chance happeneth to them all."

In polymers, we deal with slow and sluggish charge carriers (present at 1 million cm^{-3} level) which at an electric field as high as 1 MV cm^{-1}, hardly manage to drift across one centimetre length in a second's time. And here, we deal with the 'hesitating' dipoles which take years to settle down to the thermodynamic equilibrium (upon the application or withdrawal of an electric stress). But still the polymers conduct, and their dipoles rotate, and when we subject them to a changing temperature, radiation or electric field, they do respond!

In the first chapter, a survey of the current trends in the study of the dielectric and electronic processes in polymers is presented. Some of the practical applications of polymers such as in 'electrets' and 'electrophotography' are critically reviewed. The last section of this chapter presents the scope of the present work - analysis of the photocrosslinking in Poly(vinyl cinnamate) (PVCn) by the dielectric and electrical methods and the investigation of the photocarrier generation and trapping in Poly(N-vinyl carbazole) (PVK) and their applications in electrophotography.

Chapter II contains the details of sample preparation and measurement techniques employed in the present study. Design and development of a number of experimental setups for the different studies are also briefly described.

In Chapter III, the photocrosslinking in PVCn is analysed using a.c. and d.c. techniques. Activation energies for dipolar relaxation and charge carrier generation for PVCn and its crosslinked product are obtained from the isothermal relaxation and steady state current data.

Chapter IV illustrates the utility of non-isothermal relaxation (thermally stimulated discharge current or TSC) technique in analysing the photocrosslinking process in PVCn. TSC is employed to study the dipolar relaxation times, their distribution and activation energies. The capture cross section, attempt to escape frequency and low frequency dielectric loss are also computed from the TSC data.

Chapters V and VI respectively deals with the photoconduction and photoelectret state in PVK. The effect of illumination intensity, temperature, electric field, purity and crystallinity on the photo and dark carrier generation, transport and trapping are investigated. The studies lead to the conclusion that the high field photoconduction in PVK is due to the field-assisted carrier detrapping.

Corona-induced surface activation in polymers is of immense academic and practical interest. The decay of the surface charge sprayed onto the polymer foil from the corona discharge can yield valuable information about its transport parameters. The thermal and photodissipations of the surface charge, which form the basis of electrostatic printing techniques, have considerable technological applications. The surface activation technique could also be used in the fabrication of very strong foil homo-electrets and to improve the self-adhesion of polymer films. Chapter VII contains an analysis of the mechanism and dynamics of the corona-induced surface activation of polymers. Many of the above mentioned aspects as applied to PVK and PVCn are also studied.

Chapter VIII could be considered as totally application-oriented. PVK and its charge transfer complexes (with electron acceptor dyes) are the best organic photoconducting systems. They possess charge acceptance and decay characteristics well suited for electrophotographic applications. The studies show that double layer structure consisting of a PVK:trinitrofluorenone layer coated over pure PVK exhibits excellent electrophotographic performance. Thus, PVK offers an alternative to the costlier selenium 'master plates'

in Xerography. Moreover, the flexibility of the polymer system suggests the possibilities of developing detachable 'master sheets' that could be fixed to a metallic drum in the automatic 'electroprinting' machines, in place of the selenium coated metallic drums.

Chapter IX features the summary of the results from the different studies on PVCn and PVK. It is shown that comparison and correlation of the results yielded from different investigations give useful information about the microscopic properties of the polymer system with special reference to PVCn and PVK.

It is hoped that the present work will be of some interest to the solid state scientists in general and the experimental polymer physicists in particular. It offers a new method for the study of the photocrosslinking process in polymers - a field which is gaining interest because of the importance of photolithography in all microminiaturization techniques. It also explains, to a certain extent, the mechanisms responsible for the high field photoconduction in PVK - a polymer which offers immense prospects in the electrical and electronic industry. The work is also believed to be of technological importance, as it provides an alternative photoreceptor system, with added advantages, over the costly selenium plates and drums now prevalent in the electrophotographic machines.

A part of the work presented and referred to in this thesis has also resulted in the following research papers (communicated/accepted for publication):

1. Study of polymer crosslinking by thermally stimulated current - Polymer (accepted for publication).

2. Non-isothermal decay of normal and photocrosslinked PVCn electrets - (communicated).

3. Evaluation of very low frequency dielectric loss factor in Poly(vinyl cinnamate) - (communicated).

4. On the field dependent photoconduction in Poly(vinyl carbazole) - Polymer (accepted for publication).

5. Photoelectret state in Poly(vinyl carbazole) - J. Polym. Sci. Polym. Phys. (accepted for publication).

6. TSC reversals in ZnO photoelectrets - (communicated).

7. Determination of recombination and trapping kinetics in ZnO photoelectrets - (communicated).

8. Non-isothermal relaxation in ZnO photoelectrets - (communicated).

9. Double layer structures for transfer electrophotography - IEEE-IAS Conf., Chicago (Oct. 1976) (accepted).

10. Binder type plate for electrophotography - IEEE-IAS Conf., Chicago (Oct. 1976) (accepted).

11. ZnCdS-Ag binder layers as applied to charge transfer electrophotography - Photo. Sci. & Eng. (accepted for publication).

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