

## Relaxation Studies in Polymer Dielectrics - A Review

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### Abstract

*Dielectric materials play an important role in defence, data sensing, guidance control, navigation and communication through electronic means which are dependent on proper functioning of thousands of tiny circuit elements fitted on certain dielectric substances and separators. The dielectric parameters of such materials are therefore extremely important. Polymer dielectrics are the most needed materials nowadays as they have applications in almost every field and they are easy to process. Dielectric relaxation studies in polymers, blends and composites are being done by a large group of researchers.*

**Keywords:** Dielectric relaxation; Polymers; Blends ; Composites

### Introduction

Polymers are large class of materials and they consist of a large number of small molecules called “monomers” that can be linked together to form a very long chain. Thus they can be called “huge molecules” or “Macromolecules “ the word comes from the origin 'makros', which mean large and 'molecula' which mean small mass.

Relaxation is a classical phenomena and it is about a process by which the system goes from non-equilibrium state to equilibrium state. Relaxation processes have different names according to their origin thus we have thermal relaxation, dielectric relaxation or dipole relaxation and structural relaxation. Study of relaxation processes in semi-crystalline polymers is a subject of continuing great scientific and technological interest. Number of investigations have been undertaken with the purpose of characterizing the relaxations in these materials and there has been great scientific interest in the detailed description of the molecular processes underlying them. Molecular interpretation of the relaxation processes is slow and conflicting that even if it is the same process the molecular interpretation may differ. In the past

view years there have been a number of development, which clarify the nature of many of the relaxation phenomena. In semi-crystalline polymers in the range between liquid nitrogen temperature (77K) and melting temperature often three or at least two processes are commonly observed  $\alpha$ ,  $\beta$ , and  $\gamma$  or  $\beta$ , and ( $\alpha_a$ ) in some semi-crystalline polymers which do not show  $\alpha$  process. Each of these processes has distinct characteristics. In a semi-crystalline polymer, which shows all the three processes,  $\alpha$ - process, which is a high temperature relaxation process, is commonly considered to be connected to the amorphous phase and associated with the glass-rubber relaxation. The  $\beta$ - process in such a polymer has been connected also to the amorphous phase. The  $\gamma$ - processes (or  $\beta$  in the crystalline polymers which do not show  $\alpha$ -process) it is generally agreed that it has an amorphous phase origin, but many studies consider it as it have component from a crystalline phase. The relaxation processes studies in semi-crystalline polymers show that these three relaxation processes ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) are in order of decreasing temperature.

The mechanism of the first process known as “ $\alpha$ -process” is related to the main chain motions and it observed around glass transition temperature. In addition, its intensity is increasing by increasing the degree of crystallinity. The second process is the  $\beta$ -process, which related to the movement of the side group chains or branches and it related to the amorphous regions the third process is the  $\gamma$ -process, which is related to the local intermolecular relaxation at a temperature below  $T_g$ .

As the amorphous and crystalline phases are not well defined in polymers it is difficult to decide which relaxation belong to which phase. We shall consider as belonging to the crystalline phase those relaxations, which are applicably increased by increasing crystallinity, crystal form, or size. It does not necessarily mean that the units, the

motion of which is reflected by the particular relaxation are actually arranged in a crystalline lattice.

Most prominent change in the macroscopic behavior of amorphous polymers is the glass-rubber relaxation where the rigid glassy solid material becomes a viscoelastic fluid. At this relaxation the mechanical strength of the material decreases rapidly, there is an abrupt change in the thermal dilation versus temperature curve. The thermal conductivity, mechanical loss at a periodic stress, dielectric loss, and static dielectric constant also change appreciably by passing through this relaxation.

### **Dielectric materials**

Even the simplest electric circuit cannot be composed without conducting and electrical insulating materials. The purpose of electrical insulation boils down first and foremost to preventing the flow of current via the routes undesirable for the operation of a given electric circuit. The materials in which electrostatic field can persist for a long time are understood as dielectric materials. These materials offer a very high resistance to the passage of electric current under the action of applied direct-current voltage and therefore, sharply differ in their basic electrical properties from conductive materials. However, under the action of alternating voltage any dielectric material will pass alternating capacitive current (displacement current). In order to assess the applicability of the dielectric materials, it is required to know not only their electrical properties but also their general physical and chemical properties. The study of the electrical and other properties of dielectrics in relation to their chemical composition and structure will lay the basis for obtaining new materials with pre-assigned properties.

An extremely sensitive tool for the understanding of molecular behaviour is the interaction of molecular system with the electromagnetic fields. The molecular interactions in the microwave frequency region are helpful in understanding the dielectric relaxation behaviour of polar substances. Two important properties which can be studied by microwave absorption measurements are the relaxation time and dipole moment of a polar molecule. The most extensive studies have been made on the solid and liquid dielectrics [1–5].

The dielectric studies have made important contribution to the fundamental research, as they predict microscopic behaviour of these substances on one hand and secondly their findings are useful in predicting applications of dielectric materials in various fields of applied sciences. Dielectric studies are also helpful in the investigation of various diseases, viz., the presence of water in the lungs of a patient may be detected by microwave absorption measurement and the studies of scattering and absorption of microwave by living tissues, may help in detecting the presence of cancerous cells in the body [6].

Liquid dielectrics are used as impregnates for high voltage cables and capacitors, as filling compounds for transformer circuit breakers, heat transfer agents in transformers and as arc quencher in circuit breakers. Petroleum oils, synthetic hydrocarbons and halogenated acid hydrocarbons are commonly used as liquid dielectrics.

Dielectric materials play an important role in defence, data sensing, guidance control, navigation and communication through electronic means which are dependent on proper functioning of thousands of tiny circuit elements fitted on certain dielectric substances and separators. The dielectric parameters of such materials are therefore extremely important.

### **Polymer dielectrics and importance of dielectric studies**

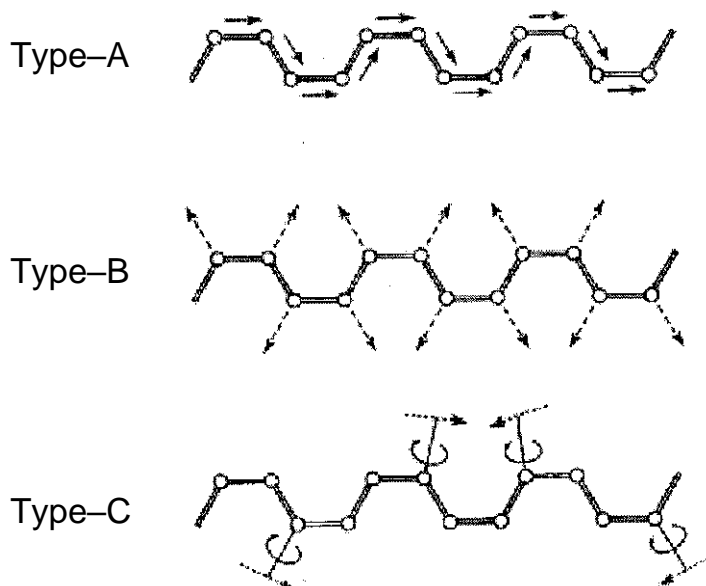
In view of the application of isolation, insulation and passivation properties of polymers in microelectronics and optical waveguide systems, the studies of dielectric properties of such materials are of considerable interest. As electrical components are miniaturized, the need for well characterized dielectric measurements on thin materials is in great demand. New packaging technology requires substrates with low permittivity. Dielectric studies [1–14] of polar molecules and polymers in pure liquid state, in dilute solutions and in solid state at microwave frequencies provide vital information on the molecular configuration of a system. The dielectric properties of organic compounds are studied by its interaction with electro-magnetic field. When polymeric substance is subjected to electric field, polarisation phenomena occurs [7–9]. The electric field may cause a small displacement of electrons, which produces an

induced electric moment in the molecules. This electric moment persists during the whole time for which the field is applied. The displacement of polar groups requires some time and is thus dependent on frequency and temperature, which leads to different dispersion phenomena according to segmental motion of the chain or orientation of pendent dipoles. At frequencies and temperatures, where dispersion occurs, only a part of the entering electric energy is stored which is proportional to the dielectric permittivity while some energy is lost which is proportional to the dielectric loss. For organic molecules the dispersion region of the energy loss lie in the microwave frequency region and hence exhibit the importance of measurements at these frequencies. Conformational changes originating in macromolecules as a consequence of their interaction with solvent have been the subject of large number of investigations. Microwave dielectric relaxation studies in non-polar solvents are very useful in determining the flexibility of chains, mobility of the polymer segment, internal group rotation and steric hindrance to the internal rotation due to hydrogen bonding. Dielectric studies of polymers at lower frequencies have been done by many researchers [29-30]

Based on chain architecture, polymers can be classified into three categories for dielectric study: type-A with dipoles oriented parallel to the backbone, type-B also with dipoles in the backbone but in the perpendicular direction, and the dipoles of type-C polymers located in the flexible side chain (Figure 1). There are also many polymers that have dipoles both parallel and perpendicular to their backbone.

The dielectric relaxation properties of polymer solutions in organic solvents have been investigated extensively [15-18] and it has been revealed that the relaxation peak due to micro-Brownian motion is observed at a frequency between 1 MHz and 10 GHz. Chain motion associated with conformational transition in the backbone of a polymer chain is a subject of particular importance for the interpretation of chain dynamics [15-22]. Microwave dielectric relaxation studies in non polar solvents are very useful in understanding the flexibility of chains, mobility of the polymer segments, internal group rotation and steric hindrance to the internal rotation due to hydrogen bonding.

A number of worker [16-18,23-28] have made extensive studies on polymers in the form of dilute solutions in non polar solvents and in films.



**Figure 1:** Schematic illustration classifies the architecture of the dipoles of polymer chains. The circles indicate atoms in the chain backbone. Type-A and type-B dipoles (solid and dashed arrows), both attached to the chain backbone, are parallel and perpendicular to the backbone. The type-C dipoles (dotted arrow) are attached to the side group

Murthy *et. al.* [16] have studied dielectric relaxations in poly (butyl acrylate), poly (butyl methacrylate) and poly (isobutyl methacrylate) solutions in the frequency region of 1 KHz to 24.42 GHz. They obtained distribution parameter and relaxation time by making Cole–Cole plots. They have evaluated activation energies by assuming dielectric relaxation to be a rate process in these solutions. Iwasa *et. al.* [17] carried out dielectric measurements in dilute solutions of isotactic and syndiotactic poly (methyl methacrylate)s in the frequency range of 1–150 MHz over a wide range of temperature. They concluded that even in dilute solution, the dipolar motion of PMMA is mainly controlled by the intramolecular interactions and the values of dielectric activation energies obtained for I and S–PMMA in dilute solution were not much affected by the solvent viscosity.

Sengwa and Choudhary [18] have studied microwave dielectric relaxation and molecular dynamics in binary mixtures of poly (propylene glycol) 2000 and poly (ethylene glycol)s of varying molecular weight in dilute solution. They have concluded that in the mixtures the relaxation time corresponding to group rotations is independent of the solvent environment and constituents of the binary mixtures.

Shukla *et. al.* [23] have studied dielectric absorption of dilute solutions of poly (ethyl methacrylate) (PEMA) and poly (n–butyl isobutyl methacrylate) (PBiBMA) at radio and microwave frequency with temperatures varying between 288 to 328 K. They have obtained enthalpies of activation to be 9.6 and 27.2 KJ/mol respectively using frequency variation for PEMA and PBiBMA. They have concluded that the dilute solution measurements seem to facilitate the orientation of even heavier substituent groups to exhibit the relaxation process, giving rise to enthalpies associated with it.

Dominguez–Espinosa *et. al.* [24] have analyzed the relaxation properties of poly (methyl cyclohexyl methacrylate)s–(P2MCHMA), (P3MCHMA), & (P4MCHMA) by using dielectric spectroscopy techniques. They observed four relaxation zones labeled  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  in decreasing order of temperature. Mohamed *et. al.* [25] measured the dielectric permittivity  $\epsilon'$ , and the loss factor,  $\epsilon''$ , of dry poly (2–hydroxyethyl methacrylate) using in the frequency range of 1 Hz to 100 KHz and between the temperature range of –150 to 275<sup>o</sup> C.

Deligoz *et. al.* [26] measured the dielectric constant and dielectric loss of the conventional and novel cross–linked polyimide films which they found to be frequency and temperature dependent. They concluded that the dielectric constant of the novel cross–linked polyimide film has lower values compared to dielectric constant of conventional polyimide film. Natarajan and Dube [27] studied dielectric behavior of doped and pure PVC samples and found that presence of iodine in PVC samples modified both the real and imaginary parts of the complex permittivity.

Khare *et. al.* [28] studied the dielectric properties of undoped and malachite green doped poly (methyl–methacrylate) (PMMA) films of approximately 20 microns in thickness by varying the temperature from 60 to 180<sup>o</sup> C. They have reported that PMMA films exhibit two dielectric loss maxima, one around 100<sup>o</sup> C and the other around 150<sup>o</sup> C, the dielectric loss maximum at 100<sup>o</sup> C corresponds to the  $\beta$ –relaxation peak and the second dielectric loss maximum in the  $\alpha$ –relaxation peak. The variation of permittivity with temperature has been attributed to the thermal expansion in the lower temperature region, to the orientation of dipolar molecules in the neighborhood of  $T_g$  and to the chaotic random thermal motion of molecules above  $T_g$ .

Fahmy *et.al.* [29] used dielectric relaxation spectroscopy and investigated for pure ABS, pure SAN and its polyblend samples in a frequency range from 100 Hz to 100 kHz at different temperatures from 303 K to 150 K. Their samples were observed to be characterized by high a dielectric constant ( $\epsilon'$ ) at low frequencies and high temperatures. They concluded that the behavior may be attributed to free charge building up at the interfaces within the bulk of the sample (interfacial or Maxwell–Wagner–Sillars (MWS) polarization) and at the interface between the sample and the electrodes (space charge polarization), particularly for polyblend samples. Their dielectric loss data revealed that all samples were characterized by a relaxation peak located in the vicinity of the glass transition temperature ( $T_g$ ). The AC conductivity ( $\sigma_{ac}$ ) behavior was examined for all samples at different temperatures by the.

### Conclusion

Dielectric spectroscopy is useful technique to investigate the relaxation processes in the semi-crystalline polymers and copolymers. An investigation into dielectric relaxation behaviour

of various polymers, blends and composites helps in choosing that particular material for microelectronics, PWB's, insulation, aeronautical industry ,aircraft structures ,space vehicles and telecommunication. Moreover such studies help in understanding of the microstructure within the material. Increasing demands of industries worldwide for new materials with tailor made properties led researchers and scientists to have better understanding of polymers, blends and composites.

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