CHAPTER 2
Materials and Experimental Studies
This chapter introduces the basic aspects of polymer modifications, experimental methods and characterization techniques employed in the research work. Experimental section provides the details of the measurement techniques such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), employed to measure the thermal properties of both synthesized and modified polymers. The important characterization techniques such as Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), and gel permeation chromatography (GPC) are also discussed in brief.

1. Polymer modification

Polymer modifications represent a valuable synthetic approach to unique polymer compositions, structure, and properties not readily available by the direct polymerization of monomers. Modified polymeric products [1-6] already exist in the commercial world, modified celluloses, for example, so the approach is not new. However, it is an interesting and challenging opportunity to develop new materials for a variety of specialty applications using the "chemistry on polymers" approach. With the vast commercial importance of polymers it is perhaps not surprising that there have been huge developments in synthetic methodology [7-13].

2. Polymer Characterization Techniques

The polymer characterization methods described in this section covers only the general information on the procedures for carrying out the spectroscopic measurements. However, detailed and specific protocols are given in the corresponding chapters.
2.1 Fourier transform infrared (FTIR) spectroscopy

Vibrational spectra of polymeric materials contain vast amounts of information about their molecular or microscopic structure, geometric and steric isomerism, molecular orientation, conformational regularity, crystallinity, and the local microscopic environment of specific functional groups of polymeric materials can be elucidated with vibrational spectroscopic analysis. In particular, Fourier transform infrared spectrometry is a convenient and powerful tool of measuring vibrational spectra of polymeric materials [14]. The characteristic IR vibrations are influenced strongly by small changes in molecular structure, thus making it difficult to identify structural fragments from IR data alone. However, there are some groups of atoms that are readily recognised from IR spectra. IR chromophores (such as carbonyl, hydroxyl and other characteristic groups) are most useful for the determination of structure [15].

2.2 Nuclear magnetic resonance (NMR) spectroscopy

The extensive chemical applications of NMR lie in the elucidation of structure, identification of the compounds, study of molecular conformation, dynamic processes and the interaction between the molecules. In some cases, the NMR method alone may be sufficient for obtaining the structure of an unknown compound, while in other cases the NMR spectrum may compliment the results obtained from the other methods. NMR Spectroscopy is a powerful technique for studying the macromolecules at the atomic level [15].
The use of NMR spectroscopy of nuclei other than $^1$H to characterise and identify organic and inorganic compounds is now common. With the development of Fourier-transform methods, extensive studies have been made on the NMR spectra of the compounds, $\delta$ which are used as a prime tool in structural analysis.

2.3 $^{13}$C NMR spectroscopy

The $^{12}$C nucleus is not magnetically active (Spin $I = 0$) but the $^{13}$C nucleus like $^1$H has a spin of $\frac{1}{2}$. In the high resolution NMR, the $^{13}$C nucleus is second in popularity to the proton. The $^{13}$C NMR spectroscopy is most useful in organic structural analysis. The magneto gyric ratio of $^{13}$C is 1.404 as compared to 5.585 for the proton, and hence the $^{13}$C signals are inherently weaker.

2.4 Thermal Analysis of Polymers

A simple example of the relationship between “structure” and “properties” is the effect of increasing molecular weight of a polymer on its physical (mechanical) state; a progression from an oily liquid, to a soft viscoelastic solid, to a hard, glassy elastic solid. Even seemingly minor rearrangements of atomic structure can have dramatic effects as, for example, the atactic and syndiotactic stereo isomers of polypropylene the first being a viscoelastic amorphous polymer at room temperature while the second is a strong, fairly rigid plastic with a melting point above 160°C. At high thermal energies conformational changes via bond rotations are frequent on the time scale of typical processing operations and the polymer behaves as a liquid (melt). At lower temperatures the chains solidifies by either of two mechanisms: by ordered molecular packing in a crystal lattice, crystallization,
or by a gradual freezing out of long range molecular motions, *vitrification*. These transformations, which define the principal rheological regimes of mechanical behavior: the melt, the rubbery state, and the semicrystalline and glassy amorphous solids, are accompanied by transitions in thermodynamic properties at the glass transition temperature, the crystalline melting, and the crystallization temperatures.

Thermal analysis techniques are designed to measure the above mentioned transitions both by measurements of heat capacity and mechanical modulus (stiffness).

2.5 Thermogravimetric analysis (TGA)

TGA is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated [16, 17]. The measurement is normally carried out in air or in an inert atmosphere, such as helium or argon, and the weight is recorded as a function of controlled temperature program, because, mass is a fundamental attribute of any material, any change is more likely to be associated with a chemical change, which may, confine on the compositional change.

2.6 Glass transition temperature

Glass transition temperature is the temperature below which a polymer is hard and above which it is soft [18]. The hard, brittle state is known as the glassy
state and the soft, flexible state as the rubbery or viscoelastic state. On further heating, the polymer becomes a highly viscous fluid and starts flowing. This state is termed the viscofluid state and the transition takes place at its flow temperature $T_f$.

2.7 Differential scanning calorimetry (DSC)

DSC is a thermal analysis technique that looks at how a material's heat capacity ($C_p$) is changed by temperature. A sample of known mass is heated or cooled and the changes in its heat capacity are tracked as changes in the heat flow. This allows the detection of transitions like melts, glass transitions, phase changes, and curing. Because of this flexibility, DSC is used in many industries including pharmaceuticals, polymers, food, paper, printing, manufacturing, agriculture, semiconductors, and electronics as most materials exhibit some sort of transitions. DSC is used widely for examining polymeric materials to determine their thermal transitions; these include the glass transition temperature ($T_g$), the crystallization temperature ($T_c$), the melt temperature ($T_m$) and the degradation or decomposition temperature ($T_d$). Chemical changes due to polymerization reactions, degradation reactions and other reactions affecting the sample under investigation can also be determined [19, 20].

2.8 Gel permeation chromatography (GPC)

A chromatographic method in which particles are separated based on their size, or in more technical terms, their hydrodynamic volume, and is applied particularly to the polymers [21]. The stationary phase consists of beads of porous
polymeric material (acts as reference). As this separation technique is based on size of the particles under study, it can also abbreviate as size exclusion chromatography (SEC), which separates the analytes basis of their sizes. GPC has many advantages. First of all, it has a well-defined separation time due to the fact that there is a final elution volume for all unretained analytes. Additionally, GPC can provide narrow bands [22], although this aspect of GPC is more complex but advantageous for polymer samples that have broad ranges of molecular weights present. For investigating the properties of polymer samples in particular, GPC can be very advantageous. GPC provides a more convenient method of determining the molecular weights of polymers. In fact most samples can be thoroughly analysed [23].

2.9 Density and Viscosity measurements

The densities of precursors were determined using the ASTM standard D-792.

Intrinsic viscosity was determined by the solution viscosity method using Ubbelhode viscometer [24]. The intrinsic viscosity (\( \eta \)) was obtained by a graphical procedure using flow times with solution in relation to flow time with the solvent. \( \eta_k = t/t_0 \), where \( \eta_k \) is relative viscosity, \( t \) is the flow time of the solution and to that of the solvent. \( \eta_k \) leads to \( \eta_{sp} \) as \( \eta_{sp} = \eta_k -1 \). \( \eta_{sp/c} \) is plotted as a function of \( C_p \) and the intercept of the linear plots gives (\( \eta \)), where \( C_p \) is the concentration of polymer in solution.
2.10 UV-Vis Absorption Spectroscopy

In this technique, the absorption of light in the ultraviolet (10-420 nm), visible (420-700 nm) and near-infrared (700-2500 nm) regions by a sample is measured. The absorption of light in the UV/Vis region depends on the nature of chemical groups presenting the structure.

A polymer molecule, in its ground state contains two electrons of equal and opposite spin in each filled molecular orbital. One of the electrons in the highest filled $\pi$ molecular orbital absorbs light and is raised to the lowest unfilled $\pi$ molecular orbital. If the spins are antiparallel, we get an excited singlet state and if they are antiparallel, an excited triplet state results. The different possible transitions are,

2.10.1 $\sigma-\sigma^*$ transition

Here the transition of electron is from a bonding sigma orbital to a higher energy antibonding sigma orbital. Since sigma bonds are very strong, this transition is a high energy process.

2.10.2 $n-\sigma^*$ transition

This transition is observed in saturated compounds having one heteroatom with unshared pair of electrons. These transitions require less energy than $\sigma-\sigma^*$ transitions.

$n-\sigma^*$ transitions are sensitive to hydrogen bonding.
2.10.3 $\pi-\pi^*$ transition

Such transitions occur in compounds with unsaturated centres and requires less energy than $n-\sigma^*$ transitions.

2.10.4 $n-\pi^*$ transition

Here an electron of unshared electron pair on a heteroatom is excited to a $\pi^*$ antibonding orbital. $n-\pi^*$ transition requires the least amount of energy than all the above transitions and consequently this transition gives rise to an absorption band at longer wavelengths.

The absorption co-efficient $\alpha$ is measured, by dividing the absorption values by the film thickness.

The photon absorption in many amorphous materials is found to obey the Tauc relation given by,

$$(\alpha h \gamma) = B (h\gamma - E)^n$$

Here $\alpha$ is the absorption coefficient in evcm$^{-1}$, $h\gamma$ the photon energy, $B$ a constant and the index $n$ is connected with the distribution of the density of states. For direct allowed transition energy gap, $n=1/2$ and for indirect allowed transition energy gap, $n=2$. $(\alpha h\gamma)^2$ as a function of photon energy $h\gamma$ gives direct allowed transition energy gap. $(\alpha h\gamma)^{1/2}$ as a function of photon energy $h\gamma$ gives indirect allowed transition energy gap [25, 26].
3. References


