4. SYNTHESIS AND CHARACTERIZATION OF PMDA-ODA AND PMDA-ODA-IDDA POLYIMIDE FILMS

4.1 INTRODUCTION

In recent years, polyimides have become most demanding high performance polymers due to their excellent thermal stability, improved mechanical and electrical properties. Among these polyimides, aromatic polyimides are well known for their excellent mechanical and chemical properties, like resistance to acids as well as their solubility in polar aprotic solvents. The modifications in this type of polyimides have been made and used in aerospace, optoelectronics, and liquid crystal display (LCD) and other needful industries. In addition, polyimides have also been used in sensors, membranes in fuel cell, gas separation, ultrafiltration and nanofiltration applications due to their flexibility, toughness and thermo-oxidative resistance. In general, aromatic polyimides have high melting temperature and poor solubility in most of the aromatic solvents due to the rigid backbone and strong interaction between the polymer chains. Many modifications have been made to improve the flexibility and solubility with reservation of other advantageous properties by introducing flexible linkages, non-coplanar units or bulky substituent.

Most of the polyimides are light brown in colour which is due to inter and intramolecular charge transfer (CT) interaction between alternating electron-donating diamine and electron accepting dianhydride components. It has been shown that the polyimides with unsymmetric structure of diamine prevent the close packing of chains and also the CT interactions. It is also found that the introduction of bulky groups with unsymmetric structure into the polyimides rendered the polymer to have better solution processability, less colour and improved flexibility.
In the present study, the synthesis and characterization of two polyimides namely pyromellitic dianhydride with 4, 4’-oxydianiline (PMDA - ODA) (PAA1 & PI-1) and PMDA-ODA with 4, 4’- (4, 4’ isopropylidine diphenyl 1, 1’-diyl dioxy) dianiline (PMDA-ODA-IDDA) (PAA-2 & PI-2) have been studied with their comparative properties such as thermal stability, transparency and flexibility. More experimental determinations are provided in chapter 3 (section 3.2). The effect of phthalic iso-propylidine group and ether linkage (PMDA-ODA-IDDA) on thermal stability, optical property and flexibility is discussed. In addition to bulky, packing-disruptive $-\text{CH}_3$ groups, the unsymmetrical structure of the bis(ether amine) component will prevent the extended close packing of chains and also the CT interactions.

4.2 RESULTS AND DISCUSSION

4.2.1 Structural studies

![FT-IR spectra](image)

Figure. 4.1: FT-IR spectra of PMDA-ODA PAA-1 & PMDA-ODA-IDDA PAA-2 powders.
The conversion of the PAA to the fully cyclized polyimide was determined by Fourier Transform Infrared spectroscopy.

Figure. 4.2: FT-IR spectra of PMDA-ODA PI-1 & PMDA-ODA-IDDA PI-2 films.

Figure. 4.1 shows the FTIR spectra of PAA-1 & PAA-2 and Figure. 4.2 shows PI-1 & PI-2 films. The conversion of carboxylic amide groups to the imide ring was evidenced by the disappearance of bands at 2500 cm\(^{-1}\) - 3500 cm\(^{-1}\) corresponds to the amic acid with the appearance of bands at 1775 cm\(^{-1}\) (asymmetrical C=O stretch), 1713 cm\(^{-1}\) (symmetrical C=O stretch), 1382 cm\(^{-1}\) (C-N stretch), 745 cm\(^{-1}\) (C=O bending).

Polyimide films were characterized by wide-angle XRD studies and the diffraction patterns are shown in Figure. 4.3. A broad diffraction peak intensity was observed around 2\(\theta\) = 10° - 25° for PI films which showed amorphous nature with broad diffraction intensities peak due to the presence of flexible iso-propylidene group. There were two broad peak intensities observed around 10° and 20° (2\(\theta\)) for PAA-1 & 2 and it indicates the semi crystalline behavior of PAA.
4.2.2 Thermal properties

Typical thermogravimetry curves for polyimides are shown in Figure 4.4, as determined at nitrogen atmosphere. The PI-1 is found to be more thermally stable compared to PI-2 and decomposition temperature of PI films at 10 % w/w decomposition was found to be 541.1 °C and 531.1 °C respectively for PI-1 & PI-2. It is clear that the higher decomposition temperature of polyimide is due to the target imide ring decomposition. The nature of cleavage of the imide ring is same for all the polyimides. However, the difference in decomposition temperature is due to the presence of electron releasing or electron withdrawing groups in the polyimide chain. The slight shift in the decomposition temperature for PI-1 & PI-2 is attributed to the influence of the electronic factors (electron releasing or electron withdrawing) associated with phenoxide oxygen and the iso-propyldiene group of the dianhydride and diamine.
4.2.3 Mechanical properties

The visco-elastic relaxation behavior of polyimide films was measured by dynamic mechanical analyzer (DMS 6100). The specimen dimensions for DMA measurements were about 40 mm × 5 mm × 0.03 mm (l × w × t). The storage modulus \( E' \), loss modulus \( E'' \) and dissipation or damping factor \( \tan \delta = E'/E'' \) at 1 Hz oscillatory deformation were recorded in the temperature range from 25 °C to 300 °C. Figure 4.5 shows the DMA curve of PMDA-ODA PI-1 film and Figure 4.6 shows PMDA-ODA-IDDA PI-2 film. The glass transition temperatures were determined as the temperatures of the maxima of \( \tan \delta \) which showed 238.8 °C and 216.7 °C for PMDA-ODA and PMDA-ODA-IDDA polyimide films respectively. The damping factor (\( \tan \delta \)) value decreased from 1.265 to 1.1324.
Figure 4.5: DMA curve of PMDA-ODA PI-1 film.

Figure 4.6: DMA curve of PMDA-ODA-IDDA PI-2 film.
Tensile strength of polyimide films is listed in Table 4.1. The tensile strength and modulus of PMDA-ODA-IDDA polyimide film are lower than PMDA-ODA film. On the other hand, elongation at break % of PMDA-ODA-IDDA film increased compared to PMDA-ODA film. This is due to the flexible iso-propylidine group present in IDDA monomer.

Table 4.1 Tensile properties of PMDA-ODA and PMDA-ODA-IDDA PI films.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>PI film sample</th>
<th>Tensile strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at break</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PMDA-ODA</td>
<td>89.1±1.2</td>
<td>2.16±0.01</td>
<td>9.2±0.3 %</td>
</tr>
<tr>
<td>2.</td>
<td>PMDA-ODA-IDDA</td>
<td>85.4±1.5</td>
<td>2.12±0.02</td>
<td>9.7±0.2 %</td>
</tr>
</tbody>
</table>

4.2.4 Optical properties

Figure. 4.7: UV-Visible spectra of PI 1 & 2 films.
The UV-Visible spectra of the polyimides with film thickness of 70 µm - 90 µm are shown in Figure. 4.7. Both the polyimides show high transmission (85 % - 88 %) in the wavelength range of 800 nm - 1600 nm. The iso-propylidene group and phthalic ether groups present in dianhydride and diamine moieties were effective in decreasing the charge transfer complex between polymer backbone chains through steric-hindrance leading to increase in the intermolecular distance and thus decreased the interaction between the polyimide chains resulting in a good optical transparency.

4.3 CONCLUSION

The two different polyimide films were prepared by two stage process. The first stage involves the formation of poly(amic acid) and second stage consists of casting the PAA solution on to the glass plate and heated to 300 °C in hot air oven to convert PAA into polyimide film. The polyimide films were characterized by FT-IR spectroscopy, X-ray diffractometer, thermogravimetry analyzer, dynamic mechanical analyzer, and UV-Visible spectrophotometer.

The PMDA-ODA polyimide film showed higher value in thermal stability and tensile strength but lower elongation at break % which indicates the poor flexibility. The PMDA-IDDA-ODA polyimide has more flexibility and transparency than PMDA-ODA polyimide film which is due to the presence of iso-propylidene group and ether linkage in the dianhydride and diamine monomers.