CHAPTER 3

MATERIAL CHARACTERISTICS OF DYE DOPED POLYMER FILMS AND THE EQUIPMENTS USED

Material characterization of the dye doped polymer films is essential to know the quality of synthesized rods, the bond formed between dye molecules and the PMMA, and the dye association with PMMA.

3.1 OPTICAL QUALITY

Optical quality of the synthesized dye doped films are checked by passing a He-Ne laser ($\lambda = 632.8$ nm, 5mW) beam through the samples. The samples which showed no dispersion or distortion are used for further studies.

3.2 THERMO GRAVIMETRIC ANALYSIS : (WATERS SDT Q 600)

Thermogravimetric Analysis or TGA is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent.
TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues.

Thermo gravimetric analysis (TGA) of the Amido Black 10B dye doped polymethymethacrylate (PMMA) is carried out using Waters SDT Q 600 equipment. The thermal analysis of the samples is made from 50°C to 800°C at a heating rate of 20°C/min in nitrogen atmosphere.

The thermogram obtained for PMMA modified with ethanol (EtOH), Dye doped PMMA modified with EtOH and the Dye are shown in Figures 3.1 – 3.3.

Figures 3.1 and 3.2, reveal two-stage decomposition between 200°C to 400°C. The peak maximum for PMMA + EtOH is at 375°C while with the addition of the dye is 392°C. This characteristic raise in the peak temperature for TG of PMMA + EtOH + Dye may be due to the strong H-bonding between the carbonyl oxygen of PMMA and the phenolic and amino groups of the dye. Minute weight losses due to the first stage decomposition may be due to the loss of the entrapped EtOH in the upper and bulk portion of the polymer. Figure 3.3 shows that the dye has good thermal stability and undergoes several stage decomposition. At 755°C there is only 45% decomposition. As the phenolic (OH and amino) groups present in the dye has strong attraction with moisture, the weight loss observed at 68°C may be due to moisture.
Figure 3.1  Thermogravimetric analysis of PMMA modified with ethanol
Figure 3.2 Thermogravimetric analysis of Amido black 10B doped PMMA modified with ethanol
Figure 3.3 Thermogravimetric analysis of the dye Amido black 10B
In spite of the concentration of the dye in the system being small (< 0.01%), it affects the thermal stability of PMMA in EtOH due to strong interactive forces. Hence, retention of dye by the matrix, may be due to the strong H-bonding between the carbonyl oxygen of PMMA and the phenolic and amino groups of the dye. The polymerization is carried out between the temperatures 35°C to 60°C. The thermograms reveal that at these temperatures no decomposition of either the dye or PMMA takes place as this might affect the spectral and nonlinear studies undertaken.

3.3 FTIR SPECTROSCOPIC ANALYSIS

Fourier Transform Infrared Spectroscopy is a technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks.

Fourier Transform spectroscopy exposes the sample to a single pulse of radiation and measures the response. The resulting signal, called a free induction decay, is a direct measurement of the temporal coherence of the light and contains a rapidly decaying composite of all possible frequencies. Using a Fourier transform of this, the spectrum of the light can be calculated as for the Michelson Fourier transform spectrometer. In this way the Fourier transform spectrometer can produce the same kind of spectrum as a conventional spectrometer, but in a much shorter time.
Infrared spectra of PMMA modified with ethanol (EtOH) and Amido Black 10B dye doped PMMA modified with EtOH are recorded using Perkin Elmer FT-IR Spectrometer (Spectrum RX I model).

The samples are recorded as KBr pellets. One hundred interferograms are recorded at room temperature with a resolution of 4 cm\(^{-1}\) and the region between 4000 and 400 cm\(^{-1}\) is analyzed. For each spectrum the baseline was corrected and smoothened. The spectra are all processed by software supplied by Perkin Elmer.

The FTIR spectra are shown in Figures 3.4 and 3.5 for PMMA modified with EtOH and the dye in PMMA modified with EtOH respectively. The Fourier transform infrared spectroscopic analysis of Figure 3.4 shows the carbonyl stretching of the ester group at 1733 cm\(^{-1}\). The peaks at 2917 cm\(^{-1}\) and 2850 cm\(^{-1}\) are due to the symmetrical and asymmetrical stretching of C–H stretch of methylene and methyl groups. The broad stretch at 3336 cm\(^{-1}\) can be attributed to the H-bonding present in the alcohol.

In the spectrum of the dye in PMMA modified with EtOH, the carbonyl stretching of the ester group is observed at 1742 cm\(^{-1}\). The peaks at 2926 cm\(^{-1}\) and 2858 cm\(^{-1}\) are due to the symmetrical and asymmetrical stretching of C–H stretch of methylene and methyl groups. The broad stretch at 3406 cm\(^{-1}\) can be attributed to the NH\(_2\) and –OH i.e., the H-bonding and amine group present in the dye molecule. The two new peaks at 710 cm\(^{-1}\) and 860 cm\(^{-1}\) is due to the = C–H out of plane vibrational bending of the aromatic nuclei in the dye molecule. The FT-IR illustrates that the association of the dye with PMMA is due to the H-bonding interaction with the ester group of PMMA and the NH\(_2\) and –OH groups of the dye molecule.
Figure 3.4 FTIR spectrum of PMMA modified with ethanol
Figure 3.5 FTIR spectrum of Amido black 10B doped PMMA modified with ethanol
3.4 THERMO GRAVIMETRIC ANALYSIS OF PYRIDINE 2: NETZSCH STA 409 C/CD

Thermo gravimetric analysis (TGA) of the pyridine 2 doped polymethymethacrylate (PMMA) is carried out using NETZSCH STA 409 C/CD equipment. The thermal analysis of the samples was made from 50°C to 900°C at a heating rate of 10K/min in nitrogen atmosphere. The thermogram obtained for dye doped PMMA modified with MeOH and the dye, pyridine are shown in Figures 3.6 and 3.7.

Figure 3.6 reveal two-stage decomposition between 175°C to 400°C. It is observed that the first stage occurs only at around 188°C. Minute weight losses due to the first stage decomposition may be due to the loss of the entrapped MeOH in the upper and bulk portion of the polymer and most of the moisture/volatile impurities originally present in the monomer. The second stage decomposition takes place due to the introduction of the dye. The decomposition mechanism of the polymer changes and weight losses occur around 275°C and 345°C. Even at 1000°C, there is a residual of 6% which may be due to oxidation. Figure 3.7 shows a three-stage decomposition pattern. The first stage occurs between 20°C and 140°C which may be due to the moisture or other volatile impurities that may be originally present in the monomer and solvent entrapped in the polymer matrix. A major weight loss occurs only between 220°C and 340°C bringing a weight loss of 34% to the dye-doped polymer sample and after which there is a slow decomposition that takes place between 340°C and 900°C. Even up to 900°C there is only 72% weight loss suggesting that the dye is thermally stable. A residual of 26% still remains.
Figure 3.6 TGA spectrum of Pyridine 2 doped PMMA modified with methanol
Figure 3.7 TGA spectrum of Pyridine 2
In spite of the concentration of the dye in the system being small (< 0.01%), it affects the thermal stability of PMMA in MeOH. The polymerization is carried out between the temperatures 35°C to 60°C. The thermograms reveal that at the polymerization temperatures 35°C to 60°C, no decomposition of either the dye or PMMA takes place as this might affect the spectral and nonlinear studies undertaken.

3.5 FTIR SPECTROSCOPIC ANALYSIS OF PYRIDINE 2: (PERKIN ELMER FT-IR SPECTROMETER – SPECTRUM ONE SPECTROMETER)

Infrared spectra of PMMA modified with methanol (MeOH) and Dye pyridine 2 doped PMMA modified with MeOH are recorded using Perkin Elmer FT-IR Spectrometer (Spectrum one model).

The samples are taken in the form of films, are recorded at room temperature with a resolution of 4 cm\(^{-1}\) and the region between 4000 cm\(^{-1}\) to 450 cm\(^{-1}\) is analyzed. For each spectrum the baseline was corrected and smoothened. The spectra are all processed by software supplied by Perkin Elmer. The FTIR spectra are shown in Figures 3.8 and 3.9 for PMMA modified with MeOH and the dye in PMMA modified with MeOH respectively. The Fourier transform infrared spectroscopic analysis 3.8 shows the carbonyl stretching of the ester group at 1737 cm\(^{-1}\). The peaks at 2999 cm\(^{-1}\), 2951 cm\(^{-1}\) and 2845 cm\(^{-1}\) are due to the symmetrical and asymmetrical stretching of C–H stretch of methylene and methyl groups. The broad stretch at 3539 cm\(^{-1}\) can be attributed to the H-bonding present in the alcohol (methanol).
Figure 3.8 FTIR spectrum of PMMA modified with methanol
Figure 3.9 FTIR spectrum of pyridine 2 doped PMMA modified with methanol
In the spectrum of the dye in PMMA modified with MeOH (Figure 3.9), the carbonyl stretching of the ester group is also observed at 1737 cm\(^{-1}\). The peaks at 2989 cm\(^{-1}\), 2951 cm\(^{-1}\) and 2843 cm\(^{-1}\) are due to the symmetrical and asymmetrical stretching of C–H stretch of methylene and methyl groups. The broad stretch at 3030 cm\(^{-1}\) can be attributed to the = C–H due to the olefinic and aromatic proton present in the dye molecule. The peak at 1638 cm\(^{-1}\) is due to the C = C stretch of the olefinic double bond of the dye. The two new peaks at 751 cm\(^{-1}\) and 912 cm\(^{-1}\) is due to the = C–H out of plane vibrational bending of the aromatic nuclei in the dye molecule. CH\(_3\) bending is more defined in this case and the absorption band is larger than pyridine 1 due to the presence of more number of methyl groups.