CHAPTER IV

EXPERIMENTS

4.1 Materials

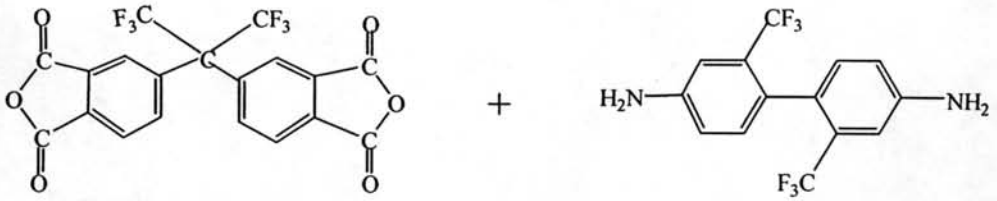
For this study, a fluorinated polyimide, 6FDA/TFDB as shown in figure 4.1 was synthesized from 4,4'-(hexafluoroisopropyllidene) diphthalic anhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-hexafluoropropane diaminobiphenyl (TFDB) because this polyimide exhibited good optical properties and optical transparency. In this process, a dianhydride and a diamine reacted in a dipolar aprotic solvent N,Ndimethylacetamide (DMAc) which was obtained from Aldrich Chemical Co. Zinc nitrate hexahydrate 99.9% (Zn nitrate) was used as zinc compound which was obtained from Aldrich Chemical Co. In this research, average diameters about 2 nm of zinc oxide nanoparticles which were obtained from Meliorum technologies, USA were used as received.

4.2 Films preparations

4.2.1 Poly(amic acid) solutions

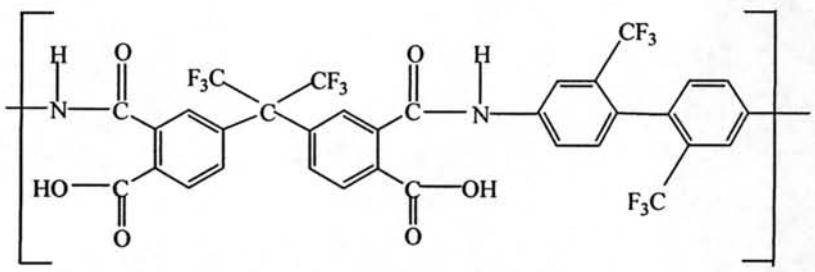
The fluorinated polyimide (PI) was prepared by the reaction between 4,4'-(hexafluoroisopropyllidene) diphthalic anhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-hexafluoropropane diaminobiphenyl (TFDB) which has 6 fluorine atoms in both monomers. 6FDA dianhydride was dissolved in N,Ndimethylacetamide (DMAc) solvent to give a clear, colorless solution. After 6FDA was dissolved completely, an equimolar amount of TFDB was added to the solution with vigorous stirring to obtain 15wt% solution. The solution was stirred at room temperature for 24 hr in order to obtain poly(amic acid) by polymerization process.

Step 1



4,4'-(hexafluoroisopropyllidene) diphthalic anhydride (6FDA) **(Dianhydride)**

2,2'-bis(trifluoromethyl)-4,4'- hexafluoropropane diaminobiphenyl (TFDB) **(Diamine)**

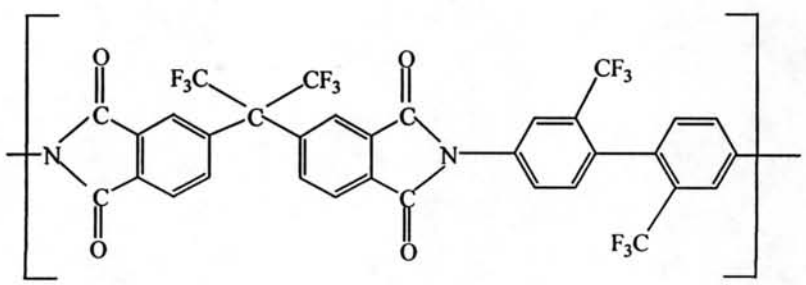


6FDA/TFDB Poly(amic acid)

Step 2

Imidization

Add Zn compounds or ZnO nanoparticles
Spin coat on glass substrate
Dry at 70 °C
Thermal cure at 300-350 °C



6FDA/TFDB Polyimide

Figure 4.1 Chemical structures of monomers and preparation of poly(amic acid) and polyimide

4.2.2 Polyimide film preparation

Zinc nitrate hexahydrate or ZnO nanoparticle with an average diameter about 2 nm were added into PAA solution at different concentration of ZnO. All the synthesizing and mixing procedures were performed in a argon atmosphere. Then the PAA solution was spinned coat onto glass substrate with 1000 to 1500 rpm speed and 15 sec, to give a thin film. The PAA solution on substrates were dried in nitrogen or argon atmosphere at 70°C for 1 hour and further imidized at curing temperature in the range of 300 to 350°C for 1 hour in nitrogen or argon atmosphere. After that they were cooled down to room temperature. Nanoparticle ZnO embedded in PI films were obtained. Note that, there were two ways of preparing hybrid films. First, adding ZnO nanoparticles into PAA solution directly. Then PAA was imidized and ZnO in PI film was obtained and was defined as ZnO/PI. The other method was adding zinc nitrate hexahydrate into PAA solution. Zinc nitrate hexahydrate in this solution was then converted to ZnO while PAA was imidized to be PI and the material was defined as Zn nitrate/PI.

4.3 Photoluminescence Characterization

Optical properties of the films were characterized by a Luminescence spectrometer (Perkin Elmer LS 50), which were carried out at room temperature using Xe as a light source at an excitation wavelength in the range of 250-450 nm and emission wavelength in the range of 350-600 nm.

4.4 Absorbance Characterization

Absorbance properties of the films were characterized by a spectrophotometer (Hewlett Packard 8452A diode array), which were measured at room temperature using Xe as a light source at an excitation wavelength in the range of 200-600 nm.

4.5 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy Characterization

Infrared spectrum of the air side and the glass side surface, of polyimide blend films were measured using a Spectrum GX FTIR spectrophotometer (Perkin Elmer, USA). Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were acquired using ZnSe as a prism at an incidence angle of 45°. The scan number and the spectral resolution were 32 and 4 cm^{-1}, respectively.

4.6 ZnO crystal structure in polyimide films

XRD was used to identify the presence of ZnO crystal from thermal decomposition of $ZnNO_3 \cdot 6H_2O$ in PI films. The sample were characterized at ambient temperature using a SIEMENS D 500 X-ray diffractometer with CuKα radiation with Ni filter in the 2 theta range of 20-70° with a resolution of 0.02°/min.

4.7 Thermal Behaviors

4.7.1 Glass transition temperature

The glass transition temperature of PI films and PI films containing ZnO nanoparticles was examined using a differential scanning calorimeter, DSC (diamond DSC Perkin Elmer). The samples, weighed 3-10 mg, were encapsulated in an aluminum pan. The experiment was performed at a heating rate of 20°C/min from 50°C to 460°C under nitrogen atmosphere.

4.7.2 Degradation temperature

The degradation temperature of PI films and PI films containing ZnO nanoparticles was examined by using thermogravimetric analyzer (TA Instruments SDT Q-600). Thermogravimetric analysis was conducted with small amounts (about 5 mg) of the films peeled from the substrates. The PI films and PI films containing ZnO

were heated to 1000 °C at 20 °C/min under nitrogen atmosphere. The weight loss profile as a function of temperature was obtained.

4.8 Transmission Electron Microscopy (TEM)

Cross-sectional transmission electron micrographs (TEM) of ZnO in PI films were taken with electron microscope (JEOL, JEM-2100). The PI films were embedded in epoxy resin and sectioned into a thickness of 20 nm with an ultra microtome (ultrotome V). The particle size and dispersion of ZnO in PI films was observed.