SYNTHESIS AND CHARACTERIZATION OF CO-POLYMER 4-FLUORO PHENYL MALEIMIDE WITH METHYL METHACEYLATE

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Abstract

Copolymerization of 4-fluoro phenyl maleimide with methyl methaceylate (MMA) was investigated in these studies. The copolymer has better thermal stability than the other polymers like vinyl monomers etc... The investigated copolymer shows excellent solubility in THF, DMF, DMSO, dioxane, chloroform and ethyl acetate. The copolymers were characterized by studies of XRD, FT-IR. The thermal properties of copolymer were studied by TG/DTA.

Keywords: N-[4-fluoro phenyl] maleimide, Monomer link, free radical, copolymerization.

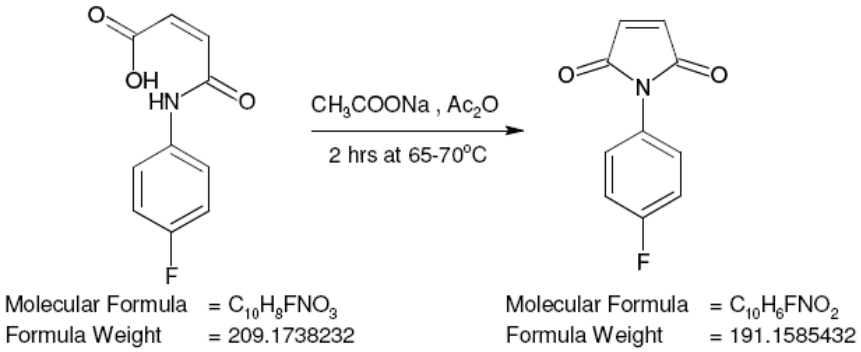
`1.Introduction

Methyl methaceylate is an organic compound and it is widely used for single molecules of methyl metha crylate monomer link together to form a very strong, hard polymer[12]. MMA is a monomer produced on a large scale of poly MMA. The present paper reports the synthesis and copolymerization of N-[4-fluoro phenyl] maleimide, with methyl methacrylate (MMA). This copolymer has better thermal stability[5]. Initially the synthesis of monomer (N-[4-fluoro phenyl] malemidie acid is prepared and then copolymerization with MMA was done. Fluoro phenyl maleimide have been polymerized by addition polymerization with either free radical or anionic initiation. In free radical process, azobisisobutylonitrile (AIBN) is used as a initiator. The maleimide groups effectively act as binding carrier for many functional groups such as vinyl polymer matrixe etc.. The nature of crystallinity of polymer, thermal stability, functional groups of polymer have been studied in order to characterize the synthesized polymer[7].

2. Experimentation

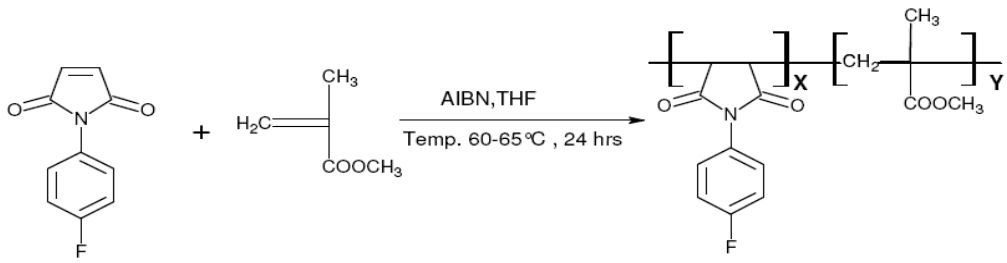
2.1 Synthesis of 4 – fluoro phenyl maleimide (FPFM)

4-fluoro phenyl maleimide was synthesized by various steps using 4-fluoro aniline and maleic anhydride. 4-fluoro aniline and maleic anhydride were taken in 30ml dimethylformamide (DMF) solvent. This reaction mixture was stirred for 3hours at room temperature 25-30° C. Then this stirred added into cursed ice water to obtain the white solid fluoro phenyl maleamic acid and further it was filtered and dried. Filtered fluoro phenyl maleamic acid was crystallized by ethanol to get a pure FPM . The 4-FPM was cyclodehydrated to form a compounds in a cyclic manner. For this 4-FPM was stirred for 3hours at 80° C with the solution of acetic anhydride and sodium acetate. Then follow the previous steps to filter and crystallize to obtain the pure 4-FPM.



2.2 Co-Polymerization

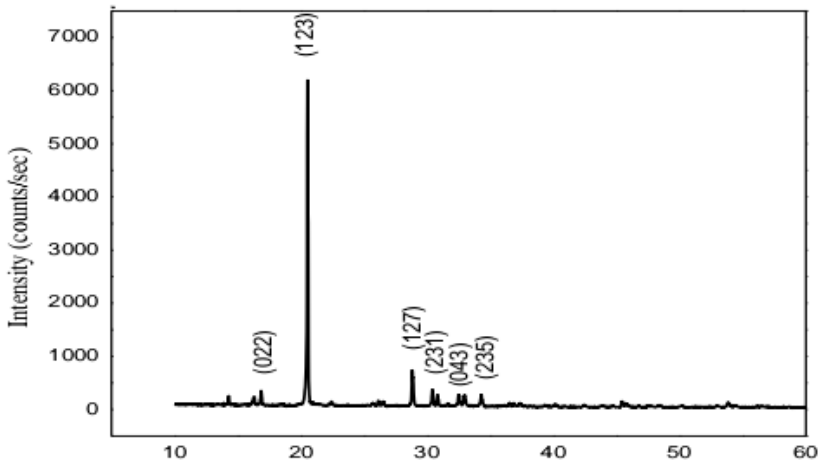
For preparation of copolymer 4-fluoro phenyl maleimide (CPFPM), the 4-FPM, methyl methacrylate (MMA), tetrahydrofuran(THF) and 20-30 mg azobisisobutylonitrile (AIBN) were refluxed in round bottom flask at 60° C for 24hours. Equal amount of methanol and water were added to precipitate the mixture. The crude product was dissolved by THF and gets a polymerization of FPM. To remove the unreacted monomer in the copolymerization, the obtained final product was reprecipitated for two times.



1. Result and discussion

3.1 XRD analysis

The Powder XRD pattern of copolymer of FPM with MMA was recorded using a Rich Seifert diffractometer with Cu Kα (λ= 1.54059 Å) radiation. The powder sample was scanned over the range of 10-80° at a rate of 1° per minute. Identification was done by comparing the diffraction patterns with the standard X- ray diffraction pattern of the synthesized copolymer that was analyzed to investigate the phase structure and the crystallinity. The crystalline of pure sample was confirmed by this analysis and diffraction peaks .The well-defined, sharp peaks in the XRD patterns signify the good crystalline of sample. The pattern show sharp peaks related to standard polymer X-ray diffraction pattern (JCPDS no. 962003122). All the peaks of copolymer can be indexed to orthorhombic phase (α=90°, β=90°,=90°). The cell parameter values are a=9.3910A°, b=11.3360A°, c=28.1730A°.

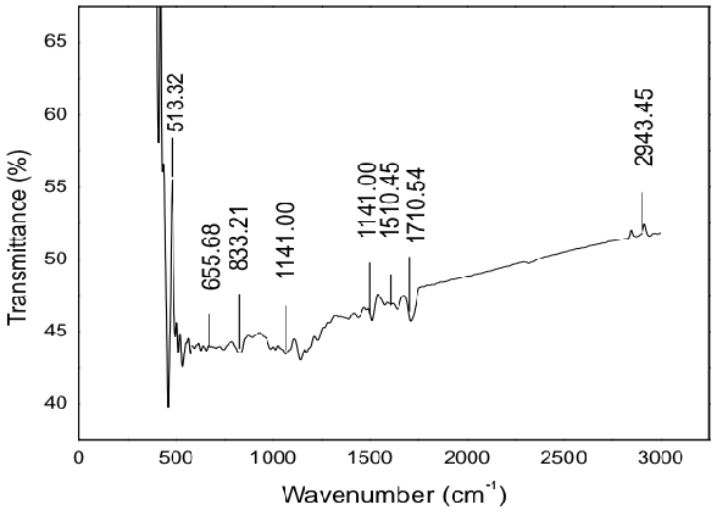


XRD of FPM with MMA

3.2 FTIR ANALYSIS

FT-IR studies on the prepared polymer were carried out using a FT-IR Perkin Elmer RX-1 spectrophotometer, over a range of 400-4000 cm-1 KBr using pellet method. Fig. shows the FTIR spectra of PFPM with MMA. The various internal modes of vibrations were observed in the spectra. FT-IR spectra of copolymer shows absorption peak at 1710Cm−1 is due to the symmetric and asymmetric stretching of the carbonyl group in imide ring and at 1640 Cm−1 is

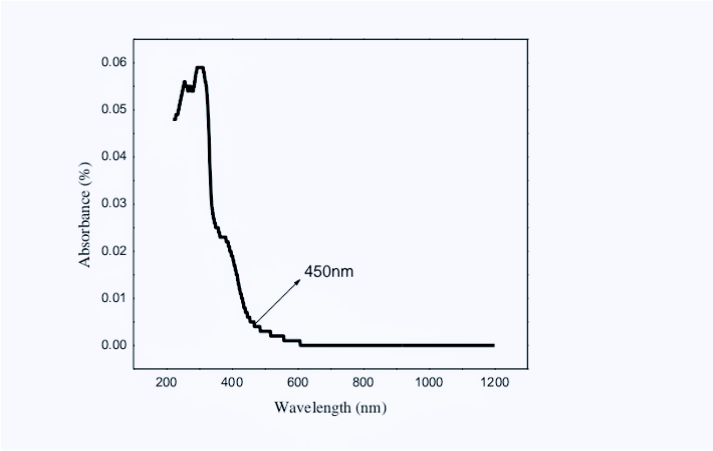
due to C=N stretching of maleic anhydride . These characteristic bands confirmed that the imide ring remains intact during the copolymerization process. The peak at 2943$Cm{-}1$ is assigned to C-H stretching in the alkyl group in MMA, it confirms that both the monomeric unit of PFPM and MMA are present in copolymer.



FTIR of FPM with MMA

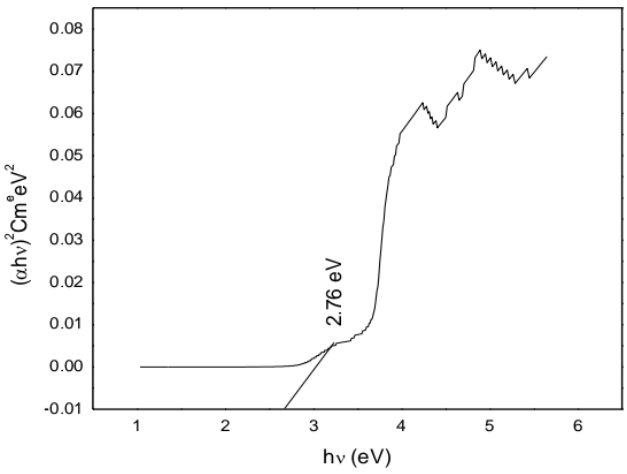
3.3 UV Analysis

UV-Vis spectrum was recorded in the range of 200-1200 nm using Shimadzu 2410 UV spectrophotometer. UV-visible spectral study may be assisted in understanding the electronic structure of the optical band gap of the polymer. The UV spectrum shows the presence of a wide transparency window lying between 450 nm and 1200 nm. The lower cut off wavelength of the sample is at 450 nm. The analysis of absorption spectrum shows that the prepared sample is transparent in the entire visible region. The optical band gap of the material is 2.76eV.



Absorbance spectrum of FPM with MMA

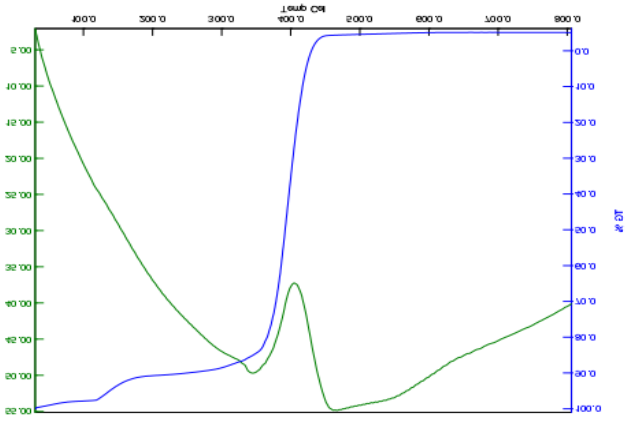
In UV spectrum, using Tauc's plot it calculate the optical band gap of the material is 2.76ev



Tauc's plots

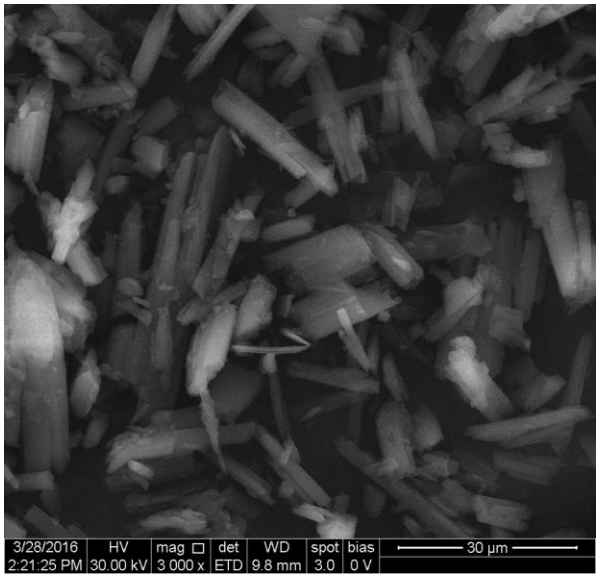
3.4 TG/DT Analysis

4-fluoro phenyl maleimide is a potential heat and chemical resistant material, so Maleimide widely used as a monomer to obtained modified polymeric system. The step degradation was observed for 4-fluoro phenyl maleimide in TGA at temperature of over 350℃. The thermo grams were obtained by heating PFPM with MMA in air 10℃/min. The results of percentage weight loss suffered from 100℃ to 450℃ at 100℃ intervals. The initial decomposition temperature (Ti), temperature is 230° c for maximum weight loss ($Tmax$) 285° c and final decomposition temperature (Tf) 355° c of first and second degradation. From the DTA curve endothermic peak seen at 350℃ is attributed to the melting point of the sample. The exothermic peak seen at 450℃.



TG/DTA of FPM with MMA

3.5 FESEM



FESEM of FPM with MMA

Field Emission Scanning Electron Microscope (FESEM) is used to study the surface of prepared polymers (copolymer of 4-fluoro phenyl maleimide with methyl methacrylate). The FESEM image of FPM with MMA is shown in fig. with the magnification of 30µm. FESEM image was taken from the magnification range 200µm to 5µm. It is evident from that the surface morphology of prepared polymer is tubeless. The molecules, which are present in the prepared polymer are unique with less defects. And also it indicates that there is no contamination in the prepared polymer for free radical copolymerization method.

Conclusion

In this project, copolymer of 4-fluoro phenyl maleimide with methyl methacrylate have been successfully prepared by polymerization method (addition polymerization). The prepared sample have been subjected to various studies like powder x-ray diffraction, FTIR analysis, and thermo gravimetric analysis. X-ray diffraction pattern shows the crystalline nature of the polymer and it is in orthorhombic structure. FTIR spectrum shows the characteristic peaks of prepared polymer. TG/DTA analysis shows the decomposition point of the polymer and weight loss of the material. UV-Vis spectrum shows the good transparent nature of polymer and the value of cut off wavelength and optical band gap are determined. FESEM Image shows the surface morphology of prepared polymer in the magnification of 30µm.

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