

Synthesis and characterization of nanoclay doped PVC/polyester composite film

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The present study deals with the synthesis, characterization of nanoclay doped PVC/polyester composite film formed from new polyester obtained from terephthaloyl chloride with Schiff base diol formed by the reaction of 4-aminophenol with 3-hydroxy-4-methoxybenzaldehyde and 4-hydroxy-3,5-dimethoxybenzaldehyde (1:1 mole ratio) in nitrogen atmosphere. The synthesized aromatic polyesters were characterized by FT-IR and ^1H NMR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and gel permeation chromatography. The resultant composite was characterized by FT-IR, SEM and TGA.

Keywords: Composite film, polyester, nanoclay.

Introduction

Polymer clay composites were prepared for various applications^{1,2} which consists of clay particles dispersed in polymer matrix. Energy efficient, strong and cost effective materials are produced by polymers containing clay fillers. Bentonite clays are capable of expand and contract their structure while maintaining the two dimensional crystallographic integrity due to presence of smectites – group of clay minerals. Bentonite clay has montmorillonite as its main component along with it contains other clays and chemicals like illite, kaolinite, quartz and carbonates. These clays are low cost, biocompatible green materials, simple processing which make it a prospective for nano architectural polymeric composites.

Bentonites are defined as a sedimentary rock consisting of a large portion of expandable clay minerals with three-layer structures (smectites) such as montmorillonites (80%), beidellite, nontronite etc. with minor amounts of non-clay minerals such as quartz, calcite, dolomite and feldspar³. The properties of modified bentonite polyester composites were studied⁴. It has been found that incorporation of bentonite clay into the polymer matrix offered significant improvement in tensile strength and toughness⁵ and also it has been reported that polymer bentonite nano composites showed greater electrical conductivity than the neat polymer⁶. Few polymer bentonite composites have been synthesized and

used for controlled release of nutrients to plants⁷. The aim of this work is to develop new polymer clay nano composite by solution blending process. The synthesized polymer and the polymer clay nano composite were characterized by FTIR, SEM and thermal studies.

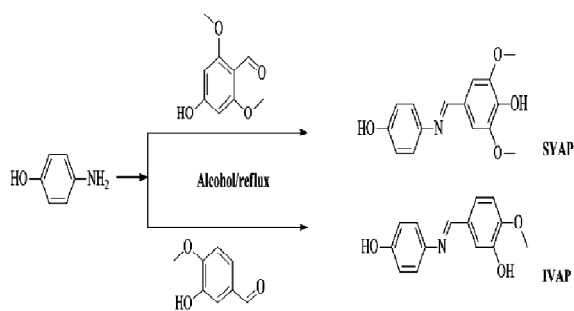
Experimental

Materials and method:

3-Hydroxy-4-methoxybenzaldehyde, 4-hydroxy-2,6-dimethoxybenzaldehyde, 4-aminophenol, terephthaloyl chloride, PVC and solvents were purchased from TCI chemicals, bentonite clay from SRL chemicals and used without further purification. FTIR spectra were recorded using Perkin-Elmer FTIR spectrometer and ^1H NMR spectra of monomer and polymer were recorded using Bruker Avance 500 MHz NMR at 25°C. Thermal analysis of polymer and composite film was carried out by Perkin-Elmer Diamond Thermal Analysis system and SEM analysis was carried out using FEI Quanta FEG 200-Scanning Electron Microscope.

Synthetic procedure of monomers (Scheme 1):

In a round bottom flask fitted with condenser and magnetic stirrer, added 3-hydroxy-4-methoxybenzaldehyde (1 mmol) dissolved in 40 ml of methanol and 1 ml of conc. HCl were added. A solution of 1 mmol of 4-aminophenol dissolved in 40 ml of methanol was slowly added to the flask using a dropping funnel. At first the mixture was stirred at room tem-

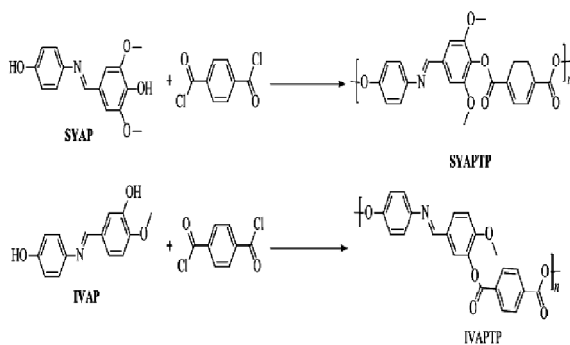


Scheme 1. Synthetic procedure of monomers.

perature for 2 h and then refluxed for 5 h for completion of reaction (monitored by TLC). After cooling, the monomer was precipitated which was filtered, washed with ethanol and dried in vacuum at 70°C for 3 h. The yield of the 5-((4-hydroxyphenylimino)methyl)-2-methoxyphenol (IVAP) was 78% and melting point was found to be 170°C, by using similar procedure 4-((4-hydroxyphenylimino)methyl)-3,5-dimethoxyphenol (SYAP) was prepared. The yield and melting of SYAP found to be 82% and 183°C.

Synthetic procedure of polyesters (Scheme 2):

Polyesterification was carried out in a 100 ml two neck round bottom flask equipped with gas inlet and dropping funnel charged with a mixture of Schiff base diol monomer (2 mmol) dissolved in 10 ml of dimethylformamide (DMF) and 0.8 ml of triethylamine. Terephthaloyl chloride dissolved in 20 ml of DMF was added drop wise to the stirred solution at ice cold condition. Then the reaction mixture was heated using oil bath at 80°C under nitrogen atmosphere for 4 h and the reaction was terminated with cold water. The product was filtered, washed with NaHCO₃ solution and dried under vacuum at 80°C for 24 h.



Scheme 2. Synthetic procedure of polyesters.

Synthetic procedure of composite film:

The polyester/PVC nanoclay composite film was prepared by solution casting method. To produce organophilic bentonite clay it has been treated with cetyltrimethyl ammonium bromide (CTAB), to exchange sodium ions of bentonite with quaternary ammonium ions of CTAB. The polyester, PVC and modified bentonite clay was taken in 1:3:1 by percentage weight respectively was dissolved in THF and stirred for 24 h then sonicated by probe sonicator with amplitude of 30% for 5 min with a pulse range of 1 s. The product was poured into petridish and allowed to dry for 24 h.

Results and discussion

IR spectra: IVAP shows a band at 3445 cm⁻¹ due to OH group. The peak at 1610 cm⁻¹ is assigned to (CH=N) stretching frequency and 1589 cm⁻¹ is characteristic of aromatic (C=C) stretching frequency. Similarly for SYAP, IR spectrum shows characteristic peaks at 3507 cm⁻¹ and 1608 cm⁻¹ due to -OH group and (CH=N) stretching frequency respectively.

¹H NMR spectra: IVAP shows OH proton peak at 9.4 ppm and a peak due to CH=N at 8.42 ppm. The peaks at 7.4 to 7.0 ppm are due to aromatic ring protons. For SYAP, peaks at 9.82 is due to -OH group and 6.6–7.7 is due to aromatic -C=C- group.

Characterization of polyester:

IR spectra: The disappearance of -OH peak in IVAPTP compared to IVAP indicates the reaction of hydroxyl group with acid chloride. The peak at 1678 cm⁻¹ in IR spectra of IVAPTP due to carbonyl group (C=O). The peak at 1574 cm⁻¹ assigned to (-C=N-) and peak at 1136 cm⁻¹ due to (C-O-C) group (Fig. 1). Similarly for SYAPTP, peak at 3507 cm⁻¹ disap-

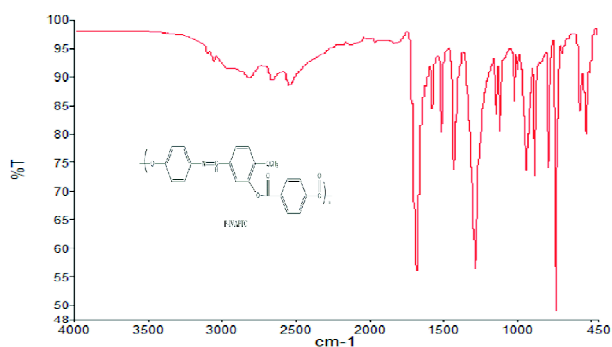


Fig. 1. FT-IR spectrum of IVAPTP.

peared in polymer due to reaction of hydroxyl group and (CH=N) stretching frequency appeared at 1640 cm^{-1} (Fig. 2).

$^1\text{H NMR}$ spectra: polyester IVAPTP shows peak at 8.0–8.49 due to -CH=N- and 6.9–7.9 due to aromatic -C=C- group (Fig. 3). $^1\text{H NMR}$ spectrum of polymer SYAPTP shows peak at 8.41 due to -CH=N- and 6.0–7.9 due to aromatic -C=C- group (Fig. 4).

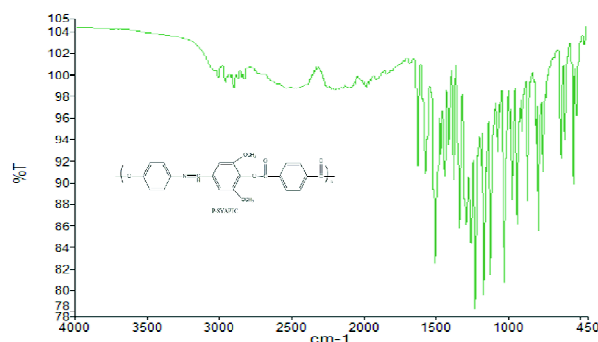


Fig. 2. FT-IR spectrum of IVAPTP.

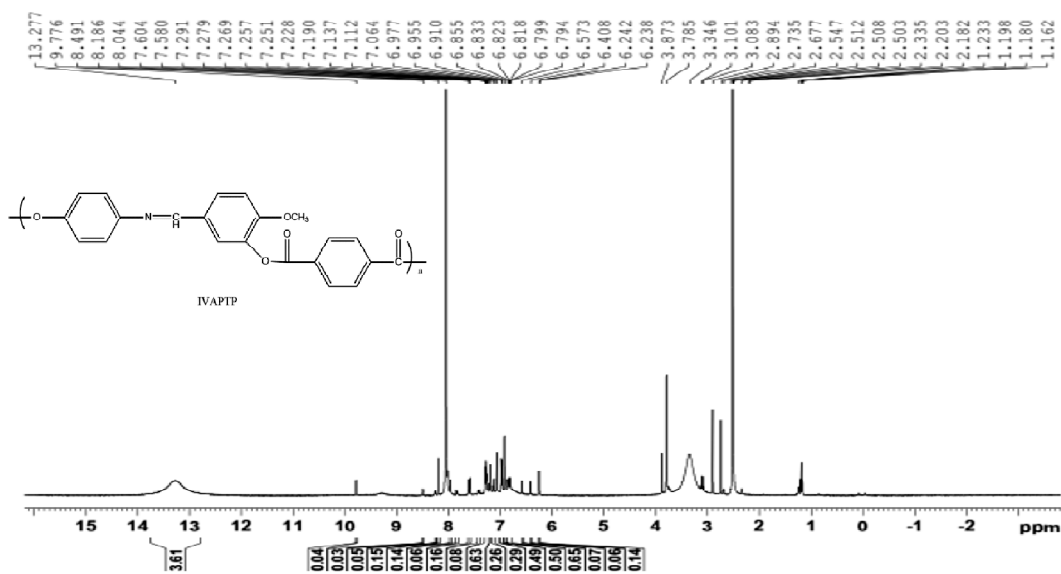


Fig. 3. $^1\text{H NMR}$ spectrum of IVAPTP.

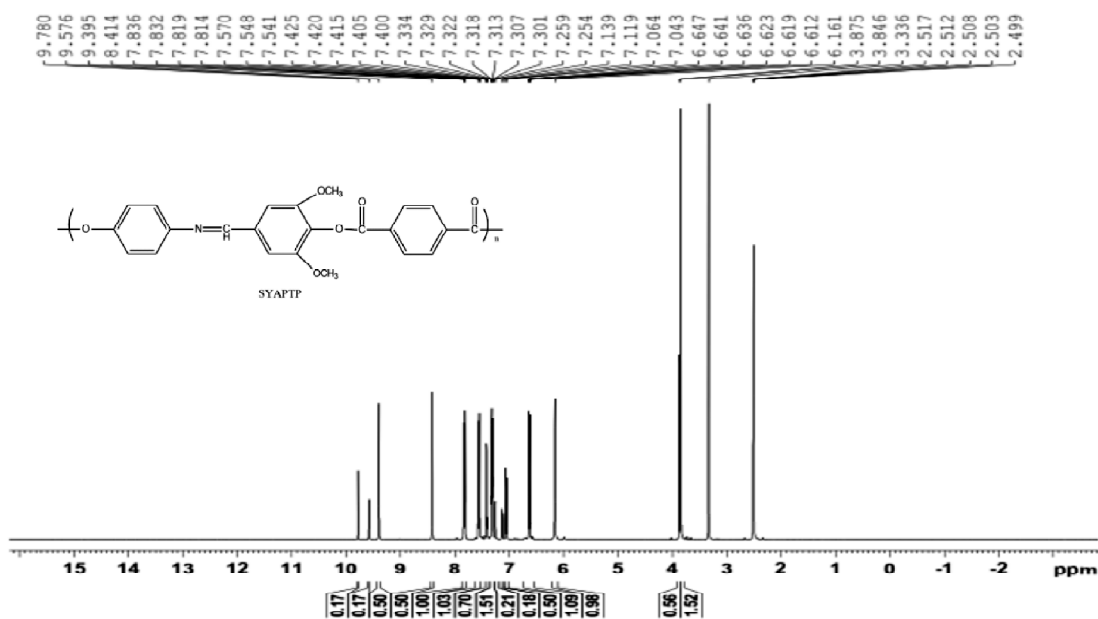


Fig. 4. $^1\text{H NMR}$ spectrum of SYAPTP.

Res characterization of composite film:

The IR spectrum of composite shows characteristic bands of both the polyester and clay which ensures the incorporation of clay in the polymer. The peak at 1650 cm^{-1} due to C=O stretching of polymer is reduced in intensity which shows that there is interaction with clay through C=O group. The composite also shows bands around 1040 cm^{-1} and 580 cm^{-1} characteristic of Si-O and Al-O linkages for bentonite⁸. The FT-IR technique therefore confirms the incorporation of clay particles in the polymer matrix⁹. Benchabane Adel *et al.*¹⁰, JörnDau *et al.*¹¹ have also reported similar results for their synthesized clay composites (Fig. 5).

Thermo gravimetric analysis (TGA):

Introduction of inorganic components into organic materials improve the thermal stability of the resulting composite¹². The thermograms of the polymer and the composite are shown in Fig. 6. From the TGA curves, it is evident that the polymer (PIVAPTP) undergoes decomposition at 196°C , the composite (PIVAPTP-bentonite) shows quite good stability upto 380°C . The thermal stability of polymer-clay composite is enhanced due to the attractive coulomb interaction between the positive group of polymer layer and negatively charged surface of the clay layer¹³.

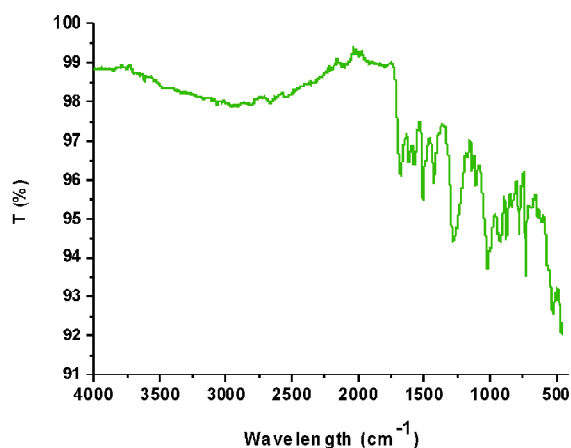


Fig. 5. FT-IR spectrum of IIVAPTP-bentonite film.

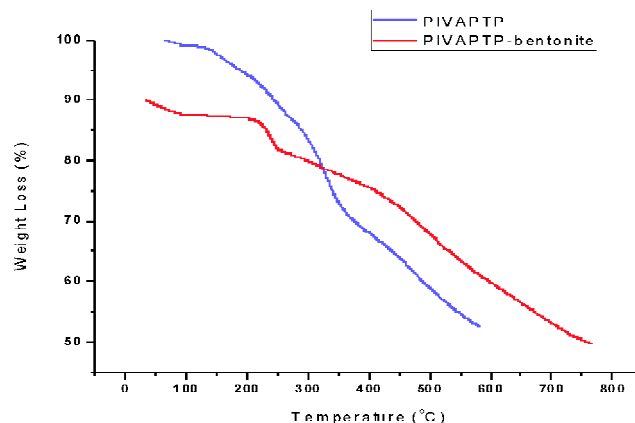
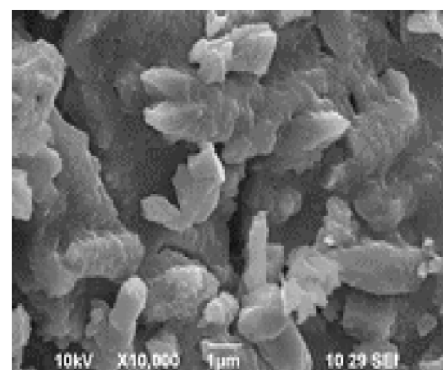
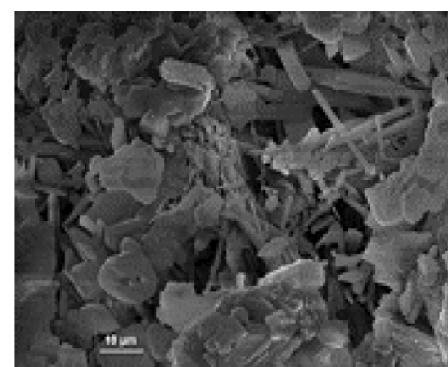


Fig. 6. TGA of PIVAPTP and PIVAPTP-bentonite.



(i)



(ii)

Fig. 7. SEM image of (i) PIVAPTP polymer and (ii) PIVAPTP-bentonite composite.

Conclusions

To improve the property of synthesized polyester, first it has been blended with PVC for workability then with modified bentonite to improve thermal stability further and for wound healing application¹⁴. The nanoclay doped PVC/polyester composite film was prepared by solution casting method and was characterized by FTIR, TGA and SEM analysis.

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