Synthesis and Characterisation of Co-Polyester and Their Composite

J Kalpana[1], C Ravichandran [2]

Jawahar Engineering College, Saligramam, Chennai, India[1]

Professor, Department of Chemistry, Easwari Engineering College, Bharathi salai, Ramapuram, Chennai, India[2]

ABSTRACT: In this paper we report synthesis of certain co-polyesters which is prepared from Di- acid ,1,4-butane diol and Azelic acid through a two step process of melt polycondensation using suitable catalyst. The synthesised random copolyesters is blended with commericially available natural polymer . The synthesized random copolyesters and their composites were characterized by means of ^{1}H NMR, ^{13}C NMR and FTIR . the polymer blends improve the properties such as surface hardness, stiffness, resistance to temperature and solvent attack. The effect of copolymer and their composite on their physical and Thermal properties were investigated.   Thermal stability was studied by Differential scanning calorimetry (DSC), between polyesters and their composite.The mechanical properties were also studied.

KEYWORDS:: Melt polycondensation, random copolyesters, Mechanical properties

I.   INTRODUCTION

There are a number of reports, concerning aliphatic polyesters due to their favourable features and biocompatibility. Generally polyester widely used in many applications due to low production cost, good mechanical properties. (PET) Poly(ethylene terephthalate) is a polyester widely used. There is considerable research on the synthesis of films and membranes using synthetic polymers to improve their biocompatibility and expanded use as biomaterials. It is proved that the crosslinking of blend strongly correlates with the increase in the strength of the membrane and the thermal stability of the blend[1]. Copolyesters composed of aliphatic and aromatic units such as1,4 butanediol, terephthalic acid and azelic acid were combined in an appropriate ratio was synthesised and blended with natural polymer. Natural polymer used here is chitosan.

 Naturally occurring polymers include collagen, chitin, silk, alginate, starch, and elastin. Natural polymers offer the advantage of being similar to macromolecular substances,the biological environment is prepared towhich recognize and to deal with metabolically. Problems associated with the stimulation of chronic inflammatory reaction and toxicity by synthetic polymers are largely suppressed or eliminated by using natural polymers. On the other hand, natural polymers are frequently quite immunogenic. Another attractive characteristic of natural polymers is their ability to be degraded by naturally occurring enzymes, implying that the implant will be degraded and eventually metabolized by physiological mechanisms. Thus, useful properties can be obtained by blending natural and synthetic polymers. Synthetic polymers used in the biomaterials field .

 In this paper, we will report on thermal properties of synthetic polyester which is synthesised and this polyesterchitosan blend systems , also mechanical properties of the blends will be seen for their blends to know theit tensile strength. We will also report on the physical and chemical properties of polymers blends in the solid state due to intermolecular interaction by means of FTIR, DSC and NMR.

II.   EXPERIMENTAL METHODS

•   Materials

Terephthalic acid (Merck AR grade), Malonic acid (Lancaster AR grade), Fumaric acid (Lancaster ARgrade) were recrystallised from deionised water and used. 1,4 Butane diol (Lancaster grade) was dried with CaO Overnight and then distilled uner reduced pressure. Titanium tetrabutoxide (Ti(OBu)$_4$ used as such. Chitosan(Extra pure)   for blending is used. All the other materials and solvents used were of analytical grade.

III.   METHOD

•   Synthesis of copolyesters

The copolyesters were synthesized by two step melt poly condensation. As an example the synthesized poly (butylenes Azelate – co- butylenes Terephthalate) PBAZBT has been described. The polycondensation flask was a three neck flask equipped with a nitrogen inlet, a condenser and a thermometer. A magnetic stirrer was used to stir the reaction mixture. The reaction mixture is purified with nitrogen and heated in an oil bath. The temperature of the reaction mixture is raised to 150°c in 20 min. Then the temperature is gradually raised in 10°C steps every minute to the reaction temperature of 210°c to remove water being the esterification by product. When water ceased to be generated, a predetermined amount of titanium tetrabutoxide (Ti(oBu)$_4$) (o.1mmol) catalyst is added to the reaction mixture. Suubsequently the pressure of the reaction system was decreased gradually and polycondensation is continued at 210°c under reduced pressure lower than 0.5mmHg. The reaction was terminated when the rotation of the mechanical stirrer is stopped. The resulting crude copolymers were dissolved in chloroform and then poured into excess of dry cold methanol to purify the polyester. The precipitated copolyesters were dried in a dessicator.

IV.   BLEND PREPARATION

A known weight of chitosan and polyester were dissolved in acetic acid and chloroform separately. The chitosan and polyester solutions were mixed at various ratios at room temperature with moderate agitation for 30 minutes. The blend solution is dried in Teflon petridish for 2 to 3 days .   The powder thus formed is the composite. This composite were dried in a dessicator for further characteristion.

V.   CHARACTERISATIONS

•   Fourier-Transform Infrared (FTIR) Spectroscopy

Chemical structure of pure and the blends were investigated by FTIR measurement, FTIR measurements were performed using KBr pelleted samples with a Perkins Elmer 200 FTIR spectrophotometer with a resolution of 4cm-1 in the range of 400 – 4000 cm-1.
• ^{1}H NMR measurements
^{1}H NMR spectra were recorded on AV 3500MHz Spectrometer by using 7% wt of CDCl3 mixed solvent.
• ^{13}C NMR measurements
^{13}C NMR spectra were recorded at 300-600 MHz in deuterated chloroform as solvent.
•   Differential Scanning Calorimetry (DSC)
The DSC scans were recorded at a heating rate of 10°c/min using Perkin-Elmer Pyris I analyzer. Indium was used as the calibration standard.

VI.   EXPERIMENTAL RESULTS

The random copolyesters were characterised by spectral sudies and thermal analysis. The copolyesters were blended with chitosan and characterisation by spectral and thermal analysis were also studied.

- FTIR of polyester and blend
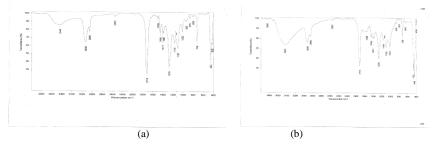

(a)   (b)

Fig.1. IR spectrum of(a) copolyesters (b) PBAZBT and its blend

FTIR spectra of copolymers derived from PBAZBT with their chitosan blends are shown in the figure (1a,& b). Band characteristics of aromatic esters are observed between 1716 cm^{-1} , for the copolyesters and their blend show similar observation between 1717 cm^{-1} , (C=O streaching). The C-H streaching of aliphatic –CH2-group observed at 2930 cm-^{1}and their polyesters at 2935cm-^{1}. C-O streaching vibrational modes are observed at 1021cm-^{1} are observed in blends and their copolyesters.

Band characteristics of OH and N-H stretching for polyesyter blends were observed at 3450 cm-1 1 which shows the characteristics of chitosan. This band is not prominent in the copolyesters synthesized.

- **Thermal properties of polyester and blend**

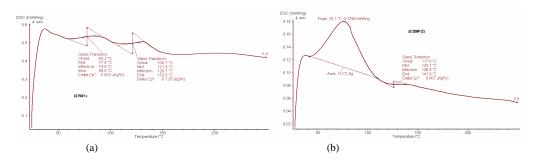(a)   (b)

Fig. 2 Thermal properties of (a)PBAZBT (b) PBAZBT blend

The above themogram shows Tg value increase for blends compared their copolyester. Two small and fairly broad exothermic peak was oberved in Fig 2(a) for PBAZBT with Tg value 77.4^{o}c and 121.3^{o}c whereas for their blends shows in Fig2(b) one large exothermic peak was observed with Tg value 122.7^{o}c. This shows that Tg value is higher for blends and hence thermal stablility is also higher for blend than their copolyester.

- ^{1}**HNMR spectral data of random copolyester and their blends**

The ^{1}HNMR spectra recorded for the copolyester are shown in the Fig 2(a)&(b). The chemical shift values observed from ^{1}HNMR spectra of the copolyester and their blends are as follows.

PBAZBTand its blend show δ = 8.09- 8.1 ppm is due to aromatic protons of Terephthalic group, Multiplet at δ = 4.95 - 4.49 ppm is due the methylene porton of CO-CH2 group and -OH- group of chitosan blends. Multiplet at δ =1.29-2.5 ppm is due to methylene protons of 1.4 butanediol. In polyester blends the chemical shift for aromatic proton of terephthalic group, multiplet due to methylene protons are seen.
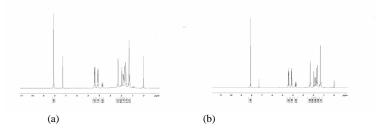
(a)   (b)

Fig. 3 ^{1}HNMR spectral data of (a)PBAZBT (b) PBAZBT blend

. It has been revealed that main proton peaks in NMR spectra correspond mainly to the signals coming from the polyester sequences Fig3(a)&(b). The proton peaks in the spectra of chitosan-PBAZBT blends are resolved as in the spectra typically observed for heteropolyesters. Thus, the NMR data confirm that the polysaccharide moieties are spread uniformly and visible in the spectra

•   ^{13}CNMR spectral data of random copolyester and their blends
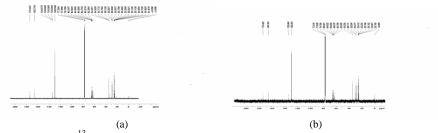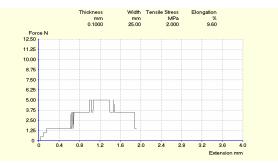

(a)   (b)

Fig4 ^{13}CNMR spectral data of (a) PBAZBT (B)PBAZBT blend

In Fig 4(a) &(b) all signals are narrow, which can be evidence that some miscibility between components of blends can be occurring. The carbonyl bends signals also showed distribution sequences of microstructures that can be assigned in the systems. Both the number and values of chemical shift for these microstructures did not change comparing to those of the initial polymers because the interaction process occurs with the same strength for all types of carbon, as it is an unselective process.

•   **Mechanical property**
•   Tensile strength

Fig 5.

Tensile property is very less for synthesised polyester and thin film for blends shows comparatively better results. Thus the yield stress and strain is higher for blends than their synthesised polyester.

VII.   CONCLUSION

Blends of polyesters with synthetic polyesters are of considerable interest in the development of biocompatible composites for medical and packaging applications. The above results shows that thermal stability is higher for polyester blends than their synthesised polyester. Similarly chitosan has moisture absorbing capacity and hence their blends can be used for commericial purpose like packaging and as biomaterials.

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