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SYNTHESIS AND CHARACTERIZATION OF CERTAIN RANDOM COPOLYESTERS CONTAINS DIOLS MOIETY

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ABSTRACT

Three biodegradable random copolyesters namely PEMC, Poly (ethylene malonate-co- ethylene citrate), PPMC-Poly (propylene malonate -co-propylene citrate), PSSC-Poly (sorbitol succinate-co-sorbitol citrate) were synthesized by direct melt polycondensation using Titanium Tetra isopropoxide as a catalyst. The biodegradable polymers Structural arrangement conformed by FT-IR, ^{1}H NMR and ^{13}C NMR analysis. The crystalline nature of synthesized polyesters was determined by X-Ray Diffraction and Differential scanning calorimetry. All the three synthesized polyesters having Biodegradability which was confirmed by weight loss method. The Synthesized biodegradable polyesters will be useful in drug delivery and Tissue Engineering.

KEY WORDS

Biodegradable Polymers, Aliphatic Polyesters, Diols moiety.

INTRODUCTION:

Polymeric materials have invaded almost every human activity. This success is primarily due to their low cost, reproducibility and durability, related to a high resistance to physical aging and biological attacks. The rapid growth of polymer production is considered as a serious source of environmental pollution. [1]. A current research area of significant environmental, economic and scientific improvement is biodegradable polymers. [2-7].

The applicability of biodegradable polymers as biomaterials provides a thrust in developing new biocompatible polymers for various applications. The usage of these polymers in biomedical field has gained importance because of its degradation in physiological conditions inside the human body. As temporary implants, they can stay intact until the healing process is complete. Subsequently they degrade and are excreted from the body as waste products. [8-11].

The use of polymer in living system depends on the mechanical, physical and surface properties of the polymers and biodegradation plays a crucial role in determining the application of polymers for a specific function inside the human body. Aliphatic polyesters, due to their favorable features of biodegradability and biocompatibility, constitute one of the most important classes of synthetic biodegradable polymers which are preferred choice of materials for *in vivo* application. (12-17)

This work focused on the synthesis and characterization of certain new random copolyesters using various diol moieties. The structure of their repeating unit was confirmed by spectral studies and thermal behavior and crystallinity of the polyesters were also studied.

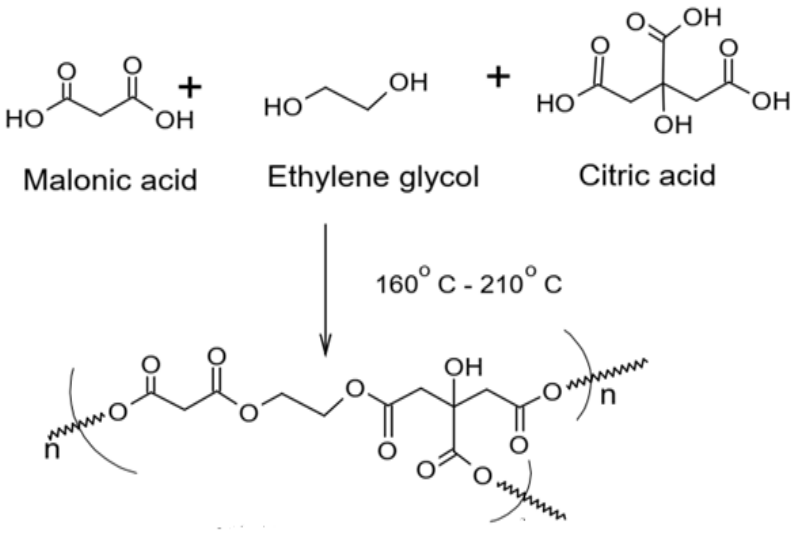
MATERIALS AND METHOD:

Materials

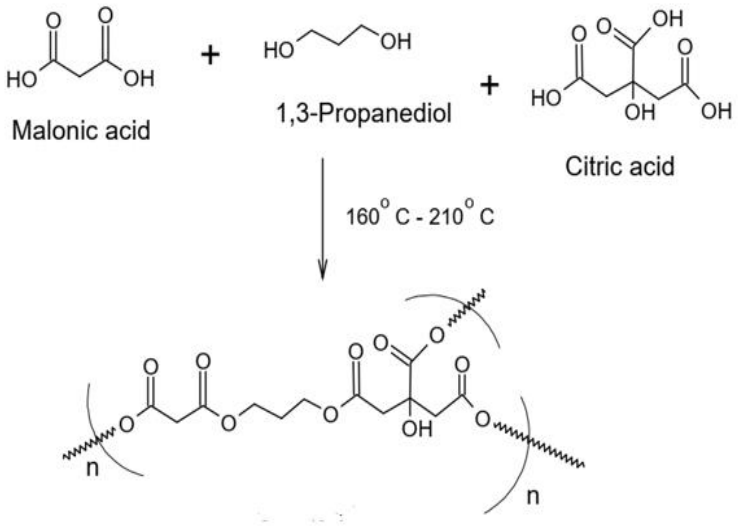
Citric acid, Malonic acid, Succinic acid, Ethylene glycol and 1.3 Propanediol, Sorbital were purchased from Sigma Aldrich used as such. Titanium Tetraisopropoxide (TTiPo) used as a catalyst was purchased from Lancaster. All other chemicals and solvents (AR Grade) were used as such.

Synthesis of copolyesters

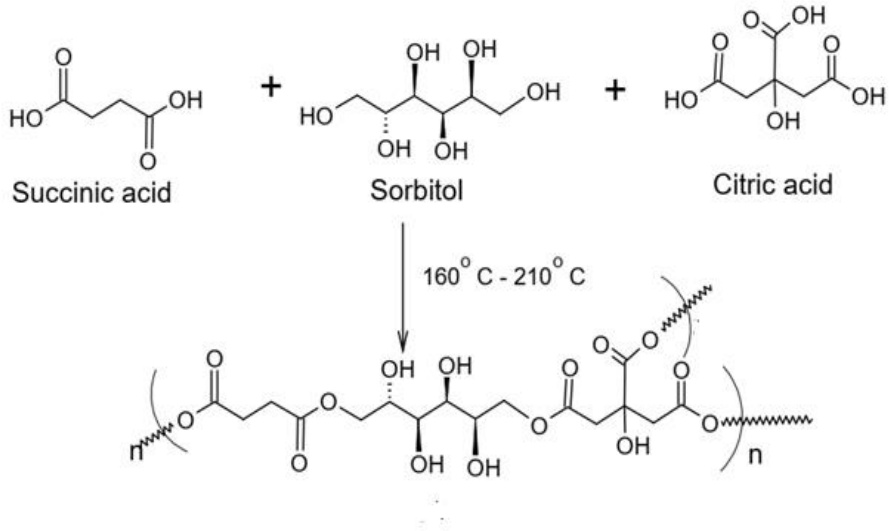
The biodegradable polyester PEMC was synthesized by predetermined amount of Malonic acid,Citric acid and Ethylene glycol were taken in a the three neck flask, The mixture was slowly heated to 160°C- 210°C for 3 hour to remove water as by product. The prepolymer heated One hour under vaccum condition with the addition of 0.1mmol TiTPO catalyst to increase the molecular weight of the polyester. The synthesized polyester was dissolved in chloroform and separated using the 10-fold cold methanol solvent. The biodegradable polymer dried in vaccum and stored in the vaccum dessicator. The biodegradable polyesters PPMC and PSSC were synthesized by same procedure used like the above polyester by direct melt poly condensation. The scheme of the polyester synthesis was follows



Scheme: 1 Synthesis of Poly (ethylene malonate-co- ethylene citrate), PEMC.



Scheme: 2 Synthesis of Poly (propylene malonate -co-propylene citrate), PPMC.



Scheme: 3 Synthesis of Poly (sorbitol succinate-co-sorbitol citrate) PSSC.

CHARACTERIZATION METHODS:

Chemical structure of pure copolyesters synthesized was investigated by FT-IR MEmeasurements has been used extensively in qualitative and quantitative analysis of Copolyesters and in determining the structural units of the polymers. The spectra were recorded using Bruker IFS 66VFT – IR spectrophotometer with KBr pellets in the range of 4000-400cm^{-1} at 25°C. ^{1}H and ^{13}C NMR spectra of copolyesters were recorded using JOEL–GSX–400 spectrometer. DMSO was used as solvent in order to prepare solutions of 5% w/v and TMS was used as internal standard. DSC Thermograms were recorded on a PERKIN ELMER PYRIS - 1 differential scanning calorimeter. About 2-4 mg of the polymer sample was heated in an Aluminium pan with pierced lid under nitrogen atmosphere at a scanning rate of 10°C / mts between a temperature range of – 100 °C and 500 °C. A Siemens D 500 diffractometer with Cu Kα filtered radiations was used for assessing the crystallinity of the polymers. The samples were scanned over the range of 2θangle, from 0º-80º. The biodegradability of the Polyesters Synthesized was determined by the following method. Polyester thin films were obtained by hot pressing method. The thin films of area 10 x 10 mm^2 and about 200μm thickness was placed in a Petri dish containing 10ml of phosphate buffer solution (pH 7.00 ± 0.01). After a specific period of incubation, the films were removed from the dish, washed with distilled water and dried weighed till constant weight. This procedure was repeated for every chosen time interval: 9,24,48,72 and 90 hours.

RESULTS AND DISSCUSSION:

Fourier – Transform Infrared (FTIR) Spectroscopy

FT-IR spectra of PEMC, PPMC and PSSC are shown in Fig4.1(a), 4.1(b). & 4.1 (c). The synthesized copolyesters showed characteristic absorption band for ester carbonyl stretching at 1724.15,1722.29 and 1722.10 respectively and between 966.50 to 1038.57 cm-^{1} C-H bending, The aliphatic C-H group symmetry stretching obtain at 2966.77,2964.80 and 2964.36. Strong vibrational modes observed at 1164.50,1170.30 ,1164.11. cm-^{1} were associated with C=O stretching vibrations mode.

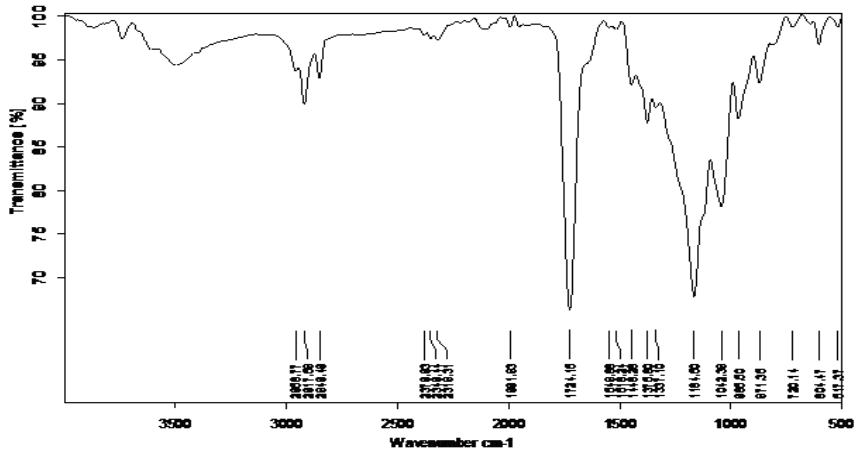


Fig.4.1 (a) IR Spectrum of PEMC

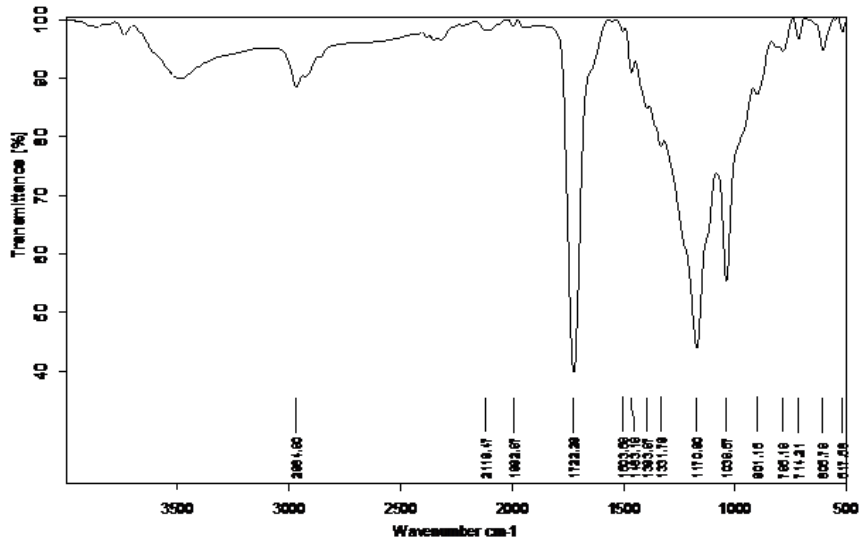


Fig.4.1 (b) IR Spectrum of PPMC

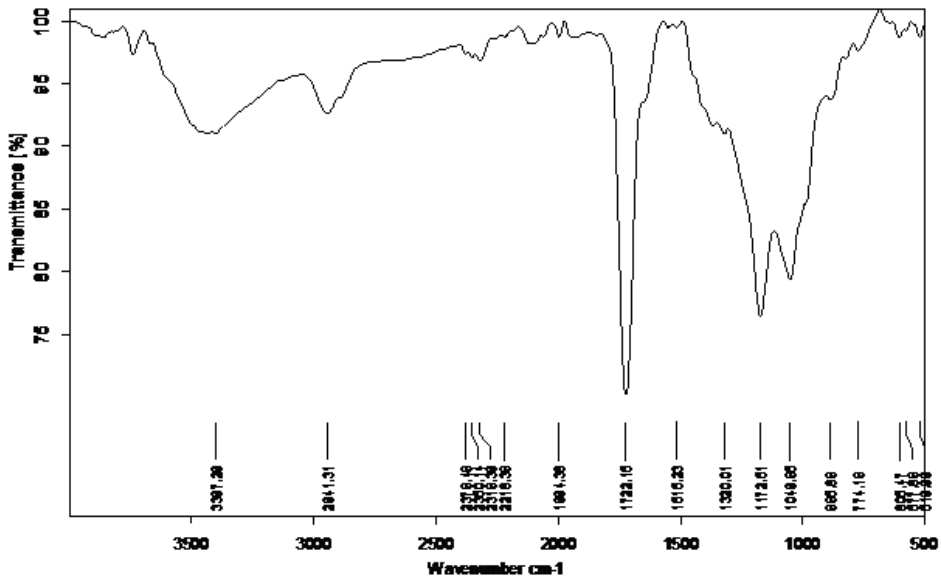


Fig.4.1 (c) IR Spectrum of PSSC

^{1}H NMR Spectral data of random copolyester

^{1}H NMR is used to study the structure of repeating units and nature of proton present in the polymer chain. ^{1}H NMR spectra of the copolyesters of PEMC, PPMC and PSSC shown in Fig 4.2(a),4.2(b) & 4.2(c) the peak at 3.20,3.25,3.23ppm was attributed to methylene protons of acids at 2.1, 2.3, 2.2ppm was attributed to central methylene proton of diols whereas 1.1, 1.4, 1.2ppm is due to terminal methylene groups of diols.

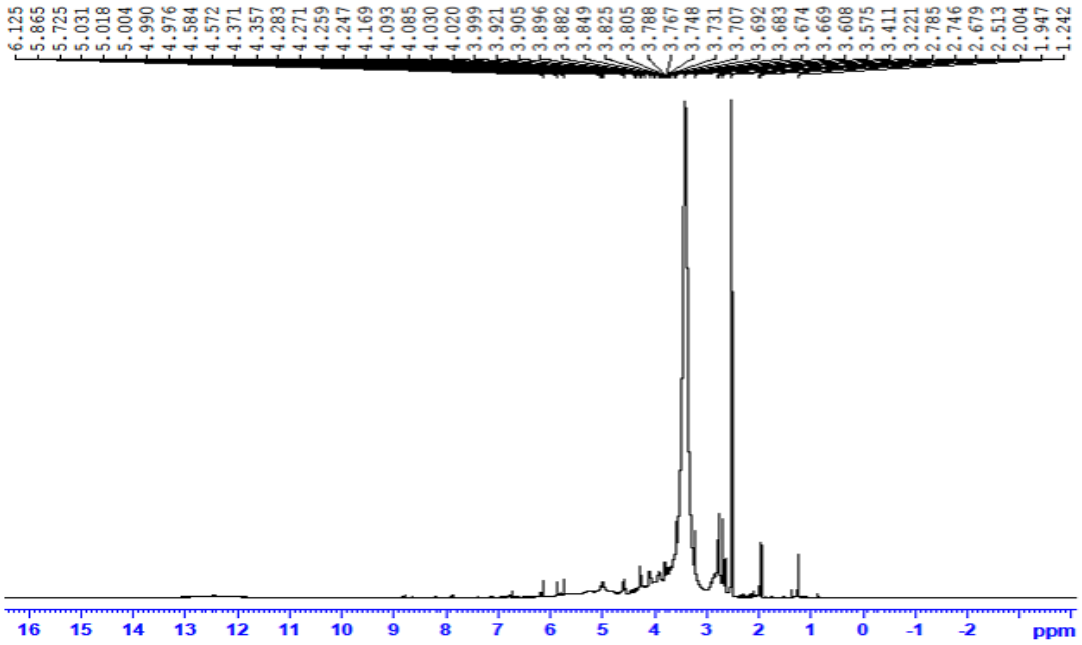


Fig.4.2(a) ^{1}H NMR Spectrum of PEMC

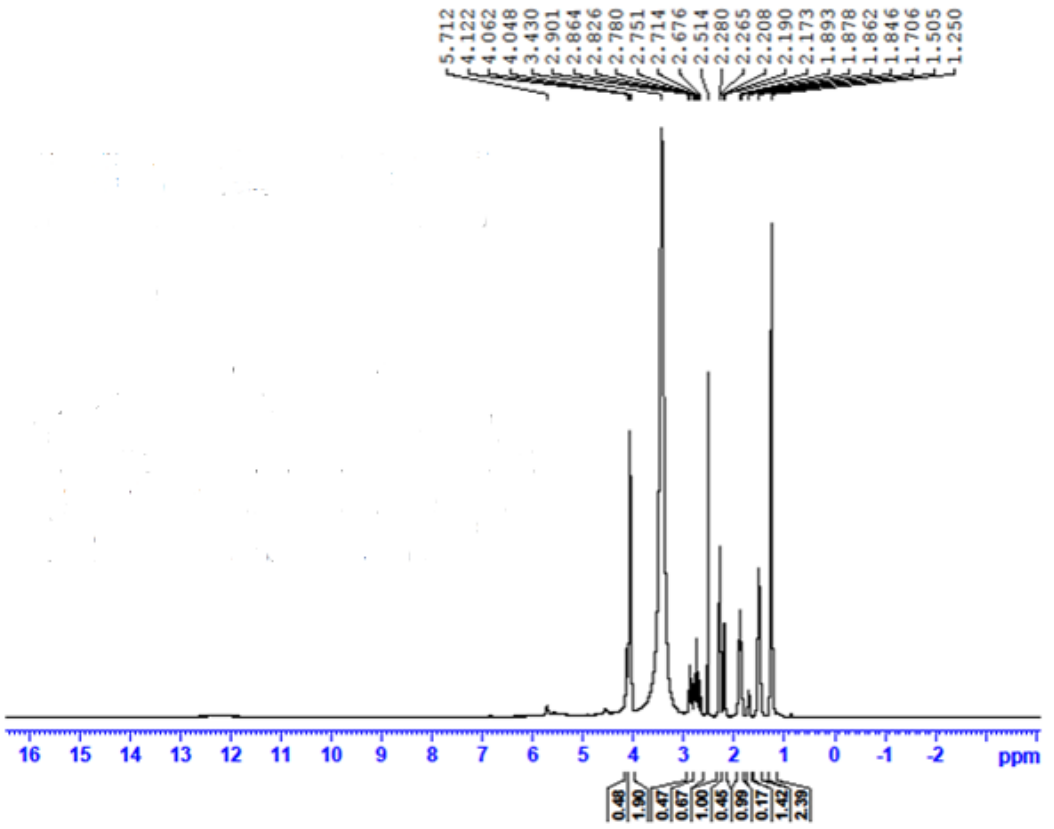


Fig.4.2 (b) ^{1}H NMR Spectrum of PPMC

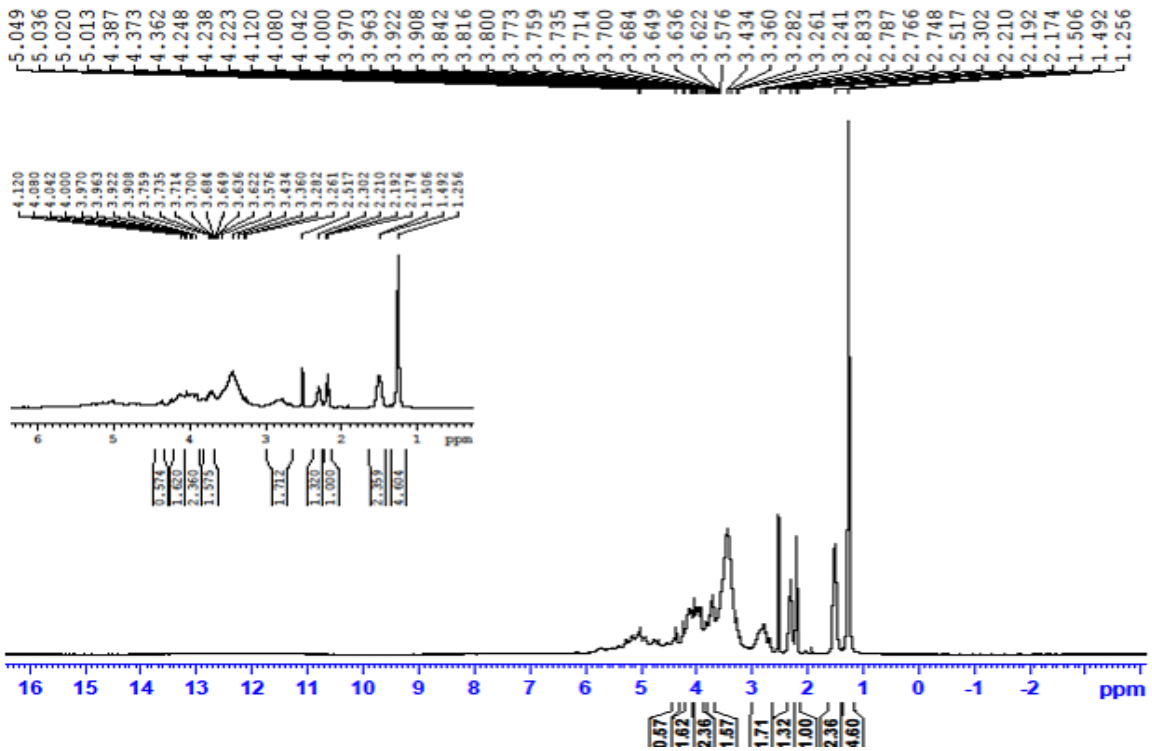


Fig.4.2 (c) ^{1}H NMR Spectrum of PSSC

^{13}C NMR Spectral data of random copolyester

^{13}C NMR Spectroscopy has considerable role in the study of the structure of the repeating units present in the random copolyesters^{13}C NMR spectra of copolyesters shows the chemical shifts at about 173.0, 63.0, 33.0, 24.0 ppm. Peaks at 173.0 ppm is attributed to the ester carbonyl carbon while the peak at 63.0 ppm is to the methylene carbon attached to oxygen, -O-CH_2-. The dicarboxylic acid moieties show lines at about 33.0 and 24.0 ppm respectively. The ^{13}C NMR spectra of characteristic polyesters are presented in Fig. 4.3(a), 4.3(b) & 4.3(c)

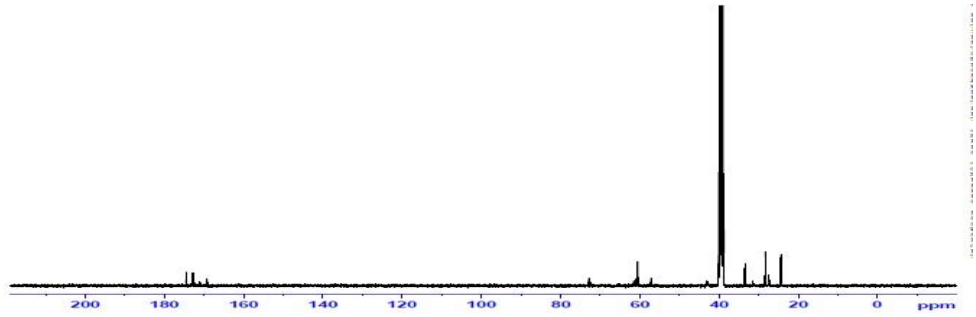


Fig. 4.3(a) ^{13}C NMR Spectrum of PEMC

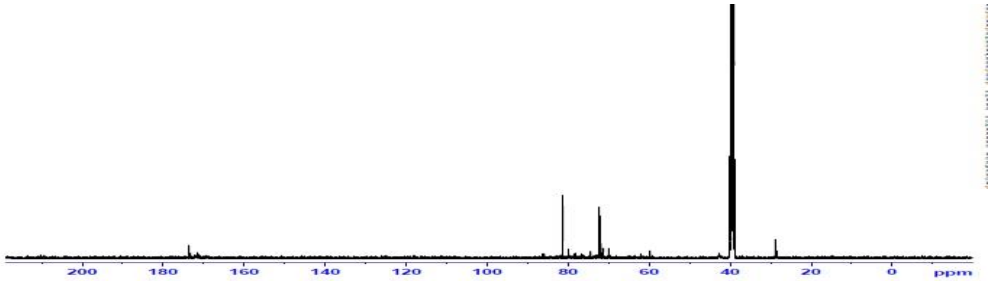


Fig. 4.3 (b) ^{13}C NMR Spectrum of PPMC

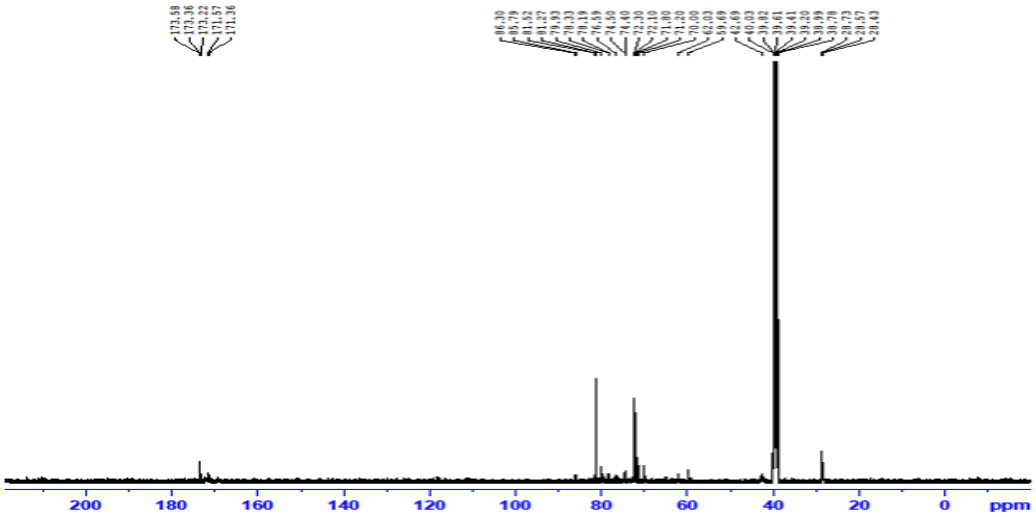


Fig. 4.3 (C) ^{13}C NMR Spectrum of PSSC

Differential Scanning Calorimetry (DSC)

Differential Scanning Colorimetry, DSC is one of the most important tools used to investigate the thermal properties of the copolyesters. The thermal properties like the melting temperature, Tm the glass transition temperature, Tg and the decomposition temperature, Td of the copolyesters have been obtained from DSC Thermograms. Generally, an increase in the number of methylene groups in the repeating units of the main chain increase the melting temperature, Tm and the crystallinity of the resultant copolyesters. The DSC thermograms of the three biodegradable copolyesters PEMC, PPMC and PSSC presented in Fig. 4.4(a), 4.4(b)& 4.4(c). It is observed from DSC data of the copolyesters that polyester PEMC exhibits the low melting point and its less crystalline nature

Polymer	T_g (°C)	T_m (°C)	T_d (°C)
PEMC	-6.5	34.46	282.0
PPMC	-10.5	46.6	298.2
PSSC	-14.5	53.92	312.6

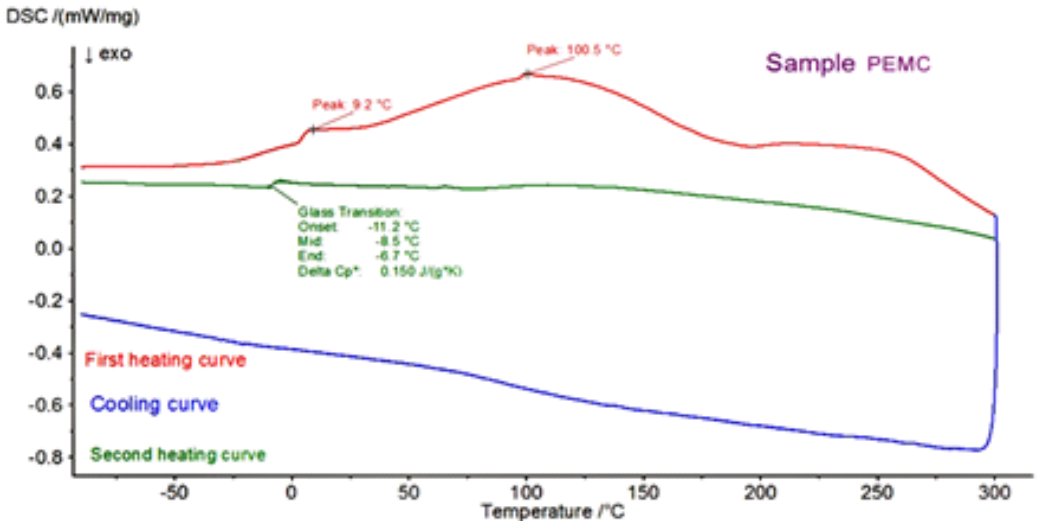


Fig. 4.4(a) DSC Thermograms of polyesters Spectrum of PEMC

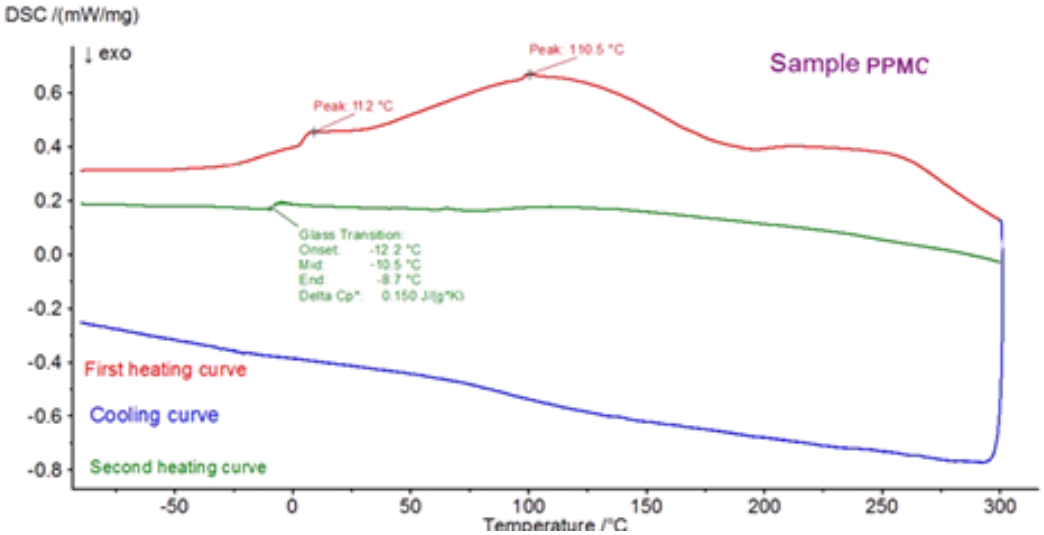


Fig. 4.4(b) DSC Thermograms of polyesters Spectrum of PPMC

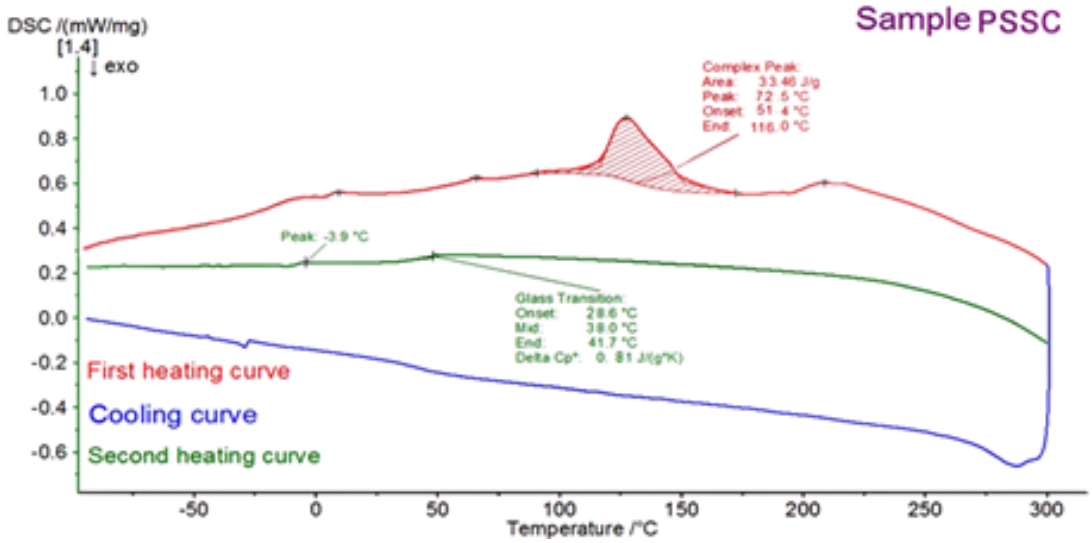


Fig. 4.4(c)DSC Thermograms of polyesters Spectrum of PSSC

X-Ray Diffraction Analysis

Wide Angle X-ray Diffraction Analysis is a primary technique used to determine the degree of crystallinity of the polymers. X-Ray diffractogram of the synthesized polymers are shown in Fig. 4.5(a), 4.5(b) & 4.5 (c) The crystalline nature of polyesters was determined from X-ray diffractogram. Gaussian curves are used to describe the amorphous phase and all crystal reflections of a diffractogram. In the X-ray diffractogram, the intensity of diffraction peaks increases with the increase in the length of the flexible spacer group. This is in accordance with the study of Chen *et al*. This indicates that the crystallinity of the polymer increases with the length of flexible segments. From the X-ray diffratogram, it is observed that PEMC is highly amorphous in nature than PPMC and PSSC.

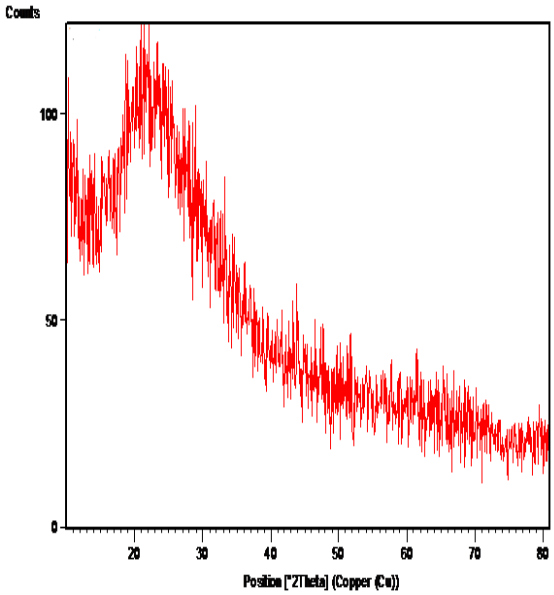


Fig. 4.5(a) WAXD Patterns of Polyesters PEMC

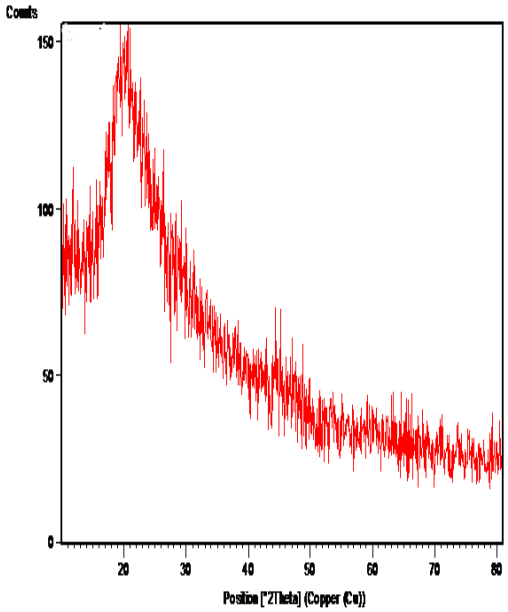


Fig. 4.5(b) WAXD Patterns of Polyesters PPMC

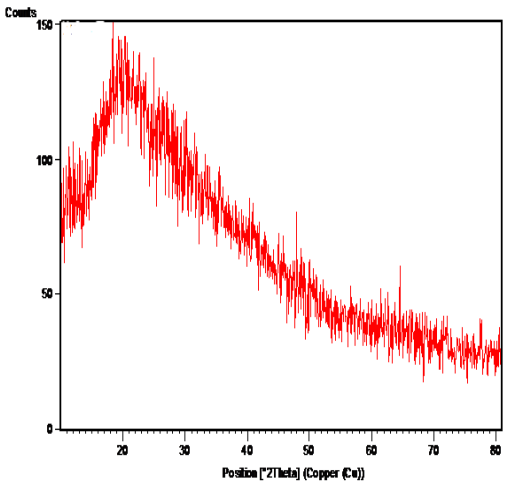


Fig.4.5 (c) WAXD Patterns of Polyesters PSSC

Biodegradation Analysis of Co polyesters PEMC, PPMC and PSSC

Polyester thin films were obtained by hot pressing method. The thin films of area 10 x 10 mm^2 and about 200μm thickness was placed in a Petri dish containing 10ml of phosphate buffer solution (pH 7.00 ± 0.01). After a specific period of incubation, the films were removed from the dish, washed with distilled water and dried weighed till constant weight. This procedure was repeated for every chosen time interval: 9,24,48,72 and 90 hours.

The weight loss percentage of polyesters, PEMC, PPMC and PSSC during biodegradation using phosphate buffer is determined with specific time interval tabulated and the weight loss percentage of the synthesized polyesters changed with its structural arrangement and crystallinity. Polyester PEMC exhibits higher degradation rate than PPMC and PSSC. The higher bio degradability of these polyester attributed to the less crystalline nature and low melting temperature of this polyester which is correlate with the DSC and XRD data of these polyester.

Weight loss Percentage of PEMC, PPMC and PSSC

Time in Hours	Weight loss (%)		
	PEMC	PPMC	PSSC
0	0	0	0
9	4.2	2.2	3.6
24	11,0	8.8	9.8
48	24.2	20.6	22.8
72	38.4	31.6	35.2
90	45.6	39.8	41..2

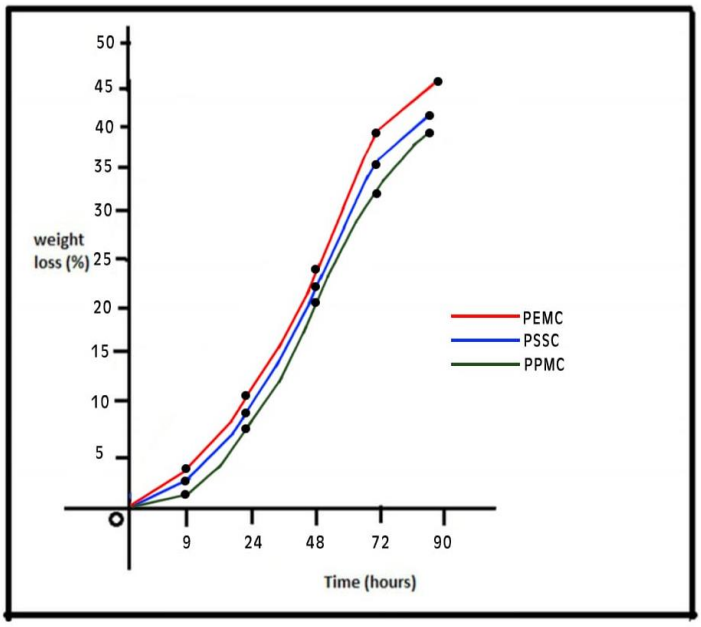


Fig.4.6 Biodegradation Graph of PEMC, PPMC and PSSC

CONCLUSION:

The three random biodegradable copolyesters PEMC, PPMC and PSSC were synthesized from by direct melt polycondensation reaction in the presence of a highly effective catalyst Titanium Tetraisopropoxide. The structure of the synthesized polyesters was confirmed by FTIR and NMR spectral studies. The degree of crystallinity was obtained from the XRD patterns of these co polyesters. The thermal behavior of the synthesized copolyesters were examined from DSC analysis. The polymer PEMC exhibits less amorphous and low melting point shows higher biodegradability than the polymers PPMC and PSSC. These studies reveled that these polyesters are good candidate having biodegradability will be used in drug delivery and biomedical applications.

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