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Synthesis and Characterization of Tartaric acid Based Polyester Nanocompositefor Biomedical Applications

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ABSTRACT

Biodegradable aliphatic polyesters have attracted significant interest in the field of healthcare such as tissue engineering, therapeutic delivery, wound healing and bio imaging applications. In terms of mechanical stability, crystallinity, hydrophobicity, and biocompability, polyesters synthesized from these monomers can display a wide range of applications. The polyester, poly (Glycerol-co-tartrate) was synthesised by catalyst free melt polycondensation. Nanohydroxyapatite powder was synthesised by sol gel method using calcium nitrate and phosphoric acid as precursors respectively. The polyester/nHAp composite was prepared by solution mixing. The solubility of polyester and polyester nanocomposite were investigated using various solvents. The synthesised polyester and polyester nanocomposite was characterised by fourier transform infrared spectroscopy (FTIR), ^{1}H nuclear magnetic resonance (^{1}H NMR) and ^{13}C nuclear magnetic resonance (^{13}C NMR). The thermal stability of polymers was studied by Differential scanning calorimetry (DSC).

Keywords: Biodegradable elastomers, Catalayst free melt polycondensation, Biomaterials, and Spectral analysis.

I. INTRODUCTION

The interesting properties of tartaric acid as a building block for the construction of biodegradable condensation polymers have been long appreciated [1-3]. Highly biodegradable polytartrateswere investigated and their potential applications as controlled releasing agents have been explored in the last few years [4]. Tartaric acid is an attractive monomer or comonomer for synthesis of functional polymers. Tartaric acid, a widely available and relatively inexpensive natural resource from a large variety of fruits, has been used in the synthesis of polyesters, [5-6]. Tartaric acid based polyesters have the potential to be used as vectors or drug carriers or controlled release agents in drug delivery [7-8].

In this study, aliphatic polyesters were synthesized by catalyst free melt polycondensation. Hydroxyapatite (HAp) has been widely investigated for both dental and orthopedic applications due to their outstanding biocompatibility and osteoconduction [9-11]. However, the brittleness of calcium phosphate and formation of micro cracks induced during harsh processing conditions limited the application of hydroxyapatite to non-load bearing parts of the skeleton. In order to overcome these limitations, many research groups have combined biodegradable polyesters with HAp to form composite [12-15]. Also, polyester/nHAp composite was prepared and characterized.

II. METHODS AND MATERIAL

2.1. Materials

Glycerol and tartaric acid (TA) were obtained and used without further purification. Phosphoric acid, Ammonia (MERCK AR grade),Calcium nitrate tetrahydrate (CNT, Aldrich) The other materials andsolvents used for the analytical methods were of analytical grade.

2.2. Synthesis of nano-hydroxyapatite

0.25M Phosphoric acid (PA) solution was prepared and ammonia solution was added in drops and stirred till a constant pH of 10. Then,1M Calcium nitrate tetrahydrate solution was prepared and was slowly added to the PA-NH_3 solution, maintaining a Ca/P ratio of 1.67. Further small amounts of ammonia was added to the solution to maintain a constant pH of 10. The solution was vigorously stirred for 1hr and kept for ageing for 24 h at room temperature. The gel obtained after ageing was dried at 65ºC for 24h in a dry oven. The powders obtained from dried gel were washed repeatedly using double distilled water to remove NH_4^+ and NO_3^-. After washing, the powder was calcined in air at 500ºC for 30 min in an electric furnace.

2.3. Preparation of Polyester and its nanocomposite

Equimolar amounts of both Glycerol and tartaric acid [Gly+TA = 1:1] were added to a round bottomed flask and melted together at 160-165ºC followed by mixing at 140-145ºC for 1h under constant steam of nitrogen to obtain pre-polymer. The pre-polymer was then mixed to incorporate 2% by weight n-HAp. PGT pre-polymer dissolved in methanol (1:1 w/v) was mixed with the desired amount of n-HAp powder. The PGT/nHAp mixture was stirred to get homogeneous solution and cast into Teflon dishes and left in an oven at 110ºC for 2 days for post-curing.

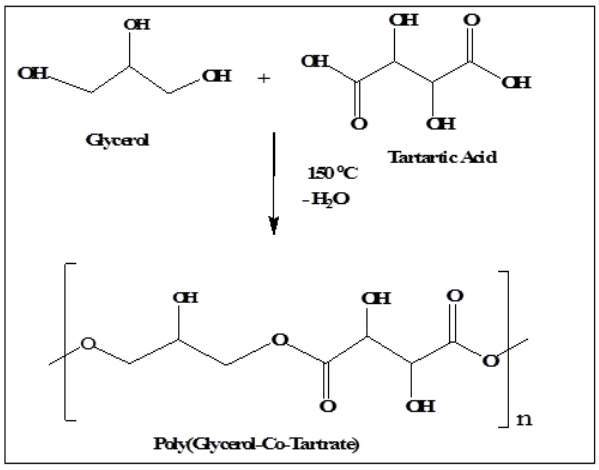


Figure 1: Synthesis of poly (Glycerol-Co-Tartrate)

2.4 Characterisation

The solubility of the synthesized polyester, PGT, was determined in various solvents qualitatively. 1H NMR spectra of the synthesized copolyester were recorded on AV 3500 MHz Spectrometer by using MeOD as solvent. 13C NMR spectra of the synthesized copolyester were recorded using deuterated methanol as solvent at 300-600 MHz. IR spectra of the n-HAp, copolyester and nanocomposite were recorded using a perkin Elmer IR spectrometer in the range of 700 cm−1 to 4500 cm−1. The samples were embedded in KBr pellets. The DSC scans of the copolyester and the nanocompositewere recorded at a heating rate of 10ºC/min using a Perkin-Elmer Pyris I analyser. Indium was used as the calibration standard.

III. RESULTS AND DISCUSSION

A. Solubility studies

The solubility of the synthesised random copolyesterwas tested qualitatively in various organic solvents and the results are presented in:

TABLE 1: Solubility of copolyester PGT

Polymer	Acetone	$CHCl_3$	1,4-Dioxane	DMF	DMSO	Ethanol	Hexane	THF	Methanol
PGT	++	+++	+++	+++	+++	+++	--	++	+++

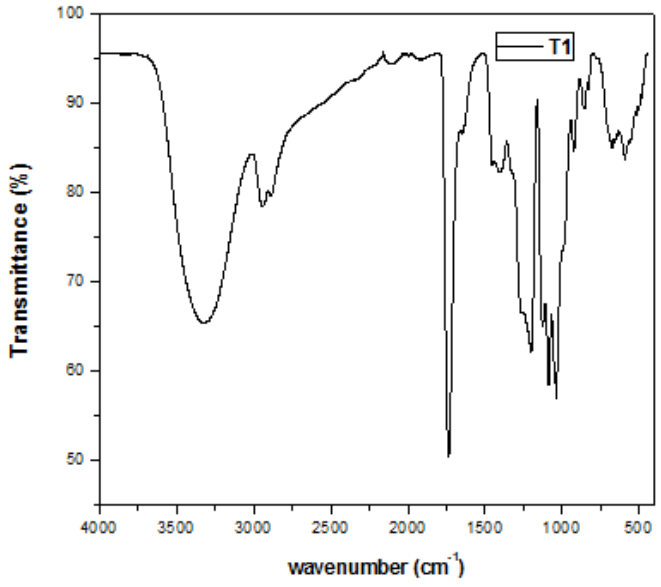
+++ - Freely Soluble, ++ - Sparingly Soluble, - - - Insoluble

The synthesised copolyester is freely soluble in CHCl3, 1, 4- Dioxane, DMF, DMSO, methanol, and ethanol. The polyester is sparingly soluble in acetone and THF and the insoluble in hexane.

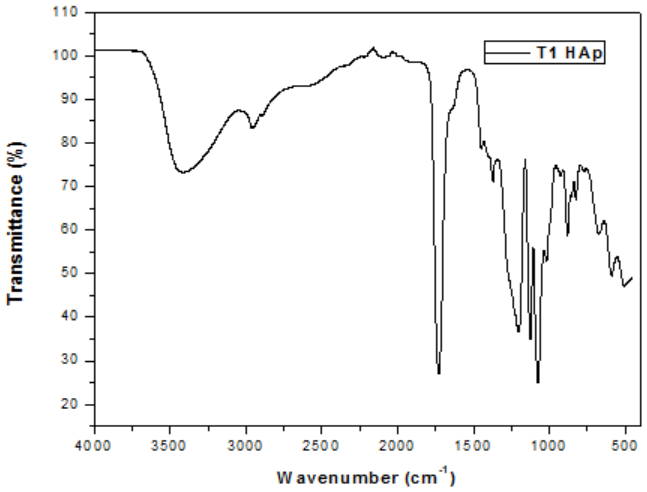
B. Fourier- Transform Infrared

(FTIR) spectroscopy of polyester

In spectra (a) a strong band of PO43- group was seen at 1042 cm-1and 1050 cm-1 due to symmetric stretching vibration. The spectra possessed a broad band ranging between 3350 cm-1 and 3550 cm-1shows the presence of –OH group. H2O band was also observed at 1632 cm-1. In spectra (b) the pronounced peaks at 1690–1750 cm−1suggest the presence of carbonyl (C=O) groups from the ester bond and pendent carboxylic acid from the tartaric acid. The bands centered at around 2944 cm−1 were assigned to methylene (-CH2-) groups for diacids/ diols. Hydrogen-bonded hydroxyl functional groups showed absorbance as a broad peak centered at 3570 cm−1. It seems that the spectra of (c) were the superimposing of n-HAp on spectra (b) and no new peaks appeared in the spectra of the nanocomposite.



(a)



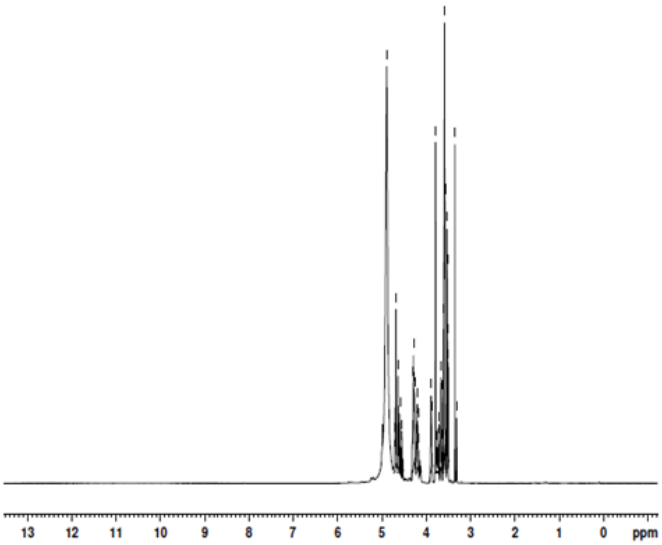
(b)

Figure 2:FTIR of (a) Copolyester PGT and (b) 2% n-HAp/PGT nanocomposite

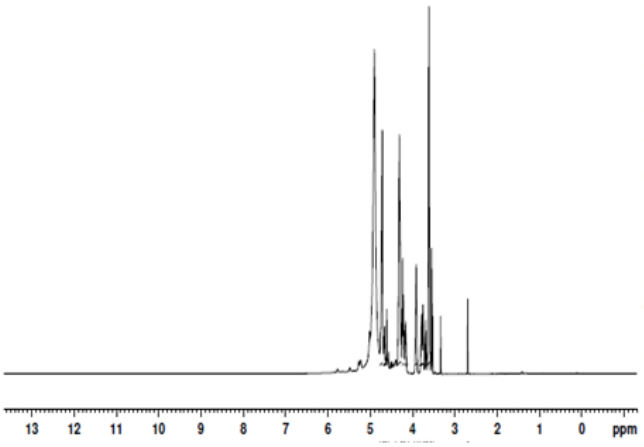
C. 1HNMR spectra of polyester

The structure of the repeating units present in the copolyester can be analysed qualitatively and quantitatively by 1H NMR spectroscopy. Figure 1 shows the 1 H NMR spectra of synthesized copolyester PGT. 1 H-NMR spectra of the sample show the expected characteristic peaks.

The chemical shift values obtained from 1H NMR spectra of copolyester are as follows. The peak observed at 2.8-2.6 ppm, was assigned to –CH2– from tartaric acid. The peak located at 3.36 ppm correspond to central methylene protons of Glycerol.



(a)

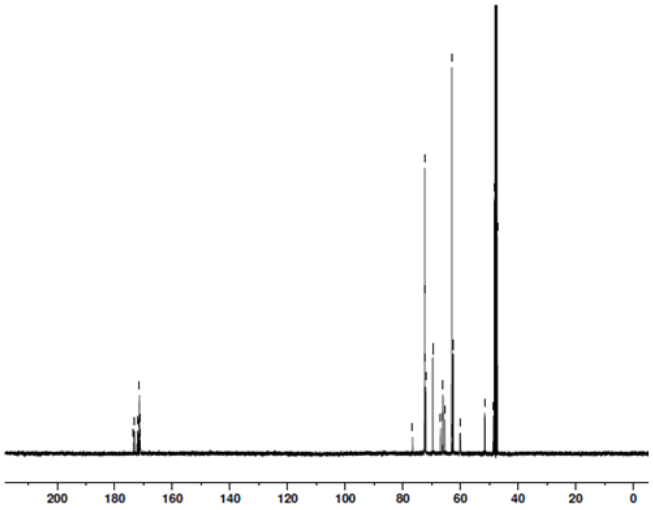


(b)

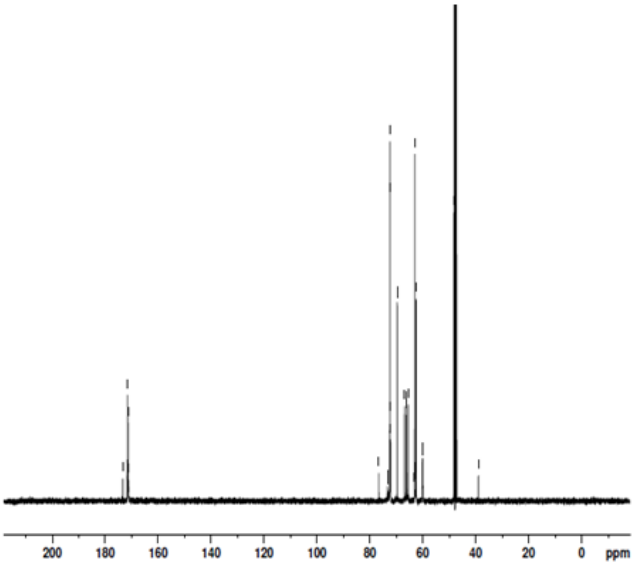
Figure 3: ^{1}H NMR of (a) copolyester PGT and (b)2% n-HAp/PGT nanocomposite

D. 13C NMR spectra of polyester

The chemical shift values of carbons present in different environments of the synthesised copolyester can be analysed by 13C NMR spectroscopy. Figure 3 shows the 13C NMR spectra of synthesized copolyester PGT. The chemical shift values obtained from 13C NMR spectra of copolyester are as follows. The peak located at 169.93 ppm was assigned to carbonyl carbon atom of the ester group and peaks located at 61–65 ppm were assigned to –CH2 -CO– group. The peak at 40.44 ppm was assigned to –CH2 – from tartaric acid.



(a)

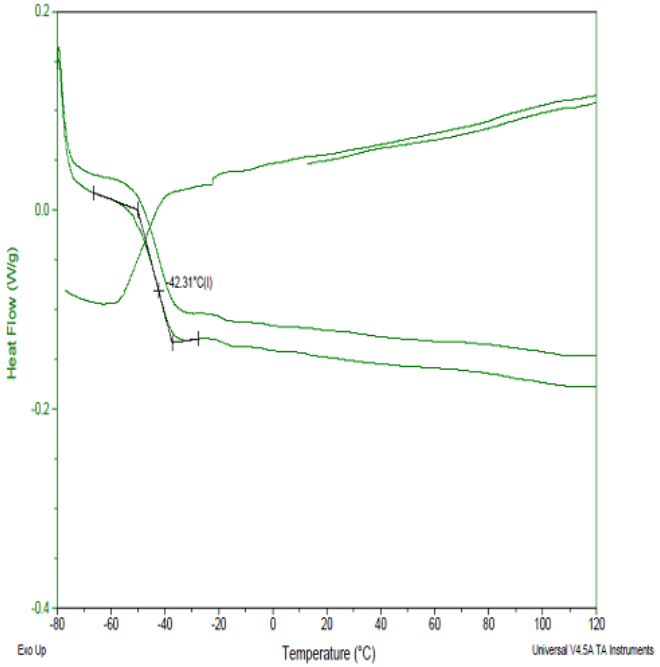


(b)

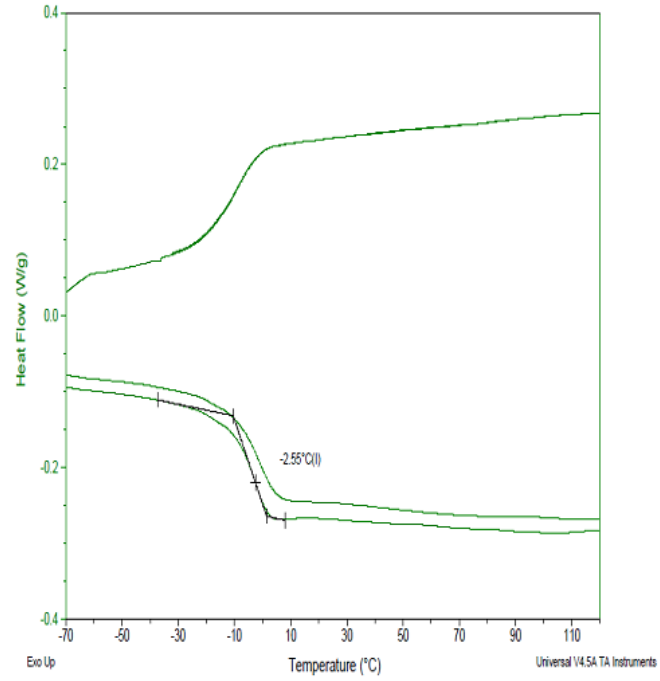
Figure 4:^{13}C NMR of (a) copolyester PGT and (b) 2%n-HAp/PGT nanocomposite

E. Thermal analysis

The thermal properties of polyesters and polymer nanocompositeswere studied from Differential Scanning Calorimetry, DSC analysis. The DSC heating thermograms of PGT and 2% of PGT/nHAp are depicted in Figure 5(a) and 5(b). It can be seen that all of the nanocomposites were amorphous, and no crystallization melting peaks were found. The glass transition temperature (Tg) of PGT matrix is around −42.31ºC. When n-HAp was incorporated, the Tg of the thenanocomposite is affected by chemical cross linking density, resulting in the glass transition temperature of −2.55ºC.As the Glass transition temperature of the polymer and the polymer nanocomposite lies well below the room temperature which infers these materials are elastomeric in nature which is one of the requirement for biomaterials.



(a)



(b)

Figure 5:DSC spectra of (a) copolyester PGT and (b)PGT/nHApNanocomposite

IV. CONCLUSION

A new type of copolyester has been synthesised by a simple catalyst-free melt polycondensation method with Tartaric acid and glycerol as starting monomers. The nanostructured hydroxyapatite powder was synthesized by sol-gel method using calcium and phosphorous precursors. The n-HAp/PGT polyester nanocomposite was prepared by solution mixing method. The PGT and n-HAp/PGT nanocomposite have appreciable mechanical and thermal properties which substantiate their cross-linking abilities. The developed new material will improve the ease of fabrication and performance of biocompatible elastomers for future tissue engineering applications.

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