A study on the effect of monomer composition on the degradation rate and mechanical properties of certain sorbitol based polyester elastomers

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Abstract-- Biodegradable synthetic polyesters have recently found widespread application in biomedical and engineering fields, such as tissue engineering, therapeutic delivery and bioimaging. Currently, many applications involving sorbitol based polyesters are being explored that are endogenous to the human metabolism. In terms of mechanical stability, crystallinity, hydrophobicity and biocompatibility, polyesters synthesised from this monomer can display a wide range of applications. In this paper, a novel biodegradable network of elastomeric aliphatic polyesters, Poly(Sorbitol sebacate-co-ethylene glycol sebacate) (PSSeEG) and Poly(Sorbitol suberate-co-ethylene glycol suberate)(PSSuEG), were synthesized using non toxic monomers such as Sorbitol, sebacic acid/Suberic acid and Ethylene Glycol by catalyst free melt polycondensation method. The pre-polymer was post-polymerized and simultaneously crosslinked in mold at 200^{o}C. The synthesised polymers were characterised by Fourier Transform Infrared Spectroscopy(FTIR), NMR Spectroscopy and thermal analysis. Thermal analysis shows the elastomeric amorphous nature of the polyesters which is suitable for biomedical applications. The mechanical properties of both the synthesised polymers are determined which confirms the typical elastomers with low hardness and large elongation. The length of the diacid had strong influence on the degradation rates and mechanical behaviour . The material was expected to be useful for drug delivery, tissue engineering scaffold and other biomedical applications.

Keywords: Biodegradable, melt polycondensation, elastomers, mechanical behaviour.

I. INTRODUCTION

The demand for biodegradable polymers in medical application is increased as they can sustain and recover from multiple deformations without causing irritation to the surrounding tissue in a mechanically demanding environment has motivated the materials community to develop new polymers.[1-4] . Recently,a versatile elastomeric material have become popular platform using polyol as the central monomer condensed with other non toxic monomers like aliphatic diacids and diols yielding various elastomers like poly (xylitol sebacate), poly (mannitol sebacate) [5], poly (sorbitol tartaric sebacate)[6] have attracted considerable attention as green materials in pharmaceutical, medical and biomedical engineering applications including drug delivery systems, artificial implants and functional materials in tissue engineering.

Sorbitol is a versatile monomer that participates in prepolymer formation through simple catalyst free condensation preserving its pendant functionality for post polymerization to produce a highly crosslinked polyester network with degradable ester bonds .Sebacic and Suberic acid is an intermediate product of ω- oxidation of long-chain aliphatic acids is more suitable for the preparation of polyesters, as short-chain aliphatic acids always conduce to intramolecular condensation[7]. However works on polyesters of sebacic acid and suberic acid are rare. To our knowledge no study has systematically investigated sorbitol-based polyesters in combination with ethylene glycol and Suberic acid/Sebacic acid . Herein we report the synthesis and characterisation of two polyesters: Poly (Sorbitol suberate -co-ethylene glycol suberate) (PSSuEG) and Poly (Sorbitol sebacate-co-ethylene glycol sebacate) (PSSeEG) .

II.MATERIALS AND SYNTHESIS

A. Materials

High purity Sorbitol(S), Suberic acid (Su), Sebacic acid (Se) and Ethylene glycol(EG)(lancaster AR grade) were used as received.1,4 dioxane and other solvents were purchased are analytical grade.

B. Synthesis of Copolyesters

Both PSSuEG and PSSeEG , were synthesised by the catalyst free melt polycondensation technique by the following procedure. Appropriate molar amounts of monomers were melted in a round bottom flask at 150^{o}C under a blanket of nitrogen gas and stirred for 2hrs to prepare prepolymers. Then, the samples were transferred into polytetrafluoroethylene moulds in a vacuum oven at 200 ^{o}C for 5 days for further polyesterification .Two different polymers using two different diacids were synthesized in

this study to investigate the effect of diacids on the physical and mechanical properties. The cured polymers were then stored in a desiccators for further use .The schematic synthesis is shown in fig.1. The resulting polymers were crosslinked at the reaction groups shown in fig.1. The –OR groups in fig.1 indicates both crosslinked or –OH groups.

C.Characterisation

a) Solubility Test

Solubility of the copolyester samples were examined in 1,4 Dioxane,Choloroform ,Ethanol, Water, Dimethyl Sulphoxide etc.

a) Fourier transform infrared (FTIR) Spectrometry analysis.

IR spectra of all the prepolymer samples were recorded using a perkin Elmer IR Spectrometer in the range of 700cm^{-1} to 4500 cm^{-1}.The samples were embedded in KBr pellets.

b) Nuclear Magnetic Resonance (NMR) Spectroscopic analysis

All the three prepolymers were dissolved in 1,4 dioxane and precipitated in water followed by filtration and drying.^{1}H and ^{13}C NMR spectra of the polymer samples were recorded on a Bruker NMR (Bruker AXS Inc., Madison, WI)Spectroscope at 400 MHz with deuterated dimethyl sulfoxide as a solvent and tetramethylsilane as a internal reference.

c) Thermal properties

Differential Scanning Calorimetry (DSC):DSC measurement were performed by NETZSECH DSC204F1 from -100^{o}C to 500^{o}C at the rate of 10^{o}C per minute in a nitrogen atmosphere.

d) In Vitro degradation of Polymers

Disc-shaped specimens (7mm in diameter, about 1–1.5mm thickness)were placed in a tube containing 10 ml phosphate buffer saline (pH 7.4) and 0.1M NaOH to rapidly obtain relative degradation rates among samples. Specimens were incubated at 37^{o}C in PBS and NaOH solution for predetermined times, respectively. After incubation, samples were washed with distilled water, incubated in ethanol overnight, and dried to a constant weight. The percentage mass loss (%M $_{loss}$) of the polymer was calculated from the following equation(1)

$$\%M_{loss} = [(M_o - M_d)/M_o] \times 100\% \quad (1)$$

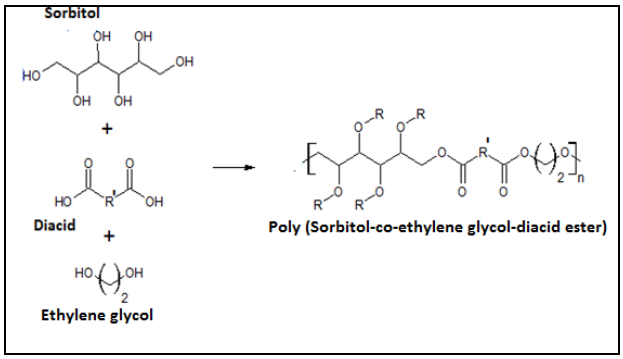
Where M_o and M_d are the masses of the polymer sample at the initial and given times.

e) Mechanical properties

The mechanical properties of polymers PSSuEG & PSSeEG were measured at room temperature with the universal testing machine (S.C. Dey Co, India)equipped with 500N load cell and data acquisition software .The dog bone shaped polymer strips were prepared according to ASTM D 638 (35x4x2 mm^3,Length x Width x Thickness = 1-2mm) and pulled at a strain rate of 10mm/min. The Young modulus(E_0) was calculated from the initial slope of tensile stress versus strain . The cross link density of the polymer sample was calculated with Equation (2) according to the theory of rubber elasticity [5].

$$n = E_0 /3RT \quad (2)$$

where n is the number of active network chain segments per unit volume (mol/m^3), E_0 is the Young's modulus (Pa), R is the universal gas constant (8.314 J/mol.K)



Diacid = Suberic acid & Sebacic acid

R' = -CH_2 - of diacid; R= crosslinked copolymer

Fig.1 Schematic representation of Synthesis of Sorbitol polyesters

III. RESULTS AND DISCUSSION

A. Solubility studies

Solubility of polymers were shown in Table-1

Table-I. Solubility of the Copolyesters

+++ Free Soluble,++ Partially Soluble,---Insoluble

Polyester	1,4 Dioxane	CHCl3	DMSO	Ethanol	Water
PSSuEG	+++	+++	+++	++	---
PSSeEG	+++	+++	+++	++	---

B. Fourier transform infrared (FTIR) Spectrometry analysis.

Fig.2 depicts the FTIR spectra of the synthesized Polymers. The absorption peak around 1700 cm^{-1} ,corresponding to ester (C=O) groups confirms the formation of ester bond[8,9,10] the peak assigned around 1250cm^{-1} & 1160 cm^{-1} due to C-O stretching absorption of diacid and the peak centered at 2940 cm^{-1} were assigned to methylene (-CH_2)stretching absorption [11] from diacid, additional stretch around 1050 cm^{-1} is associated with the vibration of ether bond existing between sorbitol and ethylene glycol, the

broad peak centered at 3500 cm^{-1}were attributed to the (O-H) stretching [12,13] the weak band at 1406 cm^{-1} was probably due to C-O stretching in unreacted diacid[14].

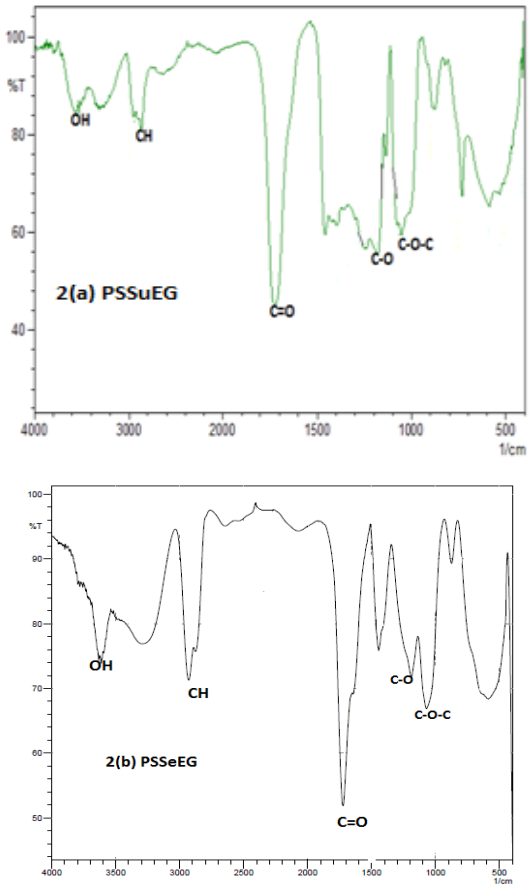
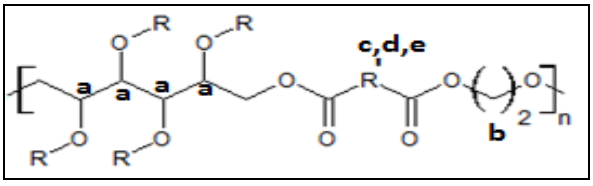


Fig 2. IR spectra of copolymers of 2 (a)PSSuEG & 2(b)PSSeEG

C. Nuclear Magnetic Resonance (NMR) Spectroscopic analysis

^{1}H NMR analysis

Spectra of all the synthesized polymer samples were obtained. Fig (3) shows the ^{1}H NMR spectrum.The peaks between 3.5 to 5 ppm were assigned to protons –$OCH_2[CH(OH)]_nCH_2O$- from Sorbitol [15] . The peaks around 2.3 ppm ,1.6ppm and 1.3 ppm shown in PSSuDEG and PSSeDEG were attributed to α, β and γ protons of diacids [16]. A peak around 3.5 to 4.5 ppm is due to methylene protons of ethylene glycol appeared in both the spectra.



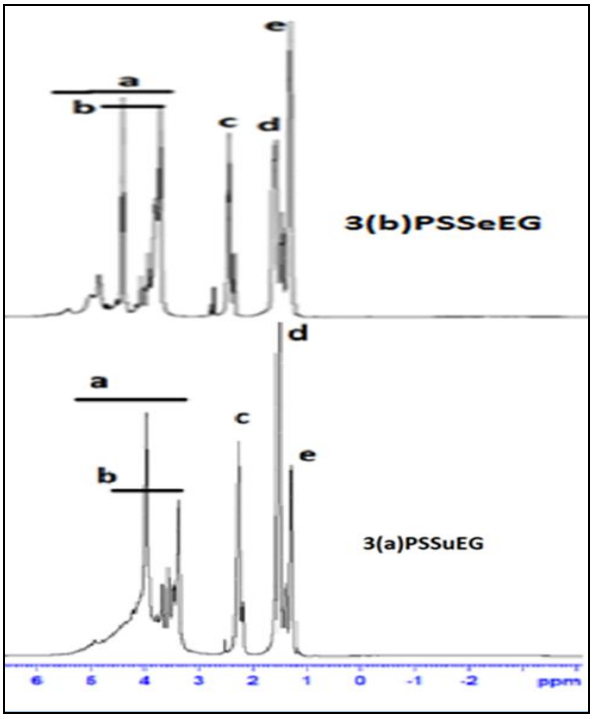


Fig.3 ^{1}H NMR spectra for 3(a)PSSuEG & 3(b)PSSeEG Polymers

^{13}C NMR analysis

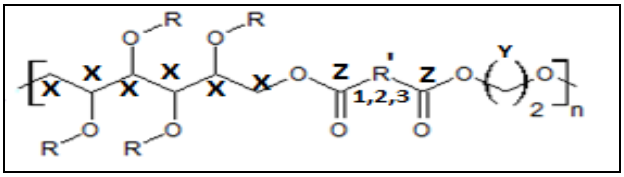
Sorbitol showed resonance peaks at 65.8,66.1,72.9,74.3,74.5 and 76.1 ppm in Fig.4 corresponds to 1-6 carbon atoms [6], in this first two peaks corresponds to the terminal carbon .The peaks in the region 60 - 65 ppm arose from carbons directly bonded to oxygen [17] , either it may be a (CO-OCH_2) of diacid or it may be (CH_2-O- CH_2) of ethylene glycol ,the peak around 173 ppm is due to COO- carbon of unreacted diacid. The peak at 35,26,30 ppm observed in PSSuDEG and PSSeDEG spectra is due to α, β and γ carbon of Suberic and Sebacic acid. A peak around 40 ppm is due to DMSO solvent.

D. Thermal Analysis

The DSC heating thermograms of PSSuEG and PSSeEG are depicted in Fig.5. The thermal studies revealed that the elastomers were thermally stable. The DSC analysis of both the polyesters showed Tg below room temperature, a characteristic feature synthesized polymers(18).The glass transition temperature (Tg) of PSSeEG matrix (-54.7°C) was higher than PSSuEG matrix (-72.3°C). This is largely due to an increase in methylene length of the diacid results in an increase in main chain flexibility of the copolymer structure which reveals that PSSeEG elastomer had better cross-linking than that of PSSuEG [19].

E. In vitro degradation

The degradation of polymers was confirmed with PBS and 0.1M NaOH. Fig 6(a,b) shows that both the polymer undergo alkaline degradation faster (100 % completed within 24 hrs) than in PBS (50% completed only after 2 months). As base catalysis causes faster chain cleavage than polymer swelling[20]. If we compare the degradation behavior for individual polymer, PSSuEG undergo faster degradation in both the medium than PSSeEG polymer. This could be due to increase in the hydrophobic group (-CH_2-) in the polymer chain, increases the cross link density decrease the degradation rate of the elastomers[21].



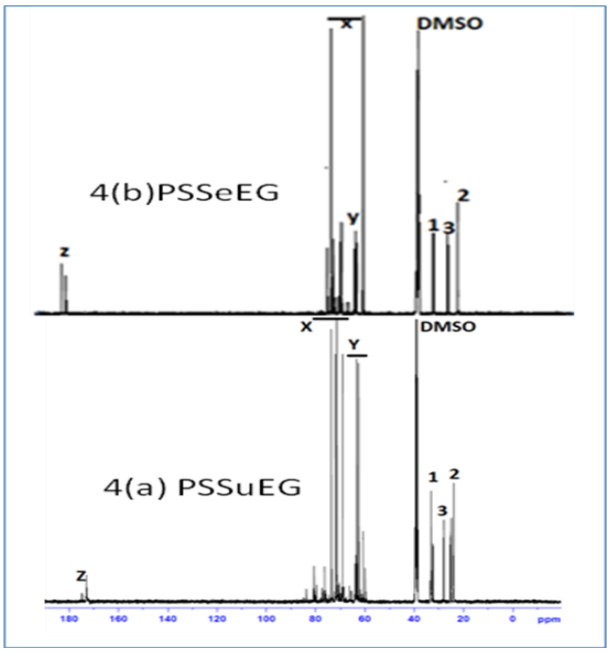


Fig.4 ^{13}C NMR spectra for 4(a) PSSuEG & 4(b) PSSeEG polymers

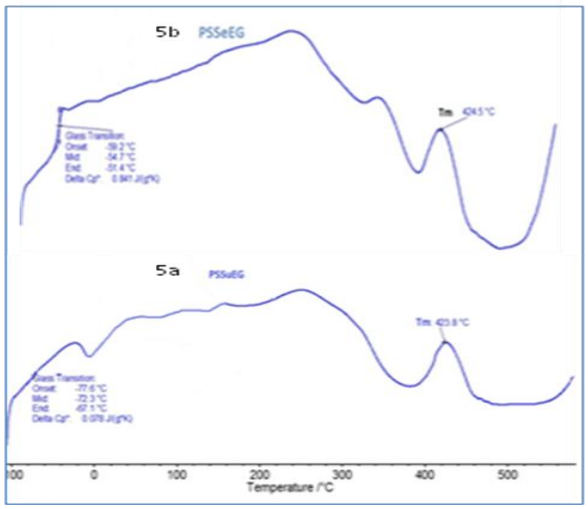


Fig.5 DSC Thermograms for 5(a)PSSuEG &5(b)PSSeEG polymers

F. Mechanical Properties

The average Young's modulus, tensile strength, Cross link density and percentage elongation at break were reported in Table-2.

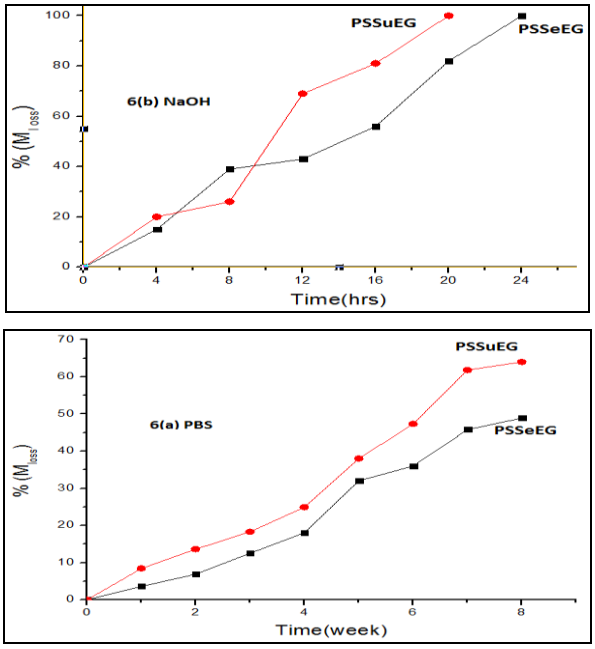


Figure 6. In vitro degradation of the Polymers in (a) PBS at 37^{o}C (b) 0.1 M NaOH at 37^{o}C

Tensile tests of the polymers exhibited characteristics similar to that of elastomers. The variation of the tensile stress with strain for the polymers is shown in Fig-7.The Young's modulus, tensile stress, cross link density & percentage elongation at break increases with increase in chain length of decides, which confirm that both the polymer behaves like elastomers. The Young's modulus and tensile stress of the

polymer were similar to knee cartilage artery [2.1-11.8 Mpa] and vascular wall elastin [0.3-0.6] [22].Thus these polymers are therefore expected to be useful for soft tissue engineering applications. Nevertheless, these polymers after appropriate modifications are suitable for drug delivery.

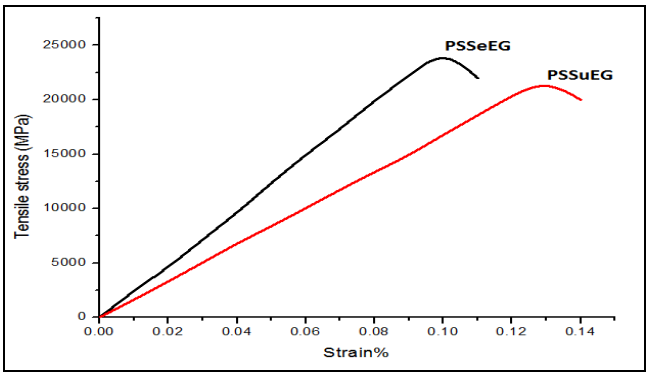


Fig 7 Tensile stress Versus strain curves for PPSuEG & PSSeEG Polymers

Table--2. Mechanical Properties of the Polyesters

Polymer	Tensile Stress (Mpa)	E_0 (MPa)	Elongation at break %	n (mol/m^3)
PSSuEG	0.57	2.46	19.8	330.8
PSSeEG	0.63	3.84	15.29	516.7

IV.CONCLUSION

This new family of sorbitol based polyesters was synthesized from monomers, which are biocompatible or found to be involved in human metabolism process. The synthesis process involves a simple procedure without any catalyst and extreme operating conditions. Two different polymers were synthesized by varying the monomer (diacid) to study the effect on the various properties. The polymers synthesized were found to be soft and flexible. Thermal mechanical and degradation properties of these polyesters can be tuned to the requirement of ligament, blood vessels and nerve applications in human body by varying the monomers or by varying the curing conditions during the post polymerization process.

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