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Synthesis and Characterisation of Sorbitol Based Copolyesters for Biomedical Applications

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Abstract: In this investigation we report on the synthesis and characterisation of certain polyester elastomers namely as Poly(Sorbitol succinate-co-ethylene glycol succinate) (PSSEG), Poly(sorbitol succinate-co-butane diol succinate) (PSSBD) and Poly(sorbitol succinate-co-hexane diol succinate) (PSSHD) by carrying out catalyst free melt polycondensation.. The synthesised polyesters were characterised by solubility, FT-IR, ^{1}H NMR and ^{13}C NMR spectral methods. The thermal properties were analysed by differential scanning calorimetry and thermogravimetric analysis. The mechanical properties evaluated for the polyester films in the tensile mode shows that the polymer has characteristics of elastomers and stiff thermosets. We demonstrate that the chemical structure , physical integrity and mechanical property of synthesized copolyester can be controlled by simply changing the monomers and suit them for the requirements of various biomedical and soft tissue engineering applications.

Key words: Polyester elastomer, catalyst free melt polycondensation, thermal and mechanical property.

1. Introduction

In recent years, considerable efforts have been taken on the synthesis and characterisation of new biocompatible polymeric materials due to their potential applications in tissue engineering. Aliphatic polyesters are the most promising biodegradable and biocompatible materials because they are readily susceptible to biological attack. A number of aliphatic polyesters with good mechanical properties have been developed to overcome problems associated with the thermoplastic materials such as rigid, bulk degradation [1-4]. To improve these properties either we use blending process or copolymerization [5-8]. In physical blending, complete biodegradability is not possible by microorganisms so we performed single step copolymerization give rise to the thermoset polymers like poly(1,2-propane diol-sebacate)-citrate [9], poly propylene sebacate [10]. Several aliphatic thermoset polyesters were synthesized such PGS poly glycerol sebacate have shown to primarily degrade by surface erosion [11, 12] retaining their structural integrity and form stability during degradation in vivo. So the polymers under this category hold great promise in cardiovascular tissue engineering application and small nerve grafts [13, 14], the introduction of a polar functional group in to the polyester enabled the application of these materials to construct novel controlled drug delivery systems and functional vectors as well as related biomedical applications. Similar to glycerol, many number of polyol based polyester were synthesized like sorbitol citric sebacate, sorbitol tartaric sebacate [15], poly1,8-octane diol citrate [16], xylitol glutamate sebacate [17], Poly sorbityl adipate [18]. Besides some other biobased polyesters using soyabean oil are attractive polyesters [19].

The advantages of using Sorbitol as a monomer, because it is derived from renewable sources and has multi functional group, to allow the formation of randomly cross linked networks as well as a wide range of crosslink densities, and it can be completely

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metabolized to carbon dioxide [20, 21] and this CO_2 is needed by the microorganism for the production of another monomer succinic acid which is also an intermediate in citric acid cycle and one of the fermentation end-products of anaerobic mechanism [22] and polyols like xylitol and sorbitol are metabolized in an insulin independent manner [23-25]. Generally, the monomer succinic acid is mainly produced by chemical process from n-butane/butadiene via maleic anhydride, utilizing the C4 fraction of naphtha in quantities of about 15,000 tons per year with a price range of about 6-9 $/kg. But more recently Mannheiimia succiniproducens MBEL55E was isolated as a natural succinic acid overproducer from bovine rumen by Lee et al [26]. So far polyols were polymerized with two diacids or one diacid and one amino acid. But in this article we polymerise polyol with one diacid and one diol to get thermally stable, highly crosslinked polymer with good thermal and mechanical property .

With regard to the high commercial potential of aliphatic copolyesters and their interesting properties, in the present investigation, we report on the synthesis and characterisation of three new class of Sorbitol based aliphatic polyesters: Poly(Sorbitol succinate-co-ethylene glycol succinate) (PSSEG), Poly(Sorbitol succinate-co-butane diol succinate) (PSSBD) and Sorbital succinate-co-hexane diol succinate) (PSSHD). The structure of their repeating units and the effect of the physical and thermal properties were also investigated.

2. Experiments

2.1 Materials

Sorbitol, S (Merck AR grade) and Succinic Acid(SA) (Lancaster AR grade) were recrystallised from distilled water and used. Ethylene Glycol(EG), 1,4 Butane diol (BD) and 1,6 Hexane diol (HD) (Lancaster AR grade) were dried with CaO overnight and then distilled under reduced pressure. All other materials and solvents used were of analytical grade.

2.2 Synthesis of Copolyesters

The polyesters PSSEG, PSSBD and PSSHD were synthesised by the catalyst free melt polycondensation method by the following procedure. The amount of diacid, diol and sorbitol in a molar ratio of 1:2:1 were placed into a 250 mL three necked round bottom flask and melted at 150 °C under the flow of nitrogen gas with stirring for 2 h. The prepolymers thus obtained were dissolved in dioxan and the resulting prepolymer solution was used for film preparation without purification. The films for mechanical and strucutural analysis were cast into Teflon petridishes and placed in an air oven maintained at 80 °C for 48 h for further polyesterification . The cured polymer films were then stored in a desiccator for further aplications. The schematic synthesis is shown in Fig. 1.

2.3 Characterisation Methods

2.3.1 Solubility Test

Solubility of the copolyester samples were examined in 1,4 Dioxane, Choloform, Methanol, Ethanol, Ether, Tetra hydro furan, Dimethyl formamide, Water, Dimethyl Sulphoxide, etc..

2.3.2 Fourier Transform Infrared (FTIR) Spectrometry Analysis

IR spectra of all the prepolymer samples were recorded using a perk in Elmer IR Spectrometer in the range of 700 cm^{-1} to 4,500 cm^{-1}. The samples were embedded in KBr pellets.

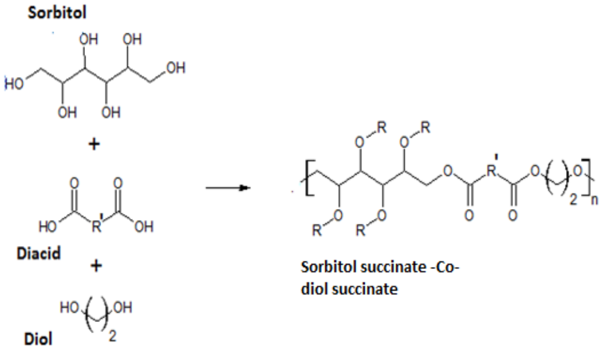


Fig. 1 Schematic representation of Synthesis of Sorbitol polyesters.

Diacid = Succinic acid R = CH_2 of diacid; R = crosslinked copolymer.

2.3.3 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.

2.3.4 Thermal Analysis

Differential Scanning Calorimetry (DSC) scans were recorded by NETZSECH DSC204F1 instrument from -100 °C to 450 °C at the rate of 10 °C per minute in a nitrogen atmosphere. Thermogravimetric Analysis (TGA) measurements were recorded by NETZSCH TGA209F1instrument under nitrogen atmosphere at the rate of 10 °C per minute from -100 °C to 600 °C

2.3.5 Mechanical Properties

The mechanical properties of the synthesised polyesters PSSEG, PSSBD and PSSHD were measured at room temperature with the universal testing machine (S.C. Dey Co, India)equipped with 500 N load cell and data acquisition software .The dog bone shaped polymer strips were prepared according to ASTM D 638 ($35 \times 4 \times 2$ mm^3, Length × Width × Thickness = 1-2 mm) and pulled at a strain rate of 10 mm/min. The Young modulus was calculated from the initial slope of tensile stress versus strain. The cross link density of the polymer sample was calculated with Eq. (1) according to the theory of rubber elasticity [27].

$$n = E_0 / RT \tag{1}$$

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).

3. Results and Discussiion

3.1 Solubility Studies

The solubility of synthesised polyesters are tested in various solvents and given in Table 1, The synhesised copolyesters maintain a good solubility in acetone, dixane, chloroform and DMSO and insoluble in water.

3.2 Fourier Transform Infrared (FTIR) Spectroscopy Analysis

The IR spectra of the synthesised copolyesters are recorded and given in the Figs. 2a to 2c.

The absorption peak around 1,700 cm^{-1}, corresponding to ester (C=O) groups confirms the formation of ester bond [28-30]. The peak assigned around 1,267 cm^{-1} and 1,160 cm^{-1} due to C-O stretching absorption of acid and the peak centered at 2,940 cm^{-1} were assigned to methylene (-CH$_2$)stretching absorption [31] from Succinic acid, additional stretch around 1,050 cm^{-1} is associated with the vibration of ether bond existing between sorbitol and diol. The broad peak appeared at 3,450 cm^{-1}was attributed to the hydrogen bonded hydroxyl groups [32, 33]. The weak band at 1,406 cm^{-1} was probably due to C-O stretching in unreacted succinic acid [34].

3.3 Nuclear Magnetic Resonance (NMR) Spectroscopic Analysis

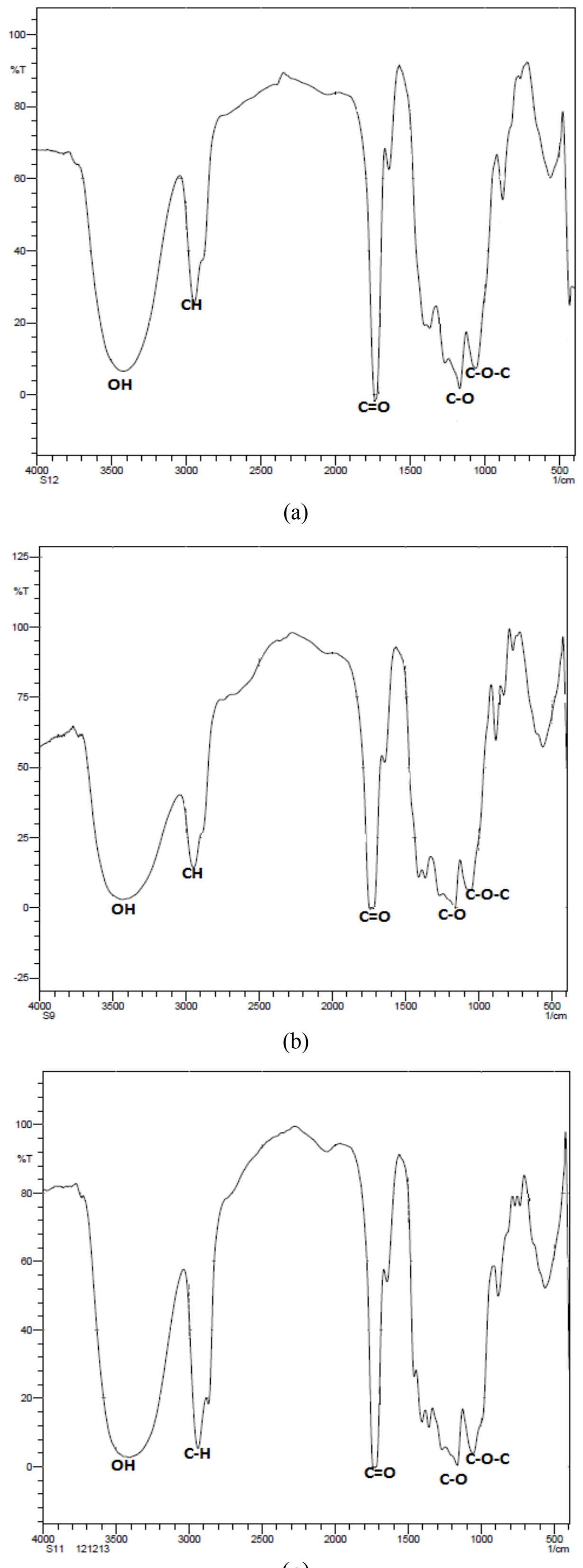
3.3.1 ^{1}H NMR Analysis

^{1}H NMR spectra of the synthesised copolyesters were recorded and presented in Figs. 3a to 3c. The peaks observed were attributed as follows. Peaks located at a chemical shift value at 5 to 3.5 ppm was

Table 1 Solubility of the copolyesters.

S.No	Polyester	Acetone	1,4 Dioxane	CHCl$_3$	DMSO	Methanol	Ethanol	Water
1	PSSEG	++	+++	+++	+++	-	-	-
2	PSSBD	++	+++	+++	+++	-	-	-
3	PSSHD	++	+++	+++	+++	-	-	-

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

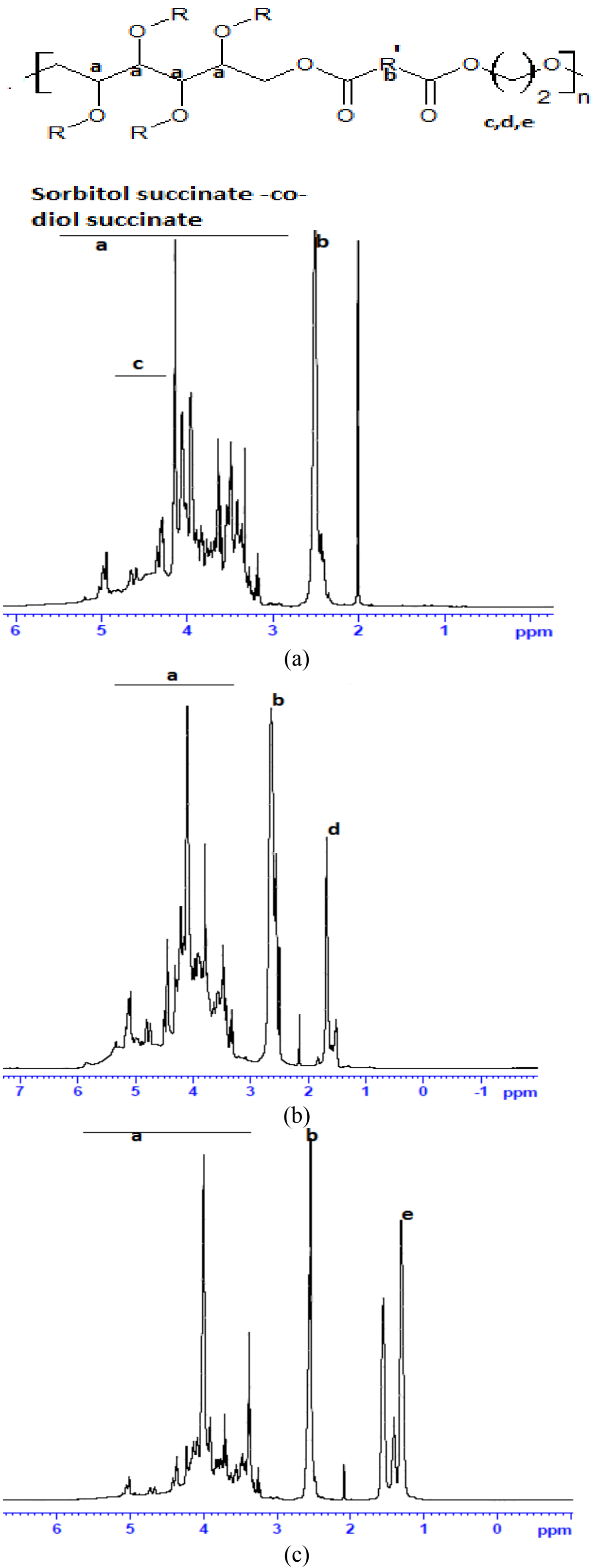


(a)

(b)

(c)

Fig. 2 IR spectra of (a) PSSEG. (b) PSSBD, (c) PSSHD.



(a)

(b)

(c)

Fig. 3 (a) ^{1}H NMR spectrum of PSSEG, (b) ^{1}H NMR spectrum of PSSBD and (c) ^{1}H NMR spectrum of PSSHD

3.3.2 ^{13}C NMR analysis.

assigned to CH_2 protons of sorbitol [27]. The multiplet peak appeared at 2.7 ppm was attributed to the protons of diacid. The multiplet observed at 1.4 to 1.2 ppm was due to the protons of CH_2 from diols [35-37].

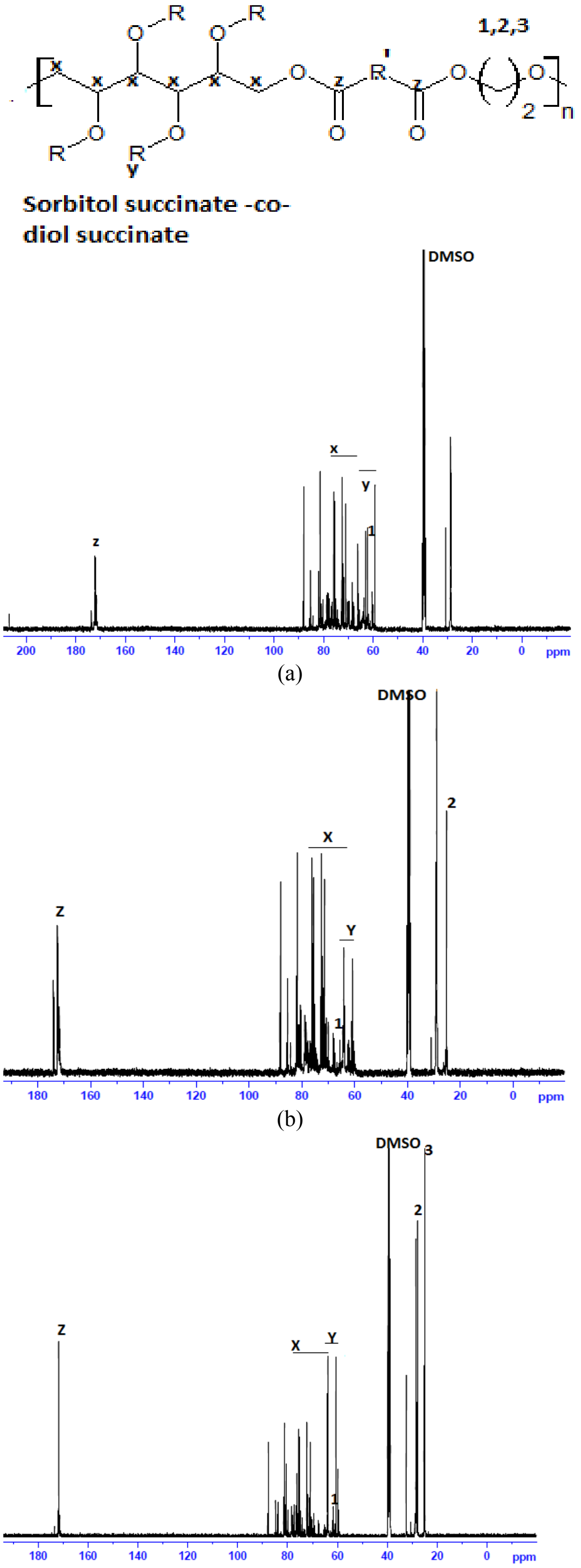
3.3.2 ^{13}C NMR Analysis

The ^{13}C NMR spectra recorded for all the synthesised copolyesters and presented in the Figs. 4a to 2c. The carbon atoms of sorbitol orbitol shows resonance peaks at 65.8, 66.1, 72.9, 74.3, 74.5 and 76.1 ppm in figure corresponds to 1-6 carbon atoms [38], and first two peaks corresponds to the terminal carbon .The peaks in the region 60-65 ppm arose from carbons directly bonded to oxygen [39], either it may be a (CO-OCH_2) from succinic acid or it may be from (CH_2-O-CH_2)from diols. The peak around 173 ppm is due to COO- carbon of succinic acid. The peak at 32 ppm present in all the spectra is due to the central methylene carbon of siccinic acid. The methylene peaks at 63.9 and 61.9 ppm were attributed to ethylene glycol in PSSEG spectra [40]. Similarly the peak at 63.9 ppm and 25.1 ppm were attributed to α and β methylene carbon of butane diol [41] which is shown in PSSBD spectra and the peak at 63.9, 29 and 25.1 ppm were attributed to α, β, γ methylene carbon of hexane diol which is shown in PSSHD spectra.

3.4 Thermal Analysis

3.4.1 Differential Scanning Calorimetry Analysis

DSC thermograms were obtained for all the synthesized polymers. The Tg ,Tm, ΔH_m and ΔS values are reported in Table 2. The representative of DSC Curves of the polymers are shown in Fig. 5. All the three polymers are semi crystalline polymer as it has both T_g and T_m value. Glass transistion temperature usually reflects the ability of polymer chains to move freely and chain movement is affected by chain length ,chemical crosslinking and hydrogen bonding . For the synthesized polymers, the T_g value decreases as the chain length of diol in polymer increases, which reveals that chain movement decreases with the length of the diol. Since T_g value is high for PSSEG polymer,



(a)

(b)

(c)

Fig. 4 **^{13}C NMR spectra for (a) PSSEG, (b) PSSBD and (c) PSSHD polymers.**

it is confirm that this polymer have more cross linkage than other two polymers ,but we cannot say that other two polymers have less cross linkage because decrease in T_g may be due to the unreacted sorbitol (hydroxyl group) which increase the free volume of the polymers [42].

Melting temperature tell us about the molecular weight and is mainly related to the degree of hydrogen bonding[30] between the chains of the polymer which ranges from 405.5-417.3 °C for the synthesized polymers, as molecular weight of the polymer increases , melting temperature increases which in turn increase the T_g value. Glass transistion temperature and Melting temperature behaves in the same way which reveals that PSSEG polymers have better crosslinking and hydrogen bonding when compare to the other two polymers (PSSBD, PSSHD). ΔH_m is an important parameter whose magnitude is directly proportional to the overall level of crystallinity *Xc* possessed by the polymer [30] and ΔS value gives the randomness of the polymers. Both the values are high for the polymer PSSBD when compared to other two polymers reveals that PSSBD are slightly crystalline in nature.

3.4.2 Thermogravimteric Analysis (TGA)

TGA and dTGA curves for all the three polymers were obtained for all the synthesized polymers are shown in Fig. 6. The thermal stability is characterized by the onset, derivative peak temperature (T^d_{max}) and the temperatures at 25% and 50% and 95% weight loss, which are referred as T_{onset}, $T_{25\%}$ and $T_{50\%}$, $T_{75\%}$ and residual mass at 599.5 °C, respectively, as tabulated in Table 3

The TGA curves show a single degradation step for all the polymers samples. For the entire samples tested, thermal decomposition is completed at a temperature range of 398.5 to 403.7 °C. No further weight loss was observed after 599 °C. The temperature range of 50 °C to 200 °C corresponds to the gradual weight loss due to evaporation of moisture. The decomposition of polymer starts at 300 °C and reaches nearly 100% at 599 °C. It is a common practice to consider 50% weight loss as an indicator for structural destabilisation [43]. From the table, it is observed that PSSBD polymer have higher stability towards thermal degradation when compared with other two polymers PSSBD and PSSEG.

3.5 Mechanical Properties

Tensile tests of the polymers exhibited characteristics similar to that of elastomers and stiff thermosets. The variation of the tensile stress with strain for the polymers is shown in Fig. 7.

The average Young's modulus, tensile strength, Cross link density and percentage elongation at break were reported in Table 4.

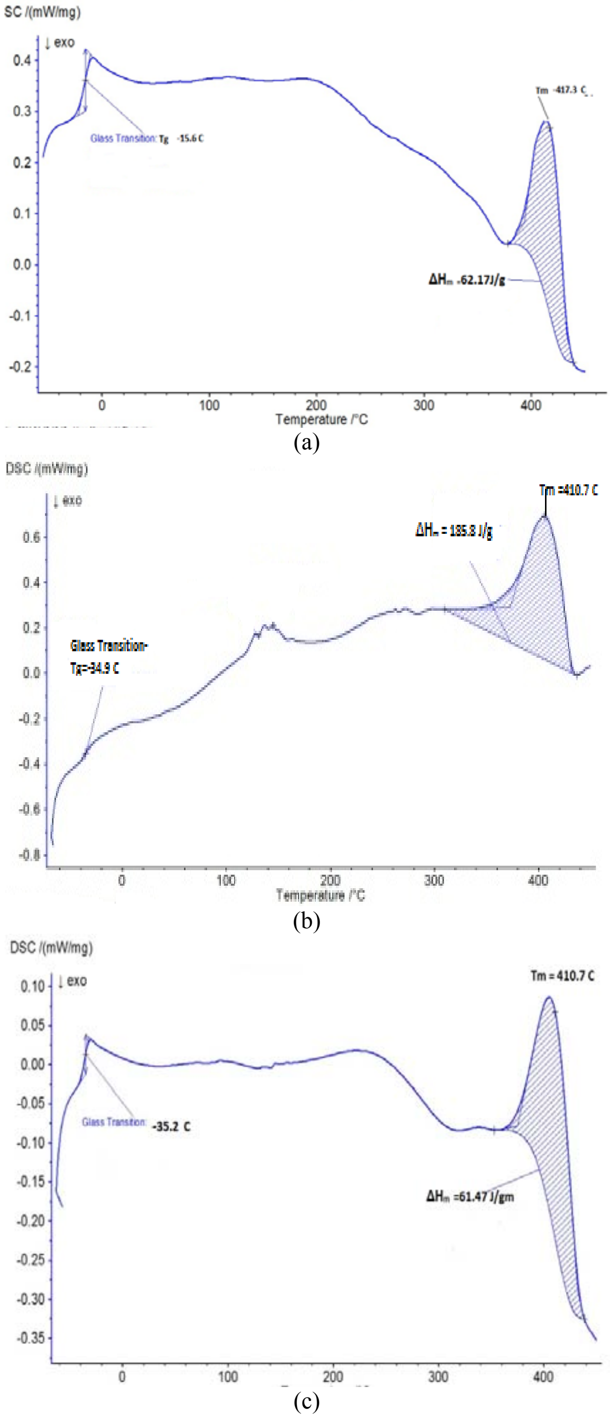
The Young's modulus, tensile stress and cross link density decreases, but percentage elongation at break increases with increase in chain length of diols, which confirm that PSSHD is a soft polymer have less cross linkage when compared with PSSEG and PSSBD.

Table 2 T_g, T_m, ΔS values of Copolyesters.

S.No	Polymer	T_g (°C)	T_m (°C)	ΔH_m (J/gm)	ΔS (J/gm/°C)
1	PSSEG	-15.6	417.3	62.17	0.15
2	PSSBD	-34.9	410.7	185.8	0.46
3	PSSHD	-35.2	405.5	61.47	0.15

Table 3 Decomposition percentage at different temperature.

S.No	Polymer	T_d under nitrogen atmosphere (°C)					Residual sample at 599.5 °C (%)
		T_{onset} (°C)	$T_{25\%}$ (°C)	$T_{50\%}$ (°C)	$T_{75\%}$ (°C)	T_{max} (°C)	
1	PSSEG	33.1	344.1	386.1	405.1	401.3	5.51
2	PSSBD	33.1	343.0	387.0	405.1	403.7	4.85
3	PSSHD	33.1	351.1	386.1	405.1	398.5	1.29

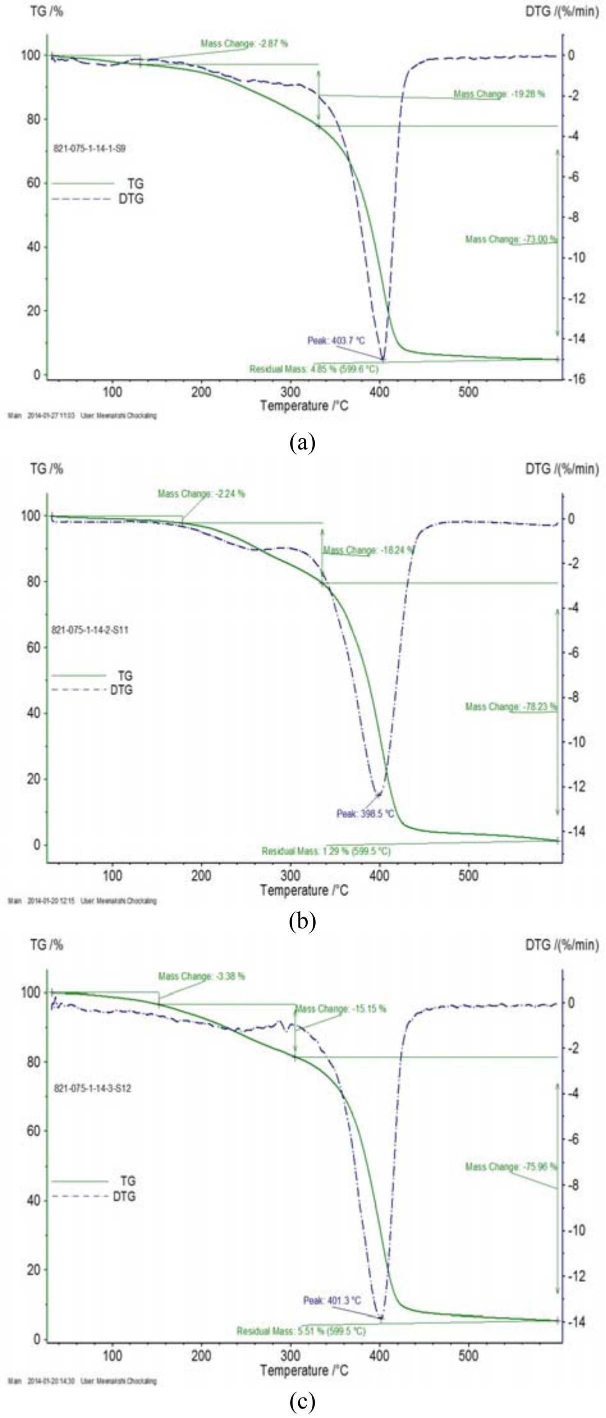


(a)

(b)

(c)

Fig. 5 DSC Thermograms for (a) PSSEG, (b) PSSBD and (c) PSSHD polymers.



(a)

(b)

(c)

Fig. 6 TGA and dTGA Curves for (a) PSSEG, (b) PSSBD and (c) PSSHD.

Table 4 Tensile strength, Young's Modulus, Elongation at break values.

S.No	Polymer	Tensile Stress (Mpa)	Young's Modulus (MPa)	Elongation at break %	Cross link density n*10^3 (mol/m^3)
1	PSSEG	10.61	554.8	18.51	74.6
2	PSSBD	7.86	320.8	23.46	43.2
3	PSSHD	0.014	20.2	38.75	2.7

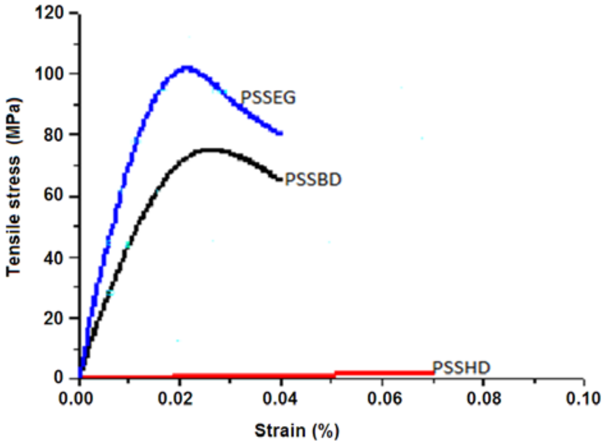


Fig. 7 Tensile stress Versus strain curves for all the three polymers PSSEG, PSSBD & PSSHD.

Other two polymers PSSBD, PSSEG polymers was observed to be the stiffest material with the Young's modulus of 554.8 and 320.8 MPa. The Tensile strength ,Young's modulus of the polymer PSSEG was comparable to that of the vertebral end plates (500 Mpa) [27]. Similarly the mechanical property of the polymers were similar to elastin from bovine ligament with tensile stress values of 1-10 MPa [44]. Thus these polymers are therefore expected to be useful for soft tissue engineering applications. Nevertheless these polymers, after appropriate surface modifications, could be suitable for drug delivery.

4. Conclusions

A new series of sorbitol based polyester elastomers have been synthesised by a simple catalyst free melt polycondensation method using sorbitol, succinic acid and various diols. These polymers are synthetic in nature but have the advantage of being composed of structural units endogenous to the human metabolism. The synthesized polyesters are characterised by spectral and thermal analysis. The degradation temperature and cystallinity for PSSBD polymer is higher than other two polymers PSSEG, PSSHD. When the mechanical property of the synthesized polymer was compared, the polymer PSSEG and PSSBD behaves like thermoplastic whereas PSSHD behaves like a elastomer. Thus it is noticed that the choice of monomers can largely influence the physical and mechanical property of the polymers so as to suit them for the requirements of various biomedical applications. We believe that this new series of polymeric elastomers will significantly improve the ease of fabrication and performance of biocompatible elastomers in tissue engineering.

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