Research Paper

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Synthesis and Characterisation of Novel Citric Acid Based Polyester Elastomers From Sunflower Oil

Chemistry

KEYWORDS : sunflower oil; epoxidation; polyols; citric acid; 1,6-hexanediol; 1, 3 - propanediol; biopolyester; soft tissue engineering

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ABSTRACT

Novel Biodegradable Polyesters are emerging and promising biomaterials for tissue scaffolding, drug delivery, biomedical and implant coatings. In this work, polyesters were obtained by thermal poly condensation technique on the effect of sunflower oil-based polyols with non-toxic monomers such as citric acid, 1,6-hexanediol, 1,3-propanediol without addition of catalyst. The prepared epoxy resin, polyol were characterized using FT-IR and 1H-NMR. Newly synthesized co-polyesters were characterized by FT-IR, swelling and solubility studies, TG-DTA, SEM analysis and mechanical analysis. These polyesters exhibit excellent properties that can be tuned by the choice of monomers.

Introduction

Biodegradable polymers have made a considerable impact in various fields of biomedical engineering including tissue engineering and drug delivery, where cell-seeded constructs are designed to replace damaged or diseased tissues[1,2]. Citric acid derived biodegradable elastomers have been shown to offer a wide range of controllable mechanical and degradation profiles along with surface affinities towards many cell types[3,4]. In this study, the sunflower oil based polyesters have the advantage of mimicking many features of extracellular matrix and have the potential to direct the migration, growth and organization of cells during tissue scaffolds, wound healing and stabilization of transported cells[5].This work refers initially to the polymerization of sunflower oil via peroxide linkages during the use of this polymeric peroxide in the polymerization of ethylene glycol to obtain sunflower oil-based polyols refers to conversion of double bonds to hydroxyl groups [6]. Herein we report the synthesis and studies of polyesters:Poly(1,6-hexanediol-co-polyolcitrate)(SHC) and Poly(1,3-propanediol-co-polyol citrate)(SPC).

Materials and methods

Citric acid (100%), H_2O_2 (99.9%), glacial acetic acid(100%) were purchased from Sigma Aldrich chemical Co. and used as such. 1,6-hexanediol and 1,3-propanediol (100%) monomers were supplied by Sigma Aldrich Co. and used as such.

Formation of epoxidised sunflower oil

Sunflower oil was epoxidised using glacial acetic acid with H_2O_2 (50%) were placed in a 250 ml round bottomed flask and the mixture was heated upto 70˚C- 80˚C for 10h. In order to remove excess H_2O_2, warm water was added to the mixture and the organic phase of the mixture was separated using separating funnel and were collected in a beaker. Thus obtained epoxidised sunflower oil were treated with ethylene glycol in presence of p-toluenesulphonic acid at 250˚ C to produce polyols.

Synthesis of polyesters

Synthesis of aliphatic polyesters was carried out by two stage melt poly condensation technique. At first stage a prepolymer was prepared by carrying out equimolar amount of diol and acids were placed in a 250 ml round bottomed flask and the mixture was heated upto 140˚C -145˚C for 30 minutes under a constant stream of nitrogen. At second stage the resultant pre-polymer was post - polymerized by cross-linking with polyols at different molar ratios , films were cast into glass plate and placed in an air oven maintained at 80˚C for 24 h, polyesters were obtained.

Polymer characterization

Fourier transform infrared (FTIR) spectra of polymers were obtained using THERMO NICOLET, AVATAR 370 FTIR SPECTROMETER with KBR crystal in the range of 4000 - 400 cm^{-1} at 27˚C. The ^{1}H-NMR spectra for epoxy resin, polyols and pre-polymers were dissolved in DMSO and recorded using BRUKER AVANCE III, 400 MHz FT NMR SPECTROPHOTOMETER. The chemical shift in ppm for ^{1}H NMR Spectra were obtained relative to TMS as internal reference. TG/DTA thermo grams of the post-polymers were obtained at a scanning speed of 10˚C min^{-1} in the range of 40˚C -700˚ C under the flow of nitrogen gas using PERKIN ELMER, DIAMOND TG/DTA. The SEM analysis of the post polymers were obtained using JOEL M ODEL JSM 6390 LV at 5 × to 300,000 × SEI magnification. The mechanical property of polyester films were measured using the UTM equipped with 500N load cell. The dog bone shaped polymer film strips were cut according to ASTM standard (45 x 5 x 2mm, length x width x thickness) and pulled at a strained rate of 10 mm min^{-1}. Values obtained were used to construct stress strain curve. Young's modulus were calculated from the initial slope of the curve.

Swelling and Solubility measurements

Swelling property

The % swelling and the sol content of the polyester was measured in DMSO. Cylindrical disc of about 7cm were cut using cork borer from cross linked polymer film. The discs were preweighed to know the initial mass (W_0) and suspended into 15 ml of DMSO at room temperature (27˚C) .The films were removed from DMSO after one week blotted dry with filter paper and weighed (W_S). The dried samples were weighed to find the dry mass (W_D). The swelling percentage was calculated using the formula :

$$\text{Swelling (\%)} = [(W_S - W_0) / W_0] \times 100$$

The sol-gel fraction was calculated using the formula

$$\text{Sol\%} = [(W_0 - W_D) / W_D] \times 100$$

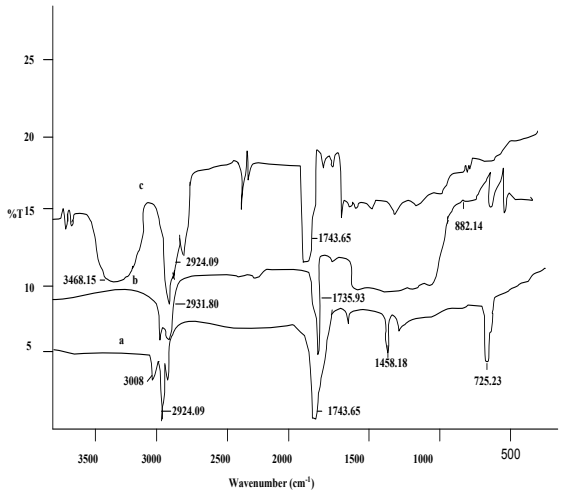

Fig 1. FT-IR Spectra of sunflower oil (a), epoxidised Sunflower oil (b) and polyol (c)

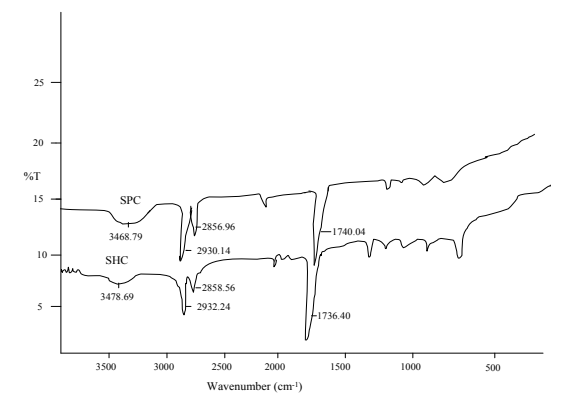

Fig 2. FT-IR Spectra of SHC and SPC

Results and discussions

Polymer characterisation

FT-IR Analysis

The FT-IR Spectra of sunflower oil, epoxidised sunflower oil and the prepared polyol are shown in fig.1. As can be noted, the signature of the double bonds, C=C-H stretch at 3008 cm^{-1} and C=C stretch at 1658 cm^{-1}(that were present in the sunflower oil spectra) completely disappear in the epoxidised oil , where spectra for the range 1500-1700 cm^{-1} are shown separately. The spectra of epoxidised oil clearly shows the epoxy groups C-O band at 882cm^{-1}.The other peaks are 725(methylene in-phase rocking), 1064(ether, antisymmetric stretch), 1165, 1242(ester, antisymmetric stretch), 1458(methyl antisymmetric deformation) and 1735(esters, aliphatic C=O stretch)cm^{-1}.The epoxy group (C-O band at 882cm^{-1}) disappear in the spectra of polyol, confirming the oxirane opening. Most importantly, the spectra of polyol shows broad hydroxyl stretching peak at around 3468cm^{-1}, confirming the incorporation of the hydroxyl groups. The FTIR spectra of all the synthesized prepolymers and polyesters show a strong absorption band at around 1736cm^{-1} (esters, aliphatic C=O stretch) thus confirmed the formation of polyesters[7,8,9] are shown in fig 2. The bands shows at around 1176 cm^{-1}, 1179cm^{-1}, 1377cm^{-1} were assigned to C-O stretching of ester group[10,11] .The band shows at 1462 cm^{-1} due to aliphatic C-C stretching. The band shows at around 2858cm^{-1} and 2930cm^{-1} were assigned to methylene (-CH_2-) groups for the diacids/diols and aliphatic C-H stretching of the polyesters[7].The broad stretch at 3468 and 3478cm^{-1} was attributed to the stretching vibrations of the hydrogen bonded carboxyl and hydroxyl groups [7].

^{1}H NMR Analysis

The ^{1}H NMR spectra recorded from sunflower oil, epoxidised sunflower oil and polyol are shown in figure 3.The spectra shows the double bond hydrogen oliphinic proton(-H-C=C-H-) between 5-5.5 ppm. This peak almost disappeared for epoxidised sunflower oil due to the conversion of double bonds from sunflower oil[12,13].The peak at 5-5.5 ppm is observed to almost disappear in the spectra of polyol and it shows appearance of new peaks between 3.2- 4.3 ppm correspond to the methylinic proton (-H-C-OH-) and the proton associated with the -OH groups [14,15].

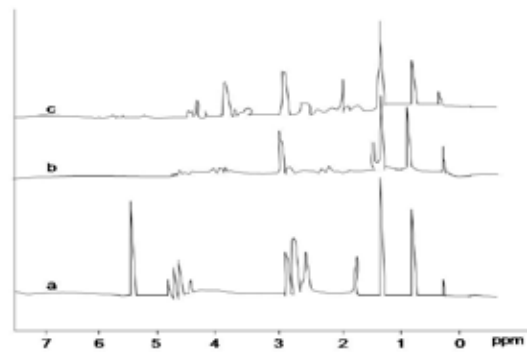

Fig 3. ^{1}H-NMR Spectra of sunflower oil(a), epoxidised Sunflower oil (b) and polyol (c)

Thermal Analysis

The thermal studies show that the synthesized polymers were thermally stable. Fig 4. reveals the TG/DTA thermogram of polymer SHC and SPC .In the TGA trace of polyesters SHC and SPC, the first mass loss corresponds to dehydration and is complete around 250˚C and the second stage decomposition takes place between 250˚C and 500˚C [16,17].

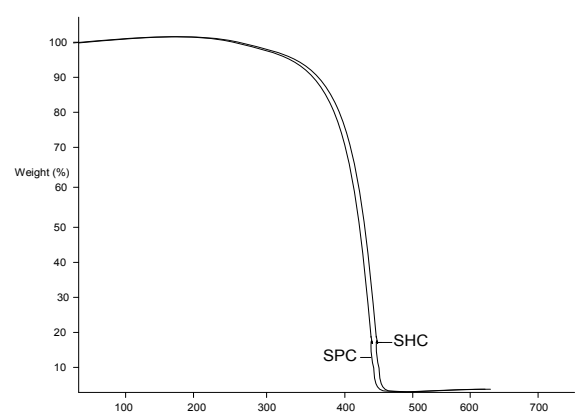

Fig .4. TGA thermogram of SHC and SPC

SEM Analysis

Scanning electron micrograph of SHC and SPC at x3000 magnification represented in figures 5 and 6 respectively. Surface sem images of the polyesters are evenly distributed which can be attributed to the well adhesion of the cells on the surface. After two months of soil burial, the percentage weight loss of SHC and SPC were 48.5% and 58%.This was due to diols with decreasing number of methylene units, faster the degradation rate. Thus confirms that the polyesters SPC degraded faster than SHC [18].

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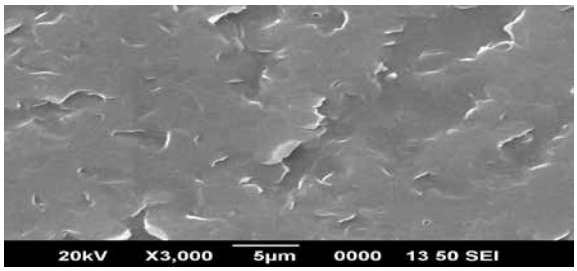

Fig 5: Scanning electron micrograph of SHC before soil burial

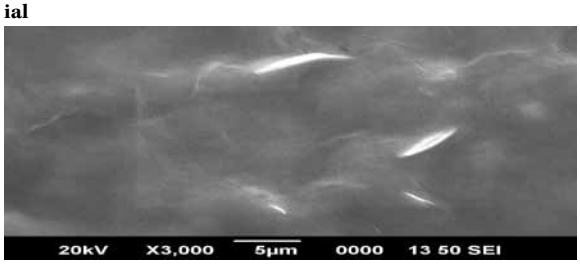

Fig 6 : Scanning electron micrograph of SPC before soil burial

Swelling and solubility behaviour

Equilibrium swelling percentage of the polymers SHC and SPC are 37% and 54.8%. The sol content for polymer SHC and SPC were 2.7% and 6.8% respectively. The low sol content indicates the successful incorporation of crosslink network during post polymerization. The pre-polymers are soluble in DMSO, the post polymers are not, since inter- molecular forces and strong hydrogen bonding exist in the post polymers. This was in agreement with the presence of hydrogen bonded hydroxyl and carboxylic groups as evidenced by FTIR analysis[16].The higher swelling of polymer SPC was due to the weakening of intermolecular forces and breaking of hydrogen bonds. The polyesters are insoluble in water, hexane, diethyl ether and ethanol.

MechanicalAnalysis

The mechanical properties of SHC and SPC are evaluated in table 1. The mechanical properties of the polymer SHC and SPC are different because of difference in diol monomer used.

Table 1. Mechanical properties of SHC and SPC (Ratio: polyol : prepolymer)

Name of the monomer Used	Ratio	Tensile Strength (MPa)	Elongation at break(%)	Young's modulus(MPa)
SHC	1:1	1.631	40	4.077
	1:2	1.715	37.7	4.549
	1:2.5	1.775	33.3	5.33
SPC	1:1	1.562	44.4	3.518
	1:2	1.638	38.4	4.265
	1:2.5	1.676	36.6	4.579

Conclusion

Citric acid-based biodegradable co-polyesters namely Poly(1,6-hexanediol-co-polyol-citrate) and Poly(1,3-propanediol-co-polyol-citrate) were synthesized by thermal condensation technique without using any catalyst or solvents. The thermal studies revealed that the elastomers were thermally stable .The thermal and mechanical properties of the polyesters showed that SHC had better cross-linking than that of SPC. The sem images shows that the samples can be used in tissue engineering due to their cell adhesion. The difference in swelling characteristics indicates that the choice of monomers influence the physical properties of the elastomers so it can potentially meet the requirements of various biomedical applications.

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