Synthesis and Characterization of Biodegradable Polyesters Based on Sesame Oil for Biomedical Field

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Abstract: The main objective of this study is to synthesize and characterization of biodegradable polyester elastomers from sesame oil. In this work, co polyesters were obtained by thermal poly condensation technique on the effect of sesame oil-based polyols with nontoxic monomers such as citric acid, 1,2-ethanediol, 1,6-hexanediol without addition of catalyst or solvents. The prepared epoxy resin and polyol were characterized using FT-IR and ¹H-NMR. Newly synthesized co polyesters were characterized by FT-IR, ¹H- NMR, Solubility studies, TG-DTA, SEM analysis and mechanical analysis. These polyesters exhibit wide range of mechanical and degradation profiles along with surface affinities towards many cell types that can be tuned by the choice of monomers.

Keywords: sesame oil; epoxidation; polyol; biopolyester; tissue engineering

1. Introduction

In recent years, biodegradable polymers have attracted much intention as green materials in biomedical engineering, soft tissue engineering and drug delivery, where cell-seeded constructs are designed to replace damaged or diseased tissues [1, 2, 3]. Vegetable oils are triglycerides of fatty acids as raw materials for the preparation of original polymeric materials with the objectives to replace petrochemical based polymers and also to develop materials for certain applications [4, 5]. Citric acid based biodegradable polyesters from vegetable oils have high strength, stiffness, environmental resistance and long life and it is the main technological advantages of these oils [6]. This work refers initially biopolyesters have the advantage of mimicking many features of extracellular matrix and have the to the polymerization of sesame oil via peroxide linkages during the use of this polymeric peroxide in the polymerization of ethylene glycol to obtain sesame oil-based polyols refers to conversion of double bonds to hydroxyl groups [7]. Herein we report the synthesis and studies of polyesters: Poly (1,6hexanediol-co-polyolcitrate) (SPHC) and Poly (1,2ethanediol-co-polyol-citrate) (SPEC).

2. Experimental

2.1 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 1,2-ethanediol (100%) monomers were supplied by Sigma Aldrich Co. and used as such.

2.2 Formation of Epoxidised Sesame Oil

Sesame 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 sesame oil were treated with ethylene glycol in presence of p-toluenesulphonic acid at 250° C to produce polyols.



Polyol Scheme 1: Synthesis of Polyol prepared from Sesame oil

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2.3 Synthesis of Polyesters

Synthesis of aliphatic polyesters was carried out by two stage thermal poly condensation technique. At first stage a prepolymer was prepared by carrying out equimolar amount of diol and acids were placed in a 250ml 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 crosslinking 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.

2.4 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 ¹H-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 ¹H 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 MODEL JSM 6390 LV at 5 \times to 300, 000 \times 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.

2.5 Soil Burial Method

Garden soil (1200 g) was taken in different pots. A weighed amount (0.5 g) of each of the samples that is, SPHC and SPEC were placed in the beaker such that the soil covered the polymer from all the sides. The pots were covered with the aluminum foil and kept at room temperature. The weight of all the samples SPHC and SPEC were taken at regular interval of time (10 days) to check for any weight loss. Percent weight loss as a function of number of days was determined as total percent weight loss after 2 months was calculated as:

Initial wt. at the beginning _

Wt. Loss = Final wt. after ten days X 100 %

Initial wt. at the beginning

% Wt.Loss Initial wt. before ten days _

(After every 10 days) = <u>Final wt. after ten days X 100</u> Initial wt. before ten days

2.6 Solubility Studies

The solubility content of the polyesters was measured in various organic solvents. Cylindrical disc of about 7cm were cut using cork borer from cross linked polymer film. The discs were pre-weighed to know the initial mass (W_o) and suspended into 15 ml of solvent at room temperature (27°C). The films were removed from the solvent after one week blotted dry with filter paper and weighed (Ws). The dried samples were weighed to find the dry mass (W_D). The sol-gel fraction was calculated using the formula: Sol% = $[(W_0-W_D)/W_D] \times 100$



Figure 1: FTIR spectra of Sesame oil (a) Sesame oil (b) and polyol (c)



Figure 2: FTIR spectra of SPHC and SPEC epoxidised

3. Results and Discussions

3.1 FT-IR Analysis

The FT-IR Spectra of sesame oil, epoxidised sesame 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 1653 cm⁻¹(that were present in the sesame oil spectra) completely disappear in the epoxidised oil .The spectra of epoxidised oil clearly shows the epoxy groups C-O band at 883cm⁻¹.The other peaks are 726(methylene in-phase rocking),1171, 1242(ester ,antisymmetric stretch),1375(methyl symmetric

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deformation), 1458(methyl antisymmetric deformation) and 1739(esters, aliphatic C=O stretch)cm⁻¹.The epoxy group (C-O band at 883cm⁻¹) disappear in the spectra of polyol, confirming the oxirane opening[8]. Most importantly, the spectra of polyol shows broad hydroxyl stretching peak at around 3443cm⁻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[9,10]are shown in fig2. The bands shows at around 1185 cm⁻¹, 1172cm⁻¹ were assigned to C-O stretching of ester group. The band shows at 1462cm⁻¹ due to aliphatic C-C stretching. The band shows at 2859cm⁻¹, 2929cm⁻¹,2855 cm⁻¹ and 2927 cm⁻¹ were assigned to methylene(-CH2-) groups for the diacids/diols and aliphatic C-H stretching of the polyesters. The broad stretch at 3458 and 3468cm⁻¹ was attributed to the stretching vibrations of the hydrogen bonded carboxyl and hydroxyl groups [11, 12, 13].

3.2 ¹H NMR Analysis



The ¹H NMR spectra recorded from sesame oil, epoxidised sesame oil and polyol are shown in figure 3.The spectra shows the double bond hydrogen oliphinic proton(-H-C=C-H-) between 5-5.4 ppm. This peak almost disappeared for epoxidised sesame oil due to the conversion of double bonds from sesame oil [14]. The peak at 5-5.4 ppm is observed to almost disappear in the spectra of polyol and it shows appearance of new peaks between 3.4- 4.3 ppm correspond to the methylinic proton (-H-C-OH) and the proton associated with -OH groups[15].

3.3 Thermal Analysis

The thermal studies show that the synthesized polymers were thermally stable. Fig 4. reveals the TG/DTA thermogram of polymer SPHC and SPEC. In the TGA trace of polyesters SPHC and SPEC, 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].



Figure 4: TG/DTA thermogram of SPHC and SPEC

3.4 SEM Analysis

Scanning electron micrograph of SPHC and SPEC at x3000 magnification represented in figures 5 and 6 respectively. Surface sem images of the polyesters are uniformly distributed which can be attributed to the well adhesion of the cells on the surface and so it meet the varying requirements of biomedical field [18].



20kV X3,000 5µm 0000 12 54 SEI Figure 5: SEM image of SPHC before soil burial



20kV X3,000 5μm 0000 12 54 SEI Figure 6: SEM image of SPEC before soil burial

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3.5 Solubility Studies

The copolyesters SPHC and SPEC are soluble in chloroform, dichloromethane and carbon tetrachloride. The prepared copolyesters are insoluble in water, hexane, ethanol and diethyl ether. The low sol content indicates the successful incorporation of crosslink network during post polymerization, since inter- molecular forces and strong hydrogen bonding exist in the post polymers as evidenced by FTIR analysis [10].

3.6 Soil Burial Method

Scanning electron micrograph of SPHC and SPEC at x3000 magnification represented in figures 7 and 8 respectively. After two months of soil burial, the sem images of the polyesters increases the gap and forming hallow cavities. The polyesters SPEC degraded faster than SPHC. This was due to diols with decreasing number of methylene units faster the degradation rate [19].



Figure 7: SEM image of SPHC after soil burial



Figure 8: SEM image of SPEC after soil burial

3.7 Mechanical Analysis

The mechanical properties of SPHC and SPEC are evaluated in table1. The mechanical properties of the polymer SPHC and SPEC are different because of difference in diol monomer used [12].

Name of the	Ratio	Tensile	Elongation	Young's
monomer Used		strength (MPa)	at break (%)	modulus(MPa)
	1:1	0.998	48.4	2.061
SPHC	1:2	1.150	46.6	2.467
	1:2.5	1.318	43.3	3.043
	1:1	0.945	54.8	1.724
	1:2	1.067	52.2	2.044
SPEC	1:2.5	1.189	50	2.378

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Lable 1: Mechanical	properties of SPHC and SPEC	(Ratio = polyol : prepolymer)

4. Conclusion

Citric acid-based biodegradable co-polyesters namely Poly(1,6-hexanediol-co-polyol-citrate) and Poly(1,2ethanediol-co-polyol-citrate) were synthesized by melt 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 SPHC had better cross-linking than that of SPEC. The sem images shows that the samples can be used in tissue engineering due to their cell adhesion. The two copolyesters were found to be freely chloroform, carbon tetrachloride soluble in and dichloromethane. The prepared copolyesters are insoluble in water, hexane, ethanol and diethyl ether. Thus it is indicated that the choice of monomers influence the physical properties of the elastomers so it can potentially meet the requirements of various biomedical applications.

References

- [1] Yang, J.; Webb, A.R.; Hageman, G Ameer, G.A. Novel citric acid-based biodegradable elastomers for tissue engineering. Advanced Materials. 2004, 16, 511–516.
- [2] Nijst, CL.; Bruggeman, JP.; Karp, JM.; et al. Synthesis and characterization of photocurable elastomers from poly(glycerol-cosebacate). Biomacromolecules. 2007, 8(10), 3067-73.
- [3] Sowbagyalakshmi Prabha, L.; Nanthini, R.; Krishnaveni, G . Synthesis and Characterisation of Novel biodegradable aliphatic copolyesterspolyethylene sebactate-co-propylene succinate) and

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poly(ethylene sebactate-co-propylene adipate). Journal of Chemical and Pharmaceutical Research. 2012, 4(5), 2442-2457.

- [4] Meier, MAR.; Metzger, JO.; Schubert, US. Plant oil renewable resources as green alternatives in polymer science. Chemical Society Reviews. 2007, 36,1788– 802.
- [5] Patricia B. Malafaya.; Gabriela A. Silva.; Rui L. Reis . Natural- origin polymers as carriers and scaffolds for biomolecules and cell delivery in tissue engineering applications. Advanced Drug Delivery Reviews. 2007,59,207-233.
- [6] Khot, S.N.; Lascala, J.J.; Can, E.; Morye, S.S.; Williams, G.I.; Palmese, G.R. Development and application of triglyceride-based polymers and composites. Journal of Appllied Polymer Science. 2001,82(3),703-723.
- [7] Gryglewicz , S.; Piechocki, W.; Gryglewicz, G. Preparation of polyol esters based on vegetable and animal fats. Bioresource Technology. 2003, 87, 35–39.
- [8] Petrovic, Z.S.; Zlatanic, A.; Snezana, C.L.; Fiser, S. Epoxidation of soybean oil in toluene with peroxoacetic and peroxoformic acids-kinetics and side reactions. European Journal of Lipid science and Technology. 2002, 104, 293-299.
- [9] Lee, L Y.; Wu, SC.; Fu, SS.; Zeng, S.Y.; Leong, W.S.; Tan, L.P. Biodegradable elastomer for soft tissue engineering. European Polymer Journal. 2009, 45(11), 3249-3256.
- [10] Djordjevic, I.; Choudhury, N.R.; Dutta, N.K.; Kumar, S . Synthesis and Characterisation of novel citric acidbased polyester elastomers. Polymer .2009, 50, 1682-1691.
- [11] Song, D.K.; Sung, Y.K .Synthesis and Characterisation of biodegradable poly(1,4-butanediol succinate). Journal of Polymer Science. 1995, 56, 1381-1395.
- [12] Pasupuleti, S.; Avadanam, A.; Madras, G. Synthesis, characterization and degradation of biodegradable poly(mannitol citric dicarboxylate) copolyesters. Polymer Engineering and Science. 2011, 51(10), 2035-2043.
- [13] Xie, D.; Chen, D.; Jiang, B.; Yang, C. Synthesis of novel compatibilizers and their application in PP/nylon-66 blends. I. Synthesis and Characterisation. Polymer. 2009, 41(10), 3599-3607.
- [14] Campanella, A.; Baltanas, M.A.; Capel-Sanchez, M.C.; Campos-Martin, J.M.; Fierro, J.L. Soybean oil epoxidation with hydrogen peroxide using an amorphous Ti/SiO₂ catalyst. Green Chemistry.2004,6 ,330-334.
- [15] Guo, A.; Cho, Y.; Petrovic, Z.S. Structure and properties of halogenated and nonhalogenated Soybased polyols. Journal of Polymer Science. Part A. Polymer Chemistry.2000, 38, 3900-3910.
- [16] Birten Cakmakli.; Baki Hazer.; Ishak Ozel Tekin.; Sait Kizgut.; Murat Koksal.; Yusuf Menceloglu. Synthesis and Characterisation of Polymeric Linseed Oil Grafted Methyl Methacrylate or Styrene. Macromolecular Bioscience. 2004, 4, 649-655.
- [17] D'Antone, S.; Bignotti, F.; Sartore, L.; D'Amore, A.; Spagnoli, G.; Penco, M. Thermogravimetric investigation of two classes of block copolymers based on poly(lactic-glycolic acid) and poly(ε-caprolactone)

- [18] Russell, S. D.; Daghlian, C. P. Scanning electron microscopic observations on deembedded biological tissue sections: Comparison of different fixatives and embedding materials. Journal of Electron Microscopy Technique. 1985, 2 (5), 489-495.
- [19] Ding, T.; Liu, Q.Y.; Shi, R.; Tian, M.; Yang, J.; Zhang, L.Q. Synthesis, characterization and in vitro degradation study of a novel and rapidly degradable elastomer. Polymer Degradation and Stability. 2006, 91, 733–739.