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Development of Novel Citric Acid Based Biodegradable Polyesters from Sesame Oil

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Abstract

Polyester elastomers obtained from natural oils are biopolymers in the sense that they are generated from renewable natural sources. In this work, polyesters were obtained by thermal poly condensation technique on the effect of sesame oil-based polyols with non-toxic monomers such as citric acid, 1, 6-hexanediol, 1, 3-propanediol without addition of catalyst or solvents. The prepared epoxy resin, polyol were characterized using FT-IR and ^{1}H-NMR. Newly synthesized co-polyesters were characterized by FT-IR, ^{1}H-NMR, swelling and solubility studies, TG-DTA, SEM analysis and mechanical analysis. These polyesters have been shown to offer a wide range of controllable mechanical and degradation profiles along with surface affinities towards many cell types that can be tuned by the choice of polyol.

Key words: sesame oil; epoxidation; polyols; biopolyester; soft tissue engineering

1. Introduction

In recent years, biodegradable polymers play an important role in emerging technologies like biomedical engineering, tissue engineering and drug delivery, where cell-seeded constructs are designed to replace damaged or diseased tissues [1, 2]. Natural oils have attracted renewed attention as raw materials for the preparation of original polymeric materials with the objectives to replace petro-chemical based polymers and also to develop novel materials for specific applications [3]. Citric acid derived biodegradable polyesters from vegetable oils have high strength as well as stiffness, environmental resistance and long life and it is the main technological advantages of these oils[4].In this study, the sesame 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, 6].This work refers initially 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, 6-hexanediol-co polyolcitrate) (SPHC) and Poly(1, 3-propanediol-co-polyol citrate)(SPPC). These are the most important bio-based polyesters due to its favorable properties widely investigated as support material for tissue regeneration.

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, 3-propanediol (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.

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 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.

2.4. Polymer characterization

Fourier transform infrared (FTIR) spectra of polymers were obtained using THERMO NICOLET, AVATAR370 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.

2.5. Swelling and Solubility measurements

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 pre-weighed to know the initial mass (W_O) 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(Ws).The dried samples were weighed to find the dry mass(Wd).The swelling percentage was calculated using the formula:

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

The sol-gel fraction was calculated using the formula:

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

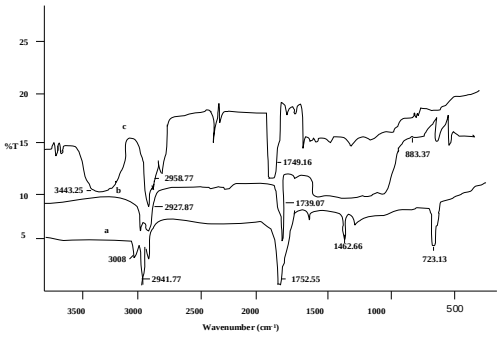

Fig 1. FTIR spectra of Sesame oil (a) epoxidised Sesame oil (b) and polyol (c)

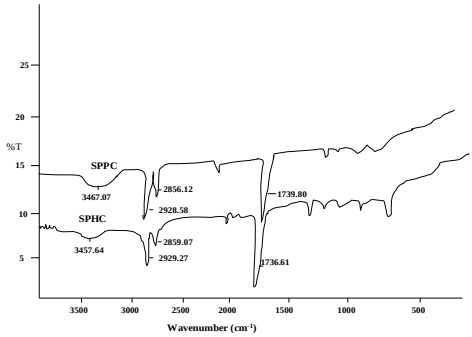

Fig 2. FTIR spectra of SPHC and SPPC

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 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. 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[8, 9, 10]are shown in fig2. The bands shows at around 1185 cm^{-1}, 1174cm^{-1} were assigned to C-O stretching of ester group.The band shows at 1462 cm^{-1} due to aliphatic C-C stretching. The band shows at around 2859cm^{-1} and 2929cm^{-1} were assigned to methylene (-CH_2-) groups for the diacids/diols and aliphatic C-H stretching of the polyesters. The broad stretch at 3458 and 3467cm^{-1} was attributed to the stretching vibrations of the hydrogen bonded carboxyl and hydroxyl groups [11, 12].

3.2. ^{1}H NMR Analysis

The ^{1}H 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. 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.

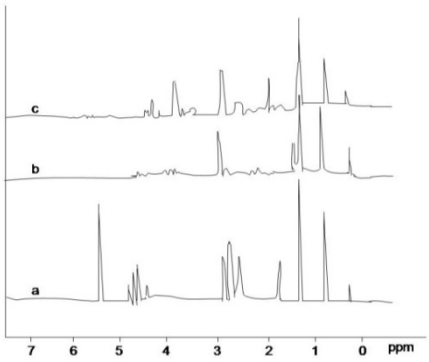

Fig 3.^{1}H-NMR Spectra of Sesame oil(a), epoxidised Sesame oil (b) and polyol (c)

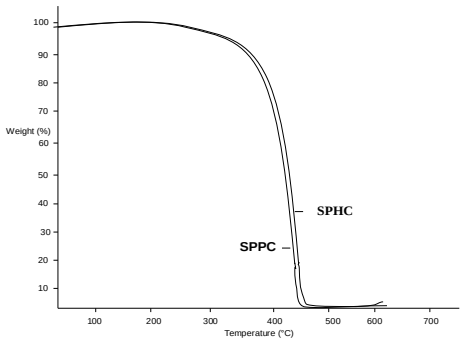

Fig.4. TG/DTA thermogram of SPHC and SPPC

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 SPPC.In the TGA trace of polyesters SPHC and SPPC, 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[13, 14].

3.4. SEM Analysis

Scanning electron micrograph of SPHC and SPPC 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[15, 16].

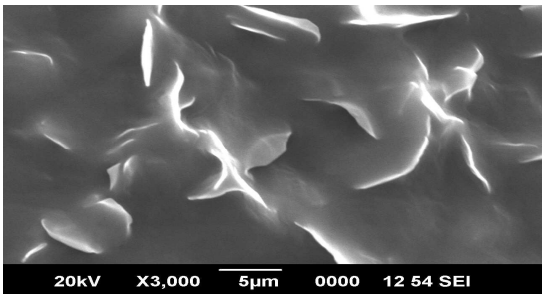

Fig 5: Scanning electron micrograph of SPHC before soil burial

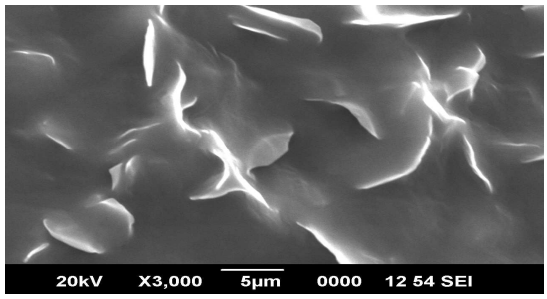

Fig 6 : Scanning electron micrograph of SPPC before soil burial

3.5. Swelling and solubility behaviour

Equilibrium swelling percentage of the polymers SPHC and SPPC were 75% and 90%. The sol content for polymer SPHC and SPPC were 5.2% and 9.8% 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[10].The higher swelling of polymer SPPC was due to the weakening of intermolecular forces and breaking of hydrogen bonds [12].

3.6. Mechanical Analysis

The mechanical properties of the post-polymers were evaluated. The tensile modulus of the polyesters SPHC and SPPC were 3.043, 2.668 MPa and elongation at break between 43.3% and 47.1% respectively. The mechanical properties of the polymer SPHC and SPPC are different because of difference in diol monomer used[12].

4. Conclusions

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 catalysts. 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 SPPC. The sem images shows that the samples can be used in tissue due to their cell adhesion. The difference in swelling characteristics indicates engineering that the choice of monomers influence the physical properties of the elastomers.

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