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SYNTHESIS AND CHARACTERISATION OF NOVEL CITRIC - ACID DERIVED POLYESTERS FROM LINSEED OIL

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ABSTRACT

Novel Biodegradable Polyester elastomers have become an integral part of various applications in drug delivery, biomedical, tissue scaffolding and implant coatings. In this work, polyesters were obtained by thermal poly condensation technique on the effect of linseed oil-based polyols with non-toxic monomers such as citric acid, 1,6-hexanediol, 1,2-ethanediol 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 studies, TG-DTA, SEM analysis and mechanical analysis. These polyester elastomers exhibit polymer properties that can be tuned by the choice of polyol.

Keywords: *Linseed Oil, Epoxidation, Polyols, Citric Acid, 1,6-Hexanediol, 1,2-Ethanediol Bioelastomer, Polyester, Soft Tissue Engineering*

INTRODUCTION

Vegetable oils are triglycerides of fatty acids, which have a number of excellent properties, so they could be utilized in producing valuable polymeric materials that can potentially meet the varying requirements for tissue scaffolds. In recent years, biodegradable polyester elastomers have attracted much attention as green materials in pharmaceutical, medical, biomedical engineering applications, drug delivery systems, artificial implants and soft tissue engineering (Prabha *et al.*, 2012). Polyesters of citric acid and diols are emerging and promising biomaterials for tissue scaffolds. In this study, the linseed 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 (Patricia *et al.*, 2007). This work refers initially to the polymerization of linseed oil via peroxide linkages during the use of this polymeric peroxide in the polymerization of ethylene glycol to obtain linseed oil-based polyols refers to conversion of double bonds to hydroxyl groups (Birten *et al.*, 2004). Herein we report the synthesis and studies of polyesters: Poly(1,6-hexanediol-co-polyol citrate) (PH) and Poly(1,2-ethanediol-co-polyol citrate) (PE).

MATERIALS AND METHODS

Citric acid (100%), H₂O₂ (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.

Formation of epoxidised Linseed oil

Linseed oil was epoxidised using glacial acetic acid with H₂O₂ (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 H₂O₂, 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 linseed 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

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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 ¹H-NMR spectra for epoxy resin, polyols and pre-polymers were dissolved in CDCl₃ 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 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 0.2mm, 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 pre-weighed to know the initial mass (W₀) 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

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

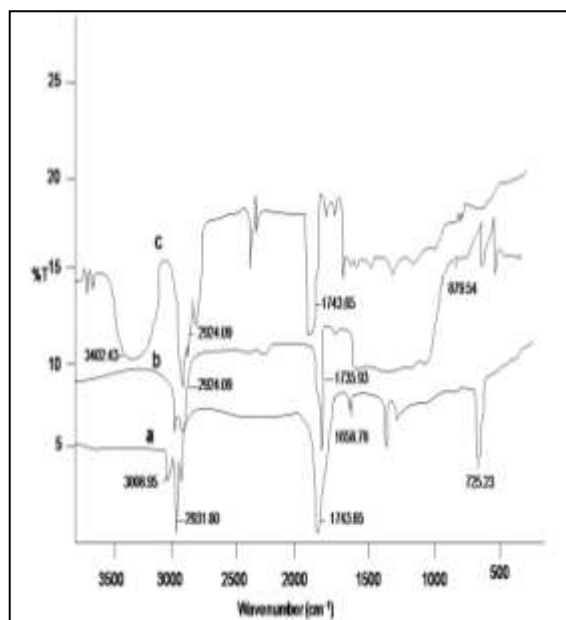


Figure 1: FT-IR Spectra of linseed oil (a), epoxidised linseed oil (b) and polyol (c)

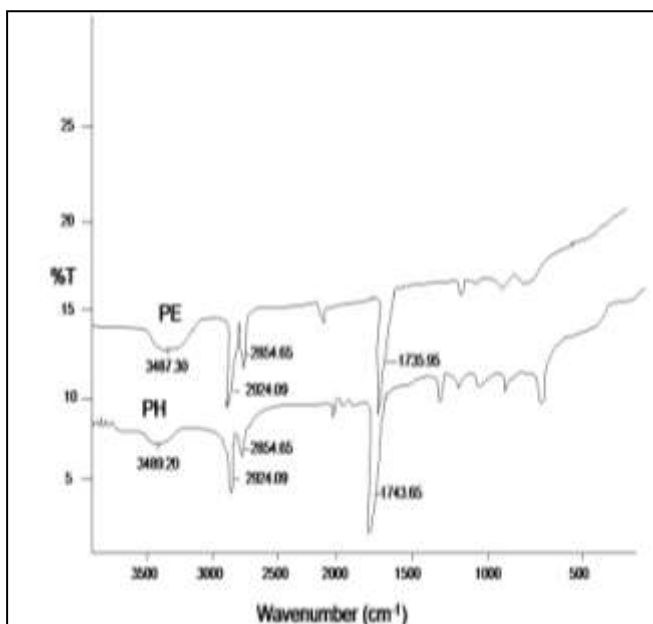


Figure 2: FT-IR Spectra of PH and PE

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RESULTS AND DISCUSSION

Polymer characterization

FT-IR Analysis

The FT-IR Spectra of linseed oil, epoxidised linseed oil and the prepared polyol are shown in Figure 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 linseed oil spectra) completely disappear in the epoxidised oil, where spectra for the range $1500\text{--}1700\text{ cm}^{-1}$ are shown separately. The spectra of epoxidised oil clearly shows the epoxy groups C-O band at 879 cm^{-1} . The other peaks are 725 (methylene in-phase rocking), 1064 (ether, antisymmetric stretch), 1172 , 1249 (ester, antisymmetric stretch), 1373 (methyl symmetric deformation), 1458 (methyl antisymmetric deformation) and 1735 (esters, aliphatic C=O stretch) cm^{-1} . The epoxy group (C-O band at 879 cm^{-1}) disappear in the spectra of polyol, confirming the oxirane opening. Most importantly, the spectra of polyol shows broad hydroxyl stretching peak at around 3402 cm^{-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 1735 cm^{-1} (esters, aliphatic C=O stretch) thus confirmed the formation of polyesters (Marie *et al.*, 2011), (Song *et al.*, 2003), (Pasupuleti *et al.*, 2011), (Lei *et al.*, 2007) are shown in Figure 2. The bands shows at around 1172 cm^{-1} , 1257 cm^{-1} , 1180 cm^{-1} , 1249 cm^{-1} were assigned to C-O stretching of ester group (Prabha *et al.*, 2012). The band shows at 1458 cm^{-1} due to aliphatic C-C stretching. The band shows at 2924 cm^{-1} and 2854 cm^{-1} were assigned to methylene ($-\text{CH}_2-$) groups for the diacids/diols and aliphatic C-H stretching of the polyesters (Marie *et al.*, 2011). The broad stretch at 3487 cm^{-1} was attributed to the stretching vibrations of the hydrogen bonded carboxyl and hydroxyl groups (Marie *et al.*, 2011) (Xie *et al.*, 2000) (Lee *et al.*, 2009).

^1H NMR Analysis

The ^1H NMR spectra recorded from linseed oil, epoxidised linseed oil and polyol are shown in Figure 3. The spectra shows the double bond hydrogen olefinic proton ($-\text{H}-\text{C}=\text{C}-\text{H}-$) between $5\text{--}5.5\text{ ppm}$. This peak almost disappeared for epoxidised linseed oil due to the conversion of double bonds from linseed oil (Maheswari *et al.*, 2005) (Petrovic *et al.*, 2002) (Campanella *et al.*, 2004). The peak at $5\text{--}5.5\text{ ppm}$ is observed to almost disappear in the spectra of polyol and it shows appearance of new peaks between $3.2\text{--}4\text{ ppm}$ correspond to the methylenic proton ($-\text{H}-\text{C}-\text{OH}-$) and the proton associated with the $-\text{OH}$ groups (Guo *et al.*, 2000) (Djordjevic *et al.*, 2009).

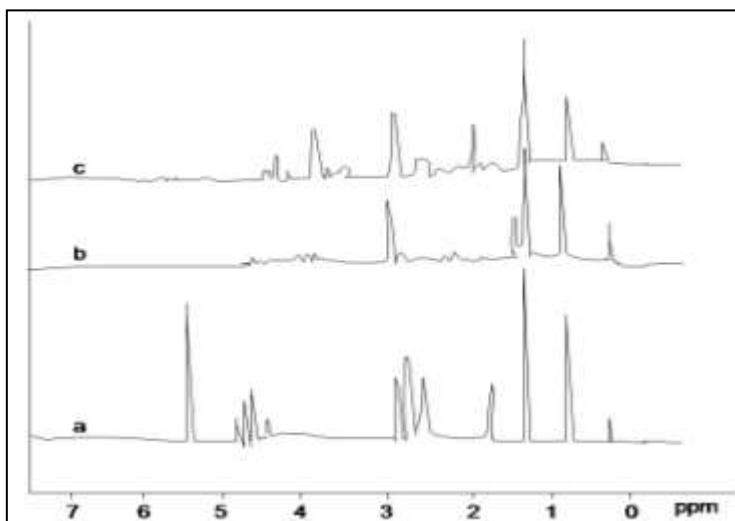


Figure 3: ^1H -NMR Spectra of linseed oil (a), epoxidised Linseed oil (b) and polyol (c)

Thermal Analysis

The thermal studies show that the synthesized polymers were thermally stable. Figure 4 reveals the TG/DTA thermogram of polymer PH and PE. The initial decomposition of PH begins at around 250°C

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with a weight loss of 10.8 % and the final decomposition temperature is around 450°C with a weight loss of 81.8%. Similarly, the initial decomposition of PE begins at around 250°C with a total mass of 10.8 % and the final decomposition is around 440°C at 81% (Birten *et al.*, 2004).The endothermic peak induces dehydration occurs from molten stage poly condensation technique confirmed in DTA analysis.

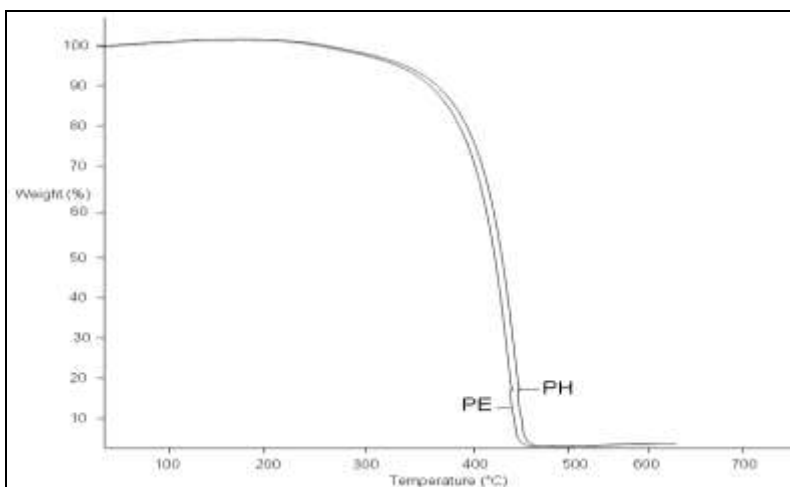


Figure 4: TG/DTA thermogram of PH and PE

SEM Analysis

Scanning electron micrograph of PH and PE at x3000 magnification represented in Figures 5 and 6 respectively. Surface sem images of both the films appear to be smooth and regular in shape which can be attributed to the well adhesion of the cells on the surface (Birten *et al.*, 2004). After sixty days of soil burial the corresponding polymers PH and PE weights are decreased, thus confirmed that the polyesters are biodegradable as noted in Figure 7.

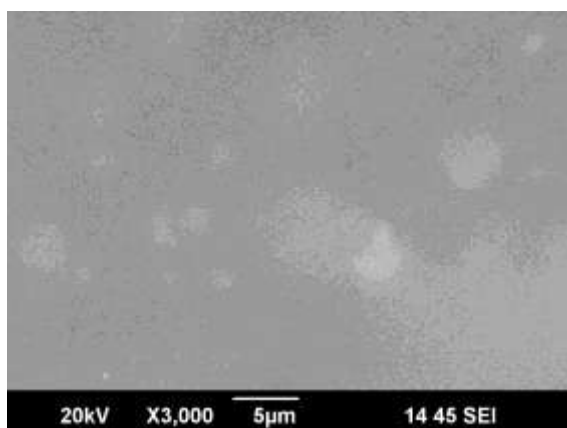


Figure 5: Scanning electron micrograph of PH before soil burial

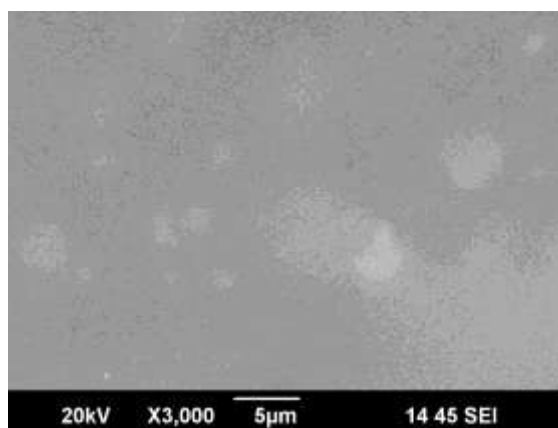


Figure 6: Scanning electron micrograph of PE before soil burial

Mechanical Analysis

The mechanical properties of the post-polymers were evaluated. The tensile test on the polymer films show the young's modulus (E) of the polymer film PH and PE were 2.46, 1.24 MPa and elongation at break between 41.52%, 29.82% respectively. The mechanical properties of the polymer PH and PE are different because of difference in diol monomer used.

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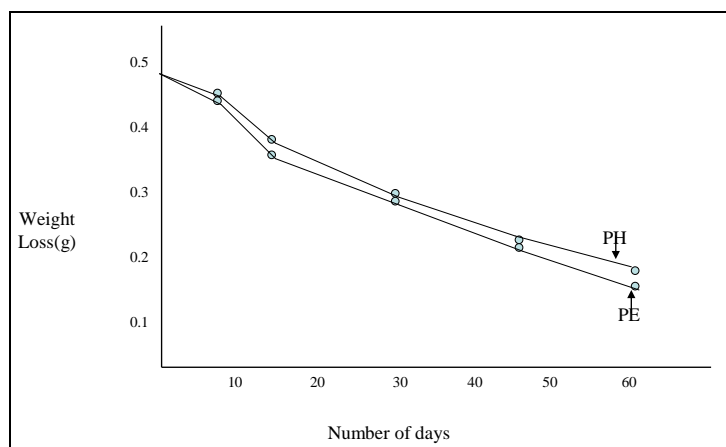


Figure 7: Graphical representation of polyesters PH and PE after soil burial

Swelling and Solubility Behaviour

The synthesized polyesters are freely soluble in Chloroform, dichloromethane, carbon tetrachloride and tetrahydrofuran. The polyesters are insoluble in water, hexane, diethyl ether and ethanol. The equilibrium swelling percentage of the polymers PH and PE are 45.16% and 62.8%. The sol content for polymer PH and PE were 3.3% and 6% respectively. The low sol content indicates the successful incorporation of cross link network during post polymerization. The pre-polymers are soluble in DMSO whereas the post-polymers are not, since intermolecular 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 (Djordjevic *et al.*, 2009). The higher swelling for polymer PE was due to the weakening of intermolecular forces and breaking of hydrogen bonds.

Conclusion

Citric acid derived biodegradable elastomers have promising potential in application for soft tissue engineering. The biodegradable polyesters PH and PE 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 PH had better cross-linking than that of PE. 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.

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