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Synthesis, Characterization and Swelling property of Poly (Diol Citrate-Co-diol Suberate) Elastomers

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ABSTRACT

The advancement in tissue engineering technology demands the identification of novel biodegradable polymers which are elastic in nature and mechanically compatible with the host tissue. Hence, we have developed two polyester elastomers from citric acid (CA), suberic acid (Su), 1, 12-dodecanediol (DD) and/or 1, 4–cyclohexanedimethanol (CHDM). These polymers were synthesized by melt condensation without using any catalyst. The presence of multifunctional group in citric acid favors cross linking during post- polymerization. The pre-polymers synthesized from citric acid, suberic acid and 1,12- dodecanediol (P5), and citric acid, suberic acid, and 1, 4-cyclohexanedimethanol(P8) were characterized by determining solubility ,FTIR- spectroscopy, ^{1}H NMR spectroscopy. The post polymers were subjected to differential scanning calorimetry, thermo gravimetric analysis, mechanical and swelling studies. The results of swelling and tensile studies show that these polymers are cross-linked elastomers. Polymer P5 and P8 displayed an initial modulus of 14.52 and 1.24 MPa and elongation at break between102% and 64% respectively. The difference in swelling % of polymers P5 and P8 indicates that the choice of monomers influence the physical properties. Both P5 and P8 were found to be susceptible for swelling, which is the required quality for any polymer prior to biodegradation.

KEYWORDS: citric acid; suberic acid; 1, 12-dodecanediol; 1, 4 – cyclohexanedimethanol; elastomer; polyester

INTRODUCTION:

The ever increasing demand for the biodegradable elastomers required for tissue engineering and drug delivery in medical field made us to think on the synthesis and characterization of new elastomers with required qualities (Ratner *et al*, 2004; Lavik *et al*, 2004). In tissue engineering, the biodegradable elastomers can be used to provide scaffolds which can withstand mechanical stress and cell attachment (Jeong *et al*, 2004). In drug delivery, these can be used alone or in conjunction to function as medical device (Saad *et al*, 1999). Most of the biodegradable elastomer syntheses require complex and costly methods and some of them require catalysts (Wang *et al*, 2002). The scaffolds used for tissue engineering purposes should posses the property of extracellular matrix to provide similar properties such as communication, swelling and mechanical stability. Soft elastomeric scaffolds should posses swelling property so that communication between tissues or organs may be pursued (Lee *et al*, 2001; Nguyen *et al*, 2002). It has been reported that citric acid acts as a prime monomer for the synthesis of poly octanediol citrate (POC), poly(1,2-propanediol-sebacate)citrate(PPSC) and (octamethylene maleate) citrate (POMC) (Wang *et al*, 2002; (Lijuan Lei *et al*, 2007; Gyawali *et al*, 2010). These polymers have been shown beneficial and applied in scaffold formation Yang *et al*, 2005). In this study we have synthesized two bioelastomers P5 made of citric acid, suberic acid, 1,12 –dodecanediol and P8 made of citric acid suberic acid,1,4-cyclohexanedimethanol. All the monomers selected here were already used in the preparation of biodegradable polymers so that the cytotoxicity was expected to be less.

MATERIALS AND METHODS:

All the chemicals utilized for the study were purchased from Sigma Aldrich and Biomaterials Bangalore, India.

Synthesis of polymers

The polymers were synthesized by using controlled condensation reaction. Citric acid, suberic acid, 1,12-dodecane diol/ 1,4-cyclohexanedimethanol were taken in a 250 ml three- necked round-bottom flask fitted with an inlet and outlet adopter. The mixture was melted under nitrogen purge with simultaneous stirring at 160-165^{o}C in a silicon oil-bath. Then the temperature was decreased to 140-145^{o}C under nitrogen purge and the reaction was allowed to occur for 3 hrs to form pre polymers. The pre-polymers were synthesized with acids to diol ratio as 1:1 in both polymer preparations. The pre-polymer was treated with 1,4-dioxane (20% w/w solution) in order to remove any un-reacted monomers and oligomers. The pre-polymer solution thus obtained was used for film preparation without further purification. The pre-polymer solution in 1,4-dioxane is poured in a clean Teflon petridish and incubated at 80^{o}C for 24 hrs and used for the determination of mechanical and thermal analysis. The pre-polymers were purified by drop wise precipitation in deionized water obtained from Millipore water purification system. The undissolved pre- polymers were collected lyophilized to obtain the purified pre-polymers (Trans *et al*, 2010). The purified pre-polymers were used for spectral analysis.

Polymer characterization:

Fourier transform infrared (FTIR) spectral analysis

Fourier transform infrared spectra (FTIR) for the pre-polymers were obtained using ABB MB 3000 FT-IR spectrometer at 27^{o}C. 5% pre-polymer in dichloromethane was prepared by solution casting technique over KBr crystal and allowed to dry for 12 hrs in vacuum hood before being used to obtain the spectra.

Nuclear magnetic resonance (NMR) spectral analysis

^{1}H NMR spectra for pre-polymers were recorded using BRUKER AV III 500 MH_z FT NMR Spectrometer. The pre-polymers were purified twice as mentioned earlier and dissolved in $CDCl_3$ in 5mm outside diameter tube. The chemical shift in ppm for ^{1}H NMR Spectra were obtained relative to TMS 0.00 ppm as internal reference.

Solubility test

Solubility of the pre-polymers was tested in different solvents such as DMSO, THF, EtOH, dioxane, acetone, hexane, water and dichloromethane.

Thermal analysis: Thermo gravimetric analysis (TGA) and Differential scanning calorimetry (DSC)

TGA thermo grams of the post-polymers were obtained at a scanning speed of 10^{o}C min^{-1} at the range of 30^{o}C to 800^{o}C under the flow of nitrogen gas by using TGA Q 500 V 20.10 Build 36. The decomposition temperature (T_d) which is the temperature at which 5% weight loss of the sample occurred. Differential scanning calorimetric (DSC) thermo grams were recorded in the range of -70 ^{o}C to 150 ^{o}C using DSC Q 200 V23.10 Build 79 at a heating rate of 10^{o}C min^{-1} under nitrogen purge.

Mechanical properties

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 (45x5x0.2mm, 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 modules were calculated from the initial slope of the curve.

Swelling property

The % swelling and the sol content of the polymers were measured in DMSO. DMSO was chosen because of its high boiling point. Briefly cylindrical disc of about 7cm were cut using cork borer from un purified cross linked polymer film. The discs were pre-weighed to know the initial mass (W_0) and suspended in DMSO for 24 hrs . The DMSO was changed for every 6 hrs. The films were removed from DMSO at different time intervals blotted dry with filter paper and weighed (W_S). The discs were suspended in de-ionized water for 24 hrs to exchange DMSO and lyophilized for 74 hrs. The dried samples were weighed to find the dry mass (W_D). The swelling percentage was calculated using the formula (Tanodekaew *et al*, 2006).

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

The sol-gel fraction was calculated using the formula

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

RESULTS AND DISCUSSION

The pre-polymer P5 and P8 were prepared through initial melt condensation reaction between citric acid, suberic acid, 1, 12-dodecanediol/1, 4-cyclohexanedimethanol. The stiochiometric ratio between acid and diol was always kept as1:1. The pre-polymers looked like a transparent viscous liquid at room temperature**.** Both the pre-polymers were soluble in 1,4-dioxane, DMSO, THF , $CHCl_3$, CH_2Cl_2 and acetone.

Polymer characterization

Fig 1a and 1b show the FTIR analysis of the pre-polymers. The strong absorption band around 1734cm^{-1} is assigned to the carbonyl stretching vibrations (C=O) of ester groups and thus shows the formation polyesters. The band centered around 2923, 2925cm^{-1} assigned to methylene group of acids and diols. Broad band around 3500, 3471 cm^{-1} was assigned to hydrogen bonded hydroxyl and carboxyl groups. Our results were in accordance with the report published (Yang *et al*, 2006).

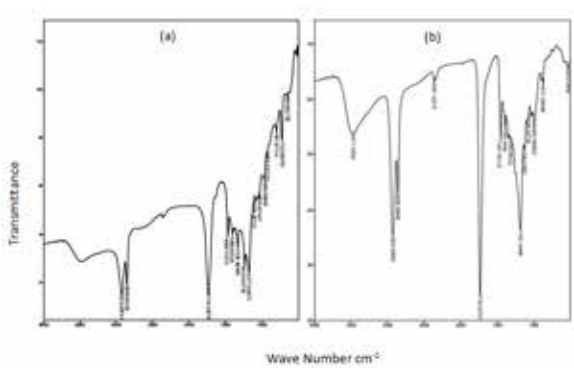

Figure 1: FTIR spectra of P5 (a) and P8 (b)

Fig 2a and 2b represent the ^{1}H NMR Spectra which confirms the resonance of various hydrogens in the pre-polymer back-bone. The peaks located at 2.8 ppm and 4.1 ppm were assigned to –C$\underline{H}_2$- and alcoholic –O$\underline{H}$-group of citric acid and the peak at 1.2 and 1.65 ppm were assigned to-C$\underline{H}_2$- of acids and diols. The peak at 2.3 ppm was assigned to –COC$\underline{H}_2$- of suberic acid. The peak at 3.6 ppm was assigned to –OC$\underline{H}_2$-CH$_2$- of diol. Similar assignments were reported by (Lei et al, 2007), (Barroso *et al* 2003) (Djordjevic *et al* ,2009).

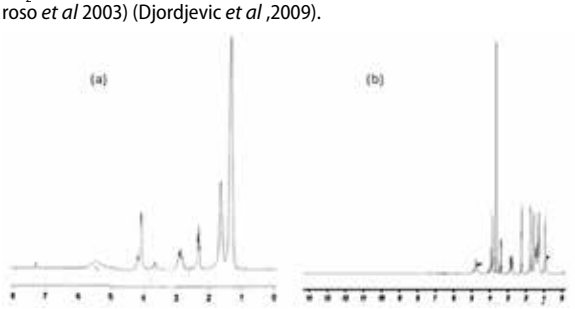

Figure 2: ^{1}HNMR spectra of P5 (a) and P8 (b)

The mechanical properties of the post-polymers were evaluated. The tensile test on the polymer films show the young's modules (E) of the polymer film p5 and p8 were 14.52, 1.24 MPa and elongation at break between102%, 64% respectively. The mechanical properties of the polymer P5 and P8 are different because of difference in diol monomer used.

Thermal Analysis

The thermal stabilities of the polymers were analyzed by TGA and DSC. The decomposition of the polymers were recorded over a various range of temperatures and the decomposition temperature (T_d) of polymers P5 and P8 were 285°C and 280°C respectively. Fig 3a and 3b show the DSC of polymer P5 and P8. DSC analysis of both the polymers showed T_g values below room temperature which is a characteristic feature of elastomer. The T_g values of polymer P5 and P8 were -4.83°C an -2.72° C

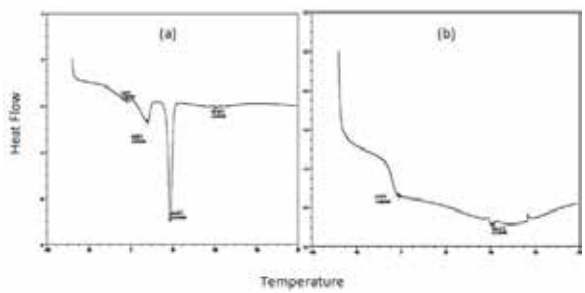

Figure 3: DSC of Polymer P5 (a) and P8 (b)

Swelling Analysis

The swelling graph of polymer P5 and P8 were shown in Fig 4. The swelling experiment shows that the swelling percentages of the polymers are 34% and 123%. The sol content for polymer P5 and P8 were 3% and 5.7% 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 P8 was due to the weakening of intermolecular forces and breaking of hydrogen bonds.

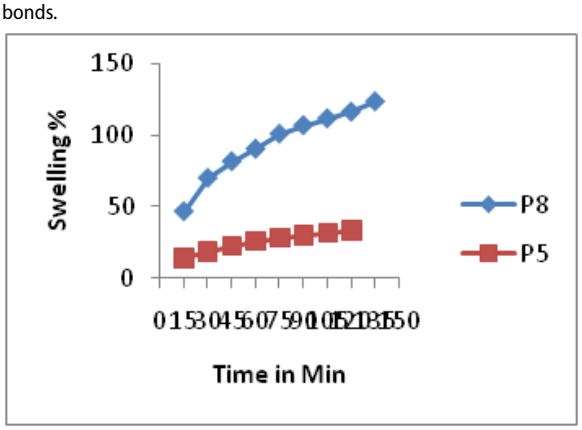

Figure 4: Swelling graph of P5 and P8.

CONCLUSION

The polyester elastomer P5 and P8 were synthesized by melt condensation reaction without using any catalyst. The results of Tg shows that the synthesized polymers are elastic in nature. The difference in swelling % of polymers P5 and P8 indicates that the choice of monomers influence the physical properties.

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