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# Synthesis and Characterisation of Certain Novel Polyester Elastomers

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***ABSTRACT***

*In this paper, we report on the synthesis of certain novel polyester elastomers namely as Poly[poly(ethylene glycol) suberate citrate], PPEGSuC and Poly[poly(ethylene glycol) sebacate citrate], PPEGSeC, by carrying out catalyst free polycondenstation of multifunctional non-toxic monomers: poly(ethylene glycol) (PEG), citric acid (CA) and suberic acid (SuA)/sebacic acid (SeA). The polyesters were characterised by solubility, viscosity measurements, IR, $^{1}H$ NMR and $^{13}C$ NMR spectral methods. The thermal properties were studied using differential scanning calorimetry. The swelling behaviour of the synthesised polyesters were studied. We demonstrate that the chemical structure, morphology, physical integrity and surface property of the synthesised copolyesters can be controlled by simply changing the monomers. These novel polyesters exhibit versatility in thermal properties, hydrolysis and hydrolytic degradation as determined by the chemical structure of the polyester elastomers. The synthesised polyesters are potential elastic biomaterials for tissue engineering.*

***Keywords:*** *Elastomers; Polycondensation; Biomaterials; Citric Acid.*

## 1. INTRODUCTION

In recent years, 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]. Tissue engineering is emerged as a new multidisciplinary research field in regenerative medicine. The main strategy involves tissue regeneration by basic, tissue specific cells that are seeded into specifically designed synthetic matrices called scaffolds [3-5]. The main guiding principle in scaffold development is that the scaffolding material should resemble the natural extracellular matrix of the target tissue. In order to successfully engineer many of the native tissues, the resulting scaffold must be strong enough to withstand the mechanical demands asserted upon them once implanted inside the body, and be able to transfer mechanical stimuli to the newly developing tissues [6-10].

The synthesis of elastomeric biodegradable polyesters needs more attention due to wide range of medical applications [11-14]. Biodegradable elastomers are advantageous in that they can sustain and recover from multiple deformations without causing irritation to the surrounding tissue. Numerous biodegradable elastomers have been developed for tissue engineering and have found widespread application in the engineering of blood vessels, heart valves, nerves, cartilage, skin, bladder and bone. Among these materials, citric acid derived bioelastomers have been shown to offer a wide range of controllable mechanical profiles along with surface affinities towards many cell types. This new class of bioelastomers are synthesised with non-toxic monomers using simple and cost effective methods. The common monomer used in these biomaterial is citric acid which is a non-toxic metabolic product of the Krebs cycle and has been approved by the food and drug administration. Citric acid is also a reactive monomer that can participate in hydrogen bonding in the polyester network. Herein, we report on the synthesis and characrisation of new polyester elastomers containing citric acid in combination with aliphatic diols as comonomers by catalyst free reaction. The synthesis and characterization of two polyesters: Poly[(ethylene glycol) citrate-co-poly(ethylene glycol)suberate], PPEGSuC and Poly [(ethylene glycol) citrate-co- poly(ethylene glycol) sebacate], PPEGSeC. The monomers used for the synthesis are biodegradable polymers and so toxicity was expected to be low.

## 2. EXPERIMENTAL

### *2.1. Materials*

Citric acid (Merck AR grade), Suberic acid (Lancaster AR grade) and Sebacic acid (Merck AR grade) were recrystallised from deionised water and used. Poly(ethylene glycol) (Merck AR grade) was dried with CaO overnight and then distilled under reduced pressure. All the other materials and solvents used were of analytical grade.

### *2.2. Synthesis of Copolyesters*

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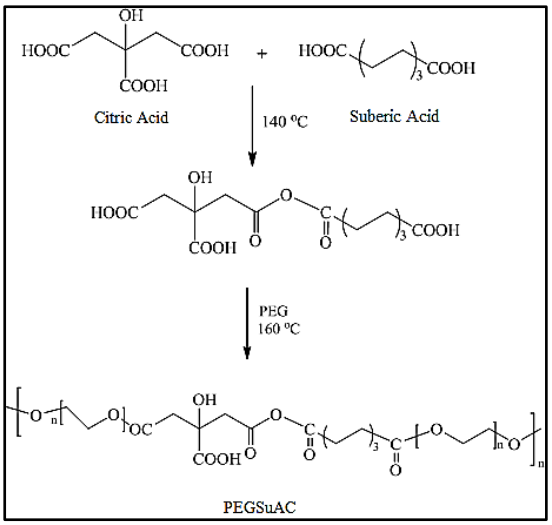


**Figure1:** Scheme of the synthesis of copolyester, PPEGSuC.

The copolyesters were synthesized by catalyst free melt polycondensation method. As an example, the synthesis of Poly[poly(ethylene glycol) suberate citrate], (PPEGSuC), has been described. The polycondensation flask was a three neck flask equipped with a nitrogen inlet, a condenser and a thermometer. A magnetic stirrer was used to stir the reaction mixture. The reaction mixture consists of equimolar amounts of Citric acid, Suberic acid and Poly(ethylene glycol). The reaction mixture was heated in an oil bath. The temperature of the reaction mixture is raised to 140 $^{o}$C in 30 minutes. Then, the temperature is gradually raised in 10$^{\circ}$C steps every minute to the reaction temperature of 165 $^{o}$C for 2 hours under a stream of nitrogen. Subsequently, the pressure of the reaction system is gradually decreased and condensation polymerisation was continued under a final reduced pressure lower than 0.5mm Hg. applied for 2 hours. Finally, the reaction was terminated when the viscosity of the reaction mixture is so high the rotation of the magnetic stirrer is not possible.

The viscous slurry was cooled in the reaction flask. The crude copolyesters was dissolved in chloroform and precipitated into a ten fold amount of vigorously stirred ice cold methanol to purify the copolyesters. The precipitated polyester was dried in a vacuum to constant weight. The scheme of synthesis of copolyesters involving poly (ethylene glycol), citric acid and suberic acid is presented in Fig.1. The yield of the synthesised copolyesters is 78.5% and 76.9% for PPEGSuC and PPEGSeC respectively.

### *2.3. Characterisation methods*

The two synthesised copolyesters were characterised by solubility studies, viscosity measurements, spectral analysis, thermal analysis and swelling experiments.

#### *2.3.1. Solubility and Viscosity*

Solubility of synthesised copolyesters PPEGSuC and PPEGSeC were determined in various solvents qualitatively. The intrinsic viscosity of polymer solutions in chloroform was measured at 30°C in a constant temperature bath using Ubbelhode Viscometer.

#### *2.3.2. Fourier Transform Infrared (FTIR) Spectroscopy*

IR Spectra of the copolyesters were recorded using a Perkin Elmer IR spectrometer in the range of 700 $cm^{-1}$ to 4500 $cm^{-1}$. The samples were embedded in KBr pellets.

#### *2.3.3. $^{1}$H NMR spectra*

$^{1}$H NMR spectra were recorded on AV 3500 MHz Spectrometer by using $CDCl_3$ as solvent.

#### *2.3.4. $^{13}$C NMR spectra*

$^{13}$C NMR spectra were recorded on Jeol Model GS X at 300 to 600 MHz in DMSO $d^6$ as solvent.

#### *2.3.5. Differential Scanning Calorimetry (DSC)*

The DSC scans were recorded at a heating rate of 10° C/min using Q200 V23.10 Build 79 instrument in the nitrogen atmosphere in the range of -50°C to 200°C.

#### *2.3.6. Swelling experiments*

The swelling behavior of the synthesised copolyesters was determined by incubation method. The synthesised copolyesters were fabricated in the form of disc and incubated in deionised water at room temperature (27 °C). The disc was taken out of the solvent after 24 hours and the surface of the swollen disc was gently blotted with filter paper to remove any excess swelling agent. The sample was then weighed ($M_w$). The percentage swelling was calculated using the expression $[(M_w-M_o)/M_o]x\ 100\%$, where $M_o$ and $M_w$ represent the disc weight in dry and wet conditions. The samples was again dried for 3 days and weighed to determine the dry weight ($M_d$). The sol content of the sample was calculated using the expression $[(M_o-M_d)/M_d]x\ 100\%$, where $M_o$ and $M_d$ represent the disc weight in pre and post swelling conditions. The swelling experiments were conducted in triplicate and average deviation is calculated.

## 3. RESULTS AND DISCUSSION

### *3.1 Solubility and Viscosity*

Solubility of synthesised copolyesters was determined qualitatively in various solvents. It may be noted that the two polyester samples exhibit the similar solubility pattern despite their different compositions. Polyesters maintain a good solubility in acetone, $CHCl_3$, THF, DMF and DMSO and are insoluble in water, methanol and ethanol. The

**Table 1.** Solubility of copolyesters.

| Copolyester | Acetone | $CHCl_3$ | THF | DMF | DMSO | Methanol | Ethanol | Water |
|---|---|---|---|---|---|---|---|---|
| PPEGSuC | +++ | +++ | ++ | ++ | +++ | - - | - - | - - |
| PPEGSeC | +++ | +++ | ++ | ++ | +++ | - - | - - | - - |

+ + + = Freely Soluble , + + = Soluble - - = Insoluble,

solubility of copolyesters are presented in Table.1. The inherent viscosity of the synthesised copolyesters was measured in chloroform using Ubbelhole viscometer. The inherent viscosity of the sebacic acid (PPEGSeC) is higher than the suberic acid polyester (PPEGSuC). The viscosity values show that the synthesised polyesters have optimum value molecular weight which is basis for processing them as biodegradable elastomers. The inherent viscosity of the copolyesters is presented in Table 2.

**Table 2.** Viscosity of the copolyesters.

| Copolyester | Inherent Viscosity, ηinh ( dL/g) |
|---|---|
| PPEGSuC | 0.79 |
| PPEGSeC | 0.82 |

### *3.2. Fourier Transform Infrared (FTIR) Spectroscopy*

IR spectra were obtained at room temperature using Perkin Elmar IR spectrometer. Pre-polymer samples were prepared by a solution casting technique (5% pre-polymer solution in dichloromethane) over a KBr crystal. The IR spectra recorded for polyesters are presented in Firgure 2(a) and 2(b). The IR spectra of the synthesized pre-polymers show a strong absorption bond at around 1720 $cm^{-1}$, which is characteristic absorptions of carbonyl stretching vibration of ester groups and thus confirmed the formation of polyesters. The bonds centered at around 2933 and 2929 $cm^{-1}$ were assigned to methylene ($-CH_2-$) groups for the diacids/diols and observed in all the spectra of the polyesters. The broad stretch at 3325 and 3475 $cm^{-1}$ was attributed to the stretching vibration of the hydrogen bonded carboxyl and hydroxyl groups.

### *3.3. $^1$H NMR spectroscopy*

The $^1$H NMR spectra recorded for the copolyesters are shown in the Fig.3(a) and 3(b). The purified pre-polymers were characterized by $^1$H NMR. A structural formula for the resulting copolyesters showed the relation between the different structural components and the observed chemical shifts of the pre-polymers. The multiple peaks around 2.8 ppm and 4.1 ppm were attributed to the proton in terminal $-CH_2-$ groups and alcoholic -OH groups from the citric acid. The peak at around 3.7 ppm could be due to the proton signal of $-OCH_2CH_2-$ from diol. The peaks at 1.2 and 1.6 ppm were attributed to $-CH_2-$protons of poly(ethylene glycol).

### *3.4. $^{13}$C NMR Spectroscopy*

The $^{13}$C NMR spectra are recorded for the synthesised copolyesters. The carbons present in different environments are differentiated in the proposed structure given in $^{13}$C NMR spectrum of corresponding polyesters which are presented in Figures 4(a) and 4(b). The chemical shift values obtained from $^{13}$C NMR Spectra of the copolyesters are as follows. Ester carbon of the carbonyl was observed at 175 to 180ppm, central carbon of citric at 75 to 80 ppm, methylene carbon attached to oxygen of $-O-CH_2$ at 62 to 65 ppm and methylene carbon attached to ester of $-O-CH_2$ at 33 to 34 ppm. The central and terminal methylene carbons of ethylene glycol and dicarboxylic acids were observed at 23ppm and 26ppm respectively.

### *3.5. Thermal analysis*

Thermal analysis of copolyesters was studied by Differential Scanning Calorimetry. DSC thermograms for the synthesised polymers were shown in Fig.5. The thermal studies showed that the elastomers were thermally stable. The glass transition temperature, Tg, value was lower than the room temperature for both the polyesters which is characteristic feature that determines their elastomeric nature. The Tg value for PPEGSuC (-13.5 $^oC$) was lower than that of PPEGSeC (6.5 $^oC$). Tg is linked with the chain mobility of the polymer. It increases with the enhanced restriction of polymer chain mobility. The relatively higher Tg for PPEGSeC is attributed to the stronger intermolecular hydrogen bonding which was confirmed by FTIR. Thus, increasing cross link density resulted in decreased chain mobility, which in turn, increased the Tg of the polymer. There were no melting peaks or crystallisation peaks in DSC thermograms suggest that all monomers were completely polymerised into the cross-linked network.

### *3.6. Swelling experiments*

The degree of swelling of the polymer is an important parameter in characterizing the cross linking degree of the synthesised elastomers. The degree of swelling and sol content calculated for the synthesised polyester samples were determined and tabulated in Table 3.

The swelling experiments revealed that PPEGSuC and PPEGSeC swelled to 144.54% and 162.36% of the original size respectively. The degree of swelling of the copolyesters shows that the cross linked part of the elastomeric network, that is, gel

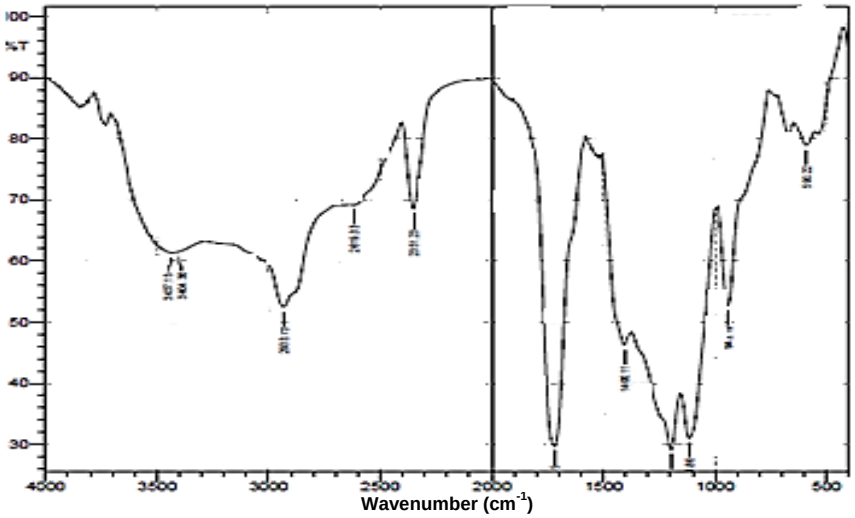


**Figure 2(a):** IR spectra of copolyester PPEGSuC.

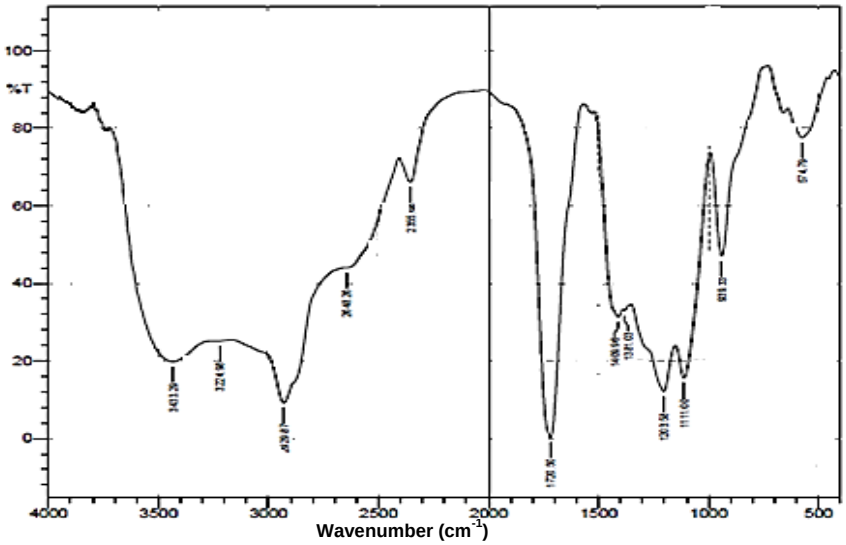


**Figure 2(b):** IR spectra of copolyester PPEGSeC.

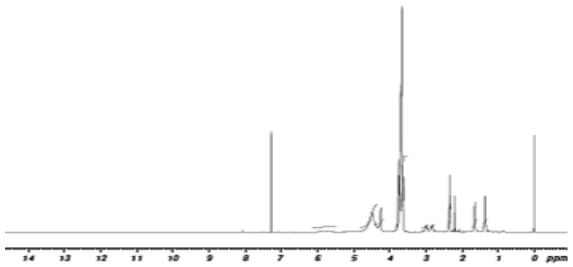

**Figure 3(a):** $^{1}$H NMR spectra of copolyester PPEGSuC.

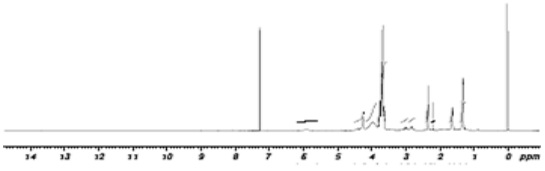

**Figure 3(b):** $^{1}$H NMR spectra of copolyester PPEGSeC.

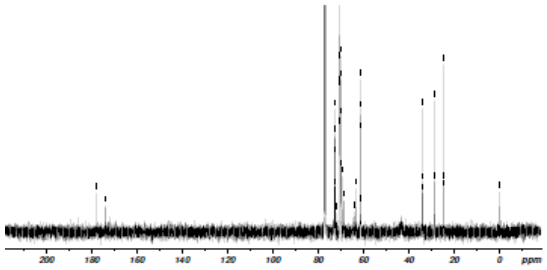

**Figure 4(a):** $^{13}C$ NMR spectra of copolyester PPEGSuC.

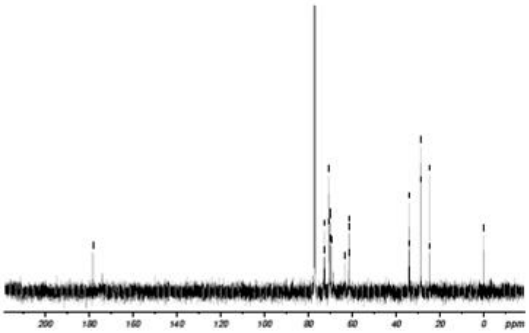

**Figure 4(b):** $^{13}C$ NMR spectra of PPEGSeC.

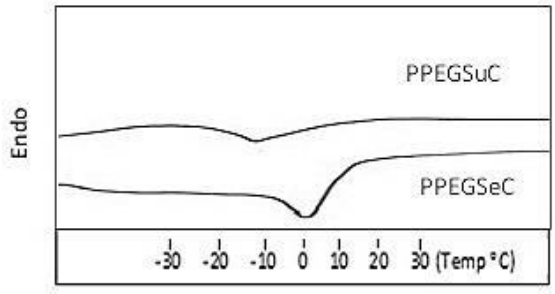


**Figure 5:** DSC thermogram of PPEGSuC and PPEGSeC.

part is fairly high. The high swelling percentage observed for PPEGSeC may be due to the weakening of the intermolecular interactions and disruption of physical cross link between the polymer chains. The sol content of the polyester elastomers PPEGSuC and PPEGSeC was calculated as 3.24% and 5.13% respectively. The relatively small amount of the sol content confirmed the formation of polymer network and indicated the very little presence of small oligomers trapped within the polymer network. The polymer samples did not completely dissolved due to cross linking and hydrogen bonding. This is in agreement with the FTIR analysis which showed the presence of hydrogen bonding.

**Table 3.** Degree of swelling and sol content of the copolyesters.

| Copolyester | Degree of Swelling (%) | Sol Content (%) |
|---|---|---|
| PPEGSuC | 144. 54 | 3.24 |
| PPEGSeC | 162.36 | 5.13 |

## 4. CONCLUSIONS

The polyester elastomers, Poly[poly(ethylene glycol) suberate-citrate], PPEGSuC and Poly[poly (ethylene glycol) sebacate-citrate], PPEGSeC were synthesized using catalyst free polycondensation method. The thermal property of the polyesters showed that PPEGSeC has better cross linking than that of PPEGSuC. The low Tg revealed by DSC thermogram for the copolyesters evidenced their elastomeric nature. The relatively higher Tg for PPEGSeC is attributed to the stronger intermolecular hydrogen bonding which was confirmed by FITR. The development of these new Citric acid based polyester elastomers presents unique opportunities for many biomedical applications such as tissue engineering and drug delivery.

## 5. REFERENCES

[1]. J. C. Middleton, A. J. Tipton, (2000) Synthetic biodegradable polymers as orthopedic devices, ***Biomaterials,*** **21**: 2335-2346.

[2]. S. Schwendeman, H. R. Constantino, R.K. Gupta, R. Langer, Challenges strategies: in controlled drug delivery; Park, K., Ed., American Chemical Society; Washington DC, 1997: 229.

[3]. M. B. Habal, W. S. Pietrzak, (1999) Key points in the fixation of the craniofacial skeleton with absorbable biomaterial, ***Journal of Craniofacial Surgery***, **10**: 491-499.

[4]. B. L. Eppley, (1997) A bioabsorbable poly-l-lactide miniplate and screw system for osteosynthesis in oral and maxillofacial surgery, ***Journal of Oral and Maxillofacial Surgery,*** **55:** 945-946.

[5]. P. Kousa, T. L. Jarvinen, P. Kannus, M. Jarvinen, (2001) Initial fixation strength of bioabsorbable and titanium interference screws in anterior cruciate ligament reconstruction: biomechanical evaluation by single cycle and cyclic loading, ***American Journal of Sports Medicine,*** **29**: 420-425.

[6]. H. Younes, E. B. Grimaldo, B. Amsden, (2004) Synthesis, characterization and in vitro degradation of a biodegradable elastomer, ***Biomaterials,*** **25**: 5261-5269.

[7]. J. Guan, M. S. Sacks, E. J. Beckman, W. R. Wagner, (2004) Biodegradable poly (ether ester urethane) urea elastomers based on poly (ether ester) triblock copolymers and putrescine: synthesis, characterization and cytocompatibility, ***Biomaterials***, **25**: 85-96.

[8]. H. J. Sung, C. Meredith, C. Johnson, Z. S. Galis, (2004) The effect of scaffold degradation rate on three-dimensional cell growth and angiogenesis, ***Biomaterials***, **25**: 5735-5742.

[9]. P. Pego, A. A. Poot, D. W. Grijpma, J. Feijen, (2003) Biodegradable elastomeric scaffolds for soft tissue engineering, ***Journal of Control Release,*** **87**: 69-79.

[10]. H. Y. Kweon, M. K. Yoo, I. K. Park, T. H. Kim, H. C. Lee, H. S. Lee, J. S. Oh, T. Akaike, C. S. Cho, (2003) A novel degradable poly caprolactone networks for tissue engineering, ***Biomaterials,*** **24**: 801-808.

[11]. B. Saad, P. Neuensch wander, G. K. Uhlschmid, U. W. Suter, (1999) New versatile, elastomeric, degradable polymeric materials for medicine, ***International Journal of Biological Macromolecules***, 25: 293-301.

[12]. G. A. Skarja, K. A. Woodhouse, (2000) Structure-property relationships of degradable polyurethane elastomers containing an amino acid-based chain extender, ***Journal of Applied Polymer Science***, **75**: 1522-1534.

[13]. Y. Wang, G.A. Ameer, B. Sheppard, R. Langer, (2002) A tough biodegradable elastomer; ***Nature Biotechnology,*** 20: 602-606.

[14]. B. S. Kim, J. Nikolovski, J. Bonadio, D. J. Mooney (1999) Cyclic mechanical strain regulates the development of engineered smooth muscle tissue, ***Nature Biotechnology,*** **17**: 979.

[15]. J. Yang, A.R. Webb, S.J. Pickerill, G. Hageman, G.A. Ameer, (2006), Folate-decorated poly(lactide-co-glycolide)-vitamin E TPGS nanoparticles for targeted drug delivery, ***Biomaterials***, **27:** 1889-1899.

[16]. P. X. Ma, R. Langer, (1995) ***Materials Research Society Symposium Proceedings,*** **394**: 99.

[17]. W. Mark, J. C. Nicholas, Long-term in vivo Degradation of Poly-L-lactide (PLLA) in Bone, (2007) ***Journal of Biomaterial Applications***, **21**: 395-411.

[18]. M. C. Serrano, E. J. Chung, G. A. Ameer, (2010) Advances and applications of biodegradable elastomers in regenerative medicine, ***Advanced Functional Materials***, **20**: 192-208.

[19]. C. J. Bettinger, (2011) Biodegradable elastomers for tissue engineering and cell-biomaterial interactions, ***Macromolecular Bioscience,*** **11**: 467-482.

[20]. D. G. Berrett, M. N. Yousaf, (2009) Design and applications of biodegradable polyester tissue scaffolds based on endogenous monomers found in human metabolism, ***Molecules,*** **14**: 4022-4050.

[21]. D. K. Song, Y. K. Sung, (2003) Synthesis and characterization of biodegradable poly (1,4-butanediol succinate), ***Journal of Applied Polymer Science,*** **56*:*** 1381-1395.

[22]. S. Pasupuleti, A. Avadanam, G. Madras, (2011) Synthesis, characterization, and degradation of biodegradable poly (mannitol citric dicarboxylate) copolyesters, ***Polymer Engineering & Science***, **51**: 2035-2043.

[23]. L. Lei, T. Ding, R. Shi, Q. Liu, D.C. Zhang, W. Tian, (2007) Synthesis, characterization and in vitro degradation of a novel degradable poly ((1,2-propanediol-sebacate)-citrate) bio elastomer, ***Polymer Degradation and Stability,*** **92**: 389-396.

[24]. M. M. Brioudea, D. H. Guimaraesa, R. D. D Fiuzaa, L.A.S. Pradob, J.S. Nadia, M. Josea, (2007) ***Materials Research,*** **10**:335.

[25]. D. Xie, D. Chen, B. Jiang, C. Yang, (2000) Synthesis of novel compatibilisers and their application in PP/nylon-66 blends. I. Synthesis and characterization, ***Polymer***, **41**: 3599-3607.

[26]. L.Y. Lee, S.C. Wu, S.S. Fu, S.Y. Zeng, W. S. Leong, L. P. Tan, (2009) Biodegradable elastomer for soft tissue engineering, ***Europian Polymer Journal,*** **45**: 3249-3256.

[27]. Y. F. Poon, Y. Cao, Y. Zhu, Z. M. Judeh, M. B. Chan-Park, (2009) Addition of β-malic acid-containing poly(ethylene glycol) dimethacrylate to form biodegradable and biocompatible hydrogels, ***Biomacromole-cules***, **10**: 2043.