Engineering PLA Nanofibers via Melt Spinning: Synthesis, Processing, and Applications

[1]Savita H. Bansode, [2]P. A. Mahanwar
[1,2] Department of Polymer and Surface Engineering, Institute of Chemical Technology, Nahalal Parekh Marg, Matunga, Mumbai – 400 019

***Abstract*—PLA is one of the most important polymers used in biomedical applications, with its degradation rate influenced by the ratio of monomers used in co-polymerization. Biodegradable and biocompatible polymers like PLA are commonly used in controlled drug delivery systems and implant devices for skin, bone, and dental repairs. Microwave irradiation is increasingly used as a heating method for polymerization because it speeds up the process compared to traditional heating methods. This approach allows efficient polymerization techniques such as polycondensation, free and controlled radical polymerization, and ring-opening polymerization (ROP).**

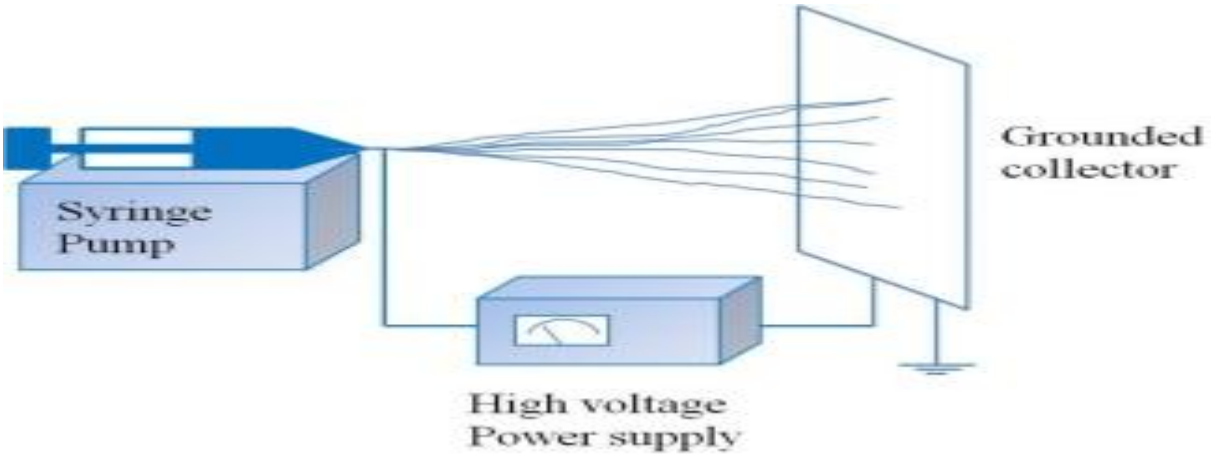
(PLA) was analysed using Fourier Transform Infrared Spectroscopy (FT-IR) and scanning electron microscopy (SEM). Polymer interactions were studied by Differential Scanning Calorimetry (DSC), and X-ray diffraction (XRD) was used to observe structural changes. PLA nanofibers were produced using electrospinning for biomedical purposes. PLA synthesis was carried out using heating polymerization, along with both electrospinning and melt spinning techniques. The input monomers and resulting products were thoroughly analysed. Key properties such as melting temperature, glass transition temperature, thermal stability, chemical composition, and monomer ratios in the synthesized copolymers were measured. These analyses confirmed there were no leftover monomers in the final products. Their excellent biocompatibility and biodegradability make them suitable for applications like long-term drug release and tissue engineering.

***Index Terms*—Synthesis, Polymerization, Electrospinning, Biodegradable, Biocompatible**

I. INTRODUCTION

Electrospinning has a straightforward setup that allows continuous drawing of fibers directly from molten polymer, eliminating the need for solvents. However, melt spinning cannot produce fibers at the nanoscale, and it is not suitable for polymers like PL that may degrade under electrospinning conditions. During the process, the spinning temperature and the take-up roll speed were

maintained at 110°C and 900 rpm, respectively. The fibers were cooled by air before being wound onto the take-up roll.



Melt electrospinning is an alternative to solution electrospinning, but it usually produces fibers with diameters in the range of tens of microns. Unlike solution electrospinning, which forms fibers through solvent evaporation, melt electrospinning relies on cooling the polymer jet to create fibers.

II. MATERIALS AND METHODS

PLA Synthesis:

Materials: Lactic acid 90% pure was purchased from Loba chemie, used as monomer. 97% pure Glycolic acid was purchased from Sigma Aldrich, as monomer. Stannous Octoate 99% pure was purchased from Sigma Aldrich and used as initiator and catalyst (it acts as both). Stearyl alcohol and Lauryl alcohol (reagent grade) from SD Fine Chemicals Pvt. Ltd used as co-catalyst. Silicon oil used in thermocouple pocket.

Apparatus: Heating mental, Overhead stirrer, stirring rod with Teflon blade, Vacuum setup, Nitrogen balloon, oil tube, thermometer, Temperature sensor, Thermocouple, thermometer pocket, four necked round bottom flask, nitrogen (gas) purging tube, Weigh machine, beakers, conical flask, pipette, water condenser, separating funnel, vacuum adaptor, stand, clamp, rubber bulk, join and bends, connector, stopper, Nitrogen balloon stand (ring clamp), fiber resistance fabric, Petri dish, Funnel, Spatulas, Glass stirring rod, Buchner funnel, wood blocks, rubber tube, etc.,Fig.1: PLA synthesis setup

Procedure

Arrange apparatus according to setup. Place mechanical stirrer in central of four neck round bottom flask, and place it in heating mental. Fill balloon with nitrogen gas, purge nitrogen from one neck with the help of gas purging tube via oil tube which help in determining rate of nitrogen gas. Keep RPM speed nearly about 500.Join vacuum through cold trap. Vacuum should apply at interval of time otherwise monomer will also remove with water. Vacuum should start after temperature reaches to 110°C, so it will remove water and since oligomerization is started monomer will not be removed.

Thermocouple place in thermometer pocket which filled with silicon oil. It can be placed in one neck or outside of heating flask but it should touch the heating solution. After arranging the whole setup check the connection before start heating and stirring also check the water inlet and outlet, then start the heating.

Add lactic acid heat for 15 min then add glycolic acid. Lactic acid added before glycolic acid because glycolic acid has higher reactivity compare to lactic acid. Add stannous octoate and/or Stearyl alcohol/ lauryl alcohol (co-initiator) after one hour (after oligomerization), and after this process vacuum is started. To check the progress of rection we determine acid value and/or saponification (sap) value. As reaction proceeds acid value decreases and sap value increases. Also determine acid value of monomer and mixture after adding initiator and/or co-initiator.

PLGA purification

Vacuum drying: Synthesized product PLA was dissolved in chloroform/ acetone, and dried in vacuum at 46°C and 55°C. After it keep for cooling.

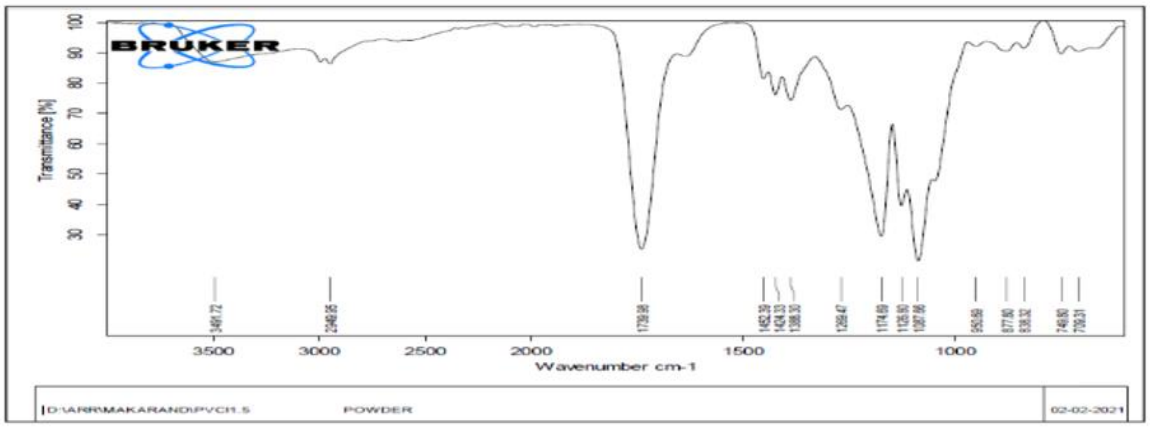
By using Desiccator: The product PLA was cooled down and then dissolved in chloroform and subsequently precipitated into diethyl ether. The precipitated mixture was collected in petri dish and dried in desiccator using vacuum. Vacuum applied by vacuum pump.

Apparatus: Electrospinning instrument, PLA

Procedure: PLA was dried in oven for 40 min. to remove moisture from polymer. About 200 grams of material PLGA used for fabrication process. Material was added to the spinneret in molten form. Optimized RPM (1200-1500) and Temperature (100-140°C) according to requirements. Polymer material is added through hopper, material was melted in single screw extruder where heating plates are attached. Material will pass to the spinneret which attached with high-speed rotatory motor. PLA melted in barrel then it passes through the nozzle to spinneret which rotate at high RPM. Figure. 2: Centrifugal melt spinning setup and Figure 3Spinneret setup with heater and spinneret respectively.

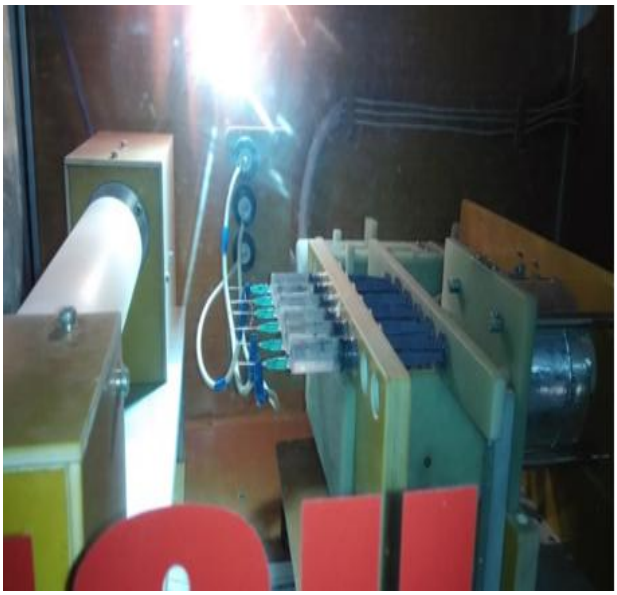
Characterization of PLA and fibers:

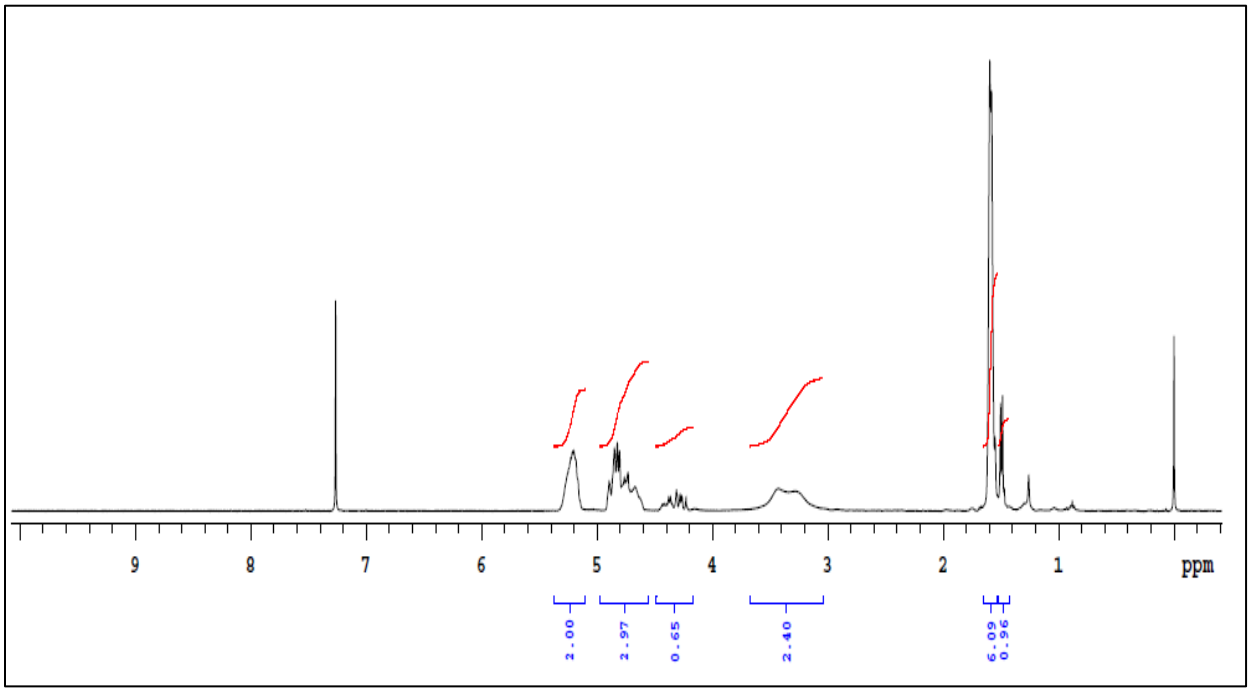
Fourier Transform Infrared (FTIR):



IR spectra is collected at 20°C from 4000 - 650 cm^{-1}. The spectra were recorded on a Bruker spectrometer operating in the ATR (Attenuated Total Reflectance) mode.

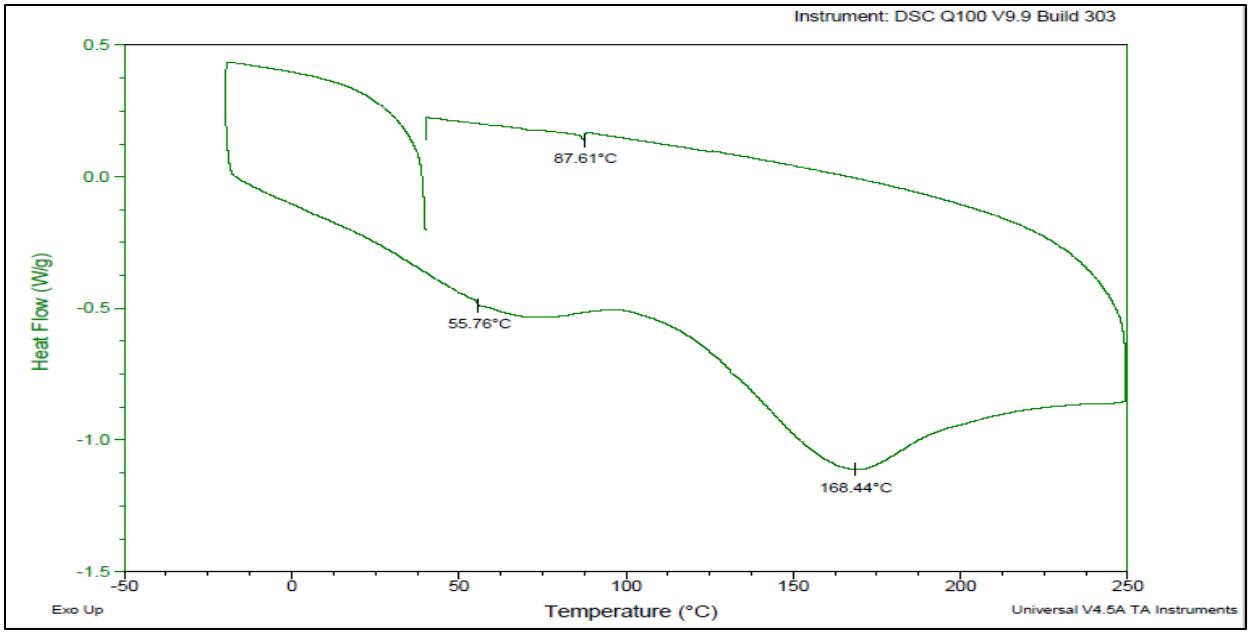
Nuclear Magnetic Resonance (NMR):





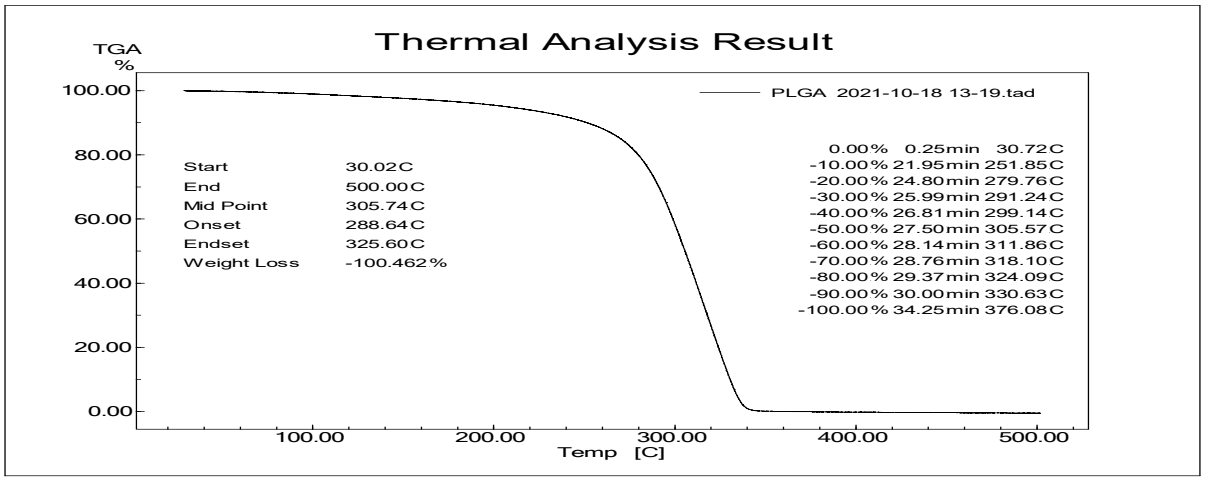
NMR samples have been prepared by dissolving the co-polymers in $CDCl_3$ from Aldrich containing TMS at 0.05%. ^1H spectra were obtained at 400 MHz. Measurement has been performed at 300 K on a Bruker spectrometer. TMS was used as internal reference.

Differential Scanning Calorimetry (DSC):



The DSC analysis was performed using a TQ Instruments DSC Q100. The samples were heated from -10°C to 200°C at a rate of 10°C per minute. An unsealed aluminum sample vessel was used, with nitrogen as the carrier gas flowing at 20 mL/min. The sample masses ranged from 5 to 10 mg. The DSC curve was used to identify the glass transition temperature (Tg) and melting temperature (Tm)

Thermogravimetry (TGA):



Thermogravimetric (TG) analysis was performed to assess the change in mass as temperature increased, along with thermal stability and the maximum degradation temperature of the samples. The test was conducted at a heating rate of 10°C per minute, ranging from 20°C to 500°C, in an open sample vessel under a nitrogen atmosphere with a flow rate of 20 mL/min. The analysis was carried out using a PerkinElmer Pyris 1 instrument, and the sample masses ranged from 5 to 10 mg.

Optical microscopy**:** Fiber diameter determined by using Olympus BX41 microscope with lens power of 20x and 50x.

Table 1. Effect of various process parameters on the resultant polymer fiber morphology

Monomer ratio (60:40)	Lactic acid = 7.5 g Glycolic acid = 1.9 g
$Sn(Oct)_2$ (1.00%)	0.08 mL
Lauryl alcohol (0.8%)	0.05 mL
Time	25 h
Temperature	130°C
Acid value of lactic acid	561.00 mg of KOH/ g of sample
Acid value of glycolic acid	728.81 mg of KOH/ g of sample
Acid value at start	563.50 mg of KOH/ g of sample
Acid value after 25 H	96 mg of KOH/ g of sample
Yield	89%

Morphology of SEM of PLGA Fibers

The morphology of Polylactic acid (PLA) was studied to understand its surface characteristics, structural arrangement, and physical texture, which are important for evaluating its suitability in various applications. Morphological analysis provides insight into particle shape, surface uniformity, porosity, and overall microstructural behaviour of the polymer. micrographs revealed that PCL relatively homogeneous semi-crystalline nature. The polymer matrix appeared continuous, indicating good film-forming ability and uniform distribution of polymer chains [176] At higher magnification, slight granular features and minor surface irregularities were observed, which may be attributed to the semi-crystalline organization of PLANo major cracks, voids, or phase separation were detected, confirming the structural integrity of the polymer. The presence of a compact morphology suggests strong intermolecular interactions and good cohesion within the material. The observed morphology is consistent with the FT-IR results, where characteristic peaks at 1720 cm^{-1} (C=O stretching), 2940 cm^{-1}, and 2863 cm^{-1} (C–H stretching) confirmed the successful formation of PCL [176,177]. The combination of FT-IR and morphological analysis supports the successful synthesis and structural stability of Polycaprolactone.

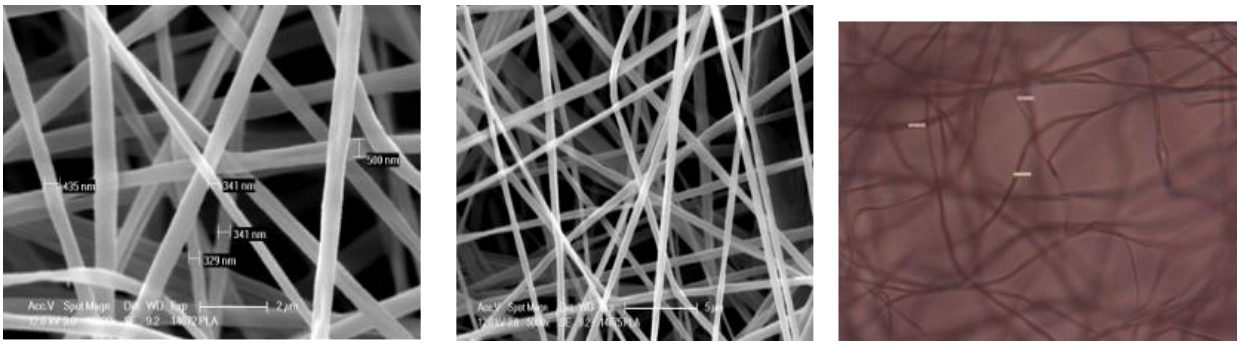


Figure 3.8 SEM of PLA

Scanning Electron Microscopy (SEM) for PLASEM image of a randomly oriented 15% PCL nanofiber deposition. Electrospun 15% PLA nanofiber diameter was 220 to 445 nm. Scale bar = 1000x Polycaprolactone (PLA) nanofibers by using electrospinning technique for 15, 20% confocal images and scanning electrospinning

III. CONCLUSION

PLGA synthesis combined with electrospinning is a simple, versatile, and cost-effective method for creating scaffolds used in biomedical applications. The fibers produced by electrospinning have unique features such as biocompatibility, biodegradability, nanometre-scale size, high surface area-to-volume ratio, adjustable fiber diameters, high porosity, and good mechanical strength. The properties of electrospun nanofibers depend on several processing factors like polymer viscosity, surface tension, conductivity, molecular weight, applied voltage, distance between the needle tip and collector, and humidity. Electrospun nanofibers have been successfully used to fabricate scaffolds for tissues such as nerves, blood vessels, heart valves, skin, and kidneys. Most applications so far have been tested in vitro, but in vivo studies are needed to better understand important factors like scaffold interaction with target organs, nutrient transfer, cell adhesion and growth, tissue development, and toxicity. Overall, electrospinning is a promising technology for producing nanofibers with significant potential in biomedical scaffold development and other related applications.

REFERENCES

[1] E. Kenawy, G. L. Bowlin, K. Mansfield, J. Layman, G. Simpson, E.H. Sanders, G.E. Wnek, Release of tetracycline hydrochloride from electrospun poly (ethylene-co-vinylacetate), poly (lactic acid), and a blend, 81 (2002) 57–64.

[2] Y. K. Luu, K. Kim, B. S. Hsiao, B. Chu, M. Hadjiargyrou, D evelopment of a nanostructured DNA delivery scaffold via electrospinning of PLGA and PLA–PEG block copolymers, 89 (2003) 341–353.

[3] X. Zong, K. Kim, D. Fang, S. Ran, B.S. Hsiao, B. Chu, Structure and process relationship of electrospun bioabsorbable nanofiber membranes, 43 (2002) 4403–4412.

[4] H. Jin, S. Min, Y. Song, H. Park, S. Yoon, composites prepared using microwave energy, 95 (2010) 1856–1861. https://doi.org/10.1016/j.polymdegradstab.2010.04.025.

[5] I. Armentano, M. Dottori, E. Fortunati, S. Mattioli, J.M. Kenny, Biodegradable polymer matrix nanocomposites for tissue engineering : A review, 95 (2010) 2126–2146. https://doi.org/10.1016/j.polymdegradstab.2010.06.007.

[6] N. Shanmugasundaram, P. Ravichandran, P.N. Reddy, N. Ramamurty, S. Pal, K.P. Rao, Collagen chitosan polymeric scaolds for the in vitro culture of human epidermoid carcinoma cells, 22 (2001) 1943–1951.

[7] F. J. O. Brien, B. A. Harley, I. V Yannas, L. J. Gibson, The effect of pore size on cell adhesion

in collagen-GAG scaffolds, 26 (2005) 433–441. https://doi.org/10.1016/j.biomaterials.2004.02.052.

[8] F. Yang, R. Murugan, S. Wang, S. Ramakrishna, Electrospinning of nano/micro scale poly (L -lactic acid) aligned fibers and their potential in neural tissue engineering, 26 (2005) 2603–2610. https://doi.org/10.1016/j.biomaterials.2004.06.051.

[9] A.S. Badami, M.R. Kreke, M.S. Thompson, J.S. Riffle, A.S. Goldstein, Effect of fiber diameter on spreading , proliferation , and differentiation of osteoblastic cells on electrospun poly (lactic acid) substrates, 27 (2006) 596–606. https://doi.org/10.1016/j.biomaterials.2005.05.084.

[10] C. Danielsson, S. Ruault, M. Simonet, P. Neuenschwander, P. Frey, Polyesterurethane foam scaffold for smooth muscle cell tissue engineering, 27 (2006) 1410–1415. https://doi.org/10.1016/j.biomaterials.2005.08.026.

[11] Y. Sumita, M.J. Honda, T. Ohara, S. Tsuchiya, H. Sagara, H. Kagami, M. Ueda, Performance of collagen sponge as a 3-D scaffold for tooth-tissue engineering, 27 (2006) 3238–3248. https://doi.org/10.1016/j.biomaterials.2006.01.055.

[12] K. Rezwan, Q.Z. Chen, J.J. Blaker, A. Roberto, Biodegradable and bioactive porous polymer / inorganic composite scaffolds for bone tissue engineering, 27 (2006) 3413–3431. https://doi.org/10.1016/j.biomaterials.2006.01.039.