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EFFECT OF DIFFERENT SOLVENT SYSTEMS ON FIBER MORPHOLOGY AND PROPERTY OF ELECTROSPUN PCL NANO FIBERS

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Abstract: Polycaprolactone (PCL) is biocompatible aliphatic polyester with many possible applications in the medical field. Porous electrospun Polycaprolactone (PCL) fibers were produced through a non-solvent induced phase separation mechanism, using binary solvent systems with different properties. The effect of single and binary solvent systems on the fiber size and surface morphology were investigated. Dichloromethane (DCM) was used as a good solvent in mixtures with a poor solvent, dimethyl sulfoxide (DMSO), in order generate to pores on the fiber surface. The effect of polymer concentrations (12%, 14% and 16%) w/v and solvents ratios (9:1, 7:3 and 5:5) v/v were investigated on nanofiber formation. During electrospun fiber production, the flow rate was 0.12mL/h, the distance between needle and collector was 15cm and the applied voltage was 12kV. SEM micrographs showed successfull production of PCL nanofibers with different solvents. With increasing the polymer concentration and changing the ratio of the solvents porous PCL electrospun nanofiber was produced. In binary solvent systems 16% PCL polymers and (7:3) % solvents ratio solution make even, beads free, smooth and porous PCL electrospun fiber. Combining the inherent properties of the PCL matrix with the characteristic of nanofibrous mats, result in promising materials that can be suitable for different applications, including biomedical applications. The advantages of nanofibrous structures include large surface area, small diameter of pores and high porosity, which make them of great interest in different applications. Porous electrospun fiber is better for cell development.

Keyword: Polycaprolactone (PCL), Electrospinning, Nanofibers, Porous fibers

FARKLI ÇÖZÜCÜ SİSTEMLERİNİN ELEKTRİK ALAN LİF ÇEKİM YÖNTEMİ İLE ÜRETİLMİŞ PCL NANO LİFLERİN LİF MORFOLOJİSİ VE ÖZELLİKLERİNE ETKİSİ

Öz: Polikaprolakton (PCL) tıbbi alanda olası birçok uygulaması bulunan biyouyumlu alifatik bir poliesterdir. Bu çalışmada farklı özelliklere sahip ikili çözücü sistemleri kullanılarak, çözücü kaynaklı olmayan faz ayırma mekanizması yolu ile elektrik alan lif çekimi yönteminde gözenekli PCL lifleri üretilmiştir. Tekli ve ikili çözücü sistemlerinin lif boyutu ve yüzey morfolojisi üzerindeki etkisi araştırılmıştır. Diklorometan (DCM), lif yüzeyinde gözenekler oluşturmak için zayıf bir çözücü olan dimetil sülfoksit (DMSO) ile karışımlarda iyi bir çözücü olarak kullanılmıştır. Nano lif oluşumuna polimer konsantrasyonlarının (%12, %14 ve %16) w/v ve çözücü oranlarının (9:1, 7:3 ve 5:5) v/v etkisi araştırılmıştır. Elektrik alan ile lif çekimimde akış hızı 0,12mL/h, iğne ile kolektör arasındaki mesafe 15cm ve uygulanan voltaj 12kV olarak seçilmiştir. SEM fotoğrafları, farklı çözücüler ile PCL nanoliflerinin başarılı bir şekilde üretildiğini göstermiştir. Polimer konsantrasyonunun arttırılması ve çözücü oranlarının değiştirilmesi ile gözenekli PCL nanolifler üretilmiştir. İkili çözücü sistemlerinde %16 PCL polimerleri ve (7:3) % çözücü oranlı çözelti ile düzgün, boncuksuz, pürüzsüz ve gözenekli PCL lifler üretilebilmiştir. PCL matrisinin kendine has özelliklerini nano lifli matların karakteristiğiyle birleştirmek, biyomedikal uygulamalar dahil olmak üzere farklı uygulamalar için uygun olabilecek umut verici malzemelerin üretimi ile sonuçlanmıştır.Nanolifli yapıların geniş yüzey alanı, küçük gözenek çapı ve yüksek gözeneklilik gibi özellikleri içeren avantajları bu lifleri farklı uygulamalarda ilgi odağı haline getirmektedir. Elektrik alan lif çekimi ile üretilmiş gözenekli lifler hücre geliştirme için daha iyi bir alternatifdir.

Anahtar Kelimeler : Polikaprolakton (PCL), Elektrik alan ile lif çekimi, nanolifler, gözenekli lifler

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1. INTRODUCTION

Natural and synthetic biodegradable polymers are consumed widely for biomedical purposes, their field of interests comprises, tissue engineering, drug delivery, regenerative medicines etc. Polymers such as Polyesters (aliphatic Polyesters) such as Polycaprolactone (PCL), poly (glycolic acid) (PGA), poly (lactic acid) (PLA), poly (trimethylene carbonate) (PTMC) have gained importance in biomaterials as of their biodegradable behaviors. Various factors such as chain length, molecular weight, degree of crystallinity, branching and the introductory system of these polyester affects their biodegradation rate. All these factors effecting biodegradability of such polyesters are tailored through polymerization techniques, polymeric reactions condition, initial reactants (monomers) and the final obtained end polymers. Subjecting to these different conditions the end polymers result in various enhanced characteristics like Tg and Tm values (glass transition and melting temperatures, respectively), solubility, stiffness and extensibility etc.

Polycaprolactone (PCL) is an aliphatic polyester produced via ring-opening polymerization (polymerization of ε-caprolactone monomers, that can proceed either via anionic, cationic, coordination or radical polymerization routes) technique has non-hazardous nature [1] (Figure1). Different methodologies have been found in literature for caprolactones, polymerizations (anionic, cationic, ring-opening mechanism) besides usage of catalyst like stannous octoate [2, 3] and aluminum alkoxides [4]. Those reactions were subjected to various reactions conditions including polymerization, time, temperature, catalyst (types and concentration) and different ratios of monomer to solvent. Changing one variable results in difference of molecular weight and polydispersity indices (PDI) that directly effects the mechanical as well biodegradable behavior of the PCL [5]. In solvents such as benzene (C_6H_6), carbon tetrachloride, chloroform, cyclohexanone, dichloromethane, toluene, 2-nitropropane, PCL has high solubility while it has lower solubility in acetone, acetonitrile, 2-butanone, dimethylformamide, ethyl acetate, and it has no affinity for dissolution in water, ethyl alcohol, diethyl ether and petroleum ether [2, 3, 6-11]. PCL emits semi crystalline nature at room as well human body normal temperature. Melting temperature (Tm) and glass transition temperature (Tg) of PCL is 60℃ and -60℃ respectively [12-15]. The amorphous regions of PCL are found to be in rubbery conditions at an amorphous temperature that provides PCL polymer chains free movement in body and hence its capacity of permeability for body metabolites enhances once replaced in body. In scaffolds preparations degradation behavior is the most important fact of consideration in tissue engineering applications of biomaterials, it is maintained in such a way that tissues generations rate is the same as the degradation rate of biomaterial used. Tissue growth rate is highly affected by it, if in any case, the biodegradation rate is slower or higher from it will hinder the connections of scaffolds and tissue as well resulting in delayed healing process [16].

PCL has a more stable nature because of less frequent ester linkages per monomer which results (when used as biomaterial) in longer degradation time via enzymatic hydrolysis in vivo. Normally the degradation of PCL takes place in time period of 2 to 3 years once used in biological medium of variable interstitial fluid [17-20]. Lipase enzymes (that is found in interstitial fluid) helps in its enzymatic degradation, by breaking the ester linkages of PCL [15, 21, 22]. PH of the medium (alkaline conditions speeds up its degradation compare to acidic) effect the degradation of PCL [23]. Degradation in presence of lipase occurs in the formation of 6-hydroxycaproic acid that is released in body fluid which is further undertaken by cells and results in 2-βoxidations to form 3-acetyl CoA molecules, which further metabolizes in the citric acid cycle and is disposed via urinary rout by filtration in renal tubules without any accumulation in body [17, 24].

Though biocompatibility of PCL is low its rubbery nature, adjustable biodegradability and easiness in blending it have been widely used in supporting devices mainly in hard tissues, scaffolds material, surgical sutures also in drug delivery on micro and nanoscale [2, 3, 18]. The surface roughness and hydrophilic nature of PCL tailored in it makes it suitable for tissue's interfacial characteristics [25, 26]. Food and Drug Administration (FDA) has approved a wide range of devices blended of PCL for human usage such as "Monocryl" sutures that are prepared by copolymerizing glycolides and ε-caprolactone in form of monofilament absorbable surgical suture (trademarked by Ethicon), "Capron or PCL in form of rods used in birth control process has been used for secretion of progestin