Gümüşhane University Journal of Science

GUFBD / *GUJS* (2024) 14(4): 1128-1137 doi: 10.17714/gumusfenbil.1508489 Research Article

Determination of biodegradation performance for fabricated by MEW chitosan/PCL composite stents with in vitro tests

MEW ile üretilmiş kitosan/PCL kompozit stentlerin in vitro testlerle biyobozunma performansının tespiti

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• Received: 01.07.2024 • Accepted: 10.09.20204

Abstract

Today, biodegradable implants have begun to become a serious alternative to permanent implant groups. Especially the development of polymer material technology can be an alternative to metallic medical instruments. An innovative manufacturing method for the fabricated of these polymeric implants is melt electrowriting (MEW). This innovative method, which emerged as a result of studies on the production quality of additive manufacturing technology, is used in products with smaller and more complex geometries, such as stents. It is anticipated that this method, which is particularly convenient for patient-specific implant models, will have an important place in the implant production market in the future. Within the framework of this perspective, in this study, a study was conducted on the polycarbolactone group using the MEW method. In order to improve the biodegradability character, biodegradability experiments of chitosan-doped stents were conducted in vitro. The degradation character of the samples subjected to immersion corrosion in two different media for 1, 7, 14 and 21 days was examined based on residual mass. It has been determined that chitosan reinforcement has a buffering effect and plays a retarding role on the degradation time. When the degradation rates were examined, it was determined that the polycarbolactone stent immersed in artificial body fluid for 21 days experienced the maximum mass loss of 1.6×10^{-2} gr. The value measured for this stent at the end of the first day was 5.8×10^{-4} gr. At the end of 21 days, the minimum loss was obtained for the chitosan-doped polycarbolactone stent in artificial body fluid (7.98×10^{-3} gr).

Keywords: Biodegradation, Chitosan, Melt electrowriting, Polycaprolactone (PCL), Stents.

Öz

Günümüzde biyobozunur implantlar kalıcı implant gruplarına ciddi alternatif olmaya başlamıştır. Özellikle polimer malzeme teknolojisinin gelişmesi metalik gruptaki tıbbi enstrümanlara alternatif olabilmektedir. İşte bu polimerik implantların üretimi için yenilikçi bir üretim metodu da melt electrowritingtir (MEW). Eklemeli imalat teknolojisinin üretim kalitesi üzerine yapılan çalışmalar sonucu ortaya çıkan bu yenilikçi yöntem stentler gibi daha küçük ve kompleks geometriye sahip ürünlerde kullanılmaktadır. Özellikle hastaya özel implant modeli için oldukça elverişli olan bu yöntemin gelecekte implant üretim pazarında önemli bir yere sahip olacağı ön görülmektedir. Bu perspektif çerçevesinde bu çalışmada da MEW yöntemi kullanılarak polikarbolakton grubu üzerine bir çalışma yürütülmüştür. Biyobozunur karakterinin geliştirilmesi amacıyla chitosan takviyesi yapılan stentlerin biyobozunurluk deneyleri in vitro ortamda gerçekleştirilmiştir. İki farklı ortamda 1,7, 14 ve 21 gün esas alınarak daldırmalı korozyona tabi tutulan numunelerin bozunma karakteri kütle kaybı esas alınarak incelenmiştir. Chitosan takviyesinin tampon etkisi göstererek bozunma süresi üzerinde geciktirici bir rol oynadığı tespit edilmiştir. Bozunma miktarları incelendiğinde, yapay vücut sıvısı içinde 21 gün bekletilmiş polikarbolakton stentin $1,6\times10^{-2}$ gr ile maksimum kütle kaybını yaşadığı tespit edilmiştir. 1. günün sonunda bu stent için ölçülen değer $5,8\times10^{-4}$ gr dir. 21 gün sonunda minimum kayıp yapay vücut sıvısı içinde kitosan takviyeli polikarbolakton stent için elde edilmiştir ($7,98\times10^{-3}$ gr).

Anahtar kelimeler: *Biyobozunurluk, Kitosan, Melt electrowriting, Polikarbolakton, Stents*

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1. Introduction

With the development of polymeric material technology day by day, the use of biodegradable implants has become widespread. They are especially preferred in the production of high-performance implants without repeated surgical interventions (Abbas, et al., 2024; Khan et al., 2023; Sammel et al., 2013; Song et al., 2022). They have begun to replace metallic alternatives for a wide variety of implant groups. They are involved in invasive interventions that will increase patient comfort thanks to their biodegradable structures in many sub-disciplines such as orthopedics, traumatology, cardiology and urology (Khan et al., 2023; Kim et al., 2022; Peng et al., 2024; Wen et al., 2024). The biodegradable stents, developed as a new alternative in the cardiovascular and urethral fields, have been the subject of important studies in the literature (Tie et al., 2020; Y. Wang et al., 2023; Wen et al., 2024). The proliferation of innovative approaches introduced recently indicates that there is a trend towards patient-specific processes for stent applications. Therefore, in vitro-based performance tests, where different patient profiles can be simulated, have become much more important in this sense.

Most of the biodegradable stents consist of polymer-based groups. One of the most important representatives of this group is polycaprolactone (PCL). It is an important alternative for stent groups that do not require high strength, especially due to its biodegradable ability, low cost, easy machinability and especially low melting temperature compared to other polymers. In addition, their ability to be shaped with many different manufacturing methods in a cost-effective manner provides significant advantages over metallic biomaterials. Looking at the literature, there are many papers on the development of PCL-based biodegradable stents. Especially studies on its biodegradable character by giving it a composite form attract attention (Ghalia & Alhanish, 2023; Ojha et al., 2023; Srivastava et al., 2024; X. Wang et al., 2024).

The application of innovative production techniques that can be used in this field together with the developed PCL-based composites increases the possibility of producing biodegradable stents in patient-specific forms. In this context, the use of additive manufacturing methods gives very successful results (Guerra et al., 2017; Puppi & Chiellini, 2020). One of the types in this group is melt electrowriting. It is a very high-performance method, especially for polymeric groups with precise geometry and low melting temperatures, such as stents. In addition, it is possible to produce stents with the desired biodegradable character in composite form in one go, without the need for extra processes such as coating. When the studies carried out in this context are examined; Somszor et al. produced stents composed of polycaprolactone and graphene oxide in different geometries using melt electrowriting (MEW) as an alternative to traditional coronary artery stents. They were able to make significant improvements to pure polycaprolactone, especially in mechanical terms. In addition, these groups, which can be produced in a patient-specific form, can be produced as composite structures without damaging cytocompatibility (Somszor et al., 2020). In another article, Brooks-Richards et al. produced scaffolds in tubular form using MEW. They have revealed that polyvinyl alcohol (PVA) and poly- lactic acid (PLA) structured fibers will be an important alternative in vascular, urological and gastrointestinal treatments as a result of designing them with different geometries (Brooks-Richards et al., 2022). Some studies in the literature have focused on increasing polymeric fiber quality with MEW. For example, in a study conducted with Du et al., he was able to produce Poly(ε-caprolactone) scaffolds (25×25 μm) with very high resolution with the MEW method (Du et al., 2024). Similarly, another study examining the control and effective parameters related to fiber solubility was conducted by Mieszczanek et al. It has been commented that fiber quality can be improved with real-time monitoring (Mieszczanek et al., 2021). The idea of producing composite fibers with the help of MEW and converting these fibers into stents with different textures is a relatively new field of study in the literature and is represented by a small number of studies.

In particular, producing patient-specific approaches with this model is a very new field of research. The addition of different oxide-based compounds, hydrogels and many different complex structures into the skeletal structure will change future medical equipment preferences with the MEW method (Xu & Du, 2023).

When viewed from this perspective, it is thought that the specific value of PCL-based chitosan-reinforced stents produced by the MEW method, which is the subject of the study, will be quite high. In addition, simulating biodegradation performances in vitro using two different media (Dulbecco's Modified Eagle Medium and Simulated Body Fluid) distinguishes the study significantly from the literature. In the studies in the literature, stent models produced using the MEW method are quite rare. Therefore, determining the advantages and disadvantages of this production method is a necessary research area. Whether it is specific

products or studies in the context of surface engineering, all will serve this purpose. Addressing this study method in a specific dimension will allow for the presentation of detailed analyses. The production of all types of implants in the biomaterial group and their development as an alternative to existing products are of great importance at this point. For this purpose, the samples were produced in stent geometry with the MEW method and then subjected to degradation tests, with separate measurements taken each day for a total of 1, 7, 14 and 21 days. In particular, the effect of chitosan on the degradation character was evaluated on samples with stent morphology.

2. Material and method

PCL (ESUN Polymorph) and chitosan (Fluka Analytical chitosan low-viscous) doped PCL (CHPCL) stents were produced by the MEW (Axolotl Biosystems, Axo MEW) method (Figure 1). PCL and CHPCL stents were produced by the MEW method, following the production conditions given in Table 1. The two groups of stents produced were subjected to FTIR analysis (Bruker VERTEX 70v) to determine their chemical composition. For morphological analysis of the produced stents, microscope images were taken from different regions (ZEISS Axio Scope A1). Before stent manufacturing, PCL or CHPCL was loaded into the MEW system in granular form. Then, the system was allowed to reach a stable temperature (150°C). After reaching a stable temperature, the printing process was started for the stent model prepared in CAD (Computer Aided Design) . After the printing process, the stent was separated from the rod body and was ready for the immersion corrosion test. Immersion corrosion tests were applied within the scope of in vitro experiments (Figure 2). Two different solutions were used and the chemical compositions of these solutions are given in Table 2. The stents were removed from the solutions were rinsed with distilled water and dried at room temperature. Mass losses were calculated.

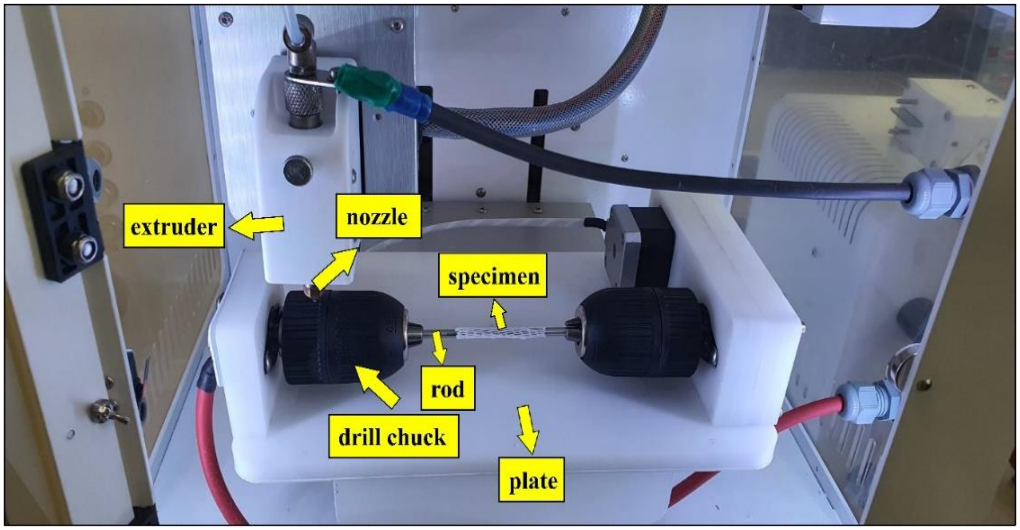

Figure 1. Component of melt electrowriting (MEW) system

Figure 2. Test setup for biodegration process

Table 1. Parameters of MEW

Extruder velocity (mm/s)	Rotation velocity (rpm)	Rod diameter (mm)	Air pressure (psi)	Melting temperature (°C)	Writing voltage (kV)	Chitosan amount (g)	PCL amount (g)
30	10	2	32	150	3	0.2	5

Table 2. Chemical compositions for SBF and DMEM (Xin et al., 2011)

Ion concentration	SBF	DMEM
Na^+ (mmol L^{-1})	142	127.3
K^+ (mmol L^{-1})	5.0	5.3
Ca^{2+} (mmol L^{-1})	2.5	1.8
Mg^{2+} (mmol L^{-1})	1.5	0.8
HCO_3^- (mmol L^{-1})	4.2	44.1
Cl^- (mmol L^{-1})	147	90.8
HPO_4^{2-} (mmol L^{-1})	1	0.9
SO_4^{2-} (mmol L^{-1})	0.5	0.8
Tris (g L^{-1})	6.069	-
Protein (g L^{-1})	-	-
Amino acid (g L^{-1})	-	1.6
Glucose (mmol L^{-1})	-	4.5
Hepes (g L^{-1})	-	5.96

3. Results

3.1. FTIR analyzes

Fourier transform infrared spectrophotometry (FTIR) with wavenumber from 40 to 4000 cm was used to analyze the chemical structure of PCL and CHPCL stent samples produced by MEW (Figure 3). In the FTIR graph of the PCL sample in Figure 3a, signals corresponding to asymmetric and symmetric groups, respectively, were observed with peaks at 2945.29 cm^{-1} and 2866.21 cm^{-1}. Additionally, peaks at 1238.29 cm^{-1} and 1163.07 cm^{-1} corresponding to asymmetric and symmetric C-O-C stretching were obtained. The sharpest absorption peak at approximately 1722.42 cm^{-1} indicates C=O stretching vibrations (Elzein et al., 2004; Malheiro et al., 2010). The peak obtained at 1294.23 cm^{-1} indicates C-C stretching vibrations, and the absorption peaks at 1043.48 cm^{-1} and 1043.48 cm^{-1} indicate C-O stretching vibrations (Ahmed et al., 2020; Kamalipooya et al., 2024). In the FTIR graph of the CHPCL sample given in Figure 3b, a wide peak in the range of 3000-3600 cm^{-1} was obtained due to the overlap of O-H and N-H stretching vibrations of the amine and amide groups of chitosan (Witecka et al., 2021; Zheludkevich et al., 2011). The peaks at 2945.29 cm^{-1} and 2864.14 cm^{-1} show C-H vibrations (Witecka et al., 2021). The peaks between 1540-1400 cm^{-1} indicate the amine groups of chitosan and are characteristic of chitosan. The peaks at approximately 1639.49 cm^{-1} and 1365.59 cm^{-1} represent the amide I and amide III bands of chitoson, respectively. Additionally, a small peak at 1062.77 cm^{-1} corresponds to the C-O stretching vibration of chitosan (Loperena et al., 2024).

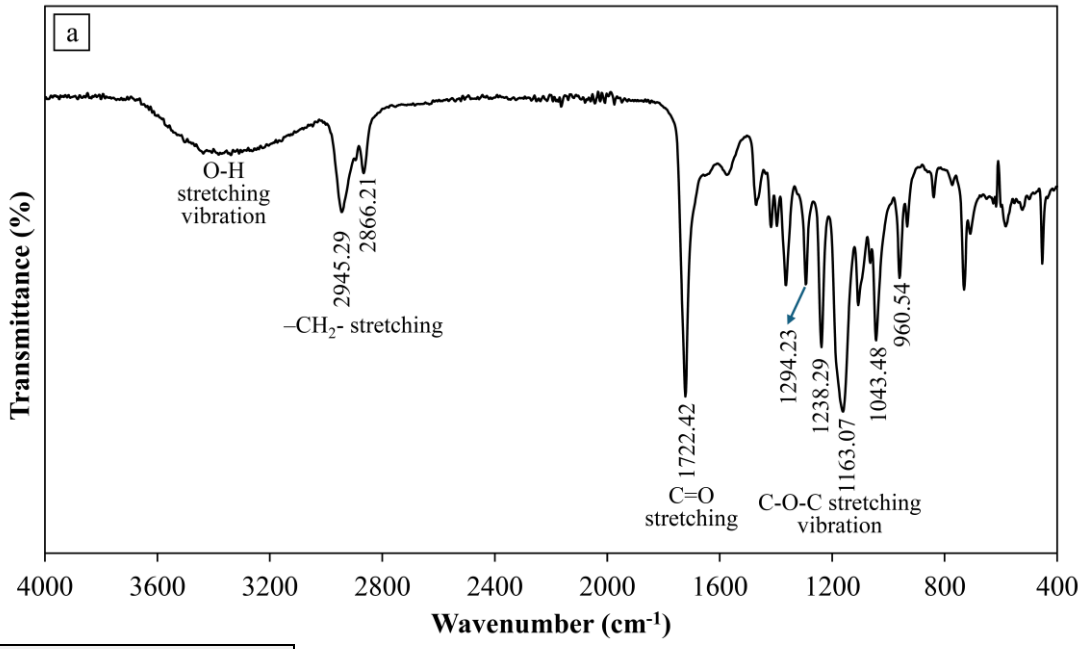

Figure 3 continued next page ▼

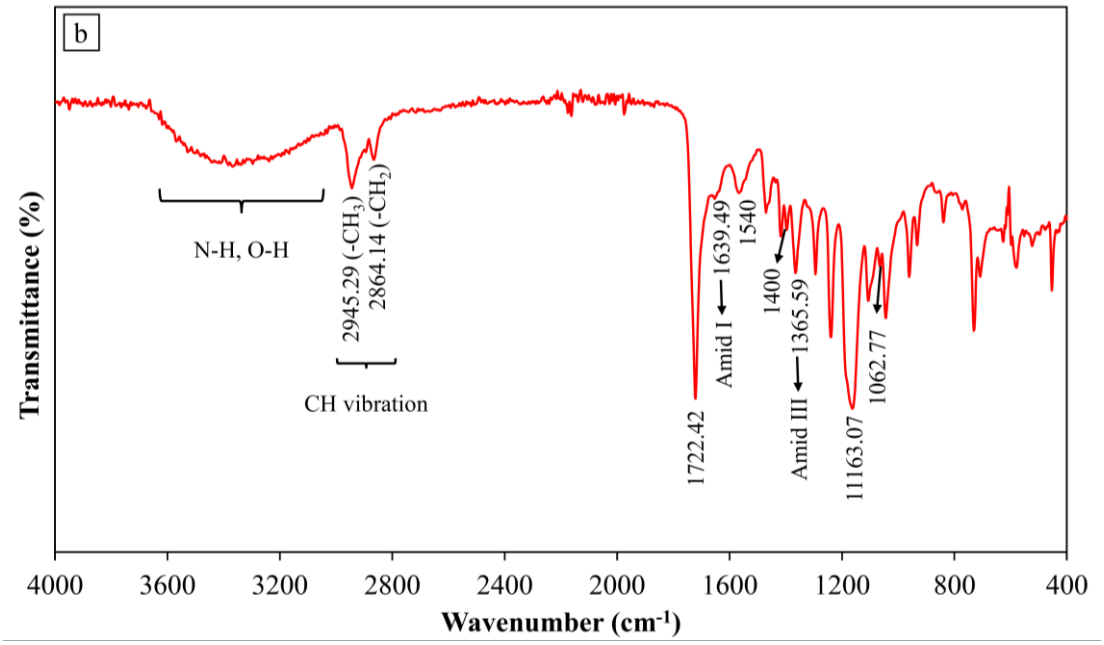

Figure 3. FTIR graph for PCL stent (a) and CHPCL (b).

3.2. Optical microscope images

Optical microscope images are given in Figure 4. Especially the difference in fiber structures and morphological changes are given in detail (Figure 4a and Figure 4b). In the PCL sample, peeling in a single fiber is clearly visible (Figure 4c and Figure 4e). This peeling is considered an important control mechanism on the degradation time. The gaps and fractures in this structure reduce the degradation time. The chitosan particles added to the molten PCL form on CHPCL surfaces have been added to the structure in a way that reduces the existing peeling during the cooling process (Figure 4d and Figure 4f). It was concluded that by reducing voids and fractures, it will provide a gradual increase in degradation time.

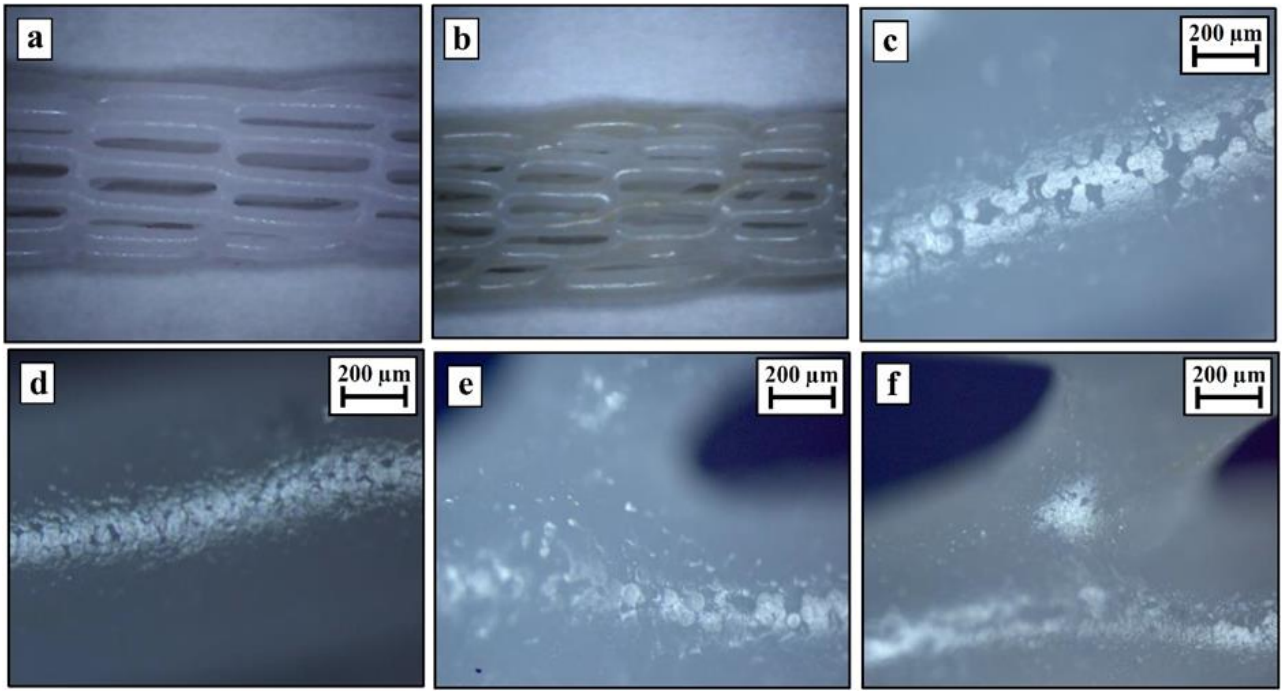

Figure 4. Optical microscobe image for PCL stent (a), CHPCL stent (b), PCL stent – 10x zoom (c and e), CHPCL stent – 10x zoom (d and f).

3.3. Immersed corrosion

PCL and CHPCL stents with a diameter of 2 mm and a length of 45 mm were immersed in 100 ml of SBF and DMEM solutions. Mass loss in stents was evaluated in direct proportion to the biodegradation period. Therefore, any intervention to prevent mass loss will increase the biodegradation time. Chitosan supplementation in CHPCL stents played an active role at this stage. As evidenced by the morphological change, the presence of chitosan increased the adhesion in the fibers and increased the degradation period both in more aggressive media (DMEM) and in SBF solution. Decomposition amounts due to mass loss following periods of 1, 7, 14 and 21 days are given in Figure 5. The effect of different ion concentrations could be examined in detail through the available solutions. In this context, as the time required for the degradation process increased, marginal changes in mass loss began to be observed. It is not possible to talk about an effective mass loss after the 1st day (Figure 5a). Significant mass changes began after 7 days (Figure 5b). The maximum mass loss occurred in the PCL sample in SBF (~ 0.00693 g). The decrease continued after 14 days (Figure 5c) and it is thought that the fiber breakage reached its maximum after 21 days (Figure 5d). At the end of 21 days, the largest degradation resulted in a loss of 0.01598 g. However, it was concluded that there was no change in the total stent geometry during this period. It can be said that the degradation rate of this environment is higher as a result of the higher aggressive ion density in SBF. It is thought that the inclusion of DMEM in the system will contribute to patient-specific stent interpretation. Characterization, especially in an environment with a high glucose rate, provides the opportunity to comment on the need for stents in such patients. It is obvious that such stent developments will offer innovative solutions for cardiovascular and urethral problems that may develop parallel to diabetic problems.

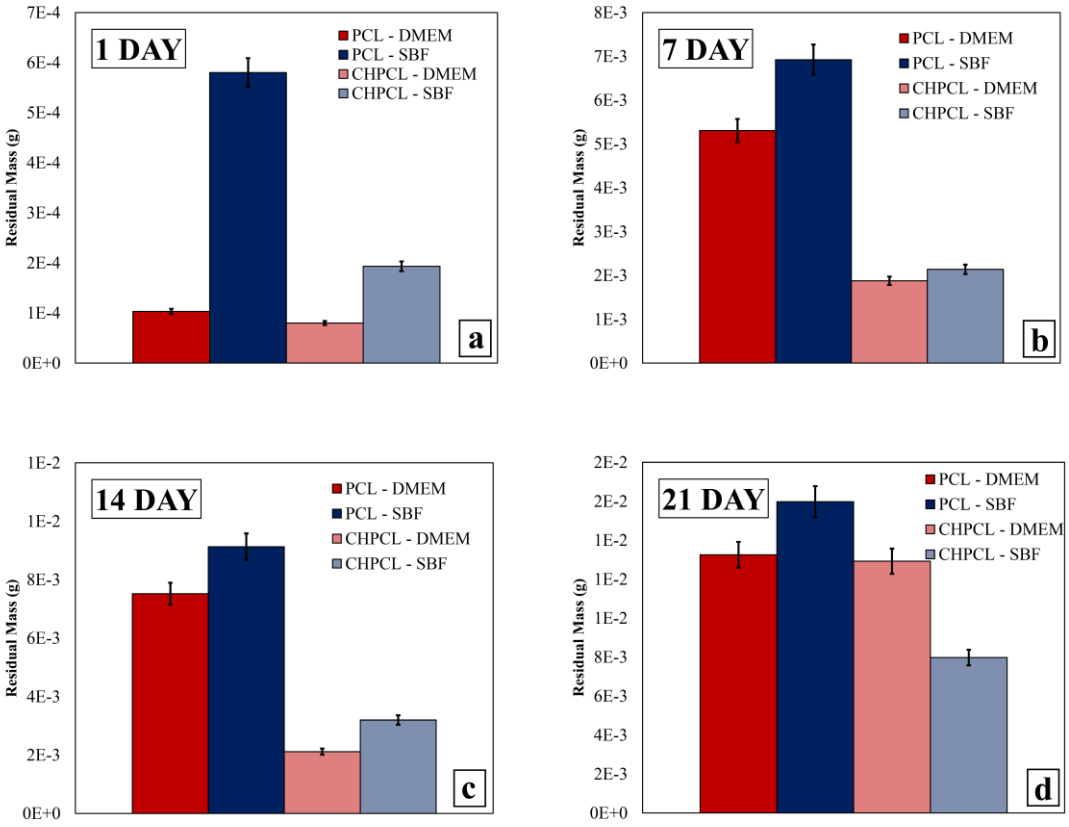

Figure 5. Immersed corrosion test results 1 day (a), 7 day (b), 14 day (c) and 21 day (d).

The morphological changes on the 21st day, when morphological changes after immersed corrosion reached their maximum, are shown in Figure 6. When the samples in DMEM are examined in Figure 6a and Figure 6b, it is clearly seen that especially solution residues started to accumulate on the fibers. It is seen that the PCL surface is exposed to much more intense corrosive damage under this condition. On the surface of CHPCL, both corrosive residue and damage are at lower levels. When the surfaces kept in SBF are examined, the damage for the PCL stent has gone as far as fragmentation (Figure 6c) and the damage development has started for CHPCL (Figure 6d). High deformation can be mentioned compared to DMEM solution.

The effect of chitosan particles on corrosion has thus been clearly demonstrated. In many studies in the literature, measures have been developed to increase electrochemical corrosion performance, especially by using chitosan-based coatings. It has been preferred both as a coating component in metallic biomaterials and as the main component of the biomaterial (Croisier & Jérôme, 2013; Kozusko et al., 2018; Zhang et al., 2021). In this context, despite the large number of studies, chitosan doped for biodegradable stents has been a very innovative approach. Further studies addressing not only corrosion performance but also other effects such as wear and tribocorrosion performance will be a great alternative for current stent technology. It can be applied not only in the cardiovascular area but also in regions where biodegradable stents are needed and contain metabolic activity.

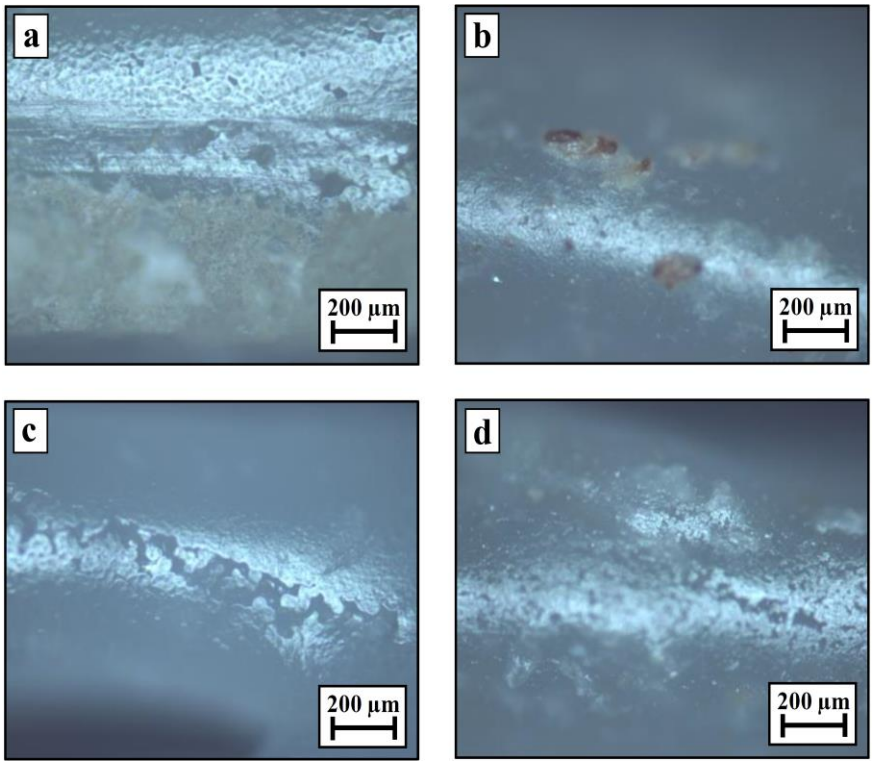

Figure 6. After immersed corrosion (21 days), optical microscobe image for PCL stent in DMEM (a), CHPCL stent in DMEM, PCL stent in SBF (c), CHPCL stent in SBF (d).

4. Discussion and conclusion

In this study, the biodegradation performances of stents consisting of two different groups (PCL and CHPCL) in two different environments (SBF and DMEM) were analyzed based on morphological and mass loss in certain periods (1, 7, 14 and 21 days) using the MEW method.

In particular, the morphological differences in the fiber structure of the stents produced in MEW were evaluated through an optical microscope. According to this evaluation, a more homogeneous and rigid formation was observed in chitosan-based fibers. This morphological development could be associated with the degradation character. The residual mass in in vitro experiments confirm this interpretation. The PCL stent in SBF solution was the sample with the highest mass loss observed after 21 days. Under the same conditions, the mass loss in the chitosan-doped sample is approximately 39 percent lower. In addition, more intense degradation was obtained in SBF than in DMEM under all experimental conditions. According to the degraded amounts, the minimum value was obtained from the CHPCL sample immersed in DMEM solution for 1 day (8×10^{-5} g). The maximum value was obtained as a result of the degradation of the PCL sample in SBF (1.6×10^{-2} g). For the stents left in DMEM solution for 21 days, the chitosan doped stents degraded 3.3×10^{-4} g less. This difference was 8×10^{-3} g for the SBF solution. In the literature, the combination of MEW and chitosan has focused more on scaffold production. However, in such studies, it has been stated that chitosan additive provides certain contributions to biodegradation and regeneration (Yoshida et al., 2021). As a specific biomaterial, chitosan-based structures have been constructed with MEW to reinforce cartilage tissue and eliminate degeneration in this region (Han et al., 2021). However, there is no similarity to the purpose of the

current study. Again, from a different perspective, studies on controlled drug release were conducted with polycaprolactone membranes produced with MEW (Martins et al., 2024; Xu et al., 2022).

Acknowledgement

As the author of this study, I would like to thank Atatürk University East Anatolia High Technology Application and Research Center (DAYTAM) and Erzurum Technical University High Technology Application and Research Center (YUTAM) for their assistance in the characterization of the materials.

Author contribution

The author contributed to all sections. The author read and approved the last version of the manuscript.

Declaration of ethical code

The author of this article declares that the material and the methods used in this study do not require ethical committee approval and/or a special legal permission.

Conflicts of interest

The author declares that he has no conflict of interest.

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