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Araştırma Makalesi / Research Article

Malva neglecta Leaves Extract / Biodegradable Diblock Copolymer Blend Biocomposites: Physicochemical and Antioxidant Properties

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Keywords
M.neglecta; poly ε-caprolactone; shape memory polymer; biocomposite; swelling degree; antioxidant activity

Abstract

In this study, it is aimed to prepare a 1:1 ratio PLA blend with PEG-*b*-PCL diblock copolymer, which is intended to be used as a drug release and biomaterial, and to obtain a biocomposite film with *M.neglecta* extract in different ratios. The obtained biocomposite films were first characterized by the ATR-IR spectrum and the characteristic functional group signals of the polymers were determined. The thermal analysis results show that the plant extract reduces the thermal stability of the polymer blend. Calorimetric measurements can be interpreted as plant-doped biocomposite films decrease the T_g temperature of the polymer blend, that is, increase the interchain free volume of the polymers. It was observed that swelling degree and moisture content of the plant treated polymer blend biocomposite films decreased with increasing plant percentage, while water solubility increased. It was observed that the plant extract slightly improved this feature of the PEG-*b*-PCL/PLA blend film, which showed shape memory. Due to the phenolic compounds in the structure *of M. neglecta*, it increased the antioxidant activities of the biocomposite films by adding it to the polymer blend.

Malva neglecta Yaprak Özü / Biyobozunur Diblock Kopolimer Karışım Biyokompozitleri: Fizikokimyasal ve Antioksidan Özellikler

Anahtar kelimeler
M.neglecta; poli ε-kaprolakton; şekil hatırlamalı polimer; biyokompozit; şişme derecesi; antioksidant aktivite

Öz

Bu çalışma ilaç salınımı ve biyomalzeme olarak kullanılması hedeflenen PEG-*b*-PCL diblok kopolimeri ile 1:1 oranında PLA blendinin hazırlanarak farklı oranlarda *M.neglecta* ekstraktıyla biyokompozit film eldesini hedeflenmektedir. Elde edilen biyokompozit filmleri öncelikle ATR-IR spektrumu ile karekterize edilmiş ve polimerlerin karekteristik fonksiyonel grup sinyalleri belirlenmiştir. Termal analiz sonuçları, bitki ekstraktının polimer blendin termal kararlılığını azalttığını göstermektedir. Kalorimetrik ölçümler ise bitki katkılı biyokompozit filmlerin, polimer blendin T_g sıcaklığını düşürdüğü yani polimerlerin zincirler arası serbest hacmini arttırması şeklinde yorumlanabilir. Bitki ile etkileştirilmiş polimer blend biyokompozit filmlerinin şişme derecesi ve nem içeriğinin artan bitki yüzdesiyle azaldığı görülürken, sudaki çözünürlüğünün ise arttığı görüldü. Şekil hatırlama özelliği gösteren PEG-*b*-PCL/PLA blend filminin bu özelliğini bitki ekstraktının da az da olsa iyileştirdiği görülmüştür. *M. neglecta* yapısında bulunan fenolik bileşiklerden dolayı, polimer blende katkılanmasıyla, biyokompozit filmlerin antioksidant aktivitelerinin artmasını sağlamıştır.

1. Introduction

Malva neglecta is a self-growing perennial herbaceous plant from the Malvaceae family. It is widely used both medicinally and as food (Güder 2008; Ingole et al. 2020). This traditionally used herb contains alkaloids, tannins, saponins, hydroxycinnamic acids, phenolics, organic acids, protein, fats and (Hassanpour Amnieh et al. 2018; Pinela et al. 2016). Roots, stems, leaves, flowers and seeds are used medicinally (Aziz et al. 2016). Due to its rich content, it is especially beneficial as

soothing plants in inflammation, wound healing, urinary, digestive and respiratory systems (Al-Snafi 2019).

Biodegradable polyesters such as poly lactic acid (PLA) and poly ε-caprolactone (PCL) have received great attention over the past two decades (Mennati et al. 2021). PLA is a versatile biodegradable polymer derived from renewable resources such as corn and sugar beet (Lipinsky and Sinclair 1986; Pekdemir, S. et al. 2022). The very good shape memory behavior of PLA is one of the reasons why it was preferred in this study (Leonés et al. 2019; Yilmaz et al. 2023). PCL is a linear chain polyester with hydrophobic properties, is biocompatible and has low immunogenicity. Due to these properties, it has been preferred in many recent studies. Approved by the Foods and Drugs Administration (FDA), PCL is a highly advantageous polymer in drug delivery systems (Brandt et al. 2019; Labet and Thielemans 2009; Sinha et al. 2004). Especially in studies such as drug delivery systems, situations where lipophilic property is a disadvantage may occur. In this case, the presence of hydrophilic molecules is needed to maintain the hydrophilic and hydrophobic ratio balance. Thus, a promising method has been developed that can change the physical and chemical properties by giving the polymer structure an amphiphilic property by the interaction of PCL and hydrophilic molecules (Li and Tan 2014; Piazza et al. 2018).

Polyethylene glycol (PEG), which has hydrophilic properties, is among the most preferred polymers due to its biological compatibility, water solubility and non-toxicity (Grossen et al. 2017; Ozer et al. 2017). At the same time, another reason why PEG is preferred is that it is a very good plasticizer (Pekdemir et al. 2023). For this reason, it has been widely used in food, pharmaceutical and medical sectors, cosmetic products and many areas of industry for many years (Pekdemir et al. 2023). PCL-*b*-PEG copolymer is produced by adding PEG chains to PCL with suitable solvents (Du et al. 2007; Fairley et al. 2008). Since the hydrophilic part of the amphiphilic block copolymers is PEG and the hydrophobic part is PCL, it is possible to show the targeted effect in medical applications and especially in drug release studies (Huang et al. 2015). In this way, the curative effect of the drugs can be increased and the toxicity to normal cells can be reduced (Dash and Konkimalla 2012; Woodruff and Hutmacher 2010).

This study aimed to produce an innovative material for drug release and medical applications, which is compatible with the environment and health, with the interaction of biodegradable polymers with plant extract. For this reason, PCL-*b*-PEG/PLA biocomposite films treated with *Malva neglecta* plant extract were prepared. The films were characterized by ATR-IR, TGA, DSC. In addition, shape memory effects and physical properties of biofilms doped with blend and plant extract were also investigated.

2. Material and Method

2.1 Material

The ε-caprolactone monomer, stannous octate [$Sn(oct)_2$] catalyst and poly ethylene glycol (PEG) initiator were purchased from Sigma-Aldrich. High molecular weight poly lactic acid (PLA) was obtained from ABG filament, Ankara, Turkey. Toluene, hexane and chloroform (purity≥99.9) solvents were purchased from Merck and used as received. In addition, the ultrasonic homogenizer that ensures the homogeneity of the composites was supplied from Fytronix company, Turkey.

2.2 Preperation of Malva neglecta ethanolic extract

Firstly, the collected plant was dried in a place out of the sun and ground into powder with the help of a blender**.** 10 g powdered plant was placed in 100 mL absolute ethanol and mixed for a while in a magnetic stirrer and then put in a shaker incubator at 35 °C for 24 hours (Pekdemir et al. 2020). After the incubation, the plant solution was filtered with Whatman filter paper no. 1 and the process was continued until the solvents were completely removed in the vacuum evaporator at 40 °C. The plant extract obtained with ethanol solvent was kept at -20 °C until experimental studies to be used.

2.3 Synthesis of PEG-b-PCL copolymer

Synthesis of PEG-*b*-PCL diblock copolymer was carried out by ring-opening polymerization under

conditions previously mentioned in the literature (Angarita et al. 2020; Arias et al. 2021). During the synthesis, ε-caprolactone was used as monomer, Sn(oct) as catalyst and PEG as initiator. 10 mmol ε-caprolactone was placed in a round bottom flask and stirred in 12 mL of toluene on a magnetic stirrer. Then, 0.25 mmol PEG and 2 drops $Sn(oct)_2$ were added to the reaction flask, respectively. The reaction was carried out under magnetic stirring and an inert atmosphere at 110 °C for 24 hours. The block copolymer was precipitated in ice-cold hexane and dissolved in chloroform. The solution precipitation process was repeated 3 times, thereby removing unreacted monomers and catalyst residues.

2.4 Preperation of (PCL-b-PEG)/PLA Blends

1:1 ratio by weight (PCL-*b*-PEG)-PLA blend was obtained by solvent casting method. For this purpose, 0.25 g (PCL-*b*-PEG) was dissolved in 5 mL chloroform by mixing in a magnetic stirrer. Then, 0.25 g of PLA was added and the mixing of the polymer blend was continued for 3 hours. The polymer blend solution, which was carefully poured into the Petri dish, was dried in a vacuum oven at 40 °C for 24 h.

2.5 Preperation of (PCL-b-PEG)-PLA blend / Malva neglecta composites

(PCL-*b*-PEG)-PLA blend composites were prepared by using different ratios of *M.neglecta* extract. To prepare the polymer blend composite film containing 10% *M.neglecta* plant extract initially, 0.05 g was weighed and mixed in 5 mL of chloroform in a magnetic stirrer. 1:1 ratio (PCL-*b*-PEG)-PLA blend solution was prepared in a separate beaker and added to the plant extract solution. The polymer blend / plant extract composite solution, which was stirred for 2 hours on a magnetic stirrer, was briefly dispersed in the ultrasonic homogenizer and poured into the petri dish. Composites were prepared with 25% *M.neglecta* extract using the same method. The composite solutions poured into the Petri dish were dried in a vacuum oven at 35 °C for 24 h, and thus (PCL-*b*-PEG)-PLA blend composite films containing *M. neglecta* were obtained (Figure 1).

Fig 1. (PCL-b-PEG)/PLA blends with different ratios of *M.neglecta* extract

2.6 Moisture content, swelling degree, and water solubility

The initial weight (W_O) of the 2x2 cm cut film samples was taken to determine the moisture content (M_t) of the biocomposite membranes. Afterwards, it was dried to a constant weight at 100 ◦C and weighed again (W_t) (Zhang et al. 2019) and then the following equation was applied:

$$M_t(\%) = (W_O - W_t)/W_O \times 100 \quad (1)$$

Studies to determine the water solubility and swelling degree were carried out simultaneously. The initial weights (W_d) of the 2x2 cm cut film samples were taken. The samples were then placed in containers filled with distilled water and shaken for 24 hours. After that, the samples were removed from the water, dried with clean filter paper and weighed (W_{sd}). Swelling degrees were calculated using Equation 2 (El-Hefian et al. 2010). Afterwards, the samples were dried to a constant weight at 100 ◦C and re-weighted (W_s). Water solubility was also calculated using Equation 3 (Liu et al. 2017)

$$Swelling\ degree\ (\%) = (W_{sd} - W_d)/W_d \times 100 \quad (2)$$

$$Water\ solubility\ (\%) = (W_d - W_s)/W_d \times 100 \quad (3)$$

2.7 Antioxidant Activity

It is important to investigate the antioxidant properties of biocomposites prepared with organic materials (Akhtar et al. 2012; Vieira et al. 2022). Therefore, the antioxidant activity of plant-based biocomposite membranes was tested according to the method of Yang and co-workers (Yang, J. et al. 2019). According to this method, samples were transferred into tubes containing 4.0 ml of methanolic 2,2-Diphenyl-1-picrylhydrazyl (DPPH) (0.1 M) solution and incubated for 60 minutes at 25 ◦C in the dark. The absorbance of the samples was

then recorded at 517 nm by a UV spectrophotometer. All analyzes were performed in 3 repetitions. The following equation 4 was used to calculate the antioxidant activity.

$$Antioxidant\ activity\ (\%) = \left[\frac{A_c - A_b}{A_c}\right] \times 100 \qquad (4)$$

A_c is the absorbance of the DPPH solution without sample added, and A_b is the absorbance of the DPPH solution remaining in the sample tube.

3. Results

3.1 ATR-IR Results

ATR-IR spectra of pure polymer blend and composites prepared with plant extract are shown in the figure 2. The signals occurring at 2881 cm^{-1} and 2948 cm^{-1} belong to –CH symmetrical and asymmetric stretching vibrations, respectively (Pekdemir et al. 2023). The very sharp and strong signal seen at 1750 cm^{-1} is attributed to the characteristic C=O stretching vibration of PLA (Niksarlıoğlu et al. 2023; Yang et al. 2023). The signal belonging to the C=O stretching vibration of the PCL seen in the shoulder shape was seen at 1720 cm^{-1} (Taşgin et al. 2023). The absorption peaks at 1357, 1182, 1086 and 1045 cm^{-1} show –CH bending vibration, C-O-C symmetrical and asymmetrical stretching vibration of ester groups and O-H bending vibrations, respectively (Ghafouri et al. 2022; Yang et al. 2020). For composites prepared with the *M.neglecta* extract, the spectra are similar to that of the blend and show characteristic bands of PLA and PCL. Unlike these signals, it was observed that the signal at 1622 cm^{-1} increased with increasing plant extract ratio, which can be attributed to the presence of a deformed aromatic ring, amino acids and flavonodes in the structure of the plant (Mabasa et al. 2021).

3.2 Thermal Analysis

In Figure 3, calorimetric measurements of pure (PCL-*b*-PEG)-PLA blend and composites containing *M. neglecta* extract in different ratios were performed with Perkin Elmer Differential Scanning Calorimetry (DSC) under N_2 gas at a flow rate of 10 °C/min. DSC curves showed a very strong signal around 60°C. It is known that this signal belongs to the melting temperature (T_m) of PCL and PEG and the glass transition temperature (T_g) of PLA, and they are all in the same region (Gürler et al. 2023; Pekdemir et al. 2023; Yilmaz et al. 2023). In composites, the decrease of this signal from 57.7 °C to 55.7 °C as the plant ratio increases can be interpreted as the increase in the distance between the polymer chains of the plant extract, that is, the free volume Pekdemir et al. 2023). The signal that appeared at 180 °C belongs to the T_m temperature of PLA and it was seen that the plant did not affect this temperature much (Bijarimi et al. 2016).

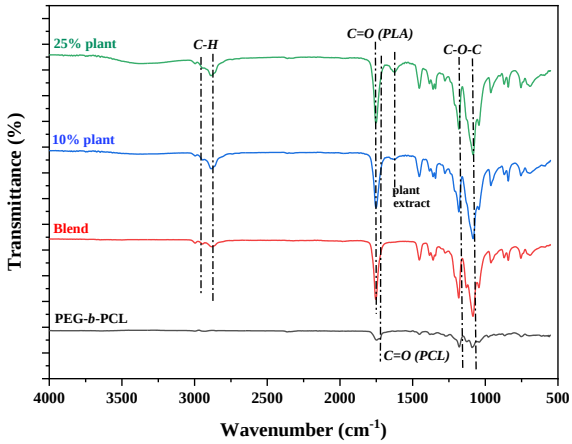

Fig 2. ATR-IR spectra of (PCL-*b*-PEG)-PLA blend/*M. neglecta* composites

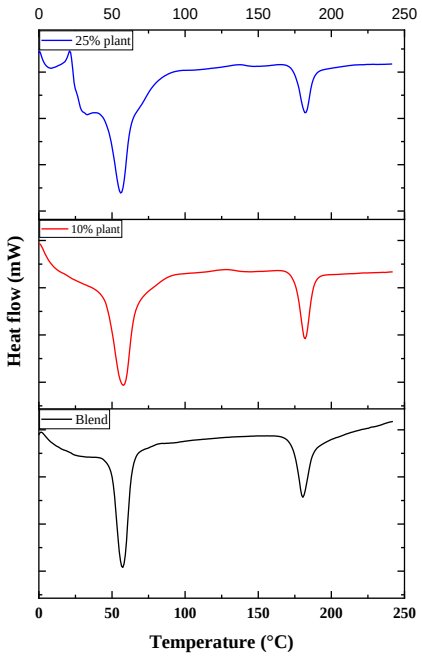

Fig 3. DSC curves of (PCL-*b*-PEG)-PLA blend/ *M. neglecta* composites

The change in mass loss of polymer blend composites was investigated with Schimadzu TG-50 under N_2 gas with a flow rate of 10 °C/min and The change in mass loss of polymer blended composites was investigated with Shimadzu TGA-50 under N_2 gas at a flow rate of 10 °C/min and the obtained TGA curves were shown in Figure 4. In the TGA curve of the (PCL-*b*-PEG)-PLA blend, it was observed that the initial decomposition temperature (T_i) was 172 °C and the degradation took place in a single step. After the *M.neglecta* extract was added, it was observed that the composites underwent a two-stage degradation and the T_i values decreased. This situation can be interpreted as the plant lowering the thermal stability of the polymer (Pekdemir et al. 2021; Pekdemir et al. 2022). Residue amounts of pure polymer blend and composites containing 10% and 25% plant extract at 500 °C were determined from the TGA curves as 4.5, 5.7 and 9.3, respectively.

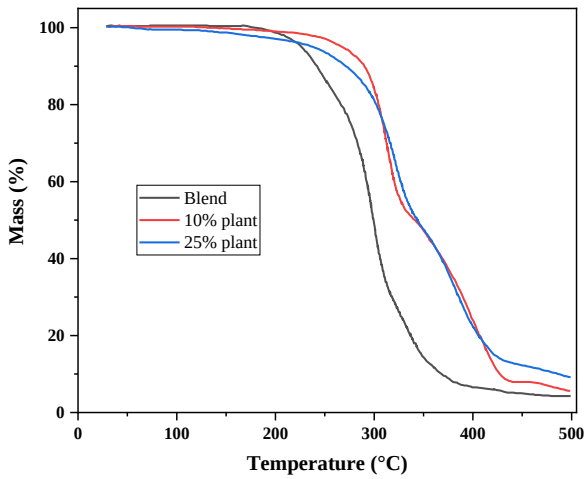

Fig 4. TGA curves of (PCL-b-PEG)-PLA blend/*M. neglecta* composites

3.3 Moisture content, swelling degree, and water solubility

Moisture content, water solubility, and swelling degrees of polymer blends and biocomposites with plant extract are shown in Figure 5. While the moisture content of the polymer blend film was higher, the moisture content of the films decreased with the addition of plant extract. The fact that the presence of OH and amino groups in the plant content can reduce the bonding presence of water molecules by interacting with the polymer, which explains the result we obtained (Souza et al. 2017). By looking at the water solubility and swelling degrees of the biocomposites, their water resistance and stability in water were determined. As shown in Figure 5, an increase in the water solubility of the films was observed with the addition of plant extract. It is seen that the water solubility of the biocomposite containing 10% plant is equivalent to the blend, while there is a significant increase in the water solubility of the biocomposite containing 25% plant extract. This is thought to be due to the weak interaction between the functional groups of the polymer blend and the plant extracts. In addition, in terms of swelling degree, it is seen that polymer blend film exhibits higher swelling values than films containing plant extracts (El Mouzahim et al. 2023). Similar results were found in studies with chitosan combined with plant extract (Souza et al. 2017).

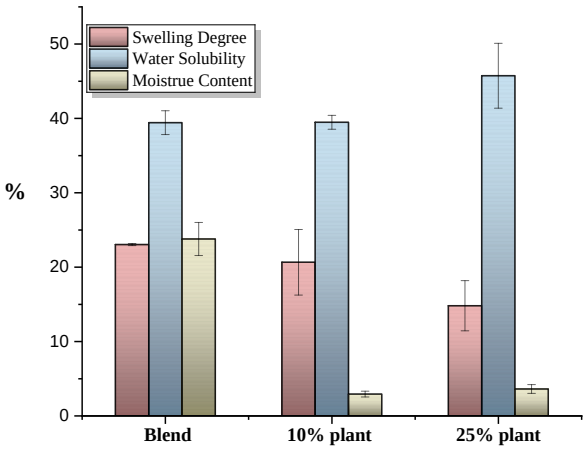

Fig 5. Moisture content, water solubility and swelling degree of (PCL-*b*-PEG)-PLA blend/*M. neglecta* composites

3.4 Shape memory Property

After doping the plant extract on the blend prepared with shape recovery polymers PLA and PCL-*b*-PEG, it was examined how it affected these properties (Figure 6). Pure blend and composite materials containing 20% plant extract were cut into a straight strip. The cut strip samples were spiralized at a temperature above their T_g. It was observed that they kept this temporary shape when left to room conditions. Then, it was determined that the samples, which were brought

to a temperature above T_g, kept their old strip shape and returned to this shape. One of the remarkable features was that the plant extract improved the shape memory property of the polymer blend (Pekdemir et al. 2022).

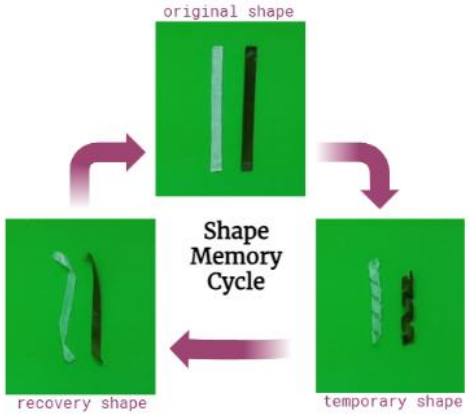

Fig 6. Shape memory cycle of (PCL-*b*-PEG)-PLA blend/*M. neglecta* composites

3.5 Antioxidant Activity

The antioxidant abilities of the samples were tested with the DPPH radical capture method, and the DPPH radical scavenging activity of biocomposite membranes containing *M.neglecta* plant extract is shown in Figure 7. It is thought that the good antioxidant activity of *M.neglecta* is caused by the phenolic components in its content, and this is due to the electron transfer or hydrogen donation of the hydroxyl groups in its structure to free radicals (DEVECİ et al. 2016; Khalid and Saleem 2018). As seen in figure 7, it was determined that the DPPH radical scavenging activity of the blend without the plant extract was significantly low, whereas the biocomposite membranes gained a certain DPPH radical scavenging capacity with the inclusion of the plant extract, and even this antioxidant activity increased with the increase of the plant content. BHT was used as a positive control. It was observed that the biocomposite containing 25% plant extract had a good antioxidant activity compared to the control.

4. Conclusion

PEG-*b*-PCL/PLA blend biocomposite films prepared by using *M.neglecta* extract at different ratios were prepared by solution casting method. When the ATR-IR spectra of the prepared biocomposite films were examined, the C=O stretching vibration, which is the characteristic signal of PLA and PCL, was seen at 1750 cm^{-1}. It was seen in the DSC curves that the decrease of the signal belonging to the T_g of PLA at 57.7 °C and T_m of PCL to 55.7 °C can be interpreted as the increase in the free volume between the polymer chains of the plant extract. The fact that *M.neglecta* extract reduces the thermal stability of the polymer blend can be explained by the decrease in T_i value.

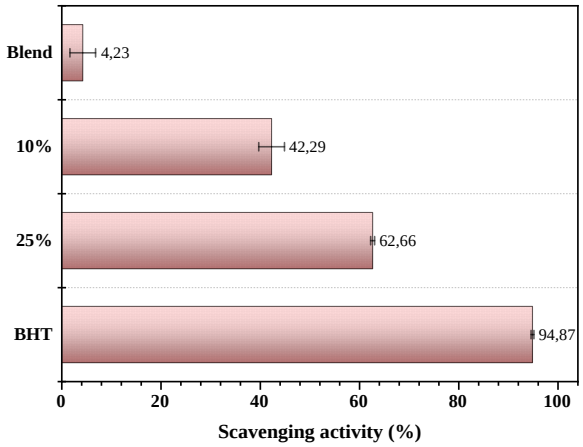

Fig 7. DPPH radical scavenging acitivty of (PCL-*b*-PEG)-PLA blend / *M.neglecta* composites

Since the presence of hydroxy and amine groups in the structure of the plant would not allow the bonding of water molecules, the plant extract reduced the moisture content of the polymer blend. Likewise, it was observed that the swelling degrees of polymer blend films doped with plant extract were lower. However, due to the weak interaction between the functional groups of the polymer and plant molecules, it was determined that the water solubility of the polymer blend increased with the increasing percentage of the plant and reached up to 46 %. It was concluded that when the plant extract was added to the blend, which consists of polymers with shape memory properties, this property was slightly improved. Finally, when the DPPH antioxidant capacities of biocomposites are examined, the fact that the biocomposite film containing 25% *M.neglecta* extract contains 62.66 % radical scavenging activity can be interpreted as showing an antioxidant activity close to BHT control.

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