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IR spectroscopy, thermal characterization and X-ray diffraction of Cd microparticles doped PLA/PHA composite films

Mustafa Ersin Pekdemir[a]*, Sibel Selçuk Pekdemir[a], Ahmet Yusuf Kavum[a] and Sedanur Altun[a]

[a]*Polymer and Biomaterials Research Laboratory, Department of Chemistry, Faculty of Science, Fırat University, Elazığ, Turkey*

**Corresponding author: E-mail: epekdemir@firat.edu.tr*

ABSTRACT

In this study, shape-memory and biodegradable poly lactic acid (PLA) and poly hydroxy alkanoate (PHA) were mixed in a 1:1 ratio and films were obtained by solvent casting method. Then, cadmium (Cd) microparticles were added to the PLA/PHA blend at different rates and the composite films were prepared using the same method. PLA/PHA/Cd composite films were characterized by Attenuated Total Reflection-Infrared (ATR-IR) spectroscopy, Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD). Finally, in the study, the crystallinity values obtained from the XRD patterns of the pure blend film and the composite films were compared.

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1. Introduction

Nanotechnology is an exciting area of scientific and economic growth that encompasses many areas of science and technology, and holds great promise. Nanoscience attempts to study materials at the nanometer level (0.1–100 nm in diameter) [1]. Applications of nanotechnology change the fundamental physical and chemical properties of conventional materials because the reduction of material size to the nanometer level leads to the formation of new materials with unique electrical, optical, and mechanical properties [1].

Nanoparticles (NPs) have a wide range of uses in various research areas, from analytical chemistry and environmental science to medicine, agriculture and pharmaceutical industry. This is due to the unique properties of NPs and the innovations they offer to such applications [2].

Polylactic Acid (PLA) and polyhydroxyalkanoate (PHA) are biotechnological polymers that were formed as alternatives to petroleum-based polymers, and these polymers offer a rapidly growing and attractive market as alternatives to petroleum-based polymers [3].

PLA is a biodegradable aliphatic polyester produced from edible corn starch and lactic acid derived from sugar cane. The glass transition temperature of PLA, a semi-crystalline polymer, was determined as 67 °C, while its melting temperature was determined as 180 °C [4]. PLA has many attractive properties, such as biocompatibility, high strength, hardness, and thermoplasticity, but it has low impact resistance. It is often used in extensive packaging applications because it is commercially available and cost-effective. It is also used in the transportation, agriculture, biomedical, textile, and electronics sectors. Other uses include biomedical sutures, bone screws and tissue engineering [5].

Polyhydroxyalkanoates (PHAs) are polyesters that accumulate as residues in various bacteria. These bacterial polymers can exhibit properties ranging from hard and brittle plastics to rubber-like materials. Due to their inherent biodegradability, PHAs are considered an attractive option for use in specialty and commercial products as non-polluting plastics and elastomers [6]. The mechanical properties and biocompatibility of PHA can be modified by further processing, modification or combining with other polymers, enzymes and inorganic materials. This allows PHA to be used in a wider range of applications [7].

Blending of polymers allows obtaining new materials with improved properties. The properties of the blends can be adjusted by selecting the appropriate polymer and changing the preparation conditions. In the literature, PLA and PHA blends have generally been studied by solvent casting method, but studies on their

preparation and characterization by melt mixing are limited [3].

Considering the previous studies on cadmium (Cd), FTIR spectra were used to determine the change in functional groups due to the presence of cadmium ions in the study conducted by NB Nanda Prakash et al. on the AC electrical conductivity of $CdCl_2$ doped PVA polymer electrolyte [8]

In a study conducted by M. Baraker et al., it was revealed that the $CdCl_2$ doped PVA-PVP sample had greater thermal stability compared to the undoped PVA-PVP blend [9].

There is another study titled "UV irradiation induced microstructural changes in $CdCl_2$ doped PVA–PVP blend" by M. Baraker and his team, where darkening was observed from 5.4 to 12.1 wt% in $CdCl_2$ doped samples when $CdCl_2$ doped polymer blend films were exposed to UV light at 254 nm wavelength [10].

This study aims to prepare PLA/PHA blend films with a weight ratio of 1:1 by solvent casting method. Then, Cd microparticles doped to the PLA/PHA blend solution at different ratios and PLA/PHA/Cd composite films will be obtained. The obtained composite films were characterized by Attenuated Total Reflection-Infrared spectroscopy (ATR-IR), Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD).

2. Material and Method

2.1. Materials

Poly lactic acid (PLA) and Poly hydroxyl alkanoate (PHA) were supplied by Türkiye ABG filament company. Cadmium (Cd) powder (purity: 99.99%) was purchased from Nanografi Co. Ltd. HPLC grade chloroform was purchased from MERCK to dissolve the polymers during the preparation of the films.

2.2. Preparation of PLA / PHA blend film

0.25 g PLA was added into a 25 mL beaker and after it was completely dissolved in 5 mL of chloroform, 0.25 g PHA was added. After the prepared blend was completely dissolved, the solution was poured into a petri dish using the solvent casting method and kept in the oven at 40 °C for 24 hours until the solvent was completely removed. At the end of this period, the PLA/PHA blend film was obtained.

2.3. Preparation of PLA / PHA / Cd composite film

Firstly, composite films were prepared using 1% cadmium microparticles. For this purpose, 0.005 g Cd microparticles were placed in a 25 mL beaker and dispersed in 5 mL of chloroform in an ultrasonic homogenizer for 1 hour. Meanwhile, 0.25 g PLA and 0.25 g PHA were mixed in 5 mL of chloroform in another beaker using a magnetic stirrer to ensure complete dissolution of the polymers. At the end of 1 hour, the PLA/PHA polymer blend was added to the Cd solution and dispersed in an ultrasonic homogenizer for another 15 minutes. The PLA/PHA solution containing Cd was poured into a petri dish using the solvent casting method and dried at room conditions until the solvent was completely removed and then in an oven at 40 °C for 24 hours. PLA/PHA blend composite films containing 5%, 10% and 20% Cd microparticles were prepared using the same method.

2.4. Characterization techniques

ATR-IR spectra of PLA/PHA/Cd composite films were performed with Attenuated total reflection (ATR) mode of an FTIR (Perkin Elmer Spectrum 100) in the wavenumber range of 400-4000 cm^{-1}. Thermal properties of the composites were measured by a Hitachi STA 200 thermogravimetric analyzer under N_2 gas at a heating rate of 10 ºC/min. The surface morphologies of Cd-doped PLA/PHA composite films were examined by LEO-EVO 40 Scanning Electron Microscope (SEM). XRD patterns of composite films were performed with RİGAKU brand Mnex 600 device.

3. Results and Discussions

3.1. ATR-IR

ATR-IR spectra of pure PLA/PHA blend and composite films containing different amounts of Cd microparticles are given in Figure 1. The double signals seen at 2995 cm^{-1} and 2946 cm^{-1} in all spectra were attributed to the aliphatic –CH stretching signals of PLA and PHA [11]. The sharp and strong signal seen at 1752 cm^{-1} belongs to the characteristic ester carbonyl (-C=O) of PLA [12, 13]. The signal seen at 1721 cm^{-1} is the –C=O signal of PHA. C-O-C symmetric and asymmetric stretching vibrations appeared at 1080 cm^{-1} and 1180 cm^{-1}, respectively [14]. Signals indicating the amorphous phase of PLA were observed at 870 cm^{-1} and the crystalline phase of PLA were observed at 754 cm^{-1} [15, 16].

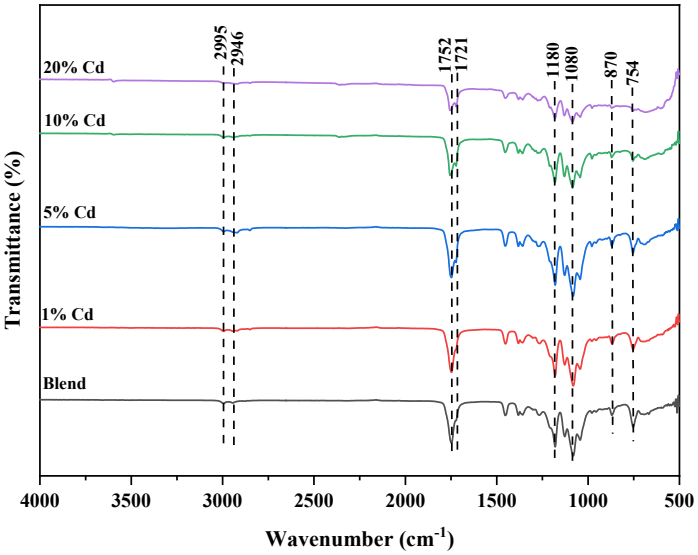

Figure 1. ATR-IR spectra of PLA/PHA/Cd composite films

3.2. Thermal Analysis (TGA)

Figure 2 shows the TGA curves of PLA/PHA/Cd composite films. It is thought that the 4% weight loss seen in the TGA curve of the pure PLA/PHA blend film up to 200 ºC is due to the loss of water molecules [17]. Apart from this, it was determined that there were two more weight losses. The first degradation (235-318 ºC) corresponds to the PHA portion, while the secondary degradation is associated with the PLA portion [18]. In the TGA curves of PLA/PHA composite films containing Cd microparticles, similar TGA curves were observed to the pure blend film, but changes were observed in the amount of residue at the end of 500 ºC. The residue percentage was found to be 1.92%, 6.84%, 9.90%, and 16.62% for PLA/PHA composite films containing 1%, 5%, 10%, and 20% Cd microparticles, respectively. The increase in the amount of residue with the increasing percentage of Cd microparticles means that the thermal stability of the PLA/PHA blend film increases due to the Cd microparticles known to be thermally stable [14, 19].

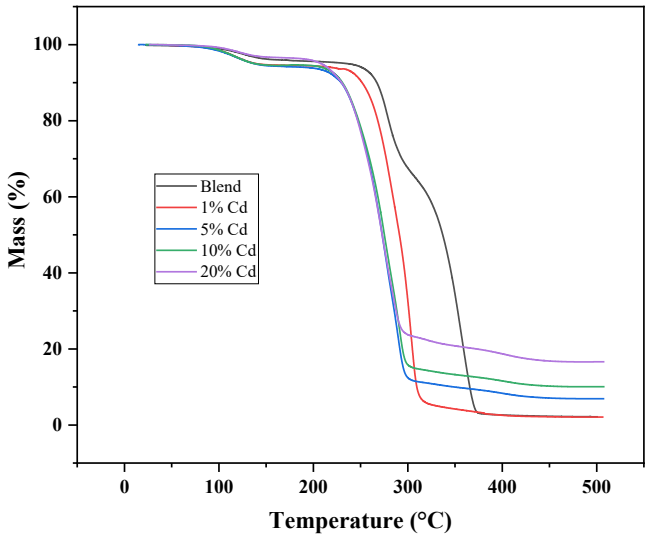

Figure 2. TGA curves of PLA/PHA/Cd composite films

3.3. Morphological structure

SEM images of pure PLA/PHA blend, 1% and 20% Cd microparticle containing composite films are given in Figure 3. When the SEM image of the pure PLA/PHA blend film is examined, it is observed that it has a flat structure [20]. It was observed that new ring-shaped structures were formed in the structure with the addition of Cd microparticle [21]. It was determined that the ring structures increase with the increasing Cd ratio and the ring structure is at most in the composite film containing 20% Cd.

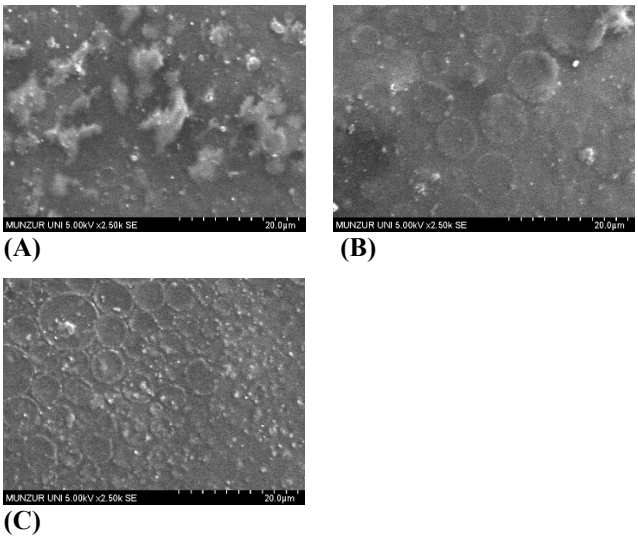

Figure 3. SEM images of **(A)** pure PLA/PHA blend **(B)** 1% Cd doped **(C)** 20% Cd doped composite films

3.4. XRD

Figure 4 illustrates the XRD spectra of the PLA/PHA blend film and composite films containing different amounts of Cd. The signal supporting the amorphous structure of PLA appeared at 2□=16.4º [13, 19]. The characteristic XRD signals and planes of PHA appeared at 2□=13.2º (020), 2□=20.9º (021), 2□=22.1º (111), 2□=26.2º (121) and 2□=29.1º (002) [22, 23]. XRD patterns of Cd-doped composite films show good crystallinity and the intensity of the peaks increases as the Cd content increases. The diffraction peaks of Cd microparticles are 2□=31.4º, 38.2º, 47.7º and 60.0º and their corresponding planes are (100), (101), (102) and (200), respectively [24]. In light of all these, all peaks are evidence that Cd microparticles have a wurtzite structure [25].

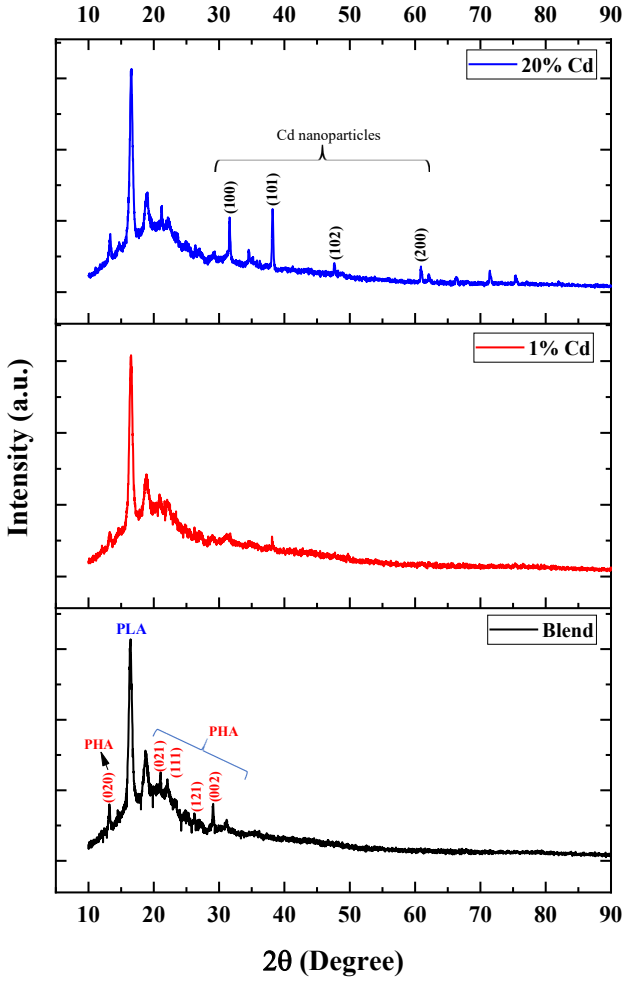

Figure 4. XRD patterns of **(A)** pure PLA/PHA blend **(B)** 1% Cd doped **(C)** 20% Cd doped composite films

X-ray patterns were used to calculate the crystallinity degree (D) of PLA/PHA/Cd composite films [19].

$$D = K\lambda/\beta cos\theta \quad (1)$$

In Equation 1, K is the Debye-Scherer constant and its value is 0.9, λ is the wavelength of the X-ray, β is the full width of the maximum half peak (FWHM) and $cos\theta$ is the cos value of the maximum peak angle. As a result of the calculations in Table 1, it was revealed that the crystallinity degree of the pure PLA/PHA blend film was 17%. It was observed that the crystallinity degree of the composite films obtained after doped 1% and 20% Cd increased to 18% and 22%, respectively. This situation can be interpreted as the increase in the crystallinity degree of the composite films with the increasing percentage of Cd, which is seen to have a crystal structure [26].

Table 1. Crystallinity degree (D) of pure PLA/PHA blend, 1% Cd doped and 20% Cd doped composite films

Sample	Crystallitinity degree(D)
PLA/PHA Blend	17%
1% Cd doped composite film	18%
20% Cd doped composite film	22%

4. Conclusion

Composite films were obtained by solvent-casting method by adding Cd particles at different rates to the PLA/PHA blend solution. First, the ATR-IR spectra of the obtained films were examined. While the characteristic signals of PLA and PHA were determined, it was observed that the characteristic polymer signals weakened with increasing Cd ratio. The significant increase in the residue rates of PLA/PHA composite films with the addition of Cd particles, which are known to have high thermal stability, can be interpreted as the Cd particles improving the thermal stability of the composite films. Cd particles also significantly affected the surface morphology of the composite films. While the pure PLA/PHA blend film initially had a flat surface, it was observed that a ring structure was formed as the Cd ratio increased in the composite films. The characteristic XRD signals of PLA, PHA and Cd particles were clearly determined and it was observed that the crystalline property of Cd increased the crystallinity of the composite films.

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Competing interests

The authors declare that they have no competing interests.

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