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Using Olive Stone Powder for Biodegradation of Bio-Based Polyamide 5.6 †

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Abstract: Polymers are extensively used as advanced materials. The most commonly used polymers in industry are non-biodegradable and petroleum derived. The increasing demand for these types of polymers results in a problem of accumulation of plastic waste in the environment and depletion of fossil resources. Because of this point, the biodegradability of polymers gains great importance as well as for the bio-based polymers produced from renewable resources. In this study, bio-based polyamide 5.6 polymer (PA56) was incorporated with olive stone powder (OSP) in order to manufacture a biodegradable polyamide compound, and its degradability was investigated. The olive stone powder was incorporated into polyamide 5.6 at 10% (w/w) with a twin-screw extruder to manufacture the compound, PA56/OSP10. The characterization of the PA56/OSP10 compound was conducted using Fourier transform infrared (FTIR) spectroscopy. The biodegradability of the PA56/OSP10 compound was examined by a natural soil burial test of six months duration. The signs of degradation were assessed by both weight loss measurements and visual observations. At the end of six months, 5.24% weight loss and surface deformation were determined for the PA56/OSP10 compound. These results suggest that olive stone powder can be considered as a green alternative to conventional biodegradation additives for polymer compounding.

Keywords: biodegradability; olive stone powder; bio-based; polyamide 5.6; compounding

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1. Introduction

Polymers are used in many applications since plastics meet a great variety of needs in numerous sectors. According to the 2019 report of Plastics Europe, the worldwide production of plastics was 348 million tonnes in 2017 and it increased to 359 million tonnes in 2018 [1]. This number is expected to reach 400 million tonnes in 2020 [2]. This increasing demand for polymers causes severe environmental problems, including depletion of fossil resources and generation of hazardous waste. Since most of the polymers are non-biodegradable, they do not decompose naturally and result in plastic waste. Because of this point, the biodegradability of polymers is of great importance.

Polyamides are petroleum derived polymers generally obtained by polycondensation of diamines with dicarboxylic acids, polycondensation of amino acids, or by ring-opening polymerization of lactams [3]. They contain a repeating amide linkage (–C(O)–NH–) in their backbone. Due to their excellent mechanical properties even at elevated temperatures, polyamides are one of the mostly preferred polymers in industry. Furthermore, their properties can be tailored by using fillers, reinforcing agents, and additives. Nonetheless, their negative effects on the environment increase the need for biobased and biodegradable polymers.

Biobased polymers are defined as polymers made from biological sources. They can be made totally or partially from renewable sourced raw materials [4]. These polymers can be formed directly in polymeric form by microorganisms or they can be manufactured ex vivo from biobased monomers [5]. Biobased polymers have many advantages over petroleum derived polymers with respect to environmental concerns [6]. Thus, biobased polymers are considered to be the most promising alternatives to petroleum derived polymers [6–8].

Polyamide 5.6 (PA56) is made by the polycondensation of 1,5-pentanediamine (cadaverine) with adipic acid. Since the used cadaverine monomer is synthesized via a biological method from renewable resources, polyamide 5.6 is classified as a bio-based polyamide [9].

Biodegradability is the breakdown of organic substances by living microorganisms [10]. This process takes place via secreted enzymes, which lead to specific chemical reactions for the cleavage of specific chemical bonds [11]. Polymers can biodegrade aerobically, anaerobically, and partly aerobically and partly anaerobically depending on the environmental conditions [10]. Besides environmental factors, the characteristics of the polymer, type of organisms involved and the nature of pretreatment are also factors which affect the biodegradation process.

Olive stone powder (OSP) is produced by grinding olive stones, which are the waste of the olive oil manufacturing industry [12]. Turkey is one of the most important olive producing countries, ranking fourth in the world, with an average of 1.7 million tonnes of olive production [13]. Thus, the utilization of olive stone is important for valorization of these solid wastes and for contributing to the national economy. Olive stone is a lignocellulosic material and its main components are hemicellulose, cellulose, and lignin [14]. It has a high value since it can be a renewable source for obtaining bio-polyols [15]. In addition, olive stone powders are used in the polymer industry. The reported researches in the literature about OSP include its use as a filler for polylactic acid matrix biocomposites [12], as reinforcement in polypropylene composites [16], and as a filler for polyvinyl composites [17]. However, there is no study in the literature on the biodegradability of bio-based polyamide 5.6 compound with olive stone powder.

In this study, a novel bio-based polyamide compound was manufactured by incorporating olive stone powder with bio-based polyamide 5.6 polymer. In addition, biodegradability of this compound was investigated through a natural soil burial test for six months. The characterization of the compound was performed with Fourier transform infrared (FTIR) spectroscopy, and the biodegradation assessed with weight loss measurements and visual observations. The aim of the present work was to evaluate olive stone powder as a green biodegradability additive for bio-based polyamide 5.6.

2. Experiments

2.1. Materials

Bio-based polyamide 5.6 (PA56), a 45% renewable polyamide grade, was obtained from Cathay Industrial Biotech Ltd., China. PA56 has a specific gravity of 1.14 g/cm^3 and a relative viscosity of 2.7 cP. The chemical structure of polyamide 5.6 is presented in Figure 1. Olive stone powder (OSP) was supplied by the Biotechnology Laboratory of Istanbul Technical University, Turkey. The materials were dried in an air-drying oven at 80 °C for 24 h in order to eliminate the moisture content before being used in compound manufacturing and the natural soil burial test.

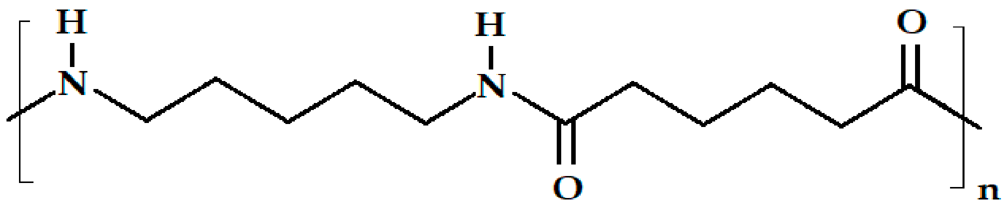

Figure 1. The chemical structure of polyamide 5.6.

2.2. Compounding and Sample Preparation

OSP was introduced to PA56 at 10% (w/w) with a twin-screw extruder, Haake MiniLab II (Thermo Fisher Scientific, Waltham, MA, USA), to manufacture the biodegradable polyamide compound, PA56/OSP10. The compounding was done at 265 °C for 10 min with a screw speed of 100 rpm. The extruded strand was pelletized and the pellets were injection molded to form test samples. Neat polyamide 5.6 pellets were also injection molded and used as controls during the applied tests.

2.3. Fourier Transform Infrared (FTIR) Analysis

The characterization of the polyamide 5.6, olive stone powder and PA56/OSP10 was carried out using an FTIR spectrophotometer, Spectrum100 (PerkinElmer, Waltham, MA, USA). The structural changes, which may have occurred in the PA56/OSP10 compound due to soil burial for 6 months, were also investigated. The applied scan range was 4000–650 cm^{-1}, the resolution was 4.0 cm^{-1} and the number of scans was 64.

2.4. Biodegradability

The biodegradability of the PA56/OSP10 compound was examined through a natural soil burial test for 6 months. The test was conducted at the Istanbul Technical University, Istanbul (latitude: 41.105595, longitude 29.025339) from February 2020 to July 2020. Meteorological data were obtained from the Turkish State Meteorological Service [18]. These data are summarized in Table 1.

Table 1. Meteorological data from February 2020 to July 2020.

Months	Average Temperature (°C)	Number of Rainy Days	Rainfall (mm)
February	7.0	13	73
March	11.1	12	55
April	12.9	8	47
May	18.7	12	71
June	22.1	6	65
July	24.0	2	4

The used test samples were 3 cm by 3 cm square pieces, and five test samples were used for PA56/OSP10 compound. The molded neat polyamide 5.6 was used as a control. The samples were weighed after drying in an air-drying oven at 80 °C for 24 h. Then they were buried in the soil. Every 30 days, the samples were dug out for examination. They were washed in distilled water and dried before undergoing weight loss measurements and visual observations.

The weight loss percentage was calculated using Equation (1);

$$\text{Weight loss (\%)} = [(w_i - w_f) / w_i] \times 100 \tag{1}$$

where w_i and w_f are the weight of the compound before and after soil burial, respectively.

For visual observation, images of the compounds and controls were taken before and after the soil burial in order to spot the differences.

3. Results

3.1. Fourier Transform Infrared (FTIR) Analysis

FTIR spectrophotometry was performed on both of the used materials; polyamide 5.6 and olive stone powder, and also on the manufactured compound PA56/OSP10.

The obtained FTIR spectrum of olive stone powder is shown in Figure 2. It showed O–H stretching at 3306 cm^{-1}, C–H stretching at 2926 cm^{-1} and C–O–C stretching at 994 cm^{-1}. In addition to these peaks, C=O stretching at 1643 cm^{-1} and O–H in plane bending at 1360 cm^{-1} were also observed.

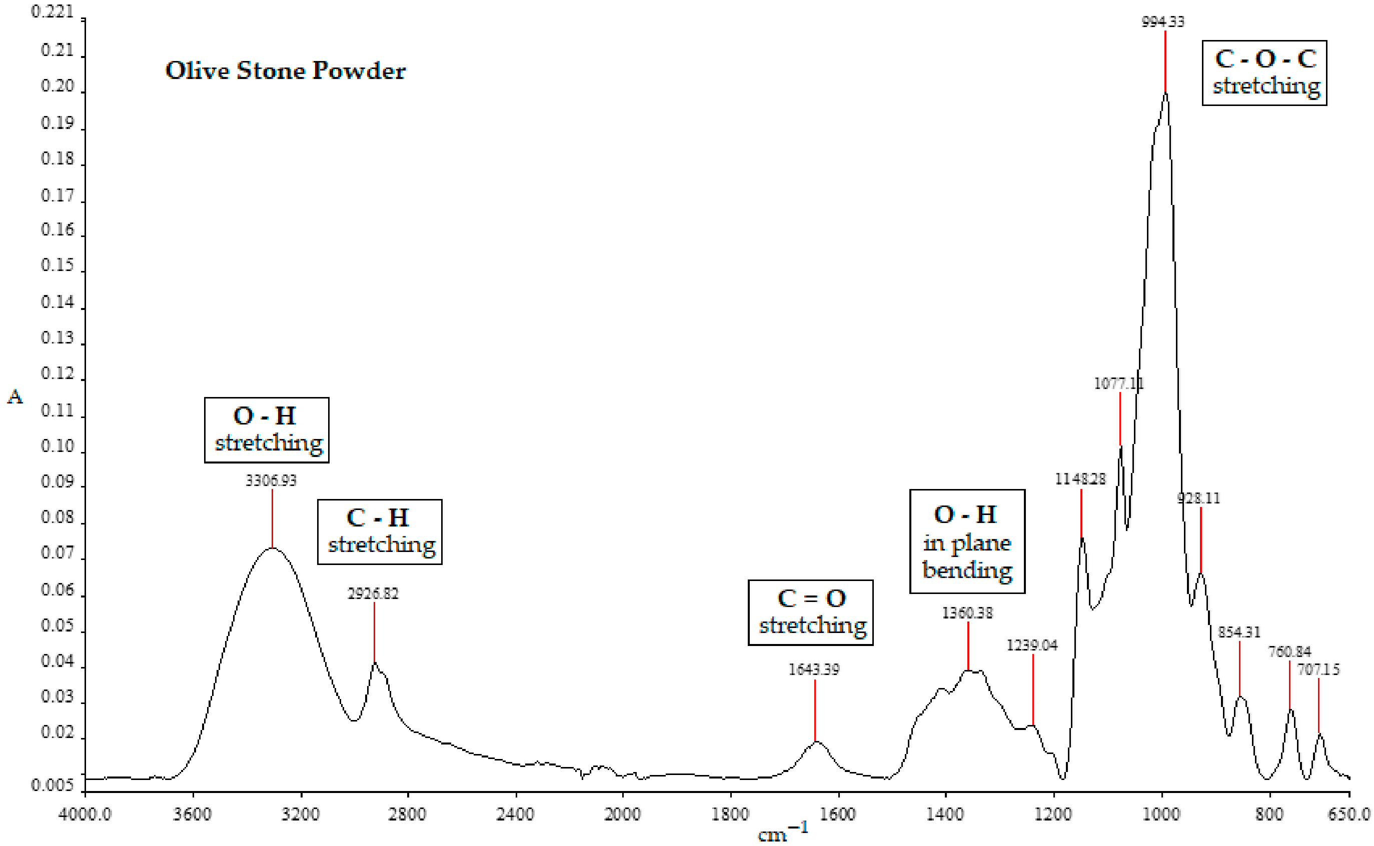

Figure 2. The FTIR spectrum of olive stone powder.

The FTIR spectrum of the manufactured PA56/OSP10 compound was overlapped with the spectrum of polyamide 5.6 and shown in Figure 3. Both spectra exhibited characteristic FTIR absorption bands of the amide linkage at 3304 cm^{-1} with N–H stretching, at 1632 cm^{-1} with C=O stretching, and at 1533 cm^{-1} with N–H bending. The main differences between the peaks of PA56 and PA56/OSP compound were observed at 1080 cm^{-1} and 1018 cm^{-1}.

The structural changes of the PA56/OSP compound after 6 months of soil burial were also analyzed and the overlapped spectrum is displayed in Figure 4. A small increase in absorbance at 1080 cm^{-1} and slight differences around 1440 cm^{-1}, 1270 cm^{-1}, and 1200 cm^{-1} were observed. On the other hand, the absorption values of the peaks associated with the amide linkage (N–H stretching, C=O stretching, N–H bending) showed a significant increase for the buried PA56/OSP10 compound.

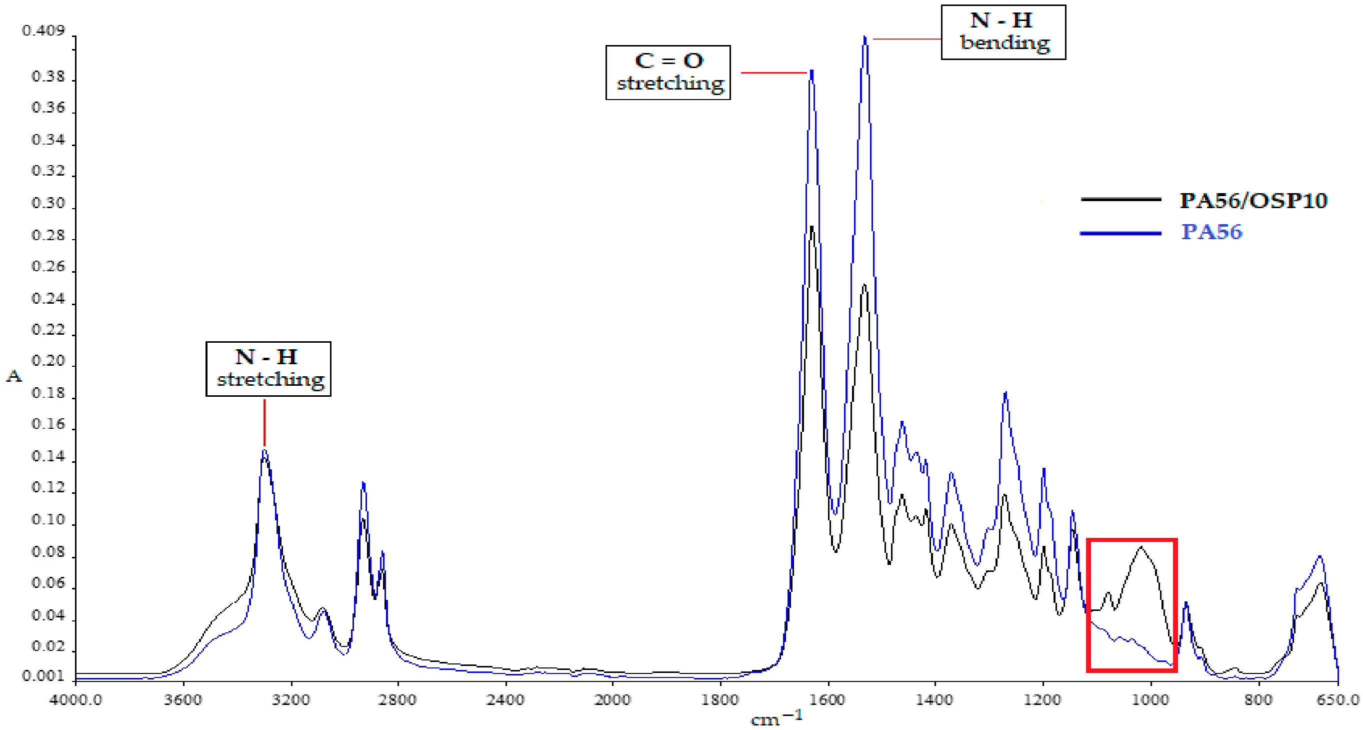

Figure 3. The FTIR spectra of the PA56/OSP10 compound and the polyamide 5.6.

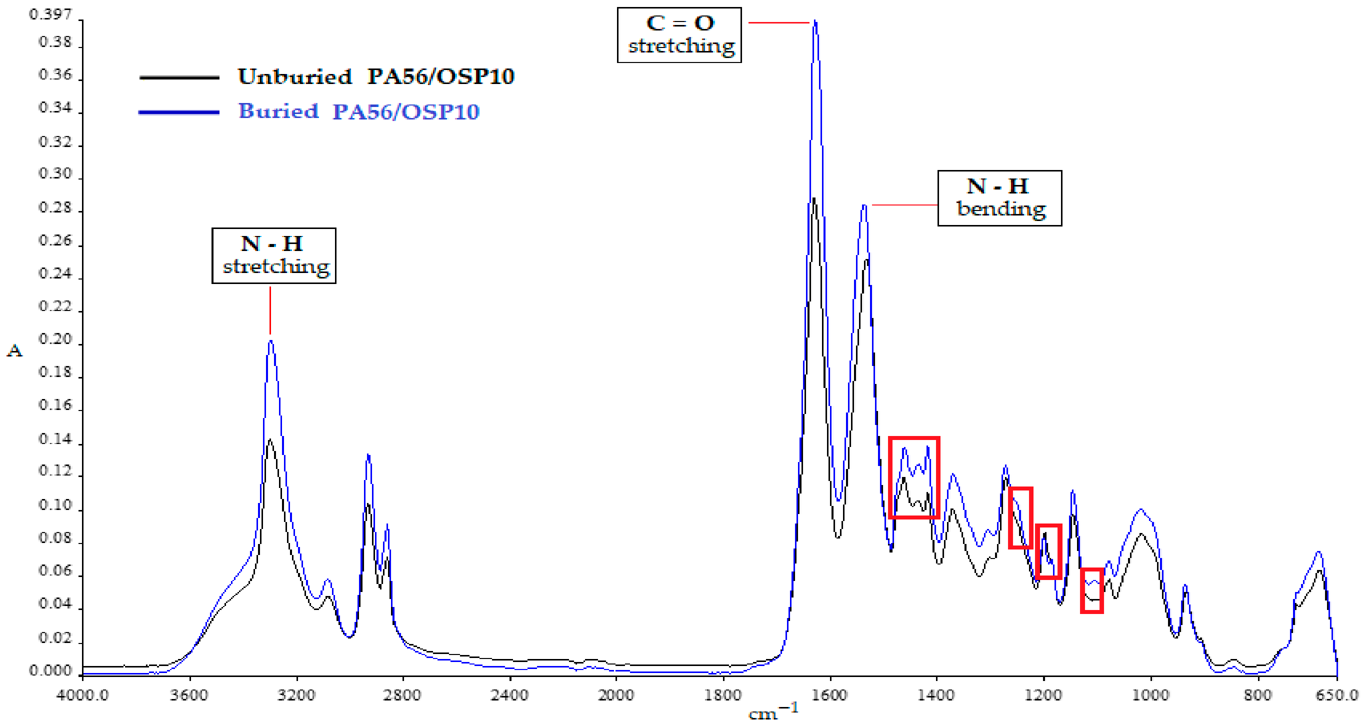

Figure 4. The FTIR spectra of the unburied and buried PA56/OSP10 compound.

3.2. Biodegradability

The natural soil burial test was applied since change in weight is a direct way to measure the biodegradability of polymers. The weight loss calculations were carried out every 30 days for 6 months. Since five test samples were buried for PA56/OSP10 compound, the average values were calculated. Figure 5 illustrates the recovered weight percentage of PA56 and of PA56/OSP10 compound.

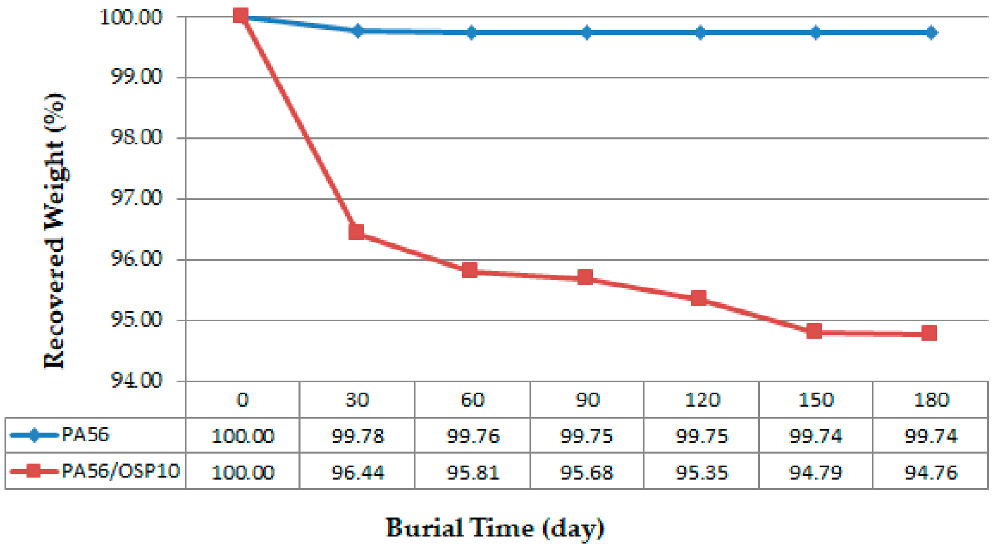

Figure 5. Recovered weight (%) versus burial time (days) graphs of PA56 and PA56/OSP10.

At the end of 6 months, 5.24% weight loss was determined for PA56/OSP10 compound and the related data for both PA56 and the PA56/OSP10 compound are given in Table 2.

Table 2. Weight loss percentages of the neat polyamide 5.6 and PA56/OSP10 compound.

Materials	PA56 Content (wt%)	OSP Content (wt%)	Weight Loss after 6 Months (%)
PA56	100%	0%	0.26%
PA56/OSP10	90%	10%	5.24%

The changes in the surface appearances of the buried and the unburied samples were documented from the images given in Figure 6. The buried PA56/OSP10 samples showed surface deformations, abrasions, and discolorations, whereas buried PA56 samples displayed only discoloration.

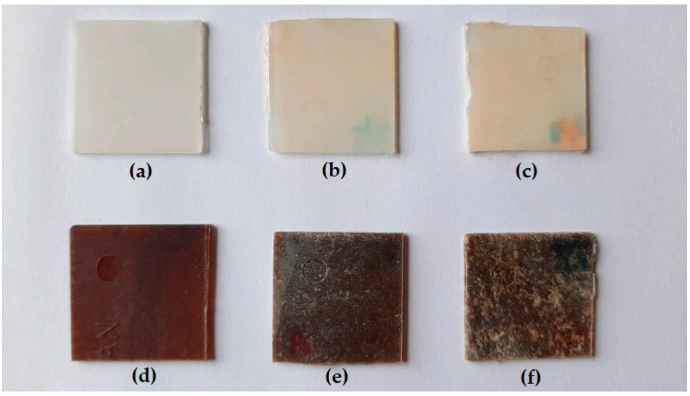

Figure 6. The images of; (**a**) Unburied Polyamide 5.6; (**b**) Polyamide 5.6 after 6 months of soil burial (sample 1); (**c**) Polyamide 5.6 after 6 months of soil burial (sample 2); (**d**) Unburied PA56/OSP10 compound; (**e**) PA56/OSP10 compound after 6 months of soil burial (sample 1); (**f**) PA56/OSP10 compound after 6 months of soil burial (sample 2).

4. Discussion

4.1. Fourier Transform Infrared (FTIR) Analysis

The spectra of the PA56 presented peaks at 3304 cm^{-1}, at 1632 cm^{-1}, and at 1533 cm^{-1} correspond to N–H stretching, C=O stretching, and N–H bending, respectively. It was an expected outcome, since all these three peaks belongs to the characteristic FTIR absorption bands of the amide linkage.

In the spectrum of OSP, which is given in Figure 2, at 3306 cm^{-1} O–H stretching, at 2926 cm^{-1} C–H stretching, at 1643 cm^{-1} C=O stretching, at 1360 cm^{-1} O–H in plane bending and at 994 cm^{-1} C–O–C stretching were determined. These peaks are characteristic of lignin, cellulose, and hemicellulose which are the main components of OSP, and are in correlation with the work of Horikawa, Y. et al. [19].

The overlapped FTIR spectrum of PA56/OSP10 and of PA56, given in Figure 3, was beneficial for determination of the OSP in the manufactured compound. As expected, both of them showed the characteristic FTIR absorption bands of the amide linkage. However, the absorption values of these peaks were lower for the PA56/OSP10 compound than the PA56. This decrease is related to the lower amount of polyamide 5.6 in PA56/OSP10 compound. The main difference between their spectra was observed when PA56/OSP10 compound presented two peaks, at 1080 cm^{-1} and at 1018 cm^{-1}, but neat PA56 showed no peaks at these wavelengths. These newly arisen peaks correspond to C–O–C stretching, which indicates the presence of the OSP in the PA56/OSP10 compound. This finding is important since it proves the incorporation of olive stone powder with the polyamide 5.6, meaning the extrusion compounding process was successful.

The structural changes, which may occur due to soil burial for six months, were also investigated with FTIR. The spectrum of the unburied and of the buried PA56/OSP10 compound were taken. Their spectra were overlapped, in Figure 4, and compared with each other. The spotted differences suggest presence of changes in chemical structure of PA56/OSP10 compound after 6 months of burial time. Most importantly, the absorption values of the peaks associated with the amide linkage showed significant increase for the buried compound. This finding was crucial, since biodegradation results in an increase in the functional end groups of the polymers [20]. The increase in the intensities of the amine stretching at 3304 cm^{-1}, carboxyl stretching at 1632 cm^{-1} and amine bending at 1533 cm^{-1} indicates that the biodegradation occurred for the buried PA56/OSP10.

4.2. Biodegradability

The biodegradability studies were conducted with bio-based polyamide 5.6 and its compound with 10% (w/w) olive stone powder, PA56/OSP10. Even though bio-based materials are composed of or derived from biological products, it does not mean that the material is biodegradable [21,22]. Thus, the biodegradability of bio-based polyamide 5.6 was investigated with the natural soil burial test.

The natural soil burial test is a bio-geophysical test. In this test, a realistic environment is provided with soil humidity, temperature, and microorganisms. All these features may vary depending on the climate and location. According to the summarized data in Table 1, throughout the experimental process the average temperature, the average number of rainy days, and the amount of rainfall changed from 7 °C to 24 °C, from 13 to 2 days, and from 73 mm to 4 mm, respectively.

The graphs of test samples with recovered weight percentage values and burial time, in Figure 5, showed that the weight of PA56/OSP10 compound decreased gradually whereas the weight of PA56 remained almost the same. The determined weight loss for PA56/OSP10 compound was 5.24% at the end of six months. The main factors affecting this biodegradability result are the weight percentage of the OSP, the types of microorganism present in the soil, meteorological data based on location, and the burial time of the samples in the soil. By changing any of these factors, the biodegradability of the polymer compounds can also be changed.

The findings of visual observations, including surface deformation, abrasion, and discoloration, also suggest the biodegradation of the PA56/OSP10 compound during the natural soil burial test.

5. Conclusions

This study investigated the biodegradability effect of olive stone powder on bio-based polyamide 5.6 polymer. For this purpose, a novel bio-based polyamide compound, PA56/OSP10, was successfully manufactured from 90% (w/w) bio-based polyamide 5.6 and 10% (w/w) olive stone powder, by an extrusion compounding method. The natural soil burial test was applied and the buried PA56/OSP10 compound showed 5.24% (w/w) degradation at the end of six months. Surface deformations, abrasions, and discolorations were also observed for these compounds. The biodegradation of PA56/OSP10 compound was further confirmed from the structural changes in the FTIR spectra. In the light of these findings, olive stone powder can be considered as a green biodegradable additive for the bio-based polyamide 5.6 polymer.

Author Contributions: Ş.G. conceived and designed the experiments; performed the experiments; analyzed the data; contributed reagents/materials/analysis tools and wrote the paper; Y.G. advised and supervised. Both authors have read and agreed to the published version of the manuscript.

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Abbreviations

The following abbreviations are used in this manuscript:

PA56	Polyamide 5.6
OSP	Olive stone powder
FTIR	Fourier transform infrared

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