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Article

Novel Functional Polycaprolactone/Hematite Composites with Improved Mechanical, Thermal, UV-Protective and Barrier Properties

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Abstract: The need for materials with advanced properties finds the candidates among modified polymers—for instance, polymer composites. Furthermore, the stated environmental concerns dictate the use of biodegradable polymers. This work studies the properties of polycaprolactone/hematite composites prepared by the incorporation of laboratory-synthesized hematite (α-Fe_2O_3) particles of different sizes into the polycaprolactone (PCL) matrix. PCL is a biodegradable, biocompatible and non-toxic polymer, while hematite is a thermally stable, corrosion-resistant, non-toxic and low-cost iron oxide. To avoid harmful solvents, PCL/hematite composites were prepared by melt mixing. PCL and PCL/hematite composites were studied by thermogravimetric analysis (TGA), FTIR and UV–Vis–NIR spectroscopy. The mechanical and barrier properties were also studied. The results indicate the influence of hematite particles on the enhancement of PCL properties, especially using the smaller hematite particles (average diameter of about 100 or 170 nm). An improvement of thermal stability, UV absorption and mechanical properties was observed. The composites prepared with the larger hematite particles (average diameter of about 1 or 2 μm) act as a significantly better barrier to water loss than pure PCL. Therefore, PCL/hematite composites can be used as novel functional materials, with enhanced mechanical, thermal, barrier and UV-protective properties, for packaging or biomedical purposes.

Keywords: polymer composites; polycaprolactone; hematite; particle size; thermal stability; UV protection; mechanical properties; barrier properties

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1. Introduction

In recent years, increasing attention has been paid to finding the most appropriate processing and recycling procedures for waste polymer materials due to the global goal of minimizing their disposal in landfills, especially those most common, conventional polymer materials that do not have the property of biodegradability. For this reason, recent trends in material production and expressed environmental concerns dictate the increasing use of biodegradable polymers. Biodegradable polymer materials include both natural and synthetic types, classified into several groups [1]: biomass products (cellulose, lignin, chitin, pectin, starch), biobased polymers (polylactide, PLA), polymers obtained from microorganisms (polyhydroxyalkanoates, PHAs) and petroleum-based polymers (polyvinyl alcohol, PVA; polyesteramides, PEAs; polycaprolactone, PCL).

Among all the listed biodegradable materials, polycaprolactone (PCL) occupies a prominent place due to its numerous advantages and various possibilities of use. PCL is a synthetic polymer from the group of aliphatic polyesters. It is produced by ring-opening polymerization of ε-caprolactone monomer. Besides biodegradability, its main properties are non-toxicity, biocompatibility, good mechanical properties (high elongation at break), resistance to various types of solvents and oils (as well as to chlorine) and hydrophobicity. It has good processability and molding ability. Due to all these properties and advantages, it is a suitable and highly desirable material in many applications, such as tissue engineering, medical devices, drug delivery systems, wound healing and biodegradable packaging [2–5]. However, there are some disadvantages of PCL, which limit its wider use and availability of PCL products, especially in the packaging field. The main disadvantages of PCL are the complex processes of its production, which dictate the high price of the final material, the low melting temperature (from 59 to 64 °C), which prevents its transportation and use at elevated temperatures [2], as well as poor mechanical strength [6]. The mentioned disadvantages of PCL can significantly limit its availability and application compared to low-cost, thermally and mechanically stable, widely used conventional synthetic polymer materials (e.g., polyethylene, PE; polypropylene, PP; polyethylene terephthalate, PET), despite their inability to biodegrade.

In order to overcome the mentioned disadvantages of PCL, it is possible to prepare different types of polycaprolactone composites, which can offer new and improved properties, such as better mechanical, thermal, barrier and other material performances [1]. Several types of fillers were used in the preparation of PCL matrix composites. Cellulose nanofibers in combination with ZrO_2 nanoparticles, prepared for biocompatible wound dressings, contributed to the improvement of the thermal stability of PCL [7]. PCL composites with zeolite were used in the preparation of homogeneous membranes for drinking water treatment [8]. Furthermore, in order to obtain polymer composites suitable for application as membranes, PCL/TiO_2 composites with improved mechanical properties due to the strengthening effect of TiO_2 were prepared [9]. Ramírez-Cedillo et al. studied composites prepared from PCL and nanoparticles such as Ag, TiO_2 or $Na_2Ti_6O_{13}$, which showed antibacterial properties, improved biocompatibility and increased tensile strength [10]. Furthermore, the SiO_2/PCL composite, which is considered an environmentally friendly polymer material with superhydrophobic properties, has been studied as an oil–water separator [11].

It is generally recognized that a synergistic effect occurs when suitable fillers are incorporated into a polymer matrix due to the contribution of both components to the overall properties of the composite. The final composite should reveal the contribution of the composite constituents through improved material performance, but at a reasonable material cost [12].

Furthermore, it is known that the processing conditions of material preparation can influence its final properties. During the preparation of biomedical materials, it is strongly recommended to avoid solvents. For that reason, melt-processing methods are preferred. The material's crystallization caused by processing has an effect on the mechanical and physical characteristics of the material. Furthermore, the reinforcement with fillers leads also to the specific material's performance [13].

Among the many types of fillers, several different iron oxides can be used to prepare composites with polycaprolactone. Iron oxides, in the form of nanoparticles, represent very important types of inorganic fillers due to their remarkable mechanical, thermal, electrical and magnetic properties, as well as their biocompatibility [14]. Among the 16 types of iron oxides, the use of hematite (α-Fe_2O_3) is highly preferable due to its numerous good characteristics. It is a readily available metal oxide, widespread in nature in soil and rocks, and can also be synthesized in the laboratory. It is often a product of the transformation of other iron oxides. Hematite is a thermally stable, non-toxic, corrosion-resistant and inexpensive material that has a strong UV absorption ability and weak ferromagnetic properties [15]. It is widely used as a pigment in paints, coatings and various materials (rubber, plastics, concrete, ceramics), as well as a catalyst in several industrial processes [15]. Also, due to its high stability, low cost and non-toxicity, nanostructured hematite is intensely investigated for various advanced applications, such as hydrogen production by photoelectrochemical water splitting [16,17], photocatalytic degradation of organic compounds [18,19], detection of harmful and flammable gases [20,21], electrode material in Li-, Na- and K-ion batteries [22,23], as well as for biomedical applications [24,25].

Due to the mentioned benefits, hematite can serve as a desirable filler for polymer composites [26]. In some studies, hematite was used in combination with a polycaprolactone matrix. PCL/hematite nanocomposite sheets prepared by solution casting were used in a catalytic application for the degradation of Rhodamine B dye [27]. In addition to the catalytic activity of PCL/hematite composites, this research revealed an improvement in thermal properties. The crystallization temperature, determined by differential scanning calorimetry (DSC), was increased compared to pure PCL polymer. Mensah et al. [28] prepared PCL/hematite composites by melt blending and investigated their microwave absorption property.

The present study is focused on the preparation and characterization of PCL matrix composites filled with hydrothermally synthesized hematite particles of different sizes. To our best knowledge, studies on the influence of hematite particles of different sizes on the properties of PCL/hematite composites have not been carried out yet. The mentioned studies [27,28] use only one size of hematite particles, while our study considers the influence of well-defined hematite particles of four different sizes on the properties of PCL/hematite composites. The influence of such specific hematite particles on the thermal, mechanical, barrier and UV absorption ability of the material was comprehensively studied in this work. It is very important to point out that all types of hematite particles used in this study were non-commercial, laboratory-synthesized, well defined and highly uniform. The uniformity of filler particles is a significant factor in obtaining polymer composites with balanced and better-defined properties. The final goal is to obtain advanced functional PCL/hematite composites as specific materials with targeted application. Such PCL/hematite composites have a potential to be used as specific packaging with improved thermal, mechanical, barrier and UV-protective properties or for biomedical uses as surgical sutures where the improvement of the mechanical properties is especially important.

2. Materials and Methods

2.1. Preparation of Hematite Particles

Uniform hematite particles of various sizes used for preparation of PCL/hematite composites were synthesized using a slightly modified method described by Sugimoto et al. [29]. This method for obtaining uniform hematite particles of various sizes from very concentrated solutions was used in the present work because significant quantities of hematite particles (several grams) are required for the preparation of polymer composites. For the syntheses of hematite particles, iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 97% Alfa Aesar, Ward Hill, MA, USA) was used as the iron source, sodium hydroxide (NaOH, p.a. Kemika, Zagreb, Croatia) as the alkali and ultrapure (Milli-Q, p.a. Kemika, Zagreb, Croatia) water as the solvent. In order to obtain a 2 mol dm^{-3} (2 M) aqueous solution of iron(III) chloride, 270.3 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 1 L of water. A 6 mol dm^{-3} (6 M) aqueous solution of NaOH was obtained by dissolving 240.0 g of NaOH in 1 L of water. For the synthesis of 4 hematite samples of various particle sizes used for preparation of PCL/hematite composites, 4 aliquots of 50 mL of 2 M iron(III) chloride aqueous solution were poured into 4 polypropylene (PP) bottles of 250 mL volume. Different volumes of 6 M NaOH solution (45 mL for the synthesis of sample HC1, 47.5 mL for sample HC2, or 50 mL for samples HS1 and HS2) were slowly added into reaction mixtures (in about 1 min for samples HC1, HC2 and HS1, or in about 2 min for sample HS2) with vigorous stirring using a magnetic stirrer (500 rpm). The resulting very dense suspensions were heated in closed PP bottles at 100 °C for 8 days. Hematite particles, precipitated as a thick red layer at the bottom of the bottles, were thoroughly washed with distilled water (5 times) and ethanol (once) using a centrifuge. The washed samples were dried at 60 °C (in air) for one day, then mixed well with a spatula and dried again at 60 °C for one more day. The presence of hematite, as the only crystalline phase in the synthesized samples, was confirmed by powder X-ray diffraction (PXRD), while the sizes and shapes of the particles were observed by scanning electron microscopy (SEM).

2.2. Preparation of PCL/Hematite Composites

Polycaprolactone/hematite composites were prepared from PCL polymer granulate (Sigma Aldrich, Burlington, MA, USA, M_n = 70,000 to 90,000 (GPC), density 1.145 g/cm^3) and the hematite particles described in the paragraph above. Polycaprolactone/hematite composites, named PCL/HC1, PCL/HC2, PCL/HS1 and PCL/HS2, were prepared by melt mixing using a Brabender kneader. The mixing temperature was 110 °C over a period of 1 min at a mixing speed of 10 rpm followed by 2.5 min of mixing at 45 rpm. The hematite content in the samples was 0.25, 0.5 and 1% (Table 1). The prepared PCL/hematite composites were then pressed into foils and plates required for characterization. Pressing was performed using a Dake (Grand Haven, MI, USA) hydraulic press, model 44-226, at a temperature of 120 °C. The prepared PCL/hematite composites in the form of the foils are shown in Figure 1.

Table 1. Composition of the prepared samples.

Sample	PCL (wt%)	Hematite (wt%)
PCL	100	0.00
PCL/0.25%HC1	99.75	0.25
PCL/0.5%HC1	99.50	0.50
PCL/1%HC1	99.00	1.00
PCL/0.25%HC2	99.75	0.25
PCL/0.5%HC2	99.50	0.50
PCL/1%HC2	99.00	1.00
PCL/0.25%HS1	99.75	0.25
PCL/0.5%HS1	99.50	0.50
PCL/1%HS1	99.00	1.00
PCL/0.25%HS2	99.75	0.25
PCL/0.5%HS2	99.50	0.50
PCL/1%HS2	99.00	1.00

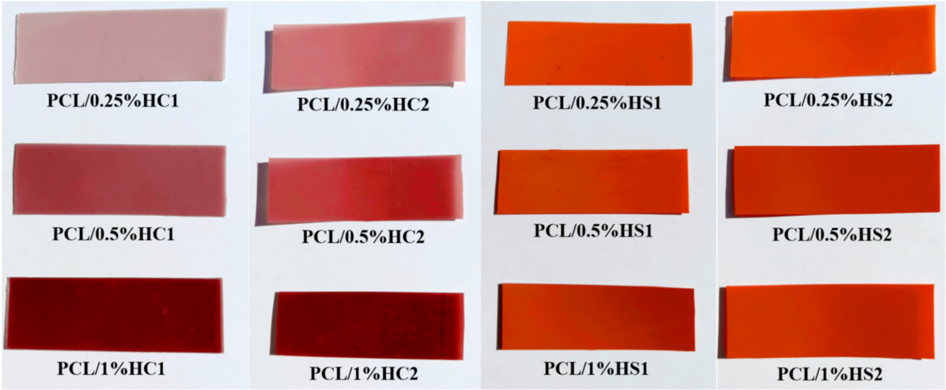

Figure 1. Photographs of prepared PCL/hematite composites in the form of the foils.

2.3. Characterization

The morphology (size and shape) of the prepared hematite particles was investigated using a JEOL (Tokyo, Japan) JSM-7000F field-emission scanning electron microscope (FE-SEM).

Phase analysis of the prepared particles was conducted by recording X-ray diffraction patterns using a Malvern Panalytical (Malvern, Worcestershire, UK) Empyrean diffractometer (Cu anode X-ray tube).

Pure PCL polymer and PCL/hematite composites were characterized by Attenuated Total Reflectance (ATR) FTIR spectroscopy using a Perkin Elmer (Shelton, CT, USA) Spectrum One FTIR spectrometer. The scanning range was from 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1}.

The thermal stability of pure PCL and PCL/hematite composites was determined using a TA Instruments (New Castle, DE, USA) Q500 thermogravimetric analyzer. Samples weighing 10 mg were analyzed in a nitrogen stream at a heating rate of 10 °C/min in the range from 25 to 800 °C.

A universal Zwick (Ulm, Germany) 1445 device was used to determine the tensile strength and elongation of break of pure PCL and PCL/hematite composites. The dimensions of the specimens were as follows: 100 mm long, 10 mm wide and ~1 mm thick. The stretching rate was 50 mm/min.

A Shimadzu (Kyoto, Japan) UV-3600 UV–Vis–NIR spectrophotometer with an integrating sphere was used to obtain the UV–Vis–NIR diffuse reflectance spectra of the studied samples. Extra-pure barium sulfate ($BaSO_4$) by Nacalai Tesque Inc. (Kyoto, Japan) was used as a reference material.

The water vapor permeability of the prepared samples was determined using a Herfeld's device. A Herfeld's device is a glass container with a metal lid, which has a circular hole (36 mm in diameter). A total of 50 mL of water was poured into a glass container. The studied sample was in the form of a foil (55 mm in diameter) and was placed under a metal lid that was tightly closed. The glass container with the water was then placed in a desiccator containing 97% sulfuric acid at the bottom. The weight of the glass container (with sample and water) was measured at the beginning of the measurement and after 24 and 48 h.

3. Results and Discussion

3.1. Properties of Synthesized Hematite Particles

For the purpose of preparing novel functional PCL/hematite composites, hematite particles of various sizes and very good uniformity (samples HC1, HC2, HS1 and HS2) were prepared using the method described in the experimental section. The sizes and shapes of the synthesized particles can be seen in the recorded SEM images (Figure 2, left). The average particle sizes (about 2 µm for sample HC1, about 1 µm for sample HC2, about 170 nm for sample HS1 and about 100 nm for sample HS2) were estimated by examining the recorded SEM images.

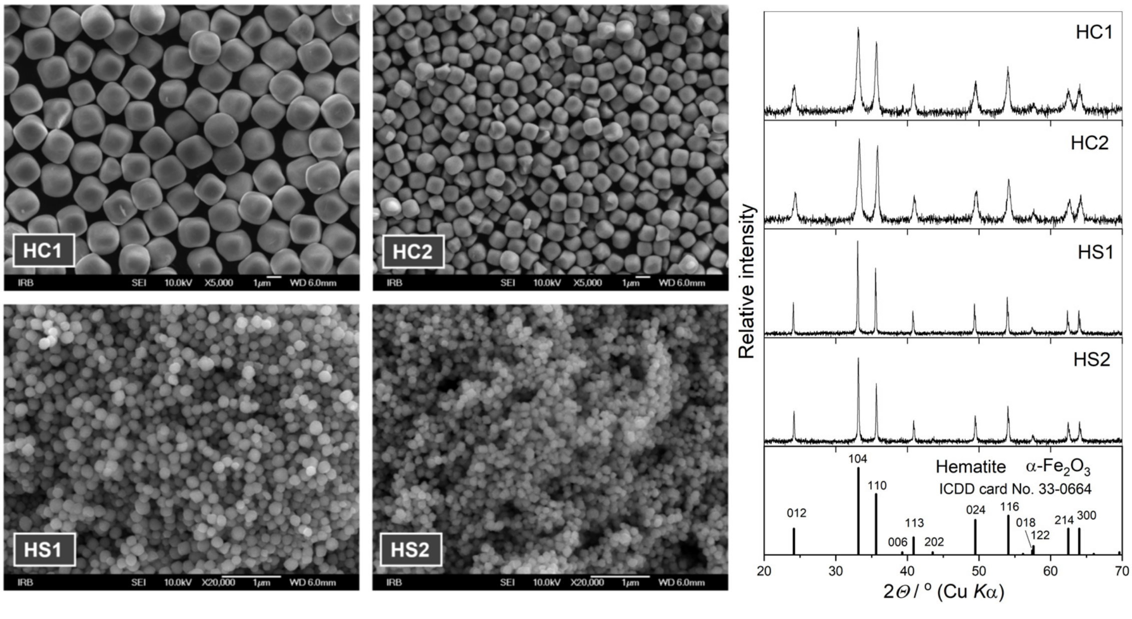

Figure 2. SEM images of synthesized uniform hematite particles of different sizes (**left**) and their XRD patterns (**right**). All bars given at the bottom of the SEM images correspond to a distance of 1 µm.

Powder X-ray diffraction (PXRD) patterns of the synthesized samples (Figure 2, right) confirmed α-Fe_2O_3 as the only crystalline phase present in these samples. The widths of the diffraction lines in the recorded patterns indicate the presence of very small crystallites (average diameter of about 20 nm estimated using the Scherrer equation [30]) in the larger hematite particles of samples HC1 and HC2, while the smaller hematite particles (samples HS1 and HS2) consist of significantly larger crystallites (average diameter of about 90 nm estimated using the Scherrer equation [30]).

3.2. FTIR Spectroscopy

The FTIR spectra of pure PCL polymer and PCL/hematite composites prepared with 1% of hematite particles of different sizes are shown in Figure 3. Infrared absorption bands characteristic of PCL were observed at 2944 and 2861 cm^{-1}, representing asymmetric CH_2 stretching and symmetric CH_2 stretching, respectively. The high-intensity band at 1720 cm^{-1} can be attributed to carbonyl stretching. Furthermore, the band at 1294 cm^{-1} can be attributed to C–O and C–C stretching in the crystalline phase, the band at 1240 cm^{-1} to asymmetric C-O-C stretching and the band at 1159 cm^{-1} to C–O and C–C stretching in the amorphous phase [31].

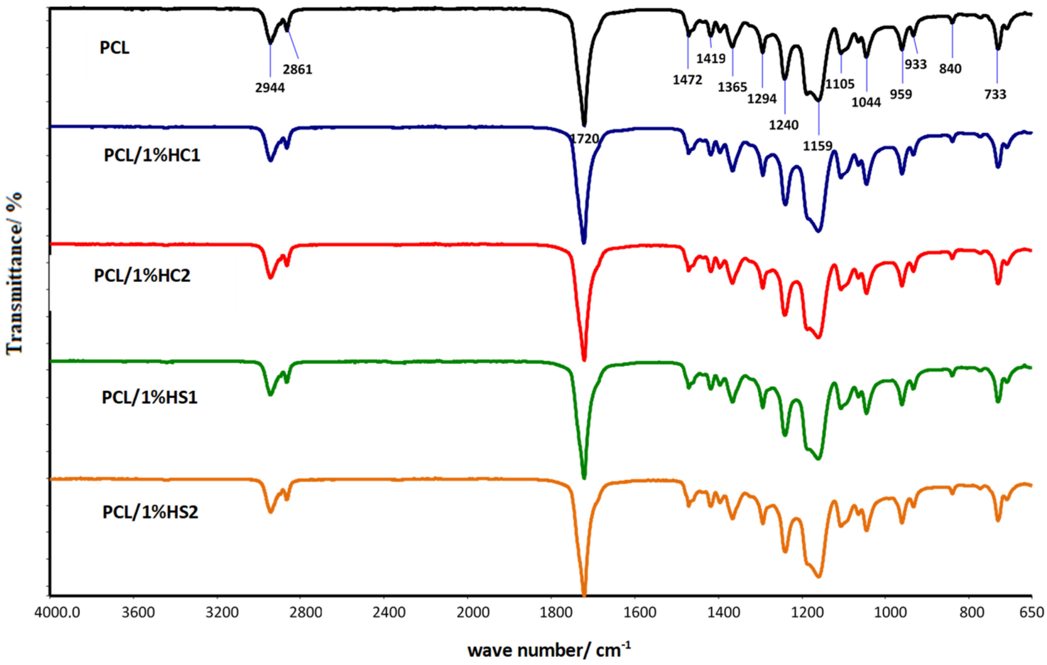

Figure 3. FTIR spectra of pure PCL polymer and PCL/hematite composites containing 1% of hematite particles of different sizes.

The FTIR spectra of pure PCL polymer and PCL/hematite composites did not show significant differences, due to the very low hematite content in the studied composites, as well as to the position of infrared bands of hematite at wavelengths below 650 cm^{-1} [32]. The spectral range of the FTIR spectrometer used in this study is from 4000 to 650 cm^{-1}, and in this spectral region, hematite does not show significant absorption of IR radiation.

It is very important to point out that the characteristic bands of the main degradation products of PCL formed by heat treatment, 5-hexenoic acid and its di- and trimers, with wavelengths of 3575 cm^{-1} and 3087 cm^{-1}, are not visible in the recorded FTIR spectra [33]. There is also no indication of the presence of a degradation product, which corresponds to the traces of carbon monoxide, with a characteristic IR band at 2176/2117 cm^{-1} [33]. It can be concluded that the melt blending of PCL and hematite does not promote PCL degradation and that adding hematite filler to the PCL matrix does not cause degradation of PCL.

3.3. Mechanical Properties

In order to study the influence of hematite filler on the properties of PCL/hematite composites, the mechanical properties were studied, and the results are given in Table 2. It is well known that the mechanical performances of the composites can highly depend on the type of the polymer matrix, the type and content of the filler, and on the interface properties of the polymer and filler particles [9]. Furthermore, the mechanical properties of the polymer composites are influenced by some other factors, such as: composite manufacturing process, surface treatment of the filler, filler dispersion and its orientation within the polymer matrix, compatibility of the components and interfacial strength [34].

Table 2. Tensile strength and elongation at break of pure PCL polymer and PCL/hematite composites.

Sample	Tensile Strength/MPa	Elongation at Break/%
PCL	12.01	461.76
PCL/0.25%HC1	12.26	461.39
PCL/0.5%HC1	12.69	459.58
PCL/1%HC1	13.92	460.43
PCL/0.25%HC2	4.85	50.24
PCL/0.5%HC2	13.10	458.49
PCL/1%HC2	12.52	459.09
PCL/0.25%HS1	14.83	461.17
PCL/0.5%HS1	12.83	460.43
PCL/1%HS1	12.86	462.50
PCL/0.25%HS2	14.99	462.44
PCL/0.5%HS2	16.19	538.12
PCL/1%HS2	16.18	460.96

It is known that the limitations of PCL polymer lie in its low tensile strength. For this reason, attempts have been made to improve its mechanical properties by using certain types of fillers [35]. However, such improvement of the material's mechanical properties is dictated by the polymer viscosity, filler content and its successful dispersion in a polymer matrix or its susceptibility to aggregation [36]. It is known that inorganic fillers can enhance the mechanical properties and the thermal stability of the polymer material [37]. Hematite presents a promising instrument for such achievements, like in the case of its incorporation into a polystyrene matrix, where it was found that the increasing content of the hematite caused an increase in the composites' elastic moduli and the magnitude of the stress relaxation [38].

The results of our study show that there is an increase in tensile strength, compared to the pure PCL polymer, for all tested composite samples, except for the PCL/0.25%HC2 sample. The decrease in the tensile strength for PCL/0.25%HC2 composite is probably caused by the agglomeration of the filler particles and formation of weak spots, which cause the deterioration of the mechanical properties [39]. The highest increase in tensile strength is observed in composite samples prepared with spherical particles (HS2), due to their small size and large surface area. That increase in tensile strength, compared to the pure PCL, ranges from 24.81% for the sample PCL/0.25%HS2 to 34.80% for the sample PCL/1%HS2. It is known that the rigidity of the filler contributes to the enhancement of the material and improves the tensile strength [6]. Additionally, it is assumed that the increased tensile strength, observed for most of the studied composite samples, is caused by the proper dispersion of the hematite particles in the PCL matrix and strong interfacial bonding between the polymer matrix and the filler particles [6,40].

Furthermore, most of the studied composite samples, except the PCL/0.25%HC2 sample, show elongation at break values that are close to those of pure PCL. The decreased elongation at break for the PCL/0.25%HC2 composite is supposed to be caused by agglomeration of the filler due to the incompatibility between the hydrophilic filler and the hydrophobic polymer matrix of PCL [35]. On the other side, the highest value for the elongation at break is observed for the sample PCL/0.5%HS2, which is about 16.5% higher than the elongation at break for the pure PCL.

It can be concluded that the best mechanical properties are obtained for the sample PCL/0.5%HS2, prepared with the spherical hematite particles of low size (about 100 nm). This improvement in mechanical properties can be explained by the very good dispersion of the spherical filler HS2 in PCL polymer, which contributed to the improved interfacial adhesion and filler/polymer compatibility. This resulted in improved stress transfer after load application during mechanical measurements [35]. It is known that increasing the surface area of the filler causes a higher strength of the polymer composite, due to a more efficient stress transfer mechanism. For a certain fraction of filler, strength tends to increase with decreasing filler particle size. Furthermore, an improvement in mechanical properties of polymer composites can be observed even at low filler contents (from 0.5 to 2 vol%) [41]. A study by Fu et al. [41] also points out that the spherical particles, due to the equal aspect ratio of the particles, can contribute to the enhancement of the material. Such filler particles act evenly in all directions in the polymer matrix. Finally, it can be concluded that the mechanical properties of the composite are influenced by the size of the filler particles, the filler loading and the interfacial adhesion of the filler particles and the polymer matrix. PCL/hematite composites with small spherical hematite particles (filler HS2 with an average particle diameter of about 100 nm) show the best improvement in mechanical properties.

3.4. Water Vapor Permeability

Among other valuable characteristics, the packaging material must have adequate barrier properties in order to secure the content of the packaging. A good packaging material offers high physical and chemical protection of the packed products. It is very important to prevent the penetration of oxygen into the packaging in order to protect the product from oxidation, which can lead to a change in color, smell and taste and the development of aerobic microorganisms. Furthermore, it is also of great importance to use packaging materials of specific water vapor permeability. In order to protect the wet product from moisture loss, it is necessary to use packaging with low vapor permeability, that is, with strong barrier properties for water vapor evaporation. Such protection can be provided by composite polymer materials, which bring the benefits to the packaging through the adequate mechanical properties and a barrier against gases and water vapor [36]. It is known that the improvement of the barrier performance of a material can be achieved by incorporating a high-barrier material into the polymer matrix. The example of a material with high barrier capacity is a polymer mixed with some type of inorganic filler. The advancement in barrier properties is achieved by increase in tortuosity, i.e., the path extension for the diffusing compound [42]. Therefore, the obtained composite material can present a powerful barrier to oxygen, water vapor and different gases [36]. Furthermore, it is also important to prevent the penetration of water from the environment into the packaged products, especially those that are sensitive to moisture and must remain dry. In general, due to the presence of fillers in the polymer matrix, such packaging material is often more durable, with many improved properties compared to the pure polymer. Therefore, packaging polymer composite materials can extend the shelf-life, quality and safety of packaged goods (food, cosmetics, drugs, etc.) [43].

This work studies the influence of iron oxide hematite particles of different sizes on the properties of a polycaprolactone polymer matrix. The measured water loss values of the studied polymer composites are listed in Table 3.

Table 3. Water loss from PCL and PCL/hematite composites after 24 h and 48 h.

Sample	Water Loss After 24 h/g	Total Water Loss (After 48 h)/g
PCL	0.065	0.117
PCL/0.25%HC1	0.035	0.051
PCL/0.5%HC1	0.046	0.075
PCL/1%HC1	0.022	0.034
PCL/0.25%HC2	0.017	0.036
PCL/0.5%HC2	0.038	0.083
PCL/1%HC2	0.037	0.061
PCL/0.25%HS1	0.048	0.090
PCL/0.5%HS1	0.037	0.061
PCL/1%HS1	0.047	0.063
PCL/0.25%HS2	0.084	0.154
PCL/0.5%HS2	0.029	0.140
PCL/1%HS2	0.047	0.089

From the results for the water loss, presented in Table 3, it can be seen that most of the studied composites lose less water vapor than pure PCL due to the better barrier performance caused by the presence of a hematite filler in the PCL matrix. It is especially seen for the samples prepared with the pseudocubic hematite particles named HC2. All prepared composites with HC2 hematite particles have significantly lower water vapor permeability than pure PCL. On the contrary, composite samples prepared with HS2 filler are not as effective in preventing water vapor loss. That can be explained by the possible agglomeration of such small hematite particles in some parts of the studied piece of the polymer material. Only the sample prepared with 1% of the hematite filler HS2 shows the improvement in barrier performance, in comparison to the pure PCL, after 24 and 48 h. On the other side, the composites prepared with the larger hematite particles (HC1 and HC2) act as a better barrier to water vapor loss than the pure PCL, probably due to the larger tortuous path needed for water to find its way out from the sample when it encounters the large hematite particles.

In general, the improvement of the barrier properties of the composite, compared to the pure polymer, can be explained by the tortuous path formed due to the presence of the filler, which forces the gas on a longer path through the polymer sample, as it has to go around the filler particles [44]. This is completely different from the passage of water vapor in a pure polymer, which takes place without obstacles. The significant reduction in permeability is characteristic for polymer–inorganic composites. The barrier performance of such materials is influenced by the factors like filler shape, size, aspect ratio and content in the composites [45]. Furthermore, the diffusion of gas molecules is prolonged due to the presence of the filler and happens by a tortuous pathway around the present filler [45]. HC1 and HC2 are large hematite particles of well-defined shape and uniform size. The permeability may be well explained and modelled by tortuosity mechanisms for fillers with regular geometries and identical shapes [45]. The presence of very small crystallites in HC1 and HC2 hematite particles (with an average size of about 20 nm) may also contribute to the slower and more difficult transport of water molecules through the PCL/hematite composites by their adsorption onto the crystallite surface.

Such an improvement in the barrier performance of the material, using hematite filler in the polymer matrix, can be used for packaging purposes in order to keep the moisture inside the package for a longer time and prevent drying of wet products.

3.5. Thermogravimetric Analysis

The results of thermogravimetric analysis of PCL and PCL/hematite composites are given in Figures 4 and 5 and in Table 4. From the TGA and DTGA curves shown in these figures, it can be concluded that PCL polymer and PCL/hematite composites are degraded in one step.

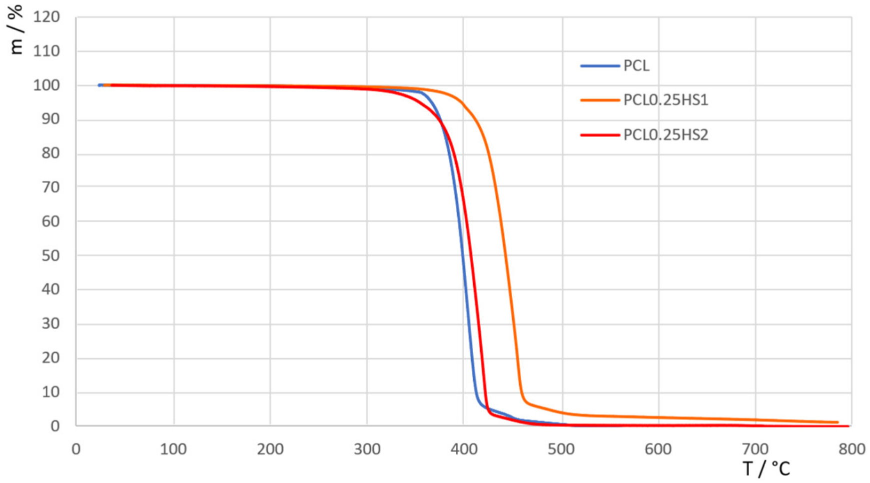

Figure 4. Thermogravimetric (TG) curves for the pure PCL and for PCL/0.25HS1 and PCL/0.25HS2 composites.

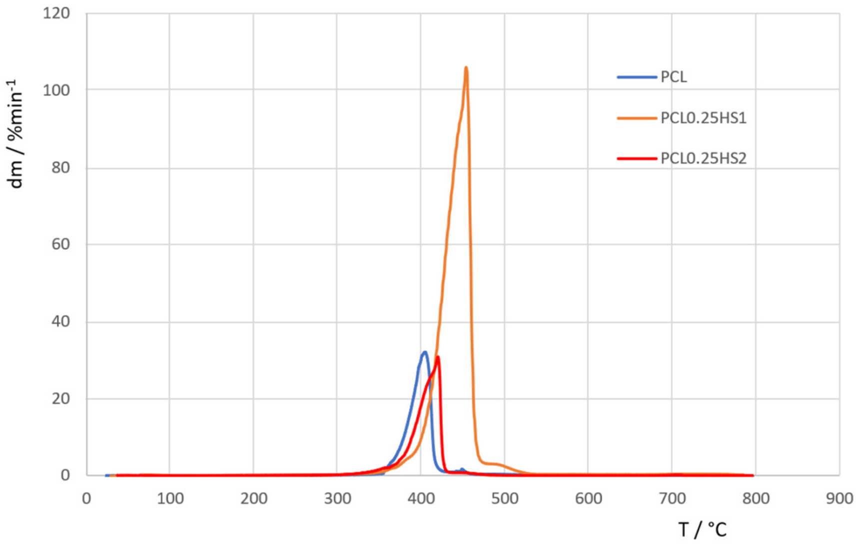

Figure 5. Differential thermogravimetric (DTG) curves for the pure PCL and for PCL/0.25HS1 and PCL/0.25HS2 composites.

Table 4. The initial decomposition temperature ($T_{95\%}$) and the temperature of the maximal rate of decomposition (T_{max}) for PCL and PCl/hematite composites.

Sample	$T_{95\%}$ (°C)	T_{max} (°C)
PCL	366.52	404.72
PCL/0.25%HC1	355.21	382.85
PCL/0.5%HC1	342.32	389.80
PCL/1%HC1	353.94	420.07
PCL/0.25%HC2	348.05	405.81
PCL/0.5%HC2	353.74	403.36
PCL/1%HC2	353.35	397.96
PCL/0.25%HS1	397.37	453,60
PCL/0.5%HS1	343.80	392.40
PCL/1%HS1	334.55	380.01
PCL/0.25%HS2	353.94	420.07
PCL/0.5%HS2	341.26	405.87
PCL/1%HS2	332.99	370.09

In order to determine the influence of hematite on the thermal properties of the PCL polymer, it is necessary to compare the thermal properties of pure PCL with the thermal properties of the PCL/hematite composites. The results listed in Table 4 show that the onset of thermal degradation ($T_{95\%}$) of the composites, compared to the pure PCL polymer, is shifted towards lower temperatures for most investigated samples except for the PCL/0.25 HS1 composite sample. It is assumed that the hematite filler particles influence the pyrolysis of PCL and increase the polymer matrix thermal decomposition. Such results indicate that hematite could be sometimes used to decrease the PCL degradation temperature [46]. Such types of composites can be used when the material must be recycled after its use, which will be more efficient due to the lower PCL degradation temperature [47].

On the other side, for the PCL/0.25HS1 sample, $T_{95\%}$ is higher for about 30 °C than $T_{95\%}$ for the pure PCL. Such material composition can be efficiently used when it is needed to produce a material with improved thermal stability.

It is also very important to point out that there is a significant increase in the temperature of the maximal degradation rate (T_{max}) for some composite samples. Such an increase is observed for the composite samples prepared with the lowest quantity of hematite (PCL/0.25%HC2, PCL/0.25%HS1 and PCL/0.25%HS2), except for PCL/0.25%HC1. For the sample PCL/0.25%HS1, T_{max} is higher for even 50 °C than T_{max} for the pure PCL. It can be concluded that the thermal stability of the PCL/hematite composites increases with the decreasing size of the hematite particles. This is explained by the fact that small particles have a larger surface area compared to larger ones for the same particle load [41]. For this reason, it can be concluded that hematite particles can significantly affect the thermal stability of composite materials due to slower diffusion of volatile decomposition products throughout the polymer matrix and reduced mobility of polymer chains, which is caused by the presence of filler particles [44,48]. In general, it is very important to mention that PCL, due to its hydrophobic and semi-crystalline nature, has a slow degradation rate and acceptable mechanical properties for various applications [49]. Adding filler into the PCL matrix, as in the case of the PCL/0.25%HS1 sample, gives the material additional thermal stability and makes it more durable. However, it is evident that only a small ratio of hematite filler causes an increase in the thermal stability of PCL. In the case of hematite particles of very small dimensions (HS1 and HS2), the thermal stability decreases with an increase in the amount of hematite in the sample.

Finally, it can be concluded that it is favorable to use fine, small, spherical hematite particles in lower proportions to achieve increased thermal stability of PCL, which can be clearly seen in Figures 4 and 5.

3.6. UV–Vis–NIR Spectroscopy

With UV blocking properties, the particular material can be considered very effective and functional. It is known that different types of metal oxides embedded in the polymer matrix can be used for this purpose, which results in polymer materials that block UV radiation [43,50,51].

The diffuse reflectance UV–Vis–NIR spectra (in the wavelength range from 200 to 1000 nm) of pure PCL polymer and prepared PCL/hematite composites with 1 wt% of different hematite particles are shown in Figure 6. The spectrum of pure PCL showed only absorption of UV radiation ($\lambda < 400$ nm) with weak absorption of UV-A radiation (315 nm $< \lambda <$ 400 nm), a moderate absorption of UV-B radiation (280 nm $< \lambda <$ 315 nm) and a strong absorption of UV-C radiation at low wavelengths ($\lambda < 280$ nm). The spectra of PCL/1% hematite composites showed very strong absorption in the entire UV and part of the visible region ($\lambda < 600$ nm) with significantly stronger absorption in the UV region compared to the spectrum of pure PCL. This means that a significant part of the UV light was absorbed by the hematite particles, which can protect the polymer from UV degradation. The strongest absorption in the UV region (i.e., the best UV protection) was shown by PCL/hematite composites containing smaller hematite particles (HS1 and HS2), and was significantly stronger compared to PCL/hematite composites containing larger hematite particles (HC1 and HC2) (Figure 6).

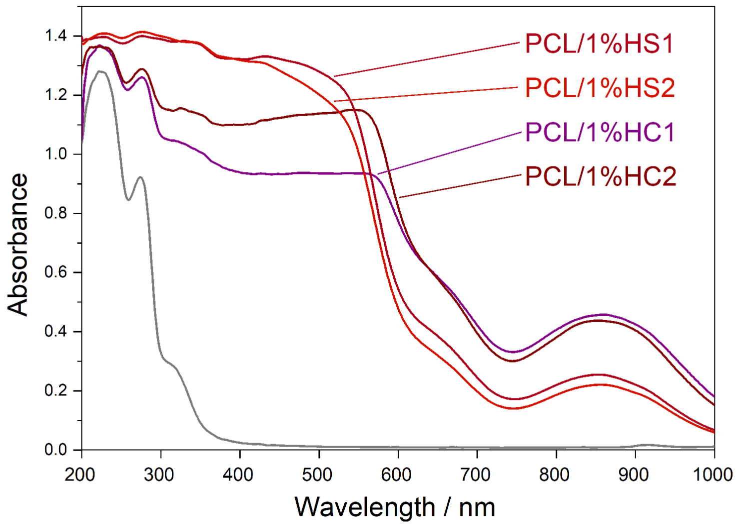

Figure 6. Diffuse reflectance UV–Vis–NIR spectra of the prepared PCL/hematite composites containing 1 wt% of uniform hematite particles of various sizes.

In the case of UV–Vis–NIR spectra of PCL/hematite composites with lower percentages of hematite (0.5% and 0.25%) (Figures 7 and 8), the absorption of UV and visible light decreased significantly with decreasing hematite content for composites containing larger hematite particles (samples HC1 and HC2), while for composites containing smaller hematite particles (samples HS1 and HS2), UV and visible light absorption remained very strong, similar to the composites with 1% of hematite.

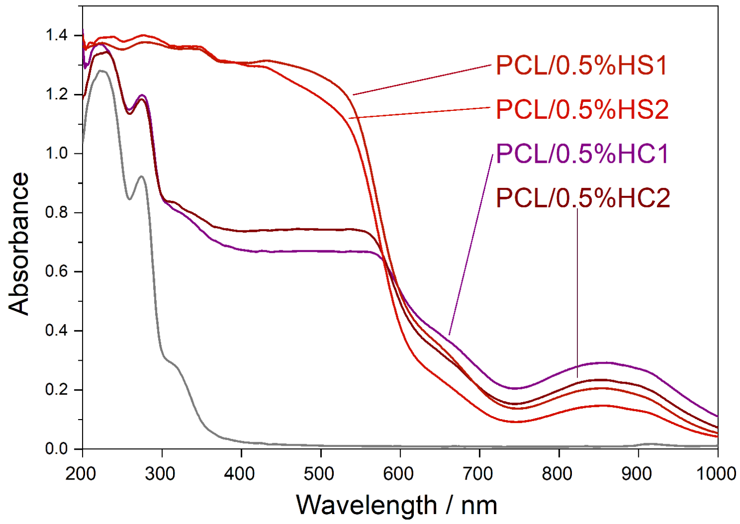

Figure 7. Diffuse reflectance UV–Vis–NIR spectra of the prepared PCL/hematite composites containing 0.5 wt% of uniform hematite particles of various sizes.

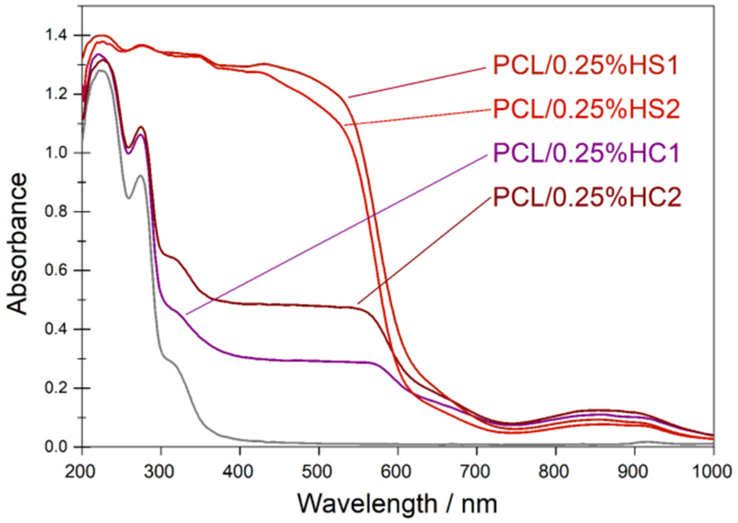

Figure 8. Diffuse reflectance UV–Vis–NIR spectra of the prepared PCL/hematite composites containing 0.25 wt% of uniform hematite particles of various sizes.

On the basis of recorded diffuse reflectance UV–Vis–NIR spectra of prepared composites, it can be concluded that smaller hematite particles (samples HS1 and HS2) provide better UV protection to PCL than larger hematite particles (samples HC1 and HC2). For good UV protection of composites with larger hematite particles, a significantly higher mass fraction of hematite particles (1%) is needed compared to smaller hematite particles, for which even a mass fraction of 0.25% is sufficient for excellent protection against UV radiation.

4. Conclusions

This study introduces novel functional PCL/hematite composites prepared with synthesized, well-defined and fairly uniform hematite particles of different sizes. The obtained results reveal that the prepared PCL/hematite composites have improved thermal, mechanical, barrier and UV-blocking properties compared to pure PCL polymer.

Hematite particles of very small dimensions, HS1 and HS2, cause an increase in the thermal stability and UV-absorbing properties of the PCL/hematite composites. The thermal properties of the composites are best for low contents of small particles and for the highest content of large particles in the PCL/1%HC1 sample. Furthermore, the improvement of mechanical properties was especially visible for the composite sample prepared with 0.5% of HS2 due to the presence of very small particles with a large surface. Such mechanical enhancement can be explained by the equal aspect ratio of the spherical particles, which act evenly in all directions in the polymer matrix.

Besides that, it is important to note that hematite particles of larger sizes (HC1 and HC2) also have a favourable effect on the improvement of the polymer material's properties, compared to pure PCL, which is evident in the better barrier properties of PCL/hematite composites prepared with HC1 and HC2. Such large filler particles act as a good barrier to water vapour loss through the polymer material. This property is very important for the potential use of such composite materials for packaging purposes.

It can be ultimately said that the significance of this research lies in the creation of new functional composite materials with advanced properties using exceptionally suitable constituent components: the biodegradable and non-toxic polymer matrix of PCL and sufficiently uniform and well-defined particles of the filler hematite, which stands out for its properties of non-toxicity and chemical stability.

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and S.K.; visualization, L.K.K., A.P. and S.K.; supervision, L.K.K. and S.K.; project administration, S.K.; funding acquisition, L.K.K. and S.K. All authors have read and agreed to the published version of the manuscript.

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