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Comparative Study on the Behavior of Virgin and Recycled Polyolefins–Cellulose Composites in Natural Environmental Conditions

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Abstract: Polypropylene–cellulose composites have great potential in many important commercial applications, and it is important to understand and properly evaluate their biodegradative behavior to achieve improved composite formulations in accordance with their future applications. In the present study, an outdoor soil burial test was performed in order to evaluate the susceptibility to degradation of polyolefins–cellulose composites. The structural and morphological changes were analyzed by Fourier transform infra-red spectroscopy with attenuated total reflectance (FTIR-ATR) and scanning electron microscopy (SEM). The weight loss of composite samples after burying in soil was recorded. The presence of new bands, as an indicator of degradation, was confirmed by FTIR-ATR spectra. The thermal stability of the composites after soil burial analyzed by TGA was slightly improved, with relatively higher temperatures being required to decompose the samples after exposure to environmental factors. SEM micrographs presented some modifications of the polymer surface, such as holes, cracks, exfoliations, and fractures. Increasing the cellulose percentage of the composite samples led to increased weight loss. From the obtained results, it can be concluded that composites based on polyolefins and renewable resources undergo a slow process of biodegradation after contact with environmental microorganisms and, with appropriate composition, could be applied to various environmental fields.

Keywords: composites; microbial degradation; polyolefins; virgin or recycled polypropylene

1. Introduction

Polypropylene (PP) is the most widely used thermoplastic polymer, presenting mechanical properties desirable for various applications. Likewise, PP is a suitable polymer matrix for obtaining composites with great potential in many important commercial applications. Several reports have described the production of composites containing natural lignocellulosic fibers from agro-industry [1–9]. Cellulose, the most abundant natural polymer, is considered a good filler with which to produce composite materials. Cellulose–polyolefins composites have found applications in numerous engineering fields, such as automotive applications, structural components, packaging, and construction (panels, window frames, decking, etc.) [10–12].

Cellulose–plastic composites are based on two polymers: a natural polymer hydrophilic cellulose and a hydrophobic synthetic polymer matrix of polypropylene. Since the polymers have different properties, it is necessary to improve the adhesion degree between both components by adding

a compatibilizer, usually based on maleic anhydride. These materials combine the advantages of cellulose and polyolefin polymers. The use of cellulose as a filler is advantageous because of its high accessibility as a renewable resource, low cost, shape flexibility, low susceptibility to fracturing during processing, and small “carbon footprint”. Therefore, it is important to understand and properly evaluate the biodegradative behavior for better composite formulations in accordance with future applications. Plastic waste management includes prevention, reuse, and recycling, and disposal is the last resort [13–15].

Interest in this domain is demonstrated by the great number of publications dedicated to natural fiber-reinforced composites. A comprehensive review was done by Faruk et al. (2013) [16], who highlighted the factors to be considered in these composites, the importance of sources and types of natural fibers, the manufacturing techniques to be used, and the properties of final product. They considered that green composite materials could be the material revolution of this century. Chauhan et al. (2012) [17] analyzed the properties of a broad range of fibers, such as hemp, flax, jute, kenaf, sisal, and ramie, as reinforcement materials for composite materials. In many cases, these reinforcements improved the mechanical behavior due to the compatibility between fibers and the polymer matrix. Ku et al. (2011) [18] provided a comprehensive overview of the influence of fibers in natural fiber-reinforced polymer composites in terms of the tensile properties of the materials. Mohammed et al. (2015) [4] presented a well-documented review evaluating the characteristics and properties of natural fiber-reinforced polymer composites, and analyzed various surface treatments (enzymatic, chemical) applied to natural fibers. The future development and extension of composite material applications were discussed by Sahari and Sapuan (2011) [19]. Another perspective on polymer–fiber composites was reported in a comprehensive review on the dynamic mechanical properties of these composites with industrial applications as construction and building materials. They considered that natural fiber-reinforced polymer composites would ensure “greener, sustainable, and smart construction development” [20].

The aim of the study was to assess composite modifications induced by soil microorganisms using several techniques, such as Fourier transform infra-red spectroscopy with attenuated total reflectance (FTIR-ATR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The samples’ weight loss over time in the soil environment was also recorded. The composites were prepared with virgin (vPP) and recycled polypropylene (rPP) at different cellulose loadings, using maleic anhydride-grafted polypropylene as the compatibilizer. The recyclability of polypropylene at the end of its useful life is economically beneficial and contributes to environmental protection by reducing plastic disposal.

2. Materials and Methods

2.1. Materials

Virgin high flow PP polymer BJ380MO (vPP) produced by Borealis AG, Vienna, Austria (white color) was kindly donated by FPK LIGHTWEIGHT TECHNOLOGIES S.COOP. rPP (granules of black color) were from auto pieces of local plastic recycling plant. Maleic anhydride grafted polypropylene (MAPP), Polybond 3200 from Crompton Corporation, Middlebury, USA, was used as compatibilizing agent. Cellulose fibers were purchased from LA.SO.LE. Est SRL, Percoto, Italy.

2.2. Composites Preparation

The composites were obtained in dynamical conditions, in a Brabender Plastograph, by directly incorporating 20, 30, or 40% of the filler into vPP or rPP melt, at 160 ± 5 °C, 100 rpm, and 7 min. Maleic anhydride as compatibilizing agent (2.5% w/w of the weight of PP) was included in materials mixture. The composites were pressed at a temperature of 190 °C for 2 min to obtain plates of 100 mm × 100 mm × 0.5 mm. The nomenclature, composition, and some characteristics of samples are presented in Table 1.

The techniques for the evaluation of biodegradation were applied to polymeric composites before and after microorganism contact. The composites are distinguished by “i” as initial (before soil burial) and “s” (after soil burial).

Table 1. Characteristics of materials investigated.

Abbreviation	Material Composition	Form and Characteristics
rPP	recycled polypropylene from auto pieces	plate; black color; 0.5 cm thickness
rPP 20cell	80% rPP+ 20% cellulose fiber	plate; black color; 0.5 cm thickness
rPP 30cell	70% rPP + 30% cellulose fiber	plate; black color; 0.5 cm thickness
rPP 40cell	60% rPP + 40% cellulose fiber	plate; black color; 0.5 cm thickness
vPP	virgin polypropylene	plate; white color; relative transparent; 0.5 cm thickness
vPP 20cell	80% vPP + 20% cellulose fiber	plate; chestnut color; 0.5 cm thickness
vPP 30cell	70% vPP + 30% cellulose fiber	plate; chestnut color; 0.5 cm thickness
vPP 40cell	60% vPP + 40% cellulose fiber	plate; chestnut color; 0.5 cm thickness

2.3. Soil Burial Test

The plastic samples were cut into pieces of 1.0 cm × 2.5 cm × 0.5 cm and buried in garden soil at the depth of 15 cm. The samples were exposed to natural weathering, such as rain, sunlight, snow etc. for 24 months.

To evaluate the biodegradation percentage by weight loss (B%), the pieces were taken off carefully from the soil and washed gently with distilled water to remove the soil particles, kept overnight at room temperature, and then kept in dessicator till constant weight. The samples were weighed and the biodegradation percentage was calculated using the following formula [21]:

$$B\% = [(W_i - W_s) / W_i] \times 100\% \quad (1)$$

where W_i = initial weight of sample and W_s = weight after burial soil.

2.4. Characterization

Morphological analysis of polymers was carried out by scanning electron microscopy (SEM) on FEI-QUANTA 200. The samples were placed on metallic support, aluminum standard stub, using a double-sided adhesive carbon tape. The SEM images were taken at an accelerating voltage of 30 kV. Micrographs of the samples were analysed at different magnifications to identify changes on the surface during the degradation process. For each polymeric sample, 4–6 micrographs were performed and only relevant images were presented.

Fourier transform infrared analysis (FTIR-ATR) spectra were acquired using a FT-IR, tensor 37 spectrometer (Bruker, Billerica, MA, USA) with ATR golden gate. All samples were recorded from 400 to 4000 cm^{-1} .

Thermal stability was proved by TGA with a TGA Q5000IR (TA instruments, New Castle, DE, USA). Samples (50–10 mg) were heated from 20 to 700 °C at a 10 °C/min scanning rate, under nitrogen atmosphere (flow rate about 200 mL·min). The onset temperature (T_{on}) was determined as the temperature corresponding to the crossover of tangents drawn on both sides of the decomposition trace, and the residue was evaluated as the residual weight at 700 °C. TGA analysis was applied to composites before and after burial soil. Additionally, cellulose, rPP, and vPP were individually analyzed for the thermal stability.

3. Results and Discussions

Environmental degradation involves both biotic and abiotic factors. Abiotic factors refer to non-living factors (sunlight, water, soil types, pollutants and nutrients, and pH values), while biotic factors mean the involvement of living organisms. Soil burial is a traditional and standard method for the investigation of biodegradation process, occurring in similar conditions to those suffered by wastes disposed on soil [22–25].

3.1. Weight Loss Determination

During the burial soil test period of 24 months, the polyolefins- based composites exhibited the normal weather changes, such as rain, snow, sun irradiation, and wind. No water or nutrients were added to soil, since the natural microorganisms from the soil were able to produce a certain level of biodegradation. As shown in Figure 1, some modifications of the color and aspect could be observed, especially for vPP-cellulose composites.

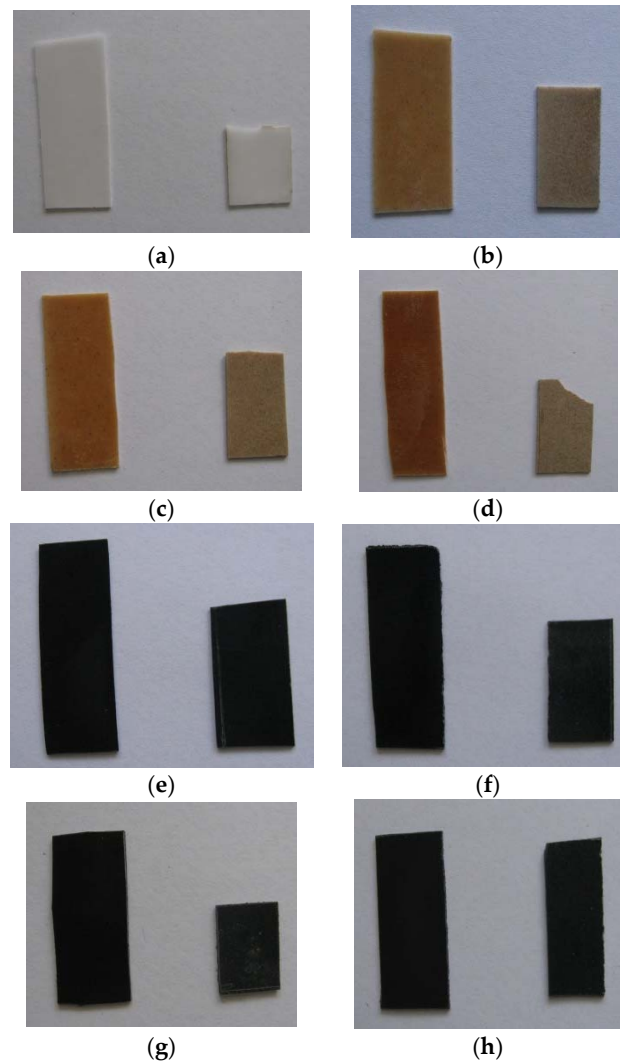


Figure 1. Images of composites before and after burial soil (left—samples before soil burial; right—samples after soil burial). (a) virgin (vPP), (b) vPP 20cell, (c) vPP 30cell, (d) vPP 40cell, (e) recycled polypropylene (rPP), (f) rPP 20cell, (g) rPP 30cell, and (h) rPP 40cell.

The percentage of composites weight loss could be considered an indicator of biodegradation level (Figure 2).

The decrease in weight observed for of the samples after soil burial is due to degradation of cellulosic component through hydrolytic depolymerization to monomeric glucose units produced by soil microorganisms, fungi, and bacteria. Generally, polymers biodegradation occurs through three main steps: (i) attachment of the microorganism to polymer surface; (ii) microbial growth using the polymer as a carbon source; and (iii) final polymer degradation up to certain compounds, depending on biodegradation mechanism pathways, whether anaerobic or aerobic [26,27]. The biodegradation of polymer composites in natural environment is governed by several factors, including the type of

microorganisms, soil characteristics (humidity, temperature, and pH), and polymer features (molecular weight, type of functional groups and substituents present in its structure, and crystallinity) [28]. Sometimes, plasticizers or additives can play a role in biodegradation.

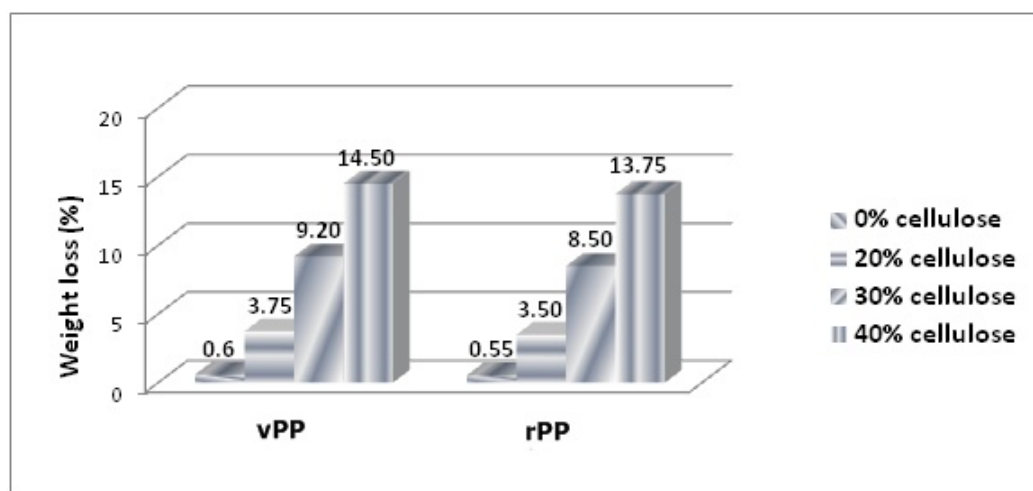


Figure 2. Weight loss of composites after 24 months of soil burial.

As expected, in our experiments the changes of weight for vPP and rPP components were very minor after 24 months of soil burial, 0.60% for vPP, and 0.55% for rPP, respectively. Generally, the values of mass loss were higher for all composites based on vPP, compared to those based on rPP. This finding is due to the multi stages heat processing of rPP component that induced a higher resistance to microbial degradation of rPP composites. It is known that rPP, being more compact, is characterized by higher density and lower porosity [29,30]. The presence of cellulose filler favored the biodegradation, with the increasing of cellulose content to 40% leading to a weight loss of 13.75% for vPP 40cell and 14.50% for rPP 40cell, respectively.

A number of studies have been published on the biodegradation extent of various composites based on polyolefins-natural components. Thus, it was reported that the degradation of pure low-density polyethylene (LDPE) and LPDE-20% (corn or potato) starch blends into the soil for 8 months leads to only 0.5% (w/w) of weight loss [31]. Polypropylene composites prepared by extrusion of PP resin with 5, 10, 15, and 20 wt % of potato starch exhibited a biodegradation increase of up to 10.6% after 120 days of being buried in soil [32]. Composites with polypropylene-cellulose fibers extracted from rice straw buried in soil for 50 days have been degraded from about 3 to 23 wt %, depending on filler content [33]. Pure and thermally pretreated polypropylene films exposed to in vitro biodegradation for 12 months, in a minimal medium with mixed soil culture, exhibited a weight loss of 10.7% and 0.4%, respectively [34].

3.2. Surface Morphology

SEM provides information about surface morphology of polymeric sheets. The technique was employed in many studies to visualize the extent of microbial degradation by polymer composite samples buried in soil [2,21,35–37]. The surface of samples became damaged and irregular with cracks, holes, exfoliation, and fractures (Figures 3 and 4). This is a general phenomenon observed in the case of thermoplastics filled with natural fibers.

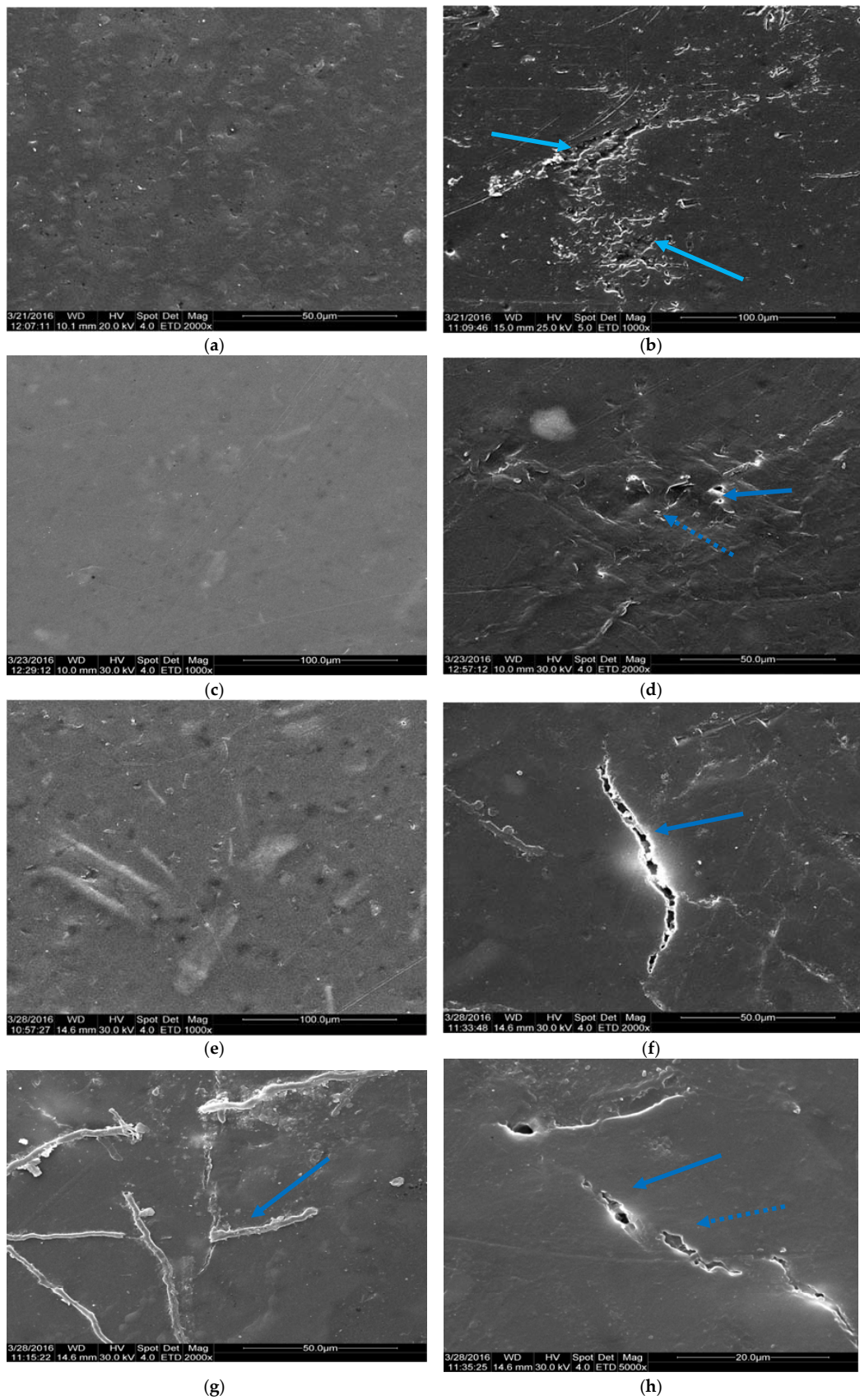


Figure 3. Cont.

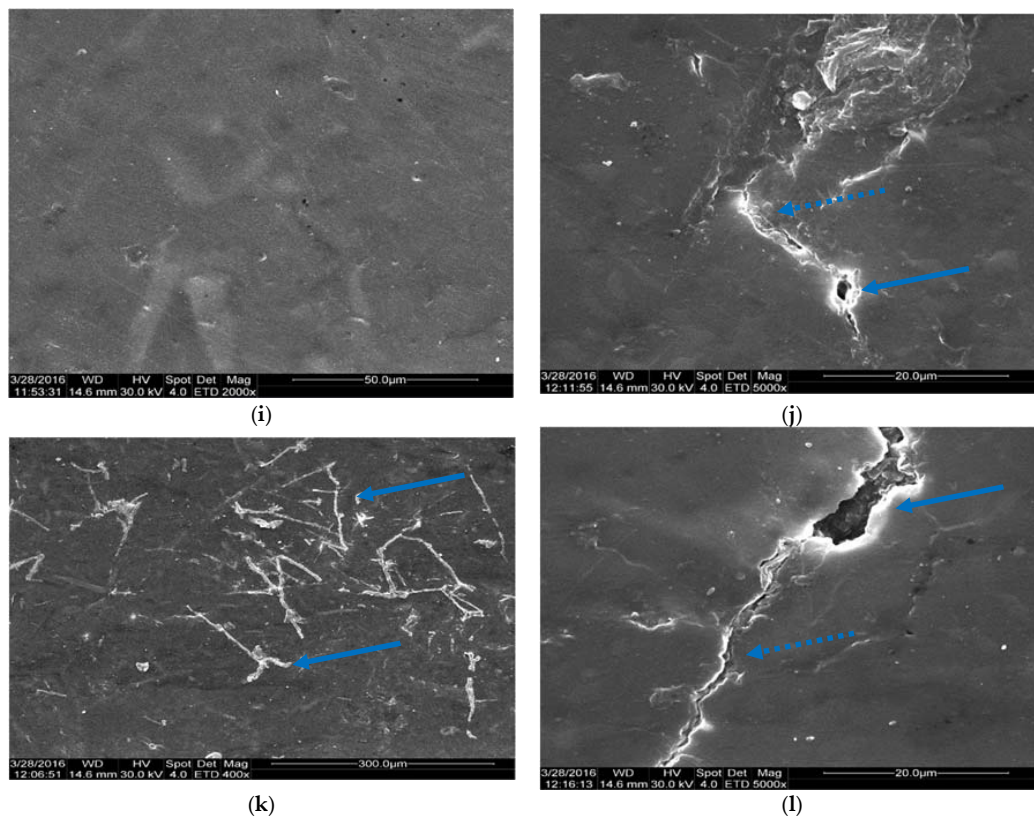


Figure 3. SEM images of the vPP-cellulose composites' surface biodegradation. (a) vPP before soil burial (2000×), (b) vPP after soil burial (arrow—damages extended on surface; 1000×), (c) vPP 20cell before soil burial 1000×), (d) vPP 20cell after soil burial (arrow—void; dotted arrow—surface exfoliation; 2000×), (e) vPP 30cell before soil burial (1000×), (f) vPP 30cell after soil burial (arrow—deep and extended fracture; 2000×), (g) vPP 30cell after soil burial network of flattened hyphae on material surface; 2000×), (h) vPP 30cell after soil burial (arrow—void; dotted arrow -surface fracture and exfoliation; 2000×), (i) vPP 40cell before soil burial (2000×), (j) vPP 40cell after soil burial (arrow—void; dotted arrow—fracture; 5000×), (k) vPP 40cell after soil burial (arrow—flattened hyphae network, 400×), and (l) vPP 40cell after soil burial (arrow—deep crater; dotted arrow—surface fracture; 5000×).

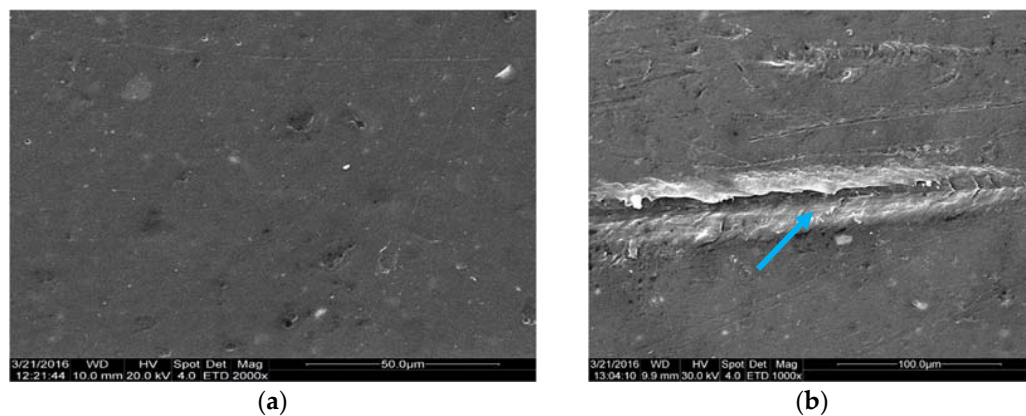


Figure 4. Cont.

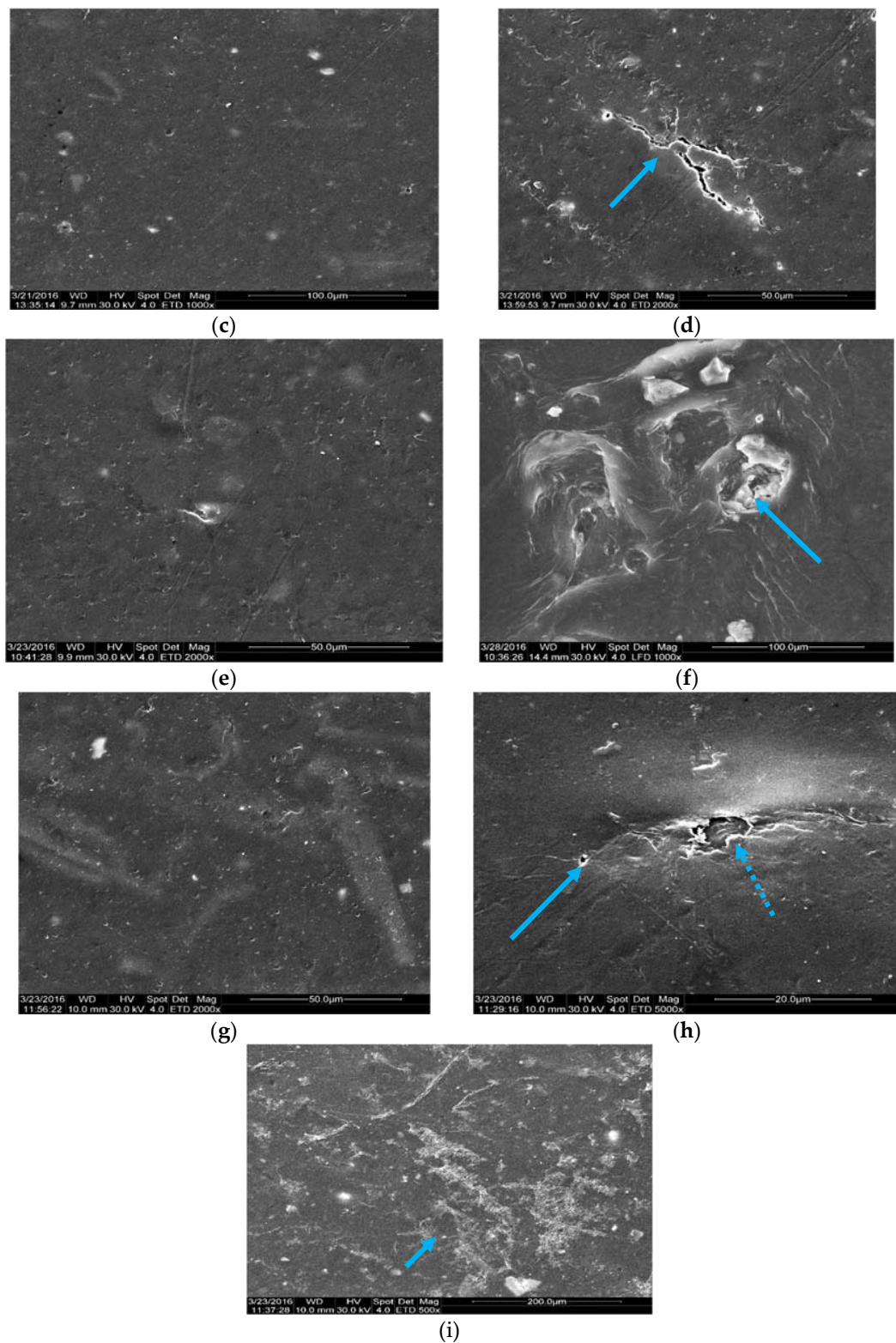


Figure 4. SEM images of the rPP-cellulose composites surface biodegradation. (a) rPP before soil burial (2000×), (b) rPP after soil burial (arrow—surface exfoliation; 1000×), (c) rPP 20cell before soil burial (1000×), (d) rPP 20cell after soil burial (arrow—surface fracture; 2000×), (e) rPP 30cell before soil burial (2000×), (f) rPP 30cell after soil (burial arrow—damaged surface;1000×), (g) rPP 40cell before soil burial (2000×), (h) rPP 40cell after soil (burial arrow—void; dotted arrow—surface exfoliation; 2000×), and (i) rPP 40cell after burial soil (arrow—traces of fungal hyphae attached to composite surface).

Generally, the initial vPP-cellulose composites have a smooth surface compared with rPP samples, and among all samples, those with 40% cellulose are more flattened. After soil burial, the samples exhibited different modifications in correlation with their composition. For all initial samples, SEM images reveal the presence of some voids, fractures, or scratches (Figure 3a,c,e,g; Figure 4a,c,e,g), which could indicate a poor interaction between the non-polar matrix of polyolefin and polar filler-cellulose. As the result of soil microorganisms-induced degradation, a series of morphological changes can be observed: damages extended on composite surface at vPP (Figure 3b); voids and surface exfoliation at vPP 20cell (Figure 3d); extended fracture with deep holes (Figure 3f) and fracture and exfoliation for vPP 30cell (Figure 3h); at vPP 40cell, voids and fracture (Figure 3j); traces of flattened fungal hyphae (Figure 3k); and deep crater connected to a long fracture for vPP 40c3l1 (Figure 3l).

A lower degradation of the samples containing rPP (Figure 4) compared to vPP samples was observed. A surface exfoliation was evidenced at rPP (Figure 4b), while rPP 20cell presented surface fracture (Figure 4d). The surface of rPP 30cell was damaged without producing holes or cracks (Figure 4f). Discrete voids and surface exfoliation were seen in images of rPP 40cell composites (Figure 4h). Fungal hyphae filaments attached to surface were visible (Figure 4i).

3.3. FTIR-ATR Analysis

FTIR-ATR analysis was applied to assess the structural modifications induced by microorganisms', revealing the rate of biodegradation based on the reduction or disappearance of some existing bonds after exposure to environment microorganisms. FTIR-ATR spectrum of cellulose presents the following characteristic bands: band at 3340 cm^{-1} assigned to hydroxyl groups stretching, bands at 2897 cm^{-1} and 1368 cm^{-1} assigned to stretching and deformation vibrations of C-H group in glucose, band at 1027 cm^{-1} assigned to -C-O- group of secondary alcohols and ethers functions from cellulose chain backbone, and band at 898 cm^{-1} characteristic of β -glycosidic linkage between glucose units [38].

In the case of recycled and virgin initial polypropylene (PP), the following bands have been identified: 2953 cm^{-1} , 2916 cm^{-1} , and $\sim 2840\text{ cm}^{-1}$ assigned to C-H stretching; 1456 cm^{-1} assigned to C-H₂ bending; 1374 cm^{-1} assigned to C-H₃ bending; 1163 cm^{-1} assigned to C-H bending, CH₃ rocking, and C-C stretching; in the range $800\text{--}1000\text{ cm}^{-1}$ assigned to CH₃ rocking, C-C stretching, and C-H and C-H₃ bendings. The spectrum was in accordance with literature data [39].

Some changes can be observed in FTIR-ATR spectra of composite samples after burial soil (Figure 5): (i) relative intensification of band in the range of $1725\text{--}1740\text{ cm}^{-1}$ assigned to carbonyl group, as an indicator of microorganisms activity and others factors upon composite samples and (ii) presence of the new bands (visible only to certain samples) at $1640\text{--}1650\text{ cm}^{-1}$ assigned to protein materials from microorganisms. The band around $1640\text{--}1650\text{ cm}^{-1}$ is due to N-H or C-N groups from N-acetyl-glucosamine units existing in soil fungi [40].

These observations are in line with the findings of others reports that mention an increase in carbonyl band after exposure to abiotic environment [34].

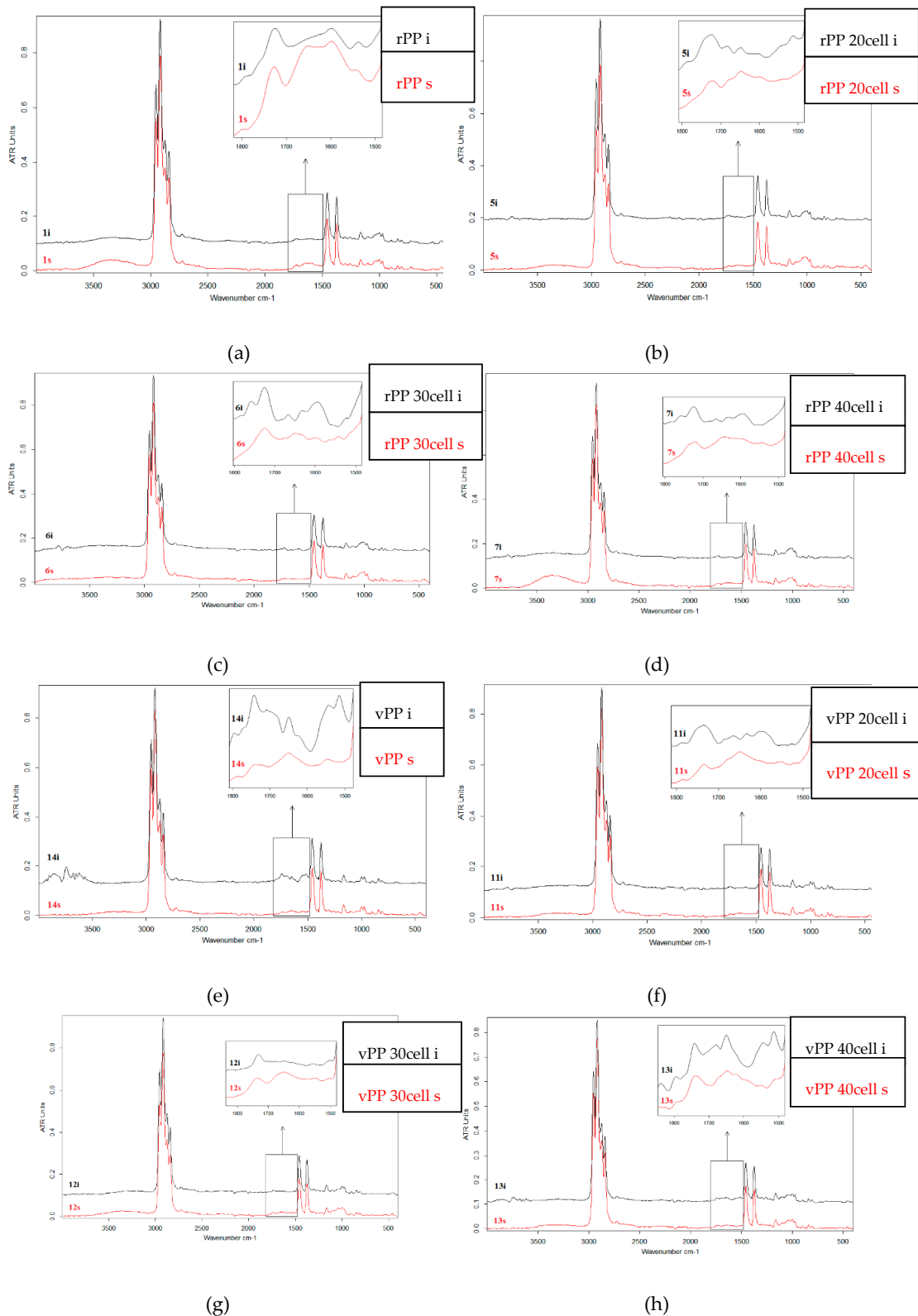


Figure 5. Fourier transform infra-red spectroscopy with attenuated total reflectance (FTIR-ATR) spectra of vPP and rPP-cellulose composites before and after soil burial (i = initial sample; s = soil buried sample). (a) rPP before and after soil burial; (b) rPP 20cell before and after soil burial; (c) rPP 30cell before and after soil burial; (d) rPP 40cell before and after soil burial; (e) vPP before and after soil burial; (f) vPP 20cell before and after soil burial; (g) vPP 30cell before and after soil burial; (h) vPP 40cell before and after soil burial.

3.4. Thermogravimetric Analysis (TGA)

TGA can determine the moisture content, thermal cleavage, thermal degradation temperature, and thermal stability of polyolefins based composites. Detailed data on thermal behavior is offered by analysis of TGA curve slope, as differential thermogravimetric analysis (Figure 6).

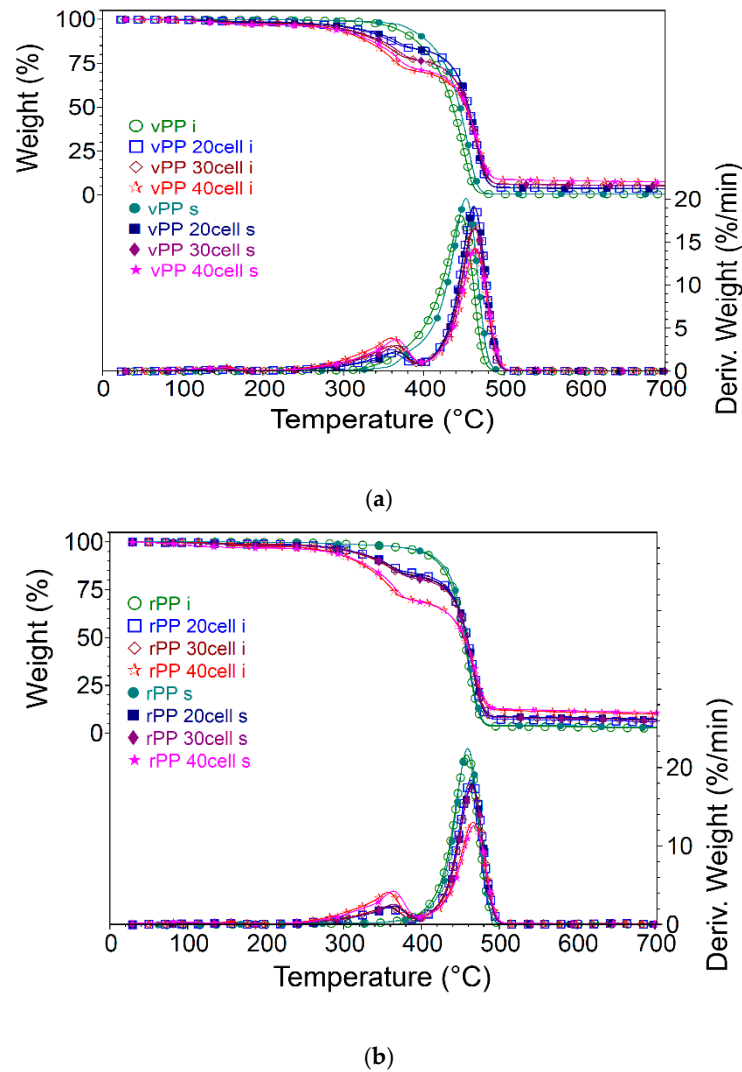


Figure 6. TGA curves of PP-cellulose composites. (a) vPP-cellulose composites and (b) rPP-cellulose composites.

The thermal stability of polymer depends on presence of monomers, aromatic rings and chemical bonds from main and side chains [41]. The evolution of weight loss in PP-cellulose composites showed typical patterns [34,42–44]. The PP-cellulose composites presented two main degradation steps. An initial weight loss was observed in the range of 30–180 °C, where water vaporization takes place. As expected, the weight loss increased with cellulose content, with the values being slightly higher for vPP cellulose samples, compared with those for rPP samples.

In the domain of 180–400 °C, cellulose decomposed at maximum temperature of 361.3 °C, a loss of 70.46% from initial weight. All composite samples presented similar evolution profiles of the thermal degradation TGA. The thermal stability after burial soil was improved, with quite small temperature differences before and after soil burial. It can be said that higher temperatures are required to decompose the samples after exposure to environmental factors during the 24 months period. The thermal weight loss was around 16% for samples with 20% cellulose, with minor differences referring to polypropylene

type. For composites with 30% cellulose, the weight loss was around 21% for vPP based composites, and around 17% for those with rPP. The weight loss values for samples containing 40% cellulose were almost similar: 28% for rPP composites and 27% for vPP composites, respectively.

Temperatures ranging from 400 to 555 °C are specific to decomposition of polymeric components. The maximum decomposition in nitrogen atmosphere occurs at 458.4 °C for rPP i, and 459.4 °C for rPP s, indicating an increase of only 1 °C. The temperature values for vPP before and after soil burial were slightly higher compared to rPP.

Normally, when lowering propylene concentration from 80% to 60%, a decrease in weight loss of samples occurred from exposure to the decomposition temperature of polypropylene. Overall, thermal degradation of buried samples was shifted towards higher temperatures, noting that rPP/cellulose composites presented a higher thermal stability than vPP. In connection with cellulose content, the values of weight loss decreased in the following order: PP 20cell (i, s) > PP 30cell (i, s) > PP 40cell (i, s). The specific degradation temperature of each individual component, rPP, vPP, or cellulose was lower than that obtained after mixing with filler in composites. This could be due to the protection exercised by the thermally more stable PP that surrounded the cellulosic fibers [43,45]. It is considered that cellulose fibers are able to immobilize the free radical released through polymer degradation, and to interact and finally inhibit the diffusion of volatile compounds resulting from degradation. The weight loss as residue in nitrogen atmosphere at 700 °C was 10.72% for rPP/cellulose composites and 7.51% for vPP/cellulose composites.

4. Conclusions

The main conclusions of the current study can be drawn as follows: (i) good resistance of proposed materials to natural environmental conditions, and thus a recommendation for possible outdoor applications; (ii) incorporation of plastic wastes, which is important for environmental protection and also for resources preservation; and (iii) high content of renewable sources, which is a positive aspect of resources preservation.

The modifications in morphology were shown by SEM micrographs as holes, cracks, exfoliation, and fractures of the composite surface. FTIR-ATR spectra of composites after soil burial presented a relative intensification of band in the range of 1725–1740 cm^{-1} assigned to carbonyl group, an indicator of changes in samples chemical structure. In some cases, new bands at 1640–1650 cm^{-1} assigned to protein materials from microorganisms were observed. All composite samples presented similar evolution profiles of the thermal degradation TGA, the thermal stability after burial soil being improved, with quite small temperature differences before and after burial soil. It can be said that higher temperatures are required to decompose the samples after exposure to environmental factors during the 24 months period.

As was expected, the increase of cellulose percentage in composite samples from 20% to 40% leads to the increase of weight loss after 24 months of burial soil. Maximum weight losses under the degradation conditions were obtained for the samples with 40% cellulose, 13.75% for rPP 40cell, and 14.50% for vPP 40cell, respectively.

Of particular interest, pronounced notable differences of composite behavior were not found regarding the polymer type or virgin or recycled polypropylene, which is an encouraging result. Thus, the use of recycled polypropylene could contribute to the conservation of petrochemical resources and to reducing the negative impact on the environment of plastic waste accumulation.

Therefore, the results proved that polyolefins–cellulose composites exhibited a reduced biodegradation and may be used for various outdoor applications. Since there is a great interest in incorporating renewable natural resources into conventional plastics such as polypropylene, the research will focus on the design of such materials, taking into account some economic aspects like lower cost and easily manufacturability. Further studies will be pursued to determine their self life, to improve their durability upon consolidation and use.

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