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Photo- and bio-degradation processes in polyethylene, cellulose and their blends studied by ATR-FTIR and Raman spectroscopies*

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Polyethylene, cellulose and their blends with different compositions (5–30% cellulose content) were exposed to UV radiation or composted in soil for bio-degradation. Both types of degradation were carried out under laboratory conditions (room temperature, air atmosphere). The course of degradation processes has been studied using ATR-FTIR and Raman spectroscopies. There are practically no changes in spectra of photo- or bio-degraded pure PE films and cellulose powders. In contrast, the PE/cellulose blends are less stable than pure components and the processes of photodegradation seem to depend on blend composition and irradiation time. Prolonged UV exposure (100 h) leads to efficient photo-oxidation of blends studied. Biodegradation effect was also pronounced in PE films containing 30% cellulose. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Polyolefins are very important and useful synthetic polymers because they posses good properties, well-known technology of production and low cost. At present, there is not expedient to back away from using synthetic polymers.

A representative polyolefin is polyethylene (PE), which has been extensively studied for many years [1–13]. Even though the mechanism of photochemical and thermal degradation of PE is well understood, the knowledge of the behaviour of this polymer in blends with other synthetic or natural materials is not sufficient. It was confirmed in numerous publications that physico-chemical properties of polymer blends are not a simple superposition of component properties [14–17]. The lack of additivity of polymer properties in blends is a main reason for difficulties in predicting their life-time.

The wide use of polymers in many industrial and domestic fields causes ecological problems connected with their utilization. Some synthetic plastics including polyolefins are characterized by relatively high stabilities under both photochemical and environmental conditions. The use of natural or synthetic photo- and bio-degradable polymers is promising, but still problematic, in direction of packaging materials [18–32]. Biodegradable materials are mainly produced for medical and pharmaceutical applications; the cost of their production is rather high as compared to classical synthetic polymers obtained from petroleum. Bio- and photo-degradable plastics are also extensively used in agriculture.

An important objective is to prepare non-expensive degradable polymers sensitive to natural factors such as sunlight, heat and soil (water) microorganisms. A simple way for obtaining bio- and photo-degradable plastics is to modify synthetic polymers by adding polymer agents of natural origin, such as cellulose or starch. The properties of such composites (tensile strength, thermal stability, resistance to bio- and photo-degradation) depend on the kind and amount of added modifier, on its dispersion degree in the polymer matrix, on sample morphology, interactions between components, degree of crystallinity, presence of structural defects as well as preparation or processing conditions [22, 31, 33, 34].

The aim of this work was to study the influence of added natural cellulose (Cell) polymer on photo- and bio-degradation of PE. It was also important to get a better insight into the molecular interactions between blend components (PE and Cell) and in their variations during the two types of degradation. So, we have focused this work on studies of surface properties because photo-degradation occurs mainly in thin surface layers of the polymer samples. We have chosen especially sensible methods allowing monitoring the changes in surface structure, as Attenuated Total

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Reflection Infrared Spectroscopy (ATR-IR). Conversely, bio-degradation occurs in the whole bulk sample, but it also begins at its external part; then, deeper parts are attacked by microorganisms, depending on their access to bulk. Combining both spectroscopic methods of ATR-IR and Raman scattering one could hope to get complementary information on susceptibility of studied samples to environmental degradation. Indeed, ATR is well known as a surface characterization and depth profiling technique. By using an appropriate combination of the refractive index of the crystal and of the incident angle, it is possible to control the penetration depth, which varies from sub-micrometers to several micrometers. Also, the Raman scattering technique is valuable to investigate small changes in the structure or bonding of natural and synthetic polymers. ATR-FTIR and Raman spectroscopic results of photo-degradation and bio-degradation are successively discussed for various polymer blends.

This paper is thus organized as follows: results of photo-degradation and bio-degradation processes obtained by ATR-FTIR and Raman Scattering spectroscopies for the pure polymers and their blends are successively discussed hereafter.

2. Experimental part

2.1. Materials

Low Density Polyethylene (LD-PE) produced by Plock (Poland) and cellulose (fibrous long) supplied by Sigma-Aldrich were used in this work. PE/cellulose films with different compositions were prepared by thermal pressing (up to 170°C) on Plasti-Corder PLV-151 extruder (Brabender) with sheet die. Non-transparent PE films (thickness of 0.6–0.7 mm) containing 0, 5, 10, 15 and 30% (wt) cellulose and 1% (wt) aminosilane thermal stabilizer $[H_2N(CH_2)_3Si(OCH_3)_3]$ were prepared.

2.2. Photo- and bio-degradation procedure

The conditions used for photo-degradation and bio-degradation of the samples were the following ones:

(i) Photo-degradation—Samples were UV-irradiated using a low-pressure mercury vapor lamp (TUV 30W, Philips, Holland, $\lambda = 254$ nm) in air atmosphere at room temperature. Average irradiance of the incident light, measured by the IL1400 Radiometer (International Light, USA), was 3.5 ± 5 mW/cm^2 and irradiation periods were varied from 20, 50 h up to 100 h.

(ii) Bio-degradation—Samples were composted in wet garden soil for periods of 7, 14, 21 and 28 weeks to induce their bio-degradation by microorganisms. Bio-degradation was conducted in room conditions (temperature: 20 ± 3°C); soil humidity was 40 ± 5%. Samples were taken off from soil after any 7 week periods, washed, dried and then analyzed by spectroscopy.

2.3. Spectral analyses

ATR Infrared and Raman spectroscopies were used for the characterization of cellulose powder, polyethylene and PE/Cell films before and after UV-irradiation or bio-degradation.

The ATR infrared spectra were recorded on a Magna 560A (Nicolet) FTIR interferometer equipped with a germanium coated KBr beamsplitter and a HgCdTe detector cooled at 77K. For each sample a total of 1500 scans were averaged at a resolution of 4 cm^{-1}. Two ATR accessories (Eurolabo) with incidence angle of 45° were used and equipped with two different crystals: The "Golden gate" with a diamond crystal (refractive index equal 2.417) and the "Silver gate" with a Germanium crystal (refractive index equal to 4.0). Both the spectrometer and the ATR accessory were purged with dry air to minimize atmospheric carbon dioxide and water vapor absorptions.

Raman spectra were collected on a LabRAM Analytical Raman micro-spectrograph (Jobin-Yvon, Horiba group, France) using a He-Ne laser source as exciting radiation ($\lambda = 632.8$ nm) and an air-cooled CDD detector (Wright). The laser power at the sample varied from 5.0 to 30.0 mW and the spectra were accumulated during 10–30 s periods. The order of magnitude of the spectral resolution was typically 5 cm^{-1} and an Olympus 100 X Mplan objective with 0.90 numerical aperture was used. To compare the spectra of different films, a normalization with respect to the more intense band either at 1294 cm^{-1} (for PE and its blends) or at 1094 cm^{-1} (for cellulose) was performed.

Both ATR-FTIR and Raman investigations were carried out considering the assignments of the Infrared and Raman active modes and the determination of structural changes in the analyzed samples.

3. Results of photo-degradation studies in polyethylene, cellulose samples and their blends

Since the PE blends containing a small amount of cellulose (5–15%) behave similarly, we present here typical results only for the pure components and for PE + 5% Cell films. Then, we present comparative data obtained for the PE + 30% Cell sample.

3.1. ATR-FTIR results

The ATR-FTIR depth profiling and surface characterization technique is very useful in photo-degradation studies, because UV-radiation does not penetrate the sample deeply. The most specific parameters of ATR are the crystal/sample contact and the penetration depth. Penetration depth (dp) is defined as the distance at which the evanescent electric field E is reduced by the factor "$e = Ln10$" upon penetration in the sample. Typical dp values of 0.066 and 0.194 λ (where λ represents the wavelength of the infrared radiation) can be calculated for a Germanium and diamond crystal, respectively, considering a mean refractive index of 1.5 for the polymer film [33, 39, 40].

In the following, only results from ATR spectra recorded with a Germanium crystal (called ATR Ge) are reported. Similar results were obtained using the other ATR accessory with a diamond crystal. As a consequence, the ATR technique tells us that the

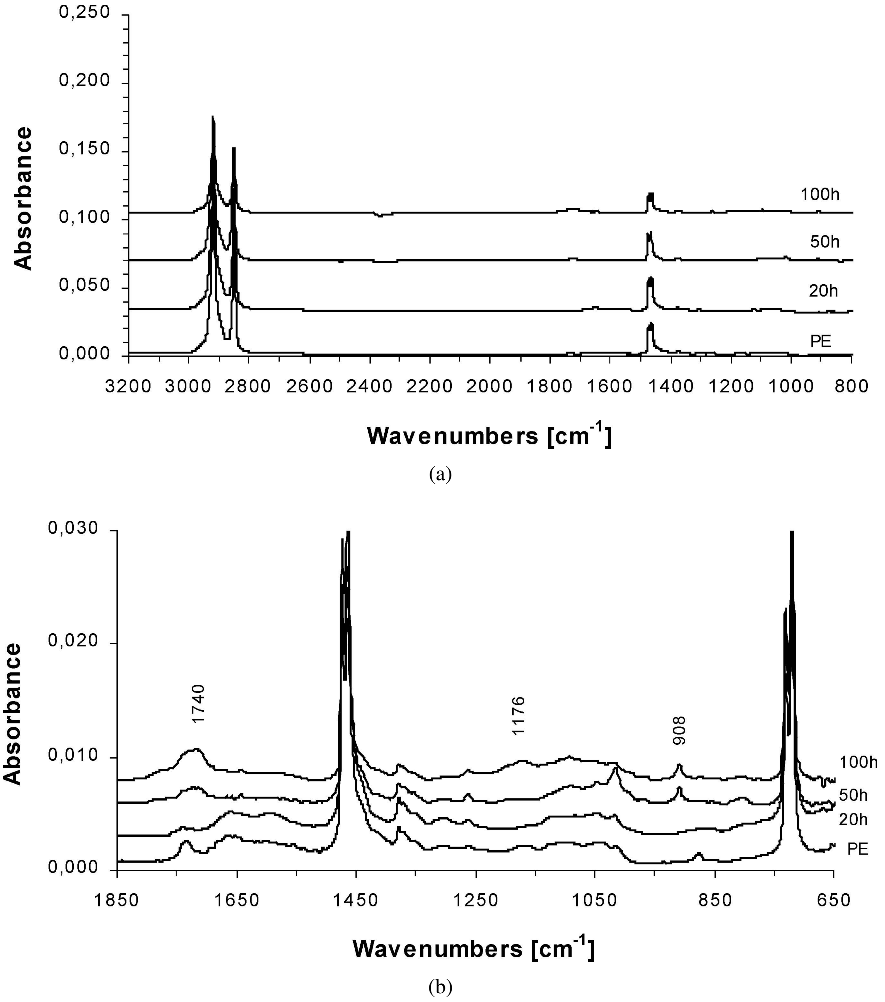

Figure 1 (a) ATR Ge spectra of PE films before photo-degradation, after 20, 50 and 100 h of UV-irradiation in the spectral range of 800–3200 cm^{-1}; (b) parts of the four above spectra in the 650–1850 cm^{-1} range.

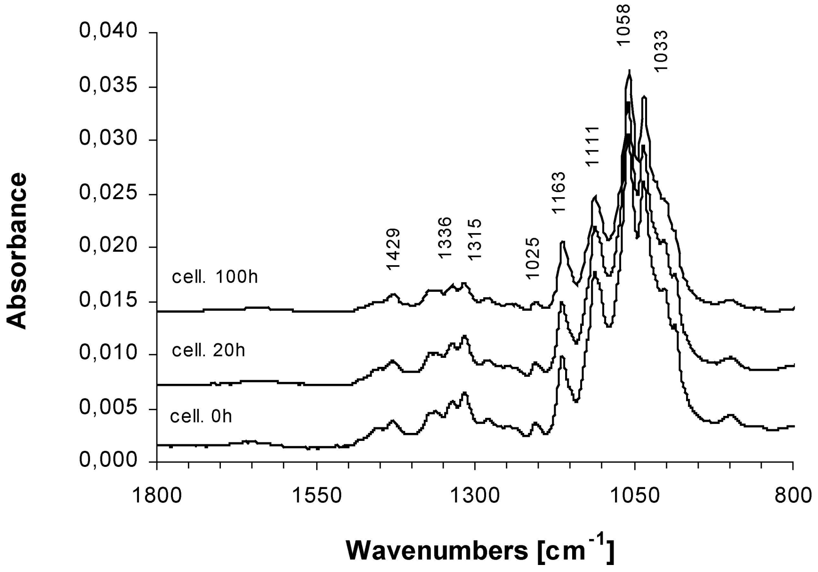

Figure 2 ATR Ge spectra in the range 800–1800 cm^{-1} of cellulose powder before photo-degradation and after 20 and 100 h of UV-irradiation.

physico-chemical properties are identical at the upper surface and within the first few micrometers inside the samples.

The ATR-FTIR spectra of samples after different irradiation times are shown on Figs 1–3. No significant changes are noted on the main absorption bands of polyethylene (Fig. 1a), the vibrational assignments of which are reported in Table I [41]. On Fig. 1b, more details in the 650–1850 cm^{-1} region are displayed for a polyethylene film before and after UV exposure. In this region, only slight changes are detected after 20 h UV irradiation, suggesting a photochemical modification of the PE film surface. Under longer times of UV-irradiation (50–100 h) changes are more distinct

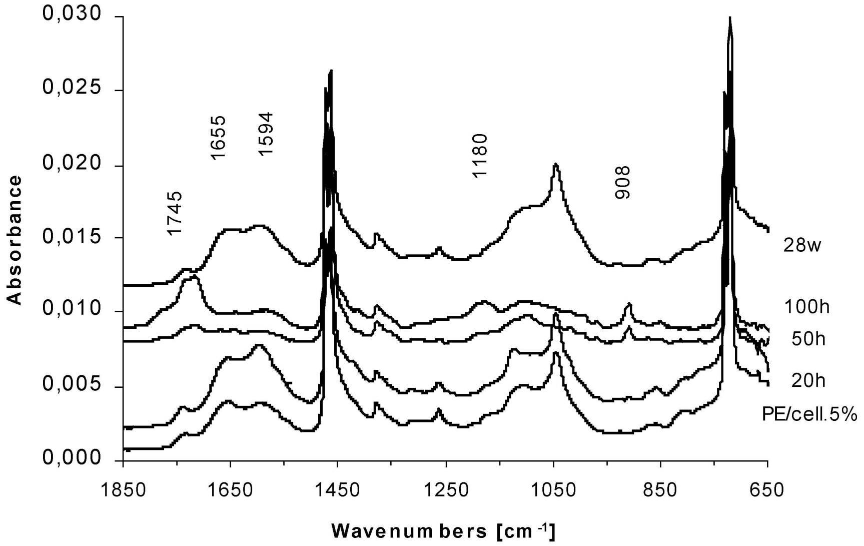

Figure 3 ATR Ge spectra of PE/Cell. (5%) film before photo-degradation, after 20, 50 and 100 h of UV-irradiation, and after 28 weeks of composting.

in the whole range of PE spectrum. New peaks appear at 1740 cm^{-1} (due to carbonyl stretching vibrations), 1170 cm^{-1} (C—O—C asymmetric stretching vibrations, which can overlap with CH_2 wagging vibrations), and at 908 cm^{-1}, and their intensities increase with irradiation time. The band at 908 cm^{-1} could be due either to CH_2 out-of-plane deformation of the vinyl groups formed as a result of photo-degradation, or to the symmetric Si—O—CH_3 stretching band of the stabilizer, which can slowly diffuse through the polymer matrix according to the so-called exudation effect. Simultaneously, notable differences in the 900–1100 cm^{-1} and 1500–1700 cm^{-1} regions were observed. In particular, water absorptions are detected as inferred from bands at 3400 and 1650 cm^{-1}. It is noteworthy that the water bands at near 1650 cm^{-1} (Fig. 1b) are already existing in the initial PE sample, but they disappear after a long time UV-irradiation. These results clearly indicate that a photo-oxidation process in PE has been already started after 20 h of UV-irradiation, but a longer time exposure is needed to obtain a higher efficiency of photoproducts collected in PE films.

Absorption spectra in 800–1800 cm^{-1} region of cellulose before and after 20–100 h UV-irradiation are reported on Fig. 2. We have intentionally omitted the region from 1800 to 2800 cm^{-1}, which is devoid of significant cellulose bands. The assignment of the different cellulose bands is given in Table II [43]. As shown on Fig. 2, there is no apparent modification of the cellulose powder after exposure, both the location and the intensity of all the bands are similar before and after irradiations as long as 100 h. Therefore, cellulose is characterized by a high photostability under the used experimental conditions.

TABLE I Main absorption bands of polyethylene and their assignments [41, 42]

Band (cm^{-1})	Assignment*
2919	CH_2 asymmetric stretching
2851	CH_2 symmetric stretching
1473 and 1463	CH_2 bending deformation (A)
1377	CH_3 symmetric deformation (C)
1366 and 1351	Wagging deformation
1306	Wagging deformation
1176	Wagging deformation (C/A)
731–720	Rocking deformation

*C-crystalline; A-amorphous.

The photostability of pure cellulose can be related to the lack of absorbing centers in its structure. Our results confirm also that the amount of chemical impurities, which usually induce photo-degradation processes in polymers, is insignificant in this natural material.

The ATR Ge spectra of UV-irradiated blends containing a low amount (5, 10 or 15%) of cellulose were not totally reproducible. Even though the PE bands were identical in all the spectra, we have observed some modifications in the spectral range associated with the cellulose absorptions. This could be due either to an inhomogeneous distribution of cellulose at the surface of the PE blends, or to particular intermolecular interactions. Moreover, since photo-degradation is a random process, only the trend of qualitative changes can be discussed comparatively using different samples.

Typical examples of ATR Ge spectra of PE/cellulose (5%) film before and after 20–100 h of UV-irradiation, and after 28 weeks of biodegradation are shown on Fig. 3. In the 1000–1200 cm^{-1} spectral range, where

TABLE II Main absorption bands of cellulose and their assignments [43]

Band (cm^{-1})	Assignment
3348	O—H stretch (hydrogen- bonded)
2902	C—H stretching
1640	Adsorbed O—H, conjugated C=O
1430	C—H deformation (asymmetric)
1372	C—H deformation (symmetric)
1336	O—H in-plane deformation
1201	O—H deformation
1163	C—O—C asymmetric vibration
1112	Glucose ring stretch (asymmetric)
1059	C—O stretch
1033	C—O stretch
897	Glucose ring stretch.

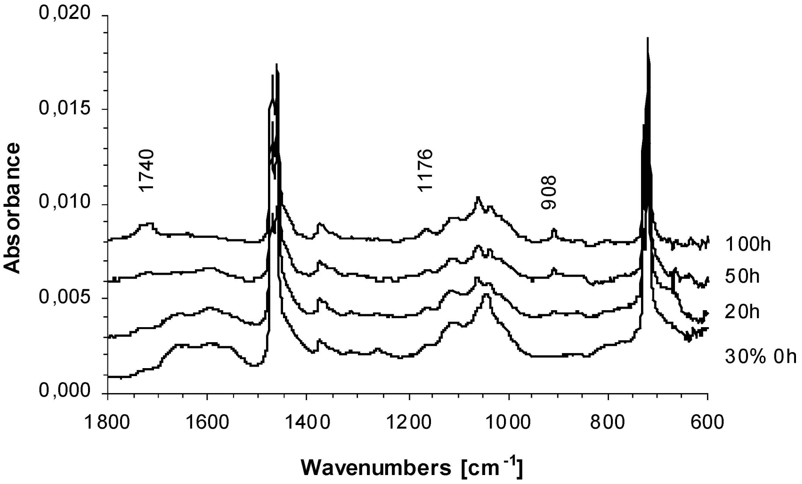

Figure 4 ATR Ge spectra of PE/Cell. (30%) film before photo-degradation, after 20, 50 and 100 h of UV-irradiation.

intense absorptions characteristic of cellulose usually appear, several bands are detected but at different wavenumbers as compared to those reported for pure cellulose. In addition, the intensities of these bands vary from one spectrum to another, so that they are likely attributed to other chemical species located at the surface of the blends. These chemical species are not produced during the photo-irradiation, since they were already existing in the spectra before irradiation. So, they are probably due to another compound added during the fabrication of the blend (for example, the stabilizer), or they could come from a chemical reaction with water during the thermal pressing (formation of carbonates, for instance). Finally, these bands are very intense and the cellulose bands can no more be detected. It is remarkable that, after a long UV-irradiation of these samples (with 5–15% cellulose) the spectra exhibit carbonyl bands maximizing at near 1745 cm^{-1}, and a new very weak band at 908 cm^{-1}, as previously discussed for the irradiated PE films.

In contrast, the ATR spectrum of the PE blend containing 30% cellulose displays very characteristic cellulose bands in the 1000–1200 cm^{-1} spectral range; they are observed before and during photo-degradation (Fig. 4). However, their intensities are still relatively weak. Only very small changes are observed in this spectral range after UV-irradiation, providing evidence for a good photo-stability. After 20–100 h of UV-irradiation the weak band at 908 cm^{-1} appears again, as discussed above in all analyzed samples. In addition, weak changes are induced by UV-irradiation in the 1500–1700 cm^{-1} range of the ATR spectra of this blend at the beginning of exposure (20–50 h) and we note the appearance of a clear carbonyl band (1740 cm^{-1}) after 100 h UV-irradiation. As above mentioned for the pure PE sample, we again observe that the disappearance of water absorptions is related to the exposure time of UV-irradiation.

The above spectra (Figs 3 and 4) suggest that processes of photo-oxidation are more efficient in PE samples containing a small amount of cellulose (5%), than in PE samples with a 30% Cell content. This can be explained by different morphologies of PE blends with small and high amounts of natural polymer. Both components are immiscible and the interpenetration of both types of macrochains into mixed domains is rendered difficult. However, in the case of a small amount of one component into the matrix of a second polymer, the dispersion degree of included particles can be higher; thus, interactions between both components, which are limited to phase boundary, are probably stronger. The more active degradation products (for example, small and mobile radicals) can diffuse into the neighbor phase, because they have a shorter way in samples containing small domains (i.e. small content of modifying polymer). Such active products could then initiate the degradation in other points of the specimen.

3.2. Raman scattering results

In Raman spectroscopy, all spectra were recorded under off resonance conditions since the exciting visible laser lines used are very far from any electronic absorption band of the cellulose sample. This scattering technique has also some important advantages for recording spectra of cellulose materials, since the absorbed water only leads to very weak signals and background contributions.

The Raman spectrum in the range 800–1800 cm^{-1} of a non-degraded cellulose sample is shown on Fig. 5 (cell. 0 h). The region 1200–1500 cm^{-1} contains numerous vibrations of mixed characteristic group frequencies [43]. Thus, the observed maxima are assigned to modes involving considerable coupling of methylene bending, methylene rocking and COH in-plane bending vibrations; excluding the internal modes of the CH_2OH groups, all motions are quite delocalized. In the intermediate region (1050–1200 cm^{-1}), some vibrational modes involve a significant amount of skeletal stretching as well as methylene bending vibrations. Their frequency distributions are sensitive to the orientation of the glycosidic linkages. The band near 895 cm^{-1} is due to the presence of crystalline and/or amorphous domains of cellulose. Broadening of this band is caused by a higher amount of disorder. Such disorder is expected to come from changes in angles around glycosidic linkages, and in hydrogen bonding arrangements. This band has been assigned to deformation modes

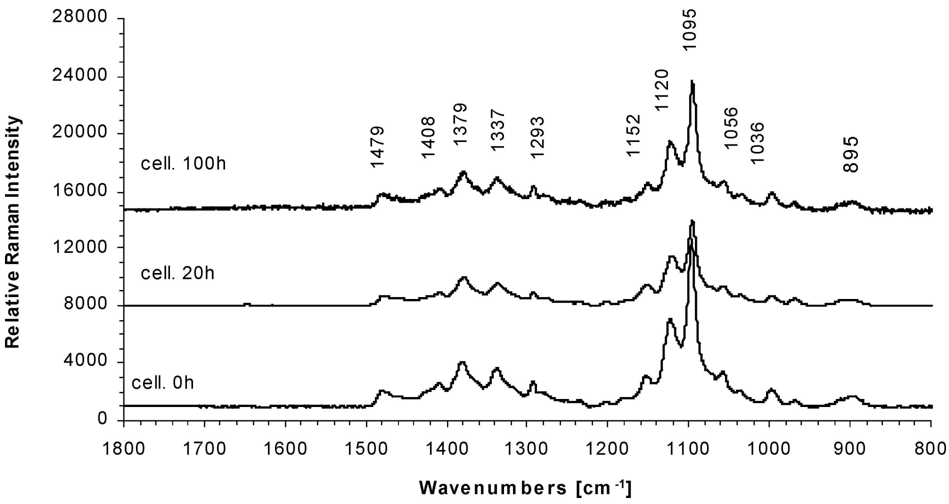

Figure 5 Raman spectra of cellulose powder before (0 h) and after 20 and 100 h of UV-irradiation; the intensity of the 1095 cm^{-1} signal has been used as normalization peak.

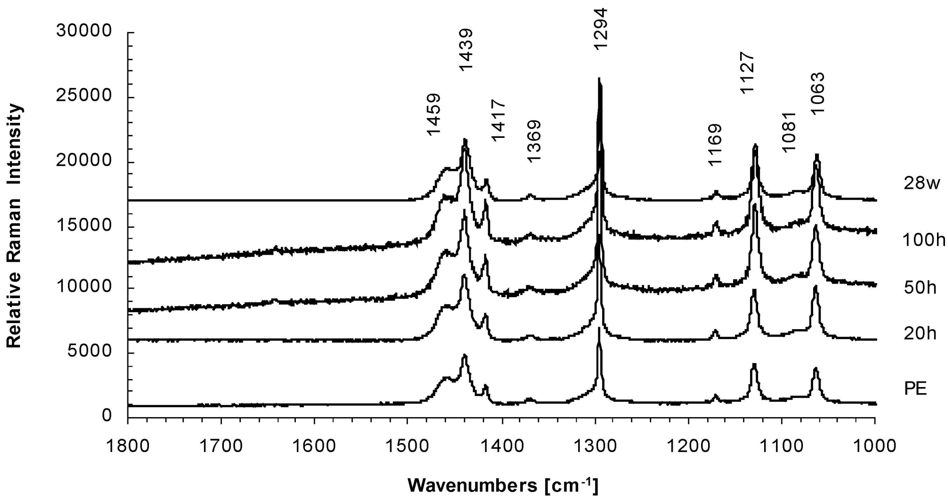

Figure 6 Raman spectra of polyethylene before (PE) and after 20, 50, 100 h of UV-irradiation and after 28 weeks of composting; the intensity of the 1294 cm^{-1} signal has been used as normalization peak.

involving COC, CCO, CCH skeletal linkages [35, 36]. Another reason for the broadening of this band could be due to interpenetration of PE and cellulose chains during the sample preparation at high temperature, since segmental mobility is increased.

After 20–100 h of UV-irradiation, no significant changes are observed in the Raman spectra of pure cellulose (Fig. 5). The lack of spectral changes even after long UV-irradiation time (100 h) confirms the high photostability of cellulose. This is in a good agreement with the ATR-FTIR results above described.

Characteristic bands for polyethylene (Fig. 6) display similar intensity and maxima at the same wavenumbers before and after UV exposure. This concerns the signals for both crystalline and amorphous regions, leading to the conclusion that there is no additional amorphization of the material under long time UV-irradiation. The Raman spectra thus demonstrate that PE bulk is photostable, even though an oxidation process was monitored after longer exposure by ATR-IR results of the PE surface.

The changes observed in the Raman spectra of PE blends containing cellulose are not so significant. For instance, results obtained for PE/cellulose (30%) are shown on Fig. 7. No new peaks are observed, but the intensity ratios of characteristic bands differ in spectra of irradiated blends as compared to those in the unexposed specimen. It is obvious that the Raman spectra are not very sensitive for photo-oxidation products (e.g. carbonyls, hydroxyls). In contrast, clear changes appear on some cellulose characteristic signals, and the bands at 1095 and 1373 cm^{-1} significantly decrease: this indicates that the degradation of the natural component is only efficient upon longer times of UV action. We have found that a longer photo-degradation (of 100 h) leads to the formation of new fluorescent impurities; they are probably responsible for further degradation of the polymer blensd, contrary to the behavior in pure polymer samples.

4. Bio-degradation of polyethylene, cellulose and their blends

PE and its blends with a 5–30% cellulose content were composted in soil during a relatively long period (up to 6 months). Samples were analyzed after every week of bio-degradation by ATR-FTIR and Raman spectroscopies. Bio-degradation of the original cellulose has

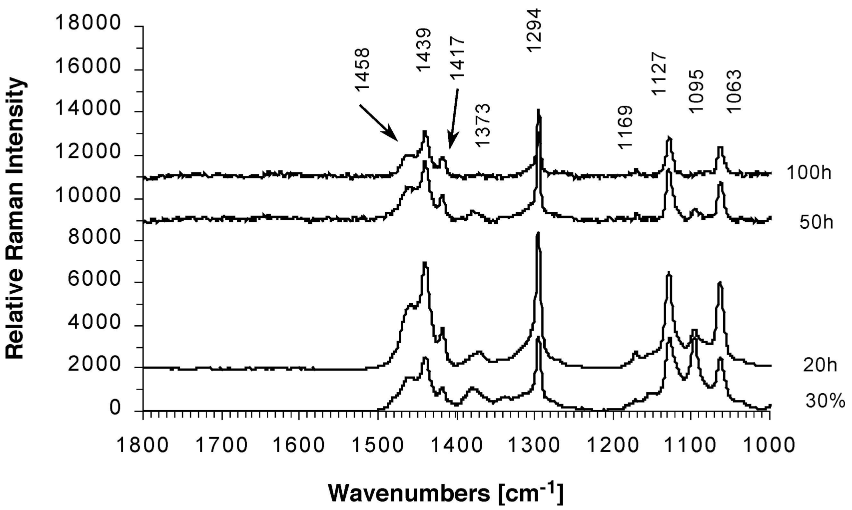

Figure 7 Raman spectra of PE blends with a 30% amount of cellulose before (30%) and after 20, 50 and 100 h UV-irradiation; the intensity of the 1294 cm^{-1} signal has been used as normalization peak.

not been investigated because of the difficulty to recover powder from the soil. The spectral changes in composted PE/Cellulose blends were found strongly dependent on the sample composition.

4.1. ATR-FTIR results

As expected, a pure PE film does not exhibit any significant change in ATR Ge spectra after composting, since this polymer is well known as non-biodegradable product.

ATR Ge spectra in the 800–1800 cm^{-1} wavenumber range for blends containing 5 and 30% cellulose (before and after bio-degradation) are shown on Figs 3 and 8, respectively. Practically, there is no significant change in spectra of samples with a low amount of cellulose (5–15%), even after 28 weeks of composting. In contrast, the ATR Ge spectra of PE + 30% cellulose, especially in the 1000–1200 and 1500–1800 cm^{-1} regions, show some significant changes appearing after only 14 weeks of bio-degradation. Indeed, in the former region the intensities of cellulose bands decrease, whereas in the latter domain two new weak bands appear at 1541 and 1577 cm^{-1}. These results are certainly related to the cellulose degradation process, and they are in agreement with similar conclusions reached using the ATR diamond accessory. They clearly indicate that the blend with 30%Cell is much more sensitive to microbial action than samples containing a lower content (5–15%) of this natural polymer.

4.2. Raman scattering results

Here again, no change in Raman spectra of biodegraded PE films was detected after a long period of composting (Fig. 6).

For PE blends with a small amount of cellulose (5–15%) the observed modifications in the Raman spectra are not so drastic as shown on Fig. 9. The composting during a 28 week period has only a small influence on the behavior of the analyzed sample. Peaks at about 1368, 1338 and 1093 cm^{-1} (assigned to asymmetric CH_2 deformation, O—H in-plane deformation and symmetric glucose ring breathing, respectively [35])

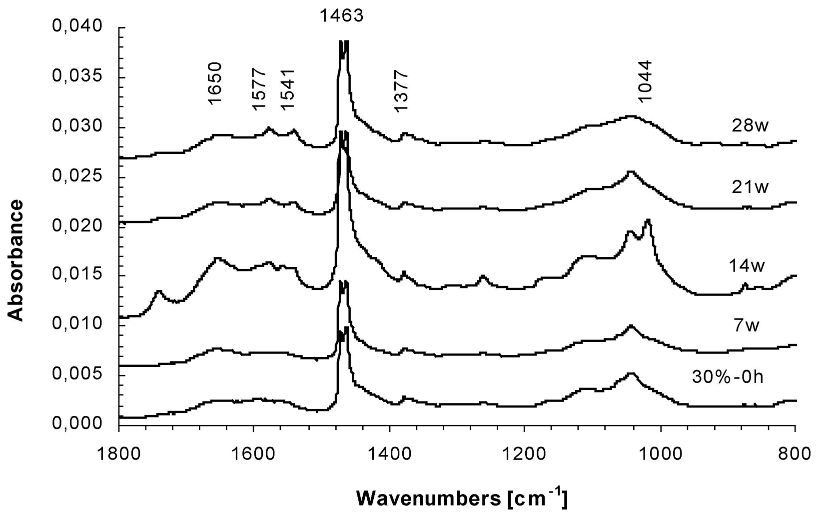

Figure 8 ATR Ge spectra in the spectral range 800–1800 cm^{-1} of PE/Cell. (30%) film before bio-degradation (0 h) and after 7, 14, 21 and 28 weeks of composting, respectively.

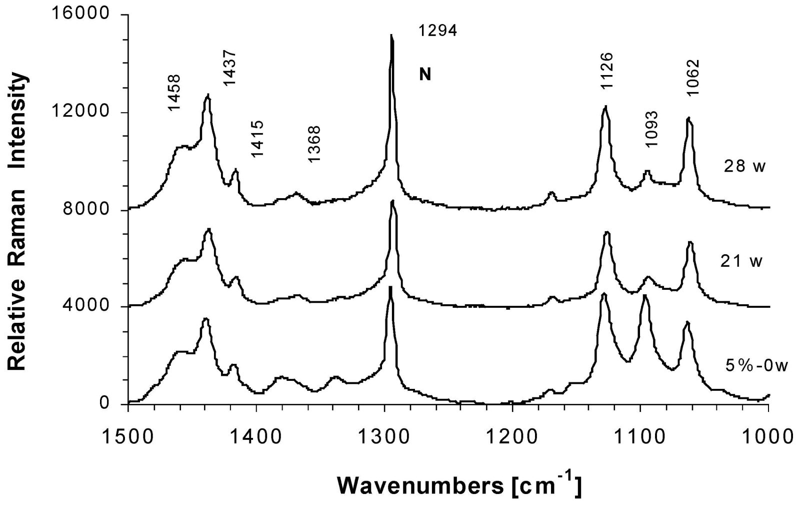

Figure 9 Raman spectra of PE blends with a 5% amount of cellulose before (0 w) and after 21 and 28 weeks of bio-degradation, respectively; the intensity of the 1294 cm^{-1} signal has been used as normalization peak.

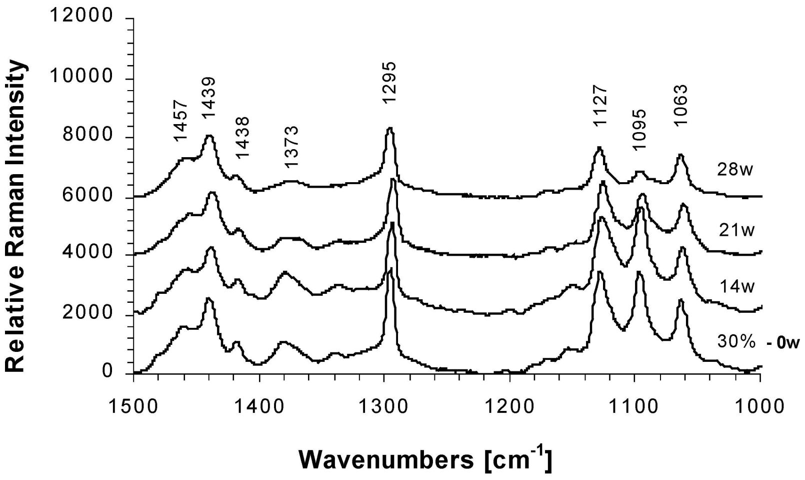

Figure 10 Raman spectra of PE blends with a 30% amount of cellulose before (0 w) and after 14, 21 and 28 weeks of composting, respectively; the intensity of the 1294 cm^{-1} signal has been used as normalization peak.

display a very weak intensity because of the small amount of cellulose in the blends; conversely, in the blends with 30% of cellulose the intensities of these peaks are much larger. After bio-degradation, their intensities decrease, whereas the peak at 1338 cm^{-1} disappears almost completely.

Blends containing 30% of cellulose have shown a similar tendency. After a period of 14 weeks of bio-degradation characteristic cellulose Raman peaks become very weak, the signal at 1337 cm^{-1} disappears and the intensity of the strong line at ~1095 cm^{-1} rapidly decreases (Fig. 10). Then, after this period the sample starts to lose its stability under composting.

All the Raman results for composted PE samples and their blends with cellulose corroborate the previous observations made in ATR-FTIR.

5. Discussion

In this Raman study we have confirmed the high stability of polyethylene, cellulose and their blends with 5–15% cellulose upon photo- and bio-degradation under normal (room) temperature and atmospheric pressure conditions. However, using the ATR technique we have detected on the surface of PE films some modifications induced upon UV-irradiation. In addition, a new peak has appeared at about 908 cm^{-1}, in both the pure polyethylene sample and the cellulose blends. It could arise either from a small amount of stabilizer (which was used in the preparation of the samples), or from vinyl groups formed mainly at PE chain-ends during degradation.

Furthermore, from ATR-FTIR results it is suggested that PE/Cell blends, although relatively resistant to short time photo-degradation, undergo a photooxidative degradation after longer exposure (when induction period is exceeded). Moreover and as expected, PE/Cell blends are more sensitive to bio-oxidation than the pure components.

Oxidation of a non-reactive polymer generally changes its susceptibility to bio-degradation. As soon as carbonyl groups are formed, they may be attacked by microorganisms and the macromolecules decompose into shorter chains. Carbonyl groups are also known as photosensitizing species, which may accelerate further photo-degradation steps. The macrochains containing carbonyl groups are also known to undergo Norrish I and Norrish II type reactions under UV exposure. Moreover, the bio-degradation of natural component leads to increased porosity and development of film surface.

Therefore, the access to the polymer bulk of free oxygen, enzymes (produced by microorganisms) and free radicals formed in primary reactions is facilitated; this significantly promotes any following degradation step.

The cellulose powder is characterized by a high stability, as it was confirmed by Raman scattering and ATR experiments. The peak at 895 cm^{-1}, which appears in the Raman spectra of PE/Cell films, is characteristic of a variable amount for the crystalline and amorphous parts in cellulose; the broadening of this band is probably due to the existence of some structural disorder.

Another interesting result is provided by the Raman spectroscopic analysis of PE/Cell 30% films after bio- and photo-degradation. We have noted a significant intensity decrease of three signals at $\sim$1373, 1337 and 1095 cm^{-1} after just 20 h. of UV-irradiation and after 14 weeks of composting. Similarly, characteristic cellulose peaks become very weak, the peak at 1337 cm^{-1} almost disappears, and a strong line at 1095 cm^{-1} is rapidly losing intensity. This suggests that samples containing a substantial amount of natural polymer are much less stable than samples with a lower content, especially at a primary period of degradation.

The differences in stability of PE blends with different compositions may also arise from various sample morphologies. In PE blend with 5–15% Cell, the cellulose can be better dispersed as small inclusions into the PE matrix—thus numerous contacts at interphase boundaries facilitate the intermolecular interactions (e.g. van der Waals interactions). In such cases, the blend resistance seems to be improved similarly as in polymer nano-composites containing fillers. The addition of 30% cellulose to PE is surely in favor of the formation of larger domains, so that interactions are not strong enough to impede degradation processes. However, two opposite effects can take place—improvement of the blend structure resulting of interaction or crosslinking and effect of the degradation products influencing the mutual destabilization of blend components. As mentioned in the case of a well dispersed natural additive in PE matrix, the diffusion of active species initiating macrochain degradation can be facilitated.

Moreover, during photo- and bio-degradation of PE new functional groups are formed (carbonyls, hydroxyls), and they modify the polarity of the polymer. This effect may induce new molecular interactions with the OH groups of cellulose. Such interactions probably facilitate the evolution of low molecular weight degradation products (for instance, water molecules), and weaken other neighboring chemical bonds.

It is emphasized in this study that clear changes appear in the blend surfaces and in their internal structures upon either bio-degradation or photo-degradation, but only after a somewhat induction period. This induction period is dependent not only on the chemical nature of blend components, but also on the sample morphologies, which control the penetration of any active low-molecular weight product.

Finally, it is well known that, in free radical photo- or bio-degradation processes, the reaction once initiated can be repeated many times before termination [38]. Thus, cyclic chain radical reactions occur through a long time during polymer aging. It should be also pointed out that in environmental conditions various kinds of degrading factors (light, heat, microorganisms) may act simultaneously on the polymers. The synergistic effect between photo-degradation and biodegradation of PE has been already described in the literature [4, 38]. Here, we can expect that the blends under study subjected to UV radiation will be more easily bio-degradable. Therefore, it would be interesting to investigate the influence of any preliminary irradiation on such bio-degradation processes in the polymer blends. Such studies will be carried out in the near future.

6. Conclusions

PE films and cellulose fibers were shown to be resistant to UV-irradiation ($\lambda = 254$ nm) and to microorganisms present in soil. Photo-degradation and bio-degradation of PE/cell blends are largely dependent on their composition. PE blends with a relatively small amount of cellulose (5–15%) behave differently than mixtures with a greater content of this natural polymer (30%). The former samples were characterized by a higher photo- and bio-resistance, while samples with 30% cellulose were less stable as inferred from both ATR-FTIR and Raman spectroscopic results. Also, the time of degradation and the sample morphology are playing a key role on the course of both degradation processes. Although the induction period of photodegradation is shorter for PE + 30% Cell, the efficiency of oxidation after long time exposure (100 h) is higher for the PE + 5% Cell sample. Such a behavior is probably due to different interactions between macrochains of both types, which in addition favorise the formation of polar groups in the PE samples.

Finally, when changing the blend compositions, it is hopeful that advanced materials for the fabrication of durable or more degradable products (e.g. for production of ecological degradable packaging) could be designed.

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