

Photochemical and Thermal Stability of Degradable PE/Paper Waste Composites Obtained by Extrusion

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ABSTRACT: The low-density polyethylene (PE)/waste paper composites with different components ratio were prepared by extrusion. The photochemical stability of these samples and crystallinity degree of PE in blends were studied using ATR-FTIR spectroscopy. The thermal properties of composites were estimated by thermogravimetric analysis. Moreover, the morphological changes were observed by SEM. It was found that after long-term exposure to UV (100 h) composites undergo more efficient photo-oxidative degra-

dation when compared with pure PE. Also the thermal stability of composites obtained is lower than that in PE. The results indicate that such a material is characterized by high susceptibility to environmental decomposition. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2197–2206, 2007

Key words: polyethylene/waste paper composites; irradiation; thermal stability; infrared spectroscopy; thermogravimetry

INTRODUCTION

Polymer composites are a class of materials with excellent properties, low production costs, and well-known technology.^{1–5} Their production systematically increases, thus, also the plastic waste amount grows. The utilization of used polymeric products has become a great problem in recent years. The solutions proposed for reduction of plastic waste (such as product reusing, disposal, recycling, incineration), besides having benefits, have disadvantages and limitations. The production of biodegradable composites is an ecological alternative for reduction of plastic waste.^{6–10} Polyethylene (PE), the most popular polyolefin, broadly used as packaging material, is not sensitive to microbial attack. The induction of its degradability by mixing with natural polymers, for example polysaccharides (starch, cellulose), is known since almost twenty years. In such blends, the biopolymer undergoes biodegradation, as a result of which the PE matrix is destroyed and dissipated in the surrounding. The biopolymer added to polyolefin plays a role of a low cost reinforcing filler.^{11,12}

Some other additives (e.g., prodegradants or prooxidants) introduced to PE can also enhance its decomposition under various environmental factors, i.e., oxygen, UV radiation, bacteria, fungi, inorganic or organic impurities. It was recently shown that pre-

liminary UV irradiation of polymeric material can induce its biodegradation.^{13,14} The reason is main chain scissions and formation of functional groups in macromolecules during photo-oxidative degradation. Such degraded polymer, containing shorter chains and incorporated hydroxyl and carbonyl groups, as well as being unsaturated, is further easily consumed by microorganisms. It was also reported that in case of mutual action of few degrading factors, it is difficult to predict the final decomposition effect because the synergism or antagonism can occur.^{15,16}

The aim of our work was to obtain biodegradable material consisting of PE and paper waste and to study their properties, especially their thermal and photochemical stability. The following topics are important from the ecological point of view:

- using of waste paper (reduction of pollution)
- using the renewable resources (because paper is made from wood)
- using cheap filler (from waste paper)
- preparation of biodegradable composites (because of paper biodegradability)

The polyolefin behavior in thermal or photochemical degradation has been widely investigated and the mechanism of reaction occurring in pure PE is well known.^{15–30} However, the presence of additives, modifiers, or other polymers can cause unexpected effects. Some introduced compounds initiate the degradation processes in polymer, whereas other additives protect them.^{15,16,31} Also the preparation method influences the polymer degradation.

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MATERIALS AND METHODS

Materials and sample preparation

The low density polyethylene (LDPE) supplied by Petrochemia Płock, Poland, was used in these studies. Paper waste was cut by shredder to get small pieces.

PE/paper waste composites were obtained using test extrusion line with strand pelletizing system, the main device of which was a corotation twin-screw extruder from Bühler (BTSK 20140D, Germany). The diameter of screws was 20 mm and working length of screws was $L = 40 D$. For the manufacture, the configuration of screws with four mixing zones has been used. The mixture of PE/paper waste was transported to the feeding hopper of the twin-screw extruder. Then, the extrudate was cooled and cut by strand pelletizer. The process of extrusion of PE/paper waste compositions was carried out at the following parameters:

- temperatures of barrel heating zones: 180, 180, 180, 185°C
- temperature of the die heating zone: 190°C
- rotary speed of screws: 250 min⁻¹.

Now, the obtained composites of PE/paper waste in the form of pellets were used to extrude the tape samples. Extrusion of tape was realized using test line from Brabender consisting of the following:

- single screw extruder with screw diameter of 19 mm and working length of screw 25 D
- flat extrusion die width of 25 mm and slot die-head of 0.5 mm
- polishing rolls unit of rolls diameter 110 mm

To extrude the mixture, the screw of compression ratio 1:3 was used.

The process of extrusion of PE/paper waste composite tape was realized at the following parameters:

- temperatures of barrel heating zones: 160, 170, 180°C
- temperature of the die heating zone: 180°C
- rotary speed of screw: 20 min⁻¹

The sample thickness was typically in the order of 0.5–1 mm.

The pure cellulose powder (Sigma–Aldrich) was used as reference for identification of absorption bands characteristic for paper. Composition and names of samples used in the work are shown in Table I.

Exposure to ultraviolet radiation

The samples were exposed to low-pressure mercury vapor lamp TUV 30 W (Philips, The Netherlands),

which has emission line at 253.6 nm. Irradiation was performed at room temperature under air atmosphere during 10–100 h. Incident light intensity, measured by radiometer IL 1400 A (International Light, USA), was 3.4 mW/cm².

FTIR spectroscopy

Photochemical processes in polymer composites were monitored by attenuated total reflectance infrared (FTIR-ATR) spectroscopy using FTIR Genesis II spectrophotometer (Mattson, USA) equipped with ATR device: MIRacle™ Pike Technologies containing ZnSe crystal. Incident beam angle was 45°. Sixty scans were acquired with a spectral resolution of 4 cm⁻¹. The carbonyl ($I_{C=O}$) and vinyl ($I_{C=C}$) indexes were calculated using intensity of bands at 1716 and 908 cm⁻¹, respectively:

$$I_{C=O} = \frac{I_{1716}}{I_{2916}}, \quad I_{C=C} = \frac{I_{908}}{I_{2916}}$$

where the band at 2916 cm⁻¹ is a standard peak due to C–H vibration.

The crystallinity degree (X , %) was calculated according to the formula³²

$$X = 100 - \frac{\left(1 - \frac{I_{729}}{I_{719}}\right) 1.233}{1 + \frac{I_{729}}{I_{719}}} 100\%$$

Bands at 729 and 719 cm⁻¹ are attributed to crystalline and amorphous phase in PE respectively.

Thermogravimetry

The thermogravimetric analysis was carried out at a heating rate of 6°C/min from room temperature up to 600°C using TA Instrument SDT 2920 Simultaneous DSC-TGA. The TG, DTG, and DTA curves were recorded under nitrogen atmosphere. The values of the following parameters were obtained from the thermograms (Fig. 1):

- T_o (°C) – on-set degradation temperature (taking the point where DTG begins to deviate from base line)

TABLE I
Assignments of Samples Used in Work

Symbol	Sample
PE	Polyethylene
PE I	Polyethylene + 5% paper
PE II	Polyethylene + 10% paper
PE III	Polyethylene + 15% paper
PE IV	Polyethylene + 20% paper
PE V	Polyethylene + 25% paper
PE VI	Polyethylene + 30% paper

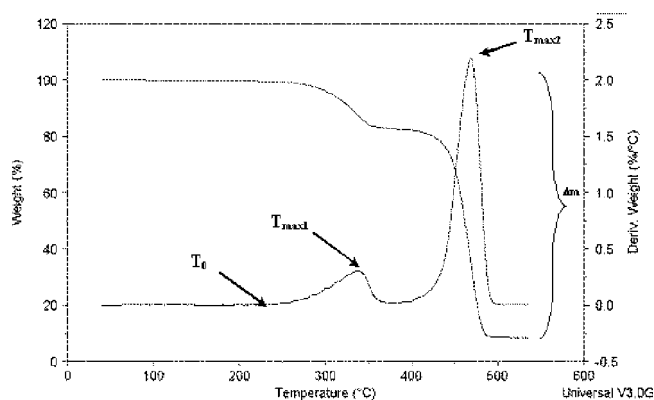


Figure 1 An example of thermogram for PE/paper waste composite—the estimation of thermal parameters.

- T_{max1} (°C) – maximum process rate temperature for the first degradation step (paper decomposition)
- T_{max2} (°C) – maximum process rate temperature for the second degradation step (PE decomposition)
- Δm – weight loss at 520°C

Scanning electron microscopy

Scanning electron microscope (SEM) – LEO 1430 VP with BSE detector (Back scattered electrons) was used for investigation of surface morphology. Accelerating voltage applied was 28 kV.

RESULTS

Characterization of PE/paper waste composites

The obtained composites were nontransparent and slightly gray. Thus, for infrared studies, the attenuated total reflectance technique was used. The ATR-FTIR spectra of pure PE and its composites with different amounts of paper waste are shown in Figure 2. Because PE is the dominant component in the blends studied, in all spectra, the following most intensive bands due to C—H stretching and deformation vibrations appear:³³

- 2919 cm^{-1} – asymmetric stretching
- 2848 cm^{-1} – symmetric stretching
- 1471 and 1463 cm^{-1} – bending deformation
- 729 and 719 cm^{-1} – rocking deformation

When the amount of paper in the composite increases, the additional bands characteristic for cellulose (at 3000–3500, 950–1300, and 872 cm^{-1} attributed to OH and C—O and ring vibrations) become more clear.

The identification of cellulose bands was done on the basis of spectrum of paper and pure cellulose (Fig. 3) as well as on the literature data.³⁴ The broadening of main PE bands at 1400–1500 cm^{-1} with the rise of intensity of branch at 1471 cm^{-1} was also observed in the blends. It can suggest some interactions of both components.

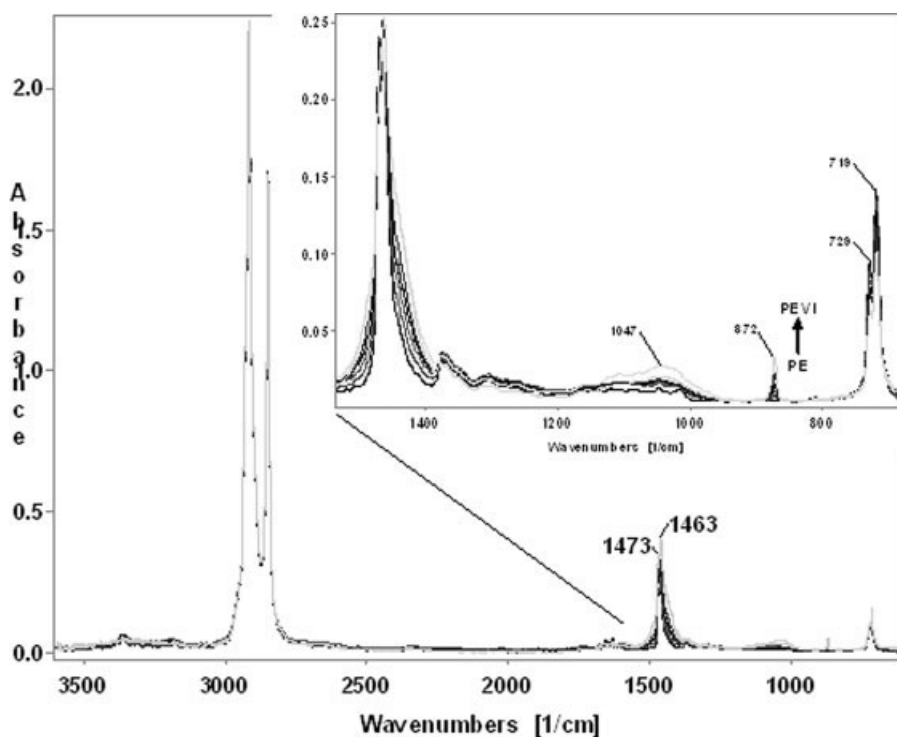


Figure 2 ATR-FTIR spectra of PE and PE composites containing 5–30% paper waste.

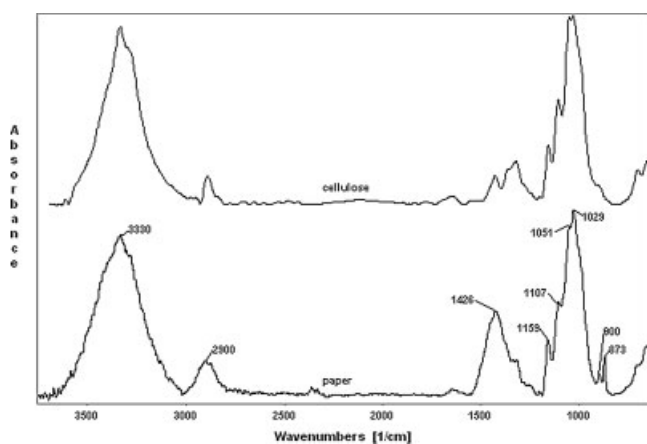


Figure 3 ATR-FTIR spectra of paper and pure cellulose powder.

The calculated crystallinity degree (X) gives an information about supramolecular changes in the PE surface. It is clearly seen from Table II that only high amount of paper (20–30%) in the blend caused about 3% X decrease, compared with PE and its blends with 5–15% paper additive.

The mechanical properties of the obtained composites are good enough for practical applications.³⁵ Such properties are the result of good homogenization of components at high temperature.

Effect of UV irradiation on PE/paper waste composites

ATR-FTIR spectroscopy is very useful for investigating the changes in UV-irradiated samples because the photochemical reactions occur mainly at the thin top layer. It was calculated that for applied ATR device the penetration depth is few micrometers¹⁴; thus, we really examined the surface structure of polymer.

As can be seen from ATR-FTIR spectra (Fig. 4), the main changes occur in carbonyl (1600–1800 cm^{-1}) and vinyl (908 cm^{-1}) regions as well as at ether bonds (1000–1200 cm^{-1}) range. Moreover, the ratio of bands at 719 and 729 cm^{-1} applied to crystallinity estimation slowly changes.

For quantitative estimation of composite photodegradation, the carbonyl ($I_{\text{C=O}}$) and vinyl ($I_{\text{C=C}}$) indexes were calculated (Table II).

It was found that $I_{\text{C=O}}$ changes observed in PE are rather insignificant, which confirms its photostability. The composites containing higher amount of paper waste (20–30%) undergo much efficient photo-oxidative degradation, whereas in samples with 5–15% paper, the $I_{\text{C=O}}$ changes are lower and irregular.

The oxidation, in which carbonyl groups are formed, accompanies the vinyl groups creation in PE. The efficiency of this process is similar in all samples investigated (see vinyl index in Table II).

It is necessary to point out that these changes concern only the surface because ATR technique was used for the estimation.

UV irradiation leads to about 4% decrease of crystallinity degree in PE after long irradiation time (100 h). The reason is photo-oxidation—the formed carbonyl groups of different types disturb the regular order of PE macromolecules. The trend of crystallinity alteration caused by UV radiation in PE/paper waste is opposite to that in PE. In all composites, besides PE + 5% paper, UV caused an increase in crystallinity. It can be explained by more efficient chain scission of macromolecules from amorphous phase, which is more sensitive to photodegradation. Shorter, degraded chains are characterized by higher mobility, which is sufficient to reorganize and crystallize. The result of high-degree degradation is also the formation of low molecular weight products, which can

TABLE II
Changes of Carbonyl Index ($I_{\text{C=O}}$), Vinyl Index ($I_{\text{C=C}}$), and Crystallinity Degree (X) in PE and Its Blends with Different Amount Cellulose After UV Irradiation

Degradation time (h)	$I_{\text{C=O}}$ (1716 cm^{-1})	$I_{\text{C=C}}$ (908 cm^{-1})	Degree of crystallinity, X (%)
PE			
0	0.43	0.22	73.2
10	0.46	0.4	73.2
30	0.43	0.3	73.2
100	0.58	0.58	69.2
PE I			
0	0.8	0.42	73.2
10	0.66	0.43	73.2
30	0.6	0.46	73.2
100	0.61	0.66	73.2
PE II			
0	1.1	0.57	73.2
10	1.09	0.49	73.2
30	0.72	0.59	79.45
100	1.01	0.79	79.45
PE III			
0	1.03	0.54	66.37
10	0.37	0.23	70.64
30	0.74	0.51	73.2
100	1.09	0.23	79.45
PE IV			
0	0.58	0.37	70.64
10	0.74	0.64	70.64
30	0.81	0.71	70.64
100	0.96	0.7	73.2
PE V			
0	1.07	0.83	70.99
10	1.31	0.93	70.64
30	1.16	0.9	70.64
100	1.33	1.1	77.58
PE VI			
0	0.37	0.32	70.99
10	1.22	1.06	70.99
30	1	0.82	70.99
100	1.27	0.98	77.58

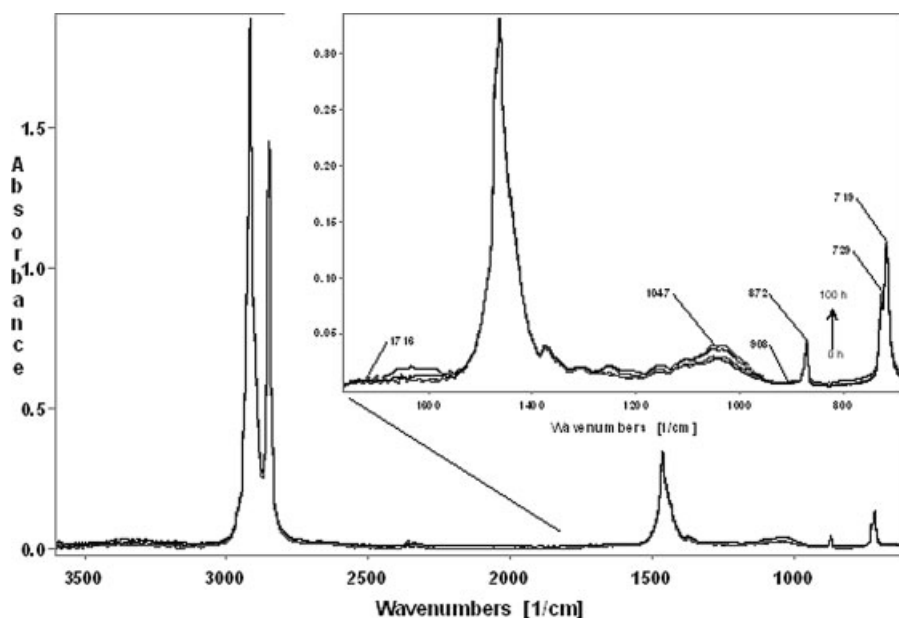


Figure 4 The changes of ATR-FTIR spectra of PE/paper waste composite (sample PE VI) caused by 10–100 h UV irradiation.

evaporate from polymer surface. Such effect of UV irradiation causing the increase in polymer order, called chemicrystallization, has been observed in other semicrystalline polymers.^{36–38}

SEM microphotographs of PE and its composite with 30% waste paper are shown in Figure 5. Pure PE is homogenous and no changes in sample morphology was observed after UV irradiation up to 100 h (not shown). The composites containing paper are characterized by high nonhomogeneity—thin pieces of paper are more or less distributed in PE matrix. Long time exposure to UV (100 h) caused visible changes in this sample—the roughness increases and small cracks (mainly at phase boundary) are formed as a result of photodegradation. It seems that the adhesion between components worsen after UV action. The development of surface can also be caused by evolution of low molecular degradation products. Such surface defects make possible the penetration of water and degrading agents (e.g., enzymes) to polymer bulk and facilitate its further environmental degradation.

Thermal stability

Figure 6 shows TG and DTG curves of PE and its blends with different amounts (5–30%) of paper waste, obtained under nitrogen atmosphere. PE alone decomposes completely in one step, which starts at 408°C. Maximum rate of this process is achieved at 465°C. Thermal degradation of paper and cellulose begins earlier—at about 260°C. Because the cellulose and paper have the tendency to absorb water, the

decrease in sample weight at just about 100°C is connected with its loss. However, in our extruded samples, no water traces were detected.

In all blends, two steps of decomposition are observed—first, at lower temperature range (250–370°C), due to thermal decomposition of paper, and second one (400–500°C), which is attributed to PE thermal degradation (Fig. 6, Table III). The separated degradation processes of both components (and practically the same values of $T_{\max 1}$ and $T_{\max 2}$ in all blends) are obvious evidence of their immiscibility. However, the T_o in the blends decreases systematically when the amount of paper increases. It suggests destabilization of paper by PE.

The weight loss at 520°C in the composites regularly decreases in the presence of paper. About 9% residue was found in the sample containing 30% paper, whereas no residue in pure PE at this temperature.

Values of T_o after 100 h of UV irradiation decrease in all samples (Table III, Fig. 7). The T_o drop in PE is low (13°C), while in composites the changes vary from about 40°C up to 60°C. It is illustrated in Figure 8. Temperature of maximum rate of paper degradation ($T_{1\max}$) also slightly decreases (about 6–13°C) in UV-irradiated composites, whereas the temperature of maximum rate for PE degradation ($T_{2\max}$) is constant. Changes of weight loss at the end of thermal degradation (at 520°C) are also negligible after UV irradiation. It again indicates that PE is photostable, contrary to paper used.

Thermal stability of composites is lower if the amount of paper waste in the composite increases.

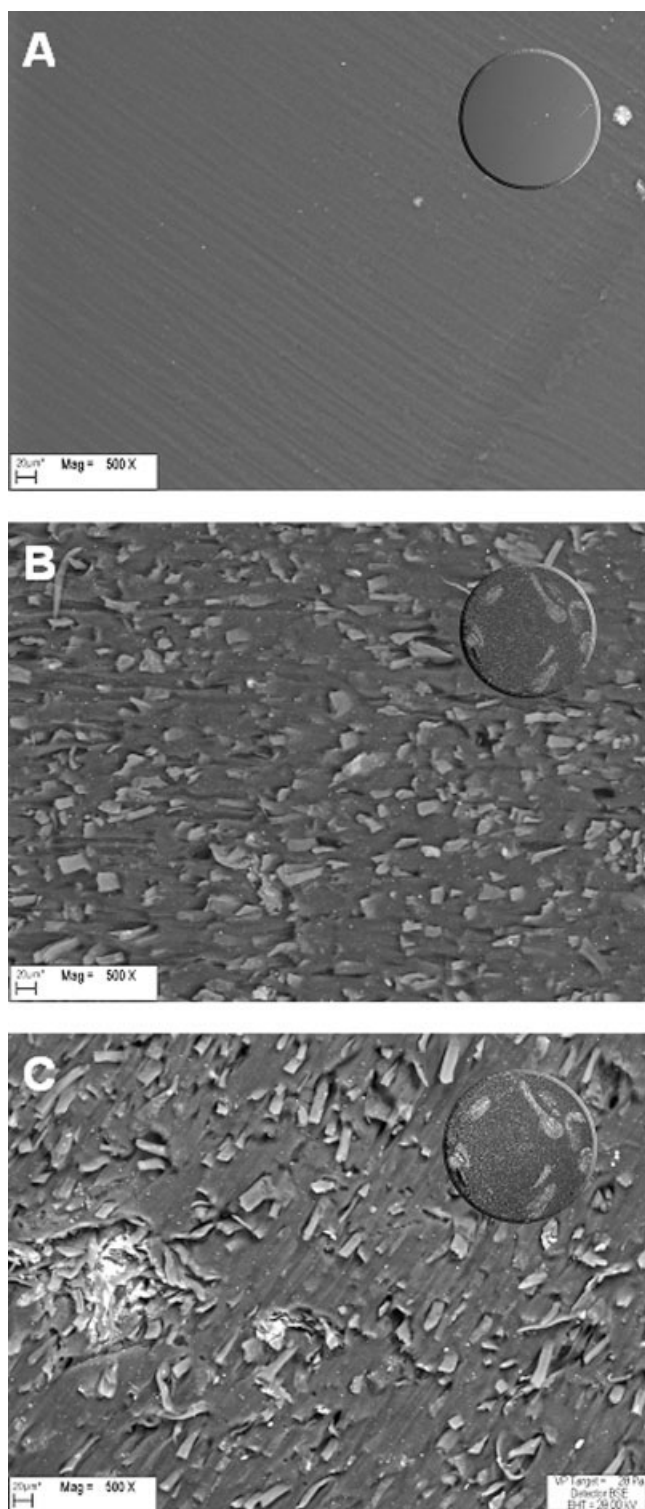


Figure 5 SEM microphotographs of composite cross section of PE (A) and PE + 30% paper waste (B) before degradation; (C) PE + 30% paper waste after 100 h UV irradiation.

DISCUSSION

Discussing the thermal and photochemical degradation of PE/paper waste, we should consider all com-

ponents involved in studied processes. Mechanism of degradation in pure PE is well known but it becomes more complicated in the presence of other substances. The main degradation reactions are typical for vinyl polymers: the random chain scission with formation of macroradicals, abstraction of hydrogen atoms, and oxidation leading to formation of various functional groups, branching, and crosslinking.^{16,17,31,38}

Second component of blend is paper. It is produced from wood pulp, which mainly contains cellulose. Minor components of paper are lignin, hemicellulose, and small amount of other organic compounds. Lignin, which is composed of macromolecules with aromatic rings and various structures repeating randomly, is mainly responsible for UV- and visible light absorption. In case of waste, paper is polluted by paint. It can contain inorganic compounds (pigments, carbon black), which often catalyze degradation, even if they are present in very low amount.

The identification of impurities in paper waste was not done in this work because of low concentration, but their sensitizing or accelerating action can not be excluded.

During photo-oxidative degradation of cellulose, the cleavage of C—H, C—OH, C—CH₂OH, and C—O—C (glycosidic) bonds occurs. Formed free radicals can react with atmospheric oxygen, giving peroxyradicals, which undergo secondary processes leading to different oxidation products.^{38–41}

We found that photochemical stability of PE/paper waste blends depends on components ratio. Composites with lower amount of paper (5–15%) are more photostable, similar to PE alone, whereas 20–30% addition of paper waste leads to photo-oxidation with generation of carbonyl groups (absorbing at 1600–1800 cm⁻¹). The vinyl groups formed during UV irradiation were also detected.

The photooxidation process in polymers is often studied also by monitoring spectral changes in hydroxyl group region (3000–3600 cm⁻¹). However, in our composites, hydroxyl groups from cellulose absorb in this range and two opposite reactions can compete upon UV action: cellulose dehydroxylation (abstraction of OH radicals) and formation of new OH and OOH groups in both PE and cellulose. It is a reason of the irregular changes in hydroxyl band (especially at the initial degradation step); those are not presented here.

Moreover, formed oxidized chains, containing different types of functional groups (OH, OOH, C=O, COOH, CHO, etc.), make the polymer photosensitive.^{16,17,31} For example, carbonyl groups formed in the first stage of photodegradation upon next photons undergo Norrish I and II type reactions. It should be added that macromolecules break off as a result of Norrish reactions. Chain scission is connected with the decrease in polymer molecular weight and forma-

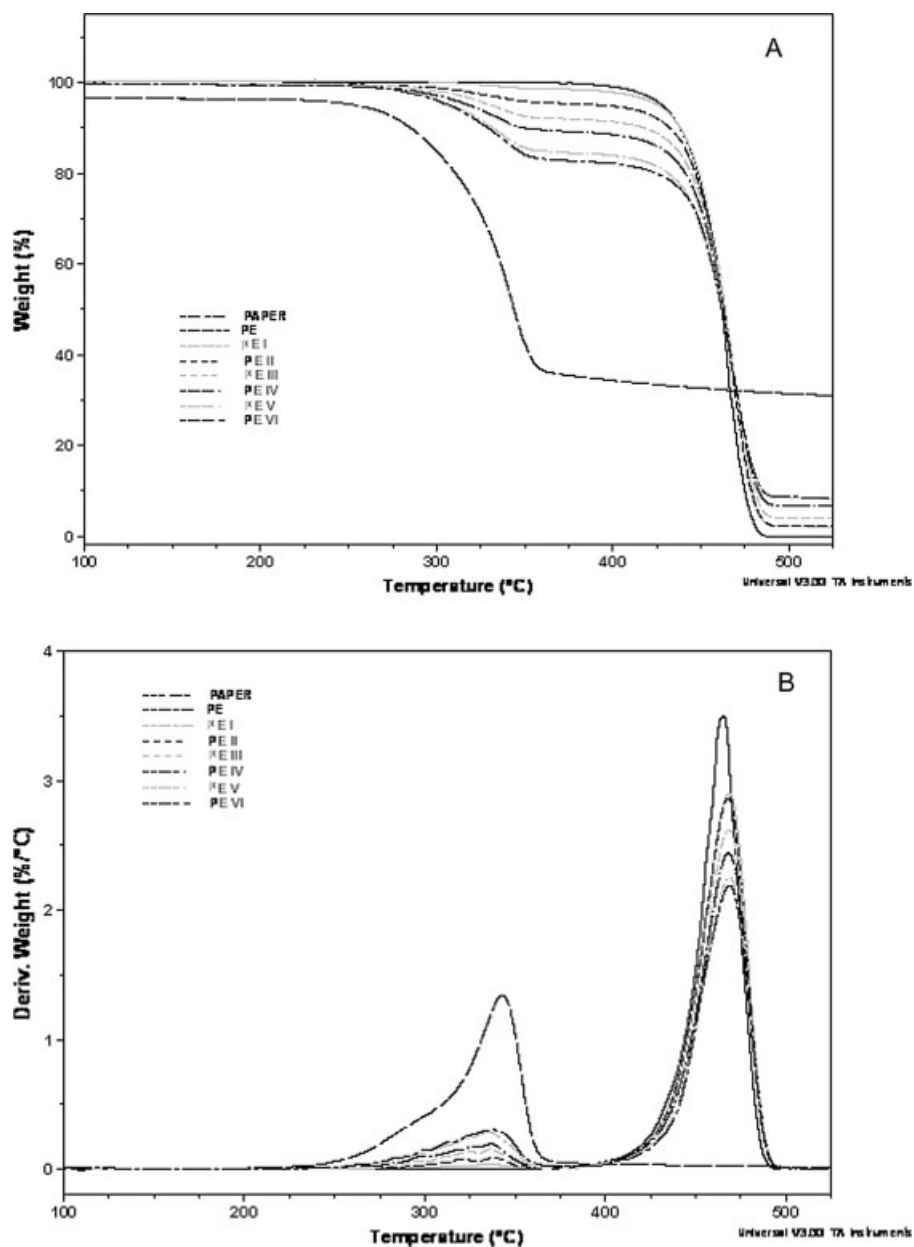


Figure 6 Thermogravimetric (A) and DTG (B) curves for PE and its blends with different amounts of paper waste.

tion of end functional groups such as aldehydes or double bonds. Main chain scission reactions are also responsible for the formation of microcracks and final damage of irradiated material. Such surface destruction after UV irradiation of PE/paper composites was observed under SEM.

Similarly, hydroperoxides easily photolyze with generation of hydroxy and alkoxy radicals, which induce the secondary reactions. It is generally accepted that hydroperoxides are mainly responsible for oxidation of polyolefins in initial stages. Carbonyl groups are characterized by higher light absorption than are hydroperoxides (and peroxides), and their effect increases upon prolonged irradiation. As a result of transfer of excita-

tion energy, even nonabsorbing polymer units can be activated.

Both the main constituents of composites (PE and cellulose) are crystalline; however, only PE crystallinity degree and its changes upon UV were estimated in this work.

Photo-oxidative degradation also leads to partial decrease of PE crystallinity in composites containing significant paper fraction. It facilitates subsequent decomposition because the amorphous phase is less stable than compact, dense, and stiff crystalline part of polymer. The access of various degrading factors (oxygen, water, enzymes, free radicals, excited molecules) is easier in disordered, flexible macrochains,

TABLE III
Thermal Parameters Estimated from Thermogravimetric Analysis of PE and Its Composites with Different Amounts of Paper Waste Before Photodegradation and After 100 h UV Exposure

Sample	Nonirradiated				Irradiated for 100 h (°C)			
	T_o (°C)	T_{max1} (°C)	T_{max2} (°C)	Δm (%)	T_o (°C)	T_{max1} (°C)	T_{max2} (°C)	Δm (%)
PE	408	–	465	100	395	–	465	100
PE I	275	337	469	98	236	329	468	99.5
PE II	270	337	468	97.5	217	324	469	98.5
PE III	260	337	468	96	200	325	469	96
PE IV	247	336	468	93.5	199	329	468	92.5
PE V	240	336	469	92	199	330	469	91.5
PE VI	243	339	468	91.5	196	331	468	88.5

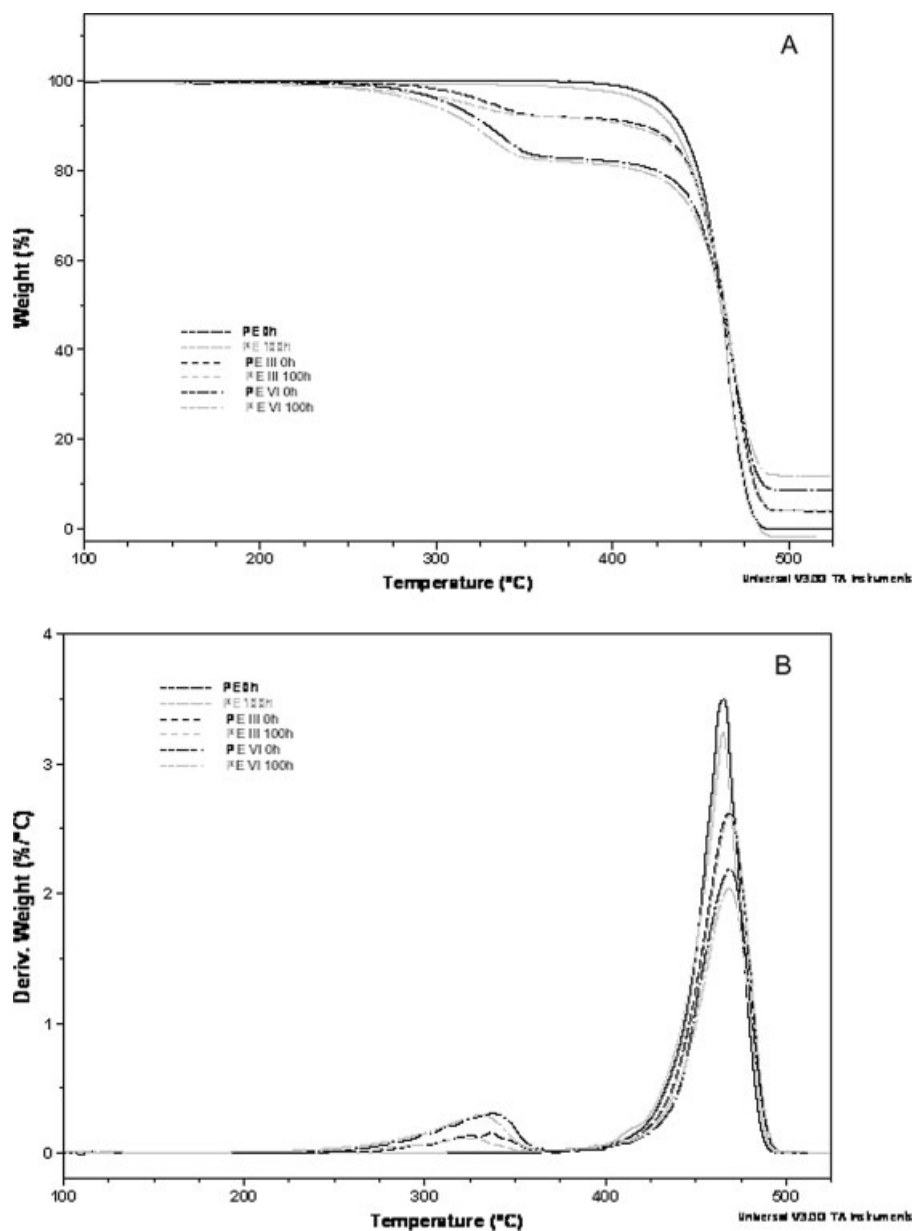


Figure 7 Thermogravimetric (A) and DTG (B) curves for PE and its blends with different amounts of paper waste after 100 h UV irradiation.

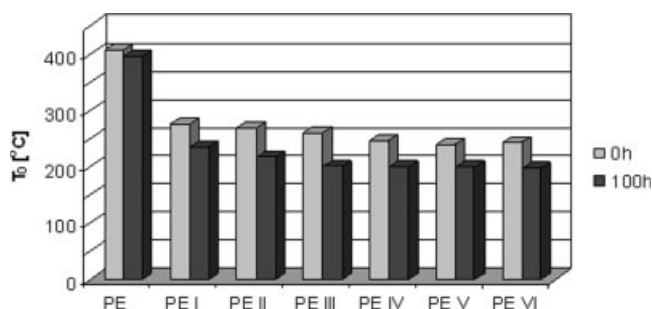


Figure 8 The changes of on-set degradation temperature (T_0) of PE and its composites with different amounts of paper added caused by 100 h UV irradiation.

where the free volume is significant. Moreover, oxidized PE chains are more polar and hydrophilic than those unoxidized. It also may increase susceptibility to biodegradation.

It was found that PE thermal stability is lower in the presence of paper waste. The higher the amount of paper in the composite, the lower the temperature of the degradation at the beginning. It is obvious because cellulose is characterized by much lower thermal resistance when compared with PE alone.

Thermal stability of PE composites decreases after UV irradiation. It can be explained by formation of less stable polymeric products during photo-oxidative degradation. Such unstable structures are carbonyl and vinyl groups, branching points, and trapped free radicals. Few percentage residue in case of composites, contrary to complete PE thermal decay can suggest that some cross reactions with formation of highly crosslinked resistant polymer can take place. It concerns both: unirradiated and UV-irradiated PE/paper composites.

Although photo-oxidative degradation is not a very fast process in case of our composites, it leads to sensitization of polymer for further degradation in natural environment. Besides macromolecules photosensibilization, the formed oxidized groups become the nutrient for microorganisms; thus, the biodegradation of composites on landfills will take place.

CONCLUSIONS

The new ecological material based on LDPE and waste paper can be obtained by extrusion, followed by preliminary reactive blending.

UV irradiation leads to slight changes of chemical structure at PE/paper waste surface, which was proved by FTIR-ATR. The photo-oxidative degradation, the result of which carbonyl groups are formed, is more efficient in composites containing 20–30% paper waste, contrary to PE and blends with low paper addition. Formed carbonyl groups are the reason of the drop of PE crystallinity degree in these samples.

The efficiency of vinyl group formation in all samples studied is low and independent of paper waste amount. UV irradiation also causes the formation of surface defects (observed by SEM), which allow further degradation (including biodegradation) in the environment.

The PE composites with paper waste are less thermally stable when compared to PE alone. Moreover, thermal stability decreases after composites exposure to UV radiation.

We can suggest that the obtained composites can be used as material relatively resistant to UV radiation in all applications (with exception of packaging destined to food) where the transparency is not needed. The biodegradation of such composites in natural environment can be predicted. The demanded properties of PE/paper waste blends, including controlled lifetime, can be regulated by proper ratio of components. On the other hand, paper waste is a cheap filler, which reduces the production costs of polymer materials.

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