

Description methods of the properties of composites from oxybiodegradable foil waste and wood

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Abstract

As part of this work oxydegradable polymer was fabricated and analyzed; it was made from the waste following a 30 day exposure in Xenotest, simulating a 2-year exposure in atmospheric conditions and undergoing a triple injection process. Similar examination was applied to composites containing 32 wt.% of wood fabricated from this polymer. In the course of the examinations two methods of degradation process evaluation of the materials were verified. It was stated that the method utilizing the relationship between peak fields originating from scissoring vibrations of the $(-\text{CH}_2-)$ group with a frequency of $\text{ca } 1463\text{cm}^{-1}$ ensures more accurate results. The results of other examinations of the two groups of materials permit us to state that the manufacturing of composites with wood constitutes an interesting form of the utilization of oxybiodegradable polymers.

Keywords: oxydegradable polyethylene, foil waste, recycling, wood.

1 Introduction

According to the data by Plastics Europe, European association of plastics manufacturers, some 230 million tons of plastics were produced in 2009 in the world (55 million tons in Europe). About 50% of the materials constitute polymers intended for the packaging industry, of which 40% are polyolefines: polyethylene (PE-LD, PE-HD, PE-LLD) and polypropylene (PP).

These polymers are made from petroleum-based synthetic polymers that do not degrade in a landfill or in a compost-like environment. However, increased use of synthetic packaging films has led to serious ecological problems. Several



approaches to solve the pollution problems caused by polyolefines were developed in the 1970s [1]. One of the solutions was the introduction of pro-oxidants to the polymers. The pro-oxidants Co, Mn, Cr, Ni, Mo and Fe on Al₂O₃ or SiO₂ support [2–6], cause that polymers become susceptible to environmental effect. Polyolefines prepared in this way are called oxo-biodegradable.

Degradation of all polymers follows a sequence in which they are converted into their single oligomeric or monomeric units and later they are utilized as carbon source by the microbes. Lower molecular weight hydrocarbons are more susceptible to attack by microorganisms than the high molecular weight polymer. The degradation of polyolefines with pro-oxidants addition proceeds in a similar way [7–18].

The presence of pro-oxidants, particularly, provided superior functionality and higher degradation rate in PE films. Though their degradation time varies between 18 and several dozen months, they often land up at the rubbish dump after a month of use. Within the framework of the works a selective collection of this type of waste was proposed along with the production of composites with wood, fabricated from them. Such composites can be used in various fields, i.e. as elements for seasonal gardening, auxiliary materials for agriculture, urban greenery, etc. Later on they can serve as valuable energy raw materials.

One of the problems connected with the utilization of products made from such composites is the assessment of their exploitation time.

The assessment of the usefulness of climatically hazard materials is carried out by Xenotest type of equipment [15]. After the exposure in such equipment various properties of polymer materials are examined including, first of all, mechanical properties and thermal analysis. However, since the availability of Xenotests is rather limited, other methods are sought after.

In the current study an attempt has been made to understand the degradation of composites from waste polyolefines with pro-oxidant and wood. The changes in the various physiochemical properties of the polymer were monitored to elucidate the degradation process. As part of work and in order to assess the oxidation process occurring during the degradation of oxydegradable polymers and their composites, methods were verified utilizing spectra obtained with the use of infrared spectroscopy.

2 Experimental

2.1 Materials

Production waste, degradable polyethylene HDPE, containing 1 wt.% of pro-oxidant d2w, from Ecoplastic Poland, (OXY) was a kind of gift from Ecoplastic Poland. Wood fibers – Lignocel C 120 with particle size 70 – 150 µm, from J. Rettenmaier & Söhne GmbH, Germany.

2.2 Sampling

Composite samples were fabricated in two stages. In the first stage, with the use of T-45-25-22T-VS single-screw extruder with screw ratio $L/D=29$ and with the head for granulation able to simultaneously extrude six 5mm profiles, a granulate was extruded containing 25 wt.% of wood flour. The extrusion process was conducted at the temperatures of 150/160/170/175/175°C (starting from the charging hopper). After cooling the extruded rods were ground using a mill for plastics. In the second stage wood flour was added to the granulate obtained from the mixture in such quantity so that its total content in the composite should reach 32% mass; next, the granulate of composite mixture (or oxybiodegradable polymer) was placed in the bunker of DrBoy 22A injection moulding machine. The regranulate and wood fibers as well as the obtained granulates were then dried before each processing stage in DAC6 dryer at 80°C for one hour. During the injection of samples the cylinder's temperature, starting from the bunker, amounted to 155, 160, 170, 178 and 180°C, injection pressure $800 \cdot 10^5$ Pa, and clamp pressure of $800 \cdot 10^5$ Pa. Injection time was ca 2 s, clamp time 12 s, cooling time 8 s; the total cycle time equaled ca 25 s. From all types of materials samples A1 were fabricated in conformity with the norm EN ISO 527-2 using a 2-cavity mould cooled with water at 40°C.

In order to verify the influence of injection process on the degradation process of oxydegradable polymers and their composites a 3-time injection process was carried out. Samples obtained in the first injection cycle were ground in an industrial mill, dried and injected. This cycle was performed twice. A description of the achieved materials is presented in Table 1.

Table 1: Description of the achieved materials.

Sample	1	2	3	1.32	2.32	3.32
Composites matrix	OXY	OXY	OXY	OXY	OXY	OXY
Amount of wood [wt.%]	-	-	-	32	32	32
Process multiplicity	1	2	3	1	2	3

2.3 Characterization

Resistance of the materials to accelerated ageing was determined on the basis of analysis of pictures taken with the use of microscopic scanning, Charpy impact tests as well as FTIR analysis of samples after irradiation. The examination was carried out in conformity with PN-EN ISO 4892-1, PN-EN ISO 4892-2 and PN-EN ISO 20105-A02:1996.

The samples underwent exposure in Xenotest Alpha High Energy equipped with xenon lamp as radiation source. The examination was carried out for 720h with samples being subjected to irradiation of $388,8\text{MJ/m}^2$ (within the scope of 300-400nm) equivalent to a 2-year exposure in natural conditions [19]. The exposure in Xenotest is shown in Table 2.



Table 2: Ageing test parameters in Xenotest alpha HE.

Parameter	Phase 1	Phase 2
Filter	Xenochrome 300	
Luminous intensity E, W/m ²	150±3	150±3
Work mode	without revolution	without revolution
Temperature control	in chamber	in chamber
Temperature in chamber °C	35±3	30±3
Rain	no	yes
Relative humidity, %	50±3	rain
Phase time, min	102	18

SEM picture from the surface of examined samples dusted with gold was achieved using an electronic scanning microscope Hitachi S-2600 with accelerating voltage of 10 kV.

Infrared spectra of PURs were collected using a FTIR spectrophotometer (Thermo Electron Corporation model Nicolet 6700). Measurements were carried out using attenuated total reflectance (ATR) technique. Each sample was scanned 64 times at a resolution of 4 cm⁻¹ over the frequency range of 4000–400 cm⁻¹. Analysis of FTIR data enabled to determine the carbonyl index.

Charpy impact resistance using Resil 5,5 hammer by Ceast, wg PN-EN ISO 179-2:2001 was defined for samples with notch, size 70 × 4 × 10 mm (cut from samples and formed via injection).

Mechanical properties at static stretching in conformity with PN-EN ISO 527-1:1998 and PN-EN ISO 527-2:1998 were examined using the strength machine MTS Q/Test 10. Five 1A samples were analyzed from each type of composite. The samples were stretched at the speed of 10 mm/min. The measurements were recorded automatically using programme TestXpertII. Determined values: strength in the area of plasticity (σ), strain at break (ε) and Young elasticity modulus (E) of polymers and composites.

Absorption after water soaking was determined basing on the change in the mass of 3 randomly selected samples from a given part of the material. The examination was carried out in conformity with the technology specified in the norm PN-EN 317:1999.

3 Results and discussion

In the course of conducted examinations the samples from oxybiodegradable polymer and its composite, fabricated via single injection process, were subjected to exposure in Xenotest. In result of the exposure, simulating a 2-year ageing process in natural conditions a degradation of the examined oxybiodegradable polymers took place (Fig. 1). The degradation was visible in the form of white ovals appearing on a sample not directly subjected to UV radiation (Fig. 1a) as well as in the form of cracking on the surface of a sample

directly subjected to action of the xenon lamp (Fig. 1b). No such visible changes were observed on the surface of composites (Fig. 2). Degradation of polymers and composites results in the decrease in their impact resistance (Table 3).

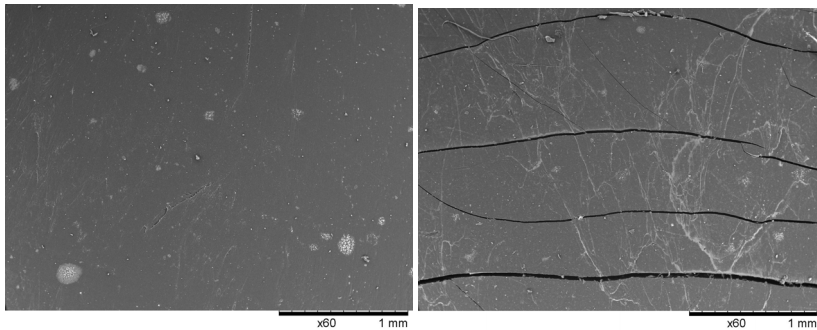


Figure 1: SEM pictures of the surface of oxybiodegradable polymer after 30 days ageing in Xenotest: surface not exposed to a direct radiation of xenon lamp (a), subjected to a direct radiation of xenon lamp (b).

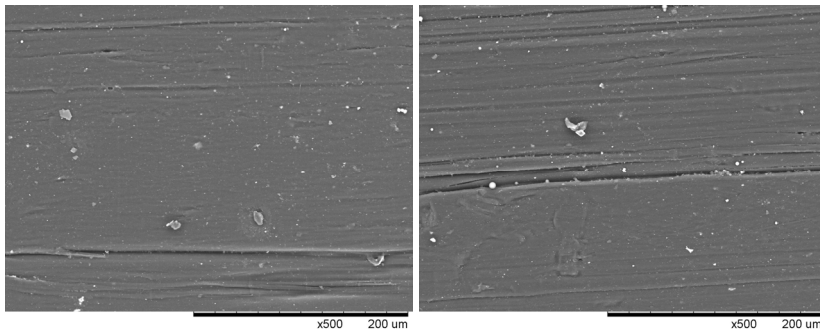


Figure 2: Rys. 2. SEM pictures of the surface of oxybiodegradable polymer with 32 wt.% of wood, not exposed to a direct radiation of xenon lamp (a), after 30 days ageing in Xenotest (b).

Table 3: The change in impact resistance of oxybiodegradable polymers and composites containing 32 wt.% of wood, caused by 30 days exposure in Xenotest. 1 – sample of oxybiodegradable polymer, 1.32 – sample of its composite, 1D and 1.32D – samples after exposure in Xenotest.

Sample	1	1.32	1.D	1.32D
U, impact resistance, kJ/m ²	43.9	9.7	33.6	9.6

In oxybiodegradable polymer the impact resistance after exposure in Xenotest decreased by ca 23% while that of the composite only by ca 1%. In order to

assess changes in the structure of polymer and composite, causing the decrease in impact resistance after exposure in Xenotest a spectroscopic analysis (FTIR – ATR) of them was carried out. The achieved spectra of polymer and composite are shown in Fig. 3.

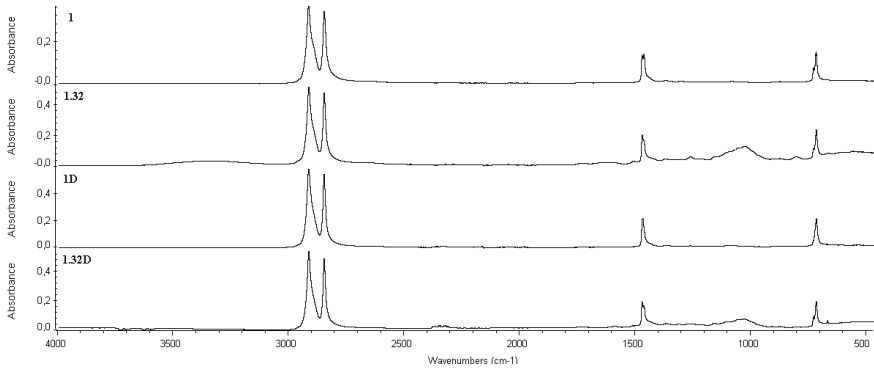


Figure 3: FTIR-ATR spectra of oxybiodegradable polymer samples before (1) and after exposure in Xenotest (1D) and composites before (1.32) and after exposure in Xenotest (1.32D).

Basing on FTIR –ATR spectra carbonyl index (COI) was calculated by two methods. In the first one, proposed by Reddy and co-authors [16] and Corti et al. [14], carbonyl index was determined as the ratio of absorbance of band 1716 cm^{-1} resulting from the vibrations of (C=O) carbonyl group and absorbance of band 1468 cm^{-1} originating from scissoring vibrations of group ($-\text{CH}_2-$).

$$COI = \frac{A_{1716}}{A_{1468}} \quad (1)$$

In the second method, proposed by Douminge and co-workers [18] and Stark and co-workers [15] carbonyl index was determined as the ratio of absorbance of band 1716 cm^{-1} , resulting from the vibrations of (C=O) carbonyl group and absorbance of band 2913 cm^{-1} , originating from the asymmetric stretching vibrations of group ($-\text{CH}_2-$).

$$COI = \frac{A_{1716}}{A_{2913}} \quad (2)$$

The fields of individual bands were determined with the use of OMNIC 7.3 programme. The analysis was carried out after correction of baseline, the spectrum in the analyzed scope was resolved into component bands using the Gaussian curve-fitting.

Table 4: Calculation results of carbonyl index.

Sample	1	1.32	1.D	1.32D
COI calculated acc. to formula (1)	0.015	0.068	0.019	0.041
COI calculated acc. to formula (2)	0.005	0.019	0.006	0.012

In the results of the calculation of carbonyl index using the first method it was stated that the index is three times higher than that calculated by the second method according to formula (2) (Table 4). Therefore, it was agreed that the first method will ensure a more accurate analysis of degradation changes in oxybiodegradable polymers and composites with wood, fabricated from them.

To verify this statement an analysis was performed of carbonyl index of the polymer and composite containing 32 wt.% of wood nanofiller after multiple processing and using the first method (Table 5). Carbonyl index is used to monitor the progress of oxidation process. An increase in COI was observed in oxybiodegradable polymers and composites, which indicates that degradation process in these materials occurs after each processing cycle. After consecutive stages of processing the speed of COI changes in composite with wood decreases, which means that the introduction of wood slows down the degradation process. Also examined were the strength properties, impact resistance and water absorption of the materials; the results are shown in Table 5.

Table 5: Examination results of oxybiodegradable polymer and composites with 32 wt.% of wood and after multiple injection process.

Sample	1	1.32	2	2.32	3	3.32
COI calculated acc. to formula (1)	0.02	0.03	0.09	0.06	0.23	0.07
U, impact resistance, kJ/m ²	38.5	8.0	36.7	9.0	31,2	11.0
A, humidity content, %	0.02	3.48	0.02	3,43	0.08	3,12
E, elasticity modulus, MPa	820	1740	210	410	205	390
σ , stress in the area of plasticity, MPa	152	19	105	26	80	27
ϵ , strain at break, %	450	4.4	280	4.9	120	5.7

The examination results of strength properties confirm that after consecutive processing cycles the degradation process of composites proceeds more slowly than the degradation process of matrix polymers. Also, after consecutive processing cycles water absorbency of the composites favourably decreases.

4 Conclusion

Within the framework of the work a possibility of manufacturing practical materials from oxybiodegradable polymers waste was assessed as well as their composites with wood flour filler. The possibility of utilizing recycled oxybiodegradable polymers requires the assessment of their degradation degree



prior to processing. To this end the use of carbonyl index is proposed. Two methods of its determination were verified. It was stated that the method utilizing the ratio of peak field originating from scissoring vibrations of group.

(-CH₂-) ensures more accurate results. This method was used for the assessment of degradation degree of oxybiodegradable polymers and their composites subjected to the exposure in Xenotest, simulating a 2-year exposure period in atmospheric conditions and following a three-time injection process. Apart from degradation itself, selected properties of the materials were also evaluated. In result of the examinations it was stated that each processing course accelerates the degradation process of oxybiodegradable polymers. The introduction of wood affects the degradation process of the matrix. Further processing causes smaller changes in the properties of composites than in polymers.

The results show that oxybiodegradable polymer waste, not often utilized so far, may constitute a valuable raw material for manufacturing practical products.

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