DOI: 10.1002/masy.200851219

Degradation Study of Polymers from Renewable Resources and their Compositions in Industrial Composting Pile

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Summary: Polyesters produced from renewable resources and susceptible to hydrolysis under the industrial composting conditions offer ecological advantages as compared to thermoplastics polymers and elastomers produced from fossil carbon sources. In this paper the degradation behaviour of polymer compositions of BTA, PLA and a-PHB in natural environment of industrial composting pile, consisting of leaves - 40%, branches - 30% and grass - 30%, have been presented. The extend of degradation was monitored by macroscopic observations of sample surfaces, changes of molecular weight, polydispersity and composition of the tested materials and their weight loss.

Keywords: (bio)degradation; blends; industrial composting pile; polyester; renewable resources

Introduction

New trends in solid waste management and rapid changes in public legislation made scientist in increase activities on the design of new generation of biodegradable polymers as important biomaterials for environmental, biomedical and pharmaceutical applications.[1,2] For the last few years, intensive research and development of new materials for packaging has been also observed.[3] The most commercially available plastics are non-degradable and their recycling is not feasible economically in many cases due to the deterioration of mechanical properties and excessive cost. Selective use of biodegradable packaging materials in certain applications may provide a solution to the above-mentioned environmental problems. One of the class of well-known synthetic hydrolysable polymers are polyesters such as poly(L-lactide), PLLA.[4] The degradation of aliphatic polyesters to common metabolites in a biological environment such as activated sludge, public waste-fields and composting facilities, including anaerobic and aerobic conditions, results from enzymatic attack or simple hydrolysis - cleavage of ester bonds, or both. Under specific conditions encountered in compost, degradation may undergo with the aid of specific enzymes formed by microorganisms such as bacteria or fungi.[5,6] Additionally, food garbage can be composted together with biodegradable packaging materials, which may contribute to a significant reduction of municipal solid waste.[7] The pilot project for marketing and recycling of compostable packaging made from biodegradable polymers was realized in Kassel (Germany). The similar system of selective collecting and industrial composting was recently introduced in Zabrze, but on smaller scale.[8] The systematic development of recycling of compostable plastics in Poland depended also from the elimination the divergences between the EU and the Polish laws, and respective EU directives e.g. with agree to

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2004/12/EC obligatory level of recycling in Poland in 2007 should be 25%. Polyesters, produced from renewable resources and susceptible to hydrolysis in natural environments such as industrial compost, dynamic sea water, standardized soil and compost with active sludge offer ecological advantages as biodegradable materials with controllable lifetime.[9] The natural polyesters (PHB, PHBV) degrade in compost with active sludge during 4–5 weeks.[10] The degradation in soil of atactic poly[(R,S)-3-hydroxybutyrate], a-PHB containing blends, with natural PHB (n-PHB) was also investigated. It has been found, that in soil degradation of this blends proceeded faster than respective reference plain n-PHB film.[11] Poly(L-lactide) is readily degraded in compost and after 90 days of degradation mineralized in compost to CO_2 in 90%.[12] Furthermore, the replace of polyethylene in the paper coatings with the new polymeric compositions going to the repulping of all packaging material and creates a real chance to eliminate difficulties connected with separation of polyethylene from paper pulp. a-PHB was selected, previously, as a blends component with natural PHA or PLLA with the aim to improve the flexibility and impact resistance of these biodegradable materials.[11,13,14]

Materials and Methods

The results of the study on biodegradation in industrial composting pile of polymer materials containing, in different weight ratio a-PHB, poly[(DL)-lactide], PLA (with 12% of [D] units, GALACTIC) and aliphatic-aromatic copolyester of terephtalic and adipic acid with 1,4-butanediol, BTA (BASF) were presented. Table 1 shown the composition of investigated materials.

Table 1.
Composition of investigated materials.

Sample	Composition [wt%]
Biomixed E	BTA
Biomixed ELB10	BTA + 10% PLA
Biomixed ELB30	BTA + 30% PLA
Biomixed ELB5A5	BTA + 5% PLA + 5% aPHB

Incubation test was performed for samples in form of monofilaments with diameter 1 mm and average length 10 cm. The blends were prepared by the mixing in the melt of polymers with using the laboratory single-screw extruder with diameter of screw 12 mm and 4 heating zone (ZMP-TW, Gliwice). The cage with polymeric materials was placed in a industrial composting pile, consisting of leaves - 40%, branches - 30% and grass - 30%, at the depth of one meter under the surface, at average temperature of 57 °C and pH = 7.4, for fourteen day. The macroscopic observations of surface changes, the weight loss and changes of molecular weight, polydispersity and composition of the samples were monitored during composting process.

GPC Analysis

Number-average molecular weight and polydispersity index M_w/M_n of investigated samples were estimated by GPC experiments conducted in chloroform solution at 35 °C and a flow rate of 1mL/min using a Spectra-Physics 8800 solvent delivery system with two Mixed C Styragel columns in series and a Shodex SE 61 refractive index detector. A volume of 10 μL of sample solutions in $CHCl_3$ (concentration 0.5% w/v) was injected. Polystyrene standards with low polydispersity were used to generate a calibration curve.

NMR Analysis

The NMR spectra were recorded using a Varian VCR-300 multinuclear magnetic resonance spectrometer. The ^1H NMR spectra were run in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard.

Results

The morphology of sample's surface can influence the degradation process. Figure 1 presents the digital photographs of investigated samples before and after fourteen

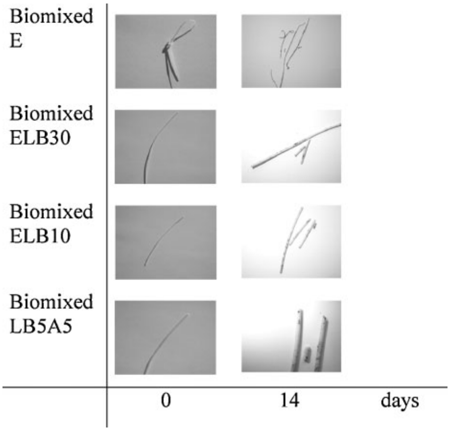

Figure 1.
The digital photographs of investigated samples before and after fourteen day degradation in industrial composting pile.

day degradation in industrial composting pile. During the composting process the macroscopic change of samples was observed. The macroscopic observations suggest the disintegration of all investigated samples, which corresponds to the weight loss results, described above and presented in Table 2. Obviously, disintegradability does not mean total sample degradation. Therefore, remaining pieces of the samples would be still degraded in environment. Moreover the results of the weight loss indicate that all blends degrade, but with different rate. The weight loss of binary blends was increase with increasing of PLA content, from 10 to 30 wt%. The weight loss for ternary blend was comparable with weight loss of binary blend containing 10 wt% PLA.

Table 2.
The weight loss of investigated samples after fourteen day degradation in industrial composting pile.

Sample	Weight loss [%]
Biomixed E	18.90
Biomixed ELB10	4.40
Biomixed ELB30	9.90
Biomixed ELB5A5	5.50

Number-average molecular weight changes have been performed using the GPC analysis. The obtained results for investigated materials before and after the fourteen day of degradation process are presented in Figure 2. The shift to lower

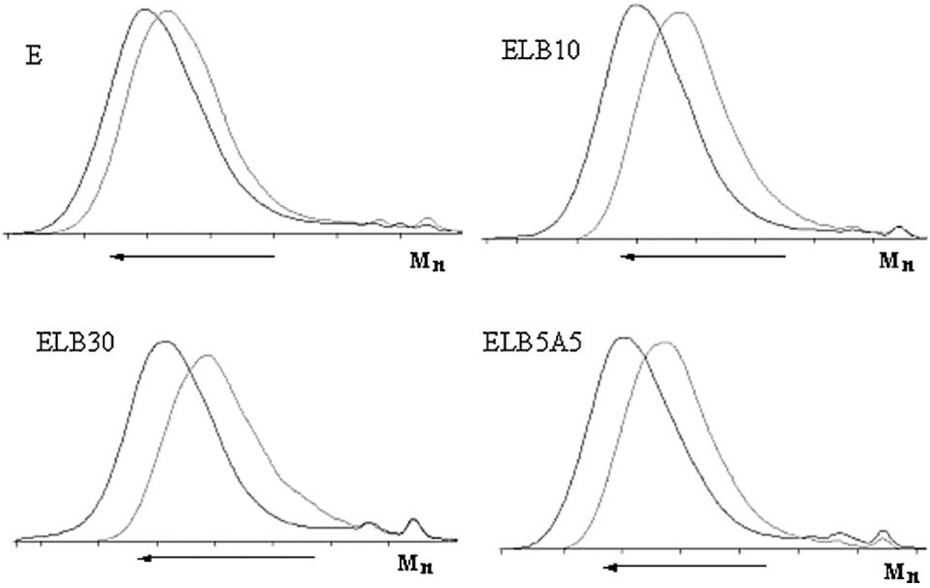

Figure 2.
Elution curves (determined by GPC method) of investigated materials: a) before degradation, b) after fourteen day incubation in the industrial composting pile.

molecular weight values was confirmed for all samples as compare with GPC traces before the degradation. The observed decreasing of molecular weight suggests that under investigated condition of industrial composting process the hydrolytic degradation was privileged.

The composition of binary and ternary blends has been determined by ^{1}H NMR spectroscopy.[15] The PLA and a-PHB content in the blends decrease after degradation process. These results reveal that degradation process occurred primarily in the amorphous phase, which is in agreement with the results of GPC observation.

Conclusion

The obtained results revealed that the investigated polyester compositions were degradable under industrial composting condition and in this environment the hydrolytic degradation was occurred. Moreover the biodegradable polyesters systems are promised materials, which can be use as paper coatings for multilayer packaging materials.

Acknowledgements: This research has been supported by a Marie Curie Transfer of Knowledge Fellowship of the European Community's Sixth Framework Programme under the contract number MTKD-CT-2004-509232. The financial support of Polish Ministry of Science and Higher Education: R&D project no. R05 055 02 is also acknowledged.

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