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Properties of blends of starch, polyethylene and poly(ethylene-co-acrylic acid) copolymer

RAPID COMMUNICATION

Summary — Using reactive extrusion in a twin-screw extruder the blends of low-density polyethylene (PE-LD) with poly(ethylene-co-acrylic acid) (EAA) copolymer 1:1 and 5–30 weight % of potato starch (oxidized — OP or non-oxidized — P) or corn starch (C) were prepared. The static tensile mechanical properties, hardness and melt flow rate (MFR) of the samples were determined. The course of biodegradation of the samples under the influence of selected, amylolytically active, bacteria strains, actinomycetes and filamentous fungi. Biodecomposition degree has been estimated on the basis of macroscopic and microscopic observations and FT-IR spectrometry. All the samples supported the growth of microbes, the blends with OP — much higher than those with C. It has been also found that biodecomposition degree increased with the starch content in the blend. The highest degree of biodecomposition was observed when *Aspergillus niger*, *Streptomyces* (strain 19) and mixture of bacteria of *Bacillus type* were used.

Key words: starch, polyethylene, poly(ethylene-co-acrylic acid), reactive blending, biodegradation, mechanical properties.

Products from agricultural sources, such as starch or proteins offer an attractive and cheap alternative in developing degradable materials. However, most of the synthetic polymers are immiscible with starch at the molecular level. Economical and commercially reasonable approach is to form graft or block copolymers *in situ* during the blend preparation by using polymers containing reactive functional groups. This method is commonly known as reactive blending. Small amounts of block or graft copolymers formed during the process, due to the reaction between the two components, are generally enough to stabilize the morphology and improve the properties of the blend. Reactive blending is known to improve the compatibility and interfacial adhesion of two immiscible polymers [1].

In this study, we present the results of investigations of the blends of starch and synthetic polymer containing carboxylic groups. The objective of this study was to blend a starch at concentration between 5 and 30 wt. %

with low-density polyethylene (PE-LD) and poly(ethylene-co-acrylic acid) (EAA). During the reactive blending of PE-LD/EAA blend with starch, the carboxylic groups in EAA can react with the hydroxyls of the starch to form hydrogen bonds [2–5]. The static tensile mechanical properties, hardness, melt flow rate (MFR), and mold growth of the samples as a function of starch concentration are reported and discussed.

EXPERIMENTAL

Materials

Industrial unmodified potato starch (P, catalogue number S9679) with chemical formula $(C_6H_{10}O_5)_n$ was obtained from Fluka. Unmodified regular corn starch (C, catalogue number S4251) containing approx. 73% of amylopectin and 27% of amylose was supplied from Aldrich Sigma. Oxidized potato starch (OP — “pudding flour”) was obtained from WPPZ S.A. Luboń (white, pH = 6.6, humidity 16%, contents of: NaCl = 0.03% and SO₂ = 19.2 mg/kg). Low-density polyethylene FABS 23 D022 (PE-LD) was supplied by PKN Orlen. Poly(ethylene-co-acrylic acid) (EAA) was obtained from Dow Chemicals. This grade of EAA contains about 10% of acrylic acid.

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Blends preparation

PE-LD/EAA (1:1) blends with unmodified and modified potato starch and corn starch were prepared in a laboratory scale twin screw extruder with co-rotating screws (diameter of 25 mm, Berstorff, Germany). The barrel length to diameter ratio was 33:1 and the extruder was divided into eight zones for temperature control. The moisture content in the starch was 10% to enhance processability. The extrusion was carried out at 140–172°C, operating at 90 rev/min. The die temperature was set at 160°C. The residence time was approximately 2 minutes.

Tensile strength

Tensile testing was done using an Instron 4505 testing machine according to the procedure outlined in ISO test method PN-EN ISO 527.

Biodegradation

Polymer samples (films, thickness = 0.5 mm) were placed in sterile Petri dishes containing solidified nutrient salt agar. A single and mixed selected microbes spore solutions were prepared from spores of amylolytically active bacteria (*Bacillus firmus* and *Bacillus coagulans*), actinomycetes (*Streptomyces* strain 19 and *Streptomyces roseochromogenes*) and filamentous fungi (*Aspergillus oryzae* and *Aspergillus niger*) [6]. The samples were then inoculated with the spore suspension (density = $10^6/\text{cm}^3$) and the covered Petri dishes were placed in plastic "sleeve" with air access and constant humidity of about 70%. Tests were carried out for 6 months at 30°C. The effect of different type of microbes on biodegradation of blends was followed by visual observations and was studied by FT-IR and polarizing microscope for the comparison of the behavior.

Thin films of the samples were compression molded at 160°C under the pressure of 15 MPa for 5 min. FT-IR spectra of these thin films were recorded by Genesis FT-IR spectrometer at room temperature using a resolution of 4 cm^{-1} .

RESULTS AND DISCUSSION

The starch/PE-LD/EAA blends were made with various starch contents ranging between 5 and 30 wt. %. Blends of a general purpose grade of PE-LD containing no functional groups, were also made at 15% starch contents for a comparison. The starch/PE-LD/EAA blends were flexible, whereas starch/PE-LD blends were rigid.

Increase in the starch content adversely affected the physical properties of the blends. Though the samples of PE-LD/EAA and starch/PE-LD/EAA blends show almost similar tensile strength (Fig. 1) then elongation at break drastically decreased with increasing the concen-

tration levels of all types of starch (Table 1). As would be expected, hardness slightly increases with the addition of starch [5]. Whereas, melt flow rate (MFR) decreases with growing amount of starch (Fig. 1). This fact indicates substantial amounts of interfacial reaction and molecular weight increase.

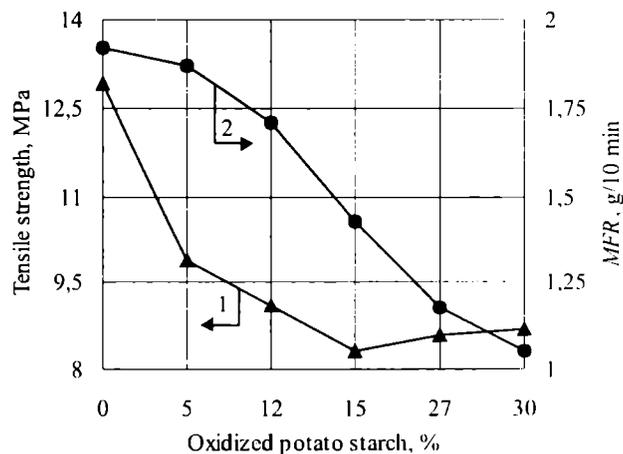


Fig. 1. Tensile strength (curve 1) and melt flow rate (curve 2) of starch/PE-LD/EAA blends as a function of oxidized potato starch (OP) content

Table 1. Elongation at break of starch/PE-LD/EAA blends as a function of starch content (oxidized potato starch — OP, potato starch — P, corn starch — C)

Starch content in starch/PE-LD/EAA	Kind of starch	Elongation at break, %
0	OP	402
5	OP	229
	P	155
12	C	325
	OP	157
	P	108
15	C	239
	OP	101
	P	94
27	C	134
	OP	39
	P	18
30	C	29
	OP	38
	P	14
	C	28

All samples supported the microbes' growth (Table 2, Figs. 2, 3). The microbes' growth could be seen by visual observations after 2–4 days. Microbes kept growing rapidly with time. The rate of microbes' growth increased with the amount of starch in the blends [7]. There is also clear from Table 2 that oxidized potato starch is more effective in the biodegradation process than corn starch. The degree of biodecomposition de-

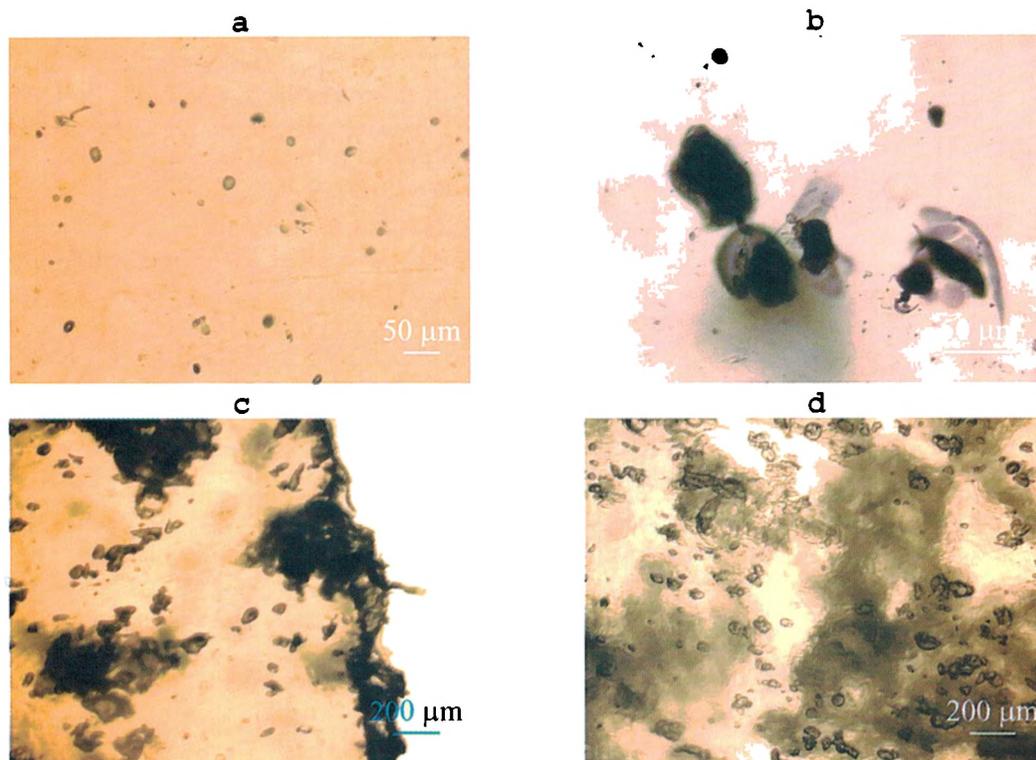


Fig. 2. Micrographs of OP/PE-LD/EAA (30/35/35) blends before (control sample a) and after biodegradation caused by: b — bacteria (*Bacillus*), c — actinomycetes (*Streptomyces*, strain 19), d — filamentous fungi (*Aspergillus niger*)

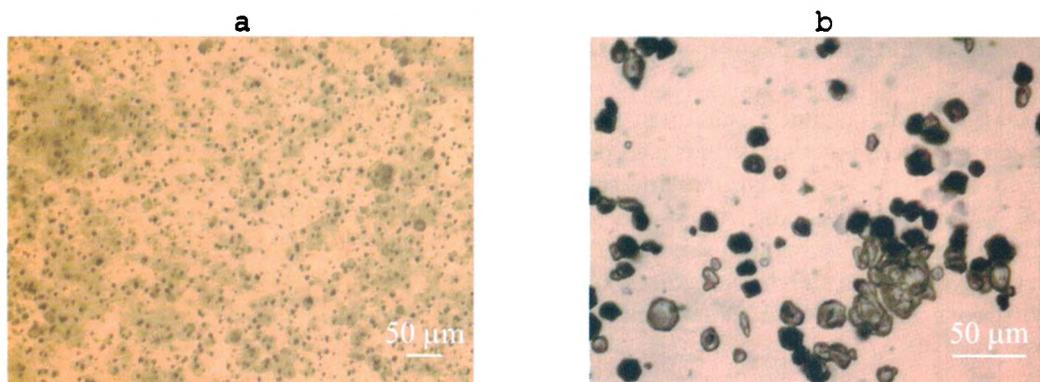


Fig. 3. Micrographs of C/PE-LD/EAA (20/40/40) blends before (control sample a) and after biodegradation caused by actinomycetes [*Streptomyces*, strain 19, sample b]

depends also on the type of microbes used. After six months of biodegradation, *Aspergillus niger*, *Streptomyces* (strain 19) and mixture of bacteria of *Bacillus* type showed the best effect.

Starch, being a natural polymer, could be readily used as a carbon source by the microbes. On the other hand, a synthetic polymer does not act as an efficient carbon source. As an example FT-IR spectra of oxidized potato starch/PE-LD/EAA (30/35/35) blend after six months of biodegradation with different microbes are presented in Fig. 4. For the samples after biodegradation the peak at $950\text{--}1200\text{ cm}^{-1}$ (characteristic for starch) was substantially weaker than for the control one. Therefore, in a starch/PE-LD/EAA blend starch component de-

Table 2. Macroscopic estimation of the growth of microbes after 6 months

Samples	Microbes growth			
	bacteria	actino- mycetes	filamen- tous fungi	mixed popu- lation
PE-LD/EAA (1 : 1)	–	–	–	–
PE-LD/EAA + 20% OP	++	++	+++	++
PE-LD/EAA + 30% OP	+++	+++	+++	+++
PE-LD/EAA + 20% C	+	++	+	+

+++ plentiful growth; ++ good growth; + moderate growth; – no growth

grades and is used up by the microbes, leaving PE-LD/EAA largely unaffected. As the starch content is

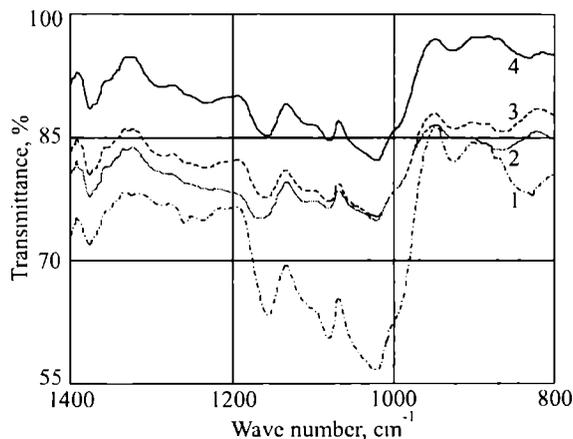


Fig. 4. FT-IR spectra of OP/PE-LD/EAA (30/35/35) blends before and after 6 months biodegradation caused by various microbes: 1 — control sample, 2— actinomycetes, 3 — filamentous fungi, 4 — bacteria

increased, the starch becomes a continuous phase in the blend and can be easily accessed by the organisms. At very low starch contents, the starch may remain encapsulated in the synthetic polymer thereby making it difficult for the organisms to access and use it as a carbon source. The control sample, made of pure PE-LD/EAA did not show any microbes' growth (Table 2).

CONCLUSIONS

Starch/PE-LD/EAA blends could be made in an extruder. The tensile strength of the blends remained practically unchanged when the starch content increased from 5 to 30 wt. %. All of the blends with starch supported the microbes' growth. The growth was faster for the blends with oxidized potato starch than corresponding samples with corn starch. The bigger amount of

starch in the samples the higher rate of microbes' growth. The degree of biodecomposition depends on the type of microbes used. The best effect show *Aspergillus niger*, *Streptomyces* (strain 19) and mixture of bacteria of *Bacillus* type.

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REFERENCES

1. Liu N. C., Baker W. E.: *Adv. Polym. Technol.* 1992, **11**, 249.
2. Otey F. H., Westhoff R. P., Doane W. M.: *Ind. Eng. Chem. Prod. Res. Dev.* 1980, **19**, 592.
3. Otey F. H., Westhoff R. P.: *Ind. Eng. Chem. Prod. Res. Dev.* 1984, **23**, 284.
4. Otey F. H., Westhoff R. P., Doane W. M.: *Ind. Eng. Chem. Prod. Res. Dev.* 1987, **26**, 1659.
5. Jeziórska R., Ratajska M., Tomaszewski W., Boryniec S., Żakowska Z.: *Proceedings of II Conference on Decomposition and Microbiological Corrosion of Technical Materials*, Łódź, May 2001, 303—308.
6. Żakowska Z., Stobińska H., Piątkiewicz A.: *Proceedings of II Conference on Decomposition and Microbiological Corrosion of Technical Materials*, Łódź, May 2001, 298—302.
7. Kuberski S., Zarzycki R., Żakowska Z., Stobińska H., Piątkiewicz A.: *Proceedings of II Conference on Decomposition and Microbiological Corrosion of Technical Materials*, Łódź, May 2001, 225—227.

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