Biodegradable polymers in the general waste stream – the issue of recycling with polyethylene packaging materials

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Abstract: This paper aims to outline the consequences of unintended mixing of polyolefin and biodegradable materials during recycling. The research was done on blends of high density polyethylene (PE-HD) and two commercial biopolymers intended for packaging applications. The mechanical properties, microstructures, water absorptions and DSC results were analyzed. A significant decrease in the blend properties compared to neat polyethylene and biopolymers is a warning against the poor waste management of biodegradable products.

Keywords: biopolymers, biodegradability, mechanical recycling, polyolefins.

Polimery biodegradowalne w strumieniu odpadów zmieszanych – problemy recyklingu polietylenowych materiałów opakowaniowych

Streszczenie: Celem przeprowadzonych badań było wskazanie konsekwencji niezamierzonego zmieszania podczas recyklingu poliolefin i polimerowych materiałów biodegradowalnych. Ocenie poddano mieszaniny polietylenu dużej gęstości (PE-HD) i dwóch dostępnych na rynku biopolimerów przeznaczonych do wyrobu opakowań. Określano ich właściwości mechaniczne i termiczne, absorpcję wody i mikrostrukturę. Właściwości mieszanin wyraźnie gorsze w porównaniu z nienapełnionym polietylenem i biopolimerami stanowią czynnik ostrzegający przed nierozważną gospodarką odpadami biodegradowalnymi.

Słowa kluczowe: biopolimery, biodegradacja, recykling mechaniczny, poliolefiny.

Biodegradable polymers and their blends are present on the world market for many years. For short-time use products of low and medium mechanical properties, especially for packaging, the application of biodegradable polymers is usually considered a solution for the growing problem of plastic waste management. There is a large number of book and journal publications on biodegradable materials and blends with biodegradable polymers, *e.g.*: [1–6]. Their authors usually discuss the synthesis, processing, performance and degradation of biopolymers, promoting them as more eco-friendly than commonly used plastics. The idea of biodegradable polymer based products has many enthusiasts. There is, however, a lack of understanding of the consequences of the introduction of new biodegradable materials onto the market without the proper preparation and education of their consumers. Unfortunately, composting of biodegradable product is an easy task only in the laboratory. In real life, such issues as industrial infrastructure (composting plant capabilities), waste sorting systems, consumer knowledge and current legislations must be taken into consideration.

Compostable polymer products should be separately collected and then composted. In practice, they are usually treated as polyolefin waste and used to produce similar packaging products, which is particularly true for plastic bags and containers. As a result, biopolymer scrap can be accidentally subjected to mechanical recycling together with polyolefins from the general waste stream. In this study, we discuss the properties of blends of polyolefins and biodegradable polymers dedicated for plastic packaging. While the problem of mixing various common plastics present in the general waste stream [*e.g.*: different types of polyethylenes, polypropylene, poly(ethylene terephthalate), polystyrene] is emphasized in the scientific and trade journals, the issue described here seemed to have been overlooked.

Blends of polyethylene (PE) or polypropylene (PP) and biodegradable polymers such as polylactide (PLA) or thermoplastic starch have been manufactured and tested in several studies [7–17]. As the purpose of those studies was to produce a good quality polymer blend, melt-compounding or other forms of extrusion process were used to produce pellets or semi-finished product for test specimen preparation. As the immiscible blends of polyolefins and polylactide or thermoplastic starch were found to have poor mechanical features (brittleness, reduced tensile strength), the researchers tried to modify

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them by introducing different compatibilizers and costly fillers. For example, Lee *et al*. [7] modified polypropylene/polylactide blends with multi-walled carbon nanotubes (MWCNT), thus enhancing the electrical conductivity, melt-crystallization rate, mechanical modulus, and thermal stability. Such features of the PLA/PP/MWCNT composite films originated from the existence of the MWCNTs dispersed selectively and uniformly in the continuous PP matrix. Nuñez *et al*. also conducted research into polypropylene/polylactide blends [8]. A poly(lactic acid) and two polypropylenes of different weight average molecular weights were used as the continuous and dispersed phases in the blends. Four polymers functionalized with maleic anhydride (MA) were used as compatibilizing agents. In these compatibilized blends, however, no morphological evidence of good adhesion between the matrix and the dispersed phases were noted. In the Kim *et al*. study, immiscible blends of PLA and PE-LD (low density polyethylene) were compatibilized using PE-GMA with glycidyl methacrylate (GMA) as a reactive compatibilizer [9]. The PE-GMA addition led to the reduction of the domain size of the dispersed phase and enhanced the tensile properties of PLA/PE-LD blends. The authors also stated that blends of PLA and polyethylene may be good candidates for excellent biodegradable packaging materials. This statement is also present in several other publications [10–12]. However, it is highly arguable and difficult to accept as polyolefins present in the blends do not undergo biodegradation and are still present in the form of a polymer material when the biodegradable part of the blend degrades to water, CO_2 and biomass. In the environment, the packaging product made of this kind of blend is only fragmented to small fractions of plastic that can be dangerous for living organisms.

Similarly to the approach taken in the present study, La Mantia *et al*. studied the issue of non-biodegradable/biodegradable material mixing during the recycling process [18]. In their study, small amounts of PLA were introduced to poly(ethylene terephthalate) (PET). The materials were collected from post-consumer water bottles and then reprocessed as neat materials and blends containing from 0.5 to 5 wt % PLA. The authors used a batch mixer and compression molding. They carried out a rheological examination and thermal analysis, as well as investigated the mechanical properties and microstructure of the blends. The rheological properties of PET are significantly lowered in the presence of small amounts of PLA and a reduction in the main tensile properties began to appear when the material was filled at 5 wt %. The scanning electron microscopy (SEM) analysis clearly showed a biphasic morphology in all of the blends. Thus, the authors also indicated the possibility of the occurrence of side effects of using both the biodegradable and non-biodegradable materials in such applications.

In this paper, blends of high density polyethylene (PE-HD) and biopolymers dedicated for packaging applications are described. The aim of the work was to indicate the possible influence of accidental mixing of such materials during mechanical recycling on the properties of such blends.

EXPERIMENTAL PART

Materials

All the materials used in the study were commercial materials intended and already used for packaging products. High density polyethylene Tipelin BS 501-17, TVK Tlc used as a matrix is a standard grade for blow molding. PLE 001 from NaturePlast was chosen as one of the two biodegradable blends added to the PE-HD matrix. It is a standard grade polylactide (PLA) used for film, sheet, and profile extrusion in food packaging, cosmetics, horticulture, medical and technical parts. The second biodegradable grade was Bioplast GS 2189 from Biotec, a plasticizer-free thermoplastic corn starch material. It is certified EN 13432 and DIN CERTCO biodegradable and compostable and has EU & FDA (USA) Food Contact Approval. It was developed for the packaging, consumer and industrial sectors. As the producer claims, it is a natural replacement for PVC [poly(vinyl chloride)], PP, PE and PET.

Specimen preparation

The blends were made with the addition of 10 wt % and 20 wt % of PLE 001 grade and Bioplast GS 2189 grade to the PE matrix. The quantity of the introduced biopolymer component was intended to reflect the local occurence of a more significant amount of biopolymer in the waste stream. After the conventional dry mixing of the components, standard dumbbell-type specimens (10 x 4 x 150 mm) were injection-molded using a Krauss Maffei KM 30-125C injection molding machine (with a screw diameter of 25 mm and *L*/*D* ratio of 23) with no previous process of extrusion and regranulation. The shot volume amounted to 20 cm^3. The process parameters were the same for all of the tested materials: barrel zone temperatures: 190 °C, die temperature: 190 °C, mold temperature: 35 °C, injection rate: 39 cm^3/s, screw rotation speed: 40 rpm, hydraulic back pressure: 0.6 MPa.

Methods of testing

– The mechanical properties were estimated by a tensile test (ISO 527) and a three-point flexural test (ISO 178) with an universal testing machine MTS Criterion 45 (30 kN force capacity). The tensile test was carried out with a constant crosshead speed of 5 mm/min and the elongation was measured with the use of a MTS axial extensometer and crosshead displacement. The flexural test was performed with a constant crosshead speed of 2 mm/min. Modulus of elasticity (E_t), tensile strength (σ_M), strain at break (ε_B), as well as flexural modulus (E_f)

and flexural stress at 3.5 % strain (σ_f) were determined. Tensile tests were carried out under standard conditions and at -20 °C and 60 °C using an Instron thermal chamber. The values of lowered and elevated temperatures reflected the lowest and highest temperatures at which PE is usually used, also in the packaging industry.

– The tensile-test fracture surfaces were studied using a scanning electron microscope. SEM images were acquired on the gold-sputtered fracture surfaces using a JEOL JSN5510LV microscope.

– Materials' density (ϱ) was measured by a hydrostatic method.

– Basic information of the materials ability to flow was evaluated from mass melt flow rate measurements (*MFR*). The measurements were performed using a CEAST Melt flow Junior 6943 tester at 190 °C/2.16 kg.

– Absorption of water was calculated after 1, 7 and 14 days of soaking, according to ISO 62 (Method 1). To determine the influence of water uptake on the mechanical properties, the tensile test was performed again after 14 days of incubation.

– DSC tests were performed using a NETZSCH model STA409CD with computer software for the test analysis. The measurements were conducted on samples of 20–30 g in an argon atmosphere with a scanning rate of 10 °C/min according to the following procedure: heating between 30 and 150 °C, holding at 150 °C for 3 minutes to erase the thermal history, cooling to 30 °C and then heating between 30 and 200 °C, holding at 200 °C for 3 minutes and cooling to 30 °C. The crystallization temperature (T_c) and melting temperature (T_m) were determined during the second heating-cooling cycle for PE-HD, neat biopolymers, and the blends (containing 20 wt % of the biopolymers). For PE and its phase in the blends, the degree of crystallinity was calculated using the following equation (1):

$$\chi_m = \frac{\Delta H_m}{w \cdot \Delta H_m^0} \cdot 100\ \% \tag{1}$$

where ΔH_m – the melting enthalpy of the tested polyethylene [J/g], ΔH_m^0– the melting enthalpy of 100 % crystalline PE assuming the value of 293.6 [J/g] [19], w – a weight fraction of polyethylene in the blends.

RESULTS AND DISCUSSION

The tested materials are preliminarily characterized in Table 1 with their acronyms used further in the text.

Table 1 includes the results of mass melt flow rate and the density of the samples. The differences in *MFR* values between the polyethylene and biopolymers are significant. Low *MFR* values for polyethylene, typical of grades dedicated to blow molding, reflect the microstructure of the blends, which is further described in the text. It should be noted that the density of polyolefins and biodegradable materials also differ considerably. This feature is useful when it comes to the identification and separation of these materials from each other in the process of industrial waste separation based on density.

Basic mechanical properties

The tensile properties and results of bending test of the examined materials are shown in Table 2.

According to the results, all of the mechanical properties of the blends are dramatically reduced compared to neat polyethylene or neat biopolymers. The biodegradable grades selected for the study possess good mechan-

Table 1. Composition and basic characteristics of the tested materials

Sample	Composition	ϱ, g/cm^3	*MFR*, g/10 min
PE	Neat PE (Tipelin BS 501-17)	0.929 ± 0.002	0.2
GS	Neat Bioplast GS 2189	1.350 ± 0.008	34.5
PE/10GS	90 wt % PE/10 wt % Bioplast GS 2189	0.959 ± 0.001	2.8
PE/20GS	80 wt % PE/20 wt % Bioplast GS 2189	1.012 ± 0.003	6.8
PLE	Neat PLE 001	1.251 ± 0.003	5.0
PE/10PLE	90 wt % PE/10 wt % PLE 001	0.944 ± 0.007	2.6
PE/20PLE	80 wt % PE/20 wt % PLE 001	0.962 ± 0.004	3.1

Table 2. Mechanical properties of the tested materials

Sample	E_t, MPa	σ_M, MPa	ε_B, %	E_f, MPa	σ_f, MPa
PE	1267 ± 270	20.2 ± 0.6	> 300	631.7 ± 50.7	22.6 ± 0.7
GS	2581 ± 109	31.8 ± 1.0	22.0 ± 0.1	–	–
PE/10GS	338 ± 66	10.5 ± 0.1	66.2 ± 7.9	180.0 ± 18.2	7.6 ± 0.1
PE/20GS	978 ± 227	10.2 ± 1.7	7.2 ± 6.9	557.9 ± 19.5	18.8 ± 0.6
PLE	3868 ± 277	72.0 ± 0.4	7.1 ± 1.6	–	–
PE/10PLE	393 ± 38	10.4 ± 0.4	46.6 ± 5.5	290.0 ± 2.0	11.4 ± 0.6
PE/20PLE	489 ± 31	9.9 ± 0.5	23.2 ± 5.7	383.0 ± 35.0	15.4 ± 2.1

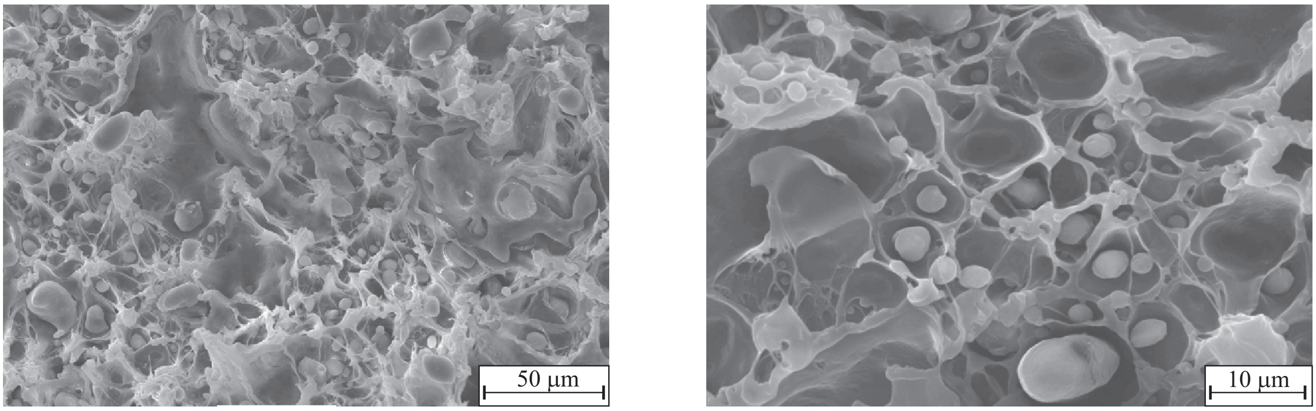

Fig. 1. Low- and high-magnification SEM images of PE/20GS tensile test fracture surfaces

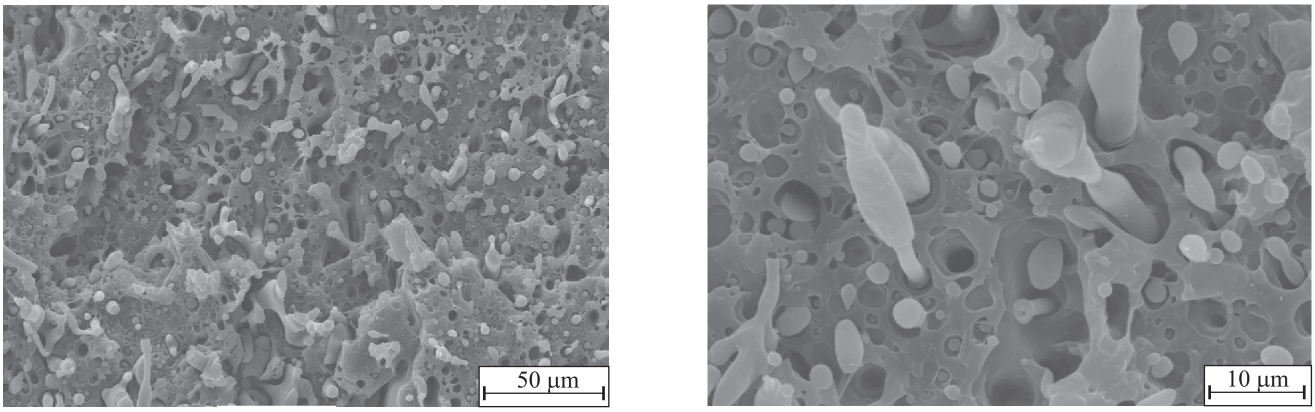

Fig. 2. Low- and high-magnification SEM images of PE/20PLE tensile test fracture surfaces

ical properties, higher than those of polyethylene resin. However, no tensile modulus enhancement can be observed for the blends compared to the value obtained for PE. The blends containing 20 wt % of the biodegradable material show greater flexural strength, as well as tensile and flexural modulus, than the blends with 10 wt % of the biopolymers but the results are unsatisfactory and the increase in biopolymer content significantly reduces the strain at break of the blends. The incompatibility and immiscibility of the blend components, as well as the use of a single-step processing without compounding (a scenario possible in mechanical recycling) resulted in poor replicability of the blends' mechanical properties.

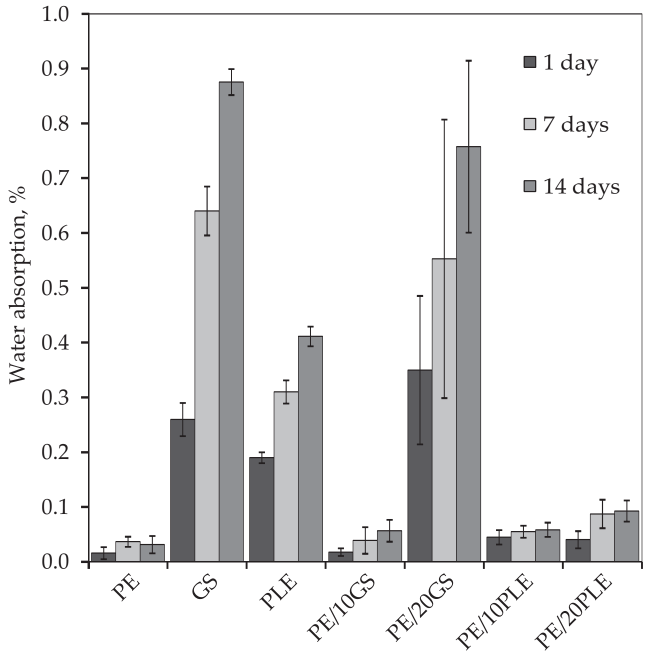

Fig. 3. Water absorption of the tested materials after 1, 7 and 14 days of soaking

Figures 1 and 2 show SEM images acquired on tensile fracture specimens of PE mixed with 20 wt % of the biopolymers. The tensile fracture images are typical of immiscible and incompatible blends with poorly dispersed phases of PLE and GS components and large voids in the interfacial areas. In PE/20PLE blends, the biopolymer phase is more elongated and separated in the PE matrix in comparison to the GS phase in PE/20GS blends.

Water absorption

The results of water absorption examination applied to the tested materials after 1, 7, and 14 days of soaking are presented in Fig. 3.

A predictable increase in water absorption of the blends is observed with an increased content of hygroscopic biopolymers. The changes can be clearly seen for

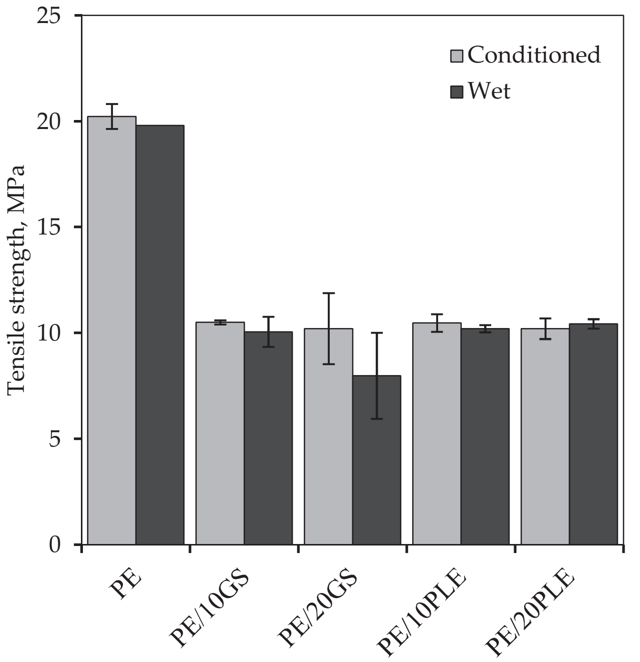

Fig. 4. Tensile strength of the conditioned materials and after 14 days of soaking

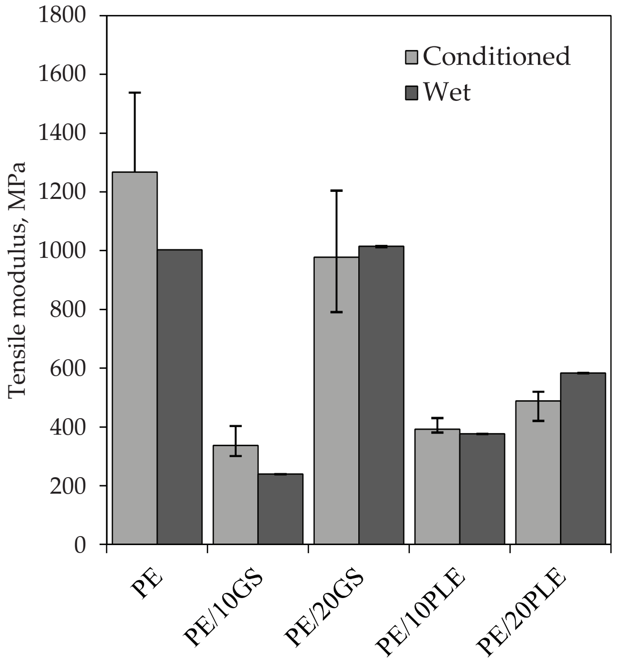

Fig. 5. Tensile modulus of the conditioned materials and after 14 days of soaking

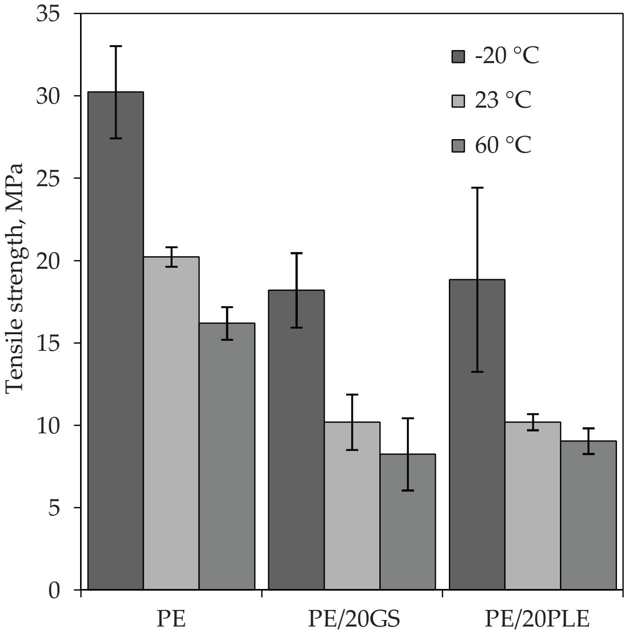

Fig. 6. Comparison of tensile strength for the neat PE and its blends with 20 wt % of biopolymers at different temperatures

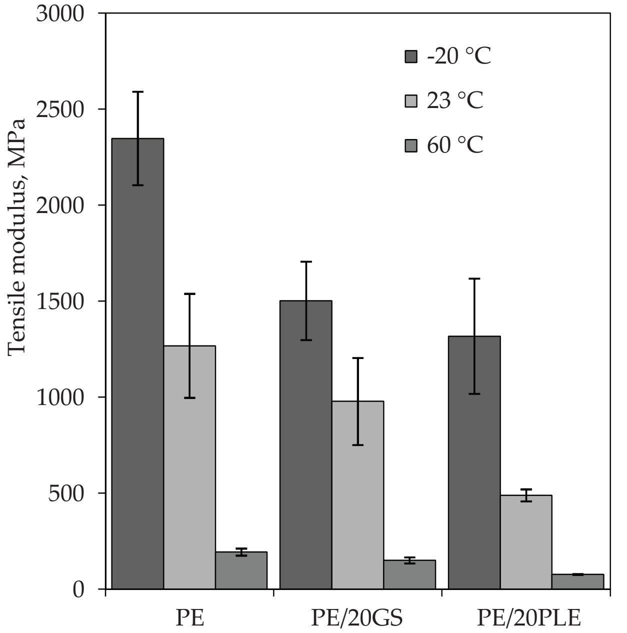

Fig. 7. Comparison of tensile modulus for the neat PE and its blends with 20 wt % of biopolymers at different temperatures

blends containing the highly water-absorbing GS grade. A net of GS biopolymer present in the blend allows water to be more easily transported inside the specimen.

Figures 4 and 5 show changes in tensile properties due to 14 days of soaking in water.

The changes were not large and irregular. The reduction in tensile strength and strain at break was noted for most blends. The effect of an increase in tensile modulus for the blends compared to neat polyethylene might be the effect of an increase in the internal stress between the blend phases. The volume of the water-absorbing biopolymer phase increased during soaking, which lead to a decrease in the void volume between the PE and biopolymer components.

This should not be considered, however, as a long-lasting, positive effect. Further decreases in all of the presented properties are expected.

Thermal and thermo-mechanical properties

The results of the tensile test for neat PE and its blend with 20 wt % of biopolymers conducted at -20 °C and at 60 °C were compared with the results obtained at room temperature as presented in Figs. 6 and 7.

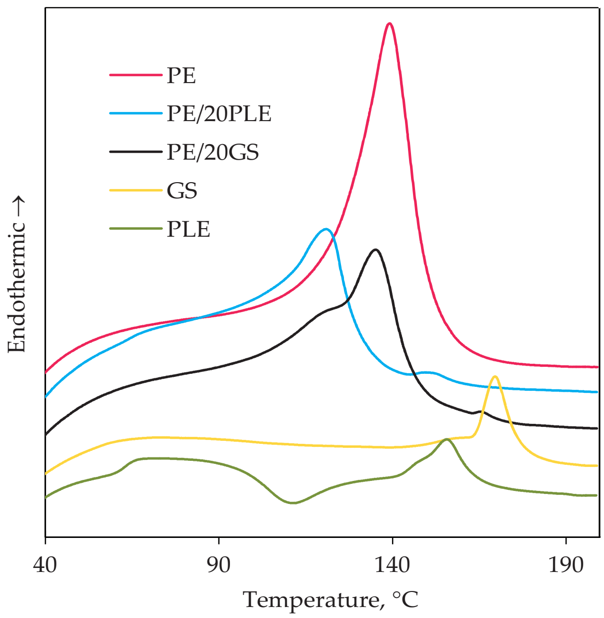

Fig. 8. DSC heating curves for neat PE, biopolymers and for PE blends with 20 wt % of biopolymers in the second heating-cooling cycle

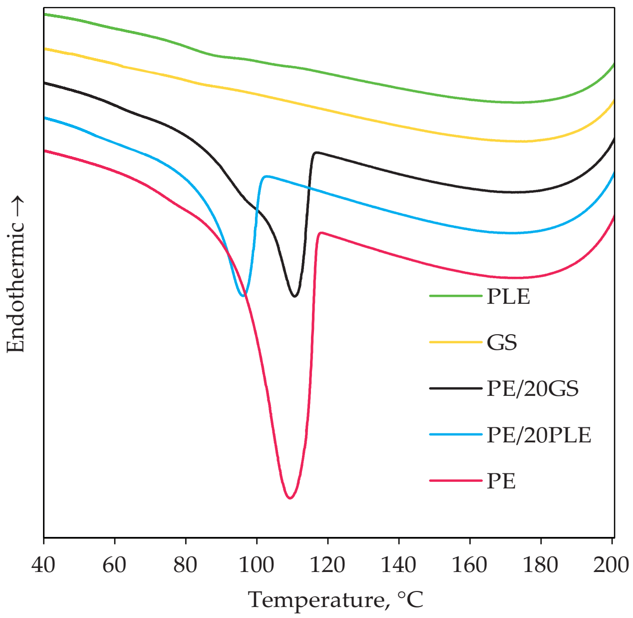

Fig. 9. DSC cooling curves for neat PE, biopolymers and for PE blends with 20 wt % of biopolymers in the second heating-cooling cycle

The changes in the properties of the blends hardly differed from those observed in the case of PE. Here, no evident influence of the biopolymer filler on the stabilization or destabilization of the properties at lowered or elevated temperatures can be proved. The changes in the mechanical properties at lower temperature are greater than those evaluated at elevated temperatures.

The thermal properties of the neat materials and the blends containing 20 wt % of biopolymers were additionally characterized by DSC analysis. The heating and cooling thermograms from the second heating-cooling cycle are shown in Figs. 8 and 9.

The data derived from the DSC analyses are listed in Table 3.

In the heating curve (Fig. 8) for the neat polylactide (PLE samples), an exothermic cold crystallization peak can be noted at 111.4 °C and no crystallization peaks appear for the tested biopolymers during the cooling phase (Fig. 9). The introduction of the biopolymers to polyethylene changed the melting (T_m) and crystallization (T_c) temperatures of PE compared to the reference sample in a typical way of inhomogeneous immiscible blends. The dominant and high melting peaks at 135 °C for PE/20GS and 120.9 °C for PE/20PLE can be assigned to the PE transition. The shift of the dominant melting or crystallization peaks towards lower temperatures can be noted especially for PE/20PLE blends. The decrease in T_m implies that the addition of biopolymers affected the crystal stability of polyethylene. The decrease in T_c indicates a decrease in the polyethylene crystallization rate with the presence of biodegradable phase inclusions. The amorphous nature of the added biopolymers hinders the crystallization of PE, which can be seen especially for PE/20PLE. The change in the degree of crystallinity (χ_m) of PE in the blends is significant (Table 2). This is another justification for the observed deterioration in the mechanical properties of the blends. Comparing PE/20PLE and PE/20GS, the results of DSC analysis are in conformity with the results of mechanical tests and SEM observations as PE/20GS showed higher tensile and flexural properties and less discontinuities, voids in structure, as well as a higher degree of crystallinity and lower shifts in transition temperatures than in the case of PE/20PLE.

CONCLUSIONS

Biodegradable polymers possess well-known advantages that make them suitable for short-term applications,

Table 3. Temperatures of melting (T_m) and crystallization (T_c), values of enthalpies of melting (ΔH_m) and crystallization (ΔH_c) of polyethylene, biopolymers and 20 wt % blends and the degree of crystallinity (χ_m) of polyethylene matrix

Sample	T_m, °C	ΔH_m, J/g	χ_m, %	T_c, °C	ΔH_c, J/g
PE	139.1	123.0	41.9	109.5	130.0
GS	169.5	–	–	–	–
PE/20GS	135.0	50.6	21.5	110.5	62.4
PLE	155.8	–	–	–	–
PE/20PLE	120.9	34.9	14.9	96.1	40.2

mainly packaging. However, the system of selective collection of compostable polymer waste is still underdeveloped. Such biopolymer waste is often disposed in the general waste stream and may then be recycled with other packaging waste, *e.g.*, polyolefin shopping bags, foils and containers. The results of the study show clearly that the unintended blending of polyolefin and biodegradable polymer packaging waste can negatively affect the properties of the final product of mechanical recycling.

The obvious question is how to prevent that situation or how to improve the properties of the presented materials. Looking for an enhancement in the physical features, one may suggest the use of compatibilizers and reinforcement, or to apply some modified manufacturing method. However, these approaches will only be adopted if they are cost-effective. The authors of the present study believe that the sensible solution of the described problem should be somehow connected with prevention methods. And these are: consumer education, technological development and legislation solutions supporting adaptation of composting plants for receiving compostable polymers, and also further implementation of waste separations methods, even those based on density. The effect of the reduced performance of the discussed blends can be neglected in the scale of the global industry when the share of biopolymers in plastic packaging market is low, but if we strive for an increase in the share, it is crucial to put particular emphasis on the effective and selective collection of compostable polymer waste.

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