Novel Microorganisms Resistant HDPE Composites with Wood Fiber and Nanosilica Containing Immobilized Nanosilver

R. Jeziórska,[*1] *M. Zielecka,*[1] *A. Szadkowska,*[1] *B. Gutarowska,*[2] *Z. Żakowska*[2]

Summary: The effect of silica containing immobilized nanosilver ($SiO_2 - Ag$) on the structure, mechanical and bactericidal properties of wood-filled high density polyethylene composites compounded in a co-rotating twin-screw extruder and then injection molded was investigated. Maleated high density polyethylene (MHDPE) was used to improve mechanical properties, while spherical nanosilica containing immobilized nanosilver modified bactericidal properties of wood-filled HDPE composites. It was found that the addition of silica in the presence of MHDPE improves adhesion between HDPE and wood fiber. DMTA measurements confirmed these observations, showing toughening effect in the presence of $SiO_2 - Ag$ and MHDPE. The gradual enhancement in tensile and flexural strength, elongation and Charpy impact of the wood-filled HDPE composites containing MHDPE and $SiO_2 - Ag$ was observed. Nanosilica practically did not affect tensile and flexural moduli of the wood-filled HDPE composites, pointing to a toughing effect. Wood-filled HDPE composites modified with nanosilica containing immobilized nanosilver were found to be active against *Escherichia coli*, *Staphylococcus aureus* and *Salmonella typhimurium* whereas unmodified (without $SiO_2 - Ag$) did not show this efficacy. Thus wood-filled HDPE composites containing $SiO_2 - Ag$ are effective bactericidal materials.

Keywords: bactericidal properties; composites; nanoparticles; silicas

Introduction

Wood polymer composites (WPC) are widely studied due to their low density, low environmental impact and low cost. Many efforts have been made to improve their properties in order to achieve specific end-use requirements.[1–3] Maleic anhydride grafted polymers, such as maleated polyethylene and maleated polypropylene, are widely used as compatibilizers to improve the mechanical properties. However, bactericidal properties of WPC are another important topic from application point of view. Among the various bactericidal agents silver is unique because of its inherent properties of high thermal stability and long-term activity.[4] Because of these unique properties, its introduction into different materials often leads to the generation of materials showing activity against a broad spectrum of microbes.

In this work, the effects of the silica containing immobilized nanosilver ($SiO_2 - Ag$) as well as high density polyethylene grafted with maleic anhydride (MHDPE) on the phase behavior, mechanical properties and water absorption of wood-filled high density polyethylene composites (HDPE/W) were studied using scanning electron microscopy (SEM) and dynamic-mechanical analysis (DMTA) in detail. Particular attention is paid to the ability of spherical silica containing immobilized nanosilver to give bactericidal properties to wood-filled HDPE composites as a function of the nanofiller content.

[1] Industrial Chemistry Research Institute, Rydygiera 8, 01-371 Warsaw, Poland
E-mail: regina.jeziorska@ichp.pl
[2] Technical University of Lodz, Wolczanska 171/173, 90-924 Lodz, Poland

Materials

High density polyethylene (HDPE, Purell GA 7760) used in this work with melt flow rate (MFR) equal to 18 g/10 min (ISO 1133, 190 °C and 2.16 kg) was supplied by Basell Service Co B.V. Standard soft wood fiber (Lignocel C 120), 70 – 150 μm, was provided by J. Rettenmaier GMbH, Germany. High density polyethylene grafted with 0.6 wt % of maleic anhydride (MHDPE) was prepared by melt blending according to the procedure published elsewhere[5] and used as a compatibilizer for nanocomposites at the concentration of 5 wt %. Spherical silica (43 nm) containing 69 500 ppm of immobilized nanosilver ($SiO_2 - Ag$), synthesized according to the developed sol-gel process[6,7] was used as a nanofiller.

Preparation of Composites

Prior to preparation of samples, wood fiber (W) was dried in an oven at 65 ± 2 °C for 24 h. Then, HDPE, wood fiber, MHDPE and nanosilica were melt mixed using a Berstorff ZE-25 × 33D twin screw co-rotating extruder with L/D = 33 (D = 25 mm) according to the process published elsewhere.[8] Samples for structural and mechanical tests were prepared by injection molding using Arburg 420 M injection machine, Allrounder 100–250 type.

Characterization

Cross-sections of fractured samples of the composites were studied using scanning electron microscope (SEM) JEOL JSM-6490LV (Japan) operating in the high vacuum mode at accelerating voltage of 15 kV. Prior to examination the samples were sputtered with gold using JEOL Fine Coater JFC-1200 for 40 s at argon pressure of 8 Pa and current of 35 mA. The dynamic mechanical properties of samples were carried out using a dynamic mechanical analyzer, model Rheometrics RDS 2. The torsion method was used with a frequency of 1 Hz, a strain level of 0.1% in the temperature range of −150 to 100 °C. The heating rate was 3 °C/min. The testing was performed using rectangular bars measuring approximately $38 \times 10 \times 2$ mm. These were prepared by injection molding. An Instron Series 4505 tensile tester operating at a crosshead speed of 5 mm/min at room temperature was used to measure the tensile and flexural properties of the composites according to ISO 527 and ISO 178, respectively. The specimens for the mechanical tests were prepared in an Arburg 420 M single screw injection machine (Allrounder 1000–250, Germany) containing five different heating zones. The temperatures of these were 175/185/200/205/195 °C, from the feeding zone to the die, while the mold was cooled with water at 20 °C. The Charpy notched impact tests were performed according to ISO 179 using Zwick apparatus. A minimum of 5 specimens for each composite were tested in order to estimate the precision of the reported data. Heat distortion temperature (HDT/A) was measured according ISO 75. *Escherichia coli strain* ATCC 8739, *Staphylococcus aureus strain* ATCC 6538 and *Salmonella typhimurium strain* ATCC 14028 were used as test organisms to check bactericidal properties. The exact initial concentration of bacteria was determined using microscopy method. Vitality of bacteria onto polymers was determined using the adenosine-5'-triphosphate (ATP) method. The HY-LiTE® (Merck) system based on bioluminescent method was applied to measure the ATP content on polymer surface.[9]

Results and Discussion

Mechanical Properties

Table 1 gives mechanical properties of wood-filled HDPE composites. Maleated high density polyethylene (MHDPE) was used as a compatibilizer of wood fiber and HDPE in the composites. It can effectively enhance tensile and flexural strengths, elongation at break and Charpy impact strength as well as tensile and flexural moduli of wood-filled HDPE composites in comparison to the sample without MHDPE. These results are attributed to

Table 1.
Properties of HDPE and wood-filled HDPE composites.

Property	HDPE	HDPE/W 70/30	HDPE/MHDPE/W/SiO_2-Ag		
			65/5/30/0	60/5/30/5	55/5/30/10
Elongation at break, %	390 ± 44	5 ± 0.4	10 ± 0.8	14 ± 0.9	16 ± 1.0
Tensile strength, MPa	22 ± 0.5	25 ± 0.3	31 ± 0.1	34 ± 0.2	35 ± 0.2
Tensile modulus, MPa	1313 ± 59	3452 ± 366	3342 ± 157	3384 ± 97	3089 ± 35
Flexural strength, MPa	24 ± 0.3	19 ± 0.4	41 ± 0.4	41 ± 0.2	40 ± 0.2
Flexural modulus, MPa	759 ± 52	1217 ± 41	2407 ± 46	2411 ± 32	2309 ± 52
Charpy impact strength, kJ/m^2	4.2 ± 0.3	2.8 ± 0.8	3.8 ± 0.4	4.4 ± 0.4	4.0 ± 0.5
HDT, °C	44	62	66	65	64
Water absorption, %	–	1.8	1.5	1.1	0.9

esterification reactions between hydroxyl on the wood fiber surface and anhydride on the polyethylene chain,[10] and the better compatibility between HDPE and the long chain in MHDPE, which was discussed by Kazayauoko et al.[11] Nanosilica containing immobilized nanosilver ($SiO_2 - Ag$) was added to wood-filled HDPE composites to improve the bactericidal properties. It is interesting to note that the $SiO_2 - Ag$ addition is beneficial to enhance tensile strength, elongation at break and impact strength of the HDPE/MHDPE/W composites. The tensile strength and elongation of the composites generally increase with increasing nanofiller content. From the above mechanical test results, it is evident that the MHDPE and $SiO_2 - Ag$ additions lead to a finer dispersion of wood fiber in HDPE matrix as discussed in the one of next sections. Similar effect was observed in our previous work for such composites filled with higher wood fiber amount, containing smaller or bigger size $SiO_2 - Ag$ particles.[12,13] However, contrary to the previous results [12,13] now when the composites contain less wood fiber the tensile and flexural moduli are practically not affected by $SiO_2 - Ag$ content.

The advantageous effects of both MHDPE and $SiO_2 - Ag$ on the water absorption of the composites have been observed. The presence of MHDPE reduces it a bit and gradual growth of $SiO_2 - Ag$ content significantly decreases water absorption (twice at 10 wt. % of $SiO_2 - Ag$).

Dynamic-Mechanical Properties

In order to evaluate the effects of wood fiber, MHDPE and $SiO_2 - Ag$ nanoparticles on the HDPE matrix, thermomechanical properties were measured. Plots of storage modulus (G'), loss modulus (G''), and loss tangent (tan δ) as functions of temperature at 1 Hz for HDPE and wood-filled HDPE composites with or without silica containing immobilized nanosilver in the presence of MHDPE, are presented in Figure 1. The storage modulus at room temperature and temperatures of α, β and γ-relaxations are shown in Table 2.

The γ-relaxation has been associated with a single relaxation process, predominantly of amorphous origin. This relaxation is typical for the joint movements of chains containing three or more methylene groups (units) in the main chain.[14,15] The γ-relaxation appears as a maximum at −108 °C for the HDPE and from −117 to −113 °C for the composites in tan δ and at slightly lower temperatures in loss modulus, with a corresponding decrease in storage modulus. This is a clear effect of wood fiber and silica containing immobilized nanosilver loading, as well as the compatibilizer used on the breadth and location of the relaxation; this process is shifted to lower temperatures in the presence of wood, MHDPE and silica, as a consequence of lower crystallinity as compared to HDPE/W composite.[12]

The α-relaxation has been defined as the reorientation of molecules within the crystal.[16] It was reported[12] that there is a relation between crystallites' thickness and

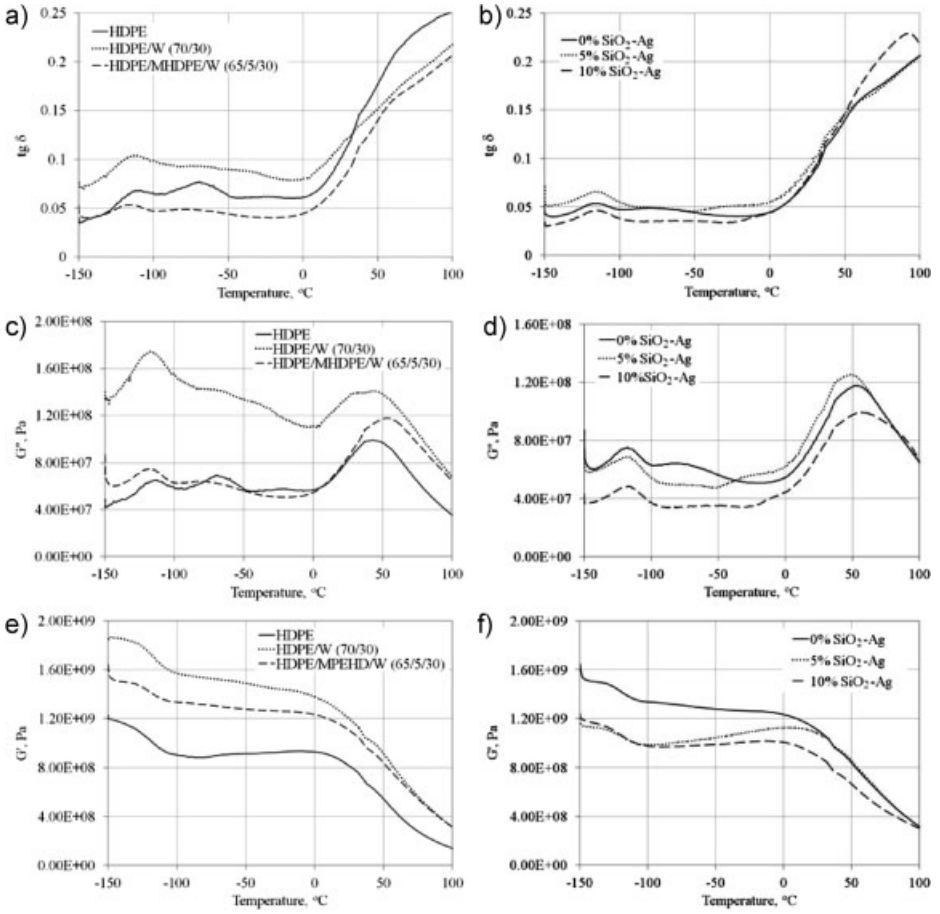

Figure 1.
Temperature dependence of loss tangent tg δ (a, b), loss modulus G'' (c, d) and storage modulus G' (e, f) of HDPE, HDPD/W 70/30, HDPE/MHDPE/W 65/5/30, HDPE/MHDPE/W/SiO_2-Ag 60/5/30/5 and HDPE/MHDPE/W/SiO_2-Ag 55/30/10.

intensity of the α-relaxation, and that this process is affected by the chain mobility of the crystallites. Therefore, chain mobility occurs at higher temperatures as crystallite thickness increases. The position and intensity of the α-relaxation maximum is usually connected with crystallites' thickness and crystallinity level, respectively.[17]

Table 2.
DMTA results for HDPE and wood-filled PEHD composites, differing in SiO_2 — Ag content.

Sample	G' at T = 23°C	Temperature (G'')			Temperature (tg δ)		
		α	β	γ	α	β	γ
	MPa	°C	°C	°C	°C	°C	°C
HDPE	832	42	−69	−114	–	−71	−108
HDPE/W 70/30	1220	42	–	−117	–	–	−113
HDPE/MHDPE/W 65/5/30	1120	53	−77	−118	–	–	−117
HDPE/MHDPE/W 60/5/30/5	1080	48	–	−118	–	–	−115
HDPE/MHDPE/W 55/5/30/10	902	58	–	−118	–	–	−117

There is no evidence of the α-relaxation in loss tangent of these samples. On the other hand, the α-relaxation shows a clear maximum in loss modulus. In the HDPE it appears centered at 42 °C. The addition of wood fiber does not affect α-relaxation temperature. However, the MHDPE significantly increases T_α value of wood-filled polyethylene (HDPE/W 70/30) to 53 °C. The addition of silica containing immobilized nanosilver decreases the α-relaxation temperature at lower content (5 wt %) and increases at higher (10 wt %). However, in both cases the α-relaxation temperature is significantly higher compared to HDPE.

Simultaneously, the β-relaxation can be observed as a clear maximum in loss modulus and tan δ (Figure 1a and 1c) for HDPE and the HDPE/MHDPE/W composite in loss modulus. However, the β-relaxation was not observed for the HDPE/W 70/30 composite and wood-filled HDPE composites containing silica with immobilized nanosilver.

The β-relaxation appears as a maximum at −69 °C for HDPE and −77 °C for the HDPE/MHDPE/W composite. Some authors have concluded that the β-relaxation results from motions of chain units in the interfacial region[17] whereas others attributed this process to the glass transition.[18]

The storage moduli of the HDPE/MHDPE/W/SiO_2 – Ag composites were slightly lower than corresponding wood-filled composites (HDPE/W and HDPE/MHDPE/W) in the whole range of temperature investigated, which is due to the toughening effect of the SiO_2 – Ag nanoparticles. For the similar composites containing higher amounts of wood fiber we observed reinforcing effect instead of toughening one.[12,13] Moreover, higher silica contents resulted in lower storage modulus as showed in Table 2. All these show that at lower amount of wood fiber the effect of compatibilizer (MHDPE) is dominant.

Morphology

In order to explain the behavior of the wood-filled HDPE composites studied in this work, the cryo-fractured surfaces of composites were examined by SEM.

Figures 2 and 3 show the dispersion state of wood-filled HDPE composites without or with nanosilica containing immobilized nanosilver. The image of the fractured surface of HDPE/W (Figure 1a) shows rough fracture surface with very poor adhesion between fiber and polymer matrix. Moreover, a fiber pull-out phenomenon can be clearly seen, although dispersion of the fibers is quite good. On the contrary, relatively smoother surface and different tendency towards the crack propagation are obtained for the HDPE/W composite containing MHDPE used as a compatibilizer (Figure 2b). It might be due

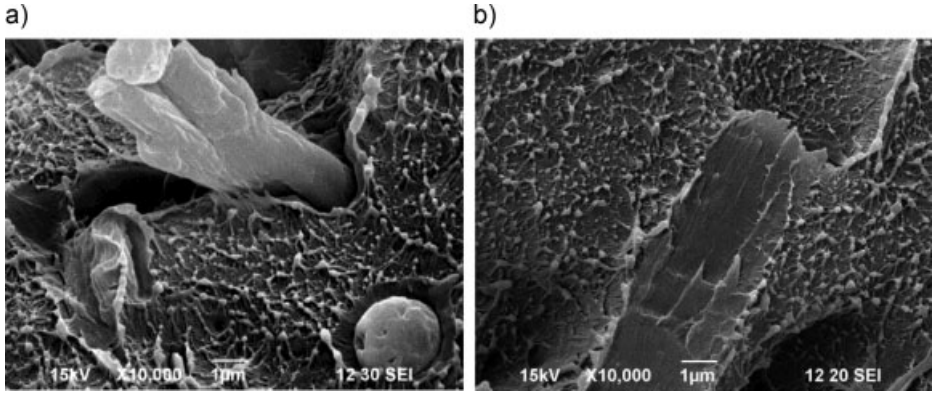

Figure 2.
SEM images of HDPE/W 70/30 (a) and HDPE/MHDPE/W 65/5/30 (b) composites.

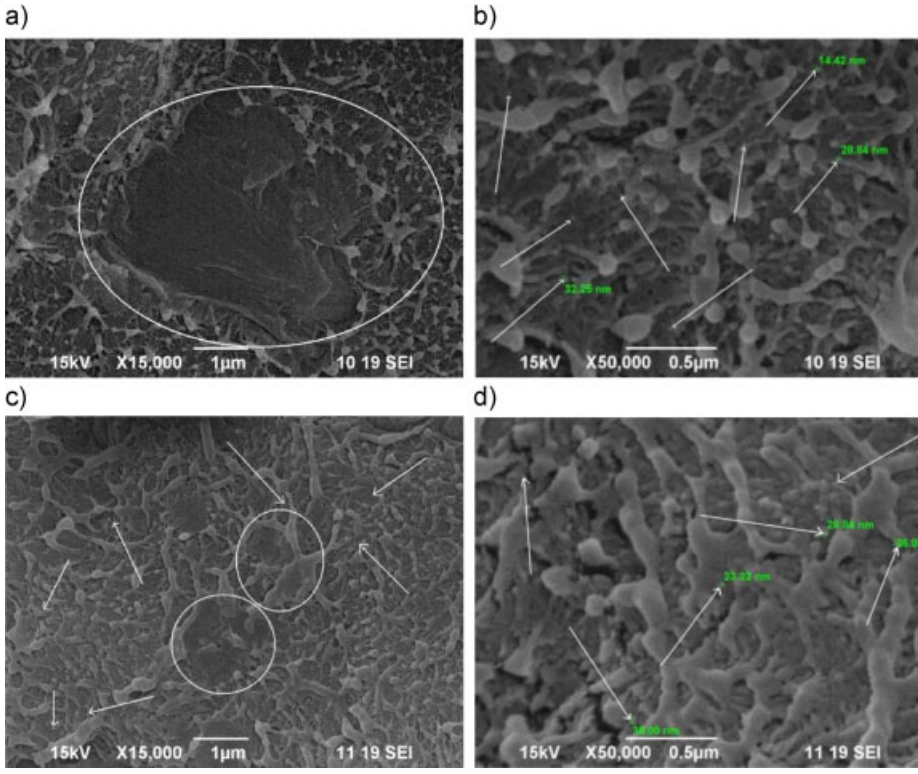

Figure 3.
SEM images of HDPE/MHDPE/W/SiO_2 – Ag composites: 5 wt% SiO_2 – Ag (a, b), 10 wt% SiO_2 – Ag (c, d) marked wood fiber (circles) and SiO_2 – Ag particles (arrows).

to the improved compatibility between HDPE and wood flour through maleic groups grafted onto HDPE and their double bonds. This phenomenon is well known from literature.[19,20] The introduction of compatibilizers affects mainly the interfacial adhesion between wood fiber and polymer matrix.

The addition of SiO_2 – Ag further smoothes the fracture surface and improves the interfacial adhesion (Figure 3). At higher magnification the individual spherical silica nanoparticles can be seen (Figure 3 b and 3 d). The diameter in the range of 14 – 36 nm could suggested that only part of the SGS – Ag particles can be observed due to the very good interfacial adhesion, which is in agreement with our previous work for higher wood fiber and smaller or bigger silica nanoparticles.[12,13]

Bactericidal Properties

The HDPE/MHDPE/W/SiO_2 – Ag composites were subjected to an evaluation of their bactericidal efficacy according to the ATP method. Tables 3 and 4 show the results of the bactericidal tests for the composites containing 5 or 10 wt. % of SiO_2 – Ag, respectively. The results indicate the composites are efficacious against

Table 3.
Vitality of *E. coli*, *St. aureus* and *Salmonella* onto the HDPE/MHDPE/W 60/5/30/5 composite surface determined using ATP method.

Bacteria	ATP content (RLU/cm^2)		F_{ATP} (%)
	HDPE/ MHDPE/W control	HDPE/MHDPE/ W/SiO_2-Ag 60/5/30/5	
E. coli	320	136	57.5
St. aureus	1300	72	94.5
Salmonella	240	90	62.5

Table 4.
Vitality of *E. coli*, *St. aureus* and *Salmonella* onto the HDPE/MHDPE/W 55/5/30/10 composite surface determined using ATP method.

Bacteria	ATP content (RLU/cm^2)		F_{ATP} (%)
	HDPE/ MHDPE/W control	HDPE/MHDPE/ W/SGS-Ag 55/5/30/10	
E. coli	320	125	61.0
St. aureus	1300	63	95.2
Salmonella	240	84	65.0

the microbes considered, due to the significant ATP reduction (57.5–95.2%).

The highest efficacy of the composites containing $SiO_2 - Ag$ against *St. aureus* was observed. Moreover, vitality of the microbes onto the composite surface slightly decreases with increasing concentration of nanosilica containing immobilized nanosilver in the range investigated. Thus wood-filled HDPE composites containing $SiO_2 - Ag$ are effective bactericidal materials.

Conclusion

It has been shown that the addition of silica in the presence of maleated high density polyethylene (MHDPE) improves adhesion between HDPE and wood fiber. DMTA measurements confirmed these observations, showing toughening effect (confirmed by storage modulus) in the presence of nanosilica and MHDPE. Moreover, higher silica contents resulted in lower storage modulus, proving that the material became toughened. It was demonstrated that both MHDPE and nanosilica obviously improved mechanical properties of wood-filled HDPE composites, such as tensile and flexural strengths, elongation and Charpy impact strength. The gradual enhancement in tensile and flexural moduli of the wood-filled HDPE composites containing MHDPE was observed. The addition of $SiO_2 - Ag$ nanoparticles to the wood-filled HDPE composites practically did not affect tensile and flexural moduli, pointing to a toughing effect. It was demonstrated that wood-filled HDPE composites with nanosilica containing immobilized nanosilver were found to be active against *Escherichia coli*, *Staphylococcus aureus* and *Salmonella typhimurium*.

Acknowledgements: This work has been financially supported by project No UDA-POIG.01.03.01-00-073/08-00 co-financed by EU (European Regional Development Fund).

[1] C. M. Clemons, R. C. Sabo, et al, *Journal of Applied Science* **2011**, *119*, 1398.
[2] R. Jeziórska, *Composite Interfaces* **2009**, *16*, 49.
[3] S. Zajchowski, J. Ryszkowska, *Polimery* **2009**, *54*, 674.
[4] C. Damm, H. Munstedt, A. Rosh, *J. Matter. Sci.* **2007**, *42*, 6067.
[5] R. Jeziórska, A. Szadkowska, in: "*Recovering and recycling of polymeric materials*", Ed., J., Kijenski, A., R. Bledzki, Jeziorska, Wydawnictwo Naukowe PWN, Warsaw **2011**, p. 168.
[6] M. Zielecka, R. Jeziórska, et al, *Polish Patent Application* P-390296. **2010**.
[7] M. Zielecka, E. Bujnowska, et al, *Progress in Organic Coatings* **2011**, *72*, 193.
[8] R. Jeziórska, M. Zielecka, M et al, *Polish Patent Applications* P-395938. **2011**.
[9] B. Gutarowska, M. Piotrowska, Z. Żakowska, K. Gwoździński, *Polimery* **2012**, *57*, 236.
[10] B. Li, J. He, *Polym. Degrad. Stab.* **2004**, *83*, 241.
[11] M. Kazayauoko, J. J. Balatinecz, R. T. Woodhams, *J. Appl. Polym. Sci.* **1997**, *66*, 1163.
[12] R. Jeziórska, M. Zielecka, A. Szadkowska, M. Wenda, L. Tokarz, *Polimery* **2012**, *57*, 192.
[13] R. Jeziórska, M. Zielecka, A. Szadkowska, Z. Żakowska, B. Gutarowska, *Journal of Biobased Materials and Bioenergy*, in print.
[14] R. Benavente, E. Perez, M. Yazdani-Pedram, R. Quijada, *Polymer* **2002**, *43*, 6821.
[15] K. H. Nitta, A. Tanaka, *Polymer* **2001**, *42*, 1219.
[16] K. Jordens, G. L. Wilkes, J. Janzen, D. C. Rohlfing, M. B. Welch, *Polymer* **2000**, *41*, 7175.
[17] R. Popli, M. Glotin, L. Mandelkern, *Journal of Polymer Science Part B: Polymer Physics.* **1984**, *22*, 407.
[18] M. L. Cerrada, R. Benavente, E. Perez, *Macromol. Chem. Phys.* **2011**, *202*, 2686.
[19] C. Gozdecki, S. Zajchowski, M. Kociszewski, A. Wilczynski, J. Mirowski, *Polimery* **2011**, *56*, 375.
[20] S. Kuciel, A. Liber-Knec, S. Zajchowski, *Polimery* **2010**, *55*, 740.

