

MARIOLA JASTRZEBSKA^{1)*}, MARIA RUTKOWSKA¹⁾, HELENA JANIK²⁾, SENO JOSE³⁾, SABU THOMAS³⁾

The morphology and mechanical properties of recycled polyethylene/polyamide laminate

Summary — The influence of the compatibilizers on the morphology and mechanical properties of the blend of polyethylene (PE) and polyamide 6 (PA6) was studied. The waste of PE/PA6 laminate obtained after processing of barrier packaging foils was studied. The waste of PE/PA6 laminate containing 80 wt. % of PE and 20 wt. % of PA6 was processed with two compatibilizers: maleic anhydride functionalized ethylene propylene random copolymer (EPM-g-MA) and carboxyl functionalized polyethylene (PE-COOH). The compatibilizers were added to the waste in the amount of 5 wt. % or 10 wt. %. The compatibilization was performed in a Brabender plasticizer at 220 °C and at rotor speed of 50 rpm in a two-step mixing procedure. In the first step the blend was melted for 2 min. That was followed by the addition of compatibilizer in the second step and the mixing was continued for the next 3 min. The mixed melted samples formed thin films by compressive molding. Morphologies were examined using transmission electron microscope TESLA BS 500. The morphology was altered by an addition of compatibilizers and the system became more homogeneous. The dimensions of PA6 domains dispersed in PE matrix decreased dramatically, compared to that of uncompatibilized system. After addition of 5 wt. % or 10 wt. % of a compatibilizer to PE/PA6 blend its mechanical properties improved (twice higher Young's modulus).

Key words: compatibilizer, blends, polyethylene, polyamide 6, morphology, mechanical properties.

MORFOLOGIA I WŁAŚCIWOŚCI MECHANICZNE RECYKLATU Z LAMINATU POLIETYLEN/POLIAMID 6

Streszczenie — W pracy badano wpływ kompatybilizatorów na morfologię i właściwości mechaniczne mieszanin polietylen/poliamid 6 (PE/PA6). Określono właściwości recyklatu uzyskanego z odpadów barierowej folii wielowarstwowej, składającej się z 80 % mas. polietylenu (PE) i 20 % mas. poliamidu 6 (PA6). W celu poprawienia kompatybilności układu zastosowano dwa kompatybilizatory: kopolimer etylen/propylen szczepiony bezwodnikiem maleinowym (EPM-g-MA) lub karboksylowany polietylen (PE-COOH) w ilości 5 % mas. lub 10 % mas. Mieszanki polimerowe z odpadów folii wielowarstwowej PE/PA6 otrzymywano za pomocą systemu uplastyczniającego Brabender w dwóch etapach w temp. 220 °C, z prędkością rotatora wynoszącą 50 obr/min. W pierwszym etapie mieszaniny topiono w ciągu 2 min, następnie, w drugim etapie, po dodawaniu kompatybilizatora mieszano je jeszcze 3 min, po czym prasowano. Strukturę morfologiczną uzyskanych materiałów polimerowych badano używając mikroskopu elektronowego TESLA BS 500. Po dodaniu kompatybilizatorów układ stał się bardziej homogeniczny. Rozmiar domen poliamidu 6 w matrycy polietylenowej kompatybilizowanych mieszanin zmalał znacznie w porównaniu z mieszaniną bez kompatybilizatora (rys. 2 i 4). Mieszanki PE/PA6 z dodatkiem kompatybilizatora i to zarówno w ilości 5 % mas. i 10 % mas. charakteryzują się lepszymi właściwościami mechanicznymi niż próbka niekompatybilizowana (dwukrotnie wyższy moduł Younga) (rys. 1 i 3).

Słowa kluczowe: kompatybilizator, mieszaniny, polietylen, poliamid 6, morfologia, właściwości mechaniczne.

Polyethylene/polyamide 6 (PE/PA6) laminate is used commonly in packaging of meat, ham, cheese and pasta. Polyethylene (PE) serves as the sealing layer and provides flexibility, whereas polyamide 6 (PA6) pro-

vides the oxygen barrier and abrasion resistance of the outer package. This laminate is used in sausage casting. European consumption of these structures is about 10 000 t/year [1].

Several studies of recycling of such films by reactive blending of polyethylene with polyamide have been reported [1—4]. Usually a thin adhesive layer is placed between the two layers to provide adhesion between the materials. These layers should give good coextrusion of the resins and provide the optimum adhesion during

¹⁾ Gdynia Maritime University, ul. Morska 83, 81-225 Gdynia, Poland.

²⁾ Gdańsk University of Technology, ul. Narutowicza 11/12, 80-952 Gdańsk, Poland.

³⁾ Mahatma Gandhi University, Priyadharshini Hills P. O., Kottayam 686560 Kerala, India.

^{*)} Author for correspondence; e-mail: mariola@am.gdynia.pl

processing but they cannot function as an optimum compatibilizer during recycling. Sometimes PE/PA6 contains ethylene-vinyl alcohol copolymer (EVOH), which tends to form gels when heated at temperature above 230 °C. This gel formation makes impossible to reuse this laminate in transparent films. To process the waste of PE/PA6 films the different compatibilizers were screened [1, 2]. Most of the studies are devoted to polyethylene/polyamide 6 blend and based on the fact that polyamide has inherent chemical functionalities (amine and carboxyl end groups) which are capable to react with the functional group present in the modified polyethylene. The most common compatibilizers are polyethylene grafted with maleic anhydride (PE-g-MA) or carboxylic acid (PE-COOH).

Subramanin [5] has shown that the addition of PE-g-MA as a compatibilizer to the PE/PA6 blends led to sufficient reduction in the interfacial tension and strengthening of the interfacial layer. It is found by Zhao *et al.* [6] that maleic anhydride grafted high-density polyethylene efficiently enhanced the compatibility of PA6 and high-density polyethylene (PE-HD) and improved the dispersion of PA6 and interfacial state of phases due to “*in situ*” forming of graft copolymer (PE-HD-g-PA6). Sanchez *et al.* [7] obtained PA6 and ethylene-1-octene copolymer blend with PE-g-MA as a compatibilizer, showing improvement of mechanical stability at high temperature. The presence of functional reactive group such as acrylic acid in polyolefin chains has a strong effect on the phase separation and mechanical properties of the blends.

The effects of acrylic groups on the phase interactions, phase morphology and compatibilization behavior was studied by Psarski *et al.* [8]. Wei *et al.* [9] have examined the radical grafting of glycidyl methacrylate onto low-density polyethylene (PE-LD) and used it for reactive blending with PA6. The compatibilization of PA6 and ultra low-density polyethylene (PE-ULD) or very low-density polyethylene (PE-VLD) was successfully reached by reactive blending of PA6 with functionalized polyethylene diethylmaleate [10, 11]. Diethylmaleate has been proposed as an alternative to maleic anhydride as a grafting moiety for polyethylene. Willis *et al.* [12, 13] used ionomer Surlyn (terpolymer of polyethylene with methacrylic acid and isobutyl acrylate, with an acid partially neutralized by zinc) to compatibilize a blend of PE/PA6. They observed that the addition of ionomer to the PE/PA6 blends resulted in smaller PA6 particles in comparison to the uncompatibilized blend.

Lahor *et al.* [14] observed that the addition of small amounts of a sodium-neutralized ethylene-methacrylic acid copolymer improved the compatibility of PA6 and PE-LD blends as evidenced by a significant reduction in dispersed phase size. Sinthavathavorn and co-workers [15, 16] studied the influence of sodium-, zinc-, or lithium-neutralized ethylene-methacrylic acid ionomers

as compatibilizers in the blends of PA6 with PE-LD. After the addition of a compatibilizer, the shear viscosity of a blend increased, tensile properties improved, the modulus drop associated with melting increased to higher temperature, and the dispersed phase size decreased.

Kudva *et al.* [17] described the effect of compatibilization of PA6/PE blends through grafting of maleic anhydride onto PE. It caused significant improvement in impact strength and reduction of the dispersed phase dimensions in these blends. Kelar *et al.* [18, 19] studied an influence of the prototype statistic and dynamic mixers on the efficiency of grafting of maleic anhydride onto PE-LD in PE-LD/PA6 blend. The poor interfacial adhesion in case of PE-LD and PA6 blended in the presence of 5 wt. % of PE-LD-g-MA, in the extruder equipped with a typical shaped head was found. However the use of the dynamic mixer essentially improves the compatibility of the mixed components PE-LD and PA6 because a graft copolymer PE-LD-g-PA6 is created *in situ*. Filippi *et al.* [20] used maleic anhydride and glycidyl methacrylate grafted onto styrene-*block*-(ethylene-*co*-1-butene)-*block*-styrene copolymer as compatibilizer precursors for blends of PE-LD with PA6 and confirmed that the anhydride functional groups showed considerably higher efficiency of the reactive compatibilization of PE/PA6 blends, than those of ethylene-acrylic acid and ethylene-glycidyl methacrylate copolymer. Minkova and co-workers [21, 22] observed significantly improved compatibility after the use of poly(ethylene-*co*-acrylic acid) (Escor 5001) as a compatibilizer for PE-LD/PA6 blend.

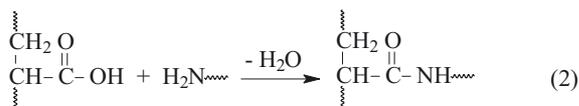
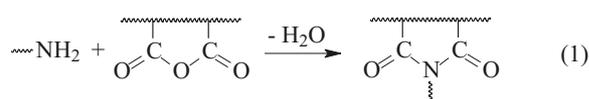
La Mantia and co-workers [23, 24] confirmed that bis-oxazoline a low molecular weight compound might promote the *in situ* formation of PA6 graft ethylene-acrylic acid copolymers in the blend of PE-LD and PA6. Jeziórska [25] observed additionally an effect of PE-LD grafting with ricinol-2-oxazoline methylmaleate on phase structure of PA6/PE-LD blends, obtained in reactive extrusion process. The blends showed heterogenic structure and stabilized microphase level. It advantageously influences the mechanical properties (increasing notched impact strength and elasticity). La Mantia *et al.* [26] studied oxazoline functionalization of PE and its blends with PA6 and the compatibilizing efficiency have been demonstrated by rheological and mechanical characterization. After the addition of epoxidized natural rubber to PA6 and polyolefin blends the interactions among components increased, toughness of the blends increased significantly while tensile strength almost did not change [27].

Coltelli *et al.* [28] studied the one-step reactive blending of the ethylene-propylene copolymer and PA6 with diethyl maleate, maleic anhydride and dicumyl peroxide. The mechanical performances of the one-step blends were slightly worse than those obtained in two-step process. The effects of reactive modifiers with anhydride or oxazoline functional groups on the morpho-

logy and mechanical properties of the blends obtained from waste of PE, polypropylene, PA6, and polystyrene have been also studied [3]. Tensile tests showed the blends had significantly improved elongation and impact strength in comparison with their unmodified analogues.

Only few studies were done on blending of PE/PA6 waste [1—4]. In the studies of the PE/PA6 waste disposal Tartakowski *at al.* [4] demonstrated that addition of dispersed silicate fillers reduced wear resistance and mechanical strength of composites.

In our studies maleic anhydride functionalized ethylene propylene random copolymer (EPM-g-MA) and carboxyl functionalized polyethylene (PE-COOH) have been applied as compatibilizers for the process of PE/PA6 laminate waste compatibilization. The functional groups (anhydride groups of EPM-g-MA or carboxylic groups of PE-COOH, respectively) can react with amine end group of PA at the interface according to equations (1) and (2) [1]:



It can be expected that the maleic anhydride grafted on to the rubber reacts with the amine end-groups of PA, forming a rubber-PA6 graft copolymer which is located between PA6 and PE and acts as a compatibilizer. The carboxylic acid in PE can react with the amine end-groups of PA at the interface and enhance the compatibility.

EXPERIMENTAL

Materials

The waste of a multilayer films consisting of 80 wt. % of PE and 20 wt. % of PA6 coming from the process of packaging were used in the study. A commercially available multilayer film was produced by Gąsiorpak using a method described in [29].

Two types of compatibilizers were used:

— maleic anhydride functionalized ethylene propylene random copolymer of molecular weight 80 000 grafted with 0.6 mole % of MA (EPM-g-MA) supplied by Exxon Chemical Company,

— carboxyl functionalized polyethylene (PE-COOH) of molecular weight 50 000 with 2 mole % of COOH group.

The compatibilizers were added to the waste multilayer films in amounts of 5 wt. % or 10 wt. %.

Blends preparation

The waste of PE/PA6 laminate was processed with two compatibilizers such as EPM-g-MA or PE-COOH. The compatibilization was performed using a Brabender plasticizer at 220 °C and at rotor speed of 50 rpm in a two-step mixing procedure. In the first step the blend was melted for 2 min. It was followed by the addition of compatibilizer in the second step and the mixing was continued for the next 3 min. The mixed melted samples were processed into thin films by compressive molding.

Methods of testing

Mechanical properties

Tensile testing of the samples was performed at 25 ± 2 °C according to standard ASTM 0412-80 with a dumb bell shaped specimen at a crosshead speed of 50 mm/min using a universal testing machine model TNE series 9200 (Facts Instrument and Engineering Pvt. Ltd., India). Tensile strength, Young's modulus and elongation at break of the blends were measured.

Morphology

The morphology of PE/PA6 blends was observed by means of transmission electron microscope (TEM) TESLA BS 500. The samples were cryogenically fractured in liquid nitrogen and thus obtained surfaces were etched with formic acid to better visualize the phases of the blends. Two-stage replicas from the surfaces of cryogenically fractured and etched samples were prepared. Poly(vinyl alcohol) (PVA) was used as a first replicating material. Then PVA matrix was shadowed with platinum and covered with carbon. After PVA dissolution, carbon-platinum replicas were observed under TEM apparatus at 60 kV. The pictures were taken at the magnification in the range from 1000 to 10 000.

RESULTS AND DISCUSSION

In Figure 1 the results of tensile properties of PE/PA6 blend and PE/PA6 blends containing 5 wt. % or 10 wt. % of EPM-g-MA compatibilizer are presented.

The tensile strength of PE/PA6 waste after the mixing in Brabender plasticizer without compatibilizers was 14 MPa, Young's modulus — 30 MPa and elongation — 470 %. The observed low values of tensile strength and Young's modulus are due to recycled laminate. In the Fig. 1 it can be seen that the addition of 5 wt. % of EPM-g-MA to PE/PA6 blend makes the samples more rigid and increases the tensile strength approximately 25 % (up to 17.5 MPa) and Young's modulus even about 100 % to 60 MPa. Elongation at break slightly decreases to 460 %. However, further addition of the compatibilizer (to 10 wt. %) does not change clearly the tensile strength, elongation at break and Young's modulus values in comparison to the sample with 5 wt. % of EPM-g-MA.

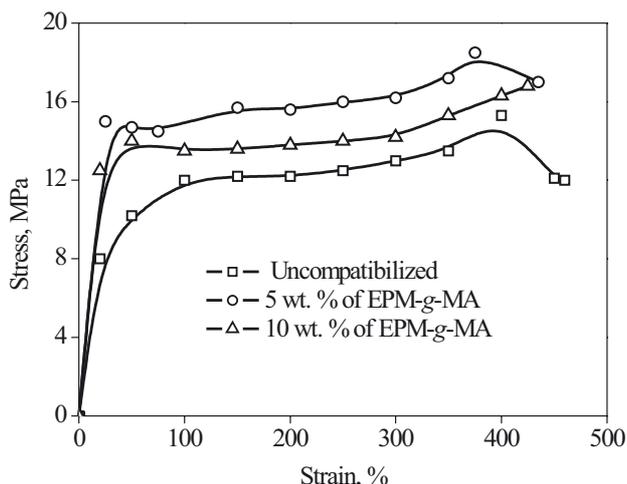


Fig. 1. Stress-strain behavior of the PE/PA6 blends with or without EPM-g-MA compatibilizer

patibilizer added. Their sizes are in the range of 0.3–0.5 μm , thus it is between that observed for PE/PA6 with no compatibilizer and PE/PA6 with 5 wt. % of it. The morphological observations confirm the results of mechanical measurement. The higher values of tensile strength are obtained for PE/PA6 blends with 5 wt. % of compatibilizer where the particles of PA6 were very fine and uniformly distributed in PE matrix.

In Figure 3 the mechanical properties of neat PE/PA6 blend and PE/PA6 blends containing 5 wt. % or 10 wt. % of PE-COOH compatibilizer are presented.

Addition of 5 wt. % or 10 wt. % of PE-COOH increases the tensile strength of the blends slightly (16 MPa, 17 MPa, respectively) in comparison to neat blend (14 MPa). The Young's modulus value increases approximately 100 % (60 MPa) by addition of 5 wt. % of PE-COOH compatibilizer. Further addition of the com-

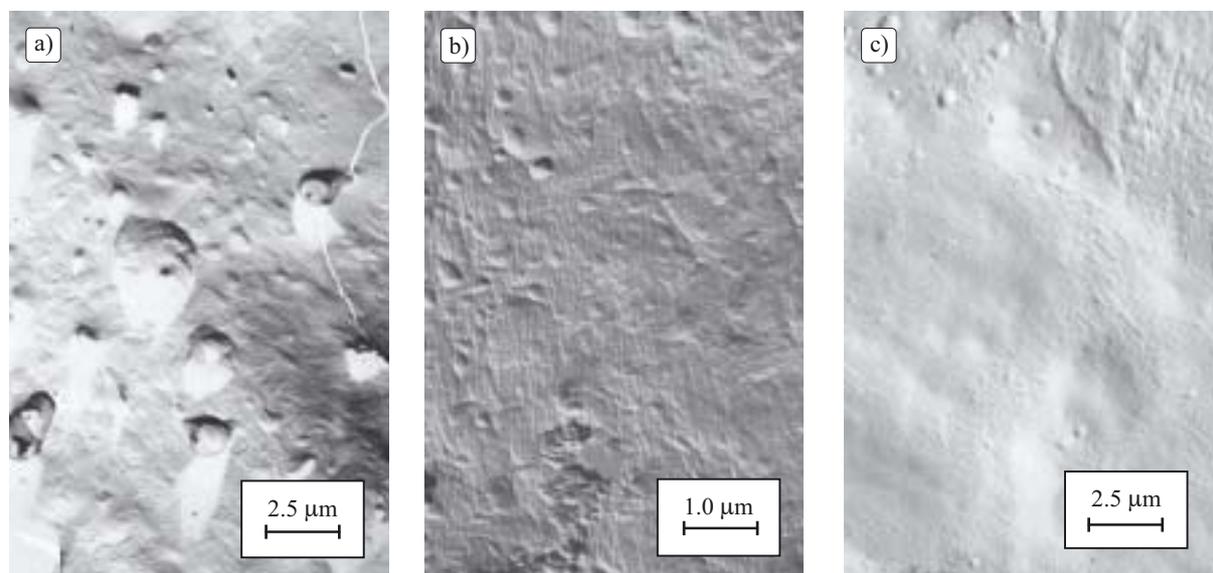


Fig. 2. Morphology of a) neat PE/PA6, b) PE/PA6 with 5 wt. % of EPM-g-MA, c) PE/PA6 with 10 wt. % of EPM-g-MA

Figure 2 shows the morphology of PE/PA6 blends with and without EPM-g-MA compatibilizer.

According to Fig. 2a the morphology of neat PE/PA6 blend is heterogeneous. PA6 particles (slightly elongated) with the size in the range of 1–2.5 μm dispersed in PE matrix can be seen. However, Fig. 2a shows that there is no adhesion between PE matrix and PA6 dispersed phase. Figure 2b presents the morphology of PE/PA6 blend with an addition of 5 wt. % of EPM-g-MA compatibilizer. It is clearly visible that PA6 particles are much smaller than before addition of the compatibilizer (Fig. 2a). Their sizes are of 0.1–0.3 μm and they are homogeneously distributed in the whole sample. Fig. 2c presents the morphology of PE/PA6 blend with addition of 10 wt. % of EPM-g-MA compatibilizer. In this picture the distribution of PA6 particles is not completely homogeneous. The amount of visible PA6 particles is smaller than in the samples without com-

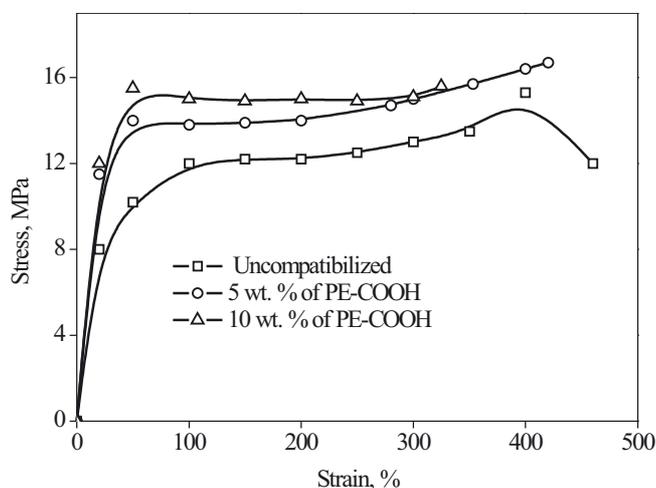


Fig. 3. Stress-strain behavior of the PE/PA6 blends with or without PE-COOH compatibilizer

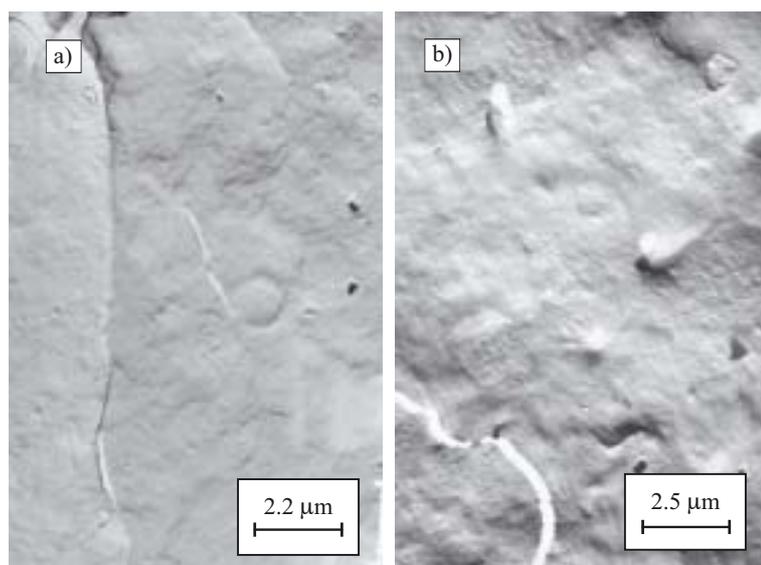


Fig. 4. Morphology of a) PE/PA with 5 wt. % of PE-COOH, b) PE/PA with 10 wt. % of PE-COOH

patibilizer (10 wt. %) to PE/PA6 blend does not change the Young's modulus value (60 MPa) but decreases approximately 28 % the elongation value (340 %) in comparison to the sample with 5 wt. % of PE-COOH.

Figure 4 shows the morphology of PE/PA6 blends with PE-COOH compatibilizer.

As it was shown before (Fig. 2a) PE/PA6 blend without compatibilizer is heterogeneous and contains particles of PA6 (1—2.5 μm in size) dispersed in PE matrix. It is visible in Fig. 4a that addition of PE-COOH compatibilizer (5 wt. %) results in decreasing size of PA6 dispersed phase (to 0.2 μm).

Further addition of PE-COOH (10 wt. %) to PE/PA6 blend makes the morphology almost homogeneous (Fig. 4b). This results in the high Young's modulus but the samples are more rigid which is clearly visible from stress-strain curve (Fig. 3).

CONCLUSIONS

The studies of mechanical properties of the PE/PA6 blends revealed that the addition of compatibilizers EPM-g-MA or PE-COOH to the waste of PE/PA6 laminate significantly improved Young's modulus.

The addition of one of both compatibilizers change clearly the heterogeneous morphology of the PE/PA6 blends and makes almost homogeneous in comparison to uncompatibilized blend system (PA6 particles in PE matrix).

It could be stated that maleic anhydride functionalized ethylene propylene random copolymer and carboxyl functionalized polyethylene act as good compatibilizers for the waste PE/PA6 blending system.

REFERENCES

1. "Polymeric Materials Encyclopedia" Vol. 2. (Ed. Salamone J. C.), CRC Press 1996.

2. Datta S., Lose D. J.: "Polymeric Compatibilizers, Uses and Benefits In Polymer Blends", Hanser Publisher, Munich 1996.
3. Jeziórska R., Szadkowska A., Studziński M.: *Polimery* 2007, **52**, 371.
4. Tartakowski Z. I., Shapovalov V. M., Zlotnikov I. I.: *Journal of Fraction and Wear* 2007, **28**, 373.
5. Subramanin P. M.: *Polym. Eng. Sci.* 1985, **25**, 483.
6. Zhao L., Yang H., Shangguan Y., Zang F., Zheng Q.: *Acta Polymerica Sinica* 2008, **9**, 849.
7. Sanchez M. S., Mathot V., Groeninckx G., Bruls W.: *Polymer* 2006, **47**, 5314.
8. Psarski M., Pracella M., Galeski A.: *Polymer* 2000, **41**, 4923.
9. Wei Q., Chionna D., Galoppini E., Pracella M.: *Macromol. Chem. Phys.* 2003, **204**, 1123.
10. Sanchez A., Rosales C., Laredo E., Muller A. J., Pracella M.: *Macromol. Chem. Phys.* 2001, **202**, 2461.
11. Lazzer A., Malanima M., Pracella M.: *J. App. Polym. Sci.* 1999, **74**, 3455.
12. Willis J. M., Favis B. D.: *Polym. Eng. Sci.* 1988, **28**, 1416.
13. Willis J. M., Caldas V., Favis B. D.: *J. Mater. Sci.* 1991, **26**, 4742.
14. Lahor A., Nihitanakul M., Grady B. P.: *Europ. Polym. J.* 2004, **40**, 2409.
15. Sinthavathavorn W., Nihitanakul M., Grady B. P., Magaraphan R.: *Polym. Bull.* 2008, **61**, 331.
16. Sinthavathavorn W., Nihitanakul M., Magaraphan R., Grady B. P.: *J. App. Polym. Sci.* 2008, **107**, 3090.
17. Kudva R. A., Keskkula H., Paul D. R.: *Polymer* 1999, **40**, 6003.
18. Kelar K., Jurkowski B.: *Polymer* 2000, **41**, 1055.
19. Kelar K., Ciesielska D., Jurkowski B.: *Polimery* 1995, **40**, 298.
20. Filippi S., Yordanov H., Minkova L., Polacco G., Talarico M.: *Macromol. Mater. Eng.* 2004, **289**, 512.
21. Minkova L., Yordanov H., Filippi S.: *Polymer* 2002, **43**, 6195.
22. Yordanov H., Minkova L.: *Europ. Polym. J.* 2005, **41**, 527.
23. La Mantia F. P., Canfora L., Tzankova Dintcheva N.: *Polym. Eng. Sci.* 2005, **45**, 1297.
24. Canfora L., Filippi S., La Mantia F. P.: *Polym. Eng. Sci.* 2004, **44**, 1732.
25. Jeziórska R.: *Polimery* 2004, **49**, 623.
26. La Mantia F. P., Scaffaro R., Colletti C.: *Macromol. Symp.* 2001, **176**, 265.
27. Xie B., Yang M., Li S., Li Z., Feng J.: *J. App. Polym. Sci.* 2003, **88**, 398.
28. Coltelli M. B., Passaglia E., Ciardelli F.: *Polymer* 2006, **47**, 85.
29. Smoliński E.: *Przemysł Spożywczy* 1999, **10**, 26.

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