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Recycling of multilayer films by reactive extrusion

RAPID COMMUNICATION

Summary — Polyethylene, polyamide 6 and poly(ethylene terephthalate) multilayer films waste were recycled by reactive extrusion in order to produce thermoplastic polymers. These wastes were extruded together with PA 6 and PET functionalized with oxazoline groups (R-PA 6, R-PET), ethylene/acrylic acid copolymer (EAA) or block copolymer styrene-ethylene/butylene-styrene-*grafted*-succinic acid (SEBS-*g*-SA). Used additives act as compatibilizers in the structurally heterogeneous initial wastes. Compatibilizers used, as well as wood fiber granulates (filler), improve the mechanical properties of compositions investigated.

Key words: thermoplastic polymers wastes, recycling, multilayer films, modifiers, reactive extrusion, mechanical properties.

Usually, recycled materials are thought to be materials with poor properties with respect to those of the virgin ones. Of course, we are referring to mechanical recycling, *i.e.* the one that allows reusing the material directly in application similar to those of virgin polymers. Multilayer films are widely used in packaging applications; thus due to the increase of environmental issues, the recycling of multilayer films was the subject of several recent studies [1–3]. The main problems during recycling operations of multilayer films are degradation and delamination phenomena. These two aspects are common to all recycled mixed polymers; these phenomena are results of the incompatibility of different polymeric phases. This latter problem is so serious that actually the multilayer films recycling is absolutely reduced and leads to the production of secondary material that can be used only to produce the items with low economical value.

Our intention was to convert the post-production multilayer films waste into thermoplastic polymers with high economical value using low-cost reactive extrusion. In this case polymers react through their functional groups while being processed, and the processing equipment, such as twin screw-extruder or mixer acts as a mini reactor [4, 5].

In this study some new recycling methods will be discussed in order to preserve or even to improve the properties of post-production multilayer films waste.

EXPERIMENTAL

Materials

Materials used were as follows:

— multilayer film waste flakes (MFW1) containing 60 wt. % of polyethylene and 40 wt. % of polyamide 6 — melt-flow rate *MFR* of 0.64 g/10 min (ISO 1133: 1991, 190°C and 2.16 kg); flakes in dimension over 8 mm were < 1% and below 6 mm < 0.5 %;

— multilayer film waste agglomerate (MFW2) containing polyamide 6, polyesters and mainly polyolefins with unknown weight fraction of the components — melt-flow rate *MFR* of 3.02 g/10 min (ISO 1133: 1991, 230°C and 2.16 kg);

— polyamide 6 (PA 6) — melt-flow rate *MFR* of 2.6 g/10 min (ISO 1133: 1991, 230°C and 2.16 kg) from Nitrogen Works Tarnów-Mościce (Poland);

— bottle-grade poly(ethylene terephthalate) (PET) — intrinsic viscosity 0.80 dL/g in phenol/1,2-dichlorobenzene, 50/50 (wt./wt.) at 25°C from Elana PET Ltd (Poland);

— 2,2'-(1,3-phenylene)bis-2-oxazoline (PBO) with chemical formula C₁₂H₁₂N₂O₂ was synthesized according to procedure published elsewhere [6, 7];

— poly(ethylene-*co*-acrylic acid) (EAA) — 9.7% of acrylic acid from Dow Plastics (USA);

— block copolymer styrene-ethylene/butylene-styrene-*grafted*-succinic anhydride (SEBS-*g*-SA), 1% of succinic anhydride from Shell Chemicals (Germany);

— wood fiber granulates LIGNOCEL C-120 from J. RETTENMAIER & SOHNE GmbH (Germany).

Before using, multilayer films waste, PET and PA 6 were dried under vacuum at 80°C, while wood fiber granulate was dried at 105°C.

Melt functionalization

The melt functionalization of polyamide 6 (PA 6) and poly(ethylene terephthalate) (PET) with bis(2-oxazoline) onto was carried out in a pilot-plant twin-screw extruder "Berstorff" ZE-25-33D at 225–245°C and 245–260°C, respectively, operating at 80 rpm.

Blend preparation

Recycling of multilayer films scraps was performed using the same Berstorff extruder as used for the functionalization process. PA 6 and PET reactively functionalized with an oxazoline group (R-PA 6, R-PET), EAA or SEBS-*g*-SA was extruded together with multilayer films waste, according to procedure published elsewhere [8]. Wood fiber granulate was added in amount of 10–30 wt. % to the reaction mixture at 15D length down the barrel. The residence time of the reactants was 2 minutes.

Aging studies

The composites with wood fiber granulate were subject to different environmental conditions:

— Conditioned at room temperature (not subject to any treatment).

— Samples were kept at 105°C in an air-circulating oven for 7 days and then slowly cooled to room temperature. The above samples were conditioned at room temperature before testing.

Testing methods

The morphology of the fracture surface of the specimens was studied *via* scanning electron microscope JSM 6100, Jeol. Samples were fractured under liquid nitrogen after 3 min and then vacuum coated with gold.

The tensile data were collected according to PN-EN ISO 527, and the tests were carried out at room temperature using Instron 4505 tensile tester at a crosshead speed of 5 mm/min.

Charpy impact tests were performed according to ISO 179.

Vicat melting temperature (T_{A120}) was obtained according to PN-93/C-89024.

The melt-flow rate (MFR) was examined by plastometer type II RT according to the standard PN-93/C-89069 (ISO 1133/1991).

RESULTS AND DISCUSSION

Phase structure studies showed that interfacial reactions between reactive modifier and multilayer films waste components are effective in the compatibilization of investigated blends (Figs. 1–3). As examples, Figures

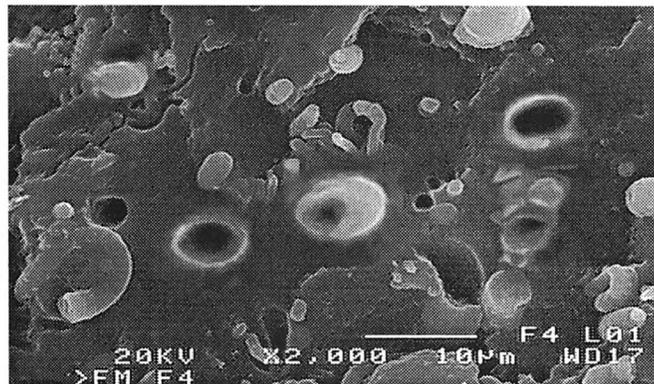


Fig. 1. SEM micrographs of recycled unmodified multilayer film waste (MFW1)

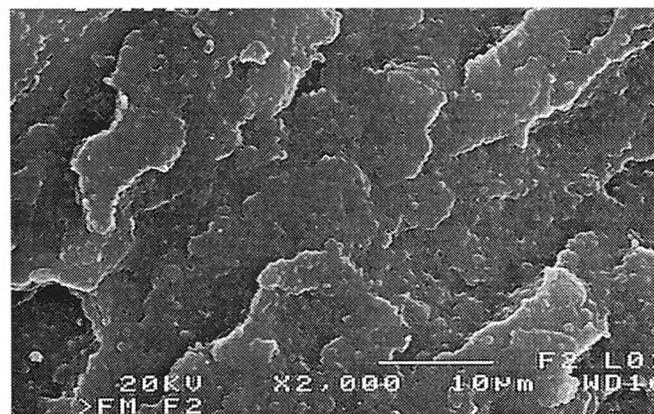


Fig. 2. SEM micrographs of recycled multilayer film waste (MFW1) modified with R-PA 6

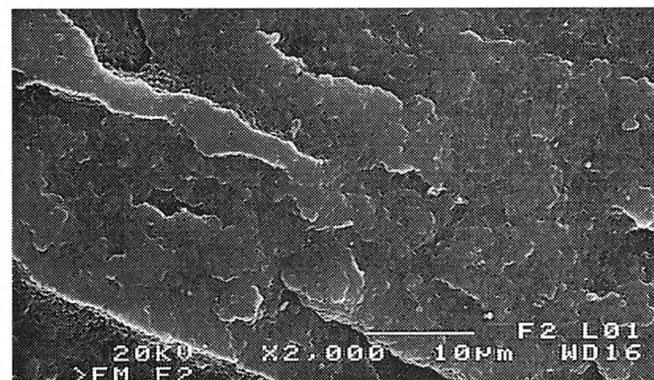


Fig. 3. SEM micrographs of recycled multilayer film waste (MFW1) modified with SEBS-*g*-SA

2 and 3 present micrographs of the impact fractured surface of the samples modified with R-PA 6 and

SEBS-g-SA. The sizes of dispersed phase of the chemically modified blends are relatively smaller than of unmodified one. As can be seen, modified recycled multilayer films show heterogeneous compatible structure with very good adhesion between the phases. The phase morphology of the blends modified with SEBS-g-SA was of interpenetrating polymer network (IPN) type (Fig. 3). This indicates indirectly intermolecular reactions between the polymers during extrusion.

Table 1. Mechanical properties of multilayer films waste (MFW1) modified with different compatibilizers

	Tensile strength MPa	Elongation at break %	Impact notched strength (Charpy) kJ/m^2	Tensile modulus MPa
MFW1	15.6	20.5	12.3	575
MFW1 + 5% R-PA 6	18.7	31.0	14.9	630
MFW1 + 5% EAA	17.2	29.0	18.6	575
MFW1 + 5% SEBS-g-SA	12.7	100.0	100.0	319

Table 2. Tensile properties of multilayer films waste (MFW2) modified with R-PET

	Tensile modulus, MPa	Tensile strength MPa	Elongation at break, %
MFW2	430	19.4	420
5% R-PET	475	17.5	450
10% R-PET	500	13.3	400

Experimental results for the blends with different compatibilizers are summarized in Tables 1 and 2. The investigated blends offer a wide range of mechanical properties and rigidity (Fig. 4). Oxazoline functionalized

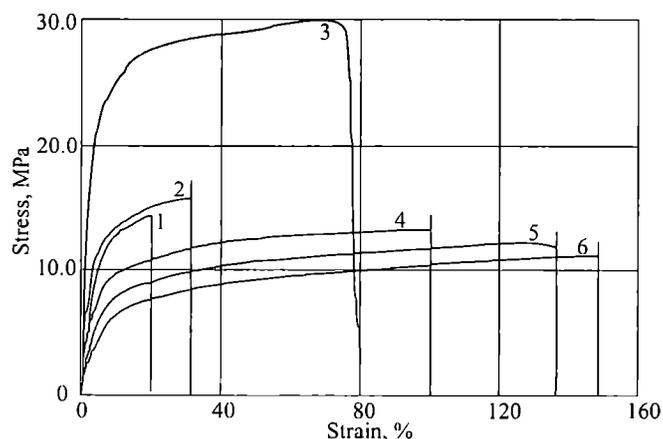


Fig. 4. Stress-strain curves: 1 — MFW1, 2 — MFW1 + 5% EAA, 3 — MFW1 + 25% R-PA 6, 4 — MFW1 + 5% SEBS-g-SA, 5 — MFW1 + 10% SEBS-g-SA, 6 — MFW1 + 15% SEBS-g-SA

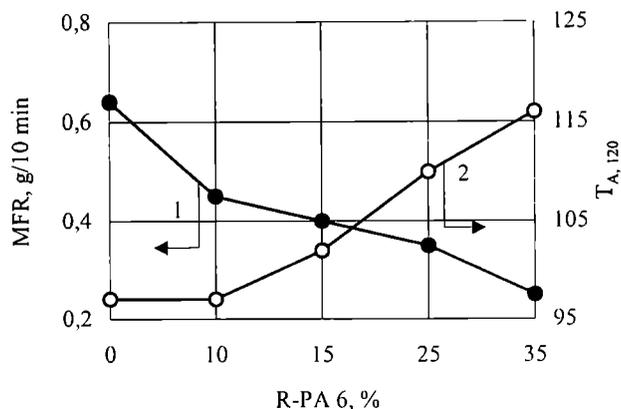


Fig. 5. Melt flow rate (MFR — curve 1) and Vicat melting temperature ($T_{A, 120}$ — curve 2) of modified multilayer films waste (MFW1) as a function of R-PA 6 amount

polyamide 6 (R-PA 6) improves tensile strength, elongation at break, modulus, impact strength and thermal properties (Table 1, Fig. 5). EAA and SEBS-g-SA improve elongation at break and impact strength, on the one hand, and decrease tensile modulus on the other. However, blends with EAA exhibit higher strength, modulus, hardness and deflection temperature as compared to the blends modified by the elastomer.

The blends show very good impact strength. No break was observed in unnotched specimens even at -30°C , and the impact strength for notched specimens in the wide range of temperatures was also high.

The melt flow rate of multilayer films waste modified by different compatibilizers decreased progressively with increasing of the modifier concentration (Figs. 5, 6). This fact can be caused by a change in intermolecular forces or increased molecular weight.

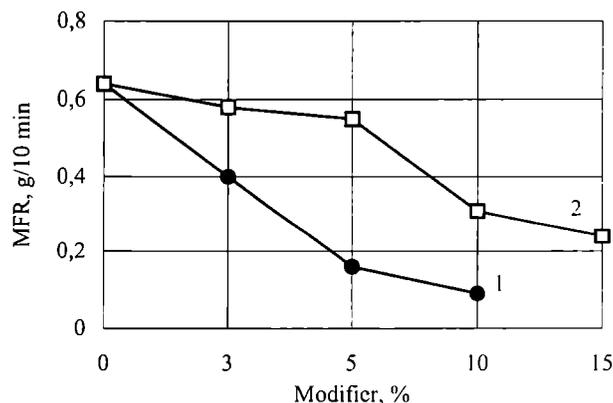


Fig. 6. Melt flow rate (MFR) of modified multilayer films waste (MFW1) as a function of modifier concentration; modifier: 1 — EAA, 2 — SEBS-g-SA

Wood fillers are new filler type that focus the interest of scientists and industry. Wood fillers, very cheap and

"environmentally friendly" can be used with the same scope as other fillers and with similar results. Tensile properties of SEBS-g-SA modified multilayer films waste (MFW2) with various wood fiber granulates concentration, before and after aging at 105°C for 7 days are presented in Table 3. The wood fiber granulates causes decrease in tensile strength and elongation at break, on the

the composites showed good maintaining of tensile properties.

CONCLUSIONS

It has been found, that interfacial reactions between reactive modifier and multilayer films waste components are effective in the compatibilization of investigated blends. Heterogeneous compatible recycled polymers show good properties, if degradation during processing is avoided, molecular weight is enlarged. Recycled multilayer films demonstrate good properties if wood fiber granulate and/or effective compatibilizers are added.

ACKNOWLEDGMENTS

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REFERENCES

1. *Japan Pat.* 05 105 786 (1993).
2. *British Pat.* 4 223 864 (1994).
3. *Japan Pat.* 05 105 731 (1993).
4. Jeziórska R.: *Macromol. Symp.* 2001, 169, 97.
5. Jeziórska R.: *Macromol. Symp.* 2001, 170, 21.
6. *U.S. Pat.* 2 569 428 (1951).
7. *U.S. Pat.* 3 419 520 (1968).
8. *Pol. Pat. Appl.* P-349 968 (2001).

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Table 3. Tensile properties of modified multilayer films waste (MFW2) with various wood fibre granulates concentration

Content of wood fibre, %	Tensile strength MPa		Elongation at break, %		Tensile modulus MPa	
	Before aging	After aging	Before aging	After aging	Before aging	After aging
0	20.1	22.4	447	305	445	450
10	14.6	15.7	305	161	720	720
20	14.5	12.6	59	46	1020	940
30	10.3	9.9	7	8.1	1380	1320

one hand, and improves modulus on the other. The strength and modulus were not much affected by aging, at 105°C for 7 days. But the situation was different in the case of elongation at break. Elongation decreased rapidly in all the cases, as the concentration of filler increased. At higher filler concentration (20, 30 wt. %), the composites showed a better maintaining of elongation compared to low (10 wt. %) filler concentration. However,