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New higher added value polymeric materials made of fabrics wastes containing poly(ethylene terephthalate)

RAPID COMMUNICATION

Summary — The post-production PET-containing fabrics wastes were recycled in order to produce new higher added value polymeric materials using reactive extrusion. These wastes were melt blended with polyamide 6 (PA6) and reactive modifier (M) elaborated in Industrial Chemistry Research Institute in Warsaw. The modifier acts as compatibilizer in the structurally heterogenous initial PA6/PET blends. PA6-*block*-M-*block*-PET copolymers formed during the reactive extrusion and located at the interface resulted in good interfacial adhesion, improved tensile properties and high impact strength of these blends.

Key words: PA6/PET blends, recycling, reactive extrusion, modification, structure, mechanical properties.

According to a recent forecast the consumption of poly(ethylene terephthalate) (PET) will still be rising by 15 %/year in the next future [1]. Major reason of this optimistic estimation is the on-going replacement of glass and aluminum containers by PET-based ones. Returnable and expendable PET bottles are widely used at present for the packaging of soft drinks, and even for beer. A further post-consumer PET source is derived from used carpets. Thus due to the increase of environmental issues, the recycling of PET bottles and carpets was the subject of several recent studies [2—5].

PET is also widely used in textile industry applications. It is worth noting that PET is in strong competition with polyamides as fibers in the fabrics production. Contrary to polyamide 6 (PA6) [6], PET can not be depolymerized. Accordingly, the recycling of PET-containing fabrics *via* reactive extrusion may have following targets: to produce PA/PET or pololefins/PET (PO/PET) blends and PET-fiber "reinforced" PA or PO-compounds. All of them should result in easy processable material with acceptable end use properties.

PET is very sensitive to thermal decomposition in presence of retained moisture and various contaminants [7, 8]. Such contaminants, *i.e.* cotton, viscose and adhesives generate acidic compounds at processing temperature, catalyzing hydrolytic ester bonds cleavage, leading to lower molecular weight and higher amount of carboxylic end groups.

Our intention was to convert the post-production PET-containing fabrics wastes into new higher added value polymeric materials using reactive extrusion. The use of extruders as continuous reactors for processes such as polymerization, polymer modification or compatibilization of polymer blends involves technologies that are gaining increasing popularity and compete with conventional operations with respect to efficiency and economics [9—12].

The aim of this study is to report on a new recycling method which may improve the properties and economics of recycling of post-production PET-containing fabrics wastes.

EXPERIMENTAL

Materials

PET-containing fabrics wastes (PET) were provided by Polontex, Częstochowa. Its melt flow rate (*MFR*), was 36 g/10 min [PN-EN ISO 1133:2002 (U), 270 °C, 1.2 kg].

The commercial polyamide 6 (PA6) was supplied by Nitrogen Works Tarnów SA, Poland. Its intrinsic viscosity was 1.13 dL/g [in phenol/1,2-dichlorobenzene, 50/50 (wt./wt.), 25 °C], the contents of carboxyl end groups was 34 meq/kg and *MFR* was 2.6 g/10 min (230 °C, 0.32 kg).

Modifier (M) with oxazoline functional groups was elaborated in Industrial Chemistry Research Institute.

Blend preparation

Before using PA6 was dried at temperature 85 °C under vacuum for 12 h. PET fabrics wastes were defibred. Figure 1 shows a view of PET-containing fabrics wastes before and after fibration.

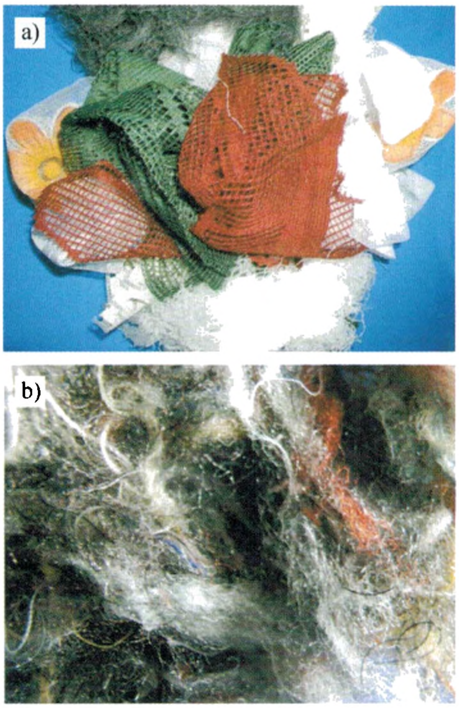

Fig. 1. PET-containing fabrics wastes: a) before fibration, b) after fibration

Investigations were carried out using Berstorff ZE-25x33D modular intermeshing co-rotating twin-screw extruder equipped with vacuum vent and of screw diameter of 25 mm and *L*/*D* of 33. Series of 60/40 PA6/PET (by weight) blends with different concentration of modifier were prepared. We expected the reaction involving functional groups of PA6, carboxyl groups of PET, and reactive groups of modifier. The thermal profile was 35/230/245/245/245/245/245/245/250/240 and the screw speed 80 rpm. The relatively high die temperature (250 °C) and screw speed allowed to work with a residence time of about 3 min, which should be sufficient for the coupling reactions occurrence to a reasonable extent [13, 14].

Injection molding process was performed using Arburg injection molder at temperature 3—5 °C higher than the melting point of the blends determined by differential calorimetry measurements.

Methods

Scanning electron microscopy (SEM) observations of the surfaces, produced by fracturing of the samples under liquid nitrogen and coating them with gold, were made using Jeol JSM-6100 microscope.

Solubility tests of the samples were carried out using a Soxhlet apparatus, in 85 wt. % formic acid at room temperature. The reaction product and polyamide 6 were dissolved in formic acid. After the time, when polyamide sample was entirely dissolved the solution were precipitated into seven volumes of methanol, filtered, washed and dried under vacuum at 75 °C for 48 h.

The tensile tests were performed according to PN-EN ISO 527-2:1998 at room temperature using an Instron 4505 tensile tester at a crosshead speed of 5 mm/min.

Charpy impact tests were performed according to PN-EN ISO 179-1:2002 (U) at room temperature.

Melt flow rate (*MFR*) was examined using plastometer type II RT, according to PN-EN ISO 1133:2002 (U) standard at 230 °C and 2.16 kg.

RESULTS AND DISCUSSION

Reactions between PA6 and PET in a molten state should result in an increase in molecular weight and viscosity. Melt flow rate measurements carried out for 60/40 PA6/PET blends in the presence of modifier are collected in Table 1. As expected, the fairly rapid decrease in *MFR* of PA6/PET blends after addition of 5 wt. % of modifier (M) is observed. This fact indicates substantial progress of interfacial reactions and molecular weight increase. Moreover, an increase in M concentration from 5 to 15 % decreases *MFR* further, which suggests that the reactive modifier promotes the compatibilization of the blend by enhancing the formation of PA6-*block*-M-*block*-PET copolymers.

Table 1. Effect of modifier on melt flow rate (*MFR*) of 60/40 PA6/PET blends

Modifier concentration, wt. %	*MFR*, g/10 min
0	13
5	2.9
10	1.4
15	0.3

Table 2. Solubility of the pure components and of the blends in formic acid (85 wt. %)

Blend composition (PA6/PET/M)	Solubility, wt. %
100/0/0	100
0/100/0	0
60/40/0	60
60/40/5	24
60/40/10	21
60/40/15	9

Data concerning the solubility of the resulting blends in formic acid can be used for qualitative evaluation of

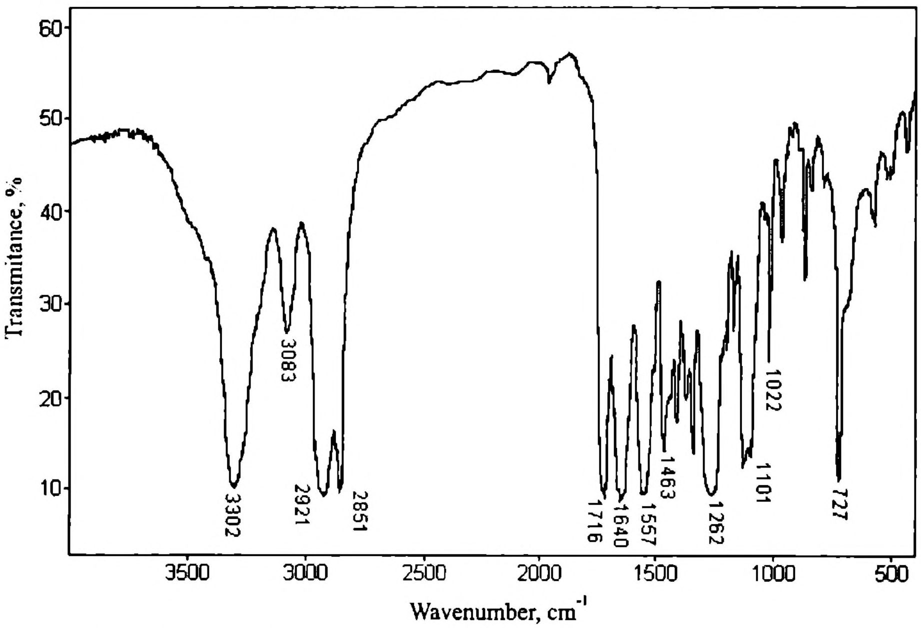

Fig. 2. FT-IR spectrum of formic acid-insoluble fraction of 60/40/15 PA6/PET/M blend

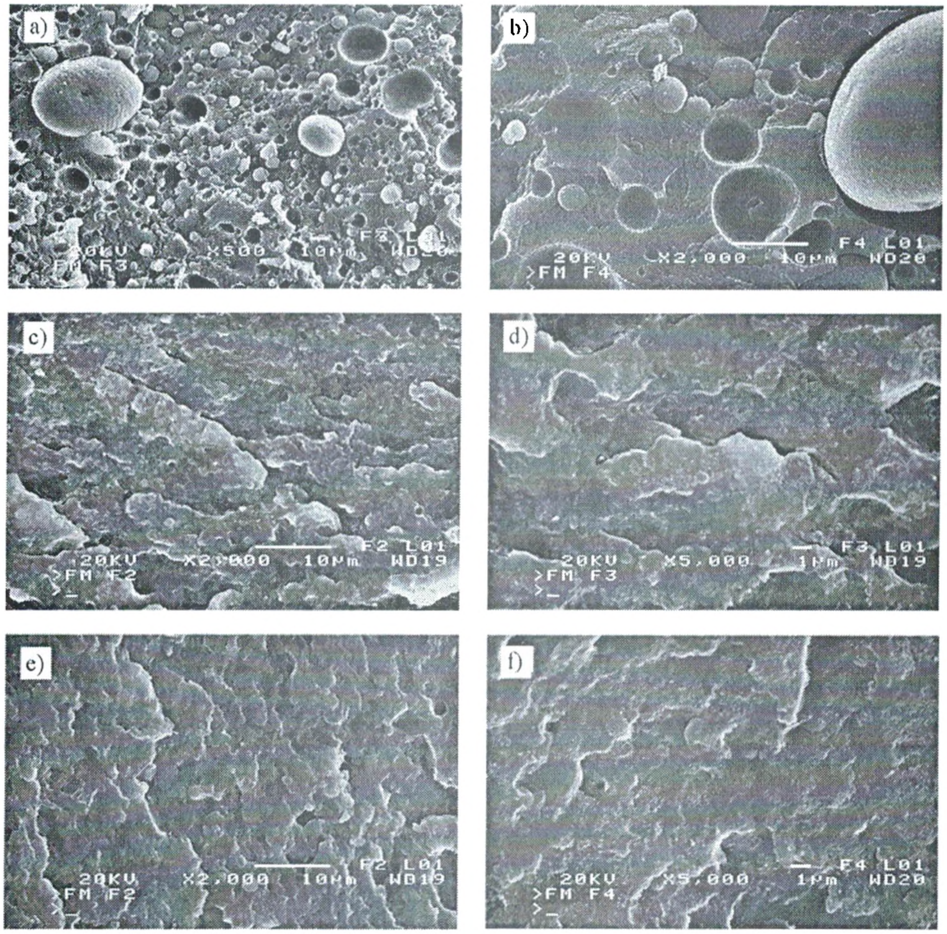

Fig. 3. Scanning electron micrographs of 60/40 PA6/PET blends as a function of modifier: a, b — 0 % of modifier, c, d — 5 % of modifier, e, f — 15 % of modifier

the final polymer composition. Solubility of the pure components and of the blends are collected in Table 2. Solubility of 60/40 PA6/PET blends in the presence of modifier decreases significantly, which confirms the formation of block copolymers. The resulting polymer system can be considered as PA6-*block*-M-*block*-PET copolymer with some content of homopolymers. It should be noted that the data of solubility tests do not provide the possibility to calculate exactly a composition of the resulting product.

Therefore the material was investigated by FT-IR spectroscopy. Figure 2 shows the spectrum of formic acid-insoluble fraction of 60/40/15 PA6/PET/M blend. The strong N-H stretching vibration at 3302 cm^{-1} and a sharp small peak at 3083 cm^{-1} indicate the presence of amide groups, characteristic for PA6. A broad small stretching vibration at 2921 cm^{-1} and a sharp small peak at 2851 cm^{-1} due to CH, CH_2 and CH_3 groups are observed. In addition pronounced peak at 1716 cm^{-1} related to C=O of the aromatic esters of intermolecular linkage is present [14, 15]. Broad small stretching vibrations at 1640 cm^{-1} and at 1557 cm^{-1} relate to I and II amide bands. The distortion stretching vibration at 1463 cm^{-1} due to CH group was also observed. However, the stretching vibration at 1101 cm^{-1} due to C-C and C-N groups and at 1022 cm^{-1} of IV amide band, and C-H absorption band of substituted ring at 727 cm^{-1} appeared. All this leads to the conclusion that the intermolecular reactions of functional groups of blend components take place during reactive processing.

Phase structure studies showed that interfacial reactions between reactive modifier, PA6 and PET are effective in the compatibilization of blends investigated. As examples, Fig. 3 presents SEM micrographs of the impact fractured surface of the samples as a function of concentration of modifier. The binary 60/40 PA6/PET blend with no modifier displays the morphology with a poor dispersion of PET droplets of various dimensions and no interfacial adhesion. The PA6/PET blends in the presence of modifier show heterogeneous compatible structure with very good adhesion between the phases. It is more reasonable to assume that a considerable number of modifier molecules react with the end groups of PA6 and the carboxyl terminal groups of PET to produce block copolymers located in the interface. The block copolymers formed during reactive processing, because of interchain exchange reactions, play a role of compatibilizers. SEM results are in accordance with conclusions from FT-IR spectra.

Table 3. Effect of modifier on tensile properties and Charpy impact strength of 60/40 PA/PET blends

Modifier concentration, wt. %	σ_B, MPa	ε_B, %	E_t, MPa	a_{cU}, kJ/m^2
0	16	0.6	1800	3
5	55	3.2	2500	37
10	53	3.9	2600	42
15	50	2.7	2680	37

PA6/PET blends, when chemically modified, showed improvement in both tensile and impact performance (Table 3). For example, the ultimate tensile strength (σ_B) and Charpy impact strength (a_{cU}) of 60/40 PA6/PET blend with 5 % of modifier increased from 16 to 55 MPa and from 3 to 37 kJ/m^2, respectively. At the same time, elongation at break (ε_B) increased from 0.6 to 3.2 % and tensile modulus (E_t) from 1800 to 2500 MPa. These features are typical for compatible blends. Moreover, an increase in the modifier concentration from 5 to 15 % improves the stiffness of the blends. The results of the mechanical characterization are in a good agreement with all other experimental data indicating that the modifier does actually help in the *in situ* formation of block copolymer.

CONCLUSIONS

In this work, a new recycling method of PET-containing fabrics wastes by reactive extrusion with PA6 has been described. Moreover, the possibility to use reactive modifier elaborated in the Industrial Chemistry Research Institute as a promoter of PA6-*block*-M-*block*-PET copolymers formation has been investigated. The morphological analysis, *MFR* characterization, the tensile behavior and, more clearly, the impact tests showed that coupling reactions between the modifier, PA6 and PET fabrics wastes were effective in the compatibilization of investigated blends. Phase morphology of the blends demonstrates heterogeneous, but compatible character according to SEM results, which was in accordance with FT-IR spectra. Solubility and FT-IR investigations evidenced chemical reactions which result in PA6-*block*-M-*block*-PET copolymers. The block copolymers formed during the reactive extrusion and located at the interface result in a good interfacial adhesion, improved tensile properties and high impact strength of these blends.

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