SECTION 14.
CHEMISTRY, CHEMICAL ENGINEERING AND BIOENGINEERING

Jerzy Korol
Doctor of Science, Associate Professor
Department of Material Engineering
Central Mining Institute, Republic of Poland

Aleksander Hejna
Doctor of Science, Assistant Professor
Department of Polymer Technology
Gdańsk University of Technology, Republic of Poland

PROCESSING, MECHANICAL AND THERMAL PROPERTIES OF RECYCLED LOW-DENSITY POLYETHYLENE STREAMS

Abstract. *The recycling of plastics is currently one of the most significant industrial challenges. Due to the enormous amounts of plastic wastes generated by various industry branches, it is essential to look for the potential methods of their utilization. Nevertheless, for the efficient application of recycled materials it is crucial to analyze their performance. Therefore, in presented paper we investigated the processing (melt flow index), as well as the mechanical (static tensile tests) and thermal (thermogravimetric analysis, differential scanning calorimetry) properties of four recycled low-density polyethylene streams obtained from the market. The impact of the impurities on the performance was analyzed.*

Introduction

For an efficient application of the recycled materials in industrial applications it is very important to assess their performance and determine the potential possible uses. Recycled materials often contain noticeable amounts of impurities, depending on the primary material composition as well as the applied treatment. They may noticeably influence the processing of plastics, affect their mechanical and thermal properties. Deterioration of the performance may be associated with the incompatibility of polymer matrix with the impurities, but also with its partial decomposition during primary use and recycling. Therefore, in presented paper we investigated the processing (melt flow index), as well as the mechanical (static tensile tests) and thermal (thermogravimetric analysis, differential scanning calorimetry) properties of four recycled low-density polyethylene streams obtained from the market. The impact of the impurities on the performance was analyzed.

Materials and methods

In the presented research work, four types of recycled low-density polyethylene were investigated. These samples were obtained from the local recycling company. Their appearance is presented in Fig. 1. It can be seen that only one of the analyzed streams was relatively pure. Others contained a noticeable amount of impurities. In the case of samples 1 and 4, which originated from the recycling of agricultural films, the impurities probably included soil residues. Sample 3, characterized by the noticeably white color was probably containing chalk, often used as an inactive filler, which is applied to reduce the materials' cost.

Fig. 1. **The appearance of analyzed recycled LDPE streams.**

Melt flow index of composites was determined at 190 °C, with a load of 2.16 kg, according to ISO 1133, using Mflow plastometer from Zwick.

The tensile strength, elongation at break, and elastic modulus were estimated following the PN-EN ISO 527 standard, using the Instron 4465 H 1937 tensile testing machine with an elongation head and an extensometer. Tensile tests were performed at a constant speed of 1 mm/min (for elastic modulus) and 50 mm/min (tensile strength and elongation at break). Five samples were analyzed for each specimen.

The thermal properties were determined by thermogravimetric analysis (TGA) with the temperature set between 30 °C and 900 °C at a heating rate of 10 °C/min under a nitrogen atmosphere using a TG 209 F1 Netzsch apparatus. The 10 mg ± 0.1 mg samples were placed in ceramic pans.

To determine the crystallization and melting temperatures, as well as the crystalline structure of analyzed composites, DSC analysis was applied. The 5 mg samples were placed in aluminum crucibles with pierced lids. They were heated from 20 to 250 °C with a heating rate of 10 °C/min and then cooled back to the initial temperature with a cooling rate of 10 °C/min. The heating/cooling cycle was performed twice to erase the polymers' thermal history during the first heating. The measurements were conducted using a Netzsch 204F1 Phoenix apparatus in an inert atmosphere of nitrogen. Oxidation induction time (OIT) of analyzed composites was determined by the differential scanning calorimetry analysis. The 5 mg samples were placed in aluminum crucibles with pierced lids. They were heated from 20 to 190 °C with a heating rate of 20 °C/min in nitrogen, then kept at 190 °C for 5 minutes in nitrogen, and then gas was switched to oxygen, and the time required for sample oxidation was measured. The measurements were conducted

using a Netzsch 204F1 Phoenix apparatus

Results and discussion

In Table 1 there are presented results of the melt flow analysis of recycled LDPE streams. Significant differences can be observed in the flow characteristics of the tested materials. This is most likely due to the impurities present in the material. As can be seen in Figure 1, samples 1 and 4 were characterized by a distinct grey color, suggesting mineral impurities, e.g. from soil, while sample 3 was characterized by a distinct white color, which could be caused by e.g. chalk added to the plastic. This is also indicated by higher values of density and viscosity for these streams in comparison with the cleanest sample 2.

Table 1

Results of the melt flow analysis of recycled LDPE streams

Sample	MFR, g/10 min	MVR, cm^3/10 min	Density at 190 °C, g/cm^3	Apparent viscosity, Pa·s
1	1.02	1.34	0.763	0.575
2	1.35	1.78	0.757	0.432
3	0.85	1.06	0.798	0.725
4	0.43	0.55	0.781	1.405

The purest material 2 had the highest melt flow rate value, and the MFR values indicate that this stream is most likely composed mostly of low density polyethylene LDPE [1]. Impurities or additives introduced during the manufacturing stage of the original material comprising streams 1, 3, and 4 resulted in a significant reduction in the melt flow index, as well as the enhancement of viscosity, which is typical of filler addition [2].

Table 2

Results of the tensile test of recycled LDPE streams

Sample	Tensile strength, MPa	Elongation at break, %	Young's modulus, MPa	Yield strength, MPa
1	16.8 ± 0.4	486 ± 31	153.4 ± 3.9	9.4 ± 0.1
2	22.0 ± 0.1	695 ± 1	286.0 ± 9.3	12.3 ± 0.2
3	13.7 ± 0.1	163 ± 12	150.4 ± 2.7	9.2 ± 0.1
4	16.6 ± 0.7	249 ± 40	183.5 ± 4.6	10.5 ± 0.1

It can be noticed that the best mechanical properties were characterized by sample 2, containing the lowest amount of impurities. Moreover, the very good strength properties may indicate the presence of linear low density polyethylene LLDPE, which is frequently present in waste streams of LDPE [3].

Other waste streams were characterized by significantly worse strength properties. This is particularly noticeable in stream 3. This confirms the assumption made in previous studies that this stream contains chalk used as a typical filler to lower the final price of the material without improving its properties.

Samples 1 and 4 showed similar tensile strength values, but the values of elongation at break and Young's modulus indicate some differences in the mechanism of matrix-filler interface interactions. These differences are most probably related to the size of the impurity particles and their chemical composition, especially their polarity, which influences, among others, the crystallinity of the polymeric phase.

The presented results of strength tests indicate that most probably the obtained waste streams do not contain polypropylene, which is characterized by higher strength values compared to polyethylene.

Table 3

Results of the TGA analysis of recycled LDPE streams

Sample	Temperature at weight loss, °C				Char residue at 900 °C, wt%
	2 wt%	5 wt%	10 wt%	50 wt%	
1	321.7	373.3	385.6	418.5	0.45
2	299.8	337.7	372.9	406.2	0.14
3	335.1	363.0	382.1	423.0	5.11
4	341.5	378.3	392.4	430.2	2.40

Table 3 presents the results of thermogravimetric analysis of analyzed samples. The results of the analysis confirm the values of the melt flow rate, which indicated the highest purity of material 2. The mass loss temperatures, especially the temperature of onset of thermal degradation assigned to 2 wt%. mass loss, indicate that the main component of this material is low density polyethylene LDPE. Streams 1, 3, and 4 showed increased thermal stability, which is most likely related to impurities present in the material. The improved thermal stability is suggested by the presence of mineral fillers, which have significantly higher stability than the lignocellulosic fillers commonly used in WPC composites. Another reason for the increase in thermal stability might be some content of plastics other than LDPE, including polypropylene PP, which has higher thermal stability and is often present to some extent in recycled polyethylene. However, this hypothesis was excluded by the tensile tests.

Thermogravimetric analysis also allows for the determination of the solid residue content after testing, which is synonymous with the content of material with a stability greater than 900 °C in the tested stream. The higher residue content for samples 1, 3 and 4, compared to sample 2, indicates the presence of mineral fillers, which may come from contaminants such as soil, or from the fillers used such as chalk (most likely used for sample 3). In the case of sample 3, despite probably the highest filler content (highest residual content after testing), the highest thermal stability is not observed. This is another argument suggesting that sample 3 most likely contains chalk, which is considered in plastics technology to be a filler to reduce the cost of the product rather than an active filler whose use is intended to impart or improve new properties to the material.

To confirm the conclusions of the thermogravimetric analysis, tests were performed using differential scanning calorimetry. Table 4 shows the results of the tests performed. Significant changes in the thermal properties of the studied waste streams were noted due to the presence of impurities. In the case of the cleanest sample 2 (it was found on the basis of previously conducted tests), the lowest value of the degree of crystallinity (X_c) and enthalpy of phase transformation, in this case melting (ΔH_m), can be observed. In addition, the width of the peak at half its height ($W_{1/2}$), is also the smallest, suggesting the most homogeneous composition. The presence of impurities in the other samples significantly affects their thermal properties. The peak widths for samples 1 and 4 are significantly higher, indicating the presence of a significant amount of impurities and changes in the structure of the polyethylene matrix. A significant increase in crystallinity was observed, which was most likely due to the stimulation of nucleation by particulate matter. This process has been repeatedly reported in the literature and is also observed for sample number 3, which most likely contains chalk. For this sample, however, no significant peak broadening was observed and a decrease in melting point was observed, which may be related to the homogeneity of the chalk particles introduced into the virgin material, as opposed to the significant size and shape scatter of random mineral particles which are probably contaminants from soil and agricultural industry [4].

Table 4

Results of the DSC analysis of recycled LDPE streams

Sample	$T_{melting}$, °C	$W_{1/2}$, °C	H, J/g	X_c, %	OIT, min
1	123.51	19.8	-81.8	27.85	3.12
2	124.37	14.5	-63.9	21.75	5.27
3	115.80	14.7	-82.7	28.17	2.68
4	126.79	20.1	-94.9	32.34	5.45

It can be seen that the values of oxidation induction time were differing between analyzed materials. Such an effect was associated with the impurities content, which may accelerate the thermooxidative decomposition of polyethylene. On the other hand, for sample 4, the enhancement compared to the almost pure PE was noted. Nevertheless, for samples 1, 2, and 4, obtained values of oxidation induction times, exceeded 3 minutes, which should guarantee the possibility of effective processing of the studied materials without their thermo-oxidative degradation.

The analysis of the obtained results indicates the possibility of using the material 6 as an outer layer of the multilayer film, whose task will be to protect the core of the material. In the case of the inner layer, it is possible to use materials 5, 7 and 8, and the content of impurities present in them will not adversely affect the properties of the multilayer film.

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