

Dominik Grzesiczak, Przemysław Postawa
Częstochowa University of Technology, Department of Polymer Processing
 19c Armii Krajowej St., 42-200 Częstochowa grzesiczak@ipp.pcz.pl

CHARACTERISTICS OF STRENGTH AND STRUCTURE OF PE - HD COMPOSITE WITH ADDITION OF PE – HD WASTE

Summary

This article presents the possibilities of using the waste material obtained from the vehicle fuel tank (high density polyethylene PE- HD) as an addition to products. The waste material is added to the original polymer in an amount of 10% , 20% and 30%. The following tests have been performed during the research: differential scanning calorimetry DSC, static tensile test, hardness degree determined by pressing a steel ball, and also optical microscopy of obtained breakthroughs in samples made of liquid nitrogen. In addition, there has also been performed an analysis of mixture of original polyethylene that contains 10%, 20 % and 30 % of HD - PE polymer, which has been turned back for recycling from the production line. The aim of the research is to determine the recycling possibilities of polymeric materials obtained from the waste that emerged on the production line and in the fuel tanks of vehicles which were withdrawn from use as materials that during the utilization process have been subjected to a long-term connection with petroleum. Description of the mechanical and structural properties is an attempt to answer the question concerning usefulness of polymeric materials after utilization.

Keywords

recycling, polyolefin processing, automotive components, HDPE processing, types of recycling, recycling of automotive components

Introduction

Dynamic development of polymeric materials and a wide range of their physical properties explain a rapid increase in their production. In the late 80-s of the last century, world production of polymers was equal to steel production. However, since 1990 the amount of polymers produced has exceeded the produced amount of steel. Polymers have won their popularity in the market due to their wide range of both physical and chemical properties, owing to a huge number of variations as well as numerous possibilities of their modification [1-6].

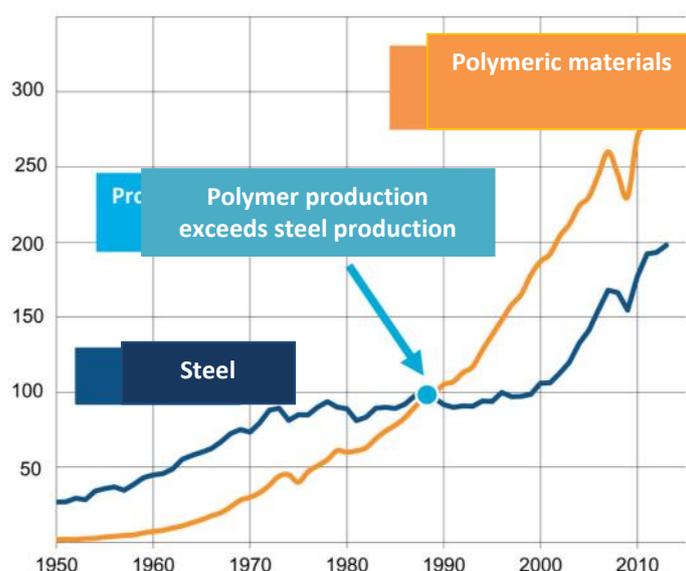


Fig. 1. The global increase in the production of polymers and steel since 1950.

Source: [3]

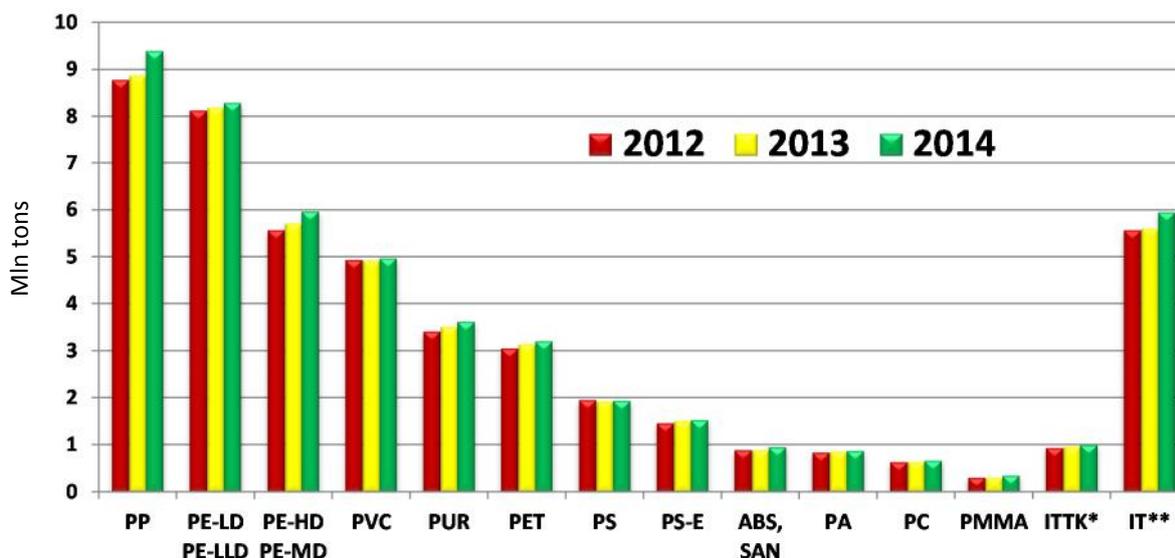


Fig. 2. Growth of demand for different types of polymers, where: *Other Thermoplastic Construction Polymers, **Other Polymers.
Source: [7]

But there is a problem concerning the waste management after production. Nowadays, the most popular solution is storing the waste materials, but the current EU Directives impose a ban on storing the waste materials in landfills, which is tantamount to their re-processing. An alternative to the defaulting on landfills polymers is recycling, which is a privileged recovery system because of the origin of molecular compounds from non-renewable raw materials.

More companies are pursuing a policy of re-use of waste products by shredded and recycling them to the production line, as mentioned by Bociąga E., Magaczewski P. in research work [8].

There are several ways to reuse the waste of polymeric materials:

- material recycling – is about grinding the polymer and then molding it by means of injection or extrusion. As a result, we get a ready-to-use product.
- chemical recycling - is about obtaining simple compounds (monomers) in order to produce some other chemicals. The result of this type of recycling is a substance that has low molecular weight.
- energy recycling – is about using the waste material as fuel in the combustion process in order to produce thermal energy.
- product recycling – is about reusing the polymeric material as a spare part.
- organic recycling – is about processing of the waste of polymers, which are not generated from petroleum. As a result, organic matter is obtained as well as water and carbon dioxide or methane, depending on the method of cultivation [8-18].

Material, research methodology and sample preparation

The aim of the research was to analyze thermal and strength properties of high density polyethylene with the addition of PE-HD waste from the production line and ground fuel tank (10, 20 and 30%). The normalized testing samples (type A1) were prepared using an injection molding machine Krauss Maffei KM 65/160/ C1. In the second step the testing samples (type A1) and a fuel tank were shredded together using a low-speed grinder type Shini SG24 series. The next step was to prepare mixtures containing the waste polymer in quantities of 10, 20 and 30%. And as a result, seven samples for the analysis were obtained.

Symbols applied for the research:

HDPE – reference sample obtained after the first injection,

HDPE + x% RO – a batch of samples with the addition of the fuel tank grinding,

HDPE + x% R L – a batch of samples with the addition of the grinding, which was turned back for recycling from the production line.

x – amount of the added material in the mixture.

Injection parameters during the preparation of test samples:

- Injection pressure: 120 MPa,
- Injection speed: 50 mm/s,
- Holding pressure: 60 MPa,
- Injection time: 1,4s,
- Holding time: 18s,
- Cooling time: 15s,
- Mold temperature: 50°C

The temperatures of individual heating zones in the plasticizing system are summarized in Table 2.

Tab. 2. The temperature of heating zones in the plasticizing system

Number of a heating zone	1	2	3	4
Temperature [°C]	215	205	195	185

Source: Author's

Following injection the sample were conditioning in temperature of 23 Celsius degrees by 48 hours. Strength properties were determined by conducting a static tensile test using a Hegewald&Peschke universal testing machine. There were 5 attempts out for each series. The samples were stretched at a speed of 50 mm/min, which made it possible to determine the maximum tension and deformation of the tested samples. The research were performed according to standard PN-EN ISO 527:1998. The strength analysis was performed using a durometer with a spherical cavity (steel ball). The obtained value of the cavity was 132N. The research were performed according to standard PN-EN ISO 2039-1:2004. Due to the heterogeneity of the tested material and to the size of cavity, the Shore D method was omitted.

Thermal analysis was performed on the basis of differential scanning calorimetry using a DSC Phox 200PC Netzsch machine. The test was carried out in a temperature range between 50 and 200°C at a speed of 10 K/min. The results are presented in the form of DSC thermograms and a table that contains characteristic values marked on the cooling curves. The structure of breakthroughs achieved by stretching the samples cooled in liquid nitrogen was also analyzed. The main purpose of using nitrogen was to get a brittle breakthrough. Breaking the samples was omitted due to the complex tension state, in which the upper part of the sample was stretched and the lower one was compressed.

Results of the research and comments

Fig. 3 and 4 show the curves recorded during the static stretching attempt (using the samples containing the grinding from the tank and from the production line). The color black indicates the tensile curves of high density polyethylene with no filler. The color green is assigned to the samples containing 10% of polymer waste; yellow 20%; red 30%. The tension and deformation values are given in the table 3.

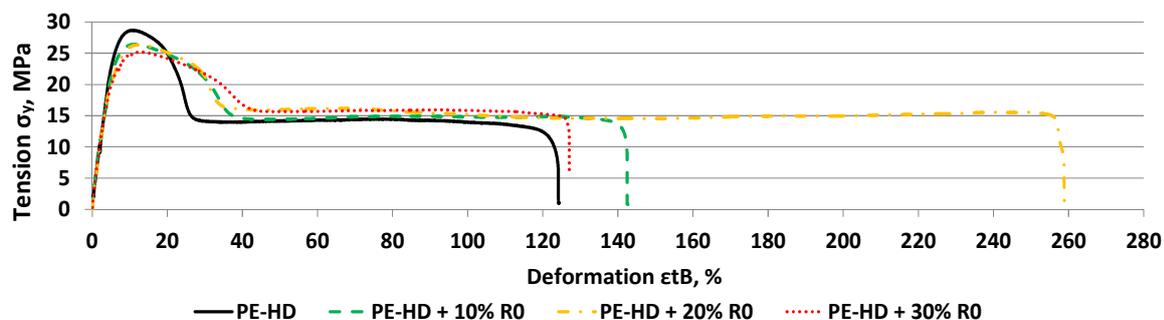


Fig. 3. Tensile curves of high density polyethylene and its mixtures with the addition of the grinding from the tank.

Source: Author's

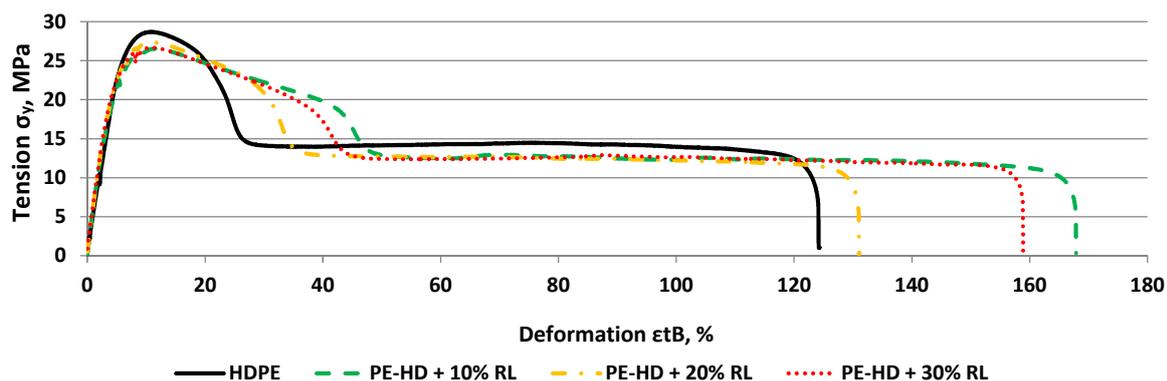


Fig. 4. Tensile curves of high density polyethylene and its mixtures with addition of the grinding from the production line.

Source: Author's

Tab. 3. The PE-HD deformation and tension values, as well as mixtures containing the PE-HD waste with standard deviations.

Symbol	Tension σ_y , MPa	Standard deviations	Deformation ϵ_{tB} , %	Standard deviations
PE-HD	28.678	0.825	124.01	12.669
PE-HD + 10% R0	26.443	0.243	142.45	10.820
PE-HD + 20% R0	26.364	0.153	258.83	13.832
PE-HD + 30% R0	25.195	0.487	127.02	8.165
PE-HD + 10% RL	26.526	0.437	167.66	7.586
PE-HD + 20% RL	27.334	0.202	130.77	8.228
PE-HD + 30% RL	27.606	1.417	154.49	13.024

Source: Author's

Analyzing the results of stretching, we can observe that the polyethylene sample, which does not contain any additives, has the largest tension value. By gradually adding 10% of the grinding originating from a fuel tank we can observe a decrease of tension. However, when adding the grinding from the production line, we can observe an opposite tendency, which is an increase of tension. Differences between these two values can be caused by the compounds containing fuel, due to which we observe a decrease of tension. While analyzing the RL batch, there has been recorded a growing trend caused by an increase of the amount of filler in the form of thermally degraded material. Deformation values for the R0 batch, on the contrary, have a decreasing trend. However, in both batches we can observe that the deformation values of the samples PE-HD + R0 and 30% HDPE + 30% RL do not correlate with the previous observations. This may be caused by poor homogenization of both polymers since they have a very diverse fractionation. As a result, a larger portion of the waste material is plasticized slower than a smaller one. Figure 5 shows the change in hardness values of individual samples.

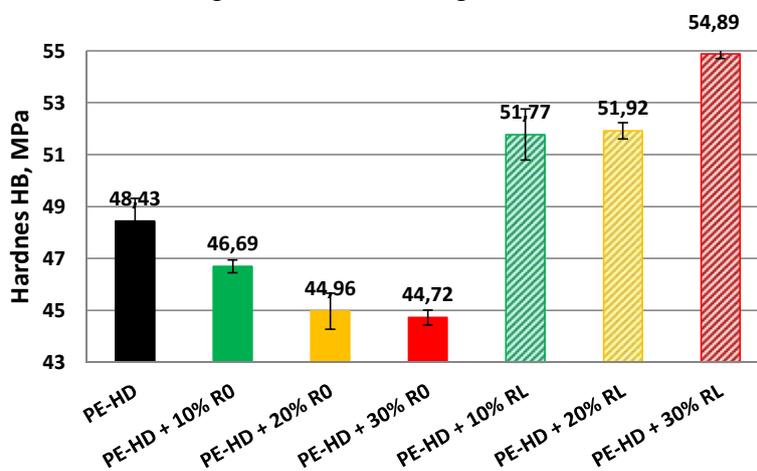


Fig. 5. Hardness values obtained by pressing the steel ball.

Source: Author's

Basing on the research we can see that an increased amount of the HDPE waste causes an increase in hardness of the obtained PE-HD mixture. In case of the RO batch, an increase of the HDPE waste amount reduces the hardness. On the contrary, the RL batch shows the opposite behavior when the PE-HD waste is added.

Figures 6 and 7 show thermographic curves of the tested batches of samples of the polyethylene and HDPE mixture (HDPE was not subjected to any modifications). The results obtained on the basis of thermograms are summarized below in form of a table (tab. 4).

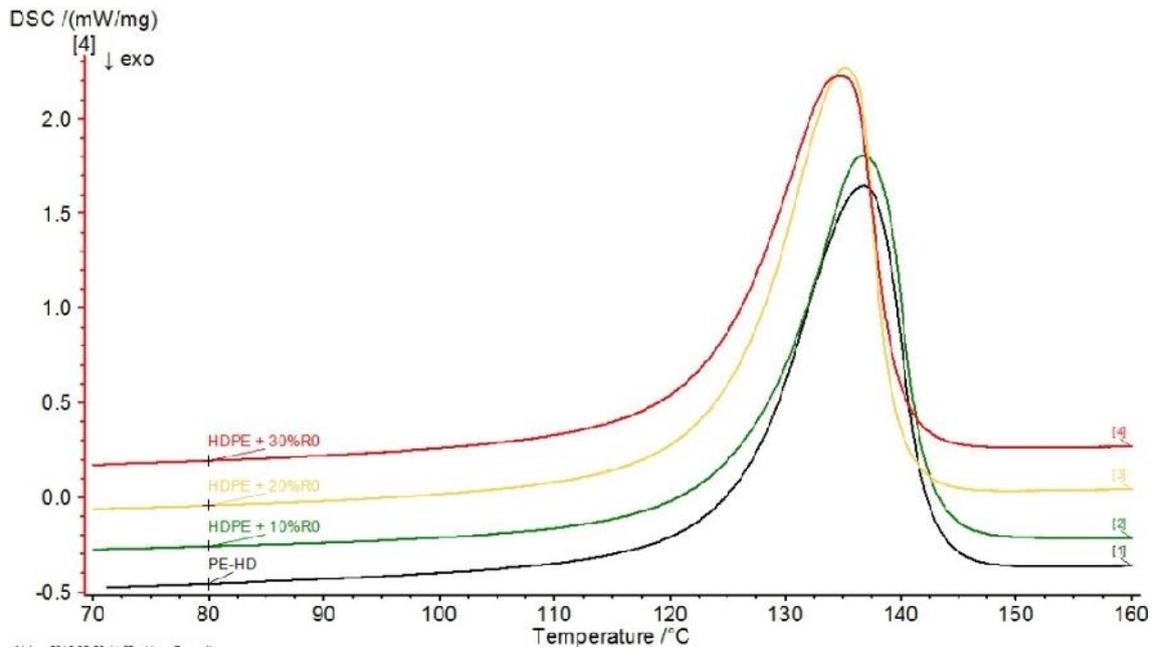


Fig. 6. DSC thermograms of the samples containing the grinding originating from the fuel tank with respect to the unmodified PE-HD.

Source: Author's

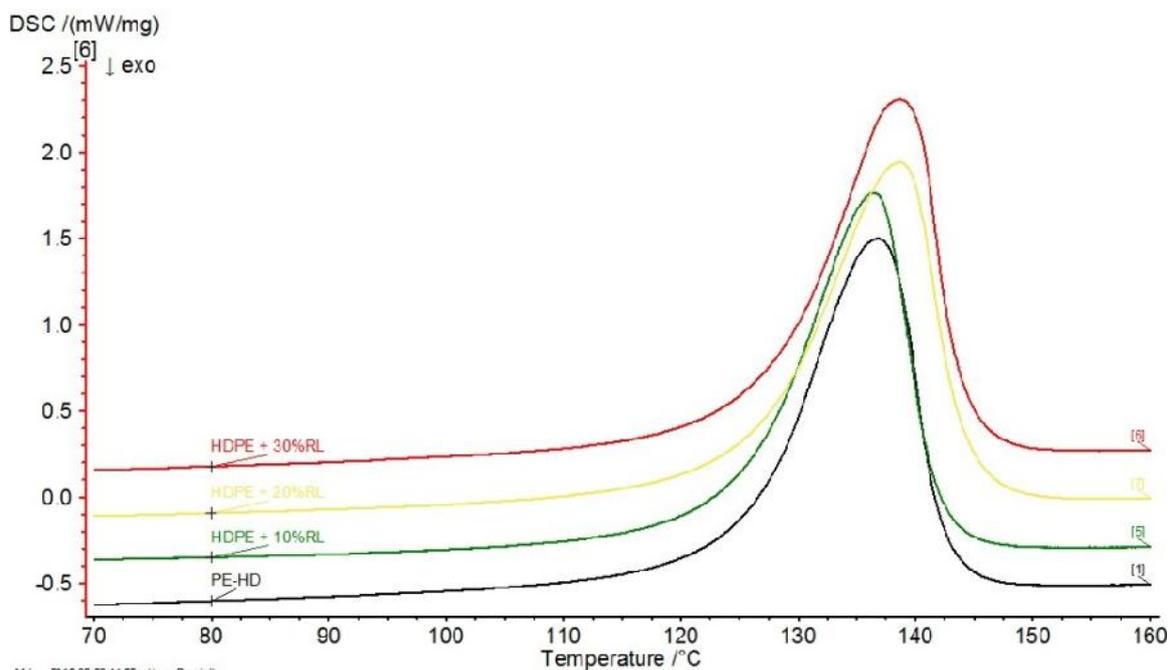


Fig. 7. DSC thermograms of the samples containing the grinding originating from the production line with respect to the unmodified PE-HD.

Source: Author's

Tab. 4. Results of the analysis using the DSC method

Symbol	Melting enthalpy [J/g]	The degree of crystallinity [%]	Maximum m.p. [°C]	Melting range of the crystalline phase [°C]
HDPE	146.9	50.13	136.8	125.8 – 142.3
HDPE +10% R0	144.9	49.45	136.7	126.7 – 142.1
HDPE +20% R0	150.1	51.24	135.2	124.9 – 139.3
HDPE +30% R0	144.5	49.32	134.7	123.6 – 139.9
HDPE +10% RL	145.6	49.68	136.4	125.3 – 141.9
HDPE +20% RL	150.8	51.46	138.5	127.3 – 143.8
HDPE +30% RL	147.5	50.34	138.6	126.5 – 143.9

Source: Author's

Analyzing the results obtained on the basis of differential scanning calorimetry, we may notice only a slight difference between the values of the melting enthalpy, with the value very similar to the corresponding polyethylene without additives. A similar correlation can be stated for the degree of crystallinity. Figure 8 shows the structure of the brittle breakthroughs in the sample of high density polyethylene. Figure 9 shows the structure of breakthroughs in the samples, to which the PE-HD waste from the tank grinding was added in an amount of 10, 20 and 30%. The structure of breakthroughs in the samples containing polymers from the production line is shown in Figure 10.

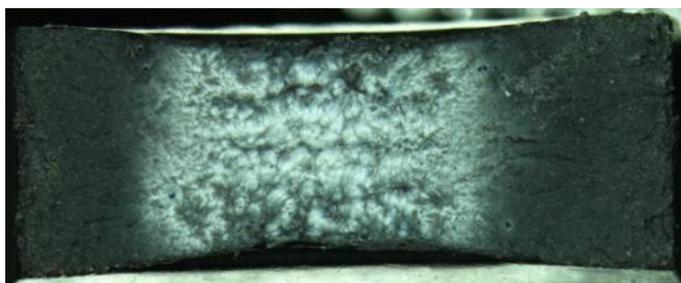


Fig. 8. The structure of breakthroughs of the original high-density polyethylene
Source: Author's

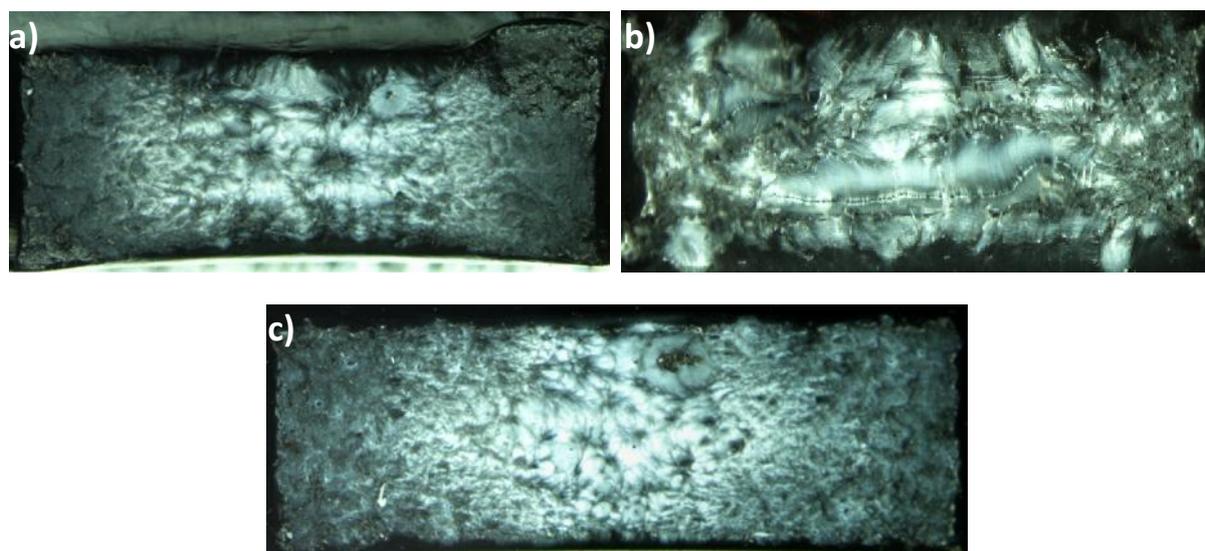


Fig. 9. The structure of breakthroughs of high density polyethylene with the addition of grinding originating from the fuel tank in an amount of: a) 10% b) 20% c) 30%.

Source: Author's

While analyzing these images that show the samples structure we can observe a characteristic bright area which is the core of the sample. Adding the waste material has led to an extension of the mentioned area. Observing the brittle breakthroughs of the samples from the fuel tank, we can notice areas, in which the fragments that have not fully melted.

In the figure 9b) we can see further delamination, or loss of consistency (the crack is formed along the section of the sample located at the bottom of the breakthrough). It should also be mentioned that there are some discontinuities caused by bad homogenization of the base HDPE polymer, which becomes the waste material before filling it back into the machine.

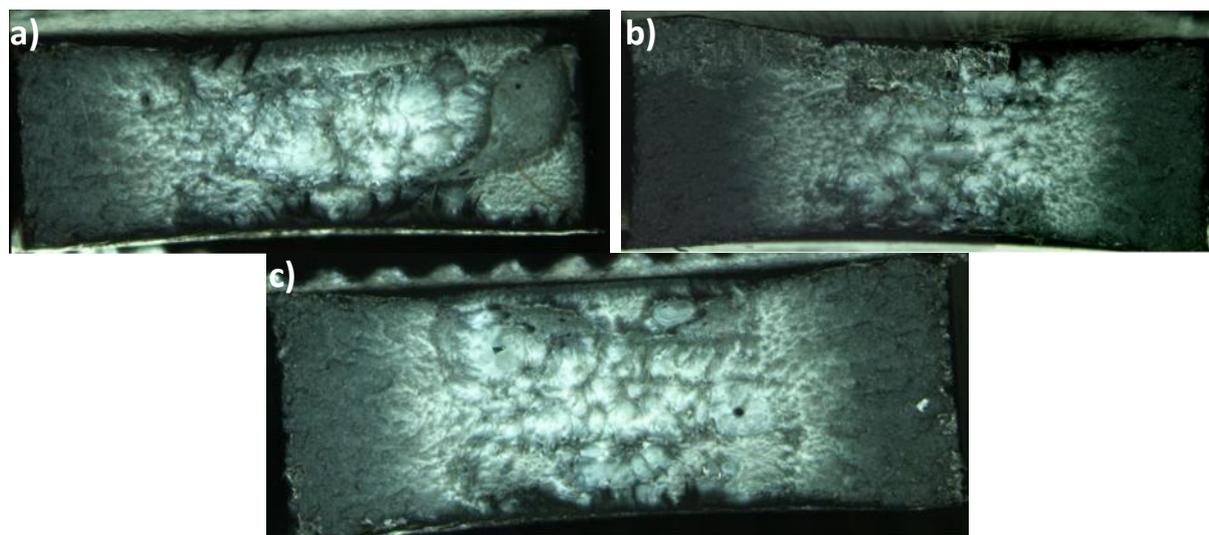


Fig. 9. The structure of breakthroughs of high density polyethylene originating from the production line in an amount of: a) 10% b) 20% c) 30%.

Source: Author's

For the samples containing ground HDPE recycled during the production stage, we can notice the ordered structure containing some particles which were homogenized in a similar way as the base material.

Summary

The research shows that the increase of the amount of additive in the form of ground fuel tank causes a decrease of tension. The waste originating from the production line causes an increase in tension, but the value is still smaller than in case of the base polyethylene. For both batches, we can observe a larger deformation than in case of HDPE, we can see the values increase in the RL batch, and the values decrease in the R0 batch.

Measurement of hardness using a device with a spherical indenter indicates a greater hardness of the samples from the RL batch, which is growing together with increasing of the amount of the waste material added. It should be added that the hardness of the reference sample is lower comparing to the one of this batch. But it is larger than in the R0 batch, where the value decreases while the amount of the waste material increases.

In the case of thermal analysis using the DSC method, there were no significant changes in the melting enthalpy and in the degree of crystallinity, which could only slightly change when there was a value close to the one assigned for a base polymer.

Analysis of the structure of brittle breakthroughs points on the problem of poor homogenization between the particles of the mixture particularly in the R0 batch, and also it points out that the polymer particles might not be plasticized well enough. In addition, a part of the image of the sample containing 20% of filler from the tank illustrates a crack along the cut indicating delamination of the material.

When increasing the amount of the waste material, which has a diverse fractionation, we must carefully adjust the processing conditions associated with its plasticization. This indicates the need to use regranulates instead of grind for the purpose of stability and repeatability of the physical properties of moldings.

References

- [1] K. Borowski, Przemysł tworzyw sztucznych – materiałów XXI wieku, *Mechanik* 4 (2015) 278-282.
- [2] A. Mroziński, Koło Naukowe TOPGran, Problemy recyklingu tworzyw polimerowych, *Inż. Ap. Chem.* 49, 5, (2010), 89-90.
- [3] M. Czop, B. Kozielska, Właściwości fizykochemiczne mieszanki odpadów z grupy poliolefin. *Archives of Waste Management and Environmental Protection* 1/12 (2010) 47-56.
- [4] R. Jeziorska, B. Świerż-Motysia, A. Szadkowska, Modyfikatory do recyklingu tworzyw polimerowych: otrzymywanie, właściwości i zastosowanie. *Polimery* 10 (2010) 748-756.
- [5] Kotiba H., Mosab K., Fawaz D., Recycling of waste from polymer materials: An overview of the recent works. *Polymer Degradation and Stability* 98, 2801-2812.
- [6] Stachurek I., Problemy z biodegradacją tworzyw sztucznych w środowisku. *Zeszyty Naukowe Wyższej Szkoły Zarządzania Ochroną Pracy w Katowicach* 2012, Nr 1, 74-108.
- [7] Plastics Europe, Tworzywa sztuczne - Fakty 2015. Analiza produkcji, zapotrzebowania oraz odzysku tworzyw sztucznych w Europie. http://www.plasticseurope.org/documents/document/20151123112635-fakty_o_tworzywach_2015_pl.pdf
- [8] Bociąga E., Magaczewski P., Badania wyprasek z obszarami łączenia strumieni tworzywa z tworzyw pierwotnych i wtórnych. *Recykling i odzysk materiałów polimerowych Nauka-Przemysł*. Warszawa 2007, s. 33-36.
- [9] Florjańczyk Z., Dębowski M., Chwojnowska E., Łokaj K., Ostrowska J., Polimery syntetyczne i naturalne w nowoczesnych materiałach polimerowych. *Polimery* 2009, Nr 10, s. 611-625
- [10] Leszczyński W., Materiały opakowaniowe z polimerów biodegradowalnych, *Przemysł Spożywczy*, 2001, T.55, nr 8, s. 81-84.
- [11] Kowalska E., Choroś M., Kuczyńska L., Wielgosz Z., Recykling odpadów dywanów i wykładzin dywanowych. *Polimery*, Nr 9, 2006, s. 671-679.
- [12] Alzereca M., Paris M., Boyron O., Orditz D., Lourab G., Correc O., Mechanical properties and molecular structures of virgin and recycled HDPE polymers used in gravity sewer systems. *Polymer Testing*, 2015, Nr 46, s. 1-8.
- [13] Gutiérrez O., Palza O., Effect of carbon nanotubes on thermal pyrolysis of high density polyethylene and polypropylene. *Polymer Degradation and Stability* 2015, Nr 120, s. 122-134.
- [14] Chamier-Gliszczyński, N., *Środowiskowe aspekty transportu*. Recykling w cyklu życia pojazdów. *Inżynieria i Aparatura Chemiczna* 2010, Nr 5, s. 26-27.
- [15] Żakowska H., System recyklingu odpadów polimerowych – wybrane problemy prawno-organizacyjne i ekonomiczne w Polsce. *Polimery* 2012, Nr 9, s. 613-619.
- [16] Błędzki K. A., Królikowski W., Recykling materiałów polimerowych z dywanowych wykładzin podłogowych. *Polimery*, Nr 1, s. 29-35.
- [17] Bociąga E., Magaczewski P., Badanie zmian wybranych właściwości tworzywa ABS po wielokrotnym przetwórstwie. *Praca zbiorowa pt. Materiały polimerowe i ich przetwórstwo*. Wydawnictwo Politechniki Częstochowskiej, Częstochowa 2004, s. 381-387.
- [18] Kijeński J., Polaczek J., Recykling tworzyw sztucznych według koncepcji zielonej chemii. *Polimery* 2004, Nr 10, s. 669-676.