Circular economy of barrier packaging produced in co-injection molding technology

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Abstract: The paper presents the study of mechanical recycling of three-layer PP/EVOH/PP packaging containers made by the co-injection molding process. It is in alignment with European Circular Economy guidelines. The main objective was to evaluate the recyclability of these packages and their reuse as a secondary material. Thin wall packaging by special cutting and grinding methods were disintegrated, and recorded cutting force allowed the determination of energy per single cut. During these processes, delamination between PP and EVOH layers was observed. The recyclate r(PP/EVOH) was used to produce samples in the standard injection molding process. The similar samples were prepared from recycled virgin PP using the same technology. The paper presents the results of the mechanical properties of samples manufactured from recyclate r(PP/EVOH) and compares them with the properties of samples obtained from recycled polypropylene (rPP). It was observed, that the content EVOH in the PP matrix does not significantly affect the mechanical properties of r(PP/EVOH) samples. It was also found that r(PP/EVOH) blends are characterized by favorable apparent viscosity and MFI and can be a valuable raw material for reuse.

1 Introduction

One of the types of injection molding is the co-injection molding process (COI) which involves producing at least three-layer applications. A dedicated material supply system ending with a specially designed nozzle allows the introduction of an additional material into the core layer of the plastic part's wall for a specific purpose (Fig. 1) [1, 2]. These can include protective functions in the form of a barrier coating (EVOH, EVA, PVDC, OPET, PA), as well as layers conducting electricity or heat (graphene) [3-7]. Giving products additional functional functions is consistent with one of the observed trends in the production of polymer products [8]. Due to the directions set by the European Commission within the Circular Economy CE, regranulates obtained from polymer packaging PCR (Post-Consumer Recycled materials) may also be used as the core layer [7].

Considering the responsible management of material resources in a closed-loop system (Circular Economy), the high propensity of thermoplastic materials for secondary utilization in the form of regranulates, and the unique characteristics of plastic packaging with a protective layer (multi-layer applications), there is a need for a better understanding of the co-injection molding process. This understanding is vital not only from the perspective of part quality but also their susceptibility to mechanical recycling processes for their secondary use in manufacturing processes [7]. The choice of material combinations depends on the performance characteristics of the barrier layer (passive or active). In packaging, the outer (skin) and inner layers are often composed of polypropylene or polyethylene, while the

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middle barrier layer is typically made of an ethylene-vinyl alcohol copolymer (EVOH) [4, 5, 7]. This material has a high barrier coefficient, significantly limiting the access of atmospheric oxygen, thereby delaying, or preventing oxidation processes of food products inside the packaging (e.g., milk, soft fruit packaging, coffee capsules). Achieving adhesion at the contact surfaces requires the skin and core layers to exhibit mutual thermodynamic compatibility or be processed with high injection speed for secondary molding [8, 9].

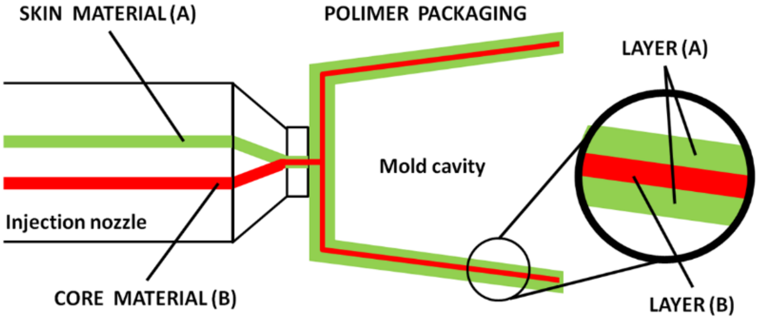

Fig. 1. Principle of co-injection molding technology (COI).

The aim of this study is to determine the susceptibility of three-layer plastic application to mechanical recycling processes and their reuse as full-value secondary material. This innovative approach to the circulation of polymeric materials in a closed-loop system aligns with the principles of the Circular Economy (CE). Thanks to this, the foundations will be developed for the production of new plastic parts from mass thermoplastic and biodegradable plastics with recyclate from PCR waste (post-consumer recycled plastics) located in the core layer. Preliminary studies on cutting and grinding PP/EVOH/PP packaging produced using COI technology were conducted, and samples from these recyclates were produced using the standard injection molding method. The secondary samples obtained were subjected to selected mechanical tests and the results were compared with the properties of samples injected from rPP regranulates.

2 Research Methodology

The object of the research was barrier triple-layer PP/EVOH/PP containers with an average total wall thickness of 1 mm, where the barrier layer of EVOH material was approximately 0,1 mm, constituting 10% of the mass. (Fig. 2).

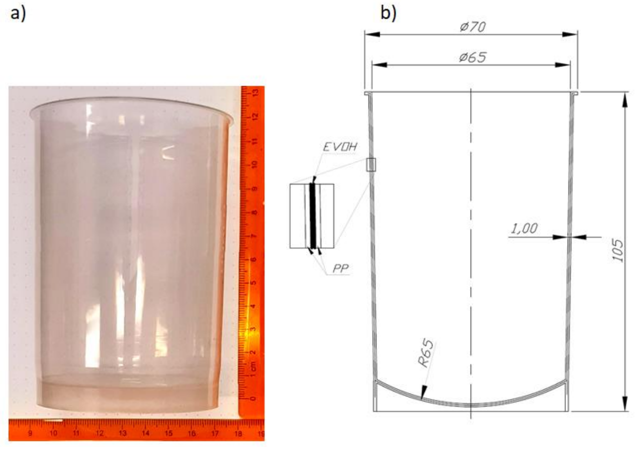

Fig. 2. Geometric features of the research object: three-layer PP/EVOH packaging container.

As the skin material, polypropylene Moplen RP390T (LyndellBasell, Switzerland) was used, while the special (barrier) layer was made from an EVOH copolymer commercially known as EVAL XEP-540 (Kuraray, Japan). The three-layer packaging containers were produced at the research and development center of Milacron LLC (Rowley, MA USA). An original, one-cavity injection mold with a special hot runner system and a 300T injection molding machine (Netstal, Switzerland) equipped with an E-Multi auxiliary injection unit (Mold-Masters, Canada) were used. Thanks to this unique configuration of the research station, it was possible to consistently produce PP/EVOH/PP three-layer packages with a total mass of 5 kg which were subjected to the processes of mechanical recycling in accordance with the diagram shown in Fig. 3.

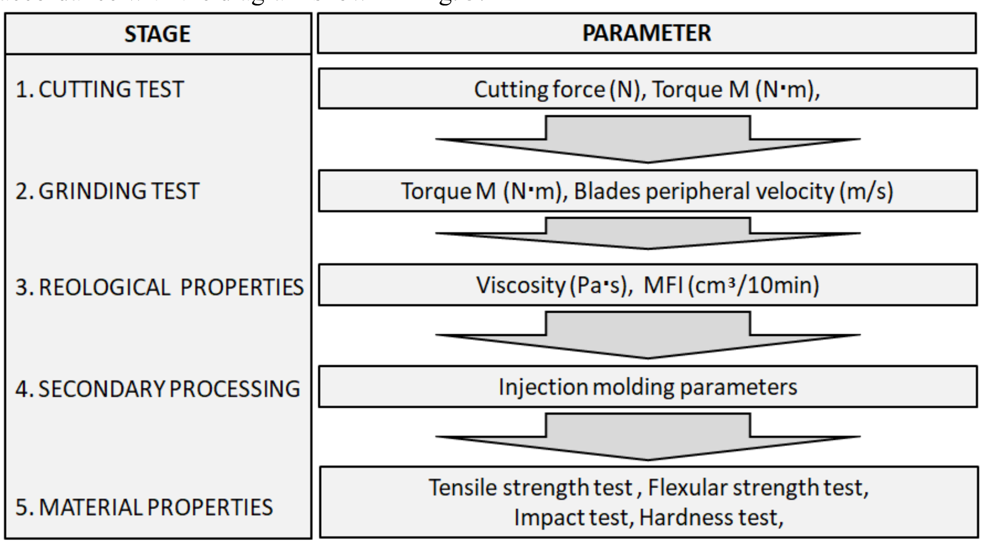

Fig. 3. Stages of research on the mechanical recycling process of three-layer PP/EVOH/PP samples for producing secondary material.

The procedure for cutting and grinding was recorded at an original research station designed for studying both processes at the Department of Manufacturing Techniques, Bydgoszcz University of Science and Technology. The characteristics of this research station and the adopted research methodology have been described in earlier literature [10, 11]. The cutting tests were carried out using moving and stationary knives with 60 degrees blades and an inclination angle of the straight cutting edges of the cooperating knives at $2\lambda = 6$ degrees relative to the rotor's axis of rotation. In the grinding investigations, 4 moving and 6 stationary knives were installed, all with straight cutting edges, and the gap between the knives was estimated to be 0,1 mm. The peripheral velocity of the cutting edges was 9 m/s, and the rotor's angular speed was 860 rpm. Sieves with an average hole size of 9 mm were used to close the working chamber of the mill in the tests.

The obtained PP/EVOH recyclate was directly fed into the hopper of the Engel e-victory 110 injection molding machine and standard injection molding samples were produced, in accordance with PN-EN 527-1. A four-cavity mold, used for producing standardized test specimens, was employed for forming secondary moldings from PE/EVOH recyclates (Fig. 3). In mold cavities, a pressure sensors (type: 6002B) and a temperature sensors (type: 4008B) were installed, which were connected to an eDAQ signal converter (type: 8102) (Fig. 4).

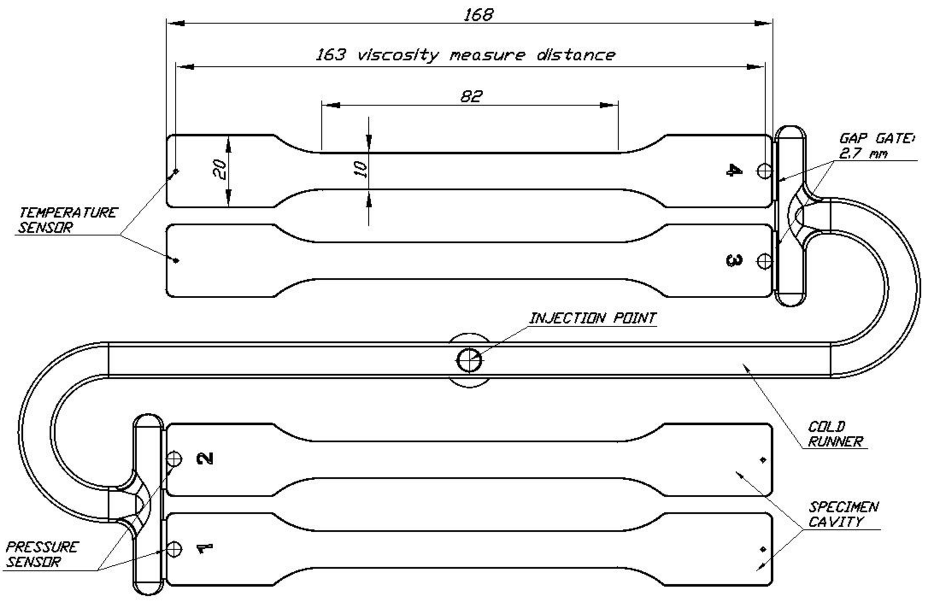

Fig. 4. Test mold cavities geometry with location of temperature and pressure sensors.

The processed signals from the pressure and temperature sensors in the injection mold were the basis for determining the in-line apparent viscosity of the PE/EVOH blend, according to the methodology described in articles [12, 13]. The Priamus system (Switzerland) was used for viscosity measurements. Rheological studies were complemented by determining the melt flow rate using a plastometer Aflow (Zwick&Roell, Germany), in accordance with the methodology consistent with PN-EN ISO 1133 for polypropylene PP.

The obtained secondary rPP and r(PP/EVOH) samples underwent multi-criteria evaluation in line with the research program outlined in Table 1. Tests were performed in accordance with the standards. Tensile tests were conducted using a Z30 Zwick&Roell testing machine (Germany), impact resistance was determined by the Izod method by using HIT 50 pendulum impact tester (Zwick&Roell, Germany).

Table 1. Test conditions on samples manufactured from secondary materials r(PP/EVOH) and rPP.

Parameter	Standard
Elastic modulus, MPa, Tensile strength, MPa	PN-EN ISO 527
Flexular modulus MPa, Flexular strength, MPa	PN-EN ISO 178
Izod impact strength, kJ/m^2	PN-EN ISO 180
Shore D Hardness, ShD	PN-EN ISO 868
Brinell Hardness, N/mm^2	PN-EN ISO 2039
Melt Flow Index, g/10min	PN-EN ISO 1133

The hardness of the samples was determined using the Brinell method and with a Shore hardness tester, using equipment from Zwick&Roell (Germany) for this purpose.

3 Results and discussion

Analysis of single-cut trial of the research objects shown that the proper orientation of packaging in the feeding system (the way of feeding into the cutting chamber) and the angle of the cutting knives significantly influence the cutting process and the tendency for the individual layers of the molding to separate. The impact of the cutting edges of the knives on the packaging results in its separation into smaller fragments. Near the bottom of the container the EVOH and PP layers separate (Fig. 5).

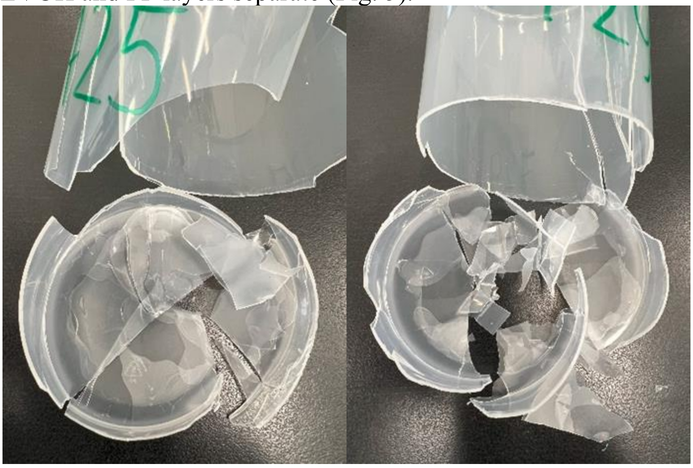

Fig. 5. Image of exemplary three-layer PP/EVOH/PP packaging after a single-cut test with a visible delamination area at the bottom.

The process of a single-cut of the packaging is unstable and can be divided into several stages (Fig. 6). In the first phase, the packaging fed parallel to the rotor axis is divided into two main fragments which undergo further deformation and cutting of fragments before leaving the cutting chamber.

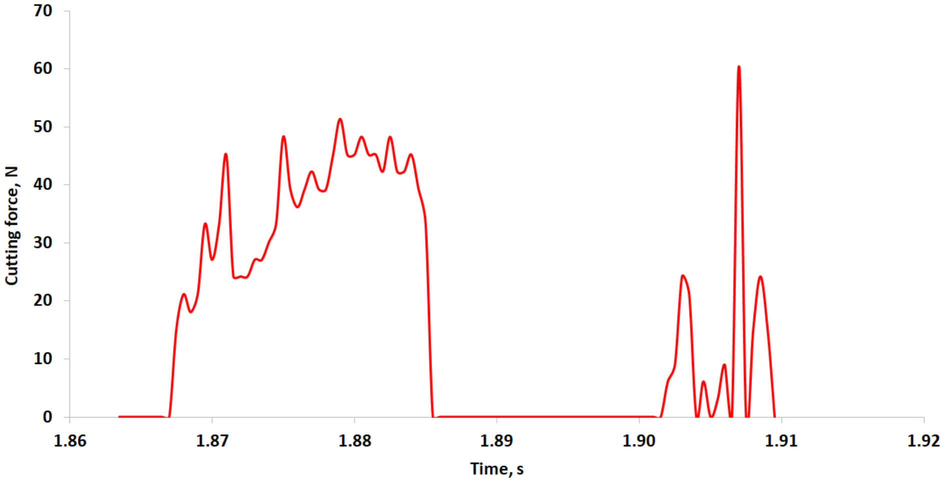

Fig. 6. Example of force changes during tests of a single-cutting of a three-layer PP/EVOH/PP packaging.

Obtained characteristics allowed for the determination of the energy required for a single cut estimated at 3.67 ± 0.2 J which corresponds to a value of 0.001 J·mm^{-2} in relation to the cut cross-section. The calculated values are significantly lower than in the case of cutting solid samples from polyolefin moldings [10]. Cut fragments of packaging were subjected to a grinding process, resulting in recyclates (grinding product) of relatively uniform flake size. The bulk density of this grinded material allowed for its direct and effective filling into the hopper of injection molding machine (Fig. 7). No excessive electrification of the charge was observed during the trials which could have caused difficulties in its further processing. The time of recording changes in the torque due to cutting forces on the rotor was long enough (about 540 seconds) to calculate average values of efficiency and specific energy required for grinding three-layer thin wall PP/EVOH/PP packaging (Fig. 7).

a) b)

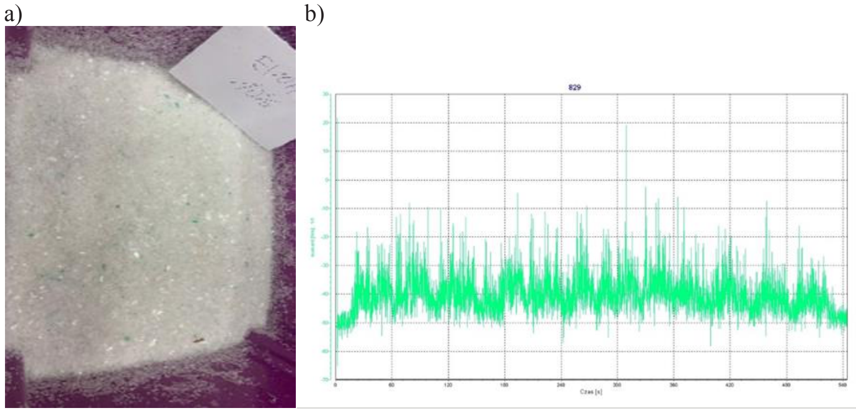

Fig. 7. Image of recyclate (a) and an example of the characteristic of torque changes on the rotor recorded during grinding tests of PP/EVOH/PP packaging (b). Visible, cyclical changes in values result from dosing an additional amount of material. In this way, the mill chamber was filled with the material.

During the moldings manufacture, the apparent viscosity of the PP/EVOH blend was measured at different injection speeds. Based on the obtained data, it was concluded that the PP/EVOH blend presents low apparent viscosity, even during the process at the lowest injection speed of 50.2 mm·s-1 (Fig. 8). Increasing its value causes a significant decrease in this processing parameter to about 120-130 Pa·s. These values were compared with the behavior of rPP under the same conditions. These values are slightly higher in the range of low injection speeds. However, it can be noted that the addition of EVOH improves the flow of the blend which is consistent with other scientific paper [5].

Furthermore, it was found that the obtained changes correspond in trend and value to the results obtained for the original (virgin) polypropylene Moplen HP 456 [14]. The advantageous rheological properties for both melts measured in the mold cavity were confirmed by the results of the melt flow index (MFI). For both materials, an MFR of $41 g \cdot 10 min^{-1}$ was obtained. These values indicate that both polymer melts, r(PP/EVOH) and rPP, showing a good flow, which is characteristic of materials used to produce thin wall moldings.

Fig. 9 shows the results of the mechanical properties of the rPP material obtained in the process of mechanical recycling of thin wall packaging made of Moplen RP390T polypropylene and a blend of this material with the EVOH barrier material (Kuraray Eval XEP-1314 TDS), derived from the recycling of three-layer r(PP/EVOH) packaging produced in the co-injection molding process. It was measured that the tensile strength does not differ significantly for both types of samples and is 29.2 ± 0.2 MPa for rPP and 29.1 ± 0.1 MPa for r(PP/EVOH), respectively. Similar results were also obtained for flexural strength. These values were 39.1 ± 0.4 MPa for rPP and 40.4 ± 0.2 MPa for r(PP/EVOH), respectively. Injection samples obtained from r(PP/EVOH) were characterized by a slightly higher value of the elastic modulus (E) of 1227 ± 19 MPa compared to the rPP samples for which E value was 1179 ± 22 MPa. A similar tendency was noted for the E modulus determined in the flexural test, obtaining values of 1296 ± 22 MPa for r(PP/EVOH) and 1281 ± 26 MPa for rPP. In the case of hardness, the same values were obtained for both types of samples. In the case of the Brinell method obtained hardness of 34.1 MPa and 63.4˚ ShD using Shore method. These results confirm previously conducted studies by other research studies [6, 8]. The addition of EVOH had a negative impact on the susceptibility of the r(PP/EVOH) samples to impact strengths. In the Charpy test, the susceptibility of this material to cracking was recorded and the average value obtained is for the r(PP/EVOH) was at a good level and amounts to 86.4 ± 38.2 kJ m^{-2}. Samples made of rPP without notches did not crack. Therefore, the impact strength was also determined using the Izod method for notched samples. In this case, the average impact strength value was 3.21 ± 0.20 kJ·m^{-2} for r(PP/EVOH) and 3.83 ± 0.22 kJ·m^{-2} for rPP samples. It is worth noting that in both cases the standard deviations are small which proves the homogeneity of the PP/EVOH blend.

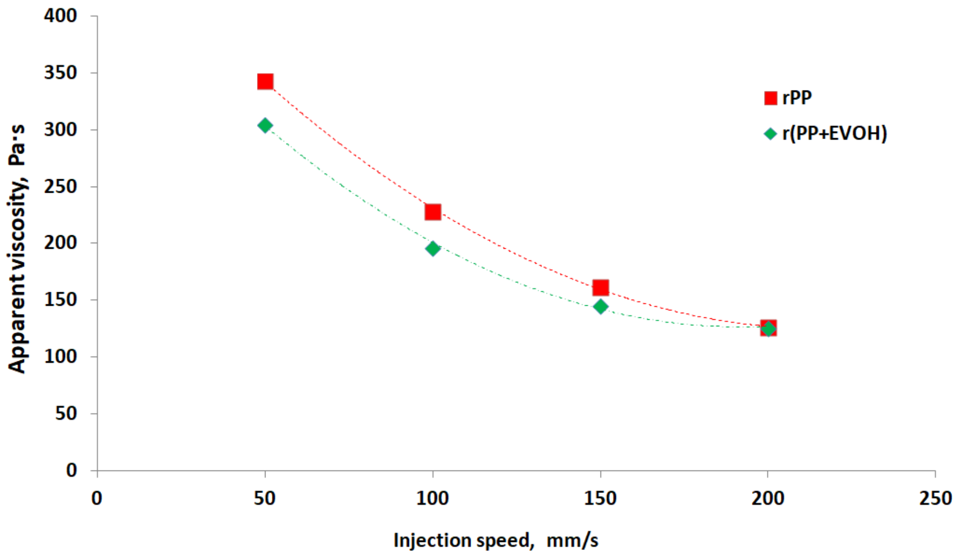

Fig. 8. Changes in the apparent viscosity of the r(PP/EVOH) melts compared to rPP as a function of injection speed.

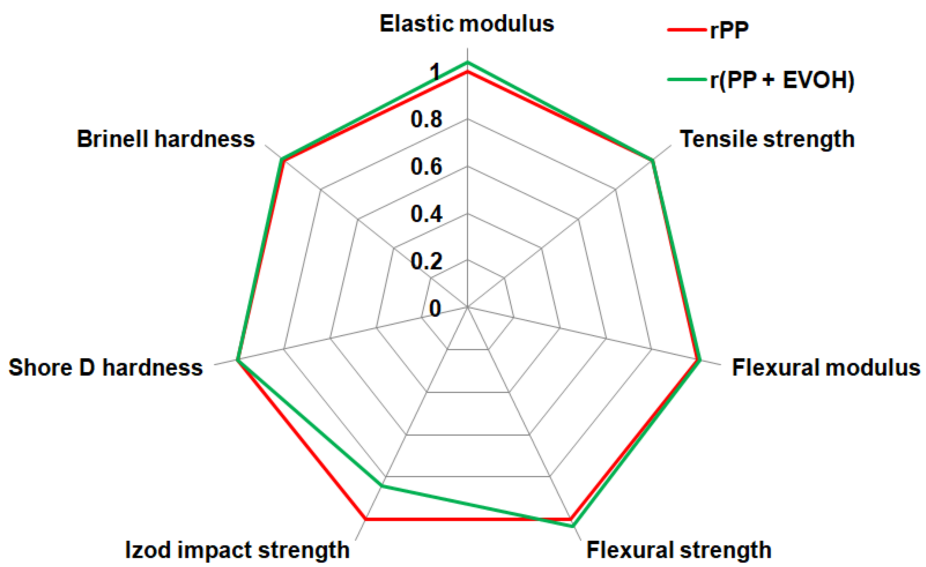

Fig. 9. Mechanical properties of samples manufactured from r(PP/EVOH) compared to rPP samples. The value obtained for rPP samples was marked as 100% (in red line) and compared with the results obtained for r(PP/EVOH) samples.

4 Conclusions

The conducted research on the components of the mechanical recycling process showed that three-layer PP/EVOH/PP barrier packaging can be effectively subjected to mechanical recycling processes using a knife mill of a special design. The estimated level of energy consumption for the cutting process is low, and the obtained recyclate can be directly dosed (bypassing the extrusion stage) into the injection molding machine. The obtained samples are characterized by favorable mechanical properties. EVOH additive did not significantly affect changes in flexural and tensile strengths and Young's modulus values compared to rPP samples. The material obtained as a result of mechanical recycling of PP/EVOH/PP barrier packaging is characterized by very good flow ability. Addition of EVOH to PP matrix causes decrease of an apparent viscosity of the PP/EVOH melt at low injection speed. For separation effectiveness important is delamination effect on the bottom layers of samples observed during cutting process. Although EVOH did not cause any unfavorable changes in strength or hardness properties, further research can verify the possibility of separating both materials (PP and EVOH) depending on the construction and technological parameters used in the cutting and grinding processes.

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