Journal of Polish CIMAC
Gdansk University of Technology
The Faculty of Ocean Engineering and Ship Technology

RECYCLING ABILITIES OF THERMOPLASTIC IONOMERS, AS EXAMPLIFIED BY SURLYN®

Dariusz Sykutera, Piotr Czyżewski
University of Technology and Life Sciences in Bydgoszcz
Faculty of Mechanical Engineering
Department of Plastics and Recycling Processing
ul. Kaliskiego 7, 85-796 Bydgoszcz, Poland
tel.: +48 52 340 82 24, fax: +48 52 340 82 22
e-mail: sykutera@utp.edu.pl

Abstract

The results presented in this paper apply to the research of grinding and cutting process of ionomer copolymer (E/MAA) under the trade name Surlyn® from DuPont company. Processing of this material is difficult and its susceptibility to mechanical recycling is limited. The results presented here are an important part of research concerning management of ionomer waste formed in the injection moulding process (defective moulded pieces with and the thick-walled injection moulding waste). The plastic material under examination is applied in the line of perfume, the products are expected to have transparency of the glass and don't have disqualifying surface defects. This requires the use of non-standard conditions in the injection moulding process and the construction of complicated structures of injection moulding tools (ie, three plate mould), along with valve gate hot runner systems.
In the structure of three plate mould we use cold runner system in hot runner injection moulds, the former of which forms the so-called injection waste, i.e. runner, which further increases the cost of the tool. In the case of plastics considered, injection waste constitutes up to 30 percent of the weight of the moulded piece, which, with high prices of this plastic (Surlyn® price is more than three times higher than the commonly used polyolefin materials) and reduced re-use possibilities, constitutes unaccepted, additional cost of production. This paper is an attempt to develop favorable conditions for the process of grinding of Surlyn® in terms of its re-use in secondary processing. The study shows that the temperature of feed has a significant impact on the level of thermal load of the material subjected to grinding and cutting, as well as on the effectiveness of disintegration.

Keywords: *ethylene/methacrylic acid copolymers, recycling of ionomers, recycling of Surlyn (E/MAA), grinding of ionomers, cutting of ionomers,*

1. Introduction

Surlyn® is the trade name of ionomer (E/MAA - *ethylene/methacrylic acid copolymers*, which has in its structure the cations of metals such as Zn and Na), produced by DuPont. Ionomers are characterized by strong electrostatic interactions between the chains of polymers and the amorphous structure. These materials have good resistance to abrasion and puncture, and good stiffness combined with the flexibility and resilience. These materials combine high tensile strength (greater than crystalline polyolefins and copolymers containing carboxylic acid groups) with good flexibility. Surlyn®, in comparison to the crystal structure of polyolefins and copolymers containing carboxylic acid groups, has much better mechanical properties, resistance to wear and damage, and good rigidity with sufficient flexibility and elasticity [1, 2].

The main areas of the application of Surlyn® are: production of cosmetic packaging (Figure 1), pharmaceutical packaging and food packaging (containers, bottles, boxes, foils, sheets, plates) and production of sports goods [1, 3, 5]. In literature, we can also find reports of attempts to use this plastic to modify the structure and properties of other thermoplastics [1, 3, 4, 8, 9]. The line of perfume expects exceptional transparency comparable to glass and moulded pieces free from visible surface defects from polymeric products. Surlyn®, with its unique properties can replace glass, giving more freedom for designing of package geometry e.g. the product with variety of wall thicknesses, sharp corners, the possibility to apply galvanic coating, the diversity in the surface finish, a wide variety of colouring, the use of overmoulding technology, safety of use) and by reducing the cost of packaging by approximately 30-40 per cent [6, 7].

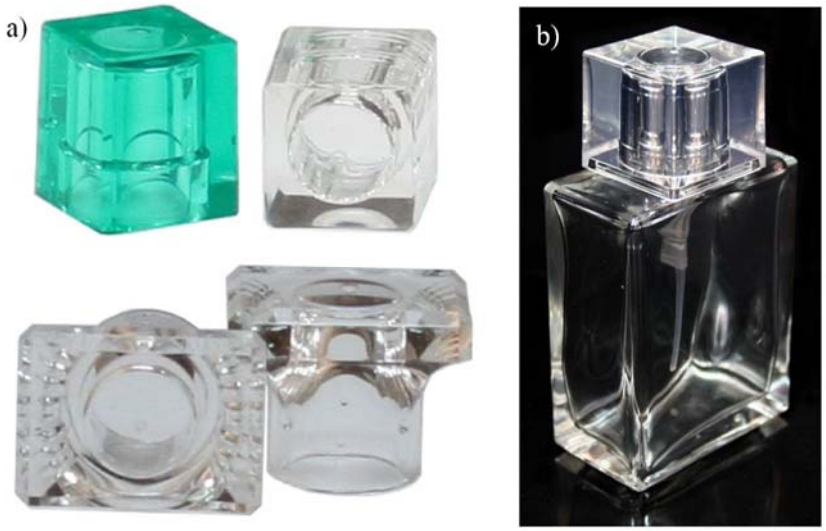

Fig. 1. Examples for using Surlyn®: a) a perfumery cap, b) complete perfumery package (bottle with cap)

Surlyn® makes lots of problems during injection moulding process, such as problems with the cooling of tool, surface defects are defects formed inside the structure of thick-walled moulded pieces. Susceptibility to mechanical recycling of ionomers is limited, due to the loss of transparency in the secondary processing (mouldings become *milky*). For these reasons, the production process often requires to apply cold runner system in hot-runner injection moulds (a three-disc mould structure arises) forming injection moulding waste, so-called "cold runner". In the case of plastics considered, injection waste constitutes up to 30 percent of the weight of the moulded piece, which, with high prices of this plastic (Surlyn® price is more than three times higher than the price of commonly used polyolefin materials) and reduced re-use possibilities, constitutes unaccepted, additional cost of production.

2. Methodology of research

In the research of cutting and grinding we used Surlyn® PC 2000 thermoplastic ionomer produced by DuPont (USA) in the form of injection moulding waste. It was cold runner, which, in case of Surlyn®, constituted as many as 32 per cent of the plastic entered to processing tool in one cycle. Before cutting and grinding, a part of the material under research was being frozen to temperature of -40°C within 24 hours in the freezer by Zwick (Germany). Cutting and grinding were carried out on the test stand whose description and research potential was presented in the paper [10]. Knives with a specific structure were equipped with extensometers by VISAY (Germany), sticked on in the Full Bridge Strain Gauge configuration [10]. The courses of strength and torque variations were registered with ESAM Traveller 1 converter (Germany). The angle of the edge of the cutting knives was $\beta=60°$, while their cutting edges were inclined by $2\lambda = 6°$ to the

rotor axis (the mill by hiperboloidal rotational cutting). Tests on cutting and grinding were conducted with tangential velocity of movable knives of 3 and 6 $m \cdot s^{-1}$ and by using sieves with diameters of ∅ 9mm of holes. Gain in weight was registered by WLC 6 scales by Radwag. Calculation of energy consumption per unit was made on the basis of a chart presenting torque variations in the realization of grinding process, according to the methodology proposed in the paper [11]. In grinding tests we also measured the temperature within the separating sieve. In order to make the data presented here more understandable, the individual cases of cutting and grinding were described in variants. Disintegration of Surlyn® with the tangential velocity of movable knives of 3 $m \cdot s^{-1}$ and at ambient temperature of 20°C was described in A variant. Cutting and grinding of Surlyn® with the tangential velocity of 6 $m \cdot s^{-1}$ and at ambient temperature of 20°C were described in B variant. Samples frozen to -40°C and disintegrated with the tangential velocity of 6 $m \cdot s^{-1}$ of movable knives were indicated as D variant, and the ones cut with the velocity of 3 $m \cdot s^{-1}$ as C variant. Proportions of graining of the recyclates obtained were estimated through sieve analyses carried out by using sieves with the diameter of holes of ∅8; 7; 6, 5; 3,5 and 2 mm. The process was realized in gyratory screen, and the analysis took 3 minutes. Moreover, recyclate grains obtained were assessed on the stand to computer analysis of view, with the help of stereo microscope with octuple magnification of the lens. Observations were made with the help of Multiscan 18 applications on Computer Scanning System from Warsaw [12].

3. Results of cutting

The analysis of cutting performance indicates that the freezing of the feed material to -40°C resulted in a significant increase in the values of the shear force. It seems to be the effect of an increase in hardness and stiffness of the material; this results in an increase of resistance to the effects of the cutting blades. At the same time, it was found out that the distribution of the frozen material is initiated by cutting owing to the cooperation of fixed and movable knives, and in the final phase of the process a brittle fracture of Surlyn® occurs, similar in its course to the disintegration of polystyrene at ambient temperature (see Figure 2).

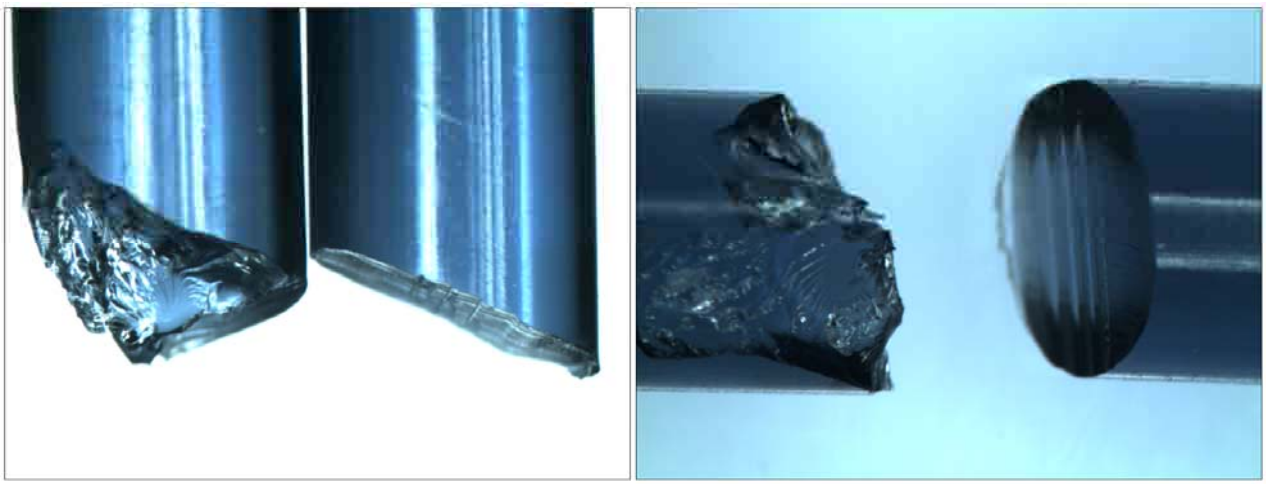

Fig. 2. Influence of temperature on disintegration type of injection moulding waste: parts of samples after cutting in -40°C. -samples on the left with frayed cutting surface- brittle cracking, parts of samples after cutting in +20°C -samples on the right with smooth cutting surface

Reduction of the tangential velocity of the cutting blades by half to 3 $m \cdot s^{-1}$ did not cause any significant changes in the course of variations of shear force or torque (see Figures 3-5). Similarly to the higher speed, the force needed to cut the sample is significantly higher for the frozen Surlyn®.

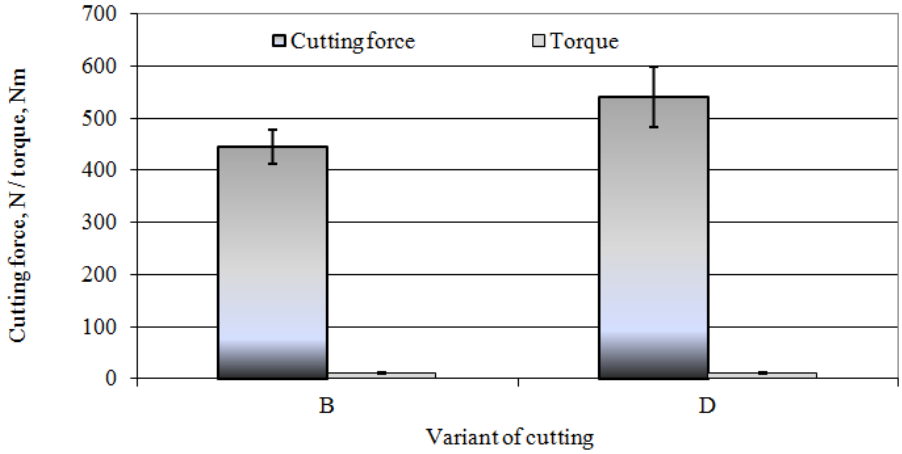

Fig. 3. Influence of the temperature of the feed on cutting force by hiperboloidal rotational cutting with tangential velocity 6 m·s^{-1} (the figure shows average values and standard deviations)

The only change observed is the prolongation of cutting time from 1ms to 3ms for the tests made for the material unfrozen (see A variant). A high percentage of cracking while cutting of Surlyn® at -40°C is evidenced by the stability of cutting time in B and D variants, despite the fact that the tangential velocity of knives was reduced twice.

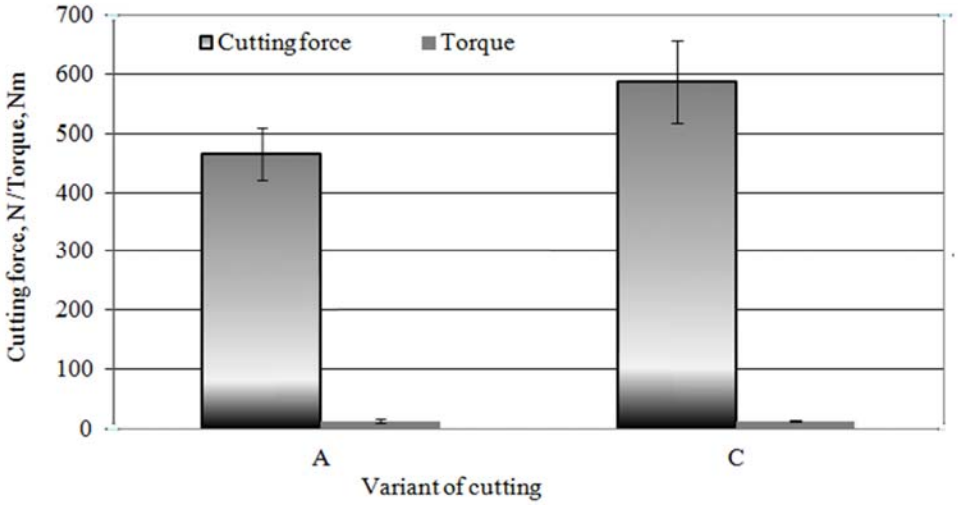

Fig. 4. Influence of temperature of the feed on cutting force by hiperboloidal rotational cutting with tangential velocity 3 m·s^{-1} (the figure shows average values and standard deviations)

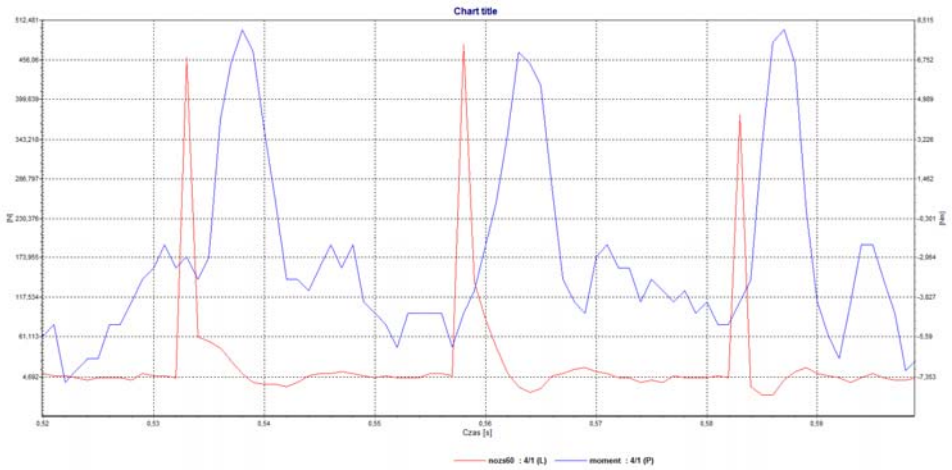

Fig. 5. Example of cutting of Surlyn® at ambient temperature with tangential velocity of 3 m·s^{-1}

4. Results of grinding

The temperature of an input affects grinding to a significant extent (see Figures 6 and 7). Reduction of the temperature of the technological waste to -40°C doubles the increase in performance in relation to A variant and causes an increase by 25 per cent as compared to the realization of the disintegration of Surlyn® at 20°C and at the same peripheral speed of 6 $m \cdot s^{-1}$ of movable knives. Similar changes can be observed in energy expenditures to be incurred in the process of disintegration of ionomer by knife. Reducing the temperature of the feed to -40°C causes the decrease in energy consumption per unit used in grinding of Surlyn® from 150 $kJ \cdot kg^{-1}$ to about 60 $kJ \cdot kg^{-1}$; which constitutes reduction in energy input by 60 per cent. For economic purposes the cost of lowering the temperature of the feed has to be taken into account.

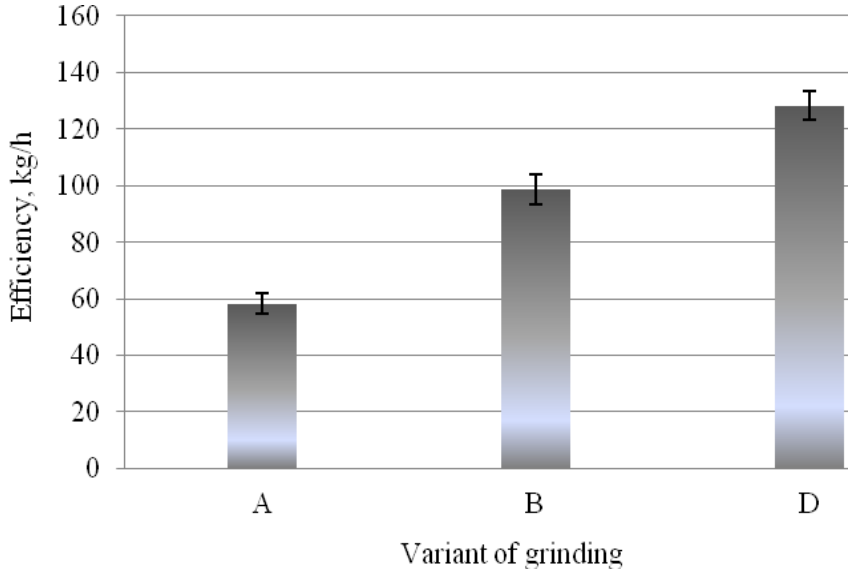

Fig. 6. Influence of conditions of grinding on efficiency during Surlyn® grinding in the cutting mill (the figure shows average values and standard deviations)

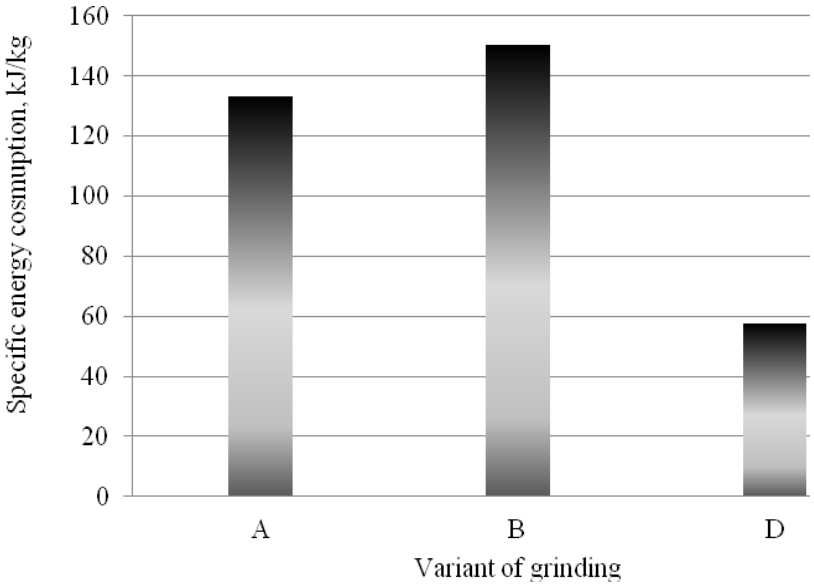

Fig. 7. Influence of conditions of grinding on energy consumption per unit during Surlyn® grinding in the cutting mill

Realization of disintegration of the material at ambient temperature is energy-consuming. Energy inputs necessary for its grinding are lower by about half when compared to a vulcanized rubber (but for graining of 1mm) and about 5 times higher then in the case of grinding of PELD to the same extent as in grinding of ionomers [11]. Using higher tangential speed of the rotor is more effective, despite the higher energy consumption per unit (see A and B variants).

Conditions for grinding processes affect temperature variations in working chamber of the tool significantly. The biggest increase of the temperature is characterized by disintegration of Surlyn® with higher tangential speed of the rotor (B variant). However, in that case, increase in temperature to about 30°C, does not constitute any thermal devastation. Freezing of the feed at -40°C caused the decrease in temperature by 10°C during grinding process, which is favourable when we take into account the sensitivity to high temperature of the disintegrated material (Figure 8). The results seem to affect the changes in structure of products obtained from recyclates. Analysis of data acquired from manufacturers of Surlyn® indicates that one of the most serious problems of recycling of Surlyn® is the loss of transparency. Thus, carefulness for maintaining relatively low temperature in a working chamber of disintegrator when carrying out the process may have a positive influence on recycling as well as on optical properties of this material.

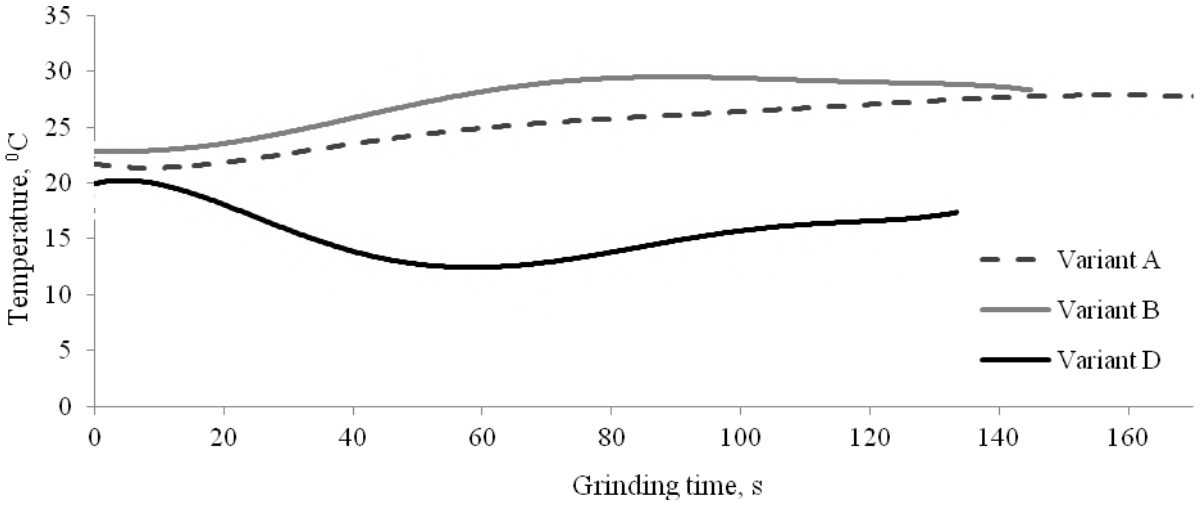

Fig. 8. Variations of temperature during the grinding process of injection moulding waste

The distribution of grains indicates that applying the ø 9mm sieves guarantees to obtain the recyclate of the proper grinding degree. It is evidenced by the fact that for all grinding variants the dominant grain group of recyclates are grains from 3,5 to 5mm, and, as for B and D variants more than 50 per cent of the total mass is comprised of the recyclate with the grain size of less than 5mm (Figure 9). Lowering the temperature of the feed did not affect the proportions of graining to any significant extent (D variant). It is worth mentioning about the importance of tangential velocity of cutting knives, but the recyclate obtained through the velocity twice as lower is characterized with the presence of larger grains. In addition, no dust was observed, while it is common for grinding of other thermoplastic materials like polyethylene or polypropylene.

Grinding of Surlyn® at 20°C leads to creating groups of grains with flat surfaces of cutting and straight edges (Figure 10). It proves the high importance of cutting in the waste material disintegration. Lowering the temperature of the feed to -40°C caused numerous fractures and roughness on surface of the grains (Figure 10). It seems to be the effect of the growing importance of cracking in disintegration of Surlyn®, which is more stiff and brittle at this temperature.

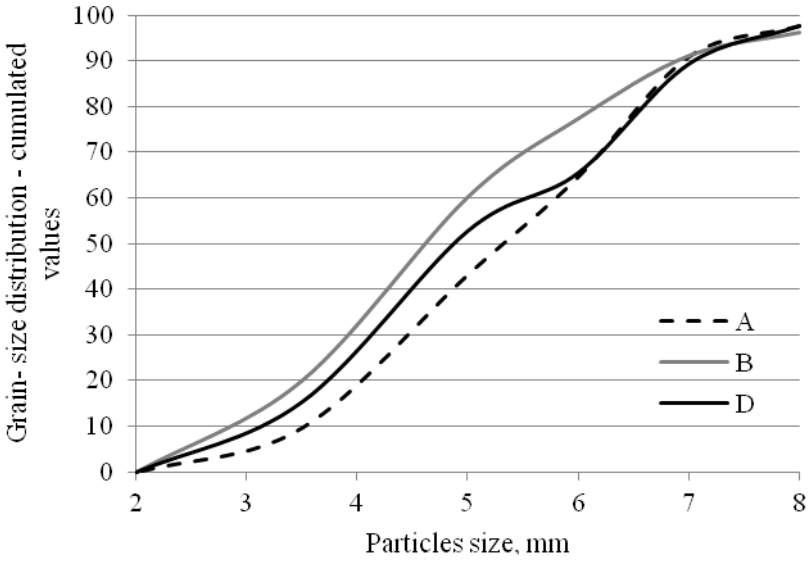

Fig. 9. Cumulated curve of ground Surlyn® PC 2000 according to grinding conditions during mill by hiperboloidal rotational cutting

Diameter of eye in screen [mm]	Temperature of grinding of injection moulding waste [°C]			
	20°C		-40°C	
8,0	5,6g 3,7%		3,4g 2,3%	
7,0	7,4g 4,9%		12,3g 8,2%	
6,0	20,0g 13,3%		35,4g 23,7%	
5,0	25,0g 16,7%		18,9g 12,6%	
3,5	58,4g 38,9%		55,6g 37,1%	
2,0	29,1g 19,4%		22,8g 15,2%	

Fig. 10. Influence of temperature of the feed on geometry and surface of grains of the recyclate. All pictures are made with the use of stereoscopic microscope (8x magnification)

5. Conclusion

Results of cutting and grinding of Surlyn® thermoplastic ionomer show the substatial importance of temperature of the feed for the effectiveness of mechanical recycling of this material. We can assume that cutting by knife at minimum gap between the blades allows to obtain ionomer recyclate with the proper grain distributions and by the relatively acceptable effectiveness and energy consumption. There is no direct dependence between the values of the cutting force and the energy consumption per unit used for grinding. Freezing of the feed to the temperature below -40°C made grinding of the material easier, since Surlyn® was flexible at ambient temperature, owing to the growing importance of cracking in disintegration.

References

[1] Company information materials of DuPont, [on-line], (28, 06, 2012), access <www2.dupont.com/Surlyn/en_US/>

[2] Czaja, K., *Poliolefiny*, Wydawnictwo Naukowo-Techniczne, Warszawa 2005.

[3] Dziadur, W., Litak A., *Wpływ jonomerycznego kopolimeru etylenu na strukturę krystaliczną i własności mechaniczne poliacetalu*, Inżynieria Materiałowa 1998, R. XIX, nr 4, pp. 946 - 949.

[4] Dziadur, W., Litak A., *Efekty modyfikacji poliacetalu kopolimerem etylenu*, Zeszyty Naukowe. Mechanika 43 (216), ATR Bydgoszcz, pp. 15-21, Bydgoszcz 1998.

[5] Kuzia, A., *Opakowania żywności*. Praca pod red. Bohdana Czerniawskiego i Jana Michniewicza, Wydawnictwo Agro Food Technology 1998.

[6] Information materials, *Żywica Surlyn DuPont wykorzystywana w opakowaniach*, [on-line], (27, 06, 2012), access < http://www.plastech.pl/wiadomosci/artykul_1964_1/ Zywica-Surlyn-DuPont-wykorzystywana-w-opakowaniach >

[7] Information materials, *DuPont: Nowa technologia obtrysku daje ogromne możliwości w dziedzinie projektowania opakowań*, [on-line], (27,06,2012), access <http://opakowania.com.pl/Wiadomości/DuPont-Nowa-technologia-obtrysku-daje-ogromne-możliwości-w-dziedzinie-projektowania-opakowań-26378.html >

[8] Garcíaa, S.L., Sánchez-Valdésb, S., Ramos-Devallec, L.F., *Effect of type and concentration of ionomer compatibilizer on the HDPE/Ionomer/Clay nanocomposites morphology*, Materials Science Forum, (2010), 644, pp. 17-20.

[9] Lim, H.T., Liu, H., Ahn, K.H., Lee, S.J., Hong, J.S., *Effect of added ionomer on morphology and properties of PP/organoclay nanocomposites*, Korean Journal of Chemical Engineering, (2010), 27 (2), pp. 705-715.

[10] Sykutera, D., *Stanowisko badawcze i wstępne wyniki badań cięcia termoplastycznych tworzyw porowatych*, Przetwórstwo Tworzyw, 4 (136), pp. 214-217, Gliwice 2010.

[11] Sykutera, D., *Badanie procesu rozdrabniania odpadów gumy cięciem hiperboloidalnym w aspekcie wykorzystania otrzymanego proszku gumowego do napełniania poliamidu 6*, Rozprawa doktorska, Politechnika Poznańska, Poznań 1998.

[12] Sykutera D., *Properties of solid polyurethane recyclat obtained in the compact multistage system of cutting mills*, Journal of POLISH CIMAC, Vol.5, No. 3, pp. 201-206, Gdańsk 2010.