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# **Rheometric research of polypropylene** Licocene PP2602 melts

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#### ABSTRACT

**Purpose:** To comprehend and ascertain reasons of the transition into the non-Newtonian viscosity zone for the melted polypropylene material, depending upon the number of recycling series.

**Design/methodology/approach:** There were carried researches on rheological features of the primary material of the melted polypropylene Licocene PP2602, subjected to be processed repeatedly in as many series as needed, using the Brookfield viscometer CAP2000+ within the temperature range 130-200°C and the shear rate range 166-3000 s<sup>-1</sup>.

**Findings:** There were obtained dependence of polypropylene melt viscosity against the shear rate at fixed temperatures, and dependence of polypropylene melt shear stress against the shear rate at fixed temperatures with the non-Newtonian viscosity transient zone shifting into the zone of greater shear rate values as the temperature increases. Also there was obtained dependence of the shear stress critical value on the number of recycling series, where the corresponding critical shear rate value grows as this number increases. This may be applied for predetermining the state of the repeatedly processed polymer material.

**Research limitations/implications:** The found rheometric regularities reflect behaviour for a homologous series of the polymer, but most probably they are generic for all polyolefines, what should be investigated and ascertained subsequently.

**Practical implications:** On the ground of the ascertained temperature-rate dependences of the polypropylene melt flow, there has appeared a possibility to gain a quantitative response about the secondary low-density-polyethylene material state, what allows selecting strategically the way of controlling this material properties, and that let develop new composites of those recycled materials for manufacturing footwear at enterprise "Vzuteks" (Khmelnytskyy).

**Originality/value:** The present paper states that processing the polymer materials repeatedly influences directly on their rheological parameters, increasing, particularly, the melt shear rate critical value.

**Keywords:** Polymer materials; Engineering polymers; Recycling polymer; Polymer rheological parameters; Non-Newtonian viscosity transition zone

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MATERIALS

## 1. Introduction

Quality and operational properties of production, manufactured from secondary polymer wastes by applying the recycling technologies, are mostly determined with features (molecular, physical-mechanical, rheological) of the secondary raw materials [1-5]. For their turn, values of those features are determined with the prehistory – the number of recycling series, conditions of exploitation, i.e. with the "life series" of the material, being transformed into wastes [6, 7].

For wastes of polyolefine plastics it is the most expedient to recycle them, where there is the repeated use with adding to the primary material the 15-20% of the wasted [8-13]. The secondary raw materials from wastes of polyolefines are obtained mostly after sorting, purification, drying out wastes and their subsequent processing into agglomerate or granulated material.

Using the secondary raw material further as independent stuff or addition to the primary raw material for making production is going to be conditioned with its features, depending directly on the number of recycling series of these wastes. It is known [14-17], that after the repeated recycling of wastes there changes the modulus of elasticity and melt flow index by straining and stretching.

However, by revising these factors it is impossible to determine how many recycling series have been run on the polymer material. But with the condition of fixing the quantitative interrelationship among factors of the material features and the recycling series number there appears a real tool of effecting upon the secondary material, aiming at controlling its features [18, 19], selecting technologies of its processing and recycling the polyolefine wastes.

# 2. Materials for research and work methodology

The research was carried out on the polypropylene material, and features of the material are put into Table 1.

Tabl	e 1	

Material specifications			
Material	Cradle	Features	Values
Polypropylene (homopolymers)	Licocene PP2602 of Clariant	Density	890 kg/m <sup>3</sup>
		Softening point	98°C
		Elongating until break	580%
		Tensile strength	$9.3 \cdot 10^6 \text{ N/m}^2$
		Viscosity (at 170°C)	6.300 Pa·s

There were researches on rheological features of the primary material Licocene PP2602 and the repeatedly processed one. A processing series lies in mixing on rollers for 60 minutes at 180°C within the melting chamber of thermobinder. The rheological researches of melts of polypropylene Licocene PP2602 were carried out with Brookfield viscometer CAP2000+ (Cone 05). The range of changing temperature is 130-200°C. The range of shear rate is 166-3000 s<sup>-1</sup>.

## 3. Results and discussion

For the melt of the primary polypropylene Licocene PP2602 there is observed the classic Z-shaped dependence of viscosity against the shear rate  $\eta = \eta(\dot{\gamma})$  with clearly defined sections of maximal Newtonian viscosity, minimal Newtonian viscosity [17, 18, 20], and transient zone of the non-Newtonian viscosity (curves 1-7 in Figure 1). At the temperature 200°C and higher the material is characterized with the minimal Newtonian viscosity (curve 8 in Figure 1), and there is no section of non-Newtonian viscosity.





On the plot (Figure 2) of shear stress  $\tau$  against shear rate  $\dot{\gamma}$  dependence  $\tau = \tau(\dot{\gamma})$  there may be observed the monotonous increment of  $\tau$ , but by  $\dot{\gamma}$  reaching the extreme value there appears the abrupt decrement of shear stress, though shear rate keeps increasing. By the melt temperature increase the values of the greatest shear stress  $\tau_{cr}$  shift into the zone of greater shear rate values [14, 21, 22]. For the polypropylene there is possibility to determine the critical value  $\dot{\gamma}_{cr}$  experimentally, when by exceeding  $\dot{\gamma}_{cr}$  the polymer melt turns from Newtonian viscosity flow mode into non-Newtonian viscosity flow mode.



Fig. 2. Dependence of the polypropylene Licocene PP2602 melt shear stress against the shear rate at fixed temperatures

In the case of processing polypropylene Licocene PP2602 repeatedly for four series the parameters of the melt flow mode change abruptly [22, 23]. At the same temperature of the melt the critical value  $\dot{\gamma}_{cr}$  shifts into the range of greater values of shear rate (Figure 3). Thus at 150°C the value  $\dot{\gamma}_{cr}$  of the primary polypropylene equals 660 s<sup>-1</sup>, and for the four series repeatedly processed polypropylene there is  $\dot{\gamma}_{cr} = 2300$  s<sup>-1</sup>. The analogous  $\dot{\gamma}_{cr}$  shifting for the processed material melt

is observed at other temperatures. It is remarkable that for the primary material the value  $\dot{\gamma}_{cr}$  is obtained right up to the temperature 190°C, while for the repeatedly processed material the value  $\dot{\gamma}_{cr}$  succeeds in being obtained only up to the temperature 160°C.



Fig. 3. Temperature dependence of  $\dot{\gamma}_{cr}$  (line 1 and 2) and  $\tau_{cr} = \tau_{cr}(\dot{\gamma})$  as line 3 for the polypropylene Licocene PP2602 melt: 1 – the primary; 2 – the recycled for four series

The observed on the plotted figures value  $\dot{\gamma}_{cr}$  relates to appearance of high-elasticity deformations of the polypropylene melt macromolecules [24]. The consequence of that is decrement of kinetic energy dissipation of movement of macromolecules gravity centres, what conditions the effective viscosity decrement, and the value  $\dot{\gamma}_{cr}$  increases disproportionately fast.

For the repeatedly processed material, due to destructive transformations, the number of long-chained macromolecules decreases, the number of macromolecules with less molecular mass grows up, and there appears the greater movability of them. As a consequence, the greater movability causes tendencies for flows at lower temperatures and greater values  $\dot{\gamma}_{cr}$ . Events of accumulation of high-elasticity reversible deformations are going to be observed for the destructed (secondary) material at greater values of shear rate. Accordingly, the greater destructions of the secondary material, the greater extent of that at the fixed melt temperature the shear rate  $\dot{\gamma}_{cr}$  shifts into the range of greater values (Figure 4). And, as it has just been figured there, the state of the repeatedly processed (secondary) material may be predetermined also over dependences  $\tau = \tau(\dot{\gamma}_{cr})$  at different melt temperatures.



Fig. 4. Dependence of  $\dot{\gamma}_{cr}$  on the number of recycling series: 1 – at 2 recycling series; 2 – at 4 recycling series; 3 – at 6 recycling series; 4 – at 7 recycling series

# 4. Conclusions

The lower temperature of the polypropylene Licocene PP2602 melt, at which the value  $\dot{\gamma}_{cr}$  is obtained and the material flows over whole range of shear rate as the Newtonian fluid, the greater extent of that the material has been endured destructive influences. Hence, on the ground of the ascertained temperature-rate dependences of the polypropylene Licocene PP2602 melt flow, there appears a possibility to gain a quantitative response about the secondary material state, what allows selecting strategically the way of controlling this material properties [25-27]. The found regularities reflect behaviour for a homologous series of the polypropylene materials.

#### References

 J. Stabik, A. Dybowska, Methods of preparing polymeric gradient composites, Journal of Achievements in Materials and Manufacturing Engineering 25/1 (2007) 67-70.

- [2] M. Bilewicz, J.C. Viana, L.A. Dobrzański, Development of microstructure affected by in-mould manipulation in polymer composites and nanocomposites, Journal of Achievements in Materials and Manufacturing Engineering 31/1 (2008) 71-76.
- [3] G. Kalay, C. Ogbonna, P.S. Allan, M. Bevis, Management, of microstructure in semi-crystalline polymers, Journal of Chemistry Engineering A 73 (1995) 798-809.
- [4] L.A. Dobrzański, M. Bilewicz, J.C. Viana, A.M. Cunha, Non-conventionally obtained polymer nanocomposites with different nano-clay ratios, Journal of Achievements in Materials and Manufacturing Engineering 31/2 (2008) 212-217.
- [5] M. Bilewicz, J.C. Viana, A.M. Cunha, L.A. Dobrzański, Morphology diversity and mechanical response of injection moulded polymer nanocomposites and polymer-polymer composites, Journal of Achievements in Materials and Manufacturing Engineering 15 (2006) 159-165.
- [6] S.-S. Lee, Y. Tae Ma, H.-W. Rhee, J. Kim, Exfoliation of layered silicate facilitated by ring-opening reaction of cyclic oligomers in PET-clay nanocomposites, Polymer 44 (2005) 2201-2210.
- [7] M. Bilewicz, J.C. Viana, L.A. Dobrzański, Self reinforced polymer-polymer composites, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 43-46.
- [8] M. Fujiyama, Polypropylene structure, blends and composites: structure and morphology, Karger-Koscis Journal 1 (1995) 167-204.
- [9] M. Arroyo, R.V. Suárez, B. Herrero, Optimization of nanocomposites based on polypropylene/polyethylene blends and organo-bentonite, Journal of Materials Chemistry 13 (2003) 2915-2921.
- [10] C.A. Silva, J.C. Viana, G.R. Dias, A.M. Cunha, Mold for Manipulation Microstructure Development, International Polymer Processing 1 (2005) 27-34.
- [11] M. Alexandre, P. Dubois, T. Sun, J.M. Garces, R. Jérôme, Polyethylene-layered silicate nanocomposites prepared by the polymerization-filing technique: synthesis and mechanical properties, Polymer 43 (2002) 2123-2132.
- [12] J. Stabik, M. Szczepanik, A. Dybowska, Ł. Suchoń, Electrical properties of polymeric gradient materials based on epoxy resin filled with hard coal, Journal of Achievements in Materials and Manufacturing Engineering 38/1 (2010) 56-63.
- [13] J. Stabik, A. Dybowska, M. Chomiak, Polymer composites filled with powders as polymer graded materials, Journal of Achievements in Materials and Manufacturing Engineering 43/1 (2010) 153-161.
- [14] G.V. Vinogradov, A.Y. Malkin, Rheology of polymers, Chemistry, Moscow, 1977, 440 (in Russian).
- [15] G. Wróbel, J. Kaczmarczyk, Numerical simulation of fatigue degradation process of polymer materials using diagnostic acoustic characteristics, Journal of Achievements in Materials and Manufacturing Engineering 36/2 (2009) 168-175.
- [16] G. Wróbel, J. Kaczmarczyk, J. Stabik, M. Rojek, Numerical models of polymeric composite to simulate fatigue and

ageing processes, Journal of Achievements in Materials and Manufacturing Engineering 34/1 (2009) 31-38.

- [17] G. Wróbel, A computer model of the process of polymer materials fatigue destruction, Journal of Achievements in Materials and Manufacturing Engineering 42 (2010) 127-133.
- [18] W. Okularczyk, D. Kwiatkowski, Prognosing the durability of polymer sealings, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 125-128.
- [19] J. Myalski, Properties of laminates containing polymer glass fiber recyclates, Journal of Achievements in Materials and Manufacturing Engineering 14 (2006) 54-58.
- [20] J. Koszkul, J. Nabiałek, Selected methods of modelling of polymer during the injection moulding process, Journal of Achievements in Materials and Manufacturing Engineering 24/1 (2007) 253-259.
- [21] A. Katunin, W. Hufenbach, P. Kostka, K. Holeczek, Frequency dependence of the self-heating effect in polymerbased composites, Journal of Achievements in Materials and Manufacturing Engineering 41 (2010) 9-15.
- [22] J. Nabiałek, J. Koszkul, The polymer flow in a mold cavity during the injection molding process. Comparison of an experiment and computer simulations, Proceedings of the

12<sup>th</sup> International Scientific Conference "Achievements in Mechanical and Manufacturing Engineering" AMME'2003, Gliwice – Wisła, 2003, 641-644.

- [23] M. Żenkiewicz, J. Richert, Influence of polymer samples preparation procedure on their mechanical properties, Journal of Achievements in Materials and Manufacturing Engineering 26/2 (2008) 155-158.
- [24] F. La Mantia, Handbook of Plastics Recycling, 2002.
- [25] E. Bociaga, M. Pietrzak, P. Postawa, The propagation of variability of polymer processing parameters in production lines, Journal of Achievements in Materials and Manufacturing Engineering 26/1 (2008) 26-32.
- [26] J. Koszkul, M. Pietrzak, A. Gzielo, P. Postawa, Influence of variability of polymer processing on the manufacturing system, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 253-256.
- [27] A. Gnatowski, J. Koszkul, Investigations of the influence of filler on the properties of chosen polymer blends with compatibilizer addition, Proceedings of the 13<sup>th</sup> International Scientific Conference "Achievements in Mechanical and Manufacturing Engineering" AMME'2005, Gliwice – Wisła, 2005, 247-250.