RHEOLOGICAL PROPERTIES OF VIRGIN, RECYCLED AND MIXED HIGH DENSITY POLYETHYLENE AND WOOD PLASTIC COMPOSITES WITH PLYWOOD SANDING DUST

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Abstract. The article summarizes investigation results of rheological properties of virgin (vHDPE), recycled (rHDPE) and mixed high density polyethylene (ratios 75/25, 50/50 and 25/75 respectively) and the corresponding composition of wood plastic composites with 50 wt.% of plywood production waste product plywood sanding dust (PSD) and 3 wt.% of coupling agent maleated polyethylene (MAPE). Pure matrices and their mixtures as well as the corresponding WPCs were mixed on two roll mills to maintain equal preparation conditions of the investigated samples. According to our studies we concluded that rheological properties of pure matrices and the corresponding composition of WPCs do not so strongly depend on the composition of composites (character of the fluidity curves and viscosity–shear deformation rate relationships are similar), but are significantly influenced by the parameters of rheological tests (shear stress and shear deformation rate). The most distinctions are observed especially at very high values of deformation rates (up to 5000 $1 \cdot s^{-1}$). The melt flow index (MFI) measurements showed the decrease of MFI values with an increase of the rHDPE content in vHDPE polymer matrix and the corresponding WPCs. The diminution of the values of MFI can reach 2 times. It shows the higher viscosity of recycled HDPE melts which can be related to prior exploitation conditions of recycled polymer. The curves of fluidity indicate the character of typical pseudo-plasticity of all investigated polymer melts because viscosity of the melts not only depends on the temperature, but also decreases with an increase of the shear stress and shear deformation rate. Pseudo-plastic properties of polymer melts confirm also the observed values of the fluidity index (n) which for pseudo-plastic, non-Newtonian liquids always is smaller than one.

Keywords: mixtures, high density polyethylene, composites, rheological properties.

Introduction

During the last 20 years, a lot of scientists have generated growing interest of utilization of recycled high density polyethylene for production of wood plastic composites [1-8]. The use of recycled matrices instead of virgin polymers allows to save fossil resources and successfully solve the ecological problems. Depending on the quality of recycled materials it is possible to make WPCs with exploitation properties what can successfully compete with WPCs based on virgin HDPE [4-7]. Due to WPCs are processed at polymer melt conditions, rheological properties of polymer melts play an important role. The rheological properties of WPCs based on virgin and recycled high density polyethylene have not been studied in many cases [1; 8-16]. Therefore, information related to rheology of WPCs is rather poor. The most used experimental method of the studies of rheological properties of polymer melts including WPCs is capillary viscosimetry what can be realized in the wide region (interval) of the shear deformation rates (10-20 up to 5000 $1 \cdot s^{-1}$ and more). That gives important information of behavior of polymer composite melts in real processing processes [1; 16-20]. Rheological properties of WPCs based on rHDPE are studied only in some works [8-10; 15]. More detailed investigations were done related to polypropylene WPCs [11-18]. The authors [13] have defined that virgin and recycled based WPCs MFI decreases with an increase of the content of mango wood waste products in WPCs and viscosity of the melts strongly depends on temperature. The authors [12; 20] indicate the coupling agent MAPP influence on the rheological properties of WPCs with wood flour [20] and viscosity of composite melts obeys to Areniuss-Ering equation [12]. That shows greater activation energy of the flowing process of WPCs melts than of the pure polymer matrix. The authors [14] observed also the visco-elastic properties of the WPCs melts. That creates some difficulties, for example, as swelling out process of the extrudate during the processing process of WPCs. The authors [1; 9; 18] in their studies have ascertained the clarity of rheological properties what essentially influence not only the content of the wood fibers in the composites but also of the prior processing of materials [1], reprocessing cycles and aging processes [10], as well as orientation of the fibers in the flow direction during the flowing process [9]. Besides, viscosity more seriously is influenced (viscosity decreases faster) at higher shear deformation rate values [9]. That means high influence of the processing parameters on viscosity of WPCs and another rheological parameter as the fluidity index. The fluidity index also indicates the degree of the difference of polymer melts from Newtonian liquids.

The goal of this study was to evaluate rheological properties of virgin, recycled and mixed HDPE matrices and the corresponding WPCs based on plywood sanding dust with the aim to clarify some composite composition which could be recommend for approbation of production of WPCs sheets.

Materials and experimental methods

For rheological investigations virgin and recycled high density polyethylene matrices and their mixtures with different vHDPE and rHDPE ratios (100/0, 75/25, 50/50, 25/75, 0/100) were prepared. As virgin HDPE was chosen the grade HMA 014 with the melt flow index (MFI) value 4.0 g per 10 min (T = 190 ºC, P = 2.16 kg, Tm = 135.41 ºC), but as a recycled HDPE served the grade produced by "Nordic Plast" Latvia, with MFI = 0.5-1.8 g per 10 min (T = 190 ºC P = 5 kg, Tm 132.85 ºC). DSC experiments showed also the presence of PP additives (Tm = 164.32 ºC) in rHDPE. As a reinforcement the birch plywood production by-product sanding dust was used with the following sizes of the fibers which contain 3 fractions with the size more than 500 microns (1.04%), between 250-500 microns (32.16%) and smaller than 250 microns (66.8%). WP composites also contain 3 wt.% maleated polyethylene (MAPE) type Licocene PE-MA4351 with defined acidity number 43 mg KOH/g (Tm = 126 ºC). All composites included pure virgin and recycled HDPE were prepared by mixing on two rolls mill equipment. Temperatures of the hot and cool rolls were 170 and 150 ºC respectively. The mixing time of the pure matrices was 10 minutes but of WP composites 15 minutes. The MFI values of mixed polymer matrices and WPCs with 50 wt.% PSD + 3wt.% MAPE were checked by IIRT viscosimeter at 190 ºC and the load 5 kg (standard LVS EN ISO 1133:2005). Rheological properties of different compositions of the composites were examined by a capillary rheometer type Malvern RH-7 (T = 190 ºC, shear deformation rate limits 50- 5020 $1·s^{-1}$ with the step of increase 50, 97, 187, 360, 695, 1346, 2600, 5020 $1·s^{-1}$). The length of the capillary was 16 and 0.25 mm but the diameter 1 mm. Equipment of Malvern RH-7 is applied with devices what ensure recording the results of experiments in the electronic shape. The computer display shows the fluidity curve from which we can calculate a lot of parameters and get a rich information about the rheological behavior of polymer melts. In this work were utilized only the most important dependences of the shear viscosity-shear deformation rate and fluidity index-shear deformation rate.

Results and discussion

The melt flow index measurement results are presented in Table 1. From these results it be can concluded that the increase of the amount of rHDPE in the mixed polymer matrix and WPC diminish the MFI values more than 40% due to the increasing of the intrinsic viscosity of polymer melts. However, MFI values of all (prior treated on two rolls mill) materials maintain at the levels of 6.41 g per 10 min and 0.28 g per 10 min (of pure rHDPE matrix and composite based on rHDPE respectively). That allows to process all investigated composites by the extrusion method. It is necessary to emphasize that the MFI values of the WPC are approximately 20 times smaller than of the corresponding pure and mixed virgin and recycled high density polyethylene matrices. That phenomena surely can be related to the presence of wood fibers in the polymer matrix what diminishes the movability of the chains of macromolecules on the surface of fibers but MAPE additive promotes and intensifies this interfacial interaction.

Table 1

Melt flow index values of WPCs based on virgin, recycled and mixed high density polyethylene matrices and composites with 50 wt.% plywood sanding dust (PSD) + 3 wt.%MAPE

Composition	Composition of matrices				
vHDPE/rHDPE	100/0	75/25	50/50	25/75	0/100
MFI, g per 10 min.vHDPE/rHDPE	11.41	10.21	8.61	7.56	6.41
vHDPE/rHDPE + 50 wt.% PSD + 3% MAPE	0.52	0.43	0.35	0.30	0.28

As it was shown in our previous investigations [17-19] of rheological properties of WPC, the melt flow index measurements do not give full information about the behaviour of the WPCs melts during

processing processes because in the real processing processes the polymer melts are subjugated of changeable shear stresses and shear deformation rates. Therefore, rheological tests by capillary rheometry give more profound and detailed information about the rheological properties of polymer composite melts. For the rheological test the temperature 190 ºC and the shear deformation rate interval 50-5020 $1 \cdot s^{-1}$ were chosen, which partially coincide with the temperatures and shear rates of processing of WPCs with PSD by the extrusion method. Basing on these data, we can predict how the composites could behave during the real processing processes. The fluidity curves of the pure and mixed matrices and WPCs with 50 wt.% PSD at 190 °C are presented in Fig. 1 and 2 respectively. Analyzing the fluidity curves of pure virgin and recycled HDPE and their mixtures, we can see that all dependences have a growing up tendency and their location is near especially at low and high shear deformation rates (50-100 $1 \cdot s^{-1}$ and 5000 $1 \cdot s^{-1}$ respectively), Fig.1. It means that the rheological properties of all polymer matrices at these conditions are similar. The main differences can be observed only at the shear deformation rate region 200-3500 $1 \cdot s^{-1}$. In this region rHDPE shows the lowest shear stresses values (80-200 kPa), but vHDPE the highest (120-240 kPa). Dependences of the shear stress-shear deformation rate of WPC practically coincide in all investigated shear deformation rate scope. Only the shear stress levels differ (120-300 kPa, Fig. 2) that is higher than of pure polymer matrices (see Fig. 1). Pseudo-plasticity of WPC melts up to 600 $1 \cdot s^{-1}$, but at shear rates more than 700 $1 \cdot s^{-1}$ the character of fluidity curves a bit changes and shows some features of dilatant liquids. In this case, the shear stress grows up slower than the shear deformation rate. Perhaps, at the higher shear rates (above 800 $1 \cdot s^{-1}$) also sliding effects of polymer melts can take place in capillary and then the flowing rate of the polymer melt increases.
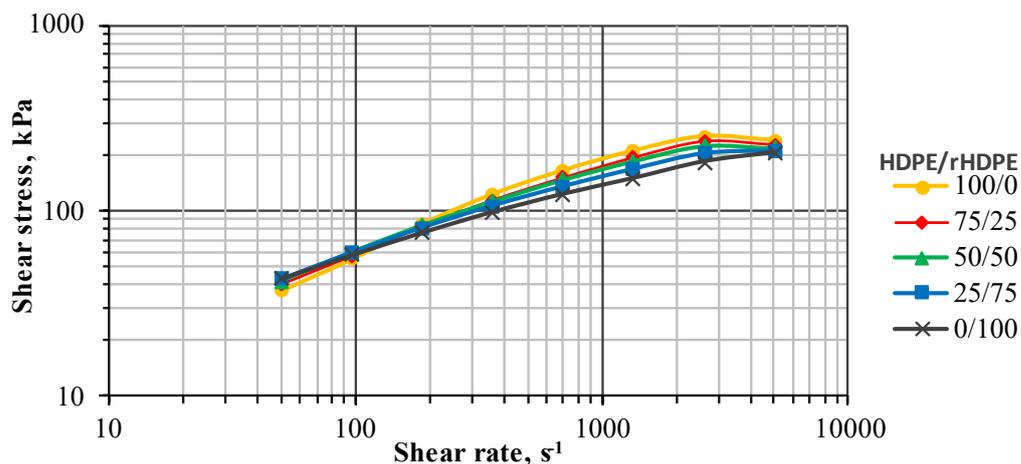

Fig. 1. **Fluidity curves of pure vHDPE/rHDPE polymer matrix of different composition at 190 ºC**
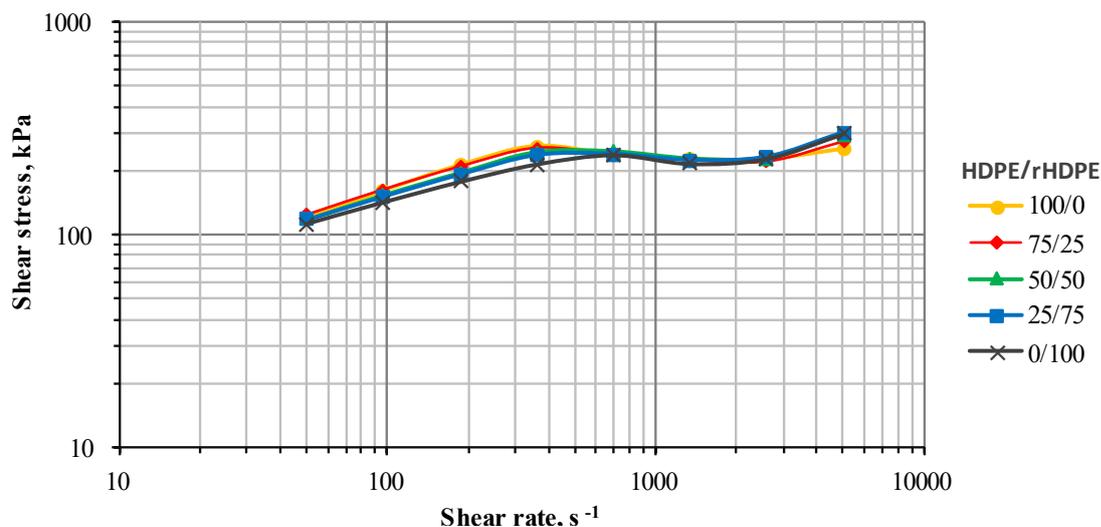

Fig. 2. **Fluidity curves of wood polymer composites of different polymer blends vHDPE/rHDPE + 50 wt.% plywood sanding dust + 3 wt.% MAPE at 190 ºC**
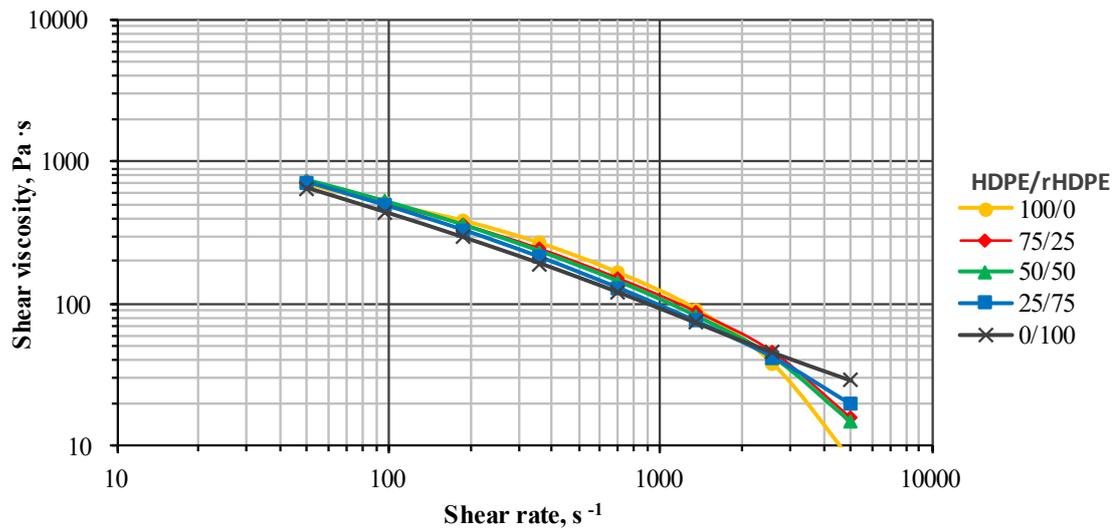
Fig. 3. **Dependences of the shear viscosity of pure v HDPE/rHDPE polymer matrices of different composition on the shear rate at temperature 190 ºC**
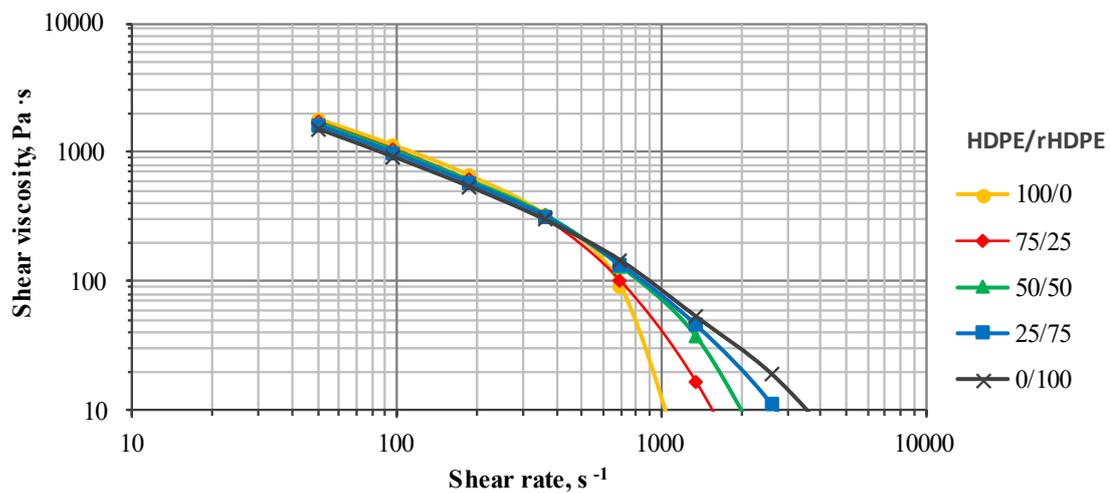

Fig. 4. **Dependences of the shear viscosity of wood polymer composites with different polymer blends vHDPE/rHDPE composition + 50 wt.% plywood sanding dust (PSD) + 3 wt.% of MAPE on the shear rate at temperature 190 ºC**

Rich information about rheology of polymer melts is given by the relationships of the shear viscosity-shear deformation rate (Fig. 3; 4) and fluidity index-shear deformation rate (Fig. 5; 6). Looking through the dependences of pure polymer matrices (Fig. 3) and WPCs (Fig. 4), we can find similarities and differences. Similarity is that all relationships have a descending character. That indicates to decrease of shear viscosity of the both pure matrices and the corresponding WP composite melts with an increase of the shear deformation rate. Besides, at the beginning of the shear rate (50-400 $1 \cdot s^{-1}$) the viscosity practically is the same for all compositions of WPCs what confirms similarity of the flowing mechanism of all composite melts. Some differences can be seen for pure polymer matrices (Fig. 3) where we can see smaller viscosity values of rHDPE melts. The essential differences of the shear viscosity-shear rate curves are observed at the shear rates more than 2500 $1 \cdot s^{-1}$ (Fig. 3) of pure polymer matrices and in 500-5000 $1 \cdot s^{-1}$ range of WPCs melts (Fig. 4). The greater influence of the shear deformation rate on the shear viscosity of pure HDPE mixtures and the corresponding WPCs can be explained by possibilities of thermal oxidation and degradation processes which could be generated at so high values of the shear deformation rate [9] (up to 2500 $1 \cdot s^{-1}$ for pure HDPE and 500-5000 $1 \cdot s^{-1}$ for WPCs). That indicates to the greater influence of the shear rate on the shear viscosity of WPCs melts what arises at faster diminishing of the shear viscosity of WPCs than of the pure polymer matrices. Nevertheless, it is necessary to emphasize that the beginning viscosity values of the pure matrices are significantly smaller (300-200 Pa.s) than of WPCs (700- 200 Pa.s). This phenomena can be explained

with the presence of the wood fibers what increases the intrinsic viscosity (friction) of polymer melts. However, at the high deformation rates (up to 5000 $1 \cdot s^{-1}$) the viscosity of WPCs polymer melts becomes smaller than of the pure polymer matrices. It could be explained also by the sliding effects when polymer melts in capillary flow as a "cork" what arises imaginary decreasing of the shear viscosity. The decrease of viscosity with an increase of the shear deformation rate indicates to the pseudo-plasticity of all polymer melts.
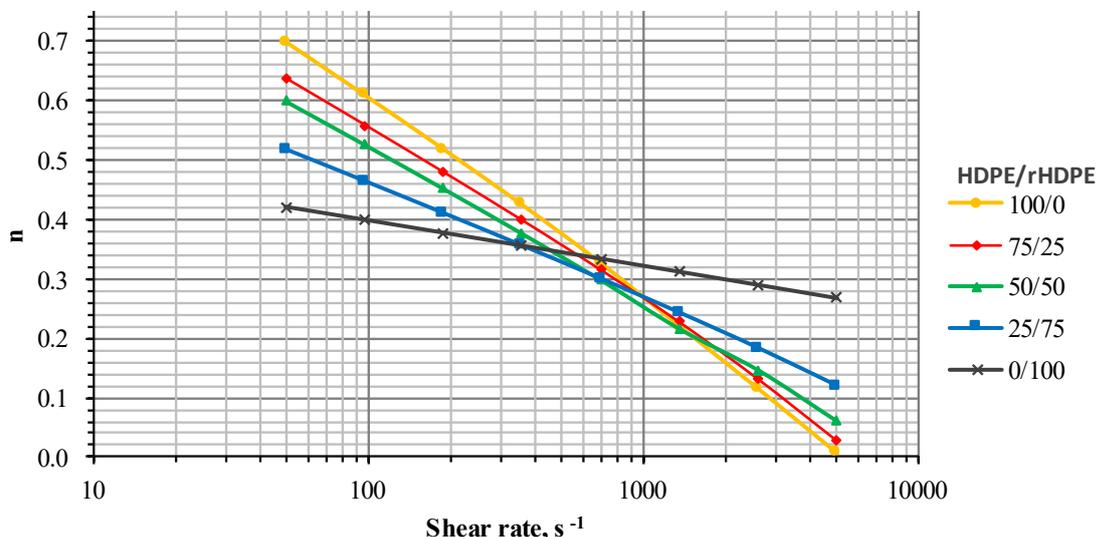

Fig. 5. **Dependences of the fluidity index (n) of pure vHDPE/rHDPE polymer matrices of different composition on the shear rate at temperature 190 ºC**

This phenomenon is affirmed also by the calculated values of the fluidity index (n) (see Fig. 5, 6). For all investigated systems n < 1, what characterizes pseudo-plastic liquids. It is necessary to mention that n values of the pure matrices are higher ($n = 0.4$-0.7) than of WPCs ($n = 0.25$-0.53). Besides, n diminishes with an increase of the shear deformation rate and decreasing of the rate depends on the chosen type of material. The highest decreasing rate of n has the system based on virgin HDPE, but the lowest – composite with rHDPE (Fig. 5). The decreasing rate of n increases with an increase of the content of rHDPE in the composite. Due to the fact that the values of the fluidity index n indicate the degree of pseudo-plasticity, we can conclude that the pure polymer matrix melts have smaller expressed pseudo-plastic properties because the n values differ from 1 smaller than of WPCs (Fig. 6).
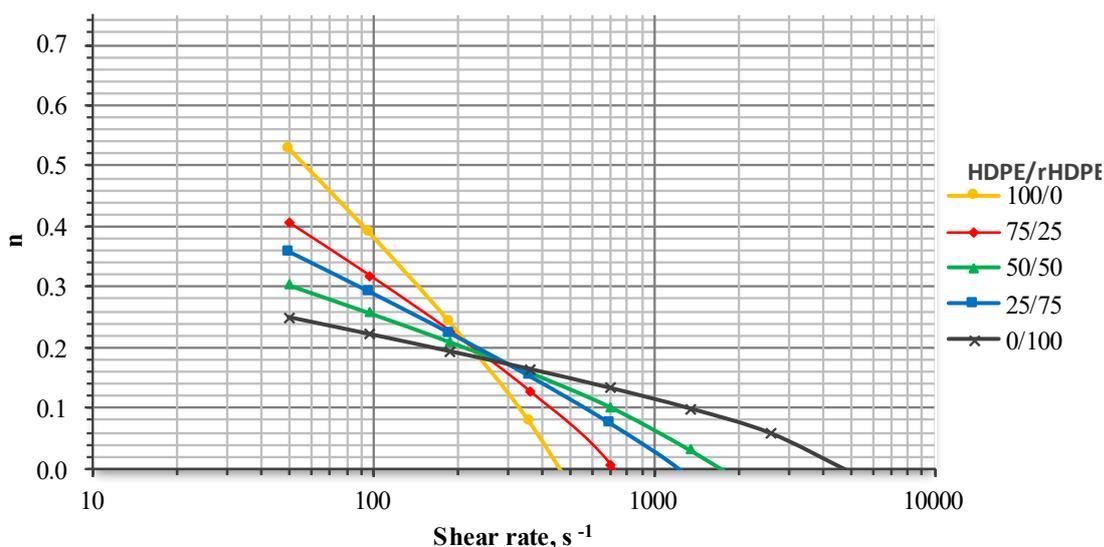

Fig. 6. **Dependences of the fluidity index (n) of wood polymer composites with different composition of polymer blends vHDPE/rHDPE + 50 wt.% plywood sanding dust (PSD) + 3 wt.% of MAPE on shear deformation rate at temperature 190 ºC**

The made investigations confirm that the presence of wood fibres in WPCs promotes the increase of the pseudo-plastic properties and faster decrease of the shear viscosity than of the pure matrices. The interesting fact is that the fluidity index-shear rate curves cross at the shear deformation rates 400-500 $1 \cdot s^{-1}$ (Fig. 5) for pure matrices, but for WPCs at 250-260 $1 \cdot s^{-1}$ (Fig. 6). That also shows of the greater and faster influence of the shear rate on the WPCs melts viscosity properties compared to the pure polyolefin matrices. In the aggregate the studies of rheological properties of pure polymer matrices and the corresponding WPCs based on PSD showed the pseudo-plasticity of all composite melts. Besides, the shear deformation rate influence on the viscosity is stronger expressed for WPCs melts.

Conclusions

In the presented work the rhelogical properties of virgin, recycled and mixed high density polyethylene and the corresponding wood plastic composites with 50 wt.% plywood sanding dust (PSD) + 3 wt.% maleated polyethylene (MAPE) were investigated. These studies showed the following results:

1. The melt flow index (MFI) values decrease with an increase of the recycled HDPE content in the polymer matrix and in the corresponding WPCs. It could be explained by the polymer structure of rHDPE and the presence of the polypropylene additive in this material.
2. The fluidity curves of all investigated materials are typical of pseudo-plastic liquids and the shear viscosity decreases with the increase of the shear deformation rate. Besides, the degree of the influence of the shear deformation rate on the shear viscosity depends on the composition of the systems and the stronger influence of the shear deformation rate on the shear viscosity of WPCs is observed.
3. Pseudo-plasticity of all investigated composites is affirmed by the fluidity index values which always were smaller than one. Besides, the smaller values of n observed of WPCs melts indicate to the greater influence of the shear deformation rate on WPCs melt rheological properties.
4. The studies of rheological properties of WPCs showed the usage possibilities of all presented mixtures for production of WPCs products, in this case WPCs sheets, but bearing in mind that WPCs based on mixed matrix (75/25% vHDPE/rHDPE) have better exploitation properties, this composition could be preferable.

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Author contributions

Conceptualization, J.K., K., and J.M.: methodology, J.K., K.K.; investigations, M.Z.; data curation, J.K. and K.K; visualization of results, M.Z. project administration J. K., K. K. and J.M.; writing – original draft preparation, K.K. writing – review and editing, J.K. All authors have read and agreed to the published version of the manuscript.

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