Examination of chemical composition of wood-plastic composites by differential scanning calorimetry and infrared spectroscopy

Tomasz Gołofit[1), *)], Tomasz Zielenkiewicz[2)], Jakub Gawron[3)], Katarzyna Cieślak[1)], Waldemar Tomaszewski[1)], Michał Chmielarek[1)], Paweł Maksimowski[1)], Wojciech Pawłowski[1)]

DOI: dx.doi.org/10.14314/polimery.2019.5.3

Abstract: Differential scanning calorimetry (DSC) and infrared spectroscopy (FT-IR) techniques were applied to analyze polymer type and its content in wood-plastic composites (WPC). Methods of analysis were developed on the basis of commercial and laboratory made WPC samples with different content of polypropylene (PP) and high-density polyethylene (HDPE). Polymer melting temperature was used to determine its type and melting enthalpy value was used to determine polymer content in the sample. The method was rewarding, both in qualitative and quantitative way. The absorption bands from FT-IR spectra (1508 cm^{-1}, *i.e.*, aromatic skeletal vibration of lignin and 1455 cm^{-1}, *i.e.*, CH_2 bending for polypropylene) were chosen to determine polymer content. Calibration curve obtained on the basis of measurements made on laboratory prepared samples with different polymer content was elaborated. Determination of polymer type with FT-IR was unequivocal, while determination of its content may cause troubles in case of samples with lower polymer content.

Keywords: differential scanning calorimetry, infrared spectroscopy, high-density polyethylene, polypropylene, wood-plastic composites.

Analiza ilościowa kompozytów polimerowo-drzewnych z zastosowaniem skaningowej kalorymetrii różnicowej oraz spektrofotometrii w podczerwieni

Streszczenie: Techniki kalorymetrii różnicowej (DSC) oraz spektrofotometrii w podczerwieni (FT-IR) zastosowano do analizy jakościowej i ilościowej kompozytów polimerowo-drzewnych (WPC). Metodykę analiz opracowano w odniesieniu do próbek WPC, komercyjnych i przygotowanych w laboratorium. Wyznaczoną wartość temperatury topnienia polimeru wykorzystano do określenia jego typu, natomiast wartość entalpii topnienia do określenia jego zawartości w kompozycie. Opracowana metoda okazała się skuteczna, zarówno do analizy jakościowej, jak i ilościowej. Pasma absorpcyjne zarejestrowane w podczerwieni przy liczbach falowych 1508 cm^{-1} (drgania szkieletowe pierścieni aromatycznych lignin) i 1455 cm^{-1} (drgania deformacyjne grupy CH_2 w polipropylenie) zastosowano do wyznaczania zawartości polimeru. Na podstawie pomiarów próbek WPC sporządzonych w laboratorium przygotowano krzywe kalibracyjne. Stwierdzono, że na podstawie widm FT-IR można jednoznacznie określić rodzaj polimeru w kompozycie oraz oznaczyć jego zawartość, jednak w wypadku niewielkiego udziału może to być problematyczne.

Słowa kluczowe: różnicowa kalorymetria skaningowa, spektroskopia w podczerwieni, polietylen dużej gęstości, polipropylen, kompozyty polimerowo-drzewne.

Manufacturing of wood products is the most ecologically safe method of wood wastes utilization. Products like fiberboards, particle boards or oriented strand boards are significant elements of wood industry. Also special

---

[1)] Warsaw University of Technology, Faculty of Chemistry, Division of High-Energetic Materials, Noakowskiego 3, 00-664 Warsaw, Poland.

[2)] Warsaw University of Life Sciences, Department of Wood Science and Wood Protection, Nowoursynowska 166, 02-787 Warsaw, Poland.

[3)] Warsaw University of Life Sciences, Department of Organization and Production Engineering, Nowoursynowska 166, 02-787 Warsaw, Poland.

[*)] Author for correspondence; e-mail: tomgol@ch.pw.edu.pl

types of this products, such as composites of wood and plastic, have been of more and more interest lately. This kind of material links wood particles with granulated plastic, which both may be industry wastes. That is why wood-plastic composites (WPC) idea is based on the utilization of wastes. Ecological advantage of such a solution is often emphasized.

Industry of WPC develops and number of its producers increases. That is why the necessity of quality control methods development occurs. Functional quality of WPC depends on its chemical composition – the ratio of wood and plastic content. The composition may be determined with different chemical methods, but they are laborious and time consuming. In order to perform fast and exact analysis, instrumental methods must be elaborated. Such a method should allow the determination of polymer content and, in some cases, polymer type (when it is unknown or uncertain).

Methods for manufacturing, variety of compositions and properties or extensive use of WPC were already presented several times. Wilczyński *et al.* [1] presented research on the flow of the WPC extrusion process. Viscosity tests of WPC were presented by Wilczyński [2]. Research on the possibility of using WPC in wastewater treatment technology was presented by Kruszelnicka *et al.* [3, 4]. The possibility of combining wood with polyhydroxyurethanes (PHU) and testing the properties of such a system has been shown by Tryznowski *et al.* [5].

Thermal analysis methods are widely used for different purposes – kinetic study (Danon and Görgens [6]), thermal stability analysis (Zhang and Weeks [7]) including wood components derivatives (Tomaszewski *et al.* [8]), thermoporometry (Książczak *et al.* [9]). Determination of polymer content may be one of these purposes. Jeske *et al.* [10] developed the method of WPC thermogravimetric analysis (TGA). They proved that it is possible to quantify the mass percentage for polypropylene copolymer in WPC. Developed method showed good agreements between analyzed and actual fractions of polymer in spite of the complex thermal degradation behavior of these composite. Authors also emphasize the lack of analytical methods for compositional analysis of samples with unknown composition.

Windt *et al.* [11] applied differential scanning calorimetry (DSC) using both melting and re-crystallization enthalpy for quantitative analysis of WPC containing different amount of polypropylene. Samples of WPC were made as particle boards in small scale, crushed and cryo-milled (under liquid nitrogen) to a powder. DSC was found as very good tool for such a task.

Mentioned technique may be also used for other purposes during WPC analyses, for instance for crystallinity studies (Mariotti *et al.* [12]). Authors made measurements under the nitrogen atmosphere of 15 mg samples of WPC prepared of refined black spruce bark fibers and high density polyethylene (HDPE). Melting process and crystallinity of WPC samples with different content of polypropylene (PP) was also analyzed (Li *et al.* [13]). Zhang *et al.* [14] performed similar studies with HDPE composites.

Besides polymer and wood, WPC contains also some other compounds (*ca.* 5 wt %). Also this part of composite may be successfully studied with DSC technique. Ou *et al.* [15] prepared samples of wood, HDPE and Kevlar fiber or grafted Kevlar fiber as nucleating agents. Authors compared different models describing non-isothermal crystallization.

Infrared spectroscopy (FT-IR) is very common technique available in many analytical laboratories. Its application is very wide, also in wood analysis. For example, this technique was used to analyze preservative content in beech wood (Gołofit *et al.* [16]). Standard samples with known content of preservative were examined and calibration curve for calculations was determined on the basis of ratio of typical peaks height. Archeological wood samples were examined with FT-IR by Traore *et al.* [17], who determined the proportion of carbohydrates and lignin in beam wood from Cathedral of Segovia (Spain). Attenuated total reflectance (ATR) unit was used in both of these papers. Other authors (Drożdżek *et al.* [18]) used FT-IR for the determination of cellulose crystallinity index in order to correlate results with crystallinity degree determined with wide-angle X-ray scattering (WAXS) technique.

FT-IR technique was also found in the literature as the method of WPC composite analysis. Migneault *et al.* [19] correlated WPC strength decrease with the increase of lignin peaks intensity. Guan *et al.* [20] applied both FT-IR and thermogravimetry technique to analyze the pyrolysis and char residue of WPC with polypropylene to estimate the improvement of flame retardancy. FT-IR was also used to perform quantitative analysis of number of WPC composites (Lao *et al.* [21]). Authors chose typical peaks for biomass (1060–1030 cm^{-1}) and plastic (1377 cm^{-1}) and used the ratio of peak intensities to analyze the content of polypropylene.

The aim of this paper is to develop a method of qualitative and quantitative determination of polymers with the application of differential scanning calorimetry on commercially available WPC with high density polyethylene which is one of the main polymers applied for this purpose. Polyethylene is mentioned in the relevant literature very rarely. Method was also used on samples with polypropylene. Additional target of this research is to verify results with FT-IR technique equipped with attenuated total reflectance (ATR) unit. DSC and FT-IR could be handy tools for quality assessment of WPC.

EXPERIMENTAL PART

Materials

PP and HDPE samples obtained from different available waste materials (Table 1) and one commercial PP sample, *i.e.*, Metocene MF650Y were analyzed.

Table 1. The studied PP and HDPE samples

PP		HDPE	
Sample	Source	Sample	Source
PP1	Pipe piece	PE1	Red bottle screw cap
PP2	Sticking plaster package	PE2	
PP3	Medical device piece	PE3	Milk bottle
PP4	Isolation needled cloth	PE4	
Metocene MF650Y	LyondellBasell	PE5	Yellow bottle screw cap
		PE6	

Composites of pine wood and polypropylene (PP) or high density polyethylene (HDPE) were examined. Pine wood flour with a particle diameter less than 0.5 mm was dried to constant weight at 100 °C.

Applied PP – Metocene MF650Y – was obtained from LyondellBasell company and the source of HDPE was milk bottle. Commercial WPC products containing 22 wt % (two different elements: C-PP22A and C-PP22B) and 47 wt % of PP (C-PP47) obtained from Polykemi (Czech Republic) were the studied material as well as laboratory made pine wood-PP (W-PP) and pine wood-HDPE (W-PE) composites.

Samples preparation

All studied composites were prepared using the following methods. The weighed amounts of polymers and pine wood flour were preheated up to 150 °C. Next the prepared mixtures were homogenized in oscillating mill MM400 (Retsch), using milling cup of 50 cm^3 volume and milling ball of 25 mm diameter. The milling time was 5 min and the milling oscillations were 30 Hz. The milling process was repeated twice. The W-PE composites were not homogenous, therefore W-PP composites were obtained using different method. At first the pine wood was milled in MM400 mill using the same parameters as described above. Next the weighed amount of PP polymer was melted at 200 °C in crucible and mixed with milled pine wood. The obtained mixtures were left alone to cool down. The quantitative composition of prepared WPC are summarized in Table 2.

Methods of testing

The melting temperatures and melting enthalpies of applied polymers were determined before composites' analysis. None of the other polymer parameters were determined because proposed method should be functional regardless the polymer origin and their detailed parameters, which are different for particular WPC manufacturers.

All calorimetric measurements were performed with TA Instruments DSC Q2000 calorimeter, with heating rate 10 °C/min, from -90 °C to 300 °C. Standard aluminum vessels were used. Onset temperature of melting peak was chosen for comparison, as its determination is more reliable in comparison to maximum peak temperature. As the endothermic polymer melting peak covers exothermic peak of wood degradation initial stage, all of the measurement were done twice. Presented below measurements are the second runs, *i.e.*, second heating run after cooling step, when exothermic effect does not repeat. The content (C_p in wt %) of polymer in WPC samples was determined according to Eq. 1, using melting enthalpies (ΔH) of samples and reference polymer:

$$C_p = \frac{\Delta H_{\text{sample}}}{\Delta H_{\text{polymer}}} \tag{1}$$

To verify DSC results, the attempt was made to apply FT-IR technique to measure polymer content in WPC composites. The spectra both of the samples of applied components and prepared PP and HDPE composites were acquired. FT-IR measurements were performed on the Thermo Fisher Scientific Inc. Nicolet 6700 spectrometer with ATR unit. Measurements were performed in the wave number range of 4000–550 cm^{-1}, with the resolution of 0.241 cm^{-1}. 16 scans of sample spectrum and 32 scans of background spectrum were made each time.

Table 2. Quantitative composition of the studied composites

Sample	PP mass g	HDPE mass g	Pine wood mass g	Polymer content in the composite, wt %	Origin of polymers
W-PE40	–	0.800	1.204	39.9	Milk bottle – waste
W-PE50	–	1.005	1.001	50.1	
W-PE70	–	1.400	0.602	69.9	
W-PE90	–	1.800	0.200	90.0	
W-PP40	3.45	–	5.17	40.0	Metocene MF650Y
W-PP50	4.02	–	4.02	50.0	
W-PP60	5.96	–	3.97	60.0	
W-PP70	5.12	–	2.19	70.0	
W-PP80	5.11	–	1.29	79.8	

T a b l e 3. Thermal characteristics of PP and PE samples

PP				HDPE			
Sample	T_{onset}, °C	T_{max}, °C	ΔH_{melt}, J/g	Sample	T_{onset}, °C	T_{max}, °C	ΔH_{melt}, J/g
PP1	153.3	158.2	96.4	PE1	123.3	131.2	200.4
PP2	151.3	161.5	87.5	PE2	125.2	131.2	198.5
PP3	145.2	163.3	78.4	PE3	124.7	133.3	187.8
PP4	159.8	165.2	96.2	PE4	122.4	130.5	185.4
–	–	–	–	PE5	120.9	128.5	166.7
–	–	–	–	PE6	120.9	129.2	162.2
Average	152.4 ± 5.2	162.0 ± 2.6	89.6 ± 8.6	Average	122.9 ± 1.7	130.6 ± 1.5	183.5 ± 14.5

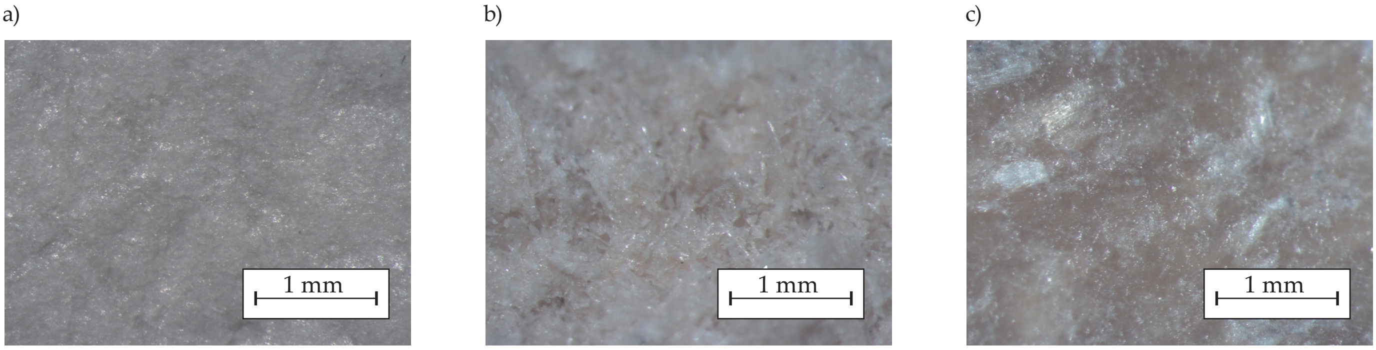

Fig. 1. An exemplary appearance of the surface of WPC containing 40 wt % of polymers: a) W-PE40, b) W-PP40, c) C-PP22A

Two adsorption peaks, *i.e.*, 1508 cm^{-1} and 1455 cm^{-1} from FT-IR spectra of WPC were chosen for quantitative analysis. Peak at 1508 cm^{-1} is assigned to aromatic skeletal vibration of lignin (Colom *et al.* [22]), and peak at 1455 cm^{-1} responds to CH_2 bending for polypropylene (Painter *et al*. [23]). The ratio of their heights (H_{1508}/H_{1455}) was applied for determination of PP content. Calibration curve was prepared using samples of laboratory made composites. The applicability of calibration curve was verified using commercial samples. Other sets of FT-IR peaks from the fingerprint regions of applied components were also studied, including this proposed in Lao *et al*. [21], but finally adsorption peaks 1508 cm^{-1} and 1455 cm^{-1} gave the best results, *e.g.*, correlation coefficient of calibration curve.

Analysis of WPC texture under the light-optical microscope was carried out using optical microscope MSt-130 (PZO) equipped with digital camera Levenhuk M500. Samples for observations were obtained by slicing of larger WPC particles with scalpel.

RESULTS AND DISCUSSION

After preparation of studied composites a preliminary examination of their homogeneity by means of microscopic observation was carried out. A comparison of exemplary composites containing 40 wt % of polymers, *i.e.*, two prepared WPC with HDPE, PP, and commercial C-PP22A is presented in Fig. 1.

It arises from the microscopic observations that the homogeneity of prepared WPC with HDPE and commercial composite with PP is comparable, and the homogeneity of the prepared WPC with PP is lower. The results are not consistent with the subsequent instrumental studies that showed lower homogeneity of WPC with HDPE in comparison to WPC with PP. This will be described underneath.

Exemplary DSC curves of PP obtained from two different sources are presented in the Fig. 2.

Shape and height of presented melting peaks for each source are different. For example peaks obtained for PP3 samples are wider, what is probably related to higher amount of impurities in that samples source. PP parameters are similar irrespectively of its supplier. Results of melting enthalpy and melting temperature determination for all PP samples are collected in Table 3.

Results are quite repeatable, but standard deviation of melting enthalpy value reaches almost 10 % of mean value. Distinctions may be caused by the presence of

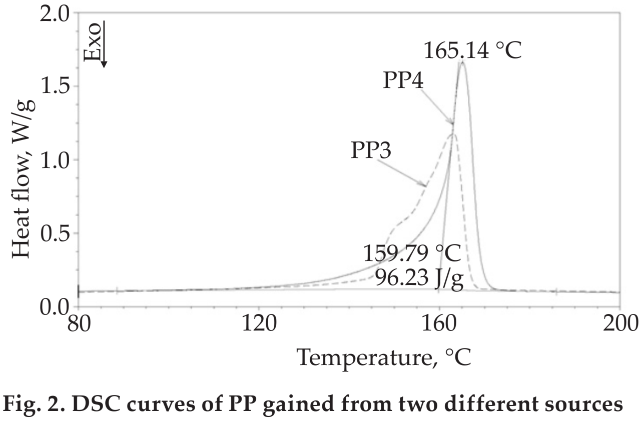

Fig. 2. DSC curves of PP gained from two different sources

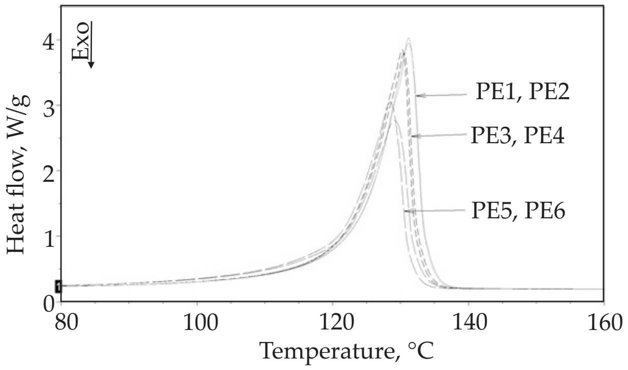

Fig. 3. DSC curves of HDPE gained from three different sources

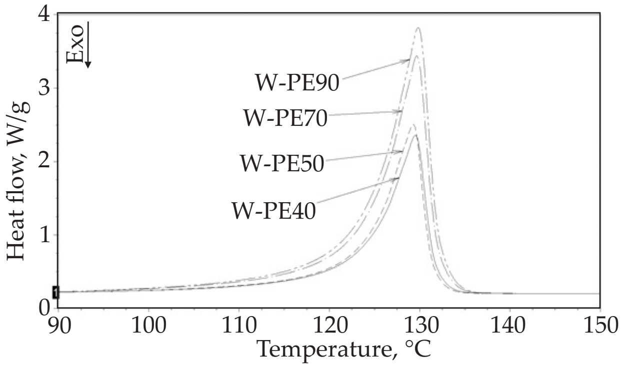

Fig. 4. DSC curves of four wood-HDPE composites with different HDPE content and pure HDPE sample

different additives in polymer. Different values of polymer average molecular weight in samples from different sources may influence the melting temperature. The crystallinity degree is the other factor which could be responsible for these differences, especially in the enthalpy values. Also the comparison of obtained melting temperature 152 °C with that measured in Windt *et al.* [11], which was 164 °C, shows significant difference. This fact may result from impurities in polymer too, but especially the way of melting temperature determination (onset temperature, but not the peak temperature) makes that difference.

Six chosen DSC curves of HDPE obtained from three different sources are presented in the Fig. 3. PE1 and PE2 samples originate from the same source – samples masses are similar, as well as melting peaks shape and height. The same may be stated in case of PE3, PE4 and PE5, PE6 sample pairs. Masses of PE5 and PE6 are slightly lower and that is why peaks are smaller. Generally, measurements are very repeatable. It means that parameters of HDPE originated from different wastes are similar irrespectively of its source. Results of melting enthalpy and melting temperature determination for all HDPE samples are collected in Table 3. Melting enthalpies of samples PE1 and PE2 are clearly higher than others but calculated standard deviation does not exceed 7 % of average value.

DSC curves of wood-HDPE composites (with different polymer content) and pure HDPE are presented in the Fig. 4.

Peak height and area clearly depend on HDPE percentage. These parameters decrease with HDPE content. It means that observed peak is totally connected with polymer phase transition. Table 4 presents values of melting temperatures and enthalpies, as well as calculated HDPE content in analyzed samples.

Table 4. Thermal properties and content of PE in studied samples

Sample	PE content (nominal), wt %	PE content (calculated), wt %	T_{onset} °C	T_{max} °C	ΔH_{melt} J/g
HDPE	100	–	123.0 ± 1.2	131.4 ± 1.3	186.2 ± 1.1
W-PE40	40	50.6	123.4	129.5	91.4
W-PE50	50	53.2	123.3	129.3	96.6
W-PE70	70	81.0	123.4	129.7	145.5
W-PE90	90	93.3	123.3	129.8	165.8

Table 5. Thermal properties and content of PP in studied samples

Sample	PP content (nominal), wt %	PP content (calculated), wt %	T_{onset} °C	T_{max} °C	ΔH_{melt} J/g
PP	100	–	144.9 ± 0.6	154.5 ± 3.3	94.6 ± 3.4
C-PP22A	22	24	154.4	159.8	21.9
C-PP22B	22	21	154.2	158.2	19.4
W-PP40	40	30	130.1 ± 2.0	141.8 ± 0.1	28.2 ± 1.2
W-PP50	50	44	140.8 ± 3.1	149.2 ± 2.0	41.3 ± 2.5
W-PP60	60	62	146.3 ± 2.5	153.2 ± 1.2	58.4 ± 0.4
W-PP70	70	68	146.3 ± 4.1	154.9 ± 1.8	64.8 ± 3.6
W-PP80	80	81	148.2 ± 2.2	153.8 ± 0.5	77.0 ± 1.4

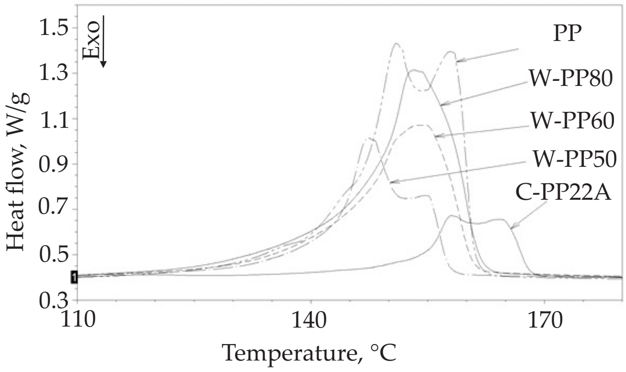

Fig. 5. DSC curves of three wood-PP composites with different PP content and pure PP sample

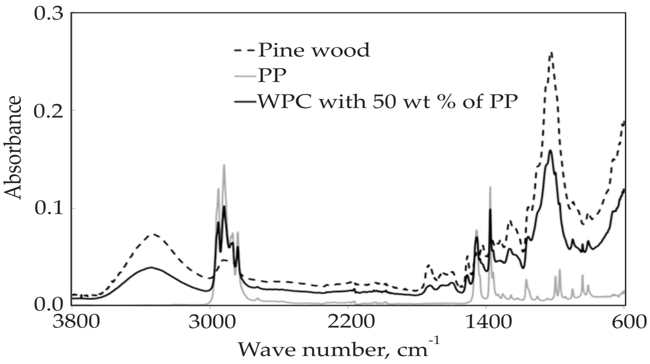

Fig. 6. Exemplary FT-IR spectra of pine wood, PP, and WPC with 50 wt % of PP

Calculation results are not quite consistent with nominal values. It is probably caused by the fact that samples were laboratory made. Samples are not homogeneous as in case of commercially made PP composites. Analyzed samples of HDPE composites are probably not representative. Problems with changes of plasticizing mechanism caused by changing composite preparation parameters were observed by Wilczyński and Buziak [24]. The method of preparation of laboratory made samples should be considered carefully in the future.

Figure 5 presents DSC curves of wood-PP composites (with different polymer content) and pure PP. It can be observed that the decrease of PP content causes the decrease of peak area what is connected with melting of lower polymer mass. Values of melting temperatures and enthalpies obtained for samples of wood-PP composites and pure PP are collected in Table 5.

For pure PP the averages were obtained from four measurements. PP content in analyzed composites was calculated based on melting enthalpy. Calculation results of determined polymer contents in commercial WPC's are consistent with the nominal values. Also for samples of laboratory made composites containing large fraction of polymers, the results are in a good agreement with nominal values. But for samples containing both 40 wt % and 50 wt % the determined polymer contents are lower than the expected ones. For these samples the measured onset temperatures of melting peak are lower, what can be an indication of polymer degradation. The degradation of polymer may results from the longer time of samples preparation, *i.e.*, longer conditioning time in higher temperature.

The attempt was made to verify obtained results with FT-IR data. Exemplary FT-IR spectra of pine wood-polypropylene composite, as well pine and polypropylene are presented in the Fig. 6. Two absorption bands above and below 1400 cm^{-1}, as well as the group of four peaks below 3000 cm^{-1} seem to be the most typical for polypropylene (fingerprint). Peaks typical for wood are also observable. Peaks at 1508 cm^{-1} and 1455 cm^{-1} were chosen as the indicators of PP content (see earlier text).

Calibration curve and results of H_{1508}/H_{1455} peaks ratio obtained for commercial samples are presented in the Fig. 7. Correlation coefficient of calibration curve is satisfactory (0.9571). However only results obtained for 47 wt % PP commercial sample seem to fit to the calibration curve. The distance from the trend line observed for the 22 wt % PP commercial sample results is significant. Moreover, two of commercial samples were of the same PP content and results of the peak height ration (H_{1508}/H_{1455}) are different for these

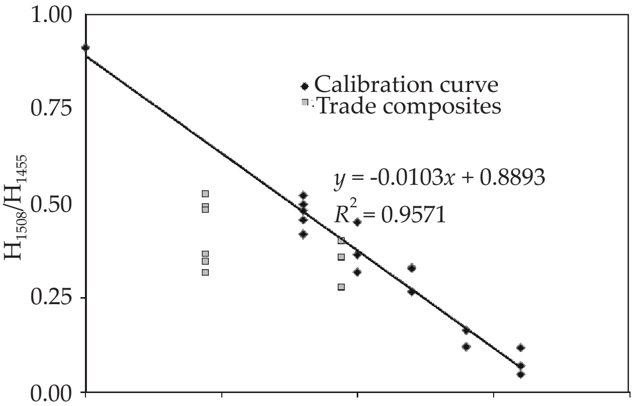

Fig. 7. Ratio of heights of 1508 cm^{-1} and 1455 cm^{-1} peaks from FT-IR spectra of trade composites including pure PP (thick line) and of laboratory made standards

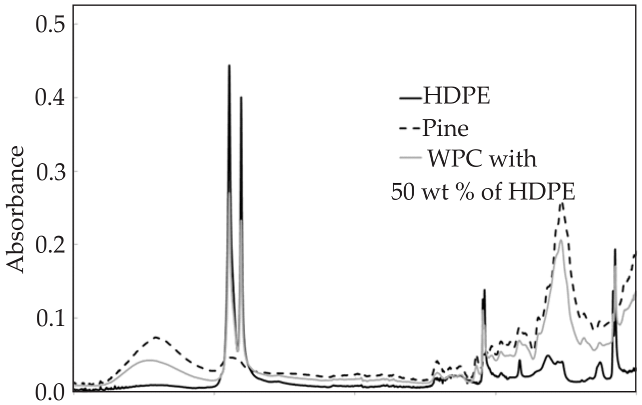

Fig. 8. Exemplary FT-IR spectra of pine wood, HDPE, and WPC with 50 wt % of HDPE

samples. Laboratory made composites and trade samples are not exactly compatible. Presence of different type or higher amount of additives in the samples with lower PP content may be the reason of such results. Homogeneity of WPC with lower polymer content causes more problems, because polymer plays a binder role. The additives may also decrease polymer viscosity or can work as binders for wood flour.

Comparing above mentioned results with these presented by Lao *et al*. [21], it must be stated that both methods are of similar quality. However, both the correlation coefficient of calibration curve (Fig. 7) and its range is higher.

Exemplary FT-IR spectra of pine wood-HDPE composite, pine and HDPE are presented in Fig. 8. There are a few significant differences between spectra presented in Figs. 6 and 8, both concerning pure polymers and composites. Absorption band below 1400 cm^{-1} is very small or invisible, while two peaks below 3000 cm^{-1} are more intense and easily observable. The identification of polymer type in analyzed composites is easily possible.

CONCLUSIONS

DSC is a very good method for determination of different polymer types and their content in WPC composites. This method is reasonably fast and requires samples of small mass. The results of the experiments show that analysis of commercial samples is easier and more reproducible, what is the advantage because the quality control of this kind of samples is the final target. Variation of polymer content values seems to be the main difficulty and is probably related to the low homogeneity of laboratory made samples. That is why preparation of small WPC samples in laboratory conditions should be performed with special care.

The insignificant, from the sample mass point of view, initial degradation may give thermal effect partially covering endothermic melting process. The analysis of the second DSC run gives the advantage of this matrix effect elimination.

Although FT-IR technique has a potential for polymer content measurements, some of commercial samples give different results than standard samples. Probably, additional substances being present in trade WPC composites disrupt the measurement. These substances are specific for each WPC manufacturer. That is why DSC technique is a better tool for polymer content determination.

The recognition of polymer type in composites is easily possible with FT-IR technique, which seems to be better for this purpose than DSC because of shorter experiment duration thanks to ATR unit. This is also non-destructive method what is additional, significant advantage.

REFERENCES

[1] Wilczyński K., Buziak K., Bartnik M.: *Polimery* **2016**, *61*, 195. https://doi.org/10.14314/polimery.2016.195

[2] Wilczyński K.J.: *Polimery* **2018**, *63*, 2013. https://doi.org/10.14314/polimery.2018.3.5

[3] Kruszelnicka I., Ginter-Kramarczyk D., Rudawska A. *et al*.: *Polimery* **2017**, *62*, 208. https://doi.org/10.14314/polimery.2017.208

[4] Kruszelnicka I., Ginter-Kramarczyk D., Michałkiewicz M.: *Polimery* **2018**, *63*, 619. https://doi.org/10.14314/polimery.2018.9.6

[5] Tryznowski M., Świderska A., Gołofit T. *et al*.: *RSC Advances* **2017**, *7*, 30 385. https://doi.org/10.1039/c7ra05455f

[6] Danon B., Görgens J.: *Thermochimica Acta* **2015**, *621*, 56. https://doi.org/10.1016/j.tca.2015.10.008

[7] Zhang X., Weeks B. L.: *Journal of Thermal Analysis and Calorimetry* **2015**, *122*, 1061. https://doi.org/10.1007/s10973-015-5005-2

[8] Tomaszewski W., Cieślak K., Zygmunt A.: *Polymer Degradation and Stability* **2015**, *111*, 169. https://doi.org/10.1016/j.polymdegradstab.2014.11.010

[9] Książczak A., Gołofit T., Tomaszewski W.: *Journal of Thermal Analysis and Calorimetry* **2008**, *91*, 375. https://doi.org/10.1007/s10973-007-8470-4

[10] Jeske H., Schirp A., Cornelius F.: *Thermochimica Acta* **2012**, *543*, 165. https://doi.org/10.1016/j.tca.2012.05.016

[11] Windt M., Meier D., Lehnen R.: *Holzforschung* **2011**, *65*, 199. https://doi.org/10.1515/hf.2011.024

[12] Mariotti N., Wang X-M., Rodrigue D. *et al*.: *Journal of Material Science Research* **2014**, *3*, 8. https://doi.org/10.5539/jmsr.v3n2p8

[13] Li L., Wang Q., Guo C.: *Journal of Thermal Analysis and Calorimetry* **2012**, *107*, 717. https://doi.org/10.1007/s10973-011-1776-2

[14] Zhang J., Rizvi G.M., Park C.B.: *Bioresources* **2011**, *6*, 4979.

[15] Ou R., Guo C., Xie Y. *et al*.: *Bioresources* **2011**, *6*, 4547.

[16] Gołofit T., Zielenkiewicz T., Gawron J.: *European Journal of Wood and Wood Products* **2012**, *70*, 907. https://doi.org/10.1007/s00107-012-0619-6

[17] Traore M., Kaal J., Martinez Cortizas A.: *Spectrochimica Acta A* **2016**, *153*, 63. https://doi.org/10.1016/j.saa.2015.07.108

[18] Drożdżek M., Zawadzki J., Zielenkiewicz T. *et al*.: *Wood Research* **2015**, *60*, 255.

[19] Migneault S., Koubaa A., Perre P. *et al*.: *Applied Surface Science* **2015**, *343*, 11. https://doi.org/10.1016/j.apsusc.2015.03.010

[20] Guan Y.H., Huang J.Q., Yang J.C. *et al*.: *Industrial and Engineering Chemistry Research* **2015**, *54*, 3524. https://doi.org/10.1021/acs.iecr.5b00123

[21] Lao W., Li G., Zhou Q. *et al*.: *Bioresources* **2014**, *9*, 6073.

[22] Colom X., Carrillo F., Nogués F. *et al*.: *Polymer Degradation and Stability* **2003**, *80*, 543. https://doi.org/10.1016/S0141-3910(03)00051-X

[23] Painter P.C., Watzek M., Koenig J.L.: *Polymer* **1977**, *18*, 1169. https://doi.org/10.1002/pol.1977.180150709

[24] Wilczyński K., Buziak K.: *Polimery* **2017**, *62*, 680. https://doi.org/10.14314/polimery.2017.680

Received 29 V 2018.