Effect of wood flour addition and modification of its surface on the properties of rotationally molded polypropylene composites

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Abstract: The aim of this study was to assess the effect of wood flour addition and the treatment of its surface on the properties and structure of rotationally molded (rotomolded) polypropylene. In this study, a random polypropylene copolymer (rPP) micropellet was rotationally molded with the direct addition of 5 wt % of commercial grade of wood flour Lignocel C120, untreated (WF) and chemically treated (mWF). Part of the natural filler was chemically modified by a silanization process using 3-aminopropyltriethoxysilane (3-APS). The structure, quality and mechanical properties of the polypropylene and composite rotomolded parts were discussed in terms of changes in the material's thermal properties, evaluated by differential scanning calorimetry (DSC), thermomechanical properties, obtained by dynamic mechanical-thermal analysis (DMTA), and dynamic rheological properties, assessed by oscillatory rheometry. The structure of composites and fillers was analyzed by means of a scanning electron microscopy (SEM), while the analysis of the chemical structure of materials and final products was carried out by a Fourier transform infrared spectrometry (FT-IR). It was found that adding the natural filler, despite the application of a preliminary drying and chemical treatment caused creation of the pores and decreased the overall mechanical properties of the composites. The lower processing ability of the composites was ascribed to a higher complex viscosity and an increase in the elastic behavior of molten composite materials in comparison to pure rPP.

Keywords: rotational molding, polypropylene, natural filler, natural composites, WPC.

Wpływ dodatku mączki drzewnej i jej modyfikacji powierzchniowej na właściwości kompozytów polipropylenowych otrzymywanych w procesie odlewania rotacyjnego

Streszczenie: Kompozyty polipropylenowe napełniane mączką drzewną otrzymywano metodą odlewania rotacyjnego. Rotowaniu poddawano kopolimer polipropylenowy (rPP) w postaci mikrogranulatu wraz z dodatkiem 5 % mas. niemodyfikowanej (WF) oraz modyfikowanej chemicznie (mWF) mączki drzewnej Lignocel C120, wprowadzonej razem z polipropylenem bezpośrednio do formy. Mączkę drzewną modyfikowano chemicznie w procesie silanizacji z zastosowaniem 3-aminopropylotrietoksysilanu (3-APS). Strukturę, jakość oraz właściwości mechaniczne odlewów polipropylenowych i kompozytowych omówiono w odniesieniu do zmodyfikowanych właściwości cieplnych ocenianych metodą różnicowej kalorymetrii skaningowej (DSC), właściwości termomechanicznych badanych za pomocą dynamiczo-mechanicznej analizy termicznej (DMTA) oraz właściwości reologicznych określanych techniką reometrii rotacyjnej. Strukturę kompozytów oraz napełniaczy badano z zastosowaniem skaningowej mikroskopii elektronowej (SEM). Zmiany struktury chemicznej napełniaczy oraz odlewów oceniano na podstawie rejestrowanych widm spektroskopii w podczerwieni z transformatą Fouriera (FT-IR). Stwierdzono, że mimo wstępnego suszenia i modyfikacji chemicznej napełniaczy naturalnych, ich dodatek do polipropylenu spowodował powstanie porowatej struktury w odlewach kompozytowych. Ograniczenie przetwarzalności kompozytów polipropylenowych napełnionych mączką drzewną przypisano zmianom ich właściwości reologicznych.

Słowa kluczowe: odlewanie rotacyjne, polipropylen, napełniacz naturalny, kompozyty naturalne, WPC.

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Rotational molding is a widely used technological process for the production of thin walled products, usually characterized by large dimensions. The main advantages in comparison to alternative processes are the inexpensive molds and the technological machines as well as a high technology flexibility. Simultaneously one of the biggest disadvantage accompanying to production of rotomolded (rotationally molded) castings is the necessity of using materials with specified geometrical characteristics and processing properties, especially rheological properties [1]. The increasing interest in rotational molding and the expansion of this technology in many industrial branches not only leads to an improvement of the quality and properties of the materials used up to date, but also enlarges their availability and stimulates the development of novel materials with lowered price. The possibility of manufacturing composite materials by rotational molding is gaining ground in the field of industrial and academic researches [1–3]. However, the production of rotomolded composite parts may be prepared in two different ways. The first approach considers the preliminary mixing of a polymeric matrix and fillers in a molten state by extrusion and the subsequent production of micropellets with defined geometry of composite granules [4]. Applying this method allows to obtain products with good dispersed filler in the final product, lowered ability to decrease surface quality and wall thickness homogeneity. However, each additional processing in molten state provides an increase of price of final product, and in the case of natural materials, it may cause thermal degradation, *e.g.*, of lignocellulosic filler. This phenomenon causes the development of a second method of polymer blends and composites production, *i.e.*, the application of polymers and fillers into the mold without preliminary mixing in molten state [5]. Despite the lowered dispersion of the filler and the possibility of its agglomeration during the melt processing in low-shearing conditions, the development of this processing method for different natural and still unused fillers may significantly reduce the production costs and simplify the application of novel composite materials in industrial conditions. As was observed for composite products manufactured by extrusion and injection molding [6–9], the application of natural fillers in rotational molding process is also gaining ground. Numerous works discuss the possibility of developing rotationally molded composites by means of natural fillers, including particle-shaped and fibrous materials such as wood flour [10], ground husks and shells from agricultural industry [11] or sisal [12], banana, abaca [13] and agave fibers [14]. In most cases, natural plant fillers are incorporated into various grades of polyethylene due to the relatively low temperature conditions during processing. Only a few works discuss the processing possibilities of natural composites based on different thermoplastic polymers [11, 15]. It's worth mentioning that the results shown by the literature are not unanimous. Adding natural fibers in low amounts into a polyethylene matrix may provide an increase in some mechanical properties such as tensile and flexural modulus, tensile strength and hardness of rotationally molded products [14, 16]. However, other studies show a decrease in those mechanical properties [17]. Improvement of mechanical properties and an adhesion between hydrophobic polyethylene matrix and hydrophilic natural filler in case of rotationally molded composites may be realized by compatibilization or modifying the filler surface including: alkali treatment with NaOH, aldehyde treatment, maleated polypropylene treatment, acrylic acid treatment, methyl methacrylate treatment or silane treatment [17, 18]. In case of polyethylene-based rotationally molded composites, applying these modification methods allows to obtain a better adhesion between composite ingredients and improve their mechanical properties, especially the elasticity modulus [17].

The aim of this work was to evaluate the influence that wood flour and the modification of its surface by silanization using 3-aminopropyltriethoxysilane (3-APS) in order to improve the compatibility with polypropylene matrix has on the properties of rotationally molded composites. The impact that adding untreated and modified fillers has on the mechanical and thermomechanical properties, as well as on the structure of polypropylene-based composites has been discussed, taking into consideration the changes in their thermal and rheological behavior. The main assumed benefit of direct incorporation of the low-cost natural filler into the mold with polypropylene micropellet, without preliminary mixing of the composites in molten state may be significant lowering the final product price.

EXPERIMENTAL PART

Materials

– The commercial random polypropylene copolymer (rPP) HD eco-tech® RM PPL 111050 UV (HD Kunstoffe GmbH, Germany) dedicated for rotational molding applications was used in this study. The melt flow index of rPP was 11 g/10 min (230 °C, 2.16 kg), while the polymer density was 0.902 g/cm³.
– Wood flour (WF) Lignocel C120 (Rettenmeier & Sohns, Germany) with particle size in the range of 70 to 150 µm was used as the natural filler.
– 3-aminopropyltriethoxysilane (3-APS) U-13, delivered by Unisilan (Poland) was used as the filler modifier.

Modification of natural wood flour

Part of the natural filler was chemically modified by 3-aminopropyltriethoxysilane. The natural filler (WF) was dried for 24 h at 80 °C before the chemical treatment. 2 wt % of 3-APS, corresponding to the weight percentage of filler, was hydrolyzed in a 50 : 50 v/v mixture of ethanol and water. After that unmodified and preliminary dried wood flour was incorporated into a solution of ethanol-water containing 3-APS and stirred for 1 h with a mechanical mixer. After that, the mixture was placed in
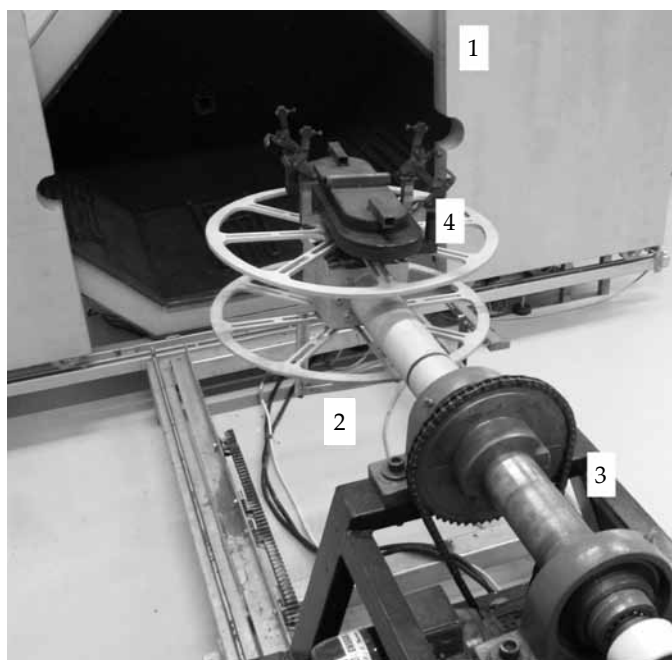
Fig. 1. Single-arm shuttle rotational molding machine: 1 – oven, 2 – clamping space, 3 – gear, 4 – steel mold

plates and dried at 80 °C for 24 h in order for ethanol and water to evaporate [19]. After drying, the modified filler (mWF) was sieved with a sieve of 400 μm mesh.

Sample preparation

The manufacturing of rotationally molded parts was carried out by means of the single-arm shuttle rotational molding machine REMO GRAF (Poznań, Poland), equipped with a production flat steel mold (Fig. 1). The total amount of material used for the manufacturing of each part was 320 g. After placing the polymer with the adequate amount of WF/mWF, the mold was closed and subjected to rotation with a rotational speed of 15 rpm (1st axis) and 5 rpm (2nd axis) and placed in a forced con-

vection oven set at 250 °C. The measured temperature inside the oven after 20 min of process was around 200 °C. Samples were processed for 60 min and later cooled for 35 min in forced cold airflow.

In Fig. 2 rotationally molded parts are presented. A visible defect in a form of incomplete mold fill in the bottom was observed in case of all parts. It's worth mentioning that only the upper part of the rotationally molded casting ascribed as P was a product ready to use. Adding both types of wood flour causes an enlargement of aforementioned holes in a place of mold clamping and an increase in the internal surface roughness, which is an effect of the modified thermal conductivity of the composite material as well the modification of the rheological properties of composites, described further in this work. It cannot be excluded that increased defects size in case of composite parts results from difficulties in pouring of polypropylene pellets during rotation caused by presence of wood flour, despite only 5 wt % of the filler was incorporated, the volumetric amount of natural filler was much higher.

Methods of testing

– Both fillers were subjected to moisture content evaluation by the moisture analyzer Axis BTS 100 (Axis, Poland). Measurements were carried out after calibration at a period of 10 min at 105 °C. Moisture content was calculated according to following formula:

$$W_\% = \frac{m_0 - m}{m_0} \cdot 100 \ \% \tag{1}$$

where: $W_\%$ – moisture content [%], m_0 – initial mass [g], m – sample mass after test [g]. Moisture content depends on the surface modification and was equal to 7.2 % for unmodified wood flour (WF) and 6.1 % for modified wood flour (mWF). Therefore, each processing in molten state was preceded by a drying process (80 °C, 24 h).
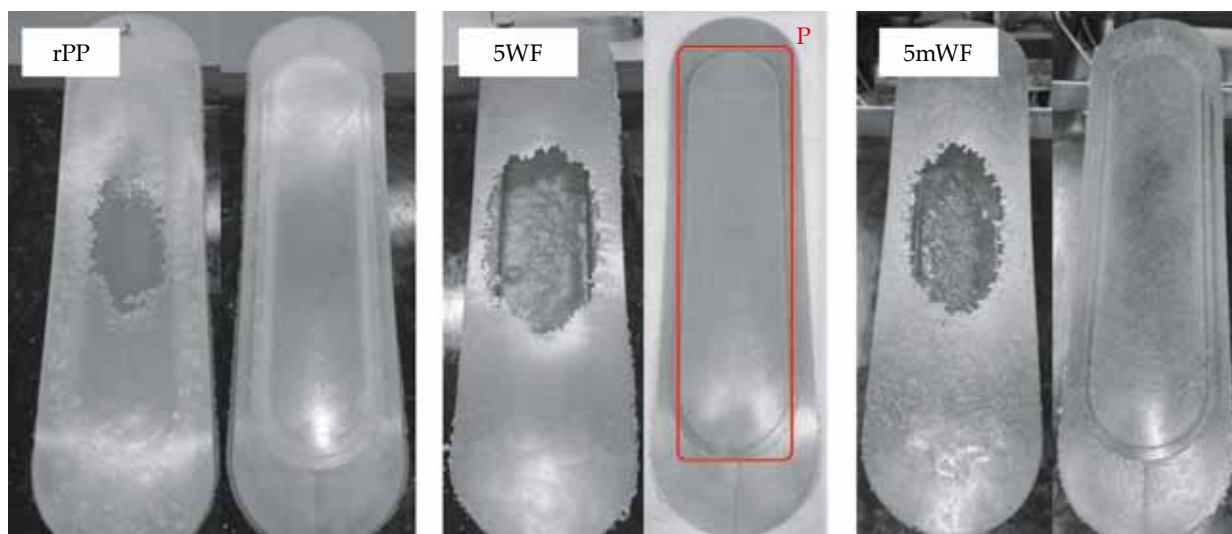

Fig. 2. Rotationally molded products made from: rPP – random polypropylene copolymer, 5WF –composite based on rPP with 5 wt % of wood flour, 5mWF – composite based on rPP with 5 wt % of modified wood flour

– Thermal stability of unmodified and modified fillers was determined by thermogravimetric analysis (TGA) realized under nitrogen atmosphere, using a TG 209 F1 Netzsch apparatus. 5 ± 0.1 mg samples were placed in aluminum pans. Two different experiments were realized under nonisothermal and isothermal conditions. Nonisothermal experiments were conducted in temperature range of 30 °C to 600 °C at a heating rate of 10 °C/min, while isothermal experiments were realized at 200 °C and time 90 min after preliminary heating with heating rate of 10 °C/min. The initial decomposition temperature was determined as a temperature at which the weight loss was 5 % (W5%). Additionally, thermal decompositions at 10 % and 50 % weight loss (W10% and W50%) were presented. The residual mass was defined at about 600 °C. Decomposition temperature was determined according to A.K. Bledzki *et al.*, as a temperature corresponding to 1 % mass loss above mass value measured at 150 °C [20].

– The Fourier transform infrared spectroscopy (FT-IR) measurements were conducted by means of a spectrometer Jasco FT/IR-4600, at room temperature (23 °C) in mode of attenuated total reflectance (ATR-FTIR). A total of 128 scans at a resolution of 2 cm^{-1} was used in all cases to record the spectra. All spectra, including the H_2O and CO_2, were submitted to weather correction. Carbonyl index (*CI*) on the basis of ATR-FTIR measurements was calculated according to following equation [21]:

$$CI = \frac{A_{1775}}{A_{2820}} \qquad (2)$$

where: A_{1775} – absorbance of carbonyl group (-CO-), A_{2820} – absorbance of reference peak.

– The scanning electron microscope (SEM), model Vega 5135MM produced by the Tescan (Czech Republic), was used in order to assess the structure of composites. The structures of the rotationally molded samples were assessed with a Back Scattered Electron signal (BSE) and a Secondary Electron signal (SE) with an accelerating voltage of 12 kV. All photographed samples were broken after being cooled in liquid nitrogen below the rPP glass transition temperature.

– The density of composites was examined by an immersion method using the Axis AD 200 equipped with a set to determine the density of solids. The study was carried out in accordance with the methodology described in the PN-EN ISO 1183-1 standard. When it comes to the immersion liquid, ethanol was used, and measurements were made for 10 samples from each series.

– Rheological investigations in small-amplitude oscillation shearing mode were carried out using an Anton Paar MCR 301 rotational rheometer with 25 mm diameter parallel plates. The experiments were conducted at 200 °C. The strain sweep experiments were realized before carrying out the dynamic oscillatory frequency sweep measurements. The strain amplitude sweep experiments of rPP and rPP-WF/mWF samples were performed at 200 °C with a constant angular frequency 10 Hz in the strain window of 0.01–100 %. The strain value determined during the preliminary investigations and used during the frequency sweep experiments was set at 0.5 %. An evaluation of zero shear viscosity (η_0) was possible due to the rheological measurements in oscillatory mode and the calculations that were performed applying the Rheoplus 32 v.3.40. Zero shear viscosity was determined by the Carreau-Yasuda model fitted to the experimental data. The Carreau-Yasuda model has been described by the following equation:

$$\eta(\dot{\gamma}) = \eta_0 \cdot [1 + (\lambda \cdot \dot{\gamma})^a]^{\frac{n-1}{a}} \qquad (3)$$

where: η_0 – zero shear viscosity, n – power law coefficient, a – adjustable exponent (equal 2 for the simple Carreau model), $\dot{\gamma}$ – shear rate, λ – characteristic time [22, 23].

– A differential scanning calorimetry (DSC) test was performed using a Netzsch DSC 204 F1 Phoenix® with aluminum crucibles and 5 ± 0.1 mg samples under a nitrogen flow. All the samples were heated to 200 °C, held in molten state for 10 min and then cooled to 20 °C at a cooling rate of ϕ = 10 °C/min. This procedure was conducted twice to evaluate the DSC curves from the second melting. The crystallinity degree (X_c) was evaluated on the basis of the melting heat (ΔH_m) during crystallization at a cooling rate of 10 °C/min. The crystallinity degree of pure rPP and rPP-WF/mWF composites was calculated using the following equation:

$$X_c = \frac{\Delta H_m}{(1 - \phi) \cdot \Delta H_0} \cdot 100 \% \qquad (4)$$

where: ΔH_0 – the melting heat of entirely crystallized iPP (its value is equal to 207.1 J/g), ϕ – the filler amount [24].

– The dynamic mechanical-thermal analysis (DMTA) test was performed using an Anton Paar MCR 301 rheometer equipped with a torsion DMA measuring tool. The investigations were carried out at a constant frequency of 1 Hz and a strain of 0.01 %. All samples were evaluated in a temperature ranging from -60 °C to 110 °C with a temperature rate of 2 °C/min.

– The mechanical properties of samples from rPP and rPP-WF/mWF composites were determined with a static tensile test according to European standard ISO 527, by means of an Instron 4481 universal testing machine with 50 kN nominal force. The tests were conducted with 50 mm/min cross speed. The hardness evaluation was carried out using a Sauter HBD 100-0 Shore D hardness tester according to ISO 868 standard.

RESULTS AND DISCUSSION

Characterization of filler

In Fig. 3 the results obtained during nonisothermal thermogravimetric analysis in a form of TG and DTG curves are presented. Moreover, detailed information about fillers thermal decomposition parameters are col-
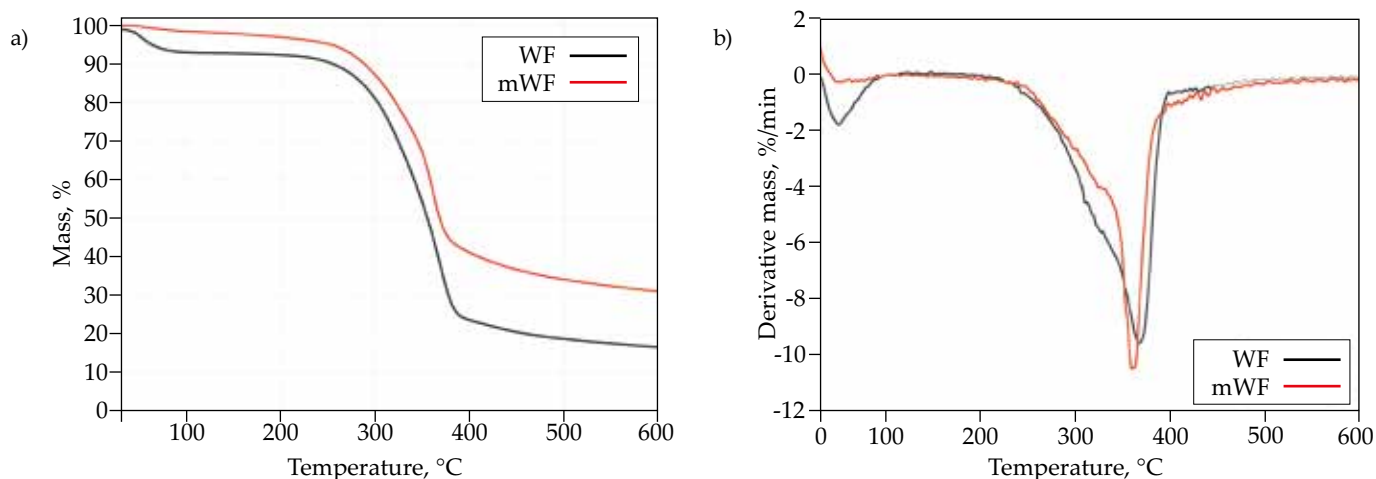
a)

b)

Fig. 3. a) TG, b) DTG curves of unmodified (WF) and modified (mWF) fillers

T a b l e 1. **Thermal degradation parameters obtained by nonisothermal TGA**

Material	W5% °C	W10% °C	W50% °C	Decomposition temperature °C	Residual mass at 600 °C %
WF	63.5	254.8	355.1	207.0	16.58
mWF	252.9	288.2	368.2	228.5	31.02

lected in Table 1. On the basis of temperature values measured at 10 % and 50 % mass loss, it can be stated that modification with 3-APS of wood flour increase its thermal stability. Calculated decomposition temperature for WF was 207.0 °C and 228.5 °C for mWF, this fact confirms that natural filler after silanization reveal higher thermal stability than unmodified one. Two-step decomposition observed for WF was connected with water evaporation, this result confirms previously mentioned higher moisture content in unmodified filler and its higher ability to water absorption. Thermal parameters of natural fillers are in a good agreement with literature data [25].

The results of additional filler thermal stability analysis evaluated at isothermal conditions are presented in

Fig. 4. Red dashed lines correspond to the beginning of isothermal annealing process after preheating and the end of the measurement after 60 minute exposure to elevated temperature. It can be seen that after 60 min annealing of wood flour 1.47 % and 2.16 % mass loss of, correspondingly, WF and mWF was observed, therefore it can be presumed that no significant degradation process occur during holding the natural fillers at a processing temperature (200 °C). DTG curves present two maxima, the first one can be related to water evaporation during preheating of the sample, while the second one is a result of changing the measurement conditions, from nonisothermal to isothermal. To summarize, it can be seen that both fillers reveal thermal stability adequate to used during processing temperature of 200 °C with no serious risk of thermal degradation.

FT-IR spectra of untreated and silanized wood flour are presented in Fig. 5. In order to evaluate the influence of processing conditions on chemical structure of lignocellulosic filler, both filler types were heated in an oxida-
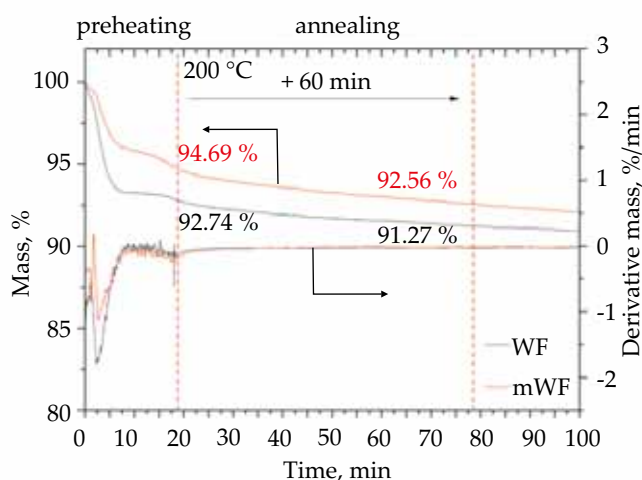

Fig. 4. TG and DTG curves obtained during isothermal measurements conducted for WF and mWF
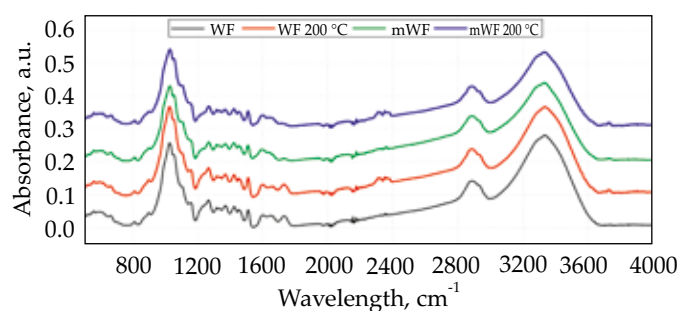

Fig. 5. FT-IR spectra of natural fillers (WF, mWF) before and after annealing at 200 °C, presented in the range from 500 to 4000 cm⁻¹
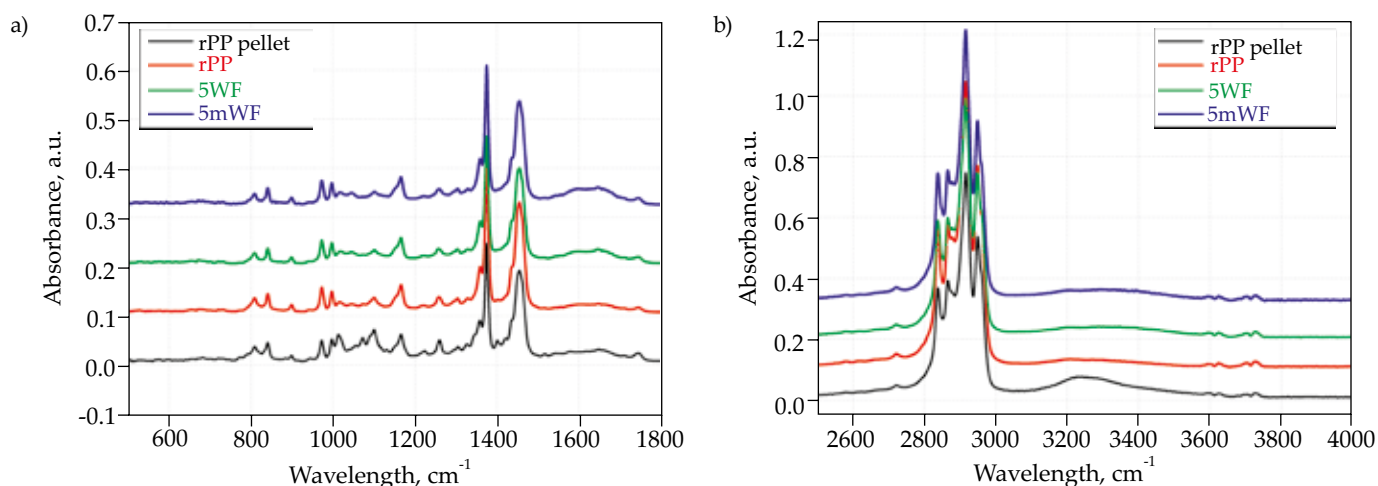
Fig. 6. FT-IR spectra of rotationally molded samples and pure rPP micropellet, presented in the range from: a) 500 to 1800 cm^{-1}, b) 2500 to 4000 cm^{-1}

tive atmosphere at a temperature of 200 °C and time corresponding to the processing time (60 min). According to Fig. 5, there were no significant changes in FT-IR spectra between pure and modified samples.

Moreover, only minor differences occurred after the annealing process. Several characteristics for lignocellulosic fillers bands were observed in all fillers, *i.e.*: OH stretching vibration within the region of 3200–3500 cm^{-1}, aliphatic CH$_2$ stretching vibration at 2886 cm^{-1}, C-H stretching vibration of hemicellulose and pectin at 1509 cm^{-1}, acetyl groups of lignin at 1264 cm^{-1} and C-O/C-C stretching vibration at 1026 cm^{-1} [26, 27]. The treatment of wood flour with 3-APS causes changes in the FT-IR spectra at 1200 cm^{-1} attributed to the presence of a Si-O-C band, visible for samples after annealing. The remaining bands corresponding to silanization reaction – such as Si-O-Si broad peak at 1050 cm^{-1}, Si-C symmetric stretching bond at 765 cm^{-1} and Si-O-Si symmetric stretching at 465 cm^{-1} were overlapped by bonds related to the complex chemical structure of wood [27]. Moreover, after the silanization process, the absorption band at 1730 cm^{-1} ascribed to C=O stretching vibration of hemicellulose and pectin decayed. What should be mentioned that, in reference to the conducted ATR-FTIR analysis, both filler types (untreated and chemically treated) were not affected by annealing.

Characterization of composites

Chemical structure analysis

Figure 6 presents the spectra of pure rPP in form of micropellet and samples taken from rotationally molded parts made from rPP and rPP-WF/mWF composites. In all figures, the dominant bands are attributed to a typical polypropylene/polyethylene copolymer, *i.e.*, rocking vibration of CH$_2$, stretching vibration of CH and CH$_3$ groups (810 cm^{-1}, 841 cm^{-1}), rocking vibration of CH$_3$, CH$_2$ and CH (899 cm^{-1}, 975 cm^{-1}), wagging vibration of CH$_3$, deformation vibration of CH$_2$ and CH (1170 cm^{-1}), CH$_2$-CH

wagging vibration (1357 cm^{-1}), symmetrical vibration deformation of CH$_3$ (1376 cm^{-1}), asymmetrical vibration deformation of CH$_3$ (1455 cm^{-1}), CH$_2$ symmetrical stretching vibrations (2837 cm^{-1}), CH$_3$ shifted symmetrical stretching vibrations (2866 cm^{-1}), asymmetrical vibration stretching of CH$_2$ (2915 cm^{-1}) and shifted asymmetrical stretching vibration of CH$_3$ (2949 cm^{-1}) [28]. The carbonyl index for rotationally molded samples and the pure polymer without thermal treatment were calculated according to Eq. (1). The following values of *CI* were obtained: 0.497 (rPP pellet), 0.328 (rPP), 0.415 (5WF), 0.556 (5mWF). *CI* was below 1 in all the assessed materials, therefore according to the literature [21], it's possible to affirm that both polymer and the composite samples were not thermally damaged and depredated during the rotational molding process.

Structure evaluation

A scanning electron microscope (SEM) was used to obtain information about structural changes in polypropylene and polypropylene-based composites rotationally molded samples induced by the incorporation of natural fillers. SEM images made with 50 and 200× magnification of cross-sections of brittle fractured materials are presented in Fig. 7. Pores were observed in both composite samples. Mean value of pore diameter evaluated in separate analysis realized with using of optical microscope was 0.24 ± 0.05 mm for 5WF and 0.12 ± 0.03 mm for 5mWF. Despite applying a preliminary drying process, adding natural filler causes an evaporation of residual water during the long-term processing in elevated temperature and/or the release of small amount of gaseous products resulting from the thermal degradation of the filler. Thanks to the SEM images prepared with higher magnification, it was possible to determine the differences in composite structure between composite materials containing pure and modified wood flour. In the case of the composite sample containing WF filler, holes are clearly visible after pulling out natural particles, while in the case of compos-
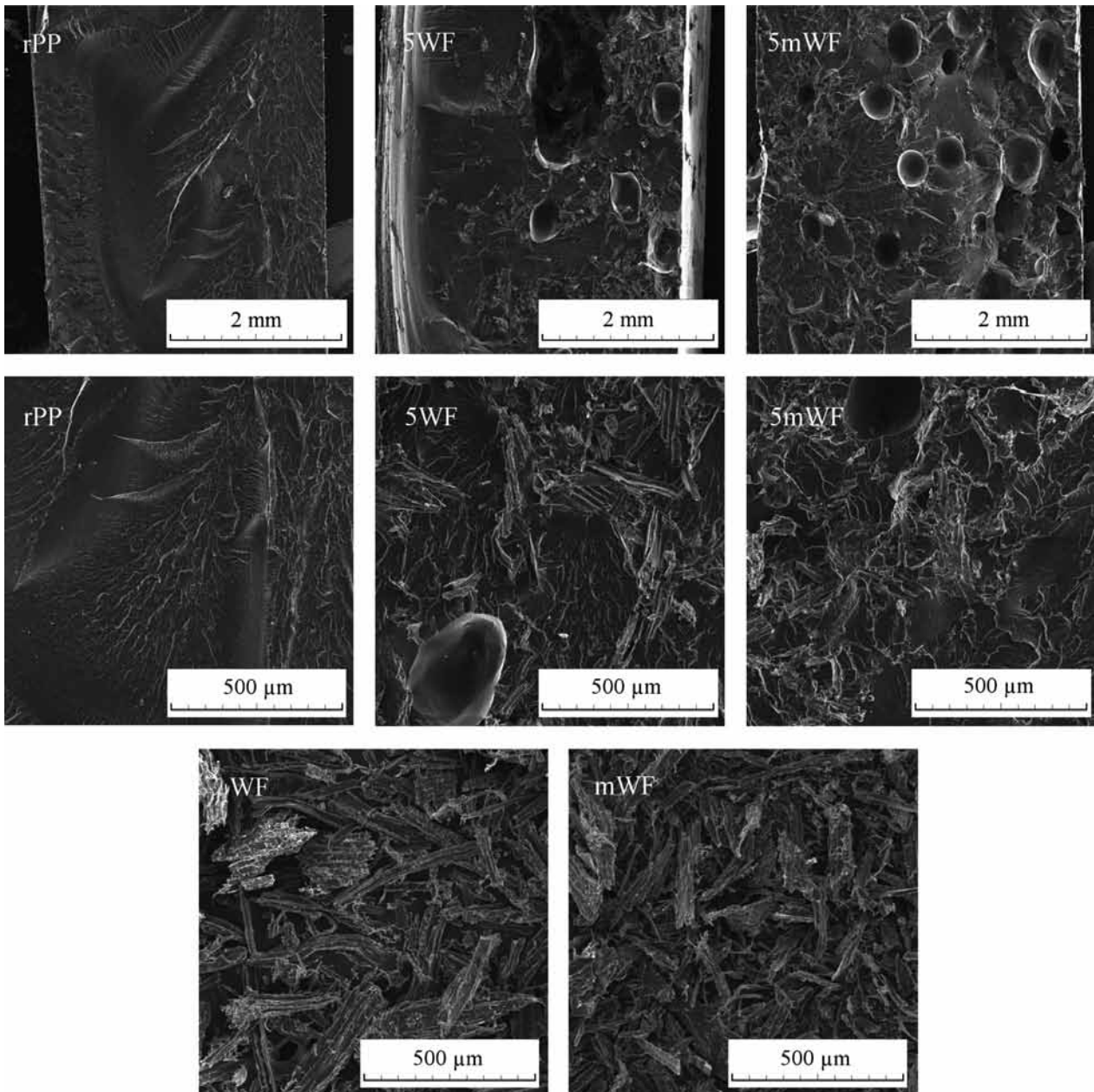
Fig. 7. SEM images of rotationally molded samples (rPP, 5WF, 5mWF) cross-sections, magnification 50× and 200×, and fillers (WF, mWF), magnification 200×

ites with mWF, the filler particles are well saturated with polymeric matrix. The analysis of filler structure was also supplemented by its structural analysis. Comparing both filler types allows to infer that the application of a silanization process (including mechanical stirring) causes a reduction of wood flour particle size. That conclusion may be referred to results presented by Girones *et al.*, who discussed the pine fiber nucleating ability on PP and the reduction of fiber length due to the silanization process [29].

Physical properties

Density of rotomolded polypropylene and polypropylene-based composite samples evaluated by an immersion method was 0.876 ± 0.004 g/cm^3 for rPP, 0.879 ± 0.013 g/cm^3 for 5WF and 0.905 ± 0.009 g/cm^3 for 5mWF. The difference between measured density and value presented by producer in technical datasheet of pure polymer results from micropores occurrence which are hindering in polymer melt during solidification of rotomolded parts. Additionally, on the basis of the components' amount, the density of polypropylene and referred to density of wood cell structure (1.45 g/cm^3) theoretical density of composites was calculated (1.075 g/cm^3). Lack of significant increase of composite materials density results from observed by SEM analysis creation of macrospores in composite structure. The differences between measured composites densities and theoretical density, confirm presence of porous structure of 5WF and 5mWF composite and higher amount of the pores in case of composite filled with unmodified filler.
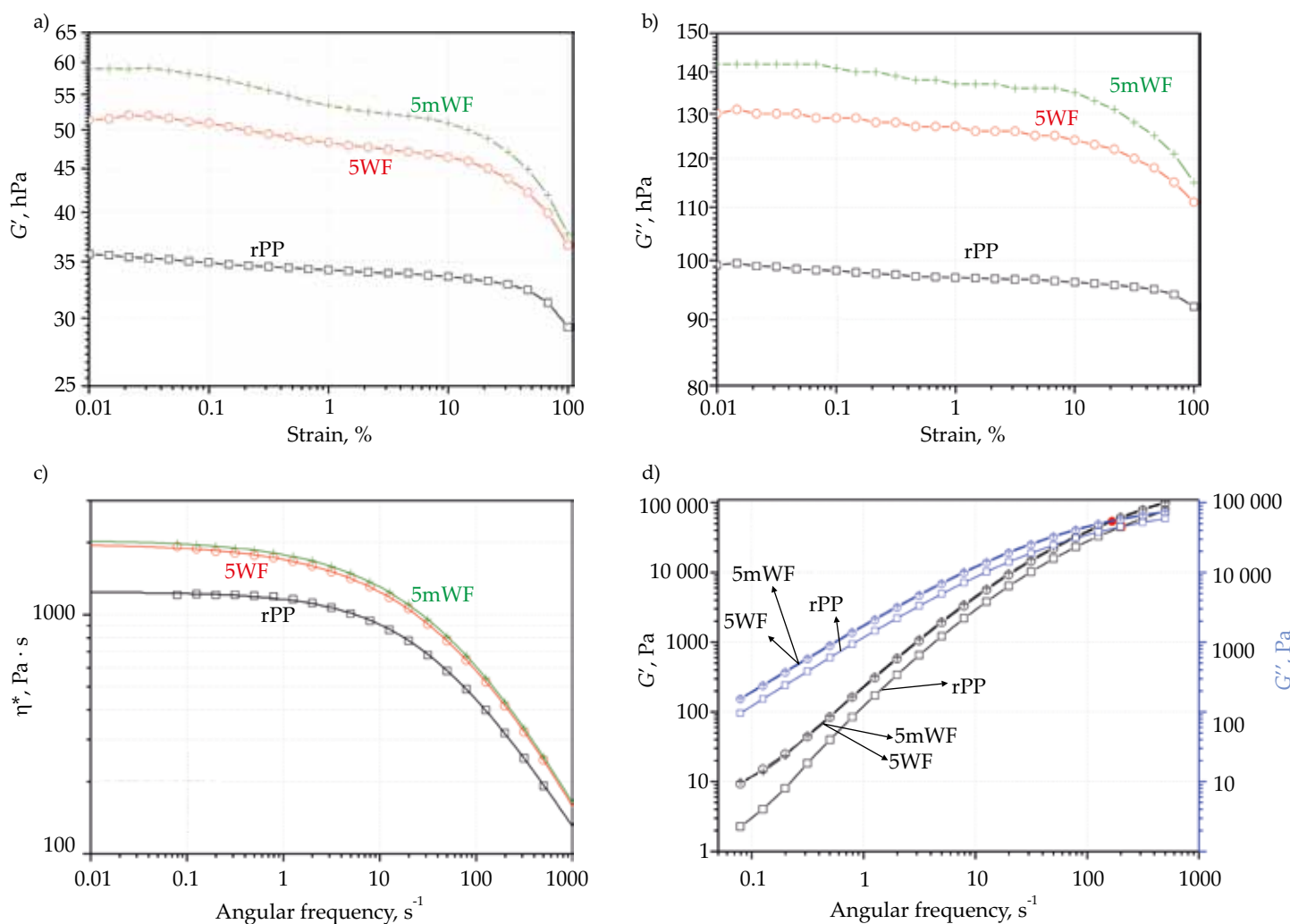
a)

b)

c)

d)

Fig. 8. Rheological properties of rPP and rPP-based composites obtained during: a, b) strain sweep test, c, d) frequency sweep test

Rheological properties

Figures 8a, 8b present the storage (G') and loss modulus (G'') changes of rPP and rPP-based composites measured during the strain sweep test. As can be seen, the application of wood flour into random copolymer results in a shift of the linear viscoelastic region range into lower strain values. Moreover, in case of both composite samples increases of storage and loss modulus were observed. This phenomenon is a result of creating rigid-structures of agglomerated wood flour particles in the polymeric matrix [30, 31]. The difference between the composites containing WF and mWF is mostly caused by changes in the wood flour's particle size, resulting from additional shear rates occurring upon mechanical stirring during the silanization [29]. However, we can't exclude that the increase in both moduli observed during the strain sweep experiments may be caused by changes in the interfacial interactions between polypropylene chains and 3-APS functionalized organic natural filler. The modification of rPP by WF and mWF also provides changes in the dynamic rheological behavior evaluated during the frequency sweep experiments (Figs. 8c, 8d). The point marked in red on G', G'' vs. ω curves cross-over points for

rPP-WF/mWF composites are shifted to lower angular frequency ranges, which suggests their more elastic rheological behavior than pure rPP [32]. In Fig. 8d increase of G' and G'' modulus was denoted, which may be attributed to intrinsic rigidity of lignocellulosic structures [30]. It can be seen that the difference between WF- and mWF-filled composites is negligible, which in reference to the strain sweep experiments confirms the creation of strain sensitive agglomerated structures of the filler in the polymeric matrix. The relatively lower increase of both moduli, considered as a function of angular frequency, results mainly from the solidification of polypropylene chains on the filler's surface [30]. The observed modification of dynamic rheological behavior described by variations of G', G'' and η^* (complex viscosity) as a function of angular frequency are in good agreement with literature data [30, 32, 33]. The higher the wood flour content, the higher the complex viscosity values observed (Fig. 8c). The increase of elastic rheological behavior and the increased viscosity, together with the modification of the composites' thermal conductivity, are the main reason why there are limitations in proper processing of rPP-based WPC composites by rotational molding. Moreover, increase of molten composites viscosity may be the reason of porous structure creation,

T a b l e 2. **Rheological data obtained during oscillatory rheological experiments**

Material	Carreau-Yasuda model		Cross-over point	
	η_0 Pa · s	R^2	$G' = G''$ Pa	ω 1/s
rPP	1242	0.9995	$4.53 \cdot 10^4$	203
5WF	1973	0.9999	$5.35 \cdot 10^4$	167
5mWF	2228	0.9999	$5.58 \cdot 10^4$	169

because of more difficult removal from the melt trapped between polypropylene micropellets and wood flour particles air residues.

Despite the fact that the strain sweep experiments suggest a hindrance of lignocellulosic particles and the creation of its agglomerated structures, the only effect of wood flour addition was the increase of complex viscosity. In all considered materials (rPP and composites), a Newtonian plateau on viscosity curves was observed. This fact allows an appropriate fitting of the Carreau-Yassuda model to the experimental data. Detailed information about rheological data based on the fitting of the Carreau-Yasuda model and cross-over point can be seen in Table 2, including zero shear viscosity (η_0) and the regression coefficient (R^2).

Thermal properties

DSC heating and cooling curves of rPP and rPP-WF/mWF are presented in Fig. 9. Supplementary DSC thermal parameters, such as crystallization temperature (T_C), melting temperature (T_M), melting enthalpy (ΔH_m) and crystallinity level (X_c) are collected in Table 3. The courses of DSC melting curves differ between first and second heating. During the first heating, one peak was denoted (137 °C), while after erasing the thermal history of the samples and cooling in controlled conditions, two distinct peaks were observed (132 °C and 141 °C). This phenomenon is an effect of a low presence of ethylene content in the rPP copolymer. The slow cooling of rotationally molded parts provides a development of higher crystallinity, which in effect caused the over-
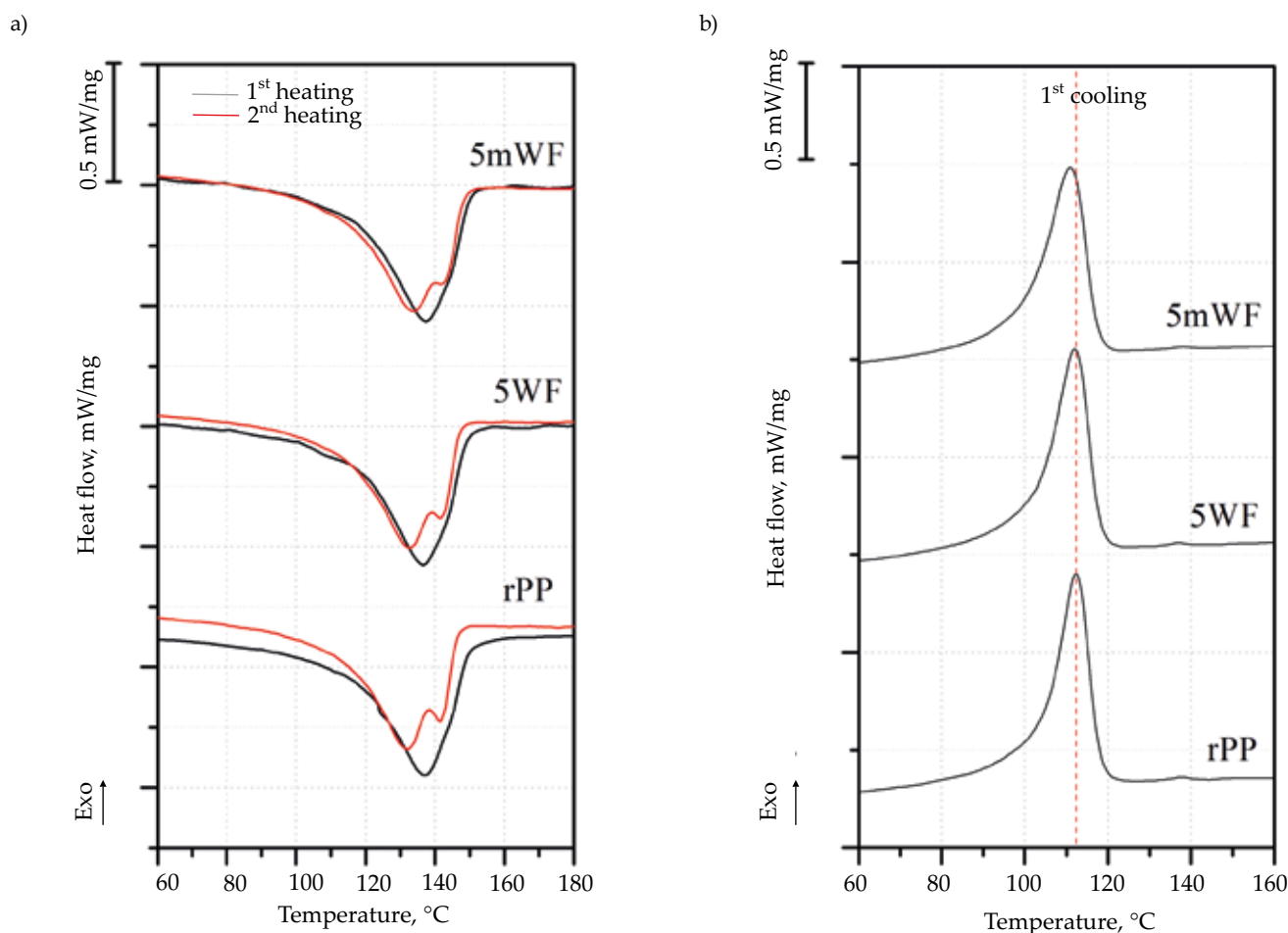
a)

b)

Fig. 9. DSC: a) melting, b) cooling curves of rPP and rPP-based composites presenting thermal property changes induced by incorporation of the natural filler

T a b l e 3. **Thermal parameters of rPP and rPP-based composites obtained from DSC**

Material	T_{M1} °C	$T_{M2\,I}$ °C	$T_{M2\,II}$ °C	T_C °C	ΔH_{m1} J/g	X_{c1} %	ΔH_{m2} J/g	X_{c2} %
rPP	137.0	131.9	141.4	112.3	99.07	47.8	89.81	43.4
5WF	137.5	132.7	141.5	112.0	101.30	51.5	90.73	46.1
5mWF	136.7	133.7	141.8	110.9	106.30	54.0	93.71	47.6

lapping of melting peaks of ethylene and propylene content in the copolymer. The melting temperature during the first heating was not influenced by the addition of both filler types. The values of the first DSC melting peak recorded during the second heating, applying WF and mWF, slightly increased. Moreover, a higher $T_{M2\,I}$ was observed in the modified filler. $T_{M2\,II}$ values were comparable between all considered materials. In composite samples, the observed values of crystallization temperature were smaller than in the unmodified rPP. Moreover, the T_C was lower in mWF-filled composites than in those containing untreated filler. The crystallinity of rPP composites increased in comparison to the pure polymer. The lignocellulosic filler revealed a nucleating ability; its addition caused a 2.7 % and a 4.2 % increase of X_c for WF and mWF, correspondingly. It should be underlined that the rPP used in this study was commercial nucleated grade, therefore each improvement of crystallinity confirms the high nucleating ability of wood flour on rPP. The higher crystallinity level of the composite containing mWF, in comparison with the WF-filled rPP sample, is in good agreement with the literature. Modifying natural fillers with silane-based coupling agents affects their efficiency to modify the crystallization of polyolefins [29]. The same tendency was observed in both heating procedures, therefore it can be stated that the observed modification of rPP crystallinity is the synergistic effect of adding lignocellulosic filler and modifying the surface, which is independent on cooling conditions occurring during the rotomolding process.

Dynamic thermomechanical properties

The dynamic mechanical properties, *i.e.*, storage modulus (G'), loss modulus (G'') and damping factor (tanδ) of random polypropylene copolymer and its composites filled with natural fillers as a function of temperature are presented in Fig. 10. In the considered temperature range, two polypropylene relaxations (β and α) are observed. The dominant β-relaxation (about 0 °C) is ascribed to the glass-rubber transition of amorphous regions in crystalline polypropylene. α-relaxation (35–90 °C) is attributed to changes in polypropylene crystalline phase. However, its intensity evaluated by DMTA analysis depends on various factors, such as the polymeric material's structure or density [34–36]. The influence of adding wood flour into polypropylene matrix on both storage and loss modulus could be observed. Moreover, the intensity of this modification was intensified by the silanization of wood flour. G' and G'' values were lower for composite materials than for neat polypropylene in the whole considered temperature range. Those results

are in good agreement with the results of the mechanical static tensile test due to the lack of reinforcing effect of natural filler and the decrease of sample stiffness subjected to dynamic load in elastic deformation range. The analysis of damping factor changes caused by the incorporation of both types of wood flour showed a decrease of tanδ intensity peak at local maxima attributed to α- and β-relaxations. The lowered values of damping factor are connected with the decreased ability of mechanical vibrations dissipation. Despite that in most of the studies presented in the literature adding wood flour to semi-crystalline polymeric matrix causes an increase of G' and a decrease of tanδ value with increasing content of the filler [37], the lowered damping properties in this case were not expected due to the porosity of composite materials observed in SEM images. The described dynamic mechanical behavior of rotomolded composites is a complex result of opposite effects, mainly: reinforcement caused by the modification of polymeric matrix crystallinity, presence of lignocellulosic rigid structures in the composite matrix and creation of pores as an effect of residual water release and/or gaseous degradation products from organic natural filler. Detailed information about the thermomechanical properties obtained by DMTA is collected in Table 4. Additionally, the effectiveness of fillers (C) on the storage modulus changes was calculated according to following formula:

$$C = \frac{(E_g'/E_r')\mathrm{comp}}{(E_g'/E_r')\mathrm{matrix}} \qquad (5)$$

where: E_g', E_r' – values of storage modulus measured in glassy and rubbery state [38]. The higher the value of constant C, the lower the effectiveness of the filler (Table 4). It can be seen that the rotationally molded sample filled with mWF was characterized with a lowered modification effectiveness calculated according to Eq. 5.

Mechanical properties

The results of mechanical properties obtained from the tensile test experiment and the hardness evaluation are presented in Table 5. Incorporation of wood flour highly influenced the mechanical properties of rPP. Both composite series reveal a lower ability to stress transfer during static load. Adding 5 wt % of WF and mWF caused a 29 % and a 40 % decrease of tensile strength in comparison with pure rPP. The same tendency occurs in the case of sample stiffness evaluation. However, both filler types decreased the composites' elasticity comparably, *i.e.*, about 9 % lower than the reference material. The reduc-
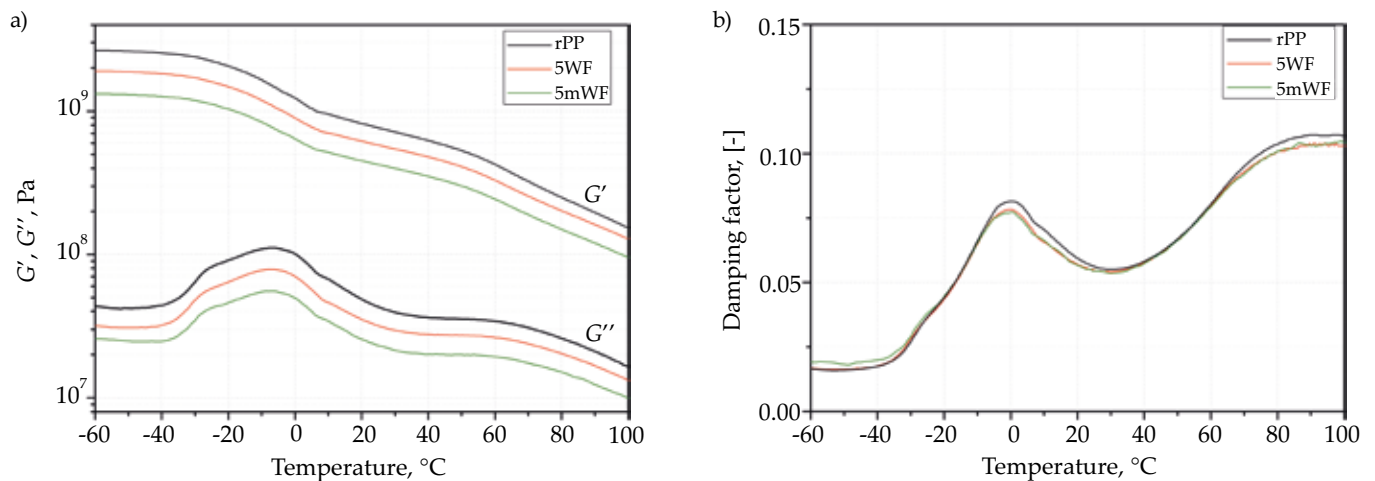
a)

b)

Fig. 10. Thermomechanical properties of rotomolded samples: a) storage modulus (G') and loss modulus (G''), b) damping factor (tanδ) *vs*. temperature obtained by DMTA

T a b l e 4. **Selected thermomechanical parameters and *C* factor obtained from DMTA measurements**

Material	$G'_{-60\,°C}$ Pa	$G'_{20\,°C}$ Pa	$G'_{60\,°C}$ Pa	$G'_{100\,°C}$ Pa	T_G °C	tanδ at T_G	C
rPP	$2.64 \cdot 10^9$	$8.16 \cdot 10^8$	$4.27 \cdot 10^8$	$1.17 \cdot 10^8$	0.3	0.082	–
5WF	$1.90 \cdot 10^9$	$6.15 \cdot 10^8$	$3.31 \cdot 10^8$	$9.91 \cdot 10^7$	1.1	0.078	0.85
5mWF	$1.32 \cdot 10^9$	$4.52 \cdot 10^8$	$2.44 \cdot 10^8$	$7.40 \cdot 10^7$	0.4	0.078	0.93

T a b l e 5. **Static tensile test results and hardness of polypropylene and polypropylene composites**

Material	Tensile strength MPa	Elasticity modulus MPa	Elongation at break %	Hardness °ShD
rPP	25.67 ± 0.04	702.5 ± 101.8	211.0 ± 82.2	65.1 ± 1.8
5WF	18.24 ± 3.08	636.5 ± 110.08	10.7 ± 4.56	58.2 ± 5.9
5mWF	15.53 ± 1.26	641.7 ± 108.26	7.32 ± 2.25	60.7 ± 4.7

tion of elongation at break is a typical behavior observed in thermoplastic polymeric composites filled with wood flour or another natural particle-shaped filler [39, 40]. In this case, the modification of mechanical properties is simultaneously an increased polypropylene crystallinity, an incorporation of rigid hydrophilic particles into hydrophobic polymeric matrix and an occurrence of macroscopic pores in the composite structure, which act as notches that provoke the weakening of rotationally molded materials. The tensile test results are in good agreement with DMTA investigations. Despite the fact that the crystallinity of composite materials was higher than that of pure rPP, their hardness decreased. The slightly higher value of mWF-filled composites may be attributed to the higher nucleating ability of silanized filler previously described. The decreased hardness values are probably caused by the presence of composites porosity observed in SEM images. The lowered mechanical properties measured by the static tensile test may result from a higher amount of pores. As we presented in our previous work, the thermal stability of natural fillers after the silanization process may be lowered in reference to untreated materials [41].

CONCLUSIONS

In this work, polypropylene-based composites filled with untreated and treated wood flour were manufactured by rotational molding technology. The incorporation of both untreated and silanized wood flour types into rPP caused significant changes in the composites' rheological properties, mainly an increase of molten material complex viscosity. Wood flour reveals a high nucleating ability and improves the crystallization level of rPP. Moreover, the surface modification of the filler provides its increased nucleating efficiency. Despite applying polypropylene random copolymer characterized by low melting temperature, it's necessary to apply a processing temperature of 200 °C and a long processing time and porosity in rotomolded castings containing natural fillers occurs. On the basis of the carried out complex analysis, it can be stated that it's possible to apply lignocellulosic fillers in the production of polypropylene-based rotomolded products, realized without a preliminary mixing of the composite ingredients by extrusion. Lack of preliminary mixing process realized by melt processing enables fabrication of composite rotomolded parts with lowered price in com-

parison to pure polypropylene. The mechanical and thermomechanical properties of composite materials became lower than pure polymers', however this fact does not exclude them from an industrial application in the production of low-demanding parts. Porous structure occurring in composite parts provides to decrease of materials density, which in several industrial applications, such as production of automobile parts, may became an advantage.

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