

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-aminopropylotrietoksy-silanu (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 dynamiczno-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 Kunststoffe 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

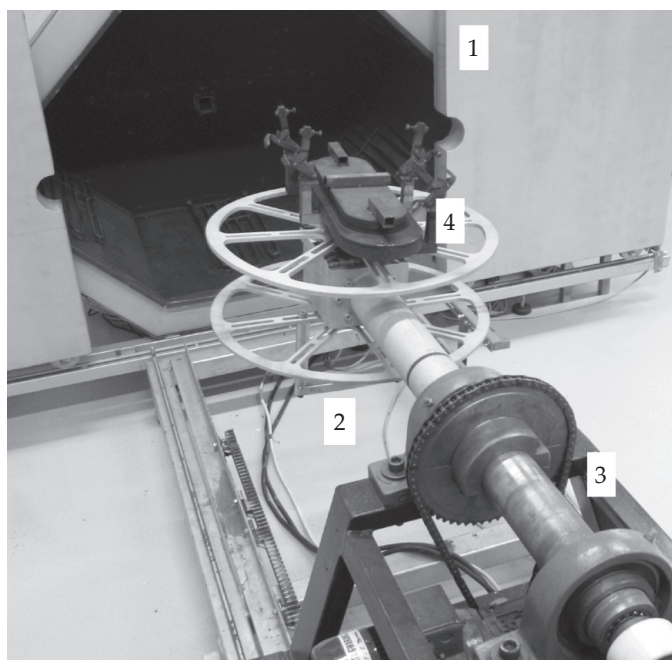


Fig. 1. Single-arm shuttle rotational molding machine: 1 – oven, 2 – clamping space, 3 – gear, 4 – steel mold

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:

$$W_{\%} = \frac{m_0 - m}{m_0} \cdot 100 \% \quad (1)$$

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).

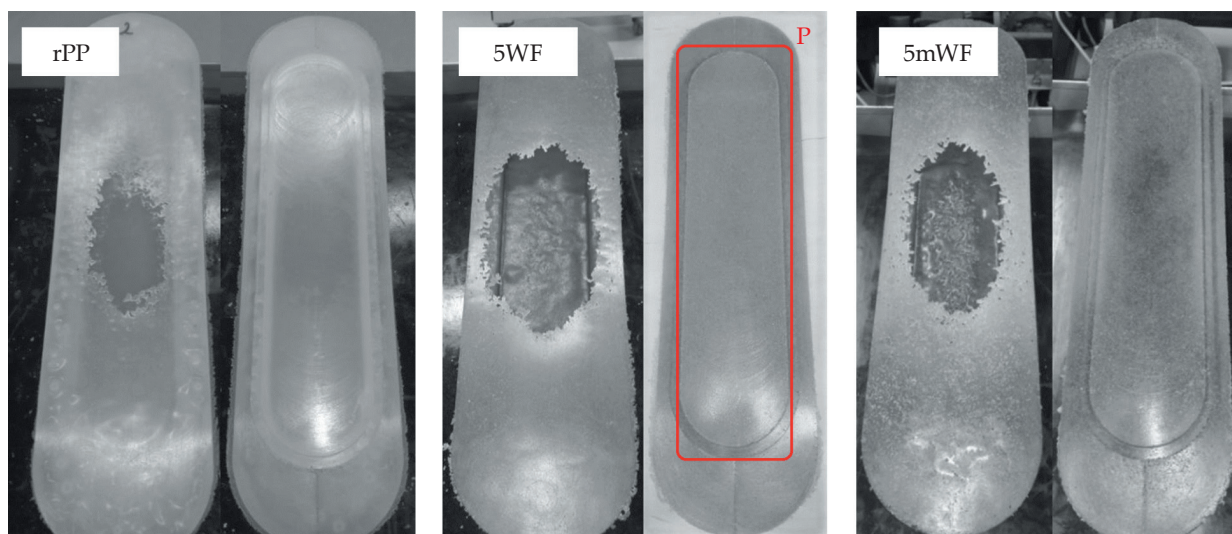


Fig. 2. Rotationally molded products made from: rPP – random polypropylene copolymer, 5WF – composite based on rPP with 5 wt % of wood flour, 5mWF – composite based on rPP with 5 wt % of modified wood flour

– 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 index₂ (CI) on the basis of ATR-FTIR measurements was calculated according to following equation [21]:

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

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 win-

dow 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:

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

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 $\phi = 10$ °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:

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

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-

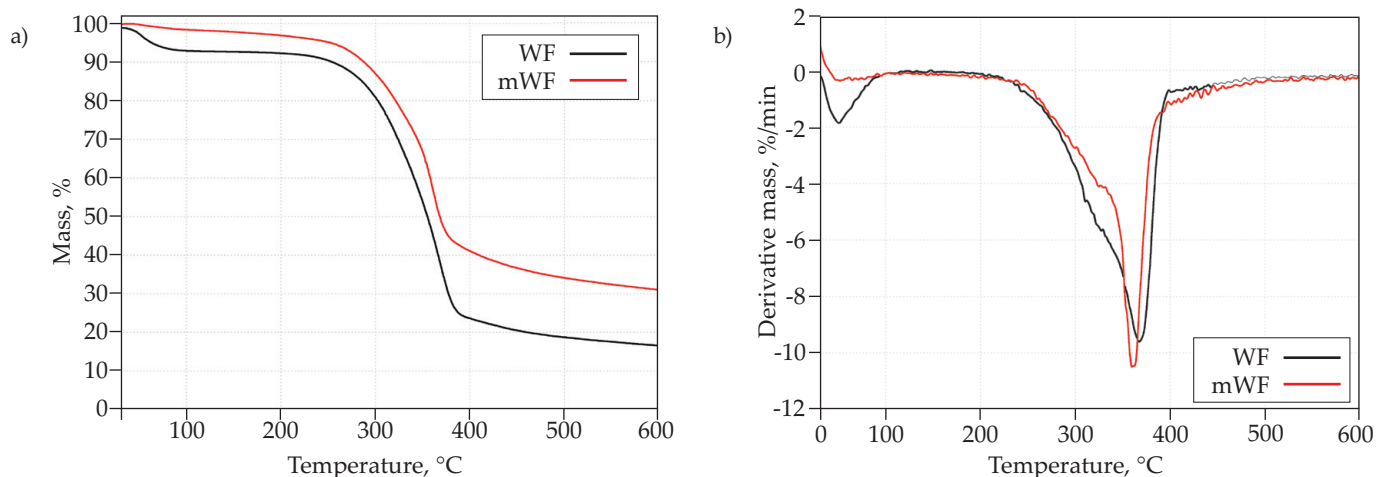


Fig. 3. a) TG, b) DTG curves of unmodified (WF) and modified (mWF) fillers

Table 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-

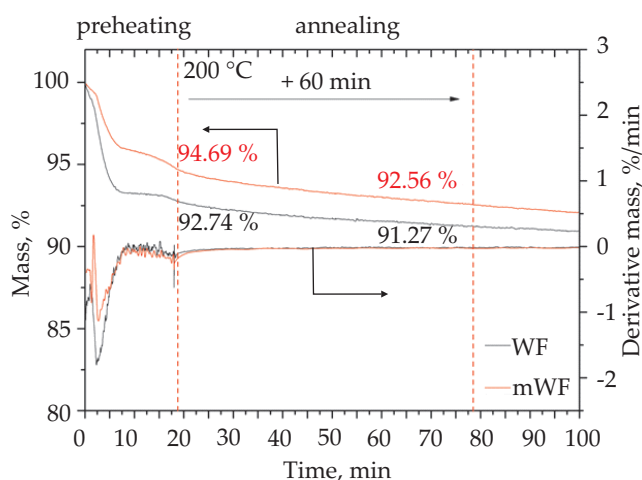


Fig. 4. TG and DTG curves obtained during isothermal measurements conducted for WF and mWF

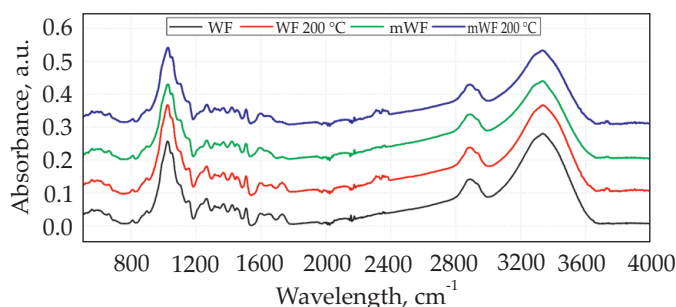


Fig. 5. FT-IR spectra of natural fillers (WF, mWF) before and after annealing at 200 °C, presented in the range from 500 to 4000 cm^{-1}

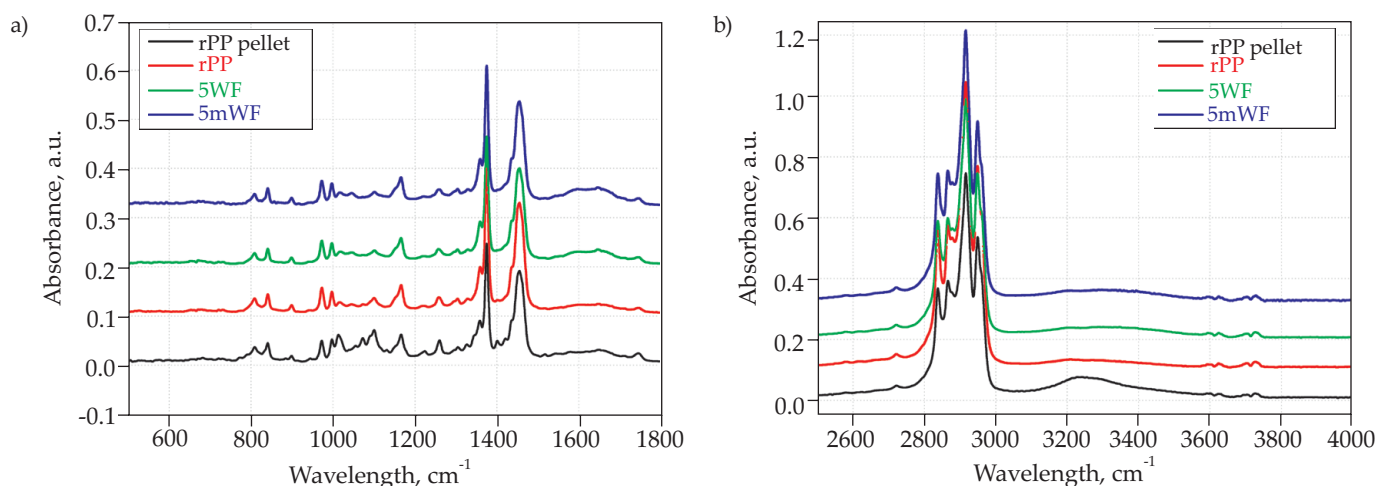


Fig. 6. FT-IR spectra of rotationally molded samples and pure rPP micropellet, presented in the range from: a) 500 to 1800 cm^{-1} , b) 2500 to 4000 cm^{-1}

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 \times 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-