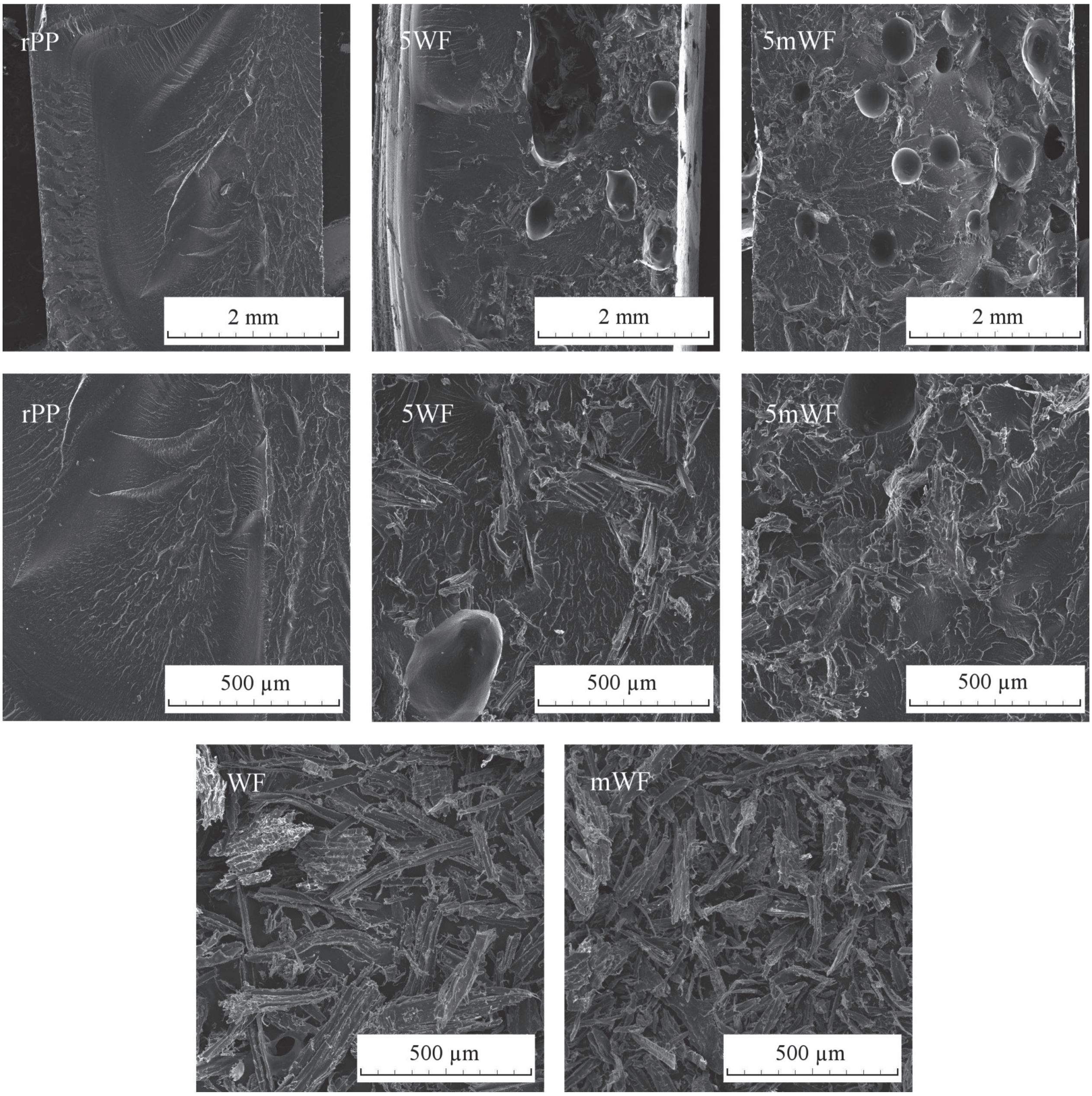

Fig. 7. SEM images of rotationally molded samples (rPP, 5WF, 5mWF) cross-sections, magnification 50× and 200×, and fillers (WF, mWF), magnification 200×

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.

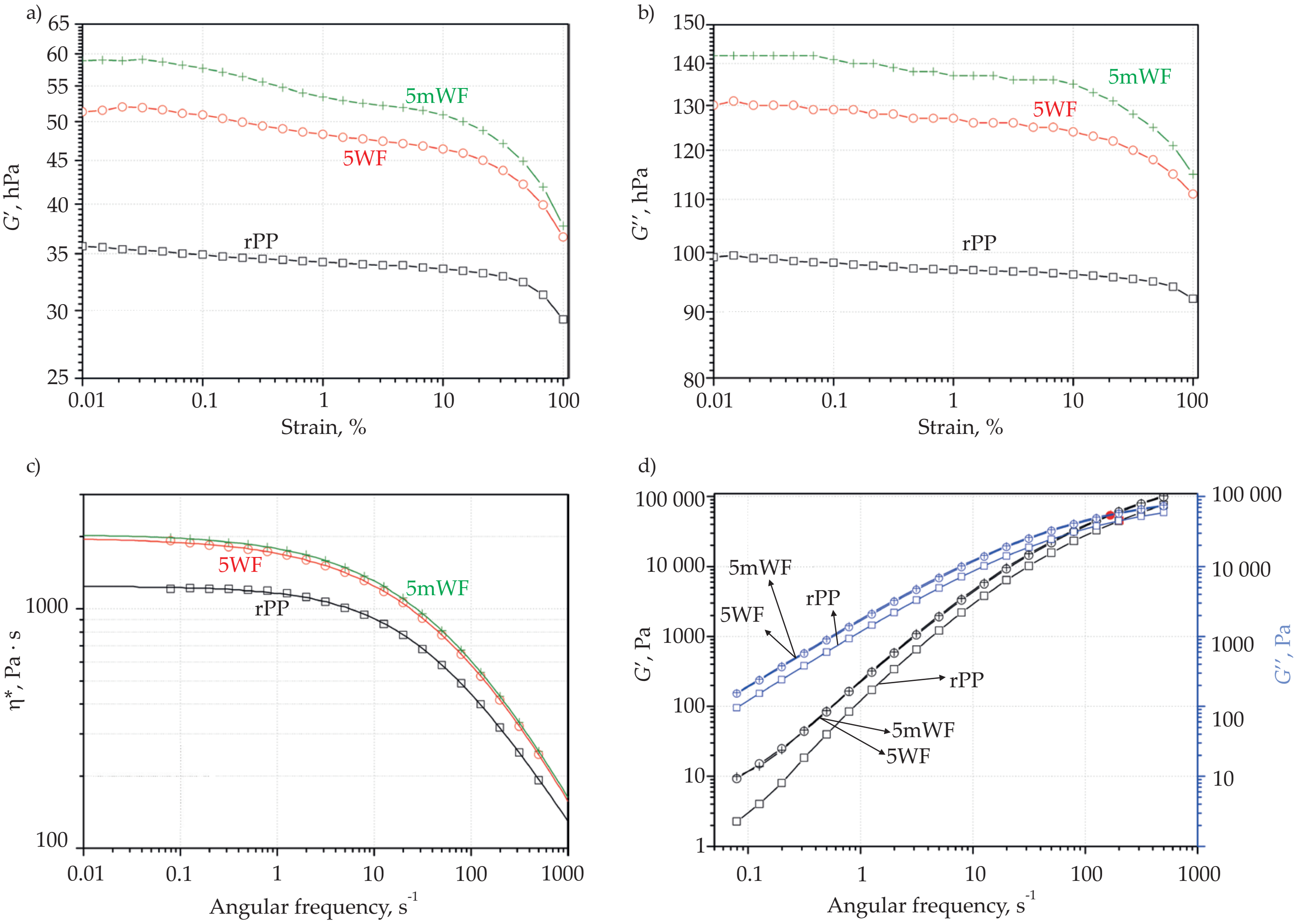

Fig. 8. Rheological properties of rPP and rPP-based composites obtained during: a, b) strain sweep test, c, d) frequency sweep test

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-Yassuda 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-

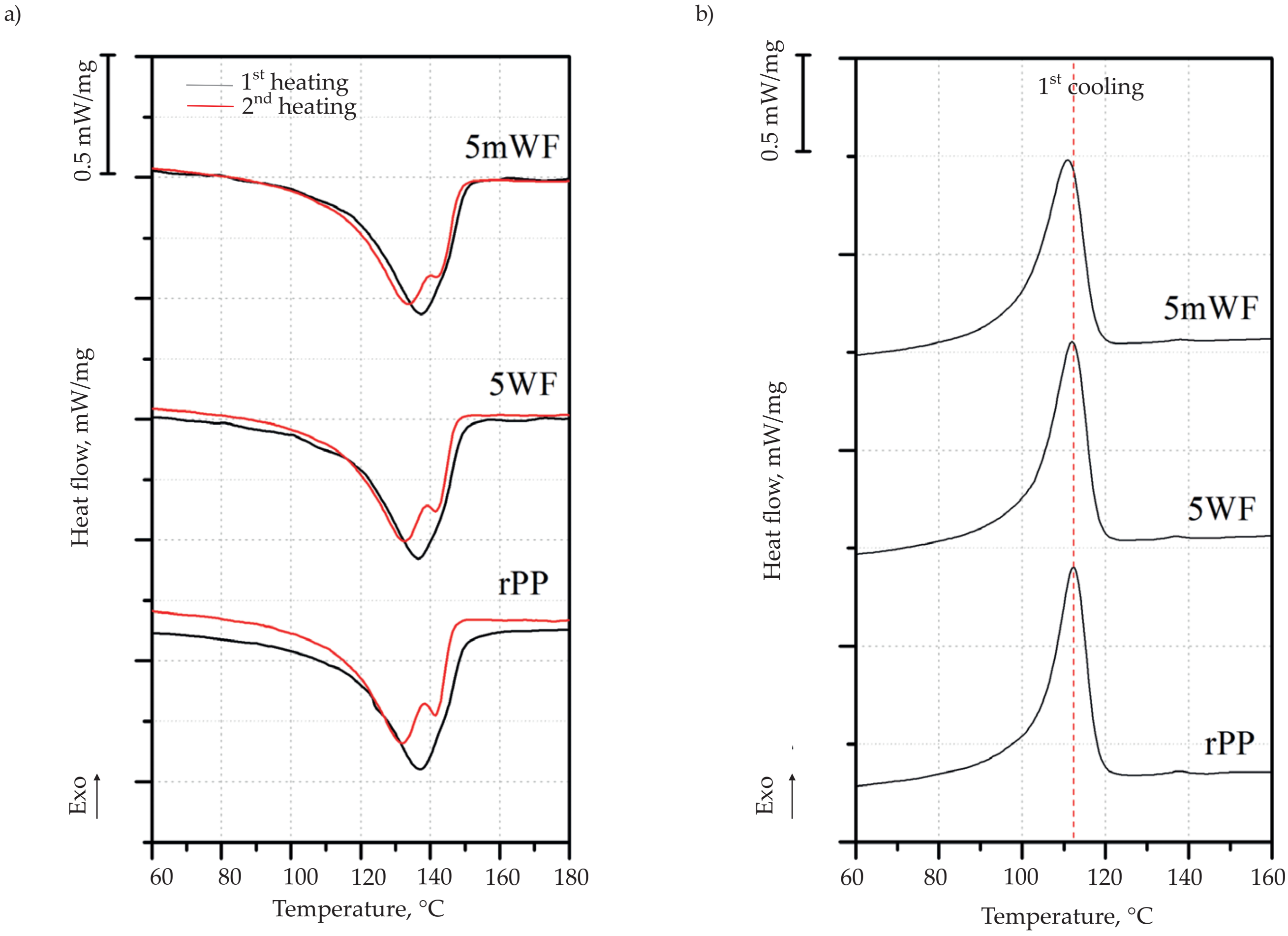

Fig. 9. DSC: a) melting, b) cooling curves of rPP and rPP-based composites presenting thermal property changes induced by incorporation of the natural filler

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-

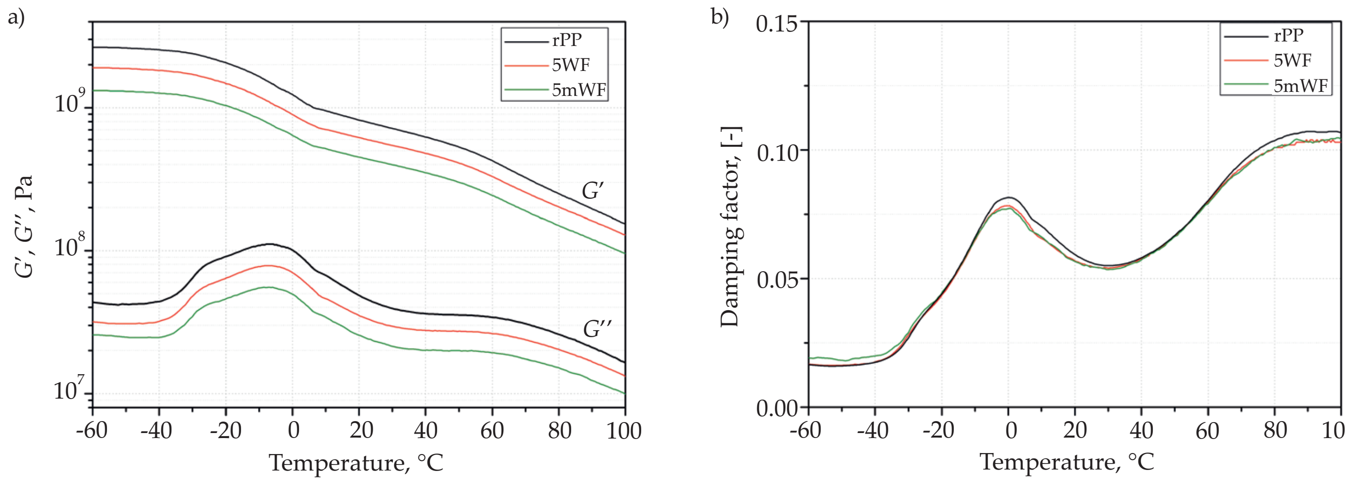

Fig. 10. Thermomechanical properties of rotomolded samples: a) storage modulus (*G′*) and loss modulus (*G″*), b) damping factor (tanδ) *vs*. temperature obtained by DMTA

Table 4. Selected thermomechanical parameters and *C* factor obtained from DMTA measurements

Material	$G'_{-60\,^{\circ}C}$ Pa	$G'_{20\,^{\circ}C}$ Pa	$G'_{60\,^{\circ}C}$ Pa	$G'_{100\,^{\circ}C}$ 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

Table 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 comparison 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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