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Influence of wood mercerization on the crystallization of polypropylene in wood/PP composites

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Abstract Mercerization process is very significant because the alkali treatment facilitates reactivity of lignocellulosic fillers, thus allowing better response to chemical modification. In the present study, the effect of mercerization of pine wood on the nucleation ability of polypropylene was investigated by means of differential scanning calorimetry. We discovered that for the composites with wood containing cellulose II, the decrease in the crystal conversion of the polymer matrix and increase in the half-time of crystallization values are significant. It can be concluded that the amount of cellulose II formed upon alkalization of lignocellulosic fillers determines their nucleation ability. To evaluate the transcrystalline effects caused by various woods, which were untreated or treated with sodium hydroxide, the polarized optical microscopy was also performed. The nucleation of polypropylene on the surface of wood was investigated by induction time measurement. It was found that surfaces of the unmodified wood generate epitaxial nucleation, whereas the mercerized wood generates nonepitaxial nucleation. The differences in the type of nucleation suggest that the effectiveness of formation of transcrystalline structures depends on the contribution of cellulose I and cellulose II. Moreover, the presence of epitaxy is not necessary for the appearance of transcrystalline structures. The results showed that the transcrystalline structures appeared in each system, even with wood containing significant contribution of cellulose II. The only difference noted was the change in the nucleation abilities of the wood surface. Results of this study imply the necessity of quantitative determination of the contributions of cellulose I and cellulose II, whose presence determine the type of nucleation and nucleation ability of the filler surface.

Keywords Polypropylene · Wood · Composites · Chemical treatment

Introduction

In the recent years, an increased interest in obtaining composite materials with natural component as wood sawdust, flax, sisal, jute, and hemp fiber has been observed [1–7]. Lignocellulosics are favored as new generation reinforcing materials in polymers since they represent renewable natural resources. Compared to glass-fiber reinforced composites, important advantages of these materials are their low density, low abrasiveness to the processing equipment, and low toxicity. Additionally, polypropylene-lignocellulosic composites are low-cost materials and may contribute to solving environmental problems considering that PP is recyclable and has low price and favorable mechanical properties while wood is cheap, highly available, and renewable.

However, the highly hydrophobic nature of certain polymers, such as polyolefins, causes compatibility problems with the hydrophilic reinforcing materials. Good interfacial adhesion between the polymer matrix and lignocelluloses is essential to transfer a stress from the matrix to the fillers and thus improve the mechanical properties of composites. Therefore, extensive studies [8–12] have examined the chemical modifications of natural filler and their effects on the interfacial adhesion mechanism of lignocellulosic and thermoplastic composites.

Alkalization is an attractive method to modify natural filler surfaces and improves their performance as

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composite reinforcement. This treatment with aqueous sodium hydroxide is called mercerization [13]. This process plays an important role. It is well know that the fine structure of cellulose materials is composed of crystalline and amorphous regions. The amorphous regions easily absorb chemicals, whereas the compactness of crystalline regions makes it difficult for chemical penetration [14]. According to literature, the mercerization process causes the decrystallization of cellulose. Consequently, the alkali treatment facilitates reactivity of lignocellulosic fillers, thus allowing better response to chemical modification such as acetylation.

Moreover, the presence of waxy substances on the filler surface contributes immensely to ineffective filler to modifier bonding, and poor surface wetting. Hon et al. [15] suggest that wood alone does not react significantly with various modificators since the hydroxyl groups in wood are not readily accessible. Hence, the lignocellulosic material must be pre-treated with sodium hydroxide. This method can eliminate a large amount of hemicelullose, lignin, waxy substances, and other impurities of the natural component [14, 16–18]. Additionally, the effect of alkali on a cellulose material is a swelling reaction, during which the natural crystalline structure of cellulose relaxes [19]. During mercerization process, the hydroxyl groups of the cellulose are converted into ONa-groups, expanding the molecule's dimensions. Consequently, after washed with water and the material dried will convert the cellulose I to a new crystalline structure of cellulose II [13, 19]. The conversion cellulose I → cellulose II depends on the concentration of the solution and treatment time [20, 21]. It is commented that the concentration of the mercerization has a significant influence on the properties of the natural component and the resultant composites [22].

It is well known that lignocellulosic materials may act as heterogeneous nucleating agents and nucleate crystallization along the interface with sufficiently high density of nuclei. The columnar crystalline layer, known as transcrystallinity (TCL), is developed at the fiber/matrix interface and plays an important role [23, 24]. The review of literature [25–31] indicates that when a chemical treatment is applied, the nature of fillers may be modified due to the interaction between the filler and polymer matrix, and, consequently, the nucleation ability of fillers may be changed. Several authors [27, 31] have reported that mercerization prevented the formation of transcrystalline layer. Quillin et al. [29] explained that TCL was caused by providing similar spacing of pyranose rings (in cellulose I) to polypropylene methyl groups in a flat manner. Authors of this concept maintain that the mercerization process causes that the pyranose rings on the face of cellulose II are not aligned in a "flat" manner and no TCL is produced. However, results presented in the literature are contradictory. On the other hand, Son et al. [26] noted completely different results. It is worth emphasizing that in the case of cellulose II without similar configuration and matching of interaction sites, lignocellulosic filler had nucleating ability to transcrystallize polypropylene matrix. In our earlier studies [28], mercerization of wood led to the development of transcrystallization layers but with very poor effectiveness.

This polymer matrix/dispersed filler exerts one of the main influences on resulting properties and is therefore the most critical point of composite materials [32].

On the basis of literature analysis, the question arises if the Wittman and Lotz [33] theory and Quillin [29] hypothesis may imply that the crystal structure matching between cellulose and polypropylene can initiate epitaxial polypropylene growth. What is the nucleation type (epitaxial and nonepitaxial) in nucleation process of semicrystalline polymer in the presence of lignocellulosic filler? A response to this question would bring interesting insights and would help verify certain inconsistencies concerning the effect of polymorphism of cellulose on the phenomena taking place at the polymer-filler interface. Problems associated with formation of interface in composite materials are closely linked to the theory of the heterogeneous nucleation [34]. The effective investigation method of the nucleation type in composite materials, using induction time measurement, was proposed by Muchova and Lednicky [32, 35]. In these excellent works, authors discuss the theoretical approach to the influence of a substrate surface on crystal nucleation. Moreover, the induction time is directly associated with the nucleation ability of a filler surface and allows evaluate the influence of a qualitative parameters on the nucleation process. Investigation of heterogeneous nucleation by the induction time of crystallization makes it possible to differentiate between epitaxial and nonepitaxial nucleation.

Although there is significant number of paper on heterogeneous nucleation [25–31, 36, 37], still many controversial results and comments could be find. Moreover, it is still difficult to define how the mercerization does affect on nucleation process in composites. However, to the best of our knowledge, there are no reports on relation between polymorphic structures of cellulose (caused by the mercerization process) and the nucleation type. Confirmation of the fact that the crystal structure matching between cellulose and polypropylene can initiate epitaxial polypropylene growth would permit verification of the hypothesis posed by Quillin et al. [29] and Felix et al. [36] based on the mechanism of crystal structure matching proposed by Wittman and Lotz [33].

In the present study, the influence of transformation cellulose I → cellulose II of wood on the polypropylene crystallization in composite materials was analyzed. The purpose of this study is to investigate the effect of alkali surface treatment on the nucleation type (epitaxial and nonepitaxial) of wood in polypropylene matrix, using differential scanning calorimetry (DSC), polarizing optical microscopy, and wide angle X-ray scattering (WAXS) method. Our intention is to study samples of different contents of different polymorphous varieties of cellulose, whose effect has not been studied so far.

Experimental

Materials

A commercially available polypropylene Malen F-401 produced by Basell Orlen Polyolefins (Plock, Poland) with melt flow index of 2.4–3.2 g/10 min (at 230 °C and 2.16 kg), isotacticity-95%, $T_{\mathrm{m}} = 163$–164 °C was used as polymeric matrix.

Unmodified pine wood (*Pinus silvestris*) particles, taken after sieve analysis from 1 mm mesh supplied by Forestry-Kaminska, Poland was used in the performed experiments.

Mercerization process of wood

The pine wood was immersed in sodium hydroxide solutions with different concentration—10, 15, and 20% for 60 min for each concentration with vigorous stirring. The samples were then washed several times with distilled water to neutralize excess NaOH. The wood was then dried to remove free water in the air at elevated temperature (ca. 110 °C).

The names of the samples are illustrated in Table 1.

Table 1 Name of the wood materials

Abbreviation	Compounds
Wood-un	Unmodified wood
Wood-merc10	Wood mercerized with 10% NaOH
Wood-merc15	Wood mercerized with 15% NaOH
Wood-merc20	Wood mercerized with 20% NaOH

Wide angle X-ray scattering (WAXS)

The structure of untreated and mercerized wood was analyzed by means of WAXS using Cu Kα radiation. The generator was operated at 30 kV and 25 mA anode excitation. The diffraction patterns were recorded between 5 and 30° (2θ-angle range) in the step of 0.04°/3 s. The deconvolution of peaks was performed by the method proposed by Hindeleh and Johnson [38], improved, and programmed by Rabiej [39]. After separation of X-ray diffraction lines, the relative amount of the polymorphic phases of cellulose (cellulose I and cellulose II) can be estimated on the basis of the separated area under the peaks of cellulose I and cellulose II. The details of this calculation procedure have been introduced in earlier publication [21]. The changes in the supermolecular structure of wood were analyzed as a function of wood treatments.

Sample preparation

The composites, containing 50% of wood by weight, was extruded by Fairex single screw extruder with a length-to-diameter ratio L/D = 25 at the barrel temperature of 195 °C. The cooled strands were subsequently pelletized into granules and dried.

Morphological analysis

The hot-stage optical microscope (Linkam TP93, made in Japan) and a polarizing optical microscope Labophot-2 (Nikon, made in Japan) equipped with a Panasonic CCD camera (KR222, made in Japan) were used to observe the isothermal crystallization process of polypropylene in presence wood. The samples were firstly heated to 210 °C and kept at this temperature for 5 min in order to eliminate their thermal history. Finally, the samples were cooled to 132, 134, 136, 138, and 140 °C, at which isothermal crystallization of the PP was allowed for various times. Dry nitrogen was introduced to eliminate any possible degradation during measurement.

The induction time t_{i}, (the beginning of the regular crystal growth) for nucleation was determined from the intercept of the TCL thickness to the time axis. According to the Muchova and Lednicky [35], induction time can be expressed by equation:

$$\ln(t_{\mathrm{i}} \cdot \Delta T) = \ln \frac{C \cdot \Delta\sigma \cdot T_{\mathrm{m}}^{\mathrm{o}}}{\Delta H_{\mathrm{m}} \cdot b_{\mathrm{o}}} + \frac{4 \cdot \sigma_{\mathrm{b1}} \cdot \sigma_{\mathrm{ab}} \cdot b_{\mathrm{o}} \cdot T_{\mathrm{m}}^{\mathrm{o}}}{k \cdot \Delta H_{\mathrm{m}}} \cdot \frac{1}{T \cdot \Delta T} \tag{1}$$

where, σ_{b1} and σ_{ab} are Gibbs specific surface energy of growing nucleus, $\Delta\sigma$ is the difference energy parameter, T_{m}^{o} is equilibrium melting temperature, ΔH_{m} is the enthalpy of crystal melting, ΔT is undercooling, b_{o} is the thickness of one layer of folding chain, C is the constant, k is the Boltzmann constant, and T is the crystallization temperature.

According to Eq. 1, the dependence of $\ln(t_{\mathrm{i}}\ \Delta T)$ on $1/T{\cdot}\Delta T$ is straight line with slope K, where:

$$K = \frac{4 \cdot \sigma_{\mathrm{b1}} \cdot \sigma_{\mathrm{ab}} \cdot b_{\mathrm{o}} \cdot T_{\mathrm{m}}^{\mathrm{o}}}{k \cdot \Delta H_{\mathrm{m}}} \tag{2}$$

and with intercept Q on the axis of $\ln(t_{\mathrm{i}}\ \Delta T)$:

$$Q = \ln \frac{C \cdot \Delta\sigma \cdot T_{\mathrm{m}}^{\mathrm{o}}}{\Delta H_{\mathrm{m}} \cdot b_{\mathrm{o}}} \tag{3}$$

The constants K and Q can be also estimated which of the nucleation types (epitaxial and nonepitaxial) is preferred in the nucleation process [35]. For nonepitaxial nucleation, *K* parameters have the same values, whereas epitaxial nucleation is characterized by changes in the *K* values. Additionally, the intercept *Q* gives information about the ability of the surface to initiate nucleation.

Theories of the crystallization process using the induction time were analyzed in detail in excellent work by Muchova and Lednicky [35].

Differential scanning calorimetry (DSC)

DSC measurements were carried out in a Netzsch DSC 200 under nitrogen atmosphere with a volume of 30 mL min^{-1}. The temperature and heat of transition were calibrated with indium standard. The samples were heated to 210 °C at a heating rate of 10 °C min^{-1}. When temperature reaches 210 °C, samples were maintained for 5 min in order to eliminate any previous thermal history and followed by a cooling rate of −5 °C min^{-1} to 40 °C the crystallization thermogram was measured. This procedure was repeated two times and only second thermograms were used to observe the crystallization behavior in the samples. The crystallization temperatures of composites were calculated from the maximum of the exothermic peak. The kinetic parameters of crystallization process of polypropylene, such as the crystal conversion and half-time of crystallization were determined.

Results and discussion

Effect of mercerization on the supermolecular structure of wood

The alkali treatment played an important role in reducing impurities including hemicellulose, lignin, and extractives [40]. Mercerization process also changes of the crystal structure from cellulose I to cellulose II [13]. Figure 1 shows the X-ray diffraction pattern for wood samples.

The diffraction pattern of unmodified wood (wood-un) in Fig. 1 showed only three peaks at $2\Theta = 15°$, 17°, and 22.7° assigned to cellulose I. The treatment of wood with 15 and 20% NaOH resulted in the formation of cellulose II. On both diffraction curves, additional peaks observed at 2θ equal ca. 12.5°, 20°, and 22°. This indicates that the cellulose I form and cellulose II form of cellulose crystals coexist in the pine wood. On the other hand, for a given concentration (15 and 20%), cellulose I is able to convert irreversibly into cellulose II. The parallel chain arrangement of the cellulose I changes into more stable anti-parallel of the cellulose II. However, the conversion from cellulose I to cellulose II depends on the concentration of the solution. As measured by X-ray diffraction, the amount of the cellulose II in wood-merc15 is 38%, and in wood-merc20 is 58%. Unexpectedly, we reported that treatment of wood with 10% NaOH (wood-merc10) is not sufficient by itself to cause the conversion to cellulose II and that the concentration of the alkali is crucial. Below a minimum concentration, the transformation does not take place. The literature [13, 15, 21, 41] reported that the original crystal structure of the cellulose I is transformed into different type of crystal structure, cellulose II, typically with NaOH concentration higher that 10% [21, 42–44]. In view of the above, to ensure getting cellulose II, it is necessary to optimize the conditions of mercerization.

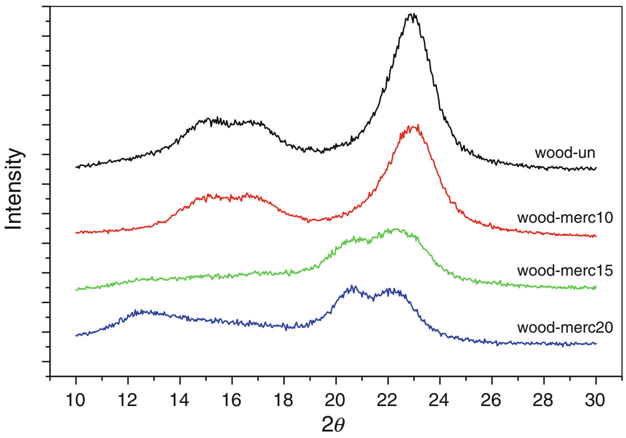

Fig. 1 Diffraction curves of wood samples

Effect of mercerization on the crystallization of polypropylene matrix (DSC)

In our previous study [45–47], we investigated the influence of esterification reaction of wood on crystallization of polypropylene matrix. It was shown that nucleation ability of polypropylene in composite materials is related to chemical treatment of surface wood.

The DSC thermographs (Fig. 2) revealed the exothermic behavior of polypropylene in wood/PP composites.

Displacement of the exotherms of composites to regions of higher temperatures (about 4 °C) can be observed. This is directly related to the fact that the wood acts as heterogeneous nucleation agents for PP. In the same way, Bouza et al. [48] and Ng et al. [49] confirmed that the presence of a foreign substrate in the PP melt reduces the critical size of the crystalline nucleus necessary for subsequent growth. The crystallization temperature of PP in PP-wood-un was measured at 115.1 °C, which is presented in Fig. 2 and almost similar crystallization phenomenon was observed in all wood mercerized/PP composites.

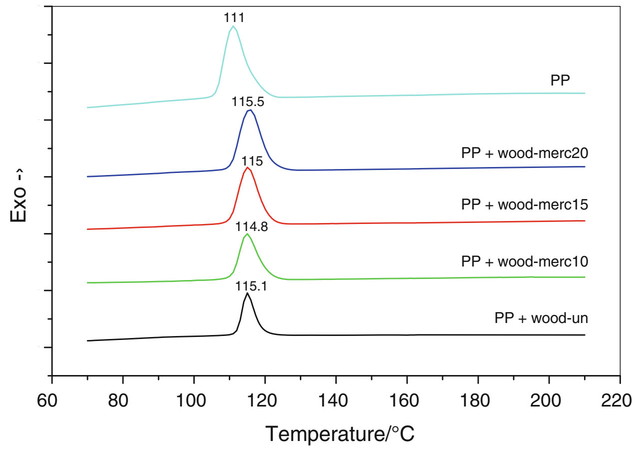

Fig. 2 Crystallization exotherms of PP and wood/polypropylene composites

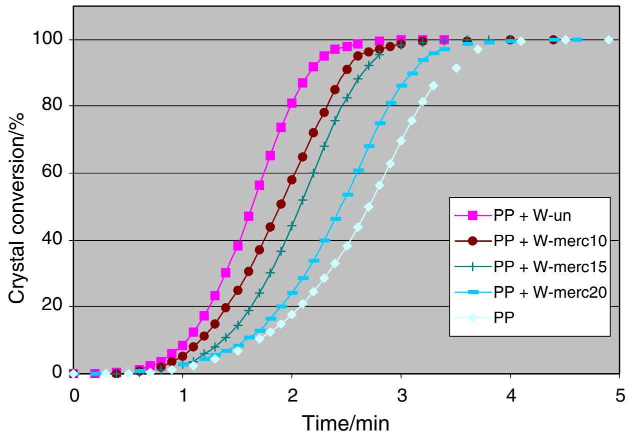

Fig. 3 Crystal conversion of the PP and wood/polypropylene composites

Moreover, in the case of pure PP and composite materials, one melting endotherm is observed with a maximum situated between 165 and 167 °C.

The evolution of the crystallization process from the melt state to the crystal state was followed by means of the variation in conversion. This is detailed in Fig. 3 for polypropylene and composites.

The highest conversion was found for polypropylene (PP) composites with unmodified wood. It is quite evident from these curves that mercerization processes of wood caused a very significant reduction of the conversion phase. Mercerization in the conditions not imposing the formation of cellulose II (PP+W-merc10) leads only to a slight decrease in the conversion. The reason may be associated with the removal of some amount of impurities, for example, waxy substances, fats and resin, and in consequence, the level of active nuclei is reduced. However, for the composites with wood containing cellulose II, the decrease in the conversion of the polymer matrix is significant. Composites with mercerized wood with 20% NaOH (highest content of cellulose II) are characterized by values of the degree of phase conversion almost identical with the pure polypropylene. Similar relationships can be found in the case of the determined values of the half-times of crystallization ($t_{0.5}$) presented in Table 2.

Table 2 Values of half-time of polypropylene crystallization

Samples	$t_{0.5}$/min
PP + wood-un	1.65
PP + wood-merc10	1.9
PP + wood-merc15	2.1
PP + wood-merc20	2.5
PP	2.6

The half-time of crystallization of the composites with unmodified wood is 1.65 min, while for those with wood subjected to alkalization with a 10% NaOH, the half-time of crystallization increased to 1.9 min. A significant increase in the half-time of crystallization values was observed for the composites with cellulose II. The half-time of crystallization of PP-W-mer20 composite is 2.5 min, which is almost the same as that of PP. It is well known that the lower the $t_{0.5}$ values are, the higher the nucleating efficiency is. The obtained significant deterioration of the nucleation ability of wood surfaces following mercerization processes (PP-merc10 and PP-merc15 or PP-merc20) was most likely associated with the formation of cellulose II. In summary, it can be concluded that the nucleation ability is decreased when wood has a cellulose II. The nucleation ability of filler in composite materials is widely regarded as the most important factor determining their mechanical properties [50] and polymer processing. Although there is significant number of paper [22, 42, 51–56] on mercerization of lignocellulosic fillers, still many controversial results and comments could be find. The review of literature on the subject indicates that an alkalization led to the deterioration of nucleation ability [25, 27, 31] and elimination of transcrystalline structure. However, some authors have reported the lack of a negative effect of mercerization on nucleation of the polymer matrix [26]. Also, in our studies [28], mercerization led to the development of transcrystallization layers but with very poor effectiveness. We expect that the results of the study will permit explanation of the inconsistencies or contradictions. The nucleation abilities have been proved to depend on the conditions of mercerization and consequently on the content of polymorphous varieties of cellulose. In the studies reported so far, no quantitative evaluation of the effect of the content of different polymorphous varieties of cellulose has been made, so it is difficult to compare the lignocellulosic fillers studied. The amount of cellulose II formed upon alkalization of lignocellulosic fillers determines their nucleation ability. In order to establish the role of cellulose in crystallization of PP matrix, it is necessary to recognize the contents of the polymorphous varieties of cellulose as the lack of such information is the source of the above-mentioned discrepancies.

Another aspect that must be considered is the analysis the adjustment of crystalline structures of the filler and the polypropylene matrix [29, 33, 36]. The next section will be devoted to the microscopy investigation of heterogeneous nucleation makes it possible to differentiate between epitaxial and nonepitaxial nucleation.

Effect of mercerization on the heterogeneous nucleation (microscopy)

The development of PP TCL on the pine wood is clearly shown in Fig. 4. The morphology of the PP matrix varies significantly with kind of wood surface. It is evident that the nucleation ability for PP on the untreated wood (Fig. 4a) is much higher than that on the mercerized wood with 15 and 20% NaOH (Fig. 4c, d). Figure 4b shows micrographs of mercerized wood (with 10% NaOH) embedded in molten PP. This wood act as nucleating agent for PP as nucleation occurs preferentially along the wood. However, for PP + W-m10 composite, the nucleation ability was lower than that for the composite with untreated wood. It is clear from Fig. 4 that polymorphic transformation cellulose I → cellulose II (in PP_W-merc15 and PP + W-merc20 samples) led to reducing of nucleation ability of wood surface. In our studies, pine mercerization with 15 and 20% NaOH led to the development of transcrystallization layers but with very poor effectiveness.

Figure 5 shows the variation of the induction times with crystallization temperatures for polypropylene to crystallize on wood at different wood treatment. It is perfectly visible that the conditions (concentration of NaOH) of the applied mercerization of pine wood exerted a significant influence on values of induction times. The shortest induction times were recorded in the case of the composite systems containing untreated wood. The alkalization of wood caused extension of the induction times required to develop transcrystalline structures. Distinctly, greatest changes of induction times were recorded for the composites containing wood subjected to the mercerization with 20% NaOH. The different composites can be ordered in terms of reducing induction time as follows: PP + W-merc20 > PP + W-merc15 > PP-W-merc10 > PP + W-un. Induction time curves provide information on the ability of nucleation sites on the filler surface.

To determine qualitatively the influence of the surface treatment of the wood on its nucleation ability, the values of the $\ln(t_i \cdot \Delta T)$ versus $1/T \cdot \Delta T$ were plotted on Fig. 6.

It may be noted that all the curves conformed linearity of these dependences. However, it is interesting that PP-W-merc15 and PP + W-merc20 composites (containing cellulose II) have a different slope of the curves of these dependences in comparison to PP-W-un and PP + W-merc10 composites (containing cellulose I only). Differences in the slope of $\ln(t_i \cdot \Delta T)$ versus $1/T \cdot \Delta T$ suggest the following hypothesis: on the surface of the mercerized wood

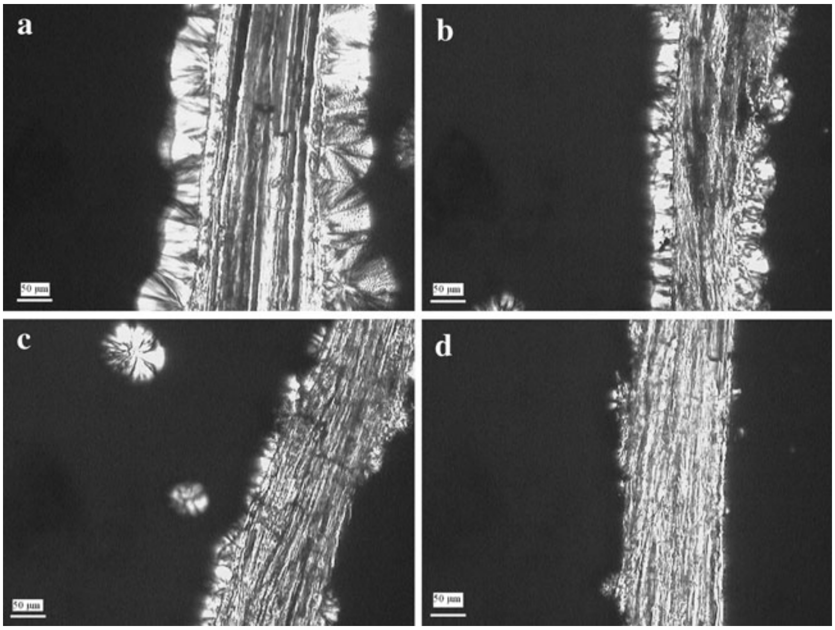

Fig. 4 Microscopy images of PP mixed with wood, at 136 °C for 5 min.: **a** PP + W-un, **b** PP + W-merc10, **c** PP + W-merc15, and **d** PP + W-merc20

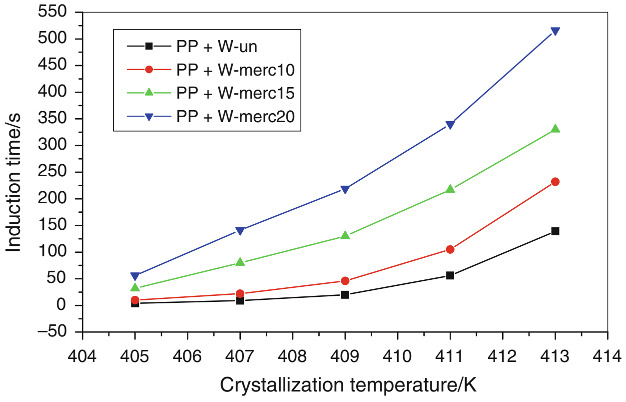

Fig. 5 Dependences of the induction time on the crystallization temperature for wood/polypropylene composites

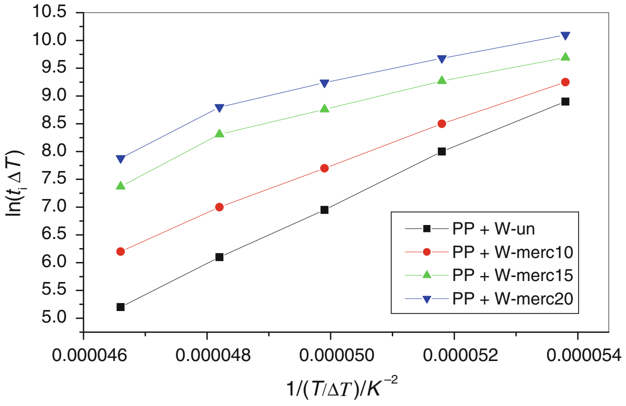

Fig. 6 Dependences of $\ln(t_i \cdot \Delta T)$ versus $1/T \cdot \Delta T$ for wood/polypropylene composites

(with 15 and 20%), there exist different types of nucleation sites that generate different types of nuclei. From these plots (Fig. 6), the slope *K* and intercept *Q* on the *y* axis of the straight lines have been calculated. These values depend on wood types are given in Table 3.

According to the results from Table 3, there is a very good agreement in *K* values for the composites containing wood mercerized by NaOH solutions of the highest concentrations. With reference to the physical interpretation of the K parameter noted in the excellent paper of Muchova [35], we assumed the nonepitaxial nucleation in these systems. For the composites containing unmodified wood and the wood modified with a 10% NaOH solution, considerable differences in *K* were observed, which indicates changes in the nucleus structure.

On the basis of theory of heterogeneous nucleation [35], we can state that epitaxial nucleation manifests itself by the changes in the values of quantity *K*. The results suggest that the wood containing only cellulose I is responsible for epitaxial nucleation, while the wood containing cellulose I and cellulose II changes the character of nucleation into nonepitaxial. The results can be correlated with those given by Quillin et al. [29]. They noted that high nucleation activity of cellulose I can be a consequence of the matching between the crystal structures of cellulose I and PP. On the grounds of the theory of Wittman and Lotz [33], Quillin et al. [29] found a good matching between the size of the cellulose I chains (0.82 nm) and the size of methyl groups of PP (0.84 nm). Elementary cell parameters of cellulose II are similar to those of cellulose I, but in the cellulose II, chains are not in planar configuration as in cellulose I. The matching of sizes at a molecular level can be the reason stimulating the epitaxial growth of transcrystalline structures on the surface of cellulose I. This hypothesis has not been experimentally verified, yet it has been done only in this work.

Table 3 The slopes *K* and intercepts *Q* values

Samples	$K \cdot 10^{-5}$	*Q*
PP + W-un	5.16	−18.8
PP + W-merc10	4.27	−13.7
PP + W-merc15	3.08	−6.75
PP + W-merc20	2.93	−5.5

It should be noted that the presence of epitaxy is not necessary for the appearance of transcrystalline structures. As shown by our results, transcrystalline structures appeared in each system, even with wood containing significant contribution of cellulose II. The only difference noted was the change in the nucleation abilities of the wood surface. The differences in the type of nucleation suggest that the effectiveness of formation of transcrystalline structures depends on the contribution of cellulose I and cellulose II. Probably, even a small content of cellulose I in mercerized wood (containing mainly cellulose II) is responsible for the possibility of formation of transcrystalline structures. The discrepancies on TCL formation in the systems with lignocellulosic components reported in literature most probably follow from the differences in the quantitative contributions of the two polymorphous variations of cellulose, which were not determined. Results of this study imply the necessity of quantitative determination of the contributions of cellulose I and cellulose II, whose presence determine the type of nucleation and nucleation ability of the filler surface. It is highly recommended to perform the studies on wood containing only cellulose II.

The intercepts *Q* give information about the quantitatively evaluate the nucleation characteristics of the materials on which crystal nucleation takes place. Based on literature, it is known that nucleation ability increases with the decreasing *Q* value [32, 35]. As follows from the results presented in Table 3, the composite with unmodified wood shows the highest nucleation ability (the lowest *Q* value).

The lowest nucleation ability was observed for the composites containing wood mercerized by NaOH solutions of the highest concentrations. The *Q* values obtained are well correlated with the microscopic images revealing similar relations between the contents of polymorphous cellulose types and the ability to form transcrystalline structures.

The performed microscopy investigations perfectly corroborated the results obtained using the DSC measurements. Both of the applied methods showed that wood nucleation activity depends significantly on the alkalization treatment. The highest activity was determined in the unmodified. The applied alkalization processes of wood resulted in a distinct deterioration of the nucleation properties of wood surface.

Conclusions

In this study, we used DSC and polarizing microscopy to investigate the type of nucleation and nucleation ability of the lignocellulosic surface in polypropylene matrix. The application of the described methods revealed that the contents of the polymorphous varieties of cellulose must be taken into account for evaluation of nucleation ability of lignocellulose fillers. The WAXS results showed that the conversion from cellulose I to cellulose II depends on the concentration of the NaOH solution. The amount of cellulose II formed upon alkalization of lignocellulose fillers determines their nucleation ability. We found that for the composites with wood containing cellulose II, the decrease in the crystal conversion of the polymer matrix and increase in the half-time of crystallization is significant. The highest nucleation ability was found for polypropylene composites with unmodified wood. Nucleation on wood containing only cellulose I (unmodified and mercerized with a 10% NaOH) were epitaxial, while wood mercerized by NaOH solutions of the highest concentrations generate nucleation that seemed to be very similar to the nonepitaxial one. Moreover, investigation of heterogeneous nucleation by the induction time of crystallization makes it possible to evaluate the ability of the surface to initiate nucleation from the parameter *Q*.

We hope that the results of the study will permit explanation of the inconsistencies or contradictions. Analyzing the hitherto published data, it was difficult to explain the reported differences in the surface nucleation activity of the lignocellulosic fillers. On the basis of this study, it is known that it is not possible to get full transformation of cellulose I to cellulose II as a result of mercerization, which has been described in detail in our earlier works [20, 21]. Therefore, lignocellulosic material after mercerization is a mixture of two polymorphic varieties of cellulose. The literature [25–28, 31] reported differences in the activation of TCL nucleation by lignocellulose materials could most probably be explained by differences in the cellulose I/cellulose II content at the wood surface. In order to establish the role of cellulose in crystallization of PP matrix, it is necessary to recognize the contents of the polymorphous varieties of cellulose as the lack of such information is the source of the above-mentioned discrepancies.

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