

# Analysis of the Nucleation Activity of Wood Fillers for Green Polymer Composites

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## Abstract

*In this work, the surface of pine wood used as a filler in polypropylene/wood composites was successfully modified by the mercerization process. It is a very significant process because it removes low-molecular components, which improves interactions between the filler and matrix and leads to a better dispersion of the filler in the matrix. Unfortunately chemical treatment may affect nucleation of the lignocellulosic filler. On the basis of XRD results, the transformation of native cellulose I to cellulose II was observed. In the present study, the effect of the mercerisation of pine wood on the nucleation ability of polypropylene was investigated by means of polarising microscopy. The results showed that the chemical modification of pine wood had a significant effect on nucleation activity in polymer composites. This effect is explained by differences in the chemical compositions of wood fibres. The content of simple sugars obtained from the methanolysis and acidic hydrolysis of cellulose and hemicellulose was determined through gas chromatography investigations. It was found for the first time that the formation of transcrystalline structures is possible for composites with a high content of glucose derived from cellulose. It is also worth emphasising that the chemical modification process can lead to cellulose depolymerisation processes and the formation of degradation products with a lower molecular weight. Knowledge of the phenomena taking place in the interphase boundary polymer/filler is very important because it permits optimisation of the processing, leading to products of target properties.*

**Key words:** wood polymer composites, cellulose, modification, nucleation.

## Introduction

Natural materials have long generated interest in the scientific community around the world. Rapid economic development and increasing demand for plastics with appropriately tailored properties cause that composites made from thermoplastic polymers filled with natural components, most often lignocellulosic material, are increasingly used. An important role is also played by the ecological aspect, as these materials are partially biodegradable [1-3]. Cellulose fibres offer an interesting alternative to the synthetic fibres currently used. Cellulose is the most abundant biopolymer on Earth, and therefore successfully used as a raw material for the preparation of composite materials [4-7]. Cellulose-reinforced plastics have many advantages over synthetic equivalents, including considerable strength and flexibility. They are also easy to process and environmental-

ly friendly. Noteworthy are also strong interactions between the components of composites with cellulose, which are the key to transfer the stresses from the matrix to the filler in the entire surface of the material [4, 6-7].

During the production of polypropylene composites with a wood filler, significant problems are encountered, which often make their potential not fully utilised [1]. First of all, attention should be paid to the poor affinity between hydrophilic wood fibres and the hydrophobic polypropylene matrix, which causes both the agglomeration of fibres (low dispersion of particles in the matrix) and less ability to transfer stresses. These phenomena are conducive to a significant deterioration in the mechanical properties of the material [1, 6-9]. In order to improve interfacial adhesion, numerous chemical modifications of wood are used, which may, however, affect the nucleating activity of lignocellulosic filler [10-14]. Obtaining good physico-chemical and mechanical properties of composites is also associated with other phenomena that occur at the interface [1].

Knowledge of the phenomena taking place in the interphase boundary polymer/filler permits optimisation of the processing, leading to products of target properties. Some fillers, e.g. flax or hemp fibre, can initiate heterogenic nucleation and significantly influence the course of

crystallisation of semicrystalline polymers [15]. The filler surface can have many active sites that can be potentially responsible for high density nucleation, leading to the growth of polymer crystallites in the direction perpendicular to the filler surface [16-19]. This phenomenon leads to the formation of a column-like crystalline layer known as the transcrystalline layer (TCL). Although the formation of transcrystalline structures has an important effect on the properties and character of the composites produced, the mechanisms of their formation have not been fully recognised and the influence of the chemical treatment of the lignocellulose component on the development of TCL structures is ambiguous and controversial [11, 17].

An important problem in the context of determination of the mechanisms of TCL structure formation can be the polymorphism of cellulose contained in natural fillers. It is known that cellulose occurs in four basic polymorphic forms: cellulose I, II, III and IV [20-22]. Naturally occurring cellulose I can be easily treated with a solution of sodium hydroxide, thereby obtaining cellulose in polymorphic form II. According to literature data, the treatment of lignocellulose materials with an alkaline chemical leads to definite deterioration of the ability to form TCL structures and often inhibits their formation [11,23]. This fact has been explained by the increased roughness of

the lignocellulose filler as a result of the removal of low-molecular components and fibrillation of the filler. Another reason behind the deterioration of the nucleation ability of cellulose II is the lack of a match between the crystallographic structures of cellulose and polypropylene matrix [24,25]. However, it should be emphasised that the results reported are often contradictory and no interpretation that could account for the differences has been proposed. Problems in explaining the real effect of the chemical modification of lignocellulosic filler on the nucleation ability performance of composites can follow from disregarding the simultaneous effects of such factors as the polymorphic variations of cellulose, and wood composition.

To the best of our knowledge, there are no studies on determining the effect of simple sugars derived from lignocellulosic fillers on nucleation ability in polymer composites. In the present study, we analysed the formation of supermolecular structures in pine wood-polypropylene composites containing cellulose with two polymorphic forms – I and II. To demonstrate the impact of wood composition on nucleation activity, the content of simple sugars obtained as a result of methanolysis and acid hydrolysis of cellulose and hemicellulose was determined. The aim of the work was to find the relationship between the chemical composition of wood components and the formation of transcristalline structures in the polymer matrix, which has not been described so far.

## Experimental

### Materials

The isotactic polypropylene – Moplen HP456J used in this study was supplied by Basell Orlen Polyolefins (Plock, Poland). It was of melt flow index  $MFR_{230/2.16}$ : 3.4g/10 min.

The pine wood (*Pinus silvestris*) was supplied by Forestry – Kaminska (Poland) in 2014, which had a particle size between 0.5-1.0 mm. The wood filler was dried at 70 °C in an air-circulating oven for 24 h prior to use. The moisture content of the pine wood was less than 1 wt. %.

### Chemical modification of wood

Pine wood dried for 24 h at 70 °C was treated at room temperature with an aqueous solution of sodium hydroxide

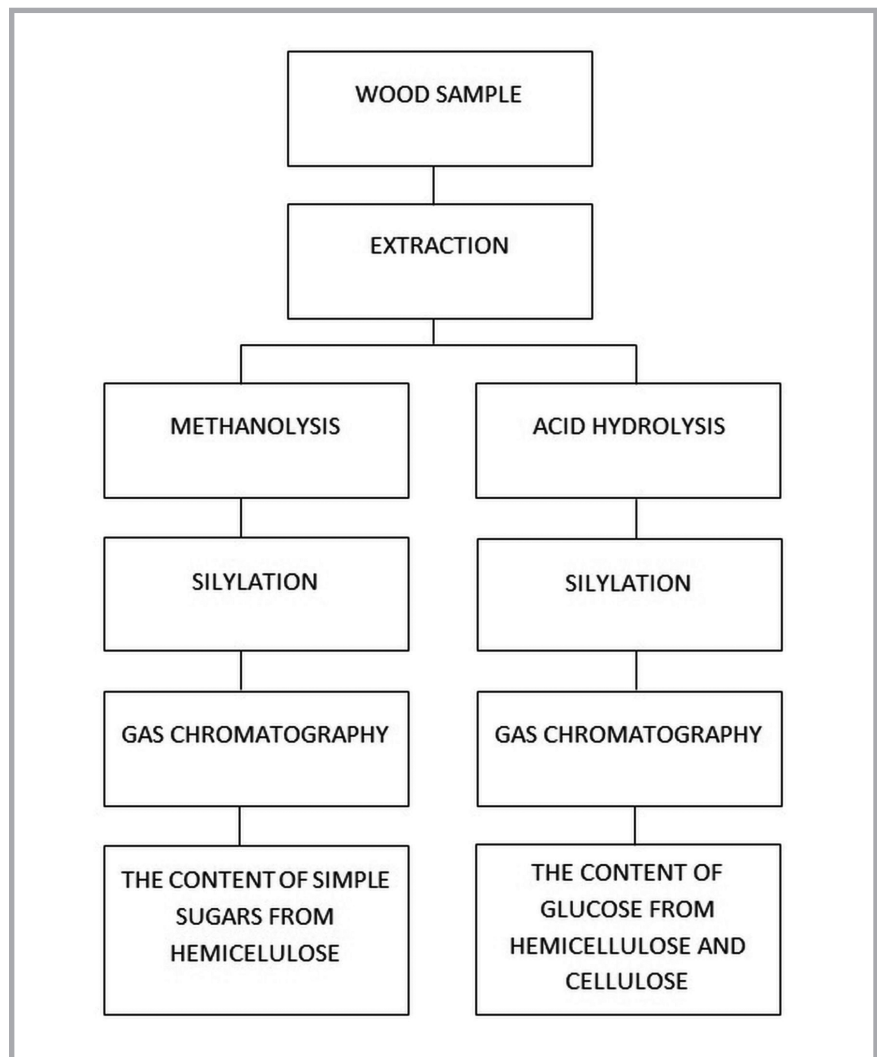


Figure 1. Scheme of procedure for determining the content of simple sugars.

at 16% (in weight) concentration for 30 min. The conditions of the mercerisation process applied are the result of the optimisation process that was presented earlier [30]. The material activated in this way was rinsed with distilled water several times to neutralise excess sodium hydroxide. Finally the wood was dried in air at an elevated temperature (ca. 110 °C) until a constant weight was achieved.

### Analysis of the chemical composition of raw and modified wood

A scheme of the procedure for determining the content of simple sugars derived from wood fillers is presented in *Figure 1*.

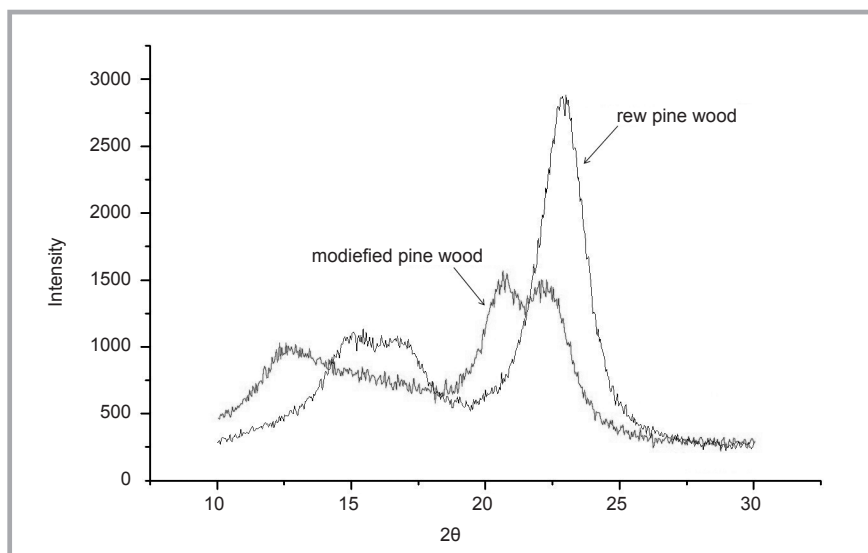
### Extraction

Wood samples were subjected to Soxhlet extraction using a mixture of ethanol: acetone (2:1, v/v) for 8 hours and then oven dried at 105 °C overnight.

### Methanolysis

The aim of methanolysis was to determine the content of simple sugars contained in hemicellulose.

To wood samples (unmodified and modified), hydrochloric acid in ethanol methanol was added. The samples were stirred and then placed in an oven (110 °C) for 6 hours. After this time the samples were cooled to room temperature and excess HCl in the solutions was neutralised by adding pyridine. In the next stage a calibration solution (monosaccharides in ethanol – 0.1 mg/1 ml) and Sorbitol as a standard compound were added to the wood samples. The solvent was evaporated in a vacuum evaporator and then dried in a vacuum desiccator (80 °C) for 10 minutes. The silylation process was realised by adding hexamethyldisilane (HMDS) and trimethylchlorosilane (TMCS) to the dried wood samples. The mixtures were then



**Figure 2.** X-ray diffraction patterns of raw wood and modified wood.

stirred in a bath with ultrasound. Finally the samples were left at room temperature for 18 h and then analysed by gas chromatography.

#### Acid hydrolysis

The aim of acid hydrolysis was to determine the content of glucose derived from cellulose and hemicellulose.

The acid hydrolysis of wood samples was performed with 72% sulfuric acid (VI) in a vacuum oven. Then distilled water was added, and they were left to stand for 24 h. Subsequently the samples were placed in an autoclave at 80 °C for 120 minutes. After cooling to room temperature, barium carbonate was added to the samples in the presence of a bromocresol green indicator.

In the next stage, a standard compound (Sorbitol in distilled water) was added to wood samples, and then they were centrifuged. After centrifugation for 10 min at 8000 rpm, the supernatant was removed and acetone added to it. Subsequently the mixtures were evaporated under inert gas (argon) and then placed in a vacuum oven for 60 minutes. Finally samples were subjected to the silylation process according to the procedure described during methanolysis.

#### Gas chromatography

The purpose of the chromatographic analysis was to determine the content of simple sugars. A gas chromatograph with a 300 mm column and internal diameter of 0.5 mm was used for the measurement. The samples were dispensed through

a flow divider at 240 °C, with an injection volume of 1.0 µl. On the basis of samples from the methanolysis process, the content of simple sugars contained in hemicellulose was determined. While from samples obtained after the hydrolysis process, the content of glucose derived from cellulose and hemicellulose was calculated.

#### X-ray diffraction

The structures of unmodified and modified pine wood were analysed by means of wide angle X-ray scattering (WAXS) using CuK $\alpha$  radiation at 30 kV and 25 mA anode excitation. The X-ray diffraction pattern was recorded for an angle range of  $2\theta = 10^\circ - 30^\circ$  in a step of  $0.04^\circ/3$  s. The efficiency of transformation of cellulose I (native form) to cellulose II (after chemical modification) was estimated.

The deconvolution of peaks was performed by the method proposed by Hindeleh and Johnson [26], improved and programmed by Rabiej [27].

#### Hot stage optical microscopy

The crystallization of PP in the presence of unmodified and modified pine wood was observed under a polarised optical microscope – Labophot-2 (Nikon), equipped with a Linkam TP93 hot stage. It was connected to a Panasonic CCD camera and to a computer. Samples were prepared by embedding wood between two films of PP. All the composite samples were first heated at 200 °C and kept at this temperature for 5 min in order to eliminate their thermal history. Then the samples were cooled down at a rate of 40 °C/min to 136 °C, at which

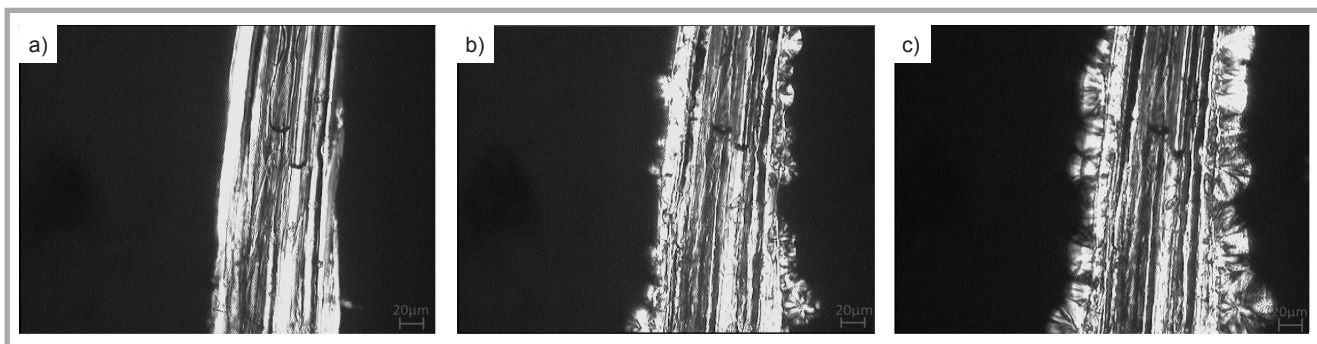
the crystallisation process took place. The growth of the transcrystalline layer was determined on the basis of observations of the PP crystallisation process in the presence of wood of various types.

## Results and discussion

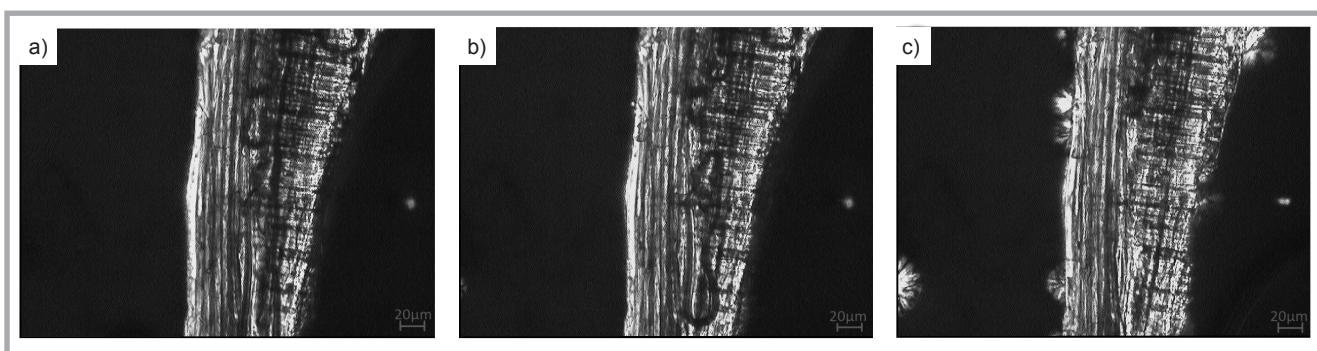
### Effect of chemical modification of wood on the supermolecular structure

A systematic evaluation of the process in which cellulose I transformed into cellulose II was undertaken. The mercerisation of wood is an important process because it permits the removal of grease from the surface and also partial removal of lignin – compounds that are responsible for the agglomeration of wood in the polymer matrix. It is also known that as a result of this process, it is possible to remove some hemicellulose content. Cellulose, however, undergoes only phase conversion; its content in the sample is constant [28]. The cellulose content in both samples tested herein was 44.7% [29]. Mercerisation leads to decreasing agglomeration potential and better dispersion of filler particles. The alkalisation process is also very important in the context of obtaining high efficiency of the chemical modification process of wood. Therefore the necessity for mercerisation as a step preceding chemical modification follows from the fact that the hydroxyl groups of native cellulose are not sufficiently reactive with the modifiers applied. Moreover the mercerisation process also leads to a change in the crystal structure and in the conversion of cellulose I to cellulose II. XRD patterns of the wood samples are presented in **Figure 2**.

It can be found that the diffraction patterns of the unmodified wood exhibit three peaks at  $2\theta = 14.7^\circ, 17^\circ$  and  $22.7^\circ$ , assigned to cellulose I. Pine wood treated with sodium hydroxide show additional peaks at  $2\theta$  equal to ca.  $12.5^\circ, 20.5^\circ$  and  $22^\circ$ , which are assigned to cellulose II. The results calculated show that cellulose I contained in the native wood was converted into cellulose II. The results obtained are consistent with the literature, which describes that the crystal structure of cellulose I is transformed into that of cellulose II, usually upon treatment with NaOH in concentrations higher than 10% [30,31]. Moreover chemical modification caused a significant reduction in crystallinity. Crystallinity index values of the fillers were 65% for untreated wood and 48% for mercerised wood.



**Figure 3.** Crystallization in iPP/unmodified wood at different times of crystallisation: a) 0 min, b) 3 min, c) 6 min.



**Figure 4.** Crystallization in the iPP/wood modified system at other crystallization times: a) 0 min, b) 3 min, c) 6 min.

### Effect of chemical treatment on the transcristallization process

**Figures 3** and **4** illustrate the process of PP crystallisation in the presence of raw and mercerised wood, taking place at 136 °C. After isothermal crystallisation from the melt, a transcristalline layer was found with crystals having grown perpendicular to the fibre axis. It is clear that the thickness of the TCL layer increases with time. However, crystallisation of the PP matrix varies significantly with the kind of wood surface.

Optical micrographs show that both the surface of raw and chemically treated wood generate the formation of transcristalline structures in each composite system, but with different effectiveness. The development of PP transcristallinity on unmodified pine wood is clearly shown in **Figure 3**. This wood acts as nucleating agent for PP as nucleation occurs preferentially along the wood. In this case, the largest nucleation densities and crystallisation rates of the polypropylene layer were recorded. The treatment of pine wood with an alkaline chemical leads to definite deterioration of the ability to form TCL structures (**Figure 4**). The nucleation density for these systems is much smaller compared

to composites containing raw pine wood. The microscopic pictures show that polymorphic transformation of cellulose I to cellulose II modified the nucleation ability of the wood surface, thereby reducing the density of the transcristalline layer. It is worth adding that the formation of a transcristalline layer in samples containing modified wood (cellulose II) may also be caused by cellulose residues with the polymorph I variant. It should be noted that it is not possible to achieve a full conversion of cellulose I to cellulose II as a result of the action of alkali [30]. In summary, differences in the cellulose I/cellulose II content at the wood surface have a decisive effect on the formation of transcristallinity.

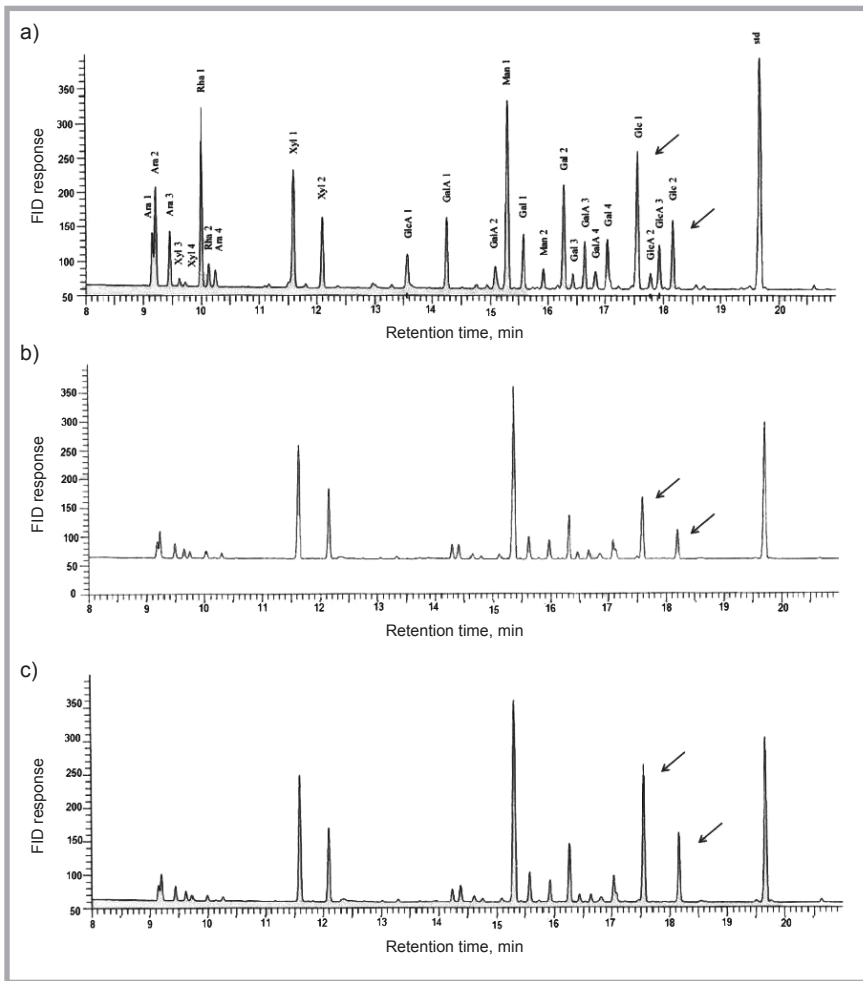
On the basis of the tests conducted, the induction time for the PP/raw wood and PP/modified wood systems was determined. A comparison of these values is shown in **Table 1**.

It is evident that the induction time for PP to nucleate on the raw wood is much shorter than on the modified wood. Moreover for the PP/unmodified wood composite, the growth rate of the TCL layer was higher than that for the composite with treated wood. It is clearly visible that the mercerisation of pine wood exerted a significant influence on reducing the nucleation ability of the wood surface. The highest activity was determined in the unmodified wood.

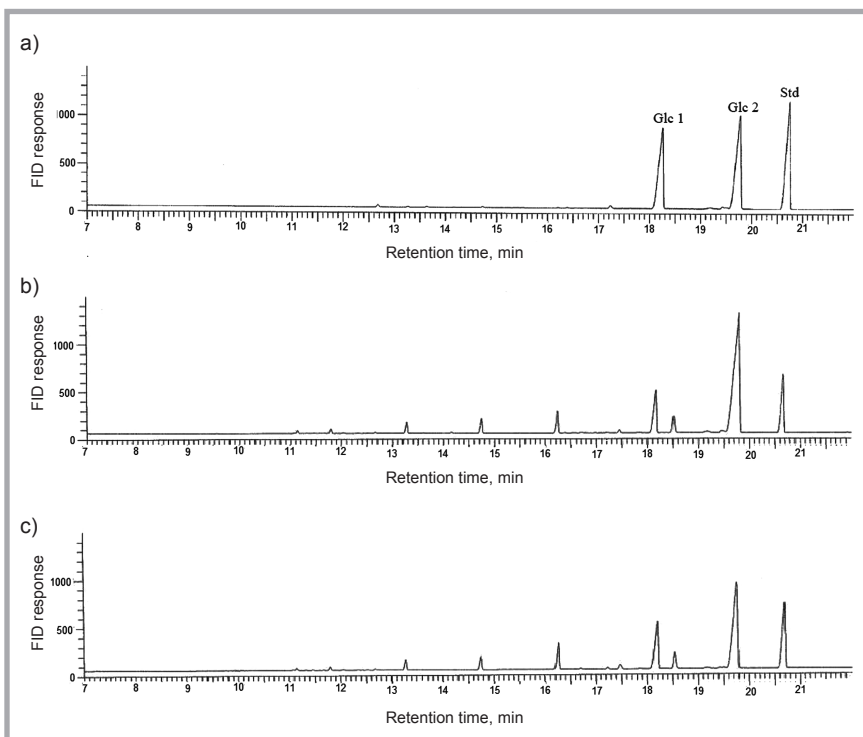
According to some authors [24, 32-35], chemical modification of the filler leads to a decrease in its nucleation abilities. Also in our studies [11] mercerisation led to the development of transcristallisation layers, but with very poor effectiveness. However, the influence of the chemical treatment of the lignocellulose component on the development of TCL structures has not been fully recognised and is controversial. There are reports in the

**Table 1.** Induction time and growth rate of the transcristalline layer in the composite materials.

	Induction time, s	The growth rate of the transcristalline layer, μm/min
PP/raw pine wood	44	6
PP/modified pine wood	160	1.5



**Figure 5.** Chromatograms showing the content of simple sugars derived from hemicellulose: a) calibration solution, b) raw pine and c) modified pine.



**Figure 6.** Chromatograms showing the content of simple sugars derived from hemicellulose and cellulose: a) calibration solution, b) raw pine wood, c) modified pine wood.

literature that the main factor responsible for reduction in the nucleation ability of the treated wood surface is the removal of low-molecular constituents [11], topography and surface energy [15]. Problems in explaining the real effect of the chemical modification of wood on the nucleation ability of composites can follow from disregarding factors related to the chemical compositions of lignocellulosic materials. Differences between the transcristalline growth of polypropylene in the presence various fillers can be explained by analysis of the contents of simple sugar derived from wood. The problems discussed above are considered in the next section.

#### Analysis of the chemical composition of wood

The quantification of individual sugars derived from hemicellulose was determined by gas chromatography. The analysis was based on the peak area, taking into account the internal standard in the calculation. A chromatogram of the calibration solution is shown in **Figure 5.a**, while chromatograms of individual sugars derived from hemicellulose is shown in **Figures 5.b** and **5.c**.

The chromatograms obtained for raw wood and modified wood are similar. However, it is possible to notice variation in the heights of glucose peaks (arrows in the Figures), which indicates the variation in sugar content. The content of simple sugars derived from hemicellulose is summarised in **Table 2**.

On the basis of **Table 1**, it can be seen that the content of compounds such as arabinose, xylose, galactose, mannose, rhamnose, glucuronic acid, galacturonic acid, and 4-O-methyl modifications of glucuronic acids is comparable in both samples. However, it was found that the hemicellulose-derived glucose content in the samples subjected to chemical modification is much more (52 mg/g dry wood) compared to the unmodified systems (25 mg/g dry wood).

The content of glucose derived from hemicellulose and cellulose was determined on the basis of the chromatograms shown in **Figure 6**. The chromatogram shown in **Figure 6.a** shows the calibration solution, while **Figure 6.b-c** contains chromatograms of raw and modified wood samples. A lower intensity of peaks in the chromatogram of samples of mercerised wood can be observed.

**Table 2.** Content of sugars, expressed in mg/g, of dry wood derived from hemicellulose of raw and modified pine wood.

	Arabinose	Xylose	Galactose	Glucose	Mannose	Rahmnose	Glucuronic acid	Galacturonic acid	4-O-Methyl modifications of glucuronic acids
Raw pine wood	15	57	23	25	70	1.8	1.32	11	7
Modified pine wood	14	61	29	52	69	1.6	2.75	8	7

Based on the chromatograms above, calculations of the glucose content originating from cellulose and hemicellulose present in both types of wood subjected to acid hydrolysis were performed (**Table 3**). It can be observed that the amount of glucose derived from hemicellulose and cellulose in raw wood is significantly higher compared to modified wood. After taking into account the content of glucose derived only from hemicellulose (**Table 2**), the content of cellulose derived exclusively from cellulose was determined. It turned out that the content of glucose from cellulose in raw wood is 171 mg/g of dry wood and is more than twice as high as the content of glucose from cellulose in wood subjected to chemical modification.

The results obtained suggest that the action of the alkaline solution (NaOH) could be responsible for the partial molecular degradation of cellulose contained in the wood, as a result of breaking the 1,4-glucosidic bond. As a consequence, cellulose with a lower degree of polymerisation and some intermediate products such as oligosucrose and cellobiose may be present in alkalisated wood. This situation may have resulted in a lower content of cellulose-derived glucose due to acid hydrolysis of the modified wood. The results are consistent with x-ray examinations, in which a significant reduction in the crystallinity of the chemically treated wood was found. It is known that arranged areas are formed in wood by cellulose particles. Lowering the crystallinity may mean degradation of cellulose chains. The hypothesis above is also consistent with literature reports, which confirm that the treatment of cellulose with concentrated solutions of hydroxides reduces the crystallinity of cellulose [36].

The results of the chemical composition of wood, with particular emphasis on glucose content, can be perfectly used to interpret the nucleation activity of raw and modified wood. Raw wood containing a high content of glucose derived from cellulose is responsible for obtaining a high nucleating activity during the crystallization of polypropylene. In the

**Table 3.** Content of glucose of dry wood, expressed as mg/g.

Sample	Glucose content derived from cellulose and hemicellulose	Glucose content derived from cellulose
Raw pine wood	196	171
Modified pine wood	136	84

case of modified wood, a significant reduction in the glucose content was found, which also results in a reduction in the nucleating capacity of this type of filler. A high content of glucose in raw wood also indicates a high value of the cellulose polymerisation degree. It is known from the literature that cellulose is responsible for obtaining high nucleation activity [24, 25, 37]. Our previous studies [29] also showed that as the content of cellulose is reduced in wood treated with  $\gamma$ -radiation, a decrease in nucleation activity is observed. In this study, it was shown that the content of glucose in wood, which is indirectly related to the degree of polymerisation, also determines the nucleating ability in composite systems. A filler with a high content of glucose from cellulose is responsible for the generation of transcrystalline structures. The results may help to explain many controversies recorded in the literature that describe a different effect of chemical modifications applied during the formation or absence of formation of transcrystalline structures, and the variation in mechanical properties obtained. A valuable conclusion from the research conducted is the necessity to take into account the change in the chemical composition of wood in the selection of adhesion modifiers in polymer-lignocellulose filler systems.

### Conclusions

Differences in the chemistry compounds of wood is a more attractive explanation for variations in nucleating ability. Therefore it is necessary to combine the new results of this work with those published earlier to gain a deeper understanding of the mechanism of transcrystallisation.

The findings made in this study can be briefly summarised as follows:

- Conducting the chemical modification of pine wood with sodium hydroxide is responsible for a significant reduction in the nucleation capacity, which was confirmed by the low nucleation density and low growth rate of transcrystalline layers as well as high values of the crystal induction time.
- Chromatographic examinations showed the very high importance of the chemical composition of wood with respect to the nucleation activity of the filler surface. The chemical modification of wood caused a significant reduction in the content of glucose derived from cellulose contained in the wood, indicating the possible course of cellulose depolymerisation processes and the formation of degradation products of lower molecular weight. Studies have shown that modifying wood does not significantly affect the content of other wood components.

The relationship between the chemical composition of wood and its nucleation activity was found. The formation of transcrystalline structures is possible for composites with a lignocellulosic filler with a high content of glucose from cellulose. Carrying out mercerisation is responsible for a significant reduction in the content of this simple sugar. The reduction in glucose content in the modified wood resulted in a decrease in the rate of formation of transcrystalline layers and lower density of nucleation. The results obtained indicate that the remaining wood components do not affect its nucleation activity.

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