

A study of transcrystallinity in polypropylene in the presence of wood irradiated with gamma rays

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Abstract The interest in lignocellulosic composites has been growing in recent years because of their specific properties. In this study, a new technique of wood treatment using γ -irradiation was used. This research focuses on the influence of the gamma irradiation on the chemical composition of wood and on the nucleation ability of polypropylene matrix. The inner morphology of the transcrystalline layer was investigated using hot stage optical microscopy. Differential scanning calorimetry was used to investigate the kinetic parameters of polypropylene crystallization in the presence of wood surface. The results showed that the gamma irradiation can decrease the content of the cellulose in the wood, but it has a slightly negative effect on the transcrystallization process of polypropylene. This treatment also affects the crystal conversion and the half-time of PP crystallization. These results suggested that the gamma irradiation of wood may play a useful role in changing the microstructure of the matrix near the wood. It was observed that the nucleation of the wood surface was selective, indicating that the chemical characteristics of the lignocellulosics might have influence on the polypropylene crystallization. A possible mechanism for the appearance of transcrystallinity involving chemical composition of lignocellulosic is also proposed.

Keywords Composites · Lignocellulosic · Polypropylene · Transcrystallization

Introduction

In recent years, polymer composites containing natural fillers have received considerable attention in both the scientific literature and industry [1–5]. Cellulosic components such as jute, flax, sisal, wood, etc. are derived from renewable resources and have many desirable properties for reinforcement of polymer such as low density, high stiffness and low cost. It is known that the performance, such as mechanical properties of composites, depends not only on the properties of the individual components, but also on their interfacial compatibility. The properties of the interphase play a crucial role in determining the properties of filler-reinforced materials. Interfacial interactions are very weak in wood filled composites, because the surface-free energy of both the filler and the polymer is very small [6, 7]. Different treatments have been used to improve the adhesion and/or the compatibility between fillers and polypropylene [8–11], and the use of compatibilizing agent [12, 13] has also been reported.

The introduction of filler into a polypropylene melt leads to a change in the morphology of the crystallizing polymer. When a cellulosic is embedded into a thermoplastic melt it may act as a nucleating site for the growth of spherulites. This phenomenon is manifested by a reduction in the values of basal interfacial-free energies for polypropylene in binary composites with wood, and thus a reduction in the free energy of nucleation and an increase in the global crystallization rate [14]. With sufficiently high nucleation density, the spherulites grow from the fibre in the radial direction only, to produce a cylindrical layer. The resulting interphase morphology is termed the transcrystalline layer (TCL) and is commonly found in semicrystalline thermoplastic composites with many different synthetic and natural fibres. Literature studies [15–26] indicate that the

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development of these structures is influenced by many different factors, among others: the type of the applied filler, its surface topography, thermal history, temperature of polymer crystallization, rate of cooling, the occurrence of shearing forces during crystallization, epitaxy associated with the adjustment of polymer and cellulose structures, surface energy of the constituents, adjustment of the thermal expansion coefficients of individual components. The numbers of factors that are reported to affect the transcrystallinity indicate that the mechanism by which transcrystallization occur are not yet fully understood.

In the case of natural component, there are abundant nucleation sites on the surface, because the main constituent is cellulose. Gray [27] was observed that when fibres containing higher quantities of lignin and hemicelluloses apart from cellulose were used some transcrystallization occurred. He also reported that the mercerized cellulose prevented the formation of TCL. Another explanation of the variability in the efficiency of the TCL structure development may be the adjustment of crystalline structures of the filler and the polypropylene matrix [28]. Authors of this concept maintain that there is a very good dimensional arrangement of the crystallization structure of polypropylene and cellulose I chains and this may provide sufficiently similar spacings of pyranose rings to polypropylene methyl groups to initiate epitaxial polypropylene growth. The mercerization process causes that the pyranose rings on the face of cellulose II are not aligned in a “flat” manner and do not provide the same configuration for the polypropylene chains to crystallization. In general, none of these explanations alone is sufficient to account for the appearance of a TCL region. Different surface treatments have been applied to cellulose to alter their chemical composition of the natural fillers. The previous studies [29, 30] were concerned with crystallization process of PP filled with various chemical-modified woods.

Our investigations were focused on the question of which gamma treatment of the wood changes the crystallization behaviour in conjunction with a changed cellulose content of the wood. This technique based on the irradiation is the only method introducing energy into a material generates favourable changes in its structure, provided it is used in the proper doses and under the appropriate conditions. According to the present state of knowledge, irradiation of wood with γ -rays contributes to the degradation of its constituent and changes the crystallinity in wood cellulose [31]. In consequence, this study is mainly aimed at evaluating development of a transcrystalline structure of the PP in presence of wood under the effects of different doses of gamma radiation. In this research field, there is a main question which still is under discussion. This question is whether the chemical composition of lignocellulosic is the main reason for the formation of transcrystallinity.

Experimental

Materials

The isotactic polypropylene matrix was used in this study. Isotactic polypropylene Malen F-401 was supplied by Basell Orlen Polyolefins (Plock, Poland) with a MFI_{230/2.16}, 2.4 to 3.2 g/10 min; isotacticity, 95%; $T_m = 163\text{--}164$ °C. Scotch pine wood (*Pinus silvestris*) particles, taken after sieve analysis from 1-mm mesh, were used as a filling material.

Irradiation treatment of wood

The wood particles were irradiated with γ -rays at radiation doses of 20, 60, 120, 300, 500, 1500, 4500 and 9000 kGy. The samples were exposed to gamma radiation in the type RChM-Gamma-20 apparatus with ⁶⁰Co as a radiation source. The gamma radiation exposition time varied from 6 h to 7 months, respectively. When the samples were irradiated at a dose of 9000 kGy then stored at room temperature for 7 months. The effect of gamma irradiation on the cellulose content in wood samples was determined with Seifert method [32].

Polarizing optical microscopy

Crystallization of polypropylene in the presence of irradiated wood was observed with a polarized optical microscope Labophot-2 (Nikon) equipped in the Linkam TP93 hot stage. It was connected to a Panasonic CCD camera and to a computer.

Thin polypropylene films, approximately 100- μ m thick, were obtained first by compression. Then the wood was placed between two PP films and next this “sandwich” was positioned between microscopic plates. The scheme of polarized optical microscopy investigations was the following: the samples were heated to the temperature of 200 °C at a rate of 10 °C/min and then they were kept at this temperature for 5 min in order to eliminate their thermal history. Next, the samples were cooled down at the rate of 20 °C/min to the temperature of 136 °C at which the crystallization process took place. After the crystallization process, samples were cooled down at the cooling rate of 20 °C/min to room temperature. Dry nitrogen was introduced to eliminate any possible degradation. The growth rate of the TCL was calculated as the slope of the linear part of the plot of the TCL thickness versus time. Optical micrographs of polypropylene crystallization in the presence of wood were analysed using MultiScan Base v.14.02 programme.

Differential scanning calorimetry

Differential scanning calorimetry measurements were carried out on Netzsch DSC 200. The samples were melted at a heating rate of 10 °C/min to 200 °C and maintained at this temperature for 5 min in order to eliminate the thermal history of the material. In the second step, the samples were cooled from 200 to 40 °C at cooling rate of 5 °C/min. This procedure was repeated two times and second segment was supplied to calculation part. The kinetic parameters of crystallization of the polypropylene matrix in the presence of sawdust such as the half-time of the crystallization and the crystal conversion were determined. The crystallization temperatures (T_{cp}) of composites were obtained from the maximum of the exothermic peaks. The samples sizes were kept between 8 and 10 mg and all tests were run under argon gas.

Results and discussion

Effect of radiation dose on the content of cellulose in wood

With the aim of analysing the behaviour of wood as a function of the integral dose of radiation applied and its possible influence on the structure of lignocellulosic, Seifert method was employed to study the content of cellulose. Table 1 lists the values of cellulose content in the wood, which were submitted to different irradiation dose.

The content of cellulose in wood is similar during the initial stage of gamma radiation at the dose range 20–300 kGy. For these samples, the content of cellulose in wood is in the range 40–45%. However, when the doses of irradiation increase above the level of 500 kGy then the cellulose content decreased rapidly. As can be seen, the only trace amount of cellulose in wood was obtained for the irradiation dose of 4500 kGy. The highest irradiation

dose (9000 kGy) leads to the total destruction of wood—the content of cellulose in this sample is 0%.

This behaviour means that the main degradation mechanism is chain scission, which highly influences amount of cellulose in wood. In addition, Goto et al. [33] reports that the γ -rays attack the structure of cellulose fibrils. This attack produces many crystalline defects throughout the whole fibres, but they retain their original shape. However, cellulose degradation of the samples in our study were consistent with the results of Antoine et al. [34], which reported that the total destruction of cellulose of *Picea abies* by gamma radiation at a dose of 6500 kGy was achieved. In our previous WAXS study [35], we found that the degree of crystallinity was reduced with increasing doses of gamma radiation and was declined to zero at a dosage of 9000 kGy in pine wood.

Effect of radiation dose of wood on the crystallization of polypropylene

In Fig. 1a–f the crystallization process for polypropylene in the presence of pine wood under isothermal conditions (136 °C) is shown.

It can be seen that the wood acts as a nucleating agent. It was also noted that the nucleation of polypropylene onto the wood surface was selective. The nucleation sites were more likely to appear at the lignocellulosic irradiated at lower of gamma doses. This indicates that the chemical compositions of wood play an important role in the nucleation process for polypropylene.

Figure 1a–c shows the optical microscope morphology of polypropylene in the presence of wood irradiated at lower of gamma doses (max. 300 kGy). When PP melt is allowed to cool in contact with this wood, which is a source of nucleating centres, the proximity of these sites on the surface inhibits lateral growth of the resultant spherulities, thus the crystallization develops only in a direction normal to the wood surface. The development of such a layer has

Table 1 The content of cellulose in wood after γ -irradiation treatment, values of the crystallization temperatures and the half-times of crystallization

| Samples | Radiation dose/kGy | Content of cellulose/% | The crystallization temperatures/°C | The half-time of crystallization/min |
|---------|--------------------|------------------------|-------------------------------------|--------------------------------------|
| TG0 | 0 | 44.7 | 115.1 | 1.57 |
| TG1 | 20 | 44.1 | 114.9 | 1.63 |
| TG2 | 60 | 45.2 | 115.4 | 1.66 |
| TG3 | 120 | 43.0 | 115.2 | 1.67 |
| TG4 | 300 | 40.1 | 114.9 | 1.66 |
| TG5 | 500 | 34.2 | 114.7 | 1.89 |
| TG6 | 1500 | 14.4 | 113.1 | 2.08 |
| TG7 | 4500 | Trace | 112.6 | 2.42 |
| TG8 | 9000 | 0 | 112.5 | 2.45 |

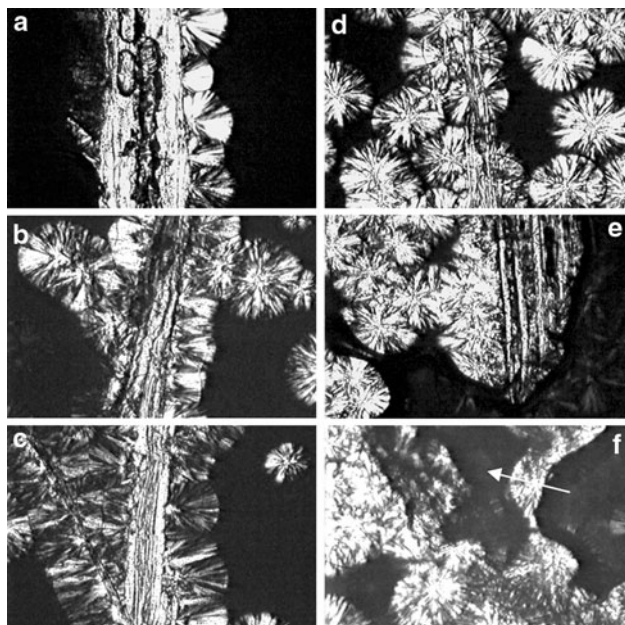


Fig. 1 Microscopy images of PP mixed with γ -irradiated wood, at 136 °C for 2.5 min: **a** TG0, **b** TG2, **c** TG4, **d** TG6, **e** TG7, **f** TG8 (arrow indicates wood); (magnification $\times 200$)

been termed “transcrystallization”. For PP/TG0-TG4 composites, transcrystalline morphology is characterized by a high density of nucleating crystallites which grow with an orientation perpendicular to the surface responsible for nucleation. The thickness of TCL is comparable in range 45 μm (after 3 min).

In Fig. 1d, transcrystallization process for polypropylene in the presence of wood irradiated at a dose of 1500 kGy is shown. Here, the situation is slightly different from the previous case. Bulk spherulites begin to form first and then they are followed by the formation of transcrystalline spherulites. Some transcrystallization at the wood surface was observed but not as much as for the TG0-TG4. The formation of the TCL is slower than that of TG0-TG4. The TCL at wood surfaces (TG6) was inhibited by irradiation at higher dose. Moreover, the final thickness of the TCL is smaller (about 25 μm after 3 min.) than with PP/TG0-TG4.

In Fig. 1e and f the crystallization process in the presence of wood (irradiated at dose of 4500 and 9000 kGy)/PP is shown. Although the bulk spherulites are well grown no TCL can be seen around the wood. It may be suggested that the differences of nucleation of PP in the presence of wood, as revealed in Fig. 1a–f, is depends on the chemical compositions of filler. Clearly, the detection of this apparent boundary in chemical composition of wood is an important step in understanding the mechanism of transcrystallization. We therefore propose that the amount of cellulose in wood plays important a role.

The growth rates of TCLs for all the analysed composite materials are shown in Fig. 2. It turned out that the highest

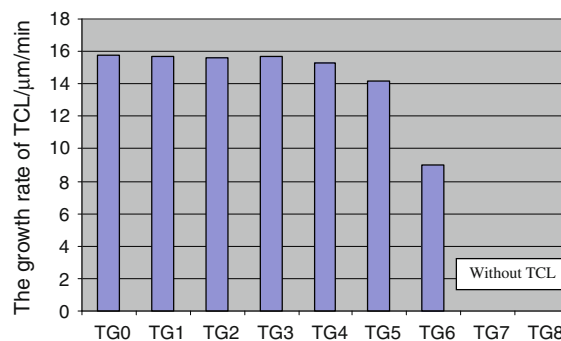


Fig. 2 The growth rate of TCL in various composites

rates of TCLs (ranging from 14 to 16 $\mu\text{m}/\text{min}$) were recorded in the case of the composite which contained wood subjected to the irradiation at the dose range 20–500 kGy. Composite systems containing wood after irradiation at dose of 1500 kGy were characterized by lower rates (of the order of 9 $\mu\text{m}/\text{min}$). Clearly, at highest irradiation doses (4500 and 9000 kGy) the transcrystalline region was not presented.

Figure 3 shows the comparison of the growth rate of TCL and the content of cellulose in irradiated wood. The growth rate of TCL decreases with decreasing content of cellulose. The presence of cellulose in wood might increase the number of active nucleating sites. However, it is likely to be responsible for the formation of transcrystallinity. Among the various mechanisms [19, 27, 36, 37] which account for transcrystalline phenomenon, the most noticeable mechanisms are those concerned with crystal structure matching between matrix and fillers.

Numerous literature items confirm that the interaction at a molecular level between the cellulose and polymer matrix is one of the possible causes of development of TCLs. The explanation of the variability in the efficiency of the TCL structure development may be the adjustment of crystalline structures of the filler and the polypropylene matrix [28]. Authors of this concept maintain that there is a very good dimensional arrangement of the crystallization structure of polypropylene and cellulose I chains and this may provide sufficiently similar spacings of pyranose rings to polypropylene methyl groups to initiate epitaxial polypropylene growth. Felix and Gatenholm [25] also suggest an adsorption configuration that involves the interaction of the α -carbon/methyl moieties of PP and the oxygens in the electron-rich glucosidic linkages in cellulose. The somewhat skewed electron density around the α -carbon/methyl moiety allows relatively strong Lifshitz–van der Waals interactions to form with the glucosidic oxygen. However, the unit cell parameter c of PP is 0.65 nm, and corresponds well with the linear distance of about 0.66 nm between the glucosidic oxygens in the cellulose. Turnbull and Vonnegut [38] have also postulated that nucleating efficiency should

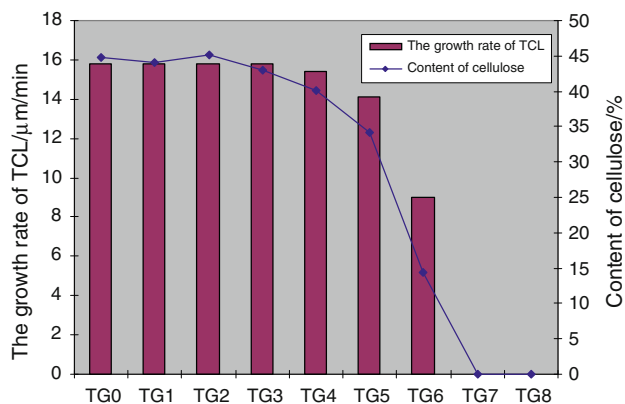


Fig. 3 The correlation of the growth rate of TCL and content of cellulose after γ -irradiation treatment

increase with increasing closeness of match between the lattice parameters of the filler and the forming crystal. The ability of cellulose fibres, such as cotton, ramie and rayon to induce TCL in PP, was first reported by Gray [27]. Gray noted that when fibres containing higher quantities of lignin and hemicelluloses (amorphous materials) were used some transcrystallization occurred.

Although many authors have studied polypropylene and filler composites in recent years, the relationship between the quantitative analysis of cellulose in wood and the nucleation ability and transcrystallization process has not yet been analysed. Therefore, we assume that the reduction of the transcrystallinity growth rate can be caused by the decrease in the effective surface of wood due to irradiation treatment. We suggested that transcrystallinity occurred by the interaction of PP and cellulose at molecular level attributable to the adsorption configuration and the matching of interaction sites. The highest irradiation doses (>4500 kGy) lead to the total destruction of wood—the content of cellulose in this sample is 0%. No wood surface nucleation activity was observed in this composite; no TCL structures were reported. The transcrystallization after this physical treatment was not presented due to the fact that the TCL is induced at cellulose component.

Differential scanning calorimetry (DSC) measurements can be used to investigate the kinetic parameters of polypropylene crystallization in PP/wood composites. From the calorimetric measurements, it can be concluded that the creation of transcrystallinity is related with kinetic of crystallization process. Figure 4 shows crystallization thermograms for the PP/wood composites at different irradiation doses. In the thermograms a single well-defined exothermic peak can be observed, corresponding to PP.

Moreover, it is detectable that values of T_{cp} are dependent of the irradiation doses of wood. Based on the thermograms presented (Fig. 4), we can infer that the values of the maximum crystallization temperature for the composites

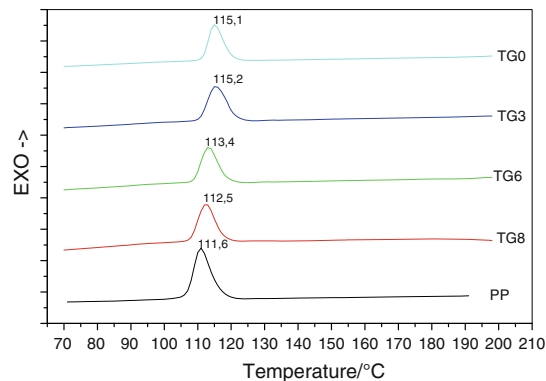


Fig. 4 Crystallization exotherms from wood/polypropylene composites and PP

which contained wood at low irradiation doses (<500 kGy) range 115–116 °C. A decrease in crystallization temperature by about 3 °C observed in composites with wood at radiation doses of 4500–9000 kGy in comparison to unmodified wood. Values of crystallization temperatures of the composites under study can be found in Table 1. As can be seen, these values remain constant at low irradiation doses and then tend to decrease as dose increases. This behaviour is caused by the decrease activity for heterogeneous nucleation of PP.

Figure 5 shows the curves of conversion of the amorphous phase into the crystalline one for the examined composite systems. It is quite evident from these curves that γ -irradiation processes of wood caused a very significant reduction of the degree of the conversion phase. Composites with irradiated wood at lower of gamma doses (max. 300 kGy) are characterized by values of the degree of phase conversion almost identical with the systems which contain unmodified wood. Moreover, the results given in Fig. 5 indicate that nucleating ability of wood surfaces irradiated at doses 500 kGy is lower than that in

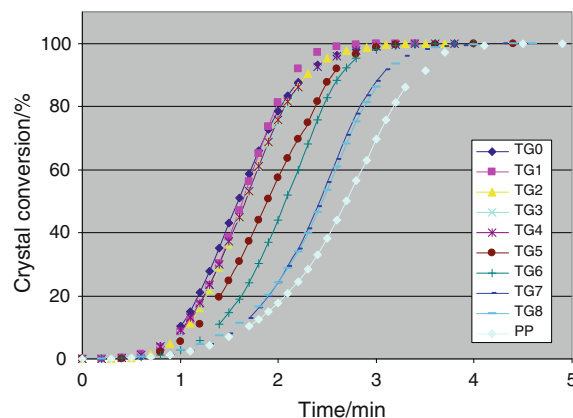


Fig. 5 Crystal conversion of polypropylene in presence of wood after γ -irradiation treatment

samples TG0–TG4 although clearly the differences are not great and the values do not appear to permit adequate discrimination between different composite materials. The obtained results are similar with the observations recorded using the microscopic technique. The crystal conversion is significantly decreased for composites with irradiated wood at dose of 4500 and 9000 kGy. As an example, in Fig. 5 the crystal conversion is reported, evidencing that irradiated wood at dose above 4500 kGy possesses lowest nucleating ability.

Similar relationships can be found in the case of the determined values of the half-times of crystallization ($t_{0.5}$) presented in Table 1. The rate of crystallization was analysed using the values of $t_{0.5}$ which corresponds to the time necessary to reach a degree of crystalline transformation of 50%. The obtained results show the highest nucleation activity of unmodified wood surface which manifests itself in the lowest values of the half-times of crystallization (about 1.5–1.6 min). It is also worth noting that TG1–TG4 composites have a crystal conversion values comparable to that of unmodified wood/PP composites. The decrease in cellulose content in wood (TG5 and TG6), following its physical treatment with γ -radiation, is responsible for the increase in the half-times of crystallization in comparison with the systems containing untreated wood. In this case, values of the half-times of crystallization reached the level of 1.9–2.1 min, i.e. they were only slightly higher than those of the composites containing unmodified wood. The highest $t_{0.5}$ values (about 2.4 min) were recorded in the case of composites containing wood after irradiation at dose of 4500 and 9000 kGy. It is worth stressing here that composites containing modified wood at highest doses are characterized by the highest half-time values which are comparable with the values obtained for polypropylene matrix. This situation can probably be attributed to the crystallization of polypropylene which takes place in the whole bulk without transcrystalline phase.

The performed DSC investigations corroborated the results obtained using the technique of polarization microscopy. Both of the applied methods showed that wood nucleation activity used as filler depends significantly on the physical treatment. The highest activity was determined in the wood which was not subjected to any irradiation treatment. The applied γ -irradiation processes of wood resulted in a distinct deterioration of the nucleation properties of wood surface. However, it must be added here that the composites containing such fillers are characterized by worse nucleation properties than the composite materials with unmodified wood.

Numerous investigations have been carried out dealing with polymer heterogeneous crystallization in the presence of fillers. However, it should be emphasized that the nucleation mechanism of supermolecular structures (including

transcrystallization) by surfaces of fillers continues to raise controversies and is still widely investigated by many researchers. As a continuation of this study we plan to investigate the impact of cellulose isolated from irradiated wood on its nucleation activity.

Conclusions

The transcrystallinity phenomenon in the wood/polypropylene system is affected by the different chemical composition of wood. The amount of cellulose seems to be an important factor affecting the morphology of the TCL and the ability of the wood to induce it. The results showed that the gamma irradiation can decrease the content of the cellulose in the wood, but it has a slightly negative effect on the transcrystallization process of polypropylene. The growth rate of TCL as well as crystallization temperatures decreases and the half-time of PP crystallization increases with decreasing content of cellulose. However, the kinetic parameters of PP crystallization in the composites with wood irradiated with doses below 1500 kGy are comparable. Small differences in the kinetic parameters of crystallization of PP in the presence of wood irradiated with different doses up to 500 kGy can follow from experimental errors related to the specific character of the filler.

It should be also taken into regard that the formation of supermolecular structure of PP can be influenced by the size and shape of the wood particles. It is, however, unquestionable that development of structures at the interface polymer–wood is completely different in the composites with the wood irradiated with doses higher than 1500 kGy than in those with the wood irradiated with lower doses. If the wood is devoid of cellulose, the nucleation abilities are significantly deteriorated leading to the lack of formation of transcrystalline structures. All composites containing the wood without cellulose (TG7 and TG8) displayed significant decrease in nucleating ability of the polypropylene.

The presence of cellulose in wood might increase the number of active nucleating sites. However, it is likely to be responsible for the formation of transcrystallinity. On the grounds of our observations and literature data, we put forward a hypothesis that one of the reasons for transcrystallinity formation is the interaction of PP and cellulose at molecular level attributable to the adsorption configuration and the matching of interaction sites. In other words, the observed transcrystallinity can be considered as an effect of the presence of cellulose in wood surfaces. The differences in transcrystallinity for various modifications of wood suggest that the formation of TCL is connected with the different ability of surface fibre nucleation and with the crystal growth rate.

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