

Fundamental Studies on Lignocellulose/Polypropylene Composites: Effects of Wood Treatment on the Transcrystalline Morphology and Mechanical Properties

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ABSTRACT: Effects of alkalization, esterification, and γ -irradiation of wood on the transcrystalline morphology of wood/polypropylene composites were investigated using X-ray diffraction, hot stage optical microscopy, and scanning electron microscopy. The occurrence of transcrystallization in wood-polypropylene composites is strongly dependent on the type of chemical modification of lignocellulosic materials. A detailed analysis of the results obtained proved that the transcrystallization is strongly influenced by conditions of mercerization process of wood and kind of anhydrides. Moreover, it has been found that amount of cellulose in wood plays a key role in the development of transcrystallinity. The absence of cellulose in wood seems to be unfavorable for the growth of transcrystallinity. A relationship between mechanical properties of composites and the phenomena taking place at the polymer-filler interface, controlled by chemical modifications of lignocellulose components has been evaluated. It has been established that the mechanical properties of wood composites depend on the proper choice of a modifier and are obtained after optimization of the process of modification. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: polypropylene/wood composites; chemical treatment; transcrystallinity; mechanical properties

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INTRODUCTION

In recent years, thermoplastic composites reinforced with a natural component, such as wood, sisal, jute, hemp, and flax fiber have been found to show a number of beneficial properties as they combine good mechanical properties with renewability and biodegradability.^{1–4} From the viewpoint of application in composites the main disadvantage of cellulose is the incompatibility between the hydrophilic surface of cellulose and the hydrophobic thermoplastic. References^{5–8} provides numerous methods of chemical modification of lignocellulosic constituents that have been developed, the majority of them employs organic acids, anhydrides, isocyanates, epoxy compounds, and silanes. Therefore, extensive studies^{9–11} have been undertaken to examine the pretreatment procedures of the natural fiber and their effects on the interfacial adhesive mechanism of natural fiber and polymer composites.

It is well known that the natural fillers can cause changes in morphology and crystallinity of the interphase regions. The fibers may act as heterogeneous nucleating agents and nucle-

ate crystallization along the interface with sufficiently high density of nuclei. The nucleation ability of certain fibers is extremely high, so that subsequent crystal growth is normal to the fiber until the growing front is impeded by the growth of spherulites nucleated in the bulk. Thus, a columnar crystalline layer, known as transcrystallinity (TCL) will develop at the fiber/matrix interface. The development of such structures has been reported for many polymer systems such as, for example: PE, PP, PA—6.6, PPS as well as fibrous fillers such as: aramide, carbon, glass, flax fibers, and jute.^{12–16} The exact mechanism for transcrystallinity is not fully understood. Literature studies^{12–16} indicate that the development of these structures is influenced by many different factors, among others: the type of filler applied, 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, and adjustment of the thermal expansion coefficients of individual components.

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The studies performed so far can be classified into two categories. The first comprises the studies on the use of compatibilizers and coupling agent in order to improve the mechanical properties. The second comprises the studies on the correlation between the chemical treatment of fibers and transcrystallization and chemical modification of cellulose components. In the latter research field there are two main questions, which still are under discussion. The first question refers to the ways in which transcrystallinity affects mechanical properties of the composite? The second question is if the surface chemistry of cellulose fiber is the main reason for the appearance of transcrystallinity? Both the questions will be discussed in this article.

The character of interfaces between the fillers and the matrix in composite materials has been widely regarded as the most important factor determining their mechanical properties.¹⁷ Although, many researches have conducted studies on TCL, the effects of transcrystallinity on the mechanical properties of composites are quite contradictory. Several researches have concluded that transcrystalline layer formation improves the interfacial strength and mechanical properties.^{18–27} The presence of a transcrystalline layer enhanced interfacial shear transfer between PP and cotton.²¹ A thorough study of PP transcrystallization at flax fiber surfaces also showed enhanced interfacial adhesion.¹⁸ Zhang et al.²⁸ reported that the interfacial morphology plays a crucial role in enhancement of load transfer. Moreover, higher modulus of transcrystallized polypropylene (PP) as compared to that of fine spherulitic material is attributed to somewhat higher orientation of polymer chains from mother lamellae. Folkes and Hardwick²⁷ have reported that the presence of transcrystalline layers leads to modest increases in flexural modulus and strength, and can thus be said to have a reinforcing effect. TCL may provide a protective sheath around fibers, which prevents them from necking during tensile loading. Chen and Hsiao²² have shown that the interfacial bond strength in a fiber/thermoplastic system could be raised by up to 40% because of the presence of TCL. Transcrystalline layers tend to be highly crystalline and oriented, and as a result have a relatively high Young's modulus, shear and tensile yield strength but low elongation at break and low failure energy. Moreover, if transcrystalline layers are relatively strong, this may be advantageous in achieving good adhesion.²⁹

However, no effect or even a negative effect on interfacial and mechanical properties has been reported in other studies.^{30–32} Xavier and Sharma have reported that transcrystallinity did not influence the interfacial bondage.³¹ Also, Son et al.³³ have shown that TCL gives a negative effect on tensile strength. A possible reason for these discrepancies may be difficulties in studying the relation between the chemical modification of the filler and crystallization of the interphase in composite systems. To the best of our knowledge, no study has been made on the quantitative evaluation of wood subjected to chemical modification. The results of this study might change the common point of view on the influence of structure of the cellulose and chemical activation of wood surface on the formation of transcrystalline structures.

The review of literature on the subject indicates that when a chemical treatment is applied or when a compatibilizer is added

to the wood-polymer system, the nature of fillers may be modified because of the interaction between the filler and compatibilizer, and consequently, the nucleation capability of fillers may be changed. The capability of transcrystallization development in the PP systems with such lignocellulosic materials such as: cotton, ramie, rayon, and wood, has been first investigated by Gray.³⁴ He has found that cotton subjected to the mercerization process failed to generate TCL structures. On the other hand, Son et al.³³ have claimed that cellulose II induced transcrystallinity in a PP matrix. In our studies,³⁵ mercerization of wood led to the development of transcrystallization layers but with very poor effectiveness. Zafeiropoulos et al.¹⁸ reported the development of transcrystallinity in the presence of flax modified with stearic acid, although the obtained filler was characterized by a poorer nucleation activity in comparison with those of unmodified flax fibers. On the other hand, Quillin et al.³⁶ have presented completely different results and reported that they did not observe the development of TCL layer after application of such a chemical modification. Moreover, surface treatment by alkyl ketene dimers and stearic acid inactivate the nucleation sites on the surface resulting in no transcrystallinity induction.³⁶ Thomas and coworkers³⁷ have found that after chemical modification of sisal fiber, TCL occurred at the interface. Lenes and Gregersen have shown that the addition of untreated cellulose materials generates a transcrystalline phase while the esterified cellulose materials do not induce TCL.³⁸

The review of literature shows that chemical modification influences the transcrystallization. Although, there is a significant number of an article on transcrystallinity, still many controversial results and comments could be found. Moreover, it is still difficult to define how the transcrystallinity does affect the interfacial adhesion between fiber and matrix. However, to the best of our knowledge, there are no reports on a relation between chemical constitution of wood and interfacial morphology.

This work is part of a comprehensive investigation of the effect of chemical (or physical) modification of wood on the interfacial phenomena and on the properties of lignocellulosic-PP composite materials. The aim of this study is to evaluate the effect of various chemical and physical surface treatments of wood on the formation of transcrystallization in PP matrix, using optical microscopy. Moreover, it is expected that the results will permit better understanding of a relationship between the mechanical properties and the growth of TCL in the treated and untreated wood. To achieve this information, the effect of the wood treatment on the properties of the composites must be clearly defined.

EXPERIMENTAL

Materials

Isotactic PP used as a matrix was Malen F-401 (MFI_{230/2.16}: 2.4–3.2 g/10 min, isotacticity- 95%, $T_m = 163–164^\circ\text{C}$) produced by Basell Orlen Polyolefins (Plock, Poland).

Two different types of wood were used as a filling material:

- unmodified pine wood (*Pinus silvestris*) particles, and
- pine wood irradiated with γ -rays at radiation dose of 9000 kGy. The procedure of γ -radiation of wood is given in our previous article.³⁹

Table 1. The Composites Studied and Their Labels

| Abbreviation | Compounds |
|--------------|--|
| PP/W-un | PP and wood—untreated |
| PP/W-m10 | PP and wood-mercerized with 10% NaOH |
| PP/W-m17 | PP and wood-mercerized with 17.5% NaOH |
| PP/W-pa | PP and wood-treated with propionic anhydride |
| PP/W-sa | PP and wood-treated with succinic anhydride |
| PP/W-gr | PP and wood-irradiated with γ -rays |

The wood used for the experiments has an average particle size of 0.5–1.0 mm.

The unmodified wood was subjected to the process of chemical modification.

Chemical Modification of Wood

Mercerization. Sawdust dried for 24 h at 70°C was treated at room temperature in the aqueous solution of sodium hydroxide with 10% and 17.5% (in weight) concentrations for 60 min with vigorous stirring. Afterward, the alkalinized pine wood was washed with distilled water for several times to remove the excess of NaOH. The wood was then dried in the air at an elevated temperature (ca. 110°C) to a constant weight.

Esterification. In this work, to improve the interaction between wood and PP, two kinds of anhydrides were used. The chemicals used for wood treatment were: propionic and succinic anhydrides. Part of the wood (after alkali treatment with a 17.5% NaOH) was immersed in a one molar solution of anhydride (propionic or succinic) in xylene and then heated at reflux temperature for 8 h. Vigorous stirring of the slurry was achieved by the use of a mechanical stirrer at a rate of 100 rpm. When the time of the reaction expired, the slurry was filtered, the modified wood was washed several times with distilled water, and extracted by the ethanol : toluene mixture [2 : 1, (v/v)] in the Soxhlet apparatus for 8 h to eliminate the unreacted anhydride. Finally, the treated wood was dried in an oven at 80°C until its weight reached a constant value. The esterification process was confirmed by the FTIR spectra and weight percent gain.^{35,40} Af-

ter esterification treatment, the absorption peak at 1710–1740 cm^{-1} was observed. The presence of these sharp and well-defined absorption peaks are because of the esterification between hydroxyl groups of the wood and acetyl groups of acid anhydrides.

X-ray Diffraction

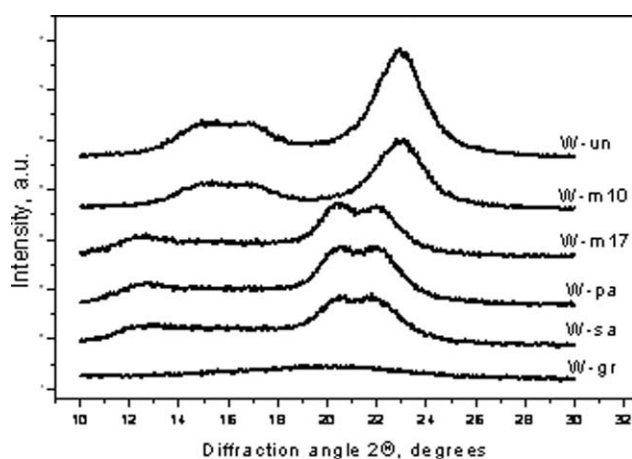
The structures of untreated and treated wood were analyzed by means of wide angle X-ray scattering (WAXS) using $\text{CuK}\alpha$ radiation at 30 kV and 25 mA anode excitation. The X-ray diffraction (XRD) pattern was recorded for the angles from the range of $2\Theta = 10^\circ\text{--}30^\circ$ in the step of $0.04^\circ/3$ s. Deconvolution of peaks was performed by the method proposed by Hindeleh and Johnson,⁴¹ improved and programmed by Rabiej.⁴² After separation of XRD lines, the crystallinity index (X_c) of wood after chemical treatment was calculated by comparison of areas under crystalline peaks and amorphous curve. Changes in the supermolecular structure of wood were analyzed as a function of wood treatments.

Hot Stage Optical Microscopy

Crystallization of PP in the presence of sawdust was observed under a polarized optical microscope Labophot-2 (Nikon) equipped in a Linkam TP93 hot stage. It was connected to a Panasonic CCD camera and to a computer. The samples were prepared by embedding the wood between two films of PP. The PP films were prepared manually between microscopy slides on a hot plate. All the composite samples were first heated at 210°C and kept at this temperature for 5 min in order to eliminate their thermal history. Then the samples were cooled down at the rate of 20°C min to 134°C at which the crystallization process took place. The growth of the transcrystalline layer was determined on the basis of observations of PP crystallization process in the presence of wood of various types. At the first stage of determination of this parameter, the transcrystalline thickness was plotted as a function of crystallization time. It is well known, that the growth rate shows a linear increase until the transcrystalline layer impinges on the spherulites at the bulk.^{30,33} The slope of the straight line represents the crystal growth rate.

Composite Preparation for Mechanical Testing

The composites were produced in a two-stage process. In the first stage, wood particles were compounded into pellets at 50% by weight with the PP using a single screw extruder with a length-to-diameter ratio $L/D = 25$. During the extrusion, the temperatures of the three processing zones were chosen as: 140,

**Figure 1.** Diffraction curves of wood samples.**Table II.** Percentage of Crystallinity of Untreated and Treated Wood Calculated According to the Area Method

| Samples | Crystallinity (%) |
|---------|-------------------|
| W-un | 70 |
| W-m10 | 58 |
| W-m17 | 42 |
| W-pa | 44 |
| W-sa | 41 |
| W-gr | 0 |

180, 195, respectively, and the extrusion die temperature of 190°C. Screw speed was 25 to 30 rpm. The cooled strands were subsequently pelletized into granules and dried. In the second stage, composite test specimens were injection molded at 210°C. Specimens were made according to ASTM specifications for tensile and impact testing. The types of composites used and their labels are given in Table I.

Mechanical Testing of Composites

The specimens were stored in a desiccator for a few days before testing. At least 10 specimens of each composite were tested. The tensile strength properties were evaluated according to ASTM D 638 specification. The tests were carried out using a Zwick (model Z020) universal mechanical testing machine with a load cell capacity of 20 kN at a cross-head speed of 5 mm/min for modulus determination as well as for tensile strength and elongation at break measurements. The tensile strength and modulus were determined from the stress–strain curves. To investigate fracture behavior Charpy impact strength test was made according to ASTM D256 standard with a Zwick 5102 impact test device.

Scanning Electron Microscopy

The fractured surfaces from Charpy impact test specimens were examined with a Carl Zeiss AG–EVO 40 Series at an acceleration voltage of 18 kV. All the specimens were sputter-coated with gold before examination.

RESULTS AND DISCUSSION

Effect of Treatment on the Supermolecular Structure of Wood

The treatment of lignocellulose with NaOH is important because it permits not only the removal of grease from the surface, but also partial a removal of lignin and hemicellulose, favoring interaction between filler and matrix.⁴³ Cellulose is a crystalline material. Alkali treatment may change its structure and properties. When native cellulose (cellulose I) is mercerized with sodium hydroxide, the transformation of its crystal structure from cellulose I to cellulose II takes place. The geometry of both cellulose is monoclinic, with parameters: $a = 8.3$, $b = 10.3$, $c = 7.9A$, $\beta = 84^\circ$ (for cellulose I) and $a = 8.1$, $b = 10.3$, $c = 9.1A$, $\beta = 62^\circ$ (for cellulose II). Polymorphic transformation of cellulose I to cellulose II involves formation of intermediate products such as alkalicellulose and hydratocellulose.

WAXS was used for the detection of changes in the crystalline structure of the wood. The XRD traces of the natural components are presented in Figure 1.

The diffraction pattern of unmodified pine wood in Figure 1, showed only three peaks at $2\Theta = 15^\circ$, 17° , and 22.7° assigned to cellulose I. The diffractograms of the samples after mercerization (with a 17.5% NaOH) revealed three additional peaks ($2\Theta = 12.5^\circ$, 20° , and 22°) assigned to cellulose II.

Unexpectedly, the XRD trace recorded on the wood (mercerized with a 10% NaOH) is characteristic of cellulose I form. Alkali treatment did not change the crystal modification of cellulose. It has been established that upon treatment of native celluloses with a water solution of NaOH, lattice I can be converted irre-

versibly to type II.^{44–46} However, similar studies on wood showed that no conversion takes place due to strong alkali treatments and in some cases only partial decrystallization occurs.^{45,47} This confirms that polymorphic transformation of cellulose depends on the concentration of hydroxide sodium solution as well as the time of chemical treatment.⁴⁶

According to X-ray data, the diffraction curves of wood samples modified with propionic anhydride or succinic anhydride are close to that of the sample mercerized with a 17.5% NaOH. This very interesting observation means that the esterified samples subjected earlier to mercerization contain cellulose II in the amount similar to that in the sample subjected only to mercerization. This result indicates a high stability of this polymorphic variety of cellulose (obtained in the process of mercerization) in esterification by acid anhydrides.

Figure 1 presents also the XRD curve for a sample of irradiated wood. As follows from this curve, the wood has been totally destroyed. The content of cellulose in this sample is 0%.

A detail analysis of γ -radiation process of wood is given in our previous article.³⁹ According to Bhuiyan et al., irradiation of wood with γ -rays contributes to the degradation of its constituents and changes the crystallinity in wood cellulose.⁴⁸ The degradation mechanism is chain scission, which highly influences the amount of cellulose in wood. In addition, Antoine et al.⁴⁹ reports that the total destruction of cellulose by gamma radiation at dose 6500 kGy was achieved.

The crystallinity of different wood samples was calculated and the results are shown in Table II.

As it can be seen, the untreated wood has the crystallinity index of 70%. Alkali treatment decreases the crystallinity index of wood to 42% (for 17.5% NaOH) and 58% (for 10% NaOH). A similar character of the dependence of cellulose crystallinity on NaOH concentration during alkali treatment has been in recent works.^{50,51} Previous investigation on mercerization of cotton or ramie has shown that the crystallinity of cellulose decreases as a result of this treatment.

Moreover, composites with esterified wood are characterized by values of the crystallinity almost identical with the systems, which contain mercerized wood (W-m-17). The observation is very interesting and implies that esterification of preliminary mercerized wood does not induce changes in crystallinity. In other words, chemical treatment can not disrupt the regularity of the crystallites of cellulose I and cellulose II obtained during the process of mercerization. Our experiments correspond to the results reported by Shiraishi et al.,⁵³ who explained that chemical reaction begins in the amorphous region of the cellulose, since the reagent cannot diffuse into the crystalline region. This decrease results in the opening of some of the hydrogen-bonded cellulose chains, producing some new amorphous cellulose and, as the reaction proceeds, more amorphous cellulose is formed.

Summarizing, for the series of treated samples a clear influence of the conditions of modification on polymorphic transformation of cellulose has been observed.

Effect of Treatment on the Transcrystallization Process

Figure 2 illustrates the process of PP crystallization in samples containing individual types of wood, taking place at 134°C. The morphology of the PP matrix varies significantly with the kind of wood surface.

Figure 2(a) shows typical PP morphologies around the untreated wood. When PP melt is allowed to cool in contact with untreated wood, which is a source of nucleating centers, the proximity of these sites on the surface inhibits lateral growth of the resultant spherulites, thus the crystallization develops only in the direction normal to the wood surface. This supermolecular structure is identified as the transcrystalline interphase. The appearance of transcrystallinity indicates a high ability of heterogeneous nucleation. It can be seen that the TCL layer formed is quite big and very uniform. It has been found that for lignocellulose/PP composites, the treatment of the wood surface with various chemicals inactivates the surface features responsible for nucleating the transcrystallinity. Figure 2(b) shows micrographs of mercerized wood (with 10% NaOH) embedded in molten PP. This wood acts as a nucleating agent for PP as nucleation occurs preferentially along the wood. However, in PP/W-m10 composite the density of nuclei in the transcrystalline layer was lower than that in the composite with untreated wood. We believe that the main factor responsible for the reduction in the nucleation ability of treated wood surface is the removal of low-molecular constituents (grease and lignin). In an earlier study,⁵⁴ mercerization and extraction processes of wood caused a very significant reduction in the degree of the phase conversion in comparison with that in the systems containing unmodified wood. Moreover, Campbell and Qayyum⁵⁵ noted that high nucleation in composite systems may be caused by the preferential adsorption of impurities in the melt onto wood filler surface. When a certain amount of impurities, e.g., grease, was removed by alkali treatment, the amount of active nuclei was reduced.

It is perfectly visible that transcrystallization is strongly influenced by the conditions of mercerization process of wood. Wood mercerization in higher alkali concentration (17.5%) did not induce the transcrystalline layer formation to the same extent as the treatment with 10% NaOH, as shown in Figure 2(c). Besides, the nucleation density on the surface of wood mercerized with 10% NaOH is higher than that on wood mercerized with 17.5% NaOH. This suggests that polymorphic transformation cellulose I → cellulose II modified the nucleation ability of wood surface, thereby reducing the density of transcrystalline layer. It is very well known that the alkali treatment results in a deterioration of nucleation ability.^{15,34} It is known that cellulose I produces transcrystallization and that cellulose II does not.^{18,34} However, Son et al.³³ have found that cellulose II induced TCL in a PP matrix. In our studies, polymorphic conversion of cellulose led to the development of transcrystallization layers but with very poor effectiveness. 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 PP matrix.^{21,36,56} The authors of this concept have shown that there is a very good size matching of the α -carbon/methyl moieties of PP and the oxygen in the electron-rich

glucosidic linkages in cellulose I, which can initiate epitaxial PP growth. The mercerization process makes the pyranose rings on the face of cellulose II not aligned in a “flat” manner and does not ensure the same configuration for the PP chains to crystallization.³⁶ Our results are also in agreement with the above statement. However, many authors have reported differences in nucleation activity of lignocellulosic fibers after alkali treatment. A possible explanation of the effect of alkali treatment of lignocellulosic materials is as follows. The necessary condition for getting cellulose II is to perform mercerization in closely fixed reaction conditions. The efficiency of mercerization is closely determined by the concentration of NaOH solution and the time of the process. Low concentration of NaOH (e.g., a 10% NaOH solution used in this study) is used to remove the impurities, fats and lignin from the surface of the lignocelluloses without prompting the conversion of cellulose I to cellulose II, while an NaOH solution of a higher concentration, e.g., 25%, can induce degradation of cellulose.⁴⁶

In view of the above, to ensure getting cellulose II it is necessary to optimize the conditions of mercerization. It should be emphasized that it is not possible to get full conversion of cellulose I to cellulose II as a result of alkali activity, which has been described in detail in our earlier works.⁴⁶ Therefore, lignocellulose material after mercerization is a mixture of two polymorphic varieties of cellulose. As shown earlier, cellulose I favors the formation of TCL, while cellulose II does not have this ability. According to Refs. 15,18,33,34, the differences in the activation of TCL nucleation by lignocellulose materials subjected to treatment with alkaline compounds could most probably be explained by different contents of the polymorphic varieties of cellulose. Summarizing, differences in the cellulose I/cellulose II content at the wood surface have a decisive effect on the formation of transcrystallinity.

An interesting conclusion follows from a comparison of the nucleation ability of unmodified wood and that of the wood subjected to mercerization by 10% NaOH. Both types of fillers contain exclusively cellulose I. It had been expected that removal of grease and other surface impurities from wood by alkalization would increase the accessibility of cellulose I for nucleating PP. However, our results did not confirm this expectation; no increased activation ability of the wood surface subjected to mercerization was observed. As follows from our results, cellulose is not the only factor determining the formation of TCL structures. Other possible factor influencing the nucleation activity of mercerized wood surface is the difference in the surface topography. The surface roughness of wood is much diversified by alkali treatment, which can lead to changes in the nucleation activity and consequently influence the formation of TCL layer, as described in the work.³⁵

Figure 2(d–e) illustrates the crystallization state of PP/W-pa and PP/W-sa composites, respectively. Figure 2(d) shows the development of transcrystallinity in the presence of wood modified with propionic anhydride, although the obtained filler was characterized by a poorer nucleation activity in comparison with that of unmodified pine wood.

This is consistent with the results obtained by Zafeiropoulos et al.¹⁸ Their observations indicated that esterification of flax

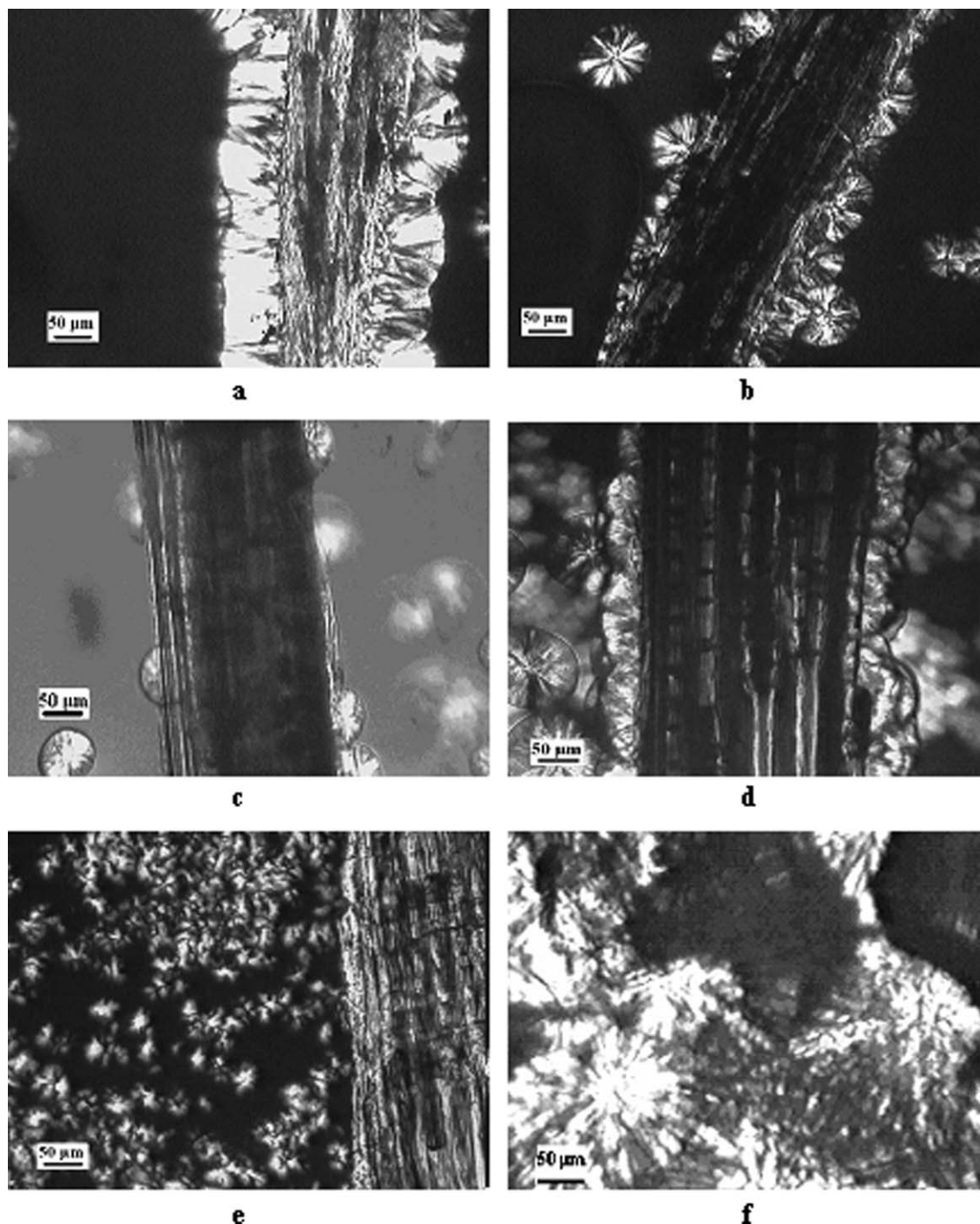


Figure 2. Optical micrographs of polypropylene morphologies obtained in the presence of: (a) W-un, (b) W-m10, (c) W-m17, (d) W-pa, (e) W-sa, (f) W-gr, by isothermal crystallization at 134°C (5 min).

fibers caused a decrease in the nucleation of TCL in comparison with unmodified fillers. However, our results are different from that reported by the authors of Refs. 36, 38. Lenés and Gregersen³⁸ and Quillin et al.³⁶ have shown that the esterified cellulose materials did not induce formation of a transcrystalline layer.

Moreover, it is found that the wood surface modification by chemical treatment (propionic anhydride) slightly

increases the nucleating ability of wood in comparison to that of mercerized (with 17.5% NaOH) wood, thereby favoring the transcrystalline behavior. The formation of a TCL layer in PP/W-pr composite may be an indication of an improved interfacial adhesion between the wood and the matrix, which resulted from the interaction between the hydroxyl groups of the wood surface and the propionic anhydride groups.

While wood modified by propionic anhydride has active surface, which induces transcrystallization, it is not the case of wood treated by succinic anhydride. Therefore, crystal morphology in a wood reinforced PP composite is strongly influenced by the surface treatment of wood.

The observed absence of TCL structures in systems containing wood modified with succinic anhydride was a considerable surprise. This behavior is perhaps caused by a different course of the esterification reaction leading to the development of a final product structure. It was shown in our earlier work³⁵ that the following phenomena can also take place during the esterification process: (1) linking to wood particles of the succinic anhydride in the form of diesters or (2) lengthening of the chain consisting, initially, in the incorporation of monoester molecules to wood active hydroxy groups and later successive monoesters to carboxyl groups, which developed in the course of these reactions. Such explanation can be confirmed by obtaining a higher weight percent gain (WPG) in the case of the esterification of wood with succinic anhydride. In previous work,³⁵ we showed that the WPG index for wood modified with succinic anhydride is 43.9%, whereas that for wood modified with propionic anhydride is only 18%. Moreover, the possibility of the reaction of anhydrides of cyclic structure in the form of monoesters and diesters has been reported by Matsuda⁵⁷ as well as by Hill and Mallon.⁵⁸

Figure 2(f) illustrates the crystallization process in irradiated wood/PP composite. Here the situation is slightly different from the previous cases. Although, the bulk spherulites are well grown no transcrystalline layer can be seen around the γ -irradiated wood. The wood (W-gr) has had no effect on the morphology of PP, which exhibits only spherulitic growth. We have suggested that the amount of cellulose in wood is of key importance for the development of transcrystallinity. In our previous study,³⁹ we have found that the content of cellulose in this gamma irradiated wood sample is 0%. It has been reported^{21,36,39,56} that transcrystallinity developed as a result of the interaction of PP and cellulose at the molecular level, which are related to the adsorption configuration and the matching of interaction sites. Therefore, the absence of cellulose (in W-gr wood) seems to be unfavorable for the growth of transcrystallinity.

Table III gives the growth rate of TCL in different composite systems.

The growth rate of TCL determined confirms the conclusions following from optical micrographs, described in detail above. The order of the growth rate is PP/W-un > PP/W-pa > PP/W-m10 > PP/W-m17. Our data reveal that for the crystallization of PP in contact with unmodified wood, the growth rate of TCL is the highest (ca. 18 $\mu\text{m}/\text{min}$). The composites containing wood treated in 10% NaOH solution were characterized by lower rates (below 10 $\mu\text{m}/\text{min}$) in comparison with PP/W-un systems. It is perfectly visible that the composites with wood subjected to mercerization (with 17.5% NaOH) were characterized by distinctly lower rates of development of TCL (below 6 $\mu\text{m}/\text{min}$). The growth rate of PP/W-pa is faster than that of PP/W-m17, though PP/W-pa and PP/W-m17 have the same

Table III. Growth Rate of TCL of the Composite Samples

| Samples | Growth rate of TCL ($\mu\text{m}/\text{min}$) |
|----------|---|
| PP/W-un | 18.1 |
| PP/W-m10 | 9.5 |
| PP/W-m17 | 5.85 |
| PP/W-pa | 12.0 |
| PP/W-sa | Without TCL |
| PP/W-gr | Without TCL |

crystal structure (cellulose II). Therefore, we assume that the enhancement of the transcrystallinity growth rate can be caused by the enlargement of the effective wood surface because of esterification treatment. It should be mentioned perhaps that earlier³⁵ we had worked on nucleation of PP matrix in the presence of chemically modified wood in the other crystallization conditions. Our previous results show that the chemical treatment of wood with other acid anhydrides (phthalic, crotonic, and maleic) plays an important role in the enhancement of nucleation ability of PP matrix. When a chemical treatment (by anhydride) is realized in a wood-polymer system, the nature of the lignocellulose may be modified because of the interaction between the wood and the modifiers, and consequently the nucleation ability of the wood may be changed.

Moreover, the wood topography can be also used to explain different nucleation ability of the wood surface. The chemical treatment of wood filler had an obvious effect on the morphology of the wood, as described in previous work.³⁵ The SEM image confirmed the chemical modification and its influence on the morphological aspects of wood.

Before treatment, wood surface is rough and showed partial breakages (cracks). After alkalization, smooth surface with only small irregularities is produced, which can be explained by the fact that mercerization can eliminate waxy layer and fats. However, after esterification the roughness of the wood surface increased. Owing to the roughness of wood surface, the nucleating ability of filler is greatly enhanced, as compared to that of the mercerized wood. Moreover, the surface roughness (similarly as in untreated wood) can be critical for development of transcrystallinity because of the increased thermal stress at the peaks, fissure, or valleys.

Summarizing, the results show that the chemical modification affects transcrystallization. This indicates that the local chemical nature of wood plays an important role in the nucleation of PP.

Mechanical Properties of the Composites

Effect of Treatment on the Mechanical Properties. Analysis of the results presented in the previous section has shown that modification of wood has essential effect on development of transcrystalline structures. In this section the subject of concern is the influence of the wood modification type on mechanical properties of composite systems. Treatments were performed to enhance adhesion between the wood and the matrix. Table IV summarizes the data on mechanical properties of PP matrix as well as composites.

Table IV. Data of Mechanical Properties of the Composite Samples (Standard Deviations are Given in Parentheses)

| Samples | Tensile strength (MPa) | Modulus (GPa) | Elongation at break (%) | Impact strength (kJ/m ²) |
|------------|------------------------|---------------|-------------------------|--------------------------------------|
| Control PP | 30.1 (0.07) | 1.43 (0.09) | 538 (7.95) | 52.3 (0.85) |
| PP/W-un | 35.3 (0.36) | 2.53 (0.16) | 3.3 (0.34) | 23.8 (0.44) |
| PP/W-m10 | 34.4 (0.32) | 2.45 (0.17) | 3.1 (0.26) | 24.1 (0.39) |
| PP/W-m17 | 30.9 (0.41) | 2.09 (0.25) | 2.2 (0.21) | 16.8 (0.27) |
| PP/W-pa | 39.7 (0.12) | 2.98 (0.11) | 5.3 (0.14) | 28.9 (0.25) |
| PP/W-sa | 37.5 (0.16) | 2.78 (0.12) | 4.4 (0.14) | 25.9 (0.19) |
| PP/W-gr | 27.4 (0.21) | 1.77 (0.15) | 2.4 (0.17) | 11.5 (0.21) |

It can be clearly seen that there is a noticeable difference between the mechanical properties of the composite materials and the PP matrix. Composite materials show slightly higher modulus and tensile strength than matrix. Additionally, the incorporation of untreated wood to PP matrix led to increased tensile strength. This behavior is very difficult to explain, since we know that some authors have reported a negative effect of untreated filler on tensile strength of composites. However, the review of literature^{59–61} on the subject indicates that the tensile properties of the composites containing untreated lignocellulosic fillers (i.e., wood, flax, and sisal) were also higher in compared to those of pure PP matrix. Our result agrees well with Refs. 59–61 claiming that untreated lignocellulosic filler had a significant effect (positive) on the strength values, which is seen when referred to the strength of pure PP matrix. A possible reason for this is that the tensile strength depends on the size of the particles, aspect ratio (length/width), and filler content.^{62–65} The divergences suggest the necessity of taking into account many factors (such as development of TLC structures) that could affect the mechanical properties, which will be more extensively discussed in section “Analysis of relation between transcrystalline layer and mechanical properties.”

Moreover, all composites showed lower impact strength than neat PP because the addition of the wood particles creates regions of stress concentrations that require less energy to initiate cracking.⁶⁶ These results suggest that the tensile properties of wood/PP composites are closely related to the method of wood treatment. The results clearly prove that the PP/W-un and PP/W-m10 exhibit almost the same mechanical properties. The treatment of wood with a 10% NaOH solution did not cause significant changes in the tensile properties and impact strength relative to those for the unmodified systems. However, it is seen that the untreated wood composites showed superior tensile properties than alkali treated (with 17.5% NaOH) composites. The results have shown that the composites containing wood with a high content of cellulose II are characterized by reduced mechanical parameters. Similar results have been presented by Marcovich et al.,⁶⁷ who also found that alkalization reaction of wood decreased the mechanical properties of composites. However, some authors such as Kaith et al.,⁶⁸ Joseph et al.,⁶⁰ Ichazo et al.,⁶¹ Albano⁴³ have found that mercerization of wood strongly improved the mechanical properties. On the other hand, the alkali treatment can have different influence on the mechanical properties of composites.

It is interesting to note that only esterification treatment enhanced the tensile properties of the composites, considerably, but to varying degrees. The composites containing wood subjected to modification with propionic anhydride reveal by far the greatest tensile strength, elasticity modulus, and impact strength. Also the composites containing wood modified with succinic anhydride show enhanced tensile properties relative to those with unmodified wood. Additionally, it is noted that esterification improves the adhesive characteristics of wood by making surface rougher and increasing more contacts in comparison with mercerized wood.³⁵ This is a clear indication that esterification of wood improved interfacial bonding, which resulted in improvement in tensile strength. It has been demonstrated that the enhancement of mechanical properties is due to the fact that chemical treatment reduced the hydrophilic nature of the wood, and thereby improved the interfacial adhesion. For the untreated systems, the interaction between the wood and the transcrystalline zone is limited to dispersive forces and topographical effects. For the modified composites, esterification reaction leads to the substitution of hydroxyl groups of cellulose by less polar groups, which reduce water absorption and the tendency towards aggregation. Reduced hydrophilicity of the wood surface means an increased strength of interaction (van der Waals type), so that there is an interfacial adhesion between esterified wood and PP matrix. The interface strength between the TCL zone and neighboring spherulites (or fillers) depends on molecular bridging between the crystals. Anhydride chains are important to maximize the effectiveness of the physical crosslinking. The improvement in mechanical performance of the composites with wood subjected to esterification of the lignocellulose component is consistent with results reported by other authors. Mahlberg et al.⁶⁹ have reported a significant improvement in the mechanical properties of wood fiber/PP composites as a result of the anhydride modifications. Similarly, Joseph et al.⁷⁰ have shown that the treatment of sisal fiber with maleic anhydride enhanced the tensile properties of the composites. It should be emphasized that according to Refs. 67, 71–74, chemical modification of the cellulose component by esterification can also give composite materials of deteriorated mechanical performance.

Introduction of W-gr wood into the polymer matrix caused a significant deterioration of mechanical properties of the composites obtained. They show the lowest breaking strength and impact strength, lower than the corresponding values

characterizing the polymer matrix. The process of γ -irradiation of wood, causing cellulose degradation³⁹ is responsible for a significant deterioration of mechanical properties of composite materials.

Effect of Treatment on the Microstructure of Composites. Discussion of the results presented in the previous section has shown that modification of wood has important effect on mechanical properties. In this section the subject of concern is the influence of the wood modification type on adhesion in the composite systems. Thorough examination of this influence will be needed for discussion of results characterizing mechanical performance of the materials obtained. The morphology is the most suitable in order to obtain the best mechanical behavior, as well be demonstrated later.

The effect of wood surface treatment on interfacial adhesion was further studied using SEM. Figure 3 shows the SEM micrographs of the fracture surfaces of different composites. The fracture surface of untreated wood [Figure 3(a)] composites shows holes and fiber ends indicating that most of the woods have come out without breaking during the fracture of untreated composites. This suggests poor adhesion between the matrix and wood.

The micrograph in Figure 3(b) shows the surface of the composite containing wood mercerized with 10% NaOH, while Figure 3(c) was taken for a composite prepared with wood mercerized with 17.5% NaOH. Although, the differences are not much pronounced, the composite prepared with the W-m17 wood seems to contain more voids and debonded particles than the one reinforced with the W-m10 wood. In both cases, the microstructure of the composites demonstrates that the interfacial adhesion between PP and wood is very weak because of weak-physical interaction based upon wood fiber break and pullout, showing the absence of plastic deformation. The images presented in Figure 3(a–c) clearly reveal that interfacial debonding took place in the composites with wood not subjected to treatment. Gaps between the wood and the PP matrix could clearly be identified, and there are a large number of holes from fiber pull-out. It is well known that one of the main factors that affect the mechanical properties of wood-reinforced material is the filler-matrix interfacial adhesion; a weak interfacial region will reduce the efficiency of stress transfer from the matrix to the filler component.

However, the use of a chemical treatment on the wood particles had an obvious effect on the surface of the wood, as shown in the SEM micrographs [Figure 3(d, e)] of the fractured composites. Figure 3(d) is the SEM photograph of impact fracture surfaces of the sample PP/W-pa. Apparently, the interfacial bonding between PP and the wood is improved. It has been evidenced that the wood surfaces are coated with a thin layer of PP matrix. This implies that the propionic anhydride group enhances the adhesion between PP matrix and wood. The existence of PP particles adhered on the wood surface can be observed in succinic anhydride treated wood composites [Figure 3(e)]. The coverage of the wood with the polymer and the relatively small number of holes related to debonding or fiber pull out indicate good adhesion. In general, the dispersion is improved for all treated wood/PP composites [Figure 3(d, e)]

and that their tensile modulus and strength are slightly higher than those of the composites with untreated or mercerized wood/PP.

Moreover, Figure 3(f) presents the fracture surface of a specimen prepared with wood irradiated with γ -rays. The number of debonded particles is quite large, the contours of particles remaining on the surface are sharp, and adhesion seems to be poor, at least compared to the wood sample subjected to chemical modification.

In summary, the SEM analysis of the fractured surface of unmodified composites (PP-W-un) has shown poor interaction between the wood and the polymer matrix with debonding phenomena of the wood. The mercerization of wood does not modify the fracture mechanism of the PP matrix. The composites (PP/W-un, PP/W-mer10, and PP/W-mer17) show similar fracture features, because the adhesion PP/wood is insufficient. However, in PP/W-pr and PP/W-su composites, the fracture surfaces of the injection-molded specimens revealed polymer adhering to the wood, which implies that the interaction between wood (esterified with anhydrides) and PP is adequate. These SEM observations confirm the FTIR and mechanical testing results. In our earlier work,³⁵ the treated wood samples were characterized by FTIR analysis. This analysis was able to reveal the main differences between the untreated and treated wood. FTIR results³⁵ indicate the absorption bands in the 1710–1740 cm^{-1} region due to ester links formed by esterification reaction between hydroxyl groups of cellulose and anhydride groups of anhydrides (propionic and succinic).

It can be inferred that the treatment of the wood has resulted in a significant improvement in the filler-PP interfacial bonding, as confirmed by SEM studies. Analysis of the mechanical properties of the composites and the FTIR results suggests that there is direct evidence of the effect of ester links on the tensile strength of the composites. In general, the improvement of mechanical properties is a result of the decrease in the hydrophilicity of wood after their treatment, which makes the fillers more compatible with the hydrophobic polymer matrix. This obviously results in an increase in the efficiency of stress transfer from the matrix to the filler, which consequently gives rise to higher modulus and tensile strength.

The fact that the interactions between the esterified wood and PP matrix are stronger is also confirmed by analysis of densities of such composites. According to the results of our earlier work,⁷⁵ the composites containing wood modified by anhydrides are characterized by higher density than those containing unmodified wood. This observation can be explained by a better wettability of the wood particles with PP, which results in a reduced number and size of pores. On the other hand, in the composites with unmodified wood, the wettability of the components is low, which results in easier capturing of air bubbles in the interphase region and thus in a greater number of pores and reduced density. This interpretation is supported by the SEM images (Figure 4).

Figure 4 presents the SEM image of the composites of lower magnification to show the degree of wood particle dispersion in

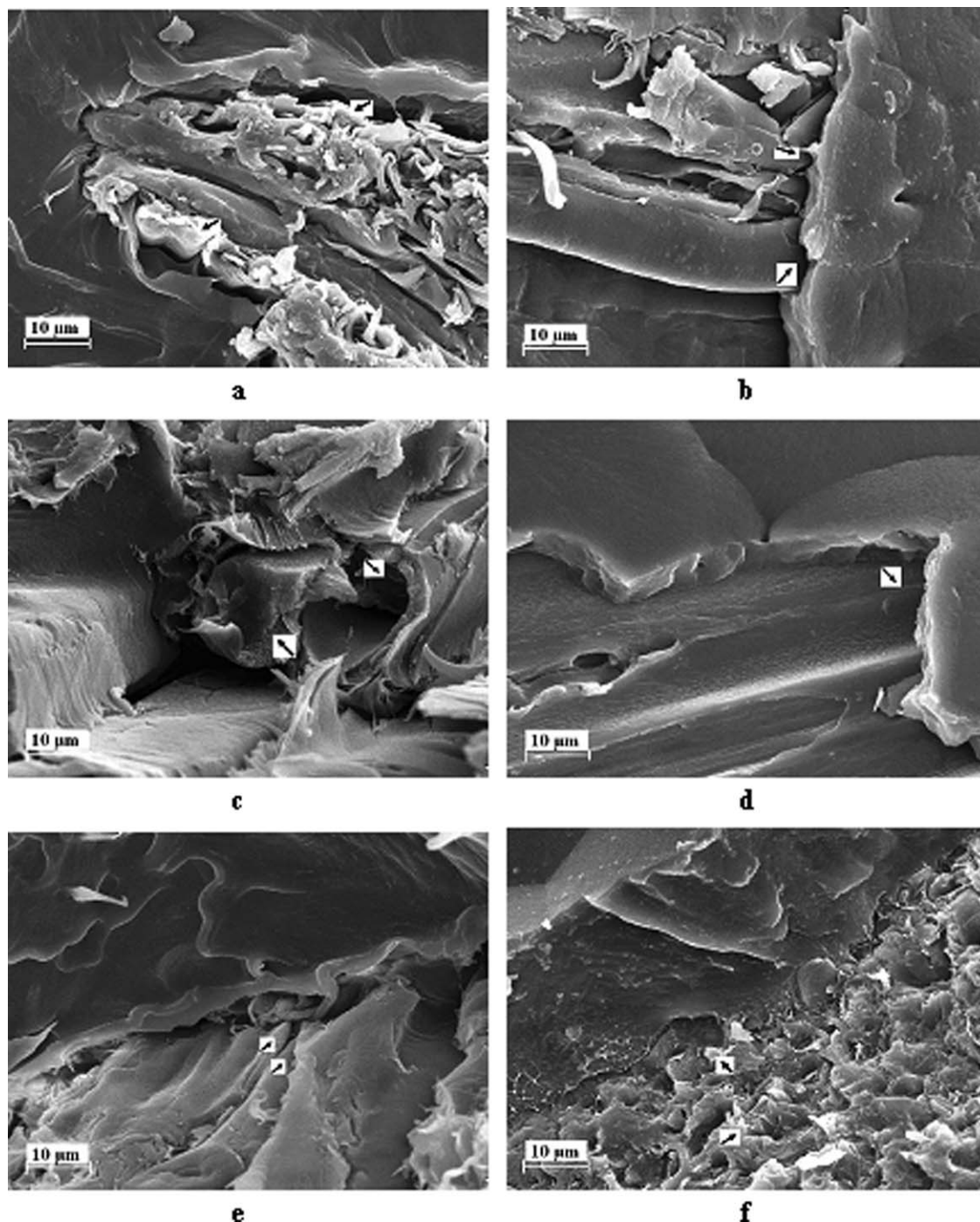


Figure 3. SEM micrographs of fracture surfaces of PP/wood composites: (a) PP/W-un, (b) PP/W-m10, (c) PP/W-m17, (d) PP/W-pa, (e) PP/W-sa, (f) PP/W-gr (arrows indicate region corresponding to the wood).

the polymer matrix. The composites containing unmodified or alkalinized wood [Figure 4(a–c)] show similar morphologies; their SEM images show poor distribution of wood particles in the matrix. A possible explanation is high polarity of wood, responsible for strong interactions favoring formation of agglomerations of the filler particles. A confirmation is high diversity of the filler particle size. The SEM of samples PP/W-un, PP/W-m10, and PP/W-m17 reveals the presence of pores and voids,

which proves low interphase adhesion leading to lower density of the composites, as described above. Figure 4(d, e) shows that dispersion of the wood (W-pr and W-su) in the polymeric matrix is improved, since a decrease in the size conglomerates can be seen. It can be explained good wettability of the particles of wood esterified by PP, leading to the absence of pores. Such a composite should show higher density, as evidenced earlier. In general, it can be said that the dispersion is improved for

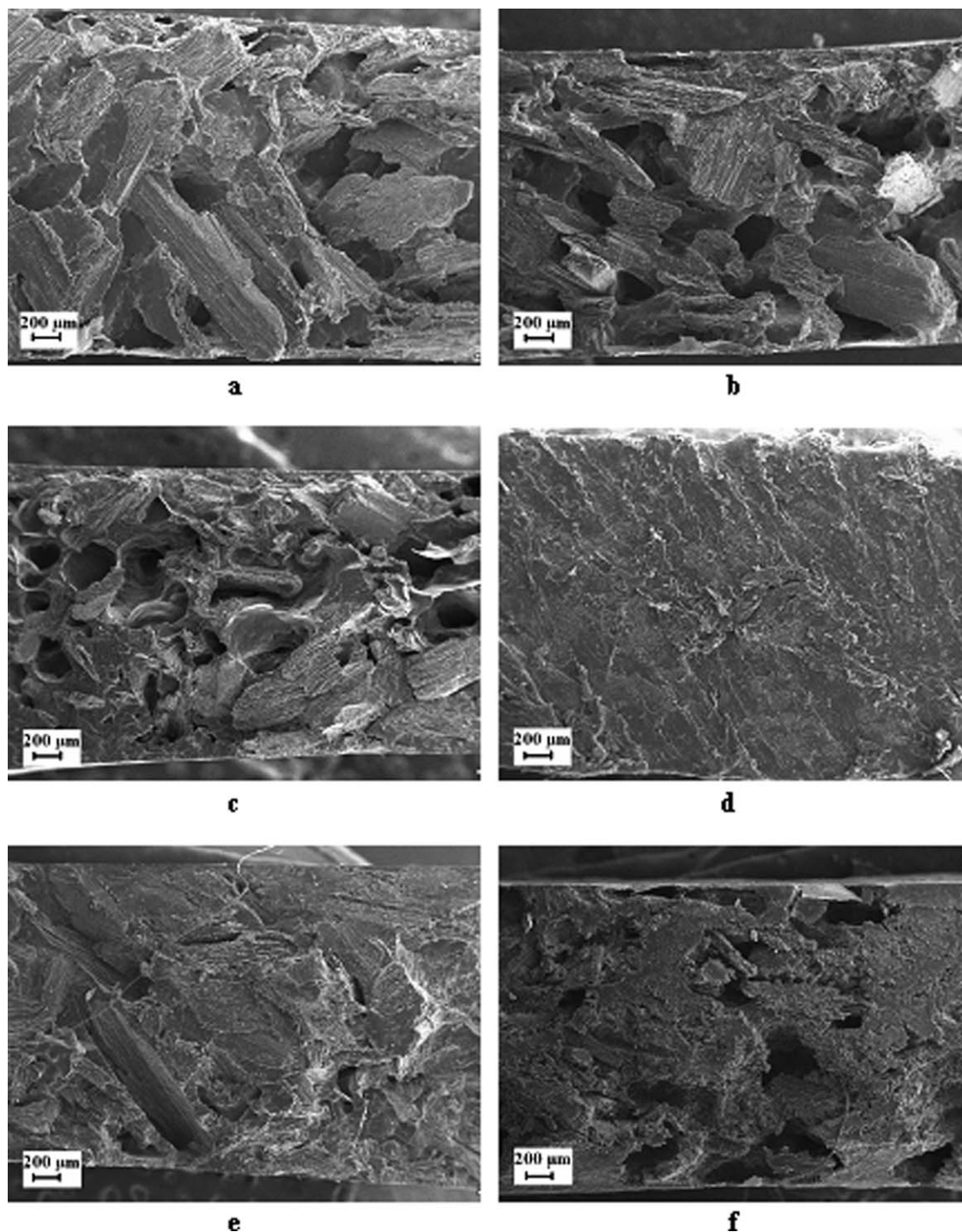


Figure 4. SEM micrographs of PP/wood composites: (a) PP/W-un, (b) PP/W-m10, (c) PP/W-m17, (d) PP/W-pa, (e) PP/W-sa, (f) PP/W-gr.

treated wood/PP composites, and that their tensile modulus and strength are higher to those of composites of untreated wood/PP. An interesting situation is illustrated in the SEM of PP/W-gr sample [Figure 4(f)]. The photograph shows rather high dispersion of wood particles in the polymer matrix as a result of high fragmentation of wood in the process of degradation. However, the morphology of this sample is not so homogeneous as that of PP/W-pr and PP/W-su, which is a

consequence of low interphase adhesion between the strongly polar filler and nonpolar polymer matrix. This low interphase adhesion leads to the presence of many pores, as shown in the SEM image.

However, the fact that PP/W-pr composites show higher strength than PP/W-su (despite the evidence of chemical reaction with both anhydrides), implies that the ester links may not

be the only factor determining the strength of the composites. The accompanied increase in mechanical strength of the PP/W-*pr* composites may be explained by taking into account an additional factor. Further analysis is needed to confirm our hypotheses and to identify the dominant factor.

The next section will be devoted to discussion of the effects of transcrystalline layer on the mechanical properties of the composites obtained.

Analysis of Relation Between Transcrystalline Layer and Mechanical Properties. It can be clearly seen that there is a noticeable difference between the mechanical properties of the composites without a TCL layer and those with a TCL layer. It should be emphasized that good interphase adhesion between PP and wood as a result of chemical modification (esterification) does not need to imply formation of transcrystalline structures, as for example happens in PP/W-*sa*.

As follows from the results obtained, the mechanical properties of wood composites are a resultant of two factors: (1) the presence of transcrystalline structures and (2) interface adhesion controlled by chemical modifications of lignocellulose components. In the composites filled with unmodified wood, their mechanical properties are determined by the efficiency of formation of transcrystalline layers. These composites are characterized by poor interphase adhesion, as has been confirmed by SEM results. Examples of such composites studied in this work are PP/W-*un*, PP/W-*m10*, and PP/W-*m17* systems. The composites having better developed transcrystalline layers and higher growth rate of TCL are characterized by greater tensile strength and higher elasticity modules.

A very interesting system whose characteristics confirm our hypotheses is PP/W-*gr*. This composite shows the poorest mechanical performance, which is a result of the absence of transcrystalline structures (a consequence of cellulose degradation) and no chemical modification of wood applied. It should be added that the composite properties depend not only on the interface, but also on the mechanical properties of the matrix and the filler. Important structural parameters in determining the mechanical properties of lignocellulosic filler are the crystallinity and the arrangement of the microfibrils in the fiber. The mechanical properties of lignocellulosic component increase with the crystallinity and degree of orientation.⁷⁶ The ordered regions of cellulose will show the typical elastic deformations of the crystalline solid, with a high modulus and strength. In W-*gr* sample the cellulose content is zero, so this wood cannot be used to reinforce the composite. This wood is amorphous and does not have so high modulus and strength values as the cellulose-containing wood; its addition will deteriorate the mechanical properties of the composite.

In the composites containing wood subjected to chemical modification with acidic anhydrides, the influence of both TCL layers and interface adhesion must be considered. The presence of TCL structures and improvement of adhesion as a result of esterification by propionic anhydride combine to give composite (PP/W-*pa*) showing very good mechanical properties. For this composite we can talk of a synergistic effect of both these factors. In PP/W-*sa* composite the situation is completely differ-

ent. Modification of wood with succinic anhydride improves the adhesion with the polymer matrix but it is also responsible for inhibition of TCL structure formation. As no synergistic effect was noted, only a small improvement in the mechanical properties was observed relative to the properties of the composites with unmodified wood. Also, Kazayawoko et al.⁷⁷ have concluded from their study that the wood surface chemistry had not direct influence on the mechanical properties of wood-PP composites but it was as important factor, which determines the wettability of wood by the polymer matrix.

To sum up, it should be emphasized that the factor determining good mechanical properties of wood composites is the choice of appropriate modifier. The chemical modification of wood is aimed at reduction of the hydrophilic properties of the lignocellulosic component but also at obtaining a filler of good nucleating properties ensuring formation of the transcrystalline structures. The significance of this double effect is illustrated by many contradictory conclusions following from results of studies of the influence of chemical modifications on the mechanical properties. The failure of taking into regard both effects is a source of difficulties in interpretation of results. In view of the above, it is necessary to perform optimization of the chemical modifications intended and to take into account the phenomena taking place at the polymer-filler interface.

Further studies on the influence of chemical nature of wood on the development of a transcrystalline layer at the filler surface and its adhesion properties are planned and will be published in the near future.

CONCLUSIONS

Differences in the surface chemistry of the wood are a more attractive explanation for the differences in nucleating ability. Therefore, it is necessary to combine the new results of this work with the results published earlier to get a deeper understanding of the mechanism of transcrystallization.

The findings made from this study can shortly be summarized as follows:

The PP transcrystallinity layer form most easily on the unmodified wood in comparison to chemically modified wood. However, the occurrence of transcrystallization in wood-PP composites is strongly dependent on the type of chemical modification of lignocellulosic materials. The alkali treated wood was able to induce a transcrystalline layer, but the efficiency of the TCL structure formation depends on the conditions of mercerization process. Moreover, the results show that the esterification reaction influences the transcrystallization. While wood modified by propionic anhydride has active surface, which induces transcrystallization, this is not observed for wood treated with succinic anhydride. Therefore, it is necessary to perform optimization of the chemical modifications. Moreover, the absence of cellulose (in γ -irradiated wood) seems to be unfavorable for the growth of transcrystallinity.

The presence of TCL in the wood/PP composites was found to have an important effect on the interface characteristics. It is assumed that the mechanical properties of composites can be correlated with TCL thickness and the growth rate of TCL. It

should be emphasized that the factor determining good mechanical properties of wood composites is the properly chosen modifier. The results clearly prove that the level of surface modification may lead to change in mechanical properties. On the basis of the results obtained in this article it follows that the mechanical properties of wood composites are a resultant of two factors: the presence of transcrystalline structures and interface adhesion controlled by chemical modifications of lignocellulose components.

In view of the above evidence, the main conclusion following from this study is that to ensure desired mechanical performance of the wood composites it is necessary to take into account the phenomena taking place at the polymer-filler interface, controlled by chemical modifications of lignocellulose components (W-m10, W-m17, W-pa, and W-sa).

However, the properties of PP/W-gr depend not only on the interface, as in the other composite systems, but also on the mechanical properties of irradiated wood. In this wood the content of cellulose, determining high modulus and strength of wood, is zero. Therefore, addition of such wood would lead to deterioration of mechanical properties of composites and the lack of a reinforcement effect. In the other composites (with cellulose-containing wood) the reinforcement effect was observed, which can be explained by the presence of cellulose and the level of reinforcement is explained as related to the interface difference.

Studies related to the transcrystallinity and the morphology are of great importance in manufacture processing, because of the fact that the resulting physical properties are strongly dependent on the morphology formed and the extend of crystallization occurring during processing. However, the question of the effect of TCL on the mechanical performance of composites has not been solved yet because of two main reasons. One is the absence of experimental technique for analysis of the transcrystallinity in processing conditions. The other is the inability in most cases to isolate the contribution of TCL from that of the crystalline matrix. The majority of articles published in the field have concerned the development of transcrystalline structures during crystallization on the hot stage optical microscopy. Only then it is possible to determine the kinetic parameters describing the process. It should be emphasized that the actual influence of TLC structures on the mechanical properties of the composites will be possible to determine for the samples obtained directly from injection molding. At present, direct observation of the nucleation processes in such samples is impossible and the use of hot stage optical microscopy is necessary. In the next stage of our study we intend to analyze the influence of such conditions of processing as high cooling rate, pressure, and orientation of molten polymer. Understanding the dependence of the properties of wood/PP composites on microstructure is an important step toward the design of optimal thermal processing protocols for these thermoplastic composites.

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