Chapter 10

The Structure, Morphology, and Mechanical Properties of Thermoplastic Composites with Ligncellulosic Fiber

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Abstract This chapter discusses the supermolecular structure and interphase phenomenon in composite-reinforced natural fibers. We analyzed the formation of the polymorphic forms in polypropylene (PP) matrix. It was found that in the composites with natural fibers, the hexagonal form arises when the fibers are in motion in relation to the polymeric matrix. of Moving temperature of the natural fibers was found to have a strong influence on the content of the hexagonal modification. If the temperature of the moving fibers is low, then the amount of β-PP significantly increases. The content of β-PP also depends on the rate of the moving of fibers; however, the chemical modification of the natural fiber's surface reduces the content of this form. Also, the processing conditions play an important role for structural changes in PP matrix.

Further, this chapter provides a survey about the formation of a transcrystalline layer in the composite system. The occurrence of transcrystallization was found to strongly depend on the type of chemical treatment of the fiber surface. Predominant nucleation ability was found for unmodified fibers. However, chemical modification of fiber surface slightly depressed the nucleation of polypropylene matrixes.

The influence of physical and chemical treatment methods of natural fibers on mechanical properties was analyzed also. Additionally, the mechanical and other physical properties of the composite are generally dependent on the length, content, and dispersion of fibrous filler and processing parameters.

Keywords Composites · Mechanical properties · Natural fibers · Supermolecular structure · Transcrystalline layer

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10.1 Introduction

It is well established that the supermolecular structure of semicrystalline matrix is of pivotal importance to the mechanical and physical behavior of composite materials. We analyzed the formation of the polymorphic forms in polypropylene composites with natural fibers. Moreover, analysis of the effect of processing conditions, during preparation of the composites, on the structure of polymer matrix is a focal issue because polymorphic changes in polypropylene can be stimulated by the temperature of processing and the shearing forces applied.

In thermoplastic/fiber systems, the fiber may act as a series of nucleating sites for the polymer, resulting in a transcrystalline region around the fiber. In this chapter, a large number of factors have been demonstrated to contribute to the interactions across the interface. The effect of various conditions such as the chemical modification of natural fibers and nucleation ability of semicrystalline matrix on the formation of transcrystallinity was investigated.

Moreover, obtaining composites filled with the lignocellulosic component with desired strength properties require consideration of many factors having an effect on the final macroscopic properties. The objectives of this study is to analyze the effect of the following factors such as the adhesion between the components, filler content, fiber length of fibrous filler, filler distribution, and the effect of processing parameters on the mechanical properties of composites.

10.2 Polymorphism in Isotactic Polypropylene Used as Composite Matrix

Polymorphism, which means existence of different crystalline forms, is a phenomenon observed in many organic and inorganic compounds. Also, natural (e.g., cellulose) and synthetic polymers show numerous polymorphic forms. Among synthetic semicrystalline polymers, which can be a matrix in composites with lignocellulosic materials, the isotactic polypropylene is the one to take a close look on this phenomenon.

In polypropylene composites containing lignocellulosic materials, one can expect two forms, α and β, because the conditions required to create for the third form – γ are not existing when forming and processing composites containing lignocellulosic materials. The most stable form is the α phase, crystallizing in a monoclinic unit. The form β, also known as hexagonal or pseudohexagonal [1, 2], is in fact a higher energetic form, crystallizing in triclinic unit. This phase used to be called a hexagonal due to the relation of network constants $a = b$ and an angle between them – 120°. This choice of an elementary cell is characteristic for hexagonal and trigonal units. However, the location of polypropylene helixes in elementary cell shows that it lacks the elements of symmetry typical for these systems.

The mechanical properties of the α phase polypropylene are generally better than that of β form, except for impact resistance. Therefore, in products specially exposed to impact, the matrix containing the pseudohexagonal form is a better choice [3].

All lignocellulosic materials contain no active nucleants that can initiate forming the hexagonal form. Therefore, this form can be present in composites under shearing forces in a temperature interval typical for these forces to appear. β phase cannot be found in products made by press molding. The structural analyses of polymers and composites are very important as the structure of these materials is determined, to a high extent, by molecular and supermolecular structure.

10.3 Analysis of Pseudohexagonal Form Created in Composites Containing Fibers

10.3.1 Influence of Fibers Pulling in Polypropylene Matrix

As reported earlier by Varga and Karger-Kocsis [4, 5] and Hoecker and Karger-Kocsis [6], the movement of glass or carbon fibers in PP matrix causes forming the β polypropylene. So, the question was asked: does the movement of natural fibers affect the formation of polypropylene matrix crystalline structure? These kinds of interactions are present in manufacturing and processing of polymers. Solving this problem may offer the way to change the polypropylene structure and consequently the properties of the final products.

To solve the problem outlined above, it is necessary to analyze the following problems and find answers to the following questions:

- How does the movement of natural fibers affect the formation of polypropylene matrix?
- How does the temperature in which the fiber is moved, the type of fiber, the modification, and the speed of fiber movement fibers affect the formation of polypropylene matrix?
- What is the range of the structural changes in the matrix in function of the distance on which the fiber is moved?

By trying to answer the above questions, the trials were made in which the polypropylene-containing fibers were heated up to 220°C. Then the samples were cooled to the predefined temperature in which the fiber was pulled at a predefined speed. The structure analysis was carried out by the WAXS technique.

We tested a stationary system and a system where flax fiber was pulled at $w = 0.62$ mm/s for different temperatures in the range 180–130°C [7, 8].

Obtained results showed clearly that the presence of the flax fiber itself, in the crystallizing polypropylene, causes no formation of hexagonal phase (Fig. 10.1). For samples where fiber was moved, the X-ray patterns revealed the diffraction maximum at 2Θ 16.2°, which proves the presence of β form. The amount of this form was calculated from the diffractograms according to the well-known Turner-Jones formula [1]. It was shown that the formation and the amount of this form in composite matrix depend on the temperature at which the fiber is moved in

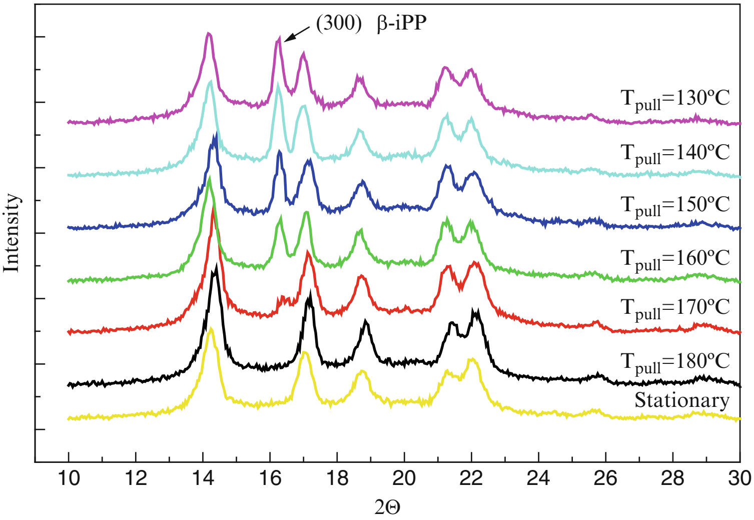

Fig. 10.1 The X-ray diffraction pattern of iPP/flax composites, where fibers were pulled with speed 0.62 mm/s in the temperature range 130–180°C [8]

the matrix. However, there is a critical temperature value of 180°C above which the hexagonal form is not induced. Thus, the formation of the polymorphic β form is connected with forced macromolecular orientation during crystallization.

Further research showed that the same effect can be obtained when using other natural fibers, for instance, hemp or sisal.

Further studies investigated the effect of earlier chemical modification of natural fibers on arising of hexagonal form of polypropylene. For these studies, it was important to consider the content of induced hexagonal phase in crystalline phase of the polypropylene matrix. Figure 10.2 shows how the content of β form changes upon the temperature in which modified and unmodified hemp fiber is moved. It is worth to mention that the curves course of modified and unmodified flax fiber is very similar to that of hemp [8, 9].

It was shown that crude natural fibers and fibers modified by mercerization process induce much better creation of polymorphic β form than fibers modified to improve adhesion with nonpolar polypropylene. It was found that the lower the temperature of the matrix during fiber movements, the higher the content for hexagonal form. Over 180°C, the hexagonal phase is not formed and polypropylene crystallizes only in a monoclinic α form. However, in the range 150–180°C, the content of hexagonal form decreases as the temperature of polypropylene matrix rises. It was also found that chemical modification of fibers causes reduction of hexagonal form generation that is formed as a result of moving the fibers. For flax fibers, this reduction is estimated to be about 25%. A similar tendency is observed for hemp fibers modified by an acetic anhydride (Fig. 10.2).

In the analysis of the induction of β from creation by lignocellulosic fibers moving in relation to the matrix, a question should be answered: does the change

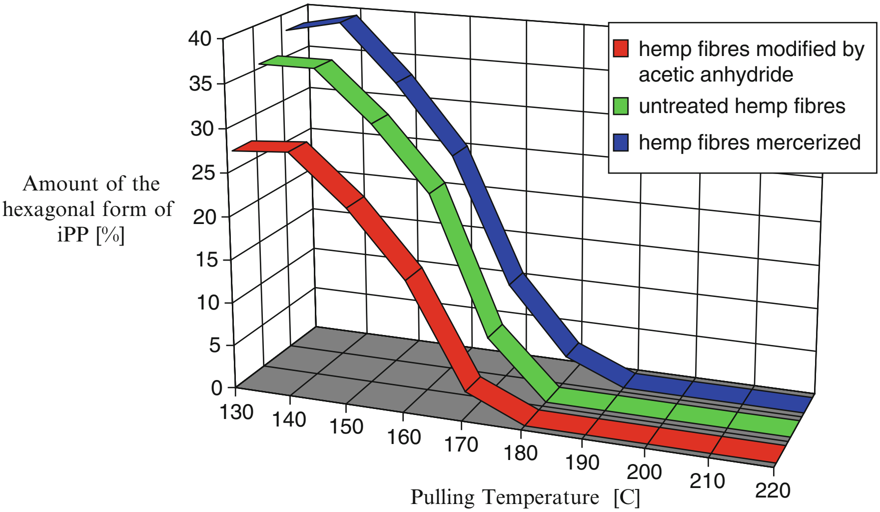

Fig. 10.2 The amount of hexagonal form of iPP versus pulling temperature for hemp fibers [8]

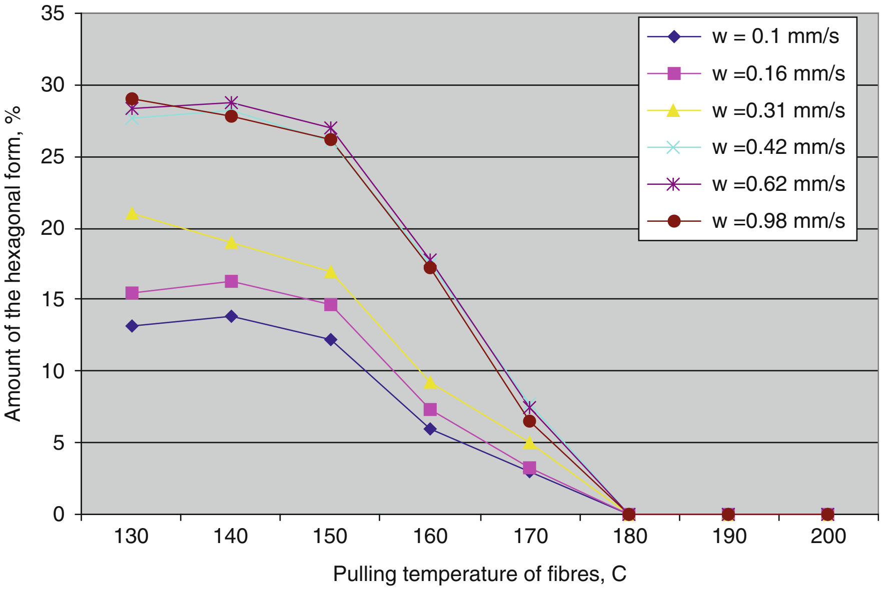

Fig. 10.3 The amount of hexagonal form versus pulling temperature of flax fibers for different speed of fiber pulling

of the speed of fiber movement in the polypropylene matrix have an effect on the observed phenomenon?

The studies were focused on unmodified flax fibers and fibers modified with an acetic anhydride. The speed of fibers moved in the matrix was from 0.10 up to 0.98 mm/s.

Figure 10.3 shows that the amount of induced hexagonal form reaches the optimum value at the speed of 0.42 mm/s. The content of β form does not increase nor decrease at higher speeds of fiber pulling. In the case of modified fibers, the dependences are similar; however, the amount of form that is being created does not exceed 25%. Additionally, the optimum speed of fiber moving, over which the content of the form β does not increase, is higher – 0.62 mm/s. Earlier findings referring to not inducing the crystalline phase above 180°C were also confirmed.

It would seem that modified fibers, in the aspect of adhesion improvement, should induce creation of polymorphic β form to a higher degree. Moreover, the experiments conducted on carbon and polypropylene fibers confirmed the adverse dependence between the adhesion and generation of hexagonal form in the surroundings of moving fiber. Thus, the alternation of interphase interactions caused by the increase of adhesion in the system polypropylene with lignocellulosic fibers is not the only factor having the effect on the polymorphism phenomenon in composite matrix.

The parallel research conducted at our laboratory by DSC, PLM, and SEM [7] techniques were to explain why the chemical modification with agents promoting adhesion decreases the nucleation activity of hexagonal form crystallization process. Mercerization of fibers only causes inducing of form β in the amount comparable to that achieved with unmodified fibers. Native flax fibers and hemp have embossment – roughness and considerable number of pores on the surface. Mercerization, to some extent, "smoothens" the surface of the cuticle, but on the other hand, it causes fiber to split. Chemical modification, e.g., with acetic anhydride, causes binding of elementary fibers in bigger strands with uniform surface. That is why moving of modified fibers is ultimately moving polypropylene chains bonded to the flax fiber by adhesion in relation to polypropylene chains of the matrix. Such movement causes no creation of such strong shearing forces as in the case of native and mercerized fiber movement – where the surface of the lignocellulosic fiber is moved against the matrix.

Thus, the topography of the outer surface of modified fibers, having higher specific surface, can be an important factor influencing the creation of β form during the fiber movement in the matrix.

Another objective of β form induction analysis, besides α form that is most often observed, is to investigate in what distance from the moved fiber the form β is present. The range of structural changes caused by moving fibers has not only a cognitive importance but also a practical dimension for composite manufacture.

Figure 10.4 shows the dependence between the content of hexagonal form and the distance from moving unmodified flax fiber. It is clearly visible that interaction is very intense in the range up to 2 mm, while in the range over 2 mm from the surface of moved fiber, the content of β form reduces drastically. In the range up to 7 mm, the amount of this form is only identified by traces, while in range over 7 mm cannot be observed at all.

It is worth mentioning an interesting analogy of increasing the crystalline degree of polypropylene matrix with the increasing presence of hexagonal form in analyzed

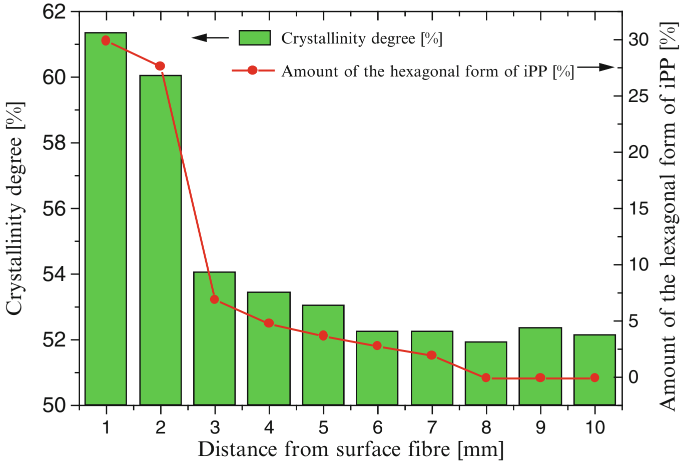

Fig. 10.4 Degree of crystallinity of iPP and the amount of the hexagonal form of iPP versus distance from surface fibers [8]

samples. The degree of matrix crystallinity increases with the reduction of temperature at which the fiber is moved. Additionally, at the nearest range from the moved fiber, the content of β form is not only the highest one but the degree of crystallinity of polymeric matrix is also much higher, which has been presented in Fig. 10.4.

Figure 10.5 shows morphology in flax fiber/polypropylene composites after crystallization in dynamic conditions. Microscopic investigations confirmed the presence of both phases (α and β) in the polypropylene layer exposed to shearing forces.

As we can seen in Fig. 10.5b, the morphology of the composite after selective melting at 150°C was observed.

It is visible that after remelting, the β-form is not present and in consequence the α phase exist only. No presence of distinct thin layer of row-nuclei was found on

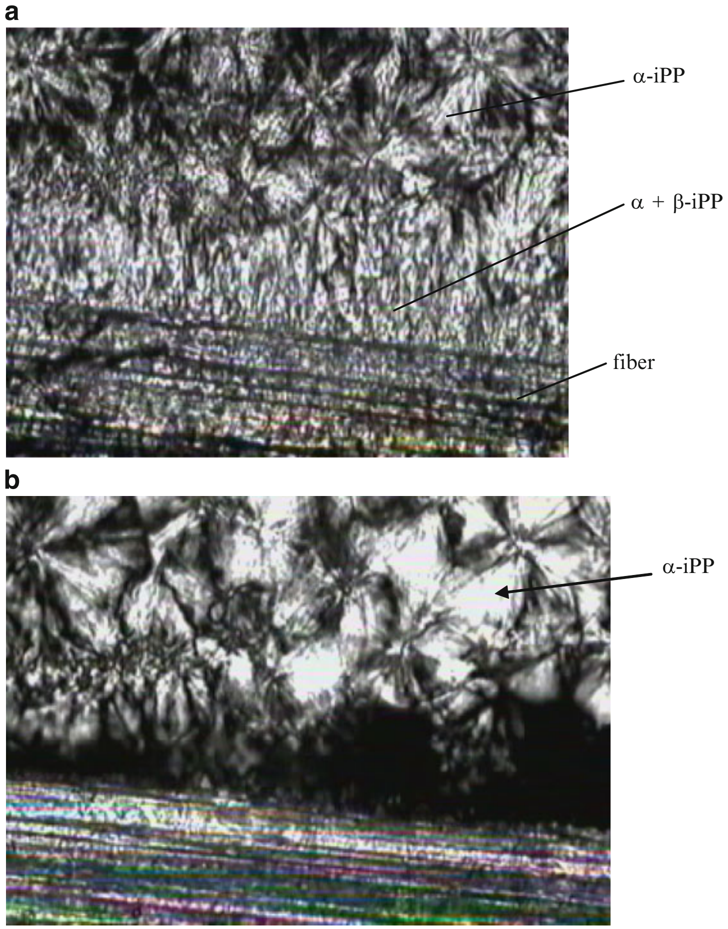

Fig. 10.5 Optical micrographs showing the transcrystallization in flax fiber/polypropylene composites. (**a**) crystallization temperature −130°C, speed of fibers pulling −0.42 mm/s, (**b**) after selective melting in temperature −150°C of sample showed in Fig. 10.5a

the surface of the fibers. According to Varga and Karger-Kocsic [4], the layer of row-nuclei forms in the close neighborhood of pulled fiber is built of form α crystallites having the ability to nucleation of hexagonal form on their surface. Our experiments do not contradict the previously mentionned considerations but we belive that topography of lignocellulosic materials results in the deterioration of the nucleation and crystallization of the polypropylene matrix. It is known that surface roughness of different fillers is one of the possible causes of development of transcrystalline layers. Transcrystallization phenomena will be described in second chapter.

10.3.2 Influence of Processing Parameters

10.3.2.1 Extrusion Process

During extrussion process, especially in the extruding die, shearing forces (similar to the model studies described above) can be the reason of structural changes in polypropylene matrix. The investigations on extrusion process of polypropylene composite containing short flax fiber, conducted at different nozzle temperatures, confirmed that at temperatures of 180–200°C no β phase can be found in the extrudate. As the processing temperature reduces, beginning from 180°C, the process of inducing form β commences. The content increase of this form in the extrudate is connected first of all with decreasing the temperature in the extruding die as well as with increasing of fiber content in the composite.

In case of obtaining composites in the form of granulate, the phase variability is not very important as the composite is meant for further processing to obtain a desired element. However, in the case of extrusion, the continuous profiles such as pipes or troughs and the presence of hexagonal phase can considerably influence the properties of the final products.

10.3.2.2 Injection Molding

The hexagonal form of polypropylene in molds can be observed more often than in extrudate due to the fact that the polymer is injected into the form of much lower temperature than the temperature at which the fibers were pulled, over which no polymorphic form of polypropylene is formed [10]. Analyzing the earlier described structural studies, this temperature was called the critical temperature of hexagonal form of isotactic polypropylene forming.

Additionally, besides the movement of fibers occurring in a whole bulk of molten polymer, the phenomenon of shearing is also present, which occurs between polypropylene chains and injection mold. It was found that a small amount (5% by weight) of flax or hemp fibers in injected polymer already causes the presence of hexagonal form in molds. As the content of fibers in the composite increases (by weight), the amount of induced β form increases and exceeds 25% at 10% fiber content in the composite. Further increasing of short fiber content in the composite causes no considerable increase of hexagonal form amount, which is in accordance with earlier described model studies conducted for single fibers pulled in the mass of the composite. It was confirmed that unmodified fibers initiate the creation of form β to a higher degree. It was also observed that in layers adjacent to walls of the injection form, i.e., where the shearing forces are stronger, the amount of polymorphic form is significantly higher than inside the molds [10].

10.3.2.3 Fiber Pulling During Press Molding

Industrial application of fiber pulling inside the crystallizing polypropylene matrix can be a method for manufacturing products characterized by a higher impact resistance and elasticity; however, the advantages of the products are the result of the presence of hexagonal form [9].

The forming method has it that isotactic polypropylene is formed as a board on which one or more parallel layers of fibers are applied. Additionally, on one side, the ends of fibers must reach out over the edge of the board to be caught and pulled. Next, the second polypropylene board is applied. The boards are heated to 175–285°C at a constant or increased pressure, and then the set is cooled down. Below 150°C, the fibers are moved to the distance up to few millimeters at 0.01–0.1 m/s. Having obtained the desired shape, the product is cooled down to the ambient temperature [3]. The technique presented in the cited patent description ensures high content of β form in the polypropylene composite reinforced with natural fiber.

10.4 Interphase Phenomenon in Fiber/Polypropylene Composites

The results of research conducted during the last decade confirm the nucleating character of lignocellulosic filler in polymeric composites. Natural fibers added to polymeric composites are the active source of creating a nucleus of crystallization. The addition of the filler reduces the interphase energy semicrystalline polymer-filler and consequently makes the crystallization process easier. A “foreign” surface as the filler structure, by its presence, makes it possible.

10.4.1 Formation of the Transcrystalline Layer in Composite Materials

A transcrystalline layer (TCL) is the supermolecular crystalline structure, induced by an oriented growth in the presence of the foreign surface. Transcrystallization occurs when the nucleation density of a solid filler that is in contact with melted

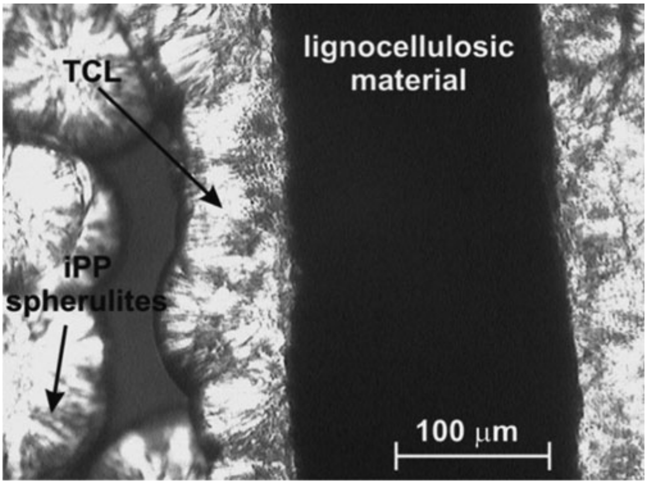

Fig. 10.6 Transcrystalline layer formed as a result of crystallization of iPP with lignocellulosic material

polymer is clearly higher on the surface than the density of nucleation in the bulk of melt.

Transcrystallization is influenced by many factors:

- Matrix topography
- Crystallization initiated by shearing
- Matrix surface energy
- Adsorption on small particles

High density of nuclei on foreign surface causes disturbance in spherulites growth, which results in the only possible growth – perpendicularly to the surface. As a result, transcrystalline front will emerge parallel to the surface. Transcrystallization is possible when nucleation energy conditions are more favorable on the surface than in the bulk of the melt. The microscopic photograph of TCL is shown in Fig. 10.6.

Presence of TCL changes the properties of crystalline matrix. Transcrystallization of isotactic polypropylene in the presence of different fibers has been thoroughly analyzed. Gray as the first one provided detailed description of isotactic polypropylene behavior in the presence of wood fibers using polarized light microscopy. He observed that when melted polymer is cooled down, it crystallizes in spherulite forms in nonisothermal and isothermal conditions, creating additionally a TCL.

Results of many researches confirm the presence of TCL as the effect of nucleation ability of different substances. Among the factors inducing transcrystallization in polyolefin matrix, the following fillers can be listed:

- Lignocellulosic material:
  - Kenaf fibers [11]
  - Wood fibers [12–14]

  - Thermomechanical pulp [15]
  - Flax fibers [16, 17]
  - Spanish Broom (*Spartium junceum*) [18]
  - Bamboo fibers [19]
  - Cotton fibers [20]
  - Cellulose nanocrystals from ramie and flax [21]
- Glass fibers [22]
- Aramid fibers [22, 23]
- Carbon fibers [22, 24]
- Carbon nanotubes [25]
- Talc [26]
- Nylon-6 fibers [27]
- PET fibers [28]
- Isotactic PP fibers [29].

Observations of polypropylene crystallization by polarized light microscopy helped to understand phenomena on interphase of polymer-filler. When analyzing the influence of the filler, many researchers noted transcrystallization of the polypropylene as a result of high enough nucleation density on the filler's surface and also in the presence polypropylene fibers. The addition of both mineral substances and natural composites containing lignocellulosic material can induce formation of TCL.

10.4.2 Transcrystallization of Isotactic Polypropylene on the Surface of Lignocellulosic Fillers

Most results of research on addition of unmodified chemically lignocellulosic filler confirm the presence of the TCL on the interphases in the composite. In this aspect, the results showing no significant effect of chemical modification on TCL forming are interesting. An example of such modification is the use of polypropylene grafted with maleic anhydride as the compatibilizing agent.

Sanadi and Caulfield [11] tested the effect of kenaf presence, with the addition of an agent improving adhesion, on the interphase – polypropylene grafted with maleic anhydride (MAPP). The tests using polarized light microscopy with a heating device showed that composites containing both MAPP fibers and unmodified fibers had a transcrystalline structure. Dynamic mechanical analysis justified a suggestion that TCL contains many defects. This could be caused not only by the presence of MAPP in TCL but also by the presence of solid body surface, which limited the crystallization process.

The PP molecular weight and amount of MAPP-grafted polypropylene has been considered an important factor influencing the adhesion. Longer PP macromolecules and smaller amounts of maleic anhydride may result in crystal defects. On the other hand, longer molecules make the physical interaction between TCL as well as spherulites and fiber surface easier [11].

Interesting results were reported by Mi et al. [19]. They analyzed polypropylene filled with bamboo fibers with the addition of polypropylene grafted with maleic anhydride. The use of the agent promoting the adhesion was aimed at improving interactions between the components. In case of systems polypropylene/bamboo fibers/compatibilizer, the TCL has been formed. This was explained by higher ability to nucleation of bamboo fibers in relation to MAPP-grafted polypropylene as compared to pure polymeric matrix.

Similar results were obtained by Son et al. [13], who treated cellulose fibers with NaOH solution and additionally modified by cellulase enzyme. He also used MAPP as an additional compatibilizing agent. It was noticed that both the unmodified cellulose and NaOH-modified cellulose have equal nucleating ability. The TCL formed around both kinds of fibers; however, it was higher for unmodified fibers. In modified fibers, the TCL around the filler was also observed. The highest layer growth of TCL was noted for the system with fibers modified by cellulase. It was explained by probable increase of TCL growth rate by the increase of surface roughness and unhomogeneity by cellulase action.

Felix and Gatenholm [20] were among the first researchers who showed results confirming the presence of TCL on the surface of lignocellulosic filler. In the manufacturing of polypropylene composites containing cotton fibers, they observed the presence of TCL around fibers. An interesting observation was that the presence of formed TCL improves the shear transfer between filler fiber and the matrix.

Sangyeob et al. [15] conducted research on heterogenic nucleation of semicrystalline polymers in the fiber surface. Using the analysis of polarized light microscopy, he noted the nucleating ability of thermomechanical pulp with the formation of TCL. The tests were conducted using fibers modified by dichloromethane extraction and rinsing with water. Modification of fibers by extraction resulted in the reduction of nucleating ability. Changes in fiber topography were noted as the result of the elimination of low molecular compounds extracted from the surface that caused the reduction of nucleating ability of lignocellulosic material. Similar observations were made by Borysiak [30] who found that applying the extraction of the lignocellulosic component results in considerable reduction of nucleating ability of the polymeric matrix. He also noted that chemical modifications, by the application of numerous acid anhydrides, are responsible for filler surface activity reduction.

Gray [21] obtained a new, interesting type of polymeric–cellulose composites. The matrix filler he used was cellulose nanocrystals extracted from cotton and ramie fibers and, next, isolated with the help of bacteria. He conducted microscopic analyses for two variants of samples. The first sample was built like a “sandwich” composite, while the other was composed of evaporated nanocrystals of cellulose covered with polypropylene disc. Gray observed the formation of TCL in both samples and explained it as a result of some kind of epitaxy. Increased nucleation was noted on the edges of the layer. It was suggested that nucleation goes better at the ends of fibers as compared to longitudinal surface.

10.4.3 Effect of Chemical Modification on Transcrystalline Layer Formation

Chemical modification to improve compatibility of composite components is very often connected with the effect of lack of TCL. The effect of filler modification on TCL formation inhibition was presented by numerous studies. Quillin et al. [29] explained the lack of TCL as a result of fiber modification by "covering" the ordered crystalline structure of cellulose chains by particles of modifiers. Gray [31], on the other hand, said that crystalline cellulose, called the cellulose II, unlike the cellulose I, causes no formation of TCLs. He explained that by the differences in crystalline structures of both types of cellulose. The results contradictory to those presented earlier were presented by Son et al. [32] – the cellulose II did initiate the transcrystallization in polypropylene matrix.

The effect of chemically modified lignocellulosic filler on the formation of TCL was thoroughly investigated by Borysiak and Doczekalska [33]. They conducted a number of pine wood modifications using different acid anhydrides: maleic, phthalic, propionic, crotonic, and succinic. The filler was also subjected to mercerization and extraction. It was found that the presence of TCL is strongly connected with chemical structure of used anhydrides. The system of the best nucleating ability was polypropylene with unmodified pine wood. It was found that mercerization and extraction slightly reduces the nucleating ability of the matrix. Unexpectedly, it was noted that wood modified with acid anhydrides may strengthen the effect of transcrystallization of polymeric matrix. The fact that the lignocellulosic filler subjected to succinic anhydride action caused no transcrystallization remained unexplained.

Lenes and Gregersen [14] found out that, analyzing the effect of cellulose fiber modification from sulphite softwood, chemical modification inhibits formation of TCL. Wood was first subjected to mercerization and next esterification with hexane and benzoic acid. Another portion of samples was knife milled sulphite fiber. All these modifications aimed at changing the fiber surface topography. Unmodified fibers showed ability to form the TCL. Even higher degree of transcrystallization was observed in composites with addition of mechanically modified fibers. The growth of TCL was noted after fibrillation. Additionally, it was observed that the differences in transcrystalline phase growth for systems containing fibers esterified with different reagents. It was explained by different degree of filler hydroxyl group substitution.

The effect of flax fiber modification and the effect on the presence of TCL were also studied by Arbelaiz et al. [17]. In his studies, fibers were subjected to maleic anhydride, vinyltrimetoxy silane, and alkali with addition of MAPP-grafted polypropylene. All applied modifications produced improvement in the thermal stability of lignocellulosic material. Analysis of the crystalline structure showed the increase of crystallinity as a result of filler addition. Nucleation density around unmodified fibers was higher than around fibers modified with maleic anhydride. Surfaces of unmodified fibers had the surface active for initialization of transcrystallization, which, in the case of modified fibers, did not occur. Son et al. [32] explained this phenomenon as the result of penetration of the MAPP molecules into the interphase areas. This blocked and inhibited the development of TCL or reduced it to trace amounts. The results obtained by Arbelaiz et al. [17] were similar to those obtained by Son et al. [32]. Transcrystallization around fibers occurred to a small degree. It was found that modifying the filler with maleic anhydride causes changes in the nucleation ability, which resulted in the formation of TCL with a low density. It was also observed that the thickness of this layer depends on the temperature of crystallization. The increase of temperature caused the reduction of the layer thickness.

Studies on lignocellulosic material modification were also conducted by Nekkaa et al. [18]. The cellulose fibers obtained from Spanish broom (*Spartium junceum*) were subjected to silane's action to improve adhesion between composite components. Thermal analysis confirmed the nucleating effect upon the addition of unmodified fibers, while the addition of modified fibers did not significantly influence the crystallinity of polypropylene matrix.

Zafeiropoulos et al. [16] used four types of flax fiber when studying the crystallization of isotactic polypropylene in the presence of fibers: unmodified, dew-retted (pectin removed), flax modified by esterification with stearic acid and flax modified by high temperature in autoclave. It was interesting to see that transcrystallization occurred in both chemically and hydrothermally modified fibers. Zafeiropoulos also found that the rate of cooling may have an effect on the morphology of TCL.

Modification by stearic acid, similar to that used by Zafeiropoulos et al. [16], was conducted also by Quillin et al. [29]. He found, however, that treating fibers with this acid inhibits development of TCL. Different results can be explained by the fact that Quillin, unlike Zafeiropoulos, used a new technique where no solvent was used, which turned out to be an advantage in terms of TCL formation. The TCL formed around particular fibers varied. The structure formed around unmodified fiber was asymmetric and had different thicknesses at different places. It also showed different optical properties from the layer formed on modified fibers in autoclave.

10.4.4 Influence of Lignocellulosic Fibers on the Nucleation and Polypropylene Crystallization Process

The aspect that is indispensably connected with polymer composites containing lignocellulosic materials is the modification of both the filler and polymeric matrix. In the last few years, intensive research has been conducted aimed at optimization of lignocellulosic composites manufacturing. General methods used to improve polymer and filler adhesion are based on chemical and physical modifications. In manufacturing composites based on polypropylene and lignocellulosic fibers, the mixing process is the important problem in preparation of composite materials. Numerous studies aiming at improvement of mixing of hydrophobic polypropylene with hydrophilic lignocellulosic filler resulted in a number of helpful modifications. Application of these modifications on lignocellulosic material has significant effect on the characteristics of temperatures and kinetic parameters.

A very commonly used method to investigate thermal properties of polymeric materials is differential scanning calorimetry (DSC). Many studies were conducted based on thermal analysis. The DSC is defined as a method in which the rate of heat flow, to which the sample is exposed, is measured in function of time or temperature, while the sample temperature (in defined atmosphere) is programmed. The DSC method allows for obtaining measurable information regarding phase transition and kinetic parameters of composite materials.

Joseph et al. [34] thermally analyzed the polypropylene composites reinforced with sisal fibers. He applied the following modifications: 10% NaOH, polypropylene glycol urethane derivative (PPG/TDI), and potassium permanganate ($KMnO_4$). He additionally investigated composites in which polymeric matrices were MAPP-grafted polypropylene.

DSC was used to determine the melting and crystallization temperatures, melting enthalpy, and the degree of crystallinity. The results showed the increase of polypropylene crystallization temperature and degree of crystallinity upon addition of sisal fibers. It was explained by the nucleating effect of fibers. Also, dependence between the amount of added filler and changes in the degree of crystallinity and melting point were observed. The addition of chemically modified sisal caused a stronger increase of crystallization temperature as compared to composites containing unmodified fibers.

Studies on a similar group of materials – polymeric composites reinforced with sisal fibers – were conducted by Manchado et al. [35]. They analyzed the presence of different fibers, such as sisal, on crystallization of polypropylene. The composites were prepared in special chamber for mixing where the matrix was plastified at 190°C. Obtained materials were subjected to thermal analysis by DSC. The analysis of thermograms allowed for a similar finding like in Joseph's studies [34]. The presence of sisal fibers, as well as other fibers used in the study, accelerated crystallization of polypropylene. This was explained by the nucleating effect of sisal filler. Also, the half-time crystallization ($t_{1/2}$) decrease was observed for polypropylene with the addition of sisal fibers in comparison with unfilled polypropylene. The analysis of nonisothermal crystallization showed that the degree of polypropylene crystallinity is higher for the composites filled with sisal fibers than for unfilled polymer.

Similar observations were made by Arbelaiz et al. [17]. Flax fibers were subjected to action of maleic anhydride, vinyltrimethoxy silane, and alkali. As an additional compatibilizing agent, a MAPP-grafted polypropylene was used. The modifications had an effect on shaping the TCL. Addition of MAPP-grafted polypropylene caused formation of TCL of lower density as compared to the systems with unmodified fibers. Calorimetric analyses of composites containing flax fibers revealed a visible increase of crystallization rate as compared to the matrix without any additives. Addition of fibers had no significant effect on the melting point, unlike the degree of crystallization and the temperature of matrix crystallization. These parameters increased together with the increase of flax fiber amount content.

The nucleating effect of lignocellulosic filler was also investigated by Yang et al. [36]. They used thermal analysis to test polypropylene composites filled with rice husks and wood flour. They used maleic anhydride-grafted polypropylene as a compatibilizer. They analyzed crystallization of the matrix in nonisothermal conditions. The analysis showed a slight effect of addition of the filler on glass transition of the matrix. The authors suggested that this proved the lack of chemical bonds between the matrix and the filler. Melting temperatures of composites showed no significant differences. No effect of filler on polypropylene melting was observed.

The consequence of lignocellulosic material addition, not only in the form of fibers but also in the form of wood flour or wood particles, is the nucleating effect. Numerous reports prove that the presence of wood origin lignocellulosic filler has an influence on crystallization of polymeric matrix.

Qiu et al. [37] observed comparable melting points of PP regardless of the amount of lignocellulosic fibers added. This refers to both the systems in which the matrix was the polyethylene with no additives and MAPP-grafted polypropylene. Different observations were made for crystallization temperature of polymeric matrix. The increase of the crystallization temperature occurred in both systems with MAPP-grafted polypropylene and in PP without additives. Modification of the filler by 1,6-diisocyanatohexane caused reduction of PP melting point and crystallization temperature, reducing also nucleating effect of wood.

Also, Amash and Zugenmaier [38] observed an increase in the crystallization temperature of polymeric matrix with the addition of cellulose fibers and MAPP, used as a compatibilizing agent. The DSC results clearly show that the addition of small amounts of cellulose fibers to PP increases the crystallization temperature of the polymer matrix. The effects observed can be explained by the assumption that the cellulose fibers act as efficient nucleating agents for the crystallization of PP.

Mucha and Królikowski [39], studying the kinetics of isothermal crystallization of polypropylene, noticed that addition of a filler, e.g., wood flour, efficiently reduces the time of crystallization. This is desirable in the processing of composites as it reduces the injection-forming cycle and forms small spherulites improving the mechanical properties of composites. Transcrystalline structures are formed during polymer crystallization in the presence of lignocellulosic filler.

Harper and Wolcott [40] conducted research aiming at the analysis of interactions between adhesion promoters and lubricants in polypropylene composites with wood. Based on calorimetric tests results, the crystallization and melting kinetics of systems with isotactic polypropylene with wood, containing adhesion promoter (MAPP-grafted polypropylene) and lubricants (e.g., zinc stearate), were analyzed. Analyses by DSC confirmed the nucleating effect of wood on polypropylene crystallization. The increase of crystallization temperature was observed. The results revealed occurrence of transcrystalline structure around cellulose fibers. The presence of wood caused increase of crystallization nuclei density in normal direction in reference to the filler surface. An interesting observation was the analyse of the presence of adhesion promoters and lubricants in amorphic areas of the polypropylene matrix. According to the authors, deposition of lubricants in amorphic areas influenced the mechanical strength of polymer and lignocellulosic materials composites.

Polymer and lignocellulosic material composites can be analyzed by wide angle X-ray scattering (WAXS) due to a character of the matrix. The necessary condition for diffraction is the fact that the wavelength of X-rays must be of the same order of magnitude as the distance between the lattice planes in polymer crystals. The most often used matrix polymers for composites containing lignocellulosic materials are thermoplastic polymers. Among the most studied ones are the systems with isotactic polypropylene. Besides PP, polyethylene (recycled and nonrecycled) is also used.

Lei et al. [41] manufactured composites from recycled high-density polyethylene, reinforced with sugarcane and wood. As a compatibilizer, the MAPP-grafted polyethylene, carboxylated polyethylene, and titanium-derived mixture (TDM) were used. Obtained composites were analyzed by the following methods: wide angle X-ray scattering, DSC, and dynamical mechanical analysis. WAXS analyses allowed for crystallinity comparison of sugarcane composite and pure matrix. The reflection plane and the degree of crystallinity were analyzed. Obtained diffractograms showed crystalline structures of cellulose present in sugarcane and wood cell walls. The peak corresponding to cellulose was visible on the diffractogram at angle $2\Theta = 22°$. Peaks for planes (110) and (200) corresponding to the crystalline structure of recycled high density polyethylene (RHDPE) were changed as a results of adding fibers and one of the compatibilizing agents. In the case when intensity of peaks changed, authors observed differences in crystallinity of particular samples. Comparison of DSC and WAXS analyses showed that the addition of lignocellulosic material results in increasing the crystallization temperature of the polyethylene matrix. Moreover, it was observed that the addition of the compatibilizing agent causes a slight decrease of crystallinity degree as compared to the material in which no compatibilizers were used.

Also, Lei et al. [42] tested composites manufactured of rice straw fibers and recycled high-density polyethylene using WAXS method. As fillers, they used fibers coming from different parts of the plant: leaves, husks, stem, and mixture of all these fibers. The filler and the two types of matrices – RHDPE and the polyethylene that is not recycled – were placed in the mixer. Obtained mixtures were pressed under 30 tons at 175°C. The WAXS technique was used to analyze the effect of the presence of fibers on polymeric matrix crystallization. The filler caused the increase of crystallinity degree of tested materials. This was explained similarly as earlier cited reports, namely that single fibers play the role of heterogenic nucleating agents.

The results of research described above prove univocally that the presence of lignocellulosic material in polymeric composites influences the crystallization process, altering the kinetic parameters, such as induction time, degree of crystallinity, conversion degree, etc., and characteristic temperatures. Using modification of the filler is not without the effect on crystallization of the matrix. An interesting phenomenon that has not been explained completely so far is the transcrystallization. Both the formation of transcrystallization and its effect on mechanical properties remain a disputable question among researchers.

10.5 The Analysis of Various Factors on Mechanical Properties of Composite Polypropylene–Natural Fibers

Within many past years, the research on polymers has concentrated, among others, on how to prolong the durability and stability. In time, this approach was supplemented by the materials that would degrade within a certain time after their life. Even if synthetic polymers make only 7% of total amount of wastes by weight, their volume share is over 30%. Therefore, for over a decade, a strong interest can be observed in using materials that are able to degrade. Among materials characterized by a partial degradability are a system of polypropylene and natural cellulose fibers. Introduction of a biodegradable component (a cellulose fiber) into a polymer causes its assimilation by microorganisms during a decomposition process, while the remaining part of a composite is safely dispersed in the environment. Additionally, such materials can be successfully recycled in terms of both material and energy.

Another important aspect that makes a wide application of such materials in industry is obtaining interesting physicochemical properties. The strength and Young's modulus parameters of natural fibers are similar to those of glass fiber [43–47], which may make them an alternative for fillers in polymers. When comparing mechanical properties of composites PP/lignocellulosic component with a system PP/glass fiber, one can notice very similar strength parameters [48]. The main advantage of introducing natural fibers into PP matrix is obtaining a material that shows a better stiffness, which is a crucial parameter in higher temperature applications.

Nevertheless, obtaining composites filled with the lignocellulosic component with desired strength properties requires to consider many factors having an effect on the final macroscopic properties. According to information from the literature, the following factors should be taken into account when designing a composite: adhesion between the components, filler content, fiber length of fibrous filler, filler distribution, the effect of processing parameters, etc. [49–53]. Achieving a good interphase adhesion between polymer matrix and fibers is necessary to transmit stress from the matrix to the fibers and finally for improvement of a material strength.

10.5.1 Effect of Improvement of an Interphase Adhesion on the Mechanical Properties of Composites

One of the most important problems occurring in composite manufacture is a low adhesion between the components, which significantly limits the application of such materials in a broader scale. Finding effective methods of improving adhesion and description of interphase interactions are the topics of numerous studies.

Literature studies showed that the most often method for improving the adhesion between the composite components is using a MAPP. This compatibilizer can be an effective adhesion promoter for a system cellulose fibers–polypropylene matrix

[54–61]. Creating covalence bonds between the cellulose –OH groups and anhydride groups of MAPP grafted to the PP chain is one of the reasons for achieving a better strength of composites [57, 62]. Obtaining a cross bond between MAPP and PP is responsible for transmission of stresses from the polymer matrix to the fiber.

Literature also reports the effect of MAPP content. The results show a certain optimum necessary for improving the mechanical properties [49]. It is also known that the content of the anhydride grafted on the polypropylene chains at the level of 0.2% is enough to obtain a positive strength effect [49]. Gauthier [63], using a microbond test, found that composites containing MAPP-modified cellulose fiber shows approximately 70% better adhesion as compared to a system with a nonmodified fiber. Oksman et al. [64] noticed that 2% addition of MAPP causes a considerable improvement of mechanical properties. In composites PP–sisal fibers, the increase of tensile strength was from 40 to 79 MPa while for the system PP–flax fiber – from 46 to 75 MPa. Similar relations were observed for Young's modulus. An addition of 10% sisal fiber into the PP matrix (in presence of MAPP) resulted in Young's modulus increase by 150% and in tensile strength increase by about 10% [65]. Bengtsson et al. [66] also noticed that the application of MAPP is responsible for the improvement of tensile strength for composites made of polypropylene and Kraft cellulose fibers. Similar observations were made for PP composites with flax fibers [53, 67, 68] and systems PP-kenaf fibers [69], where application of MAPP caused improvement of mechanical properties.

Hornsby et al. [70] noticed improvement of tensile strength, Young's modulus, and impact resistance in composites PP–flax fibers containing 5% of the MAPP compatibilizer. Also, Kim et al. [71] noticed considerable improvement of PP/cotton fiber composite tensile strength when using the MAPP as a compatibilizer.

The research results confirm that the application of silica-organic compounds for modification of cellulose fiber surface considerably improves strength properties of composites[50, 51, 72–75]. Raj et al. [72] found that the modification of cellulose fibers with silanes as well as with isocyanate caused improvement of mechanical properties of composites based on polypropylene matrix. However, studies conducted by Hornsby et al. [76] do not confirm that. His results prove that processing flax fibers with silanes has no effect on mechanical properties of composites based on polypropylene matrix. These contradictory conclusions are probably the effect of a complex anatomical structure of cellulose fiber and/or application of suitable conditions of modification reaction.

Another way to improve the adhesion is by using the process of natural fiber acetylation. Acetylation reduces the jute fiber water sorption by about 50% [77]. Liu et al. [77] investigated the effect of acetylation on cotton and rayon fibers and found that the strength of composites improved. [78] noticed the increase of fiber surface energy upon acetylation, which was explained by forming ester bonds.

Studies on acetylation as one of the methods for modification of lignocellulosic materials are conducted at our research center [7–9, 30, 33, 79–81]. Tables 10.1 and 10.2 show the values of strength of composites based on polypropylene matrix and long flax or hemp fibers. These components were obtained by compression molding according to a procedure described in a patent [82]. The developed method ensures processing of polymers containing natural fibers that are 10 cm in length and longer ones , which is not possible by extrusion and press molding methods.

Based on the results reported above, one can notice that chemical modification of natural fibers using acetic anhydride caused significant improvement of composite mechanical properties. It is also worth to emphasize that the content of lignocellulosic filler has considerable effect on mechanical parameters. The tensile strength for polypropylene composites containing 20% and 30% of unmodified fiber is comparable to polymer matrix. Only introduction of 40% of filler has caused the increase of tensile strength (by about 15%). Application of chemical modification of lignocellulosic component is responsible for the increase of tensile strength at already 20% content of natural fibers. Further increase of amount of flax or hemp fiber causes significant increase of tensile strength. The results in Tables 10.1 and 10.2 confirm that the introduction of any amount of a filler leads to the increase of Young's elasticity modulus as compared to polypropylene matrix. It is worth emphasizing that application of acetylation of lignocellulosic fibers caused the increase of the Young's modulus by about 30% as compared to unmodified composites. A very interesting observation is reduction of elongation at break for composites containing modified fibers. This situation can be a result of increasing of interphase adhesion between the polymer and hydrophobicitized natural fibers that were treated by acetic anhydride. The presence of ester groups was confirmed by IR testing.

Also isocyanates were used as adhesion modifiers. These compounds are efficient compatibilizers ensuring a significant improvement of tensile strength [50, 51, 72, 83–86]. Qiu et al. [37] showed that the application of hexamethylenedi-isocyanate causes increase of tensile strength by about 45% and bending strength by 85%, as compared to unmodified composites. Raj et al. [50, 72] noticed that application

Table 10.1 Mechanical properties of long flax/PP composites

Mechanical properties of flax/PP composites

	PP	PP + unmodified flax fibers			PP + flax fibers modified by acetic anhydride		
		20%	30%	40%	20%	30%	40%
R_m (MPa)	29.9	28.7	30.4	35.7	31.2	34.9	38.1
ε (%)	342	26.2	22.3	15.8	24.1	14.4	9.4
E (MPa)	639	789	845	1,200	921	1,079	1,469

Table 10.2 Mechanical properties of long hemp/PP composites

Mechanical properties of hemp/PP composites

	PP	PP + unmodified hemp fibers			PP + hemp fibers modified by acetic anhydride		
		20%	30%	40%	20%	30%	40%
R_m (MPa)	29.9	28.4	31.3	34.9	32.1	36.5	39.8
ε (%)	342	24.4	19.9	12.32	20.7	13.8	7.73
E (MPa)	639	802	913	1,169	1,084	1,211	1,662

of isocyanates and silanes can be an effective method to improve adhesion in composites PP–cellulose fibers, which is demonstrated by improvement of mechanical properties and better dimensional stability.

The literature reports also other methods for modification of lignocellulosic components to improve interphase adhesion. These comprise reactions with triazine derivatives [87], *n*-octadecyl vinyl-sulfone [87], potassium permanganate [86, 88], as well as dicumil or benzoyl peroxides ([89]; Jayamol [90]). Processing with peroxides in addition to significant improvement of mechanical properties of composites is also responsible for making processing of composite materials easier [86, 91, 92].

10.5.2 The Effect of Length, Content, and Dispersion of Fibrous Filler and Processing Parameters on the Mechanical Properties of Composites

Another important factor having an effect on strengthening of polymer matrix is the fiber length [89, 93, 94]. When using composites containing "short" fibers, there is a critical length that is necessary to achieve the desired mechanical parameters [52, 58, 88]. When the length of fibers is shorter than the critical value, the composites show worsening of mechanical properties. Based on a report by Joseph et al. [88], one can observe that tensile strength is increasing with increase of fiber length. It is also known that the strength of composites is higher when decreasing the critical length of fibers [52]. Those authors also noticed that the strength of composites is dependent on fiber orientation. It was found that the strength of fibers oriented unidirectionally is higher than randomly distributed ones.

Obtaining a composite with maximum high filler content is economically justified. It is known that as the content of filler increases, the price of the composite is decreasing. It is worth to mention, however, that increasing the content of fibers in the matrix causes higher stiffness of the composite [95]. Pukanszky [95] reports that mechanical properties are strongly dependent on filler particle characteristics. Composites containing a filler of spherical shape are characterized by decrease of tensile strength as the content of the filler is increased in the matrix. Oksman et al. [64] observed higher strengths of composites as the content of sisal, jute, and flax fibers increased in the matrix. The key factor responsible for improvement of mechanical properties is achieving very good dispersion of the filler in the matrix [96].

Obtaining the composite with high strength parameters is determined also by conditions of processing. It is necessary to optimize the technological processes of extrusion, injection molding, or press molding. The parameters that should be optimized are temperature plasticity, mold temperature, temperature of molded piece, rate of cooling, and process pressure. These factors are crucial for thermal resistance of lignocellulosic component, distribution and shape of the filler, and shaping the supermolecular structure of polymer matrix.

Joseph et al. [88] noticed that mechanical properties depend on the time of mixing the composite components. At shorter times, the strength and Young's modulus were lower, which can be explained by less thorough mixing and insufficient dispersion of filler in the matrix. Longer time of mixing increases the dispersion. It was also found [88] that higher temperature of processing (over 70°C) leads to decrease of strength, which can be explained by thermal degradation of cellulose component. Additionally, poorer fiber dispersion was observed, which was caused by decrease of viscosity in higher temperature.

Medina et al. [97] investigated the effect of pressure during processing on the mechanical properties. He found that a pressure of 15–60 bar results in composites of higher tensile strength as compared to higher pressures (80–200 bar). The SEM analyses explained that by occurrence of fractures in fibers at higher pressures.

10.6 Conclusions

It was found that in the composites with natural fibers the hexagonal form arises when the fibers are in motion in relation to the polymeric matrix. The processing conditions play an important role for structural changes in PP matrix. Moving temperature of natural fibers was found to have a strong influence on the content of hexagonal modification. If the temperature of the moving of fibers is low, then the amount of β-PP significantly increases. The content of β-PP also depends on the rate of moving of fibers; however, the chemical modification of the natural fiber surface reduces the content of this form.

Many factors such as adhesion between components, fiber topography, and kinetic parameters of crystallization of semicrystalline matrix have been reported to influence transcrystallinity. The transcrystallinity phenomenon in the natural fibers/polypropylene system is affected by the different type of chemical treatment of lignocellulosic materials. Moreover, the ability of natural filler to induce nucleation in polypropylene matrix is also dependent on the kind of chemical modification of surface fibers. Predominant nucleation ability was found for unmodified fibers. However, chemical modification of fiber surface slightly depressed the nucleation of polypropylene matrixes.

The mechanical and other physical properties of the composite are generally dependent on the length, content, and dispersion of fibrous filler and processing parameters.

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