



Le traitement, la structure et les propriétés des composites fondés sur les charges naturelles et les polyoléfines stereo régulières

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THESE

Présentée pour obtenir le grade de

DOCTEUR D'UNIVERSITE

Spécialité : Chimie-Physique

Par **Kristýna MONTÁGOVÁ BERKOVÁ**

**PROCESSING, STRUCTURE AND PROPERTIES OF
COMPOSITES BASED ON NATURAL FILLERS AND
STREEREOREGULAR POLYOLEFINS:
ENVIRONMENTALLY BENIGN CONCEPT**

Soutenue publiquement le 18 octobre 2013 devant la commission d'examen :

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**Processing, structure and properties of composites
based on natural fillers and stereoregular
polyolefins: environmentally benign concept**

**Zpracování, struktura a vlastnosti kompozitů založených na
přírodních plnivech a stereoregulárních polyolefinů:
Ekologicky příznivé pojetí**

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RÉSUMÉ

Ce travail porte sur l'étude des composites à base de polypropylène et de farine de bois. Seuls des composites à base d'une matrice polypropylène et de fibres végétales ont été mis en œuvre sans aucun recours à quelque agent comptabilisant que ce soit. En premier lieu nous avons regardé l'influence de la viscosité initiale de la matrice polypropylène sur la processabilité des biocomposites en utilisant des polymères de grades variés. Puis nous avons étudié l'influence de la nature et de la concentration de la farine en utilisant des farines de pin (bois mou) et de chêne (bois dur). Enfin, une attention spécifique a été portée sur la possibilité de nucléation en phase Beta de la matrice polypropylène en présence de fibres végétales. Des polypropylènes β -nucléés ainsi que des farines ayant subies des extractions par des solvants de leurs composés volatils ont été utilisées. Les mélanges obtenus ont été testés au moyen de la viscoélasticité à l'état fondu pour mettre en évidence les effets d'interaction charges-matrices et par des mesures de diffraction aux rayons X ainsi que d'analyse thermique différentielle pour la caractérisation de leurs morphologies cristallines.

ABSTRACT

This doctoral thesis is focused on composites based on polypropylene and wood flour. Firstly, the experimental work deals with preparation of composites based on wood flour with various concentrations and isotactic polypropylene with various melt flow indexes. In terms of this study, one polypropylene, which can have also practical use, was chosen. Further, this polypropylene is investigated with various types and concentrations of wood flour. Also, the attention is devoted to the modification of polypropylene by a specific β -nucleating agent. The differences are compared and described between the composites with neat and nucleated polypropylene. Further, the work is focused on solvent extraction of wood flour. The effect of extraction and solvent of wood flour is also examined in composites with neat and nucleated polypropylene. On prepared composites, the rheological, structural and thermal properties are studied. These properties differ depending on specific type of wood flour, its concentration and specific type of polypropylene.

ABSTRAKT

Předložená doktorská práce je zaměřena na kompozity polypropylenu a dřevní moučky. V experimentální části práce jsou připraveny kompozity s různými koncentracemi plniva a izotaktických polypropylenů s různými indexy toku taveniny. Na základě této studie je vybrán jeden konkrétní polypropylen, který může mít v kombinaci s dřevní moučkou i praktické využití. Tento polypropylen je dále zkoumán s různými druhy a koncentracemi dřevní moučky. Pozornost je také kladena na úpravu vlastností izotaktického polypropylenu užitím specifického β -nukleačního činidla. Jsou porovnávány a popisovány rozdíly mezi kompozity s čistým a nukleovaným polypropylenem. Práce se dále zabývá extrakcí dřevní moučky v rozpouštědle. Je studován vliv extrakce a rozpouštědla dřevní moučky na vlastnosti připravených kompozitů. Byly studovány reologické, strukturální a tepelné vlastnosti, které se lišily v závislosti na zvoleném typu plniva, jeho koncentraci a typu polymerní matrice.

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1. INTRODUCTION

Today's world faces many environmental problems and two of them are plastic waste and excessive felling. The former is connected with tremendous production and use of plastics in practically all areas of everyday living, while the latter should be related to people's demand and desire to be surrounded by natural products, particularly wood. Wood then found use not only in furniture, but also in building industry. [1, 2]

Combination of these materials – synthetic polymer, plastic, and wood, can not only reduce mentioned problems, but also bring another advantages such as low specific weight, higher specific strength or stiffness, when compared to glass reinforced composites. From this point of view, the wood fibers provide safer handling and working conditions and also less abrasive properties to mixing and molding equipment. Still the most interesting aspect about natural fillers is their potentially positive environmental impact. Wood flour is original to plants, such as other cellulose materials, it is thus included in renewable resources which production require minimum of energy. Moreover, they are carbon-dioxide neutral, which means, their contribution to CO₂ concentration in atmosphere after combustion equals to the CO₂ consumption during the wood growth. [3, 4]

In last two decades, the wood-plastic composites (WPC) gained attention of both – scientific centers and industry. Production of WPC has grown significantly. Potential applications are then found primarily in composites for use in automotive, building industry as well as furniture and household equipment industry. [5] However, the limitation is usually low interaction between the filler and matrix. Wood flour (WF) is cellulose, which bears hydroxyl groups, so its surface is hydrophilic, while most of the commodity plastics are hydrophobic, particularly polyolefins. This problem could be handled for example by use of coupling agents or chemical modification of the WF or matrix, but also by effective filling and mixing, which optimizes properties of the composite. [4, 6, 7]

Quality of the composite material depends strongly also on the origin of the wood, which may have different composition and structure of the cellulose fibers. [8] Purity of the material in connection with relatively large amount of possible accompanying substances is even more crucial. [9, 10] In present study, two materials are used – pine and oak, as representatives of softwood and hardwood, respectively. These materials are investigated, after compounding with polymeric matrices, by means of rheology, X-ray structural analysis and differential scanning calorimetry (DSC). To check possible influence of extractible wood-accompanying low-molecular substances, cyclic washing with ethanol or cyclohexane in Soxhlet apparatus was used to purify the filler.

Isotactic polypropylene (iPP) is used in the present study since it is one of extensively used plastic, which found application in many areas of living

including those for which the WPC composites are currently designed – i.e. building, automotive industry etc. iPP is an interesting material from both the scientific and industrial point of view, which is caused by its polymorphism. The strength, toughness and thermal stability is usually connected with monoclinic α phase, while tenacity, drawability, but also decreased thermal stability is typical for trigonal β phase. [11–14] The latter form is usually achieved by introduction of nucleating agent to the material. [15] There were some studies showing practically no impact of cellulose on the crystallization process, particularly α crystallites formation. [16, 17] Concerning the ability of iPP to crystallize in different structures as well as the presence of nucleating substance, one can imagine that the wood may either support or suppress the β phase formation. Both X-ray structural study and DSC were performed with purpose to check possible influence on the amount and composition of the crystalline phase.

2. AIMS OF THE WORK

Several PP with different MFI were selected for the study. These materials were filled with various concentrations and types of WF. Prepared composites should show number of attractive properties, which can offer wide range of applications. A fundamental presumption for use of composites is a need to understand interrelations between processing, structure, and properties.

Thus, the main goal of the study is experimental determination of the interrelations between processing, structure and properties of composites based on PP and WF.

These factors are studied by various experimental devices and methods such as oscillatory rheometry, wide-angle X-ray scattering (WAXS), and DSC.

Subsequently, the main attention in this work is dedicated to following points:

- to prepare PP/WF composites with various concentrations of filler in PP with various MFI,
- to compare the properties of composites with different types of wood,
- to evaluate the influence of various concentrations of wood and various MFI on structural, thermal and processing properties of final composites and increase an amount of renewable carbon.

3. STATE OF THE ART

3.1 Introduction to Wood-Plastic Composites

Composites are complex materials made from two or more distinct components which once they are combined, produce a structural and a functional new material [18].

Eco-friendly composites are made from natural renewable resources and synthetic polymer matrix. Wood flour (WF) can be considered as an example of natural filler and in combination with a wide variety of polymeric matrices, including polypropylene (PP), can be obtained wood-plastic composites (WPC).

3.1.1 Properties of Wood-Plastic Composites

The WPC are widely used modern materials, due to their environmentally friendly basis. Wood in the WPC represents the natural filler which is both renewable and biodegradable. The mentioned properties of WPC can be influenced by many factors such as concentration of fillers, size and distribution of filler particles, modification of filler or polymer matrix, processing conditions and parameters, all of these have a big impact on the properties of the WPC. Nevertheless, the WPC have some disadvantages. They are highly sensitive to humidity and have tendency to swell. They are also easily attacked by mildew which leads to lose their mechanical properties. [4, 6]

Mechanical Properties

Content of WF in WPC has significant impact on the mechanical properties. Bouafif et al. [8] found that the best mechanical properties were obtained with composites with a high WF content. Mechanical properties, namely tensile modulus of elasticity and maximum tensile strength, increase with the average particle size. This behavior is shown in the Fig 3.1 (65 mesh \approx 230 μ m, 24 mesh \approx 710 μ m). [8]

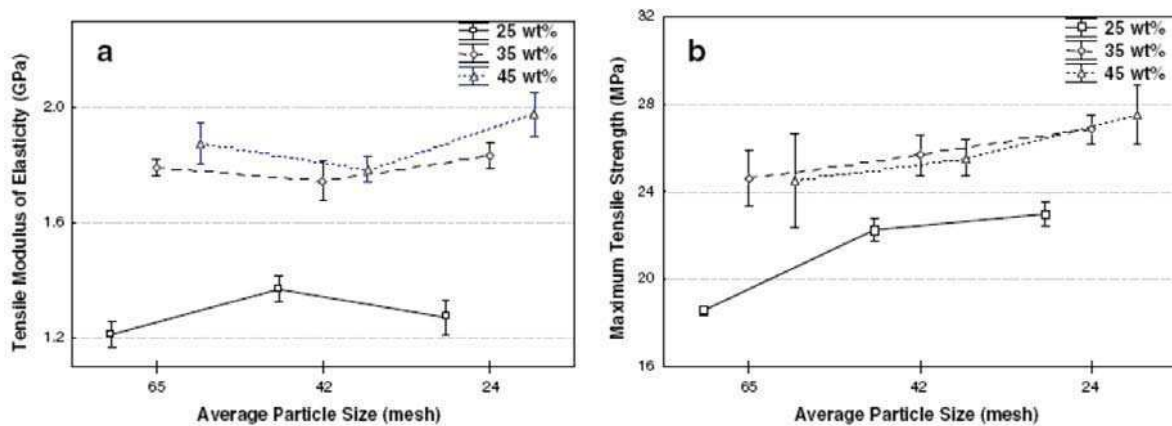


Fig. 3.1: Effect of wood particle size with various filler content on tensile modulus (a) and maximum tensile strength (b) [8]

Bledzki et al. [4] studied the effect of compounding method on mechanical properties. They investigated, that addition of maleic anhydride (MA) to PP/WF composites during compounding process improves the tensile modulus and strength while the flexural modulus and strength of composites is not changed. Composites were compounded with twin-screw extruder, two-roll mill and agglomerator. Composites with maleated PP prepared on twin-screw extruder showed better mechanical properties thanks to both better dispersion of WF in PP matrix and better adhesion between matrix and filler. [4] This finding was confirmed by Yang et al. [19] who published, that the composites prepared on twin screw extruder have better tensile properties. Ashori and Nourbakhsh [20] studied tensile strength and modulus of composites as a function of maleated polypropylene (MAPP) and fiber content. They found, that composites with MAPP exhibit improved strength since the interaction of MAPP-filler causes strong interfacial bonding. They also found, that the tensile strength and modulus decrease with higher WF content. This was explained by poor adhesion between filler and matrix and by the fact, that higher concentrations need more coupling agents. [20]

Water Absorption

The ability of wood to absorb water may cause problems in certain applications. Chemical modification of wood can decrease significantly the water absorption (WA) which was studied by Dányádi et al. [21]. Izacho et al. [22] focused on the influence of WF content on the WA. They discovered that WA increases with increasing concentration of WF in composites. This increase is logically explained by hydrophilic character of wood. Mainly the concentration of particles and their chemical modification have an influence on WA on the other hand the size of the particles does not influence WA essentially. When the amount of WF was increased, the polar character was higher and hence the WA increased. [22]

3.1.2 Processing of Wood-Plastic Composites

The WPC are commonly produced by mixing of polymer matrix and wood as filler. Some additives (colorants, stabilizers, blowing and coupling agents) can be incorporated to the composite [23]. Modification of the wood can help to obtain required properties of the WPC, as well as the modification of polymer matrix can. The most often method of matrix modification in case of PP is grafting it with MA or acrylic acid [24, 25].

The most used methods of goods and semi-finished goods production are extrusion and injection molding. However, thermoforming can also be used for processing of the WPC [26]. Extrusion is a method which is used for production of profiles, such as decks and handrails. On the other hand, goods with more complicated shape can be made by injection molding. Extrusion as well as

injection molding includes the same processing steps: compounding, melting, shaping and cooling. During these various methods of manufacturing processing factors have to be kept strictly.

Two types of extrusion can be employed for production of the WPC. Single screw extruder and twin co-rotating screw are usually used. The single screw extruder does not have a mixing part and can only feed the melted mixture to the die, thus the pre-blending is required before extrusion. On the other hand, the twin screw extruder provides feeding and mixing together. In this system, the screw has a multiplex shape and therefore the fillers and polymer matrix are blended very well. [19]

3.1.3 Application of Wood-Plastic Composites

The WPC was proposed as good candidate for many applications in various industry sectors as shown in Fig. 3.2. In the year 2008, the automotive industry made use of a significant percentage of the WPC substituting glass fiber with plant fiber. [23] Mechanical strength, lower production cost, passenger safety and shatterproof performance under extreme temperature changes are provided by the WPC for the interior parts in automotive industry. [23]

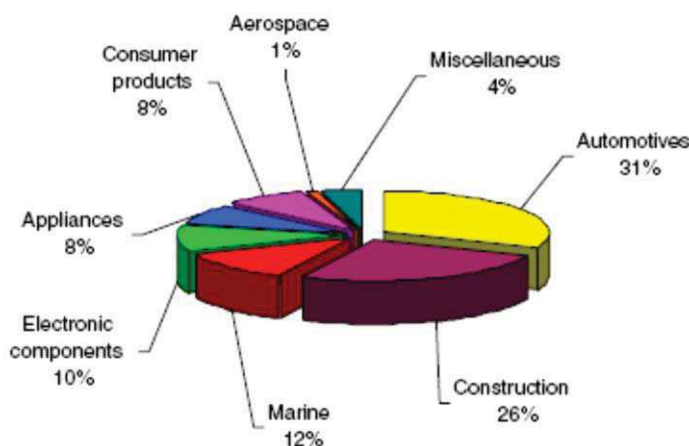


Fig. 3.2: Wood-plastic composites used worldwide in 2002 [23]

The second biggest sector regarding the use of the WPC is building industry. For example, in the United States softwoods and hardwoods are widely used for various applications. The WPC with softwood (in the form of lumbers or plywood) are applied in constructions for decking, forms, scaffolding, framing, sheathing, flooring, molding, paneling, cabinets, poles and piles, and many other building components. Hardwoods are used in the WPC for constructions of architectural woodwork, interior woodwork (flooring, furniture), and paneling. [27] Applications of WPC are as well actual in Asia, Australia, and Europe. In Germany the main areas for the application of WPC are in the automotive

industry for car interiors and also in decking (floor coverings, used mainly in outdoor areas, such as terraces and public places) [28].

The impressive growth of WPC leading up to 2010, had been followed by stagnation in 2011 to 2012, but growth is now expected to resume, North America has been the biggest inventor and producer of WPC in the world. Still Europe lags far behind North America where usage is around twice as high. However, in Europe decking continues to be the dominant application for WPC. [29]

In 2012, more than 1.5 million tons of WPC were produced worldwide, especially in North America (about 1 million tons), China (200,000 tons) and Japan (100,000 tons). Germany was the European leader with more than 70,000 tons. Nowadays, the road furniture has been studied by Muszynski who examines the possible replacement of currently used materials in many of highway applications of WPC. These street furniture products are manufactured in Australia and rarely in Europe and Asia [28-30].

3.2 Wood

Wood is a stiff tissue of coniferous and broadleaved species which is grouped among the renewable resources. It has been used since ancient times with outstanding availability. Wood can be recycled and when it reaches the end of its life it can be disposed of with minimal impact to the environment.

3.2.1 Chemical Structure of Wood

From the chemical point of view, wood is composed from 49.5 wt. % of carbon, 44.2 wt. % of oxygen, and 6.3 wt. % of hydrogen. Wood is composed primarily of organic compounds such as macromolecular components (90–98 %) which form a structure of cell wall: cellulose, hemicellulose, and lignin. [27, 31] The typical composition of wood is in Tab. 3.1.

Tab. 3.1: Typical chemical compositions of wood [31, 32]

Main components 90–98 %	Polysaccharides 70 %	Cellulose	
		Hemicellulose	
Aromatic parts 25 %	Lignin		
	Polymers		
Minor components 2–10 %	Organic	Low-molecular substances	
		Anorganic	Salts Ca, K, Mg, Na, Mn

Cellulose

Cellulose (Fig. 3.3), which is the main component of wood, is a linear homopolymer which consists of repeating β -D-glucopyranose units. These units are bonded by 1,4-glycosidic bonds. Each of the unit contains three hydroxyl groups, which play an important role in physical properties of cellulose. The length of the cellulosic chain varies considerably. The average polymeric degree of cellulose is between 8 000 and 10 000. [3, 31, 33, 34]

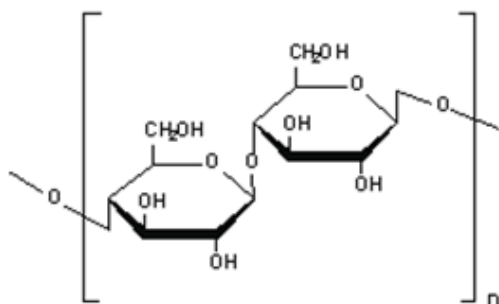


Fig. 3.3: Structure of cellulose monomer [32]

Cellulosic fibers could be used, for example, in the paper making industry. One of the most important characteristic is their natural origin. The reason of the growing interest in these fibers is that they are non-polluting, safe to use, and energy efficient. [33, 35]

Hemicellulose

Hemicellulose is a linear polysaccharide with short side chains (Fig. 3.4) and has lower molecular weight than cellulose. The average degree of polymerization of hemicelluloses is approximately 150. Hemicellulose is less chemical resistant and easily hydrolyzed. [3, 31]

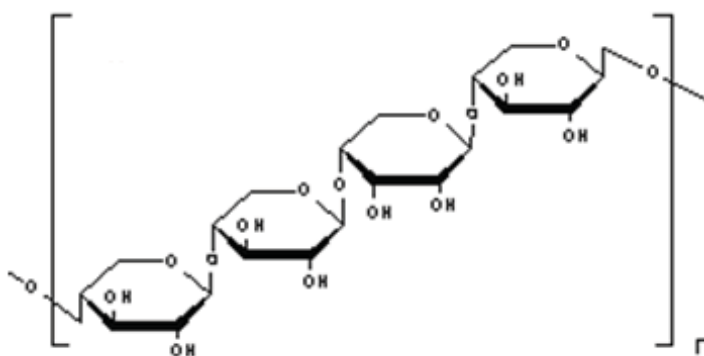


Fig. 3.4: Structure of hemicellulose [32]

Lignin

Lignin is an amorphous polymer, which has a three-dimensional structure (Fig. 3.5). This structure consists of phenylpropane units, which are variously substituted mainly with hydroxyl and methoxyl groups on the benzene ring of side chains. [31] One of the characteristics of lignin is a strong absorption of ultraviolet light. Therefore, radical-induced depolymerization of both lignin and cellulose can occur. [36]

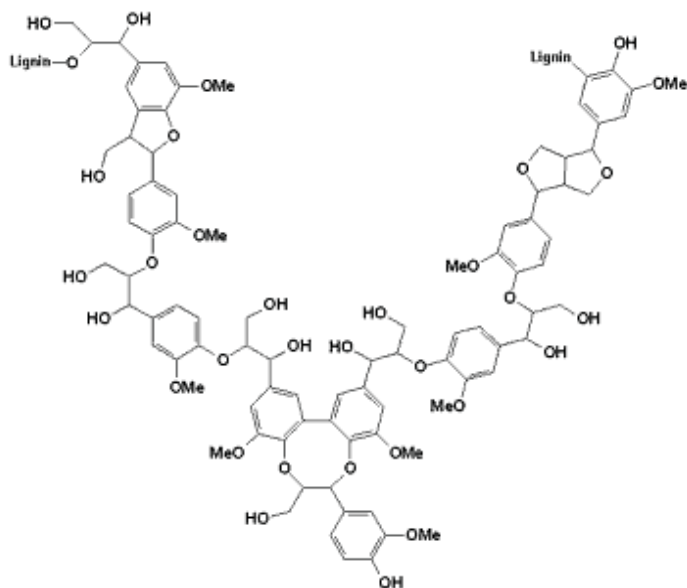


Fig. 3.5: Structure of lignin [37]

3.2.2 Properties of Wood

Differences in the characteristic compositions of wood make material with various properties. It can be heavy or light, stiff or flexible. Particular pieces have essentially the same properties as the whole wood. However, an attention on selection of wood with respect to applications must be paid. [27]

Wood can differ in many properties accordingly to the age of tree, portion, mechanical properties and others. In literature earlywood and latewood, sapwood and heartwood, softwood and hardwood are recognized. Hardness is from practical point of view the most important criterion for selection the right wood for the final product. [38, 39] Wood is classified as hardwood or softwood accordingly to their mechanical properties, but not all softwoods have soft and lightweight wood, nor do all hardwoods have hard, heavy wood. Botanically these woods can be defined by name of their origin. Softwood comes from gymnosperms, which usually are conifers, whereas hardwood comes from angiosperms, so called flowering plants. [27, 39] Softwood is non-porous,

whereas hardwood is porous material, which consists of vessel elements. These two different kinds of wood differ in their anatomy. Vessel elements have open ends of cell and thus can transport water or sap in the tree. Hardwood is oak, maple, ash, elm, chestnut, locust, hickory, poplar, alder etc. and softwood is pine, fir, spruce, cedar, larch etc. [27, 39] The main properties, which limit the use of wood in some application, are density, porosity, and moisture content. Density of wood varies around 1.5 g/cm³, depending on the wood species. Wood with thin walls and small lumen volumes has high density whereas thin walls with large lumen volumes are ascribed to wood with low density. The magnitude which is related with density is strength. Cells with thick wall endure greater stress than cells with thin wall. These cells serve as interphasing region and it is necessary to ensure strong adhesive bond as strong as the wood. [40]

The porosity of wood system influences a direction of adhesive flow and amount. Softwood does not have pores; there are pits between fibers that let and keep lateral transfer of fluids in tree, this makes complex capillary system in tree. In the capillary system it is easy to deeply penetrate adhesives. On the other hand, because of the large vessel with no end walls in hardwood, it is not possible to penetrate deeply to the grain. In hardwood, few pits for lateral transfer of adhesive can be found. [40]

Large quantity of water is contained in a tree. The residual moisture content in wood is influenced by relative humidity of the surrounding air. Water is removed by drying. Quality of wood is anisotropic, which means that its properties vary according to direction in which they are measured. Both mentioned phenomenon must be taken into account when measuring and assessing its mechanical, thermal and other properties. [41, 42]

3.2.3 Modification of Wood

It is well known, that polymers especially non-polar have hydrophobic character, whereas bio-based fillers are usually hydrophilic. Because of these opposite characters, it is uneasy to get composite with good compatibility. Modification of wood seems to be a possible method to obtain a good interfacial connection of the polymer matrix and the filler. The incorporation of coupling agents or compatibilizers can also create a good connection between wood fibers, flours, or ligno-cellulosic materials with the non-polar used polymer matrix. [40–45]

Chemical Modification

The properties of wood are determined by cell wall components. Chemical modification of cell wall can influence basic properties of wood. Modifiers or coupling agents are chosen on the basis of final required properties. Usually the main aim of this modification is to get a good interfacial linkage (Fig. 3.6), an improved adhesion between the polymer matrix and the filler (decrease of wood

hydrophilicity), and thereby certain mechanical and physical properties, fire retardancy, and weathering resistance [4, 21, 22, 44–46].

The most applied coupling agents are anhydrides such as phthalic, succinic, maleic, propionic, and butyric; acid chlorides; ketene carboxylic acids; many different types of isocyanates; formaldehyde; acetaldehyde; difunctional aldehydes; epoxides, such as ethylene, propylene, and butylene oxide; and difunctional epoxides etc. [5, 22, 47–49].

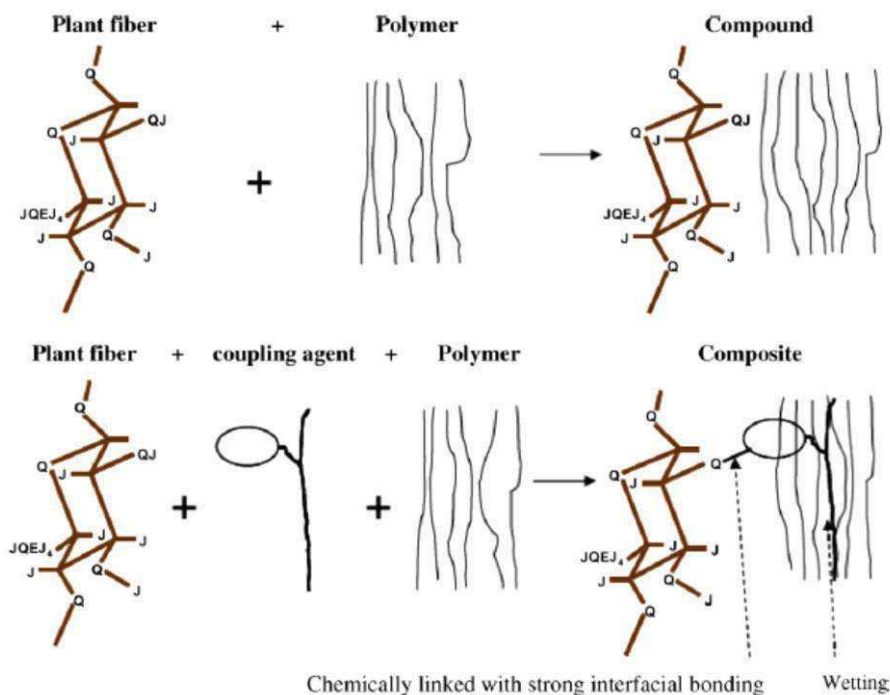


Fig. 3.6: Mechanism of coupling agent activity between hydrophilic fiber and hydrophobic polymer matrix [23]

Physical Modification

Physical modification consists in the removal of water from wood by heating in dry air. This process can take several hours and it is necessary to decrease water content under 3 %. Thermal treatment of wood changes chemical and physical properties and also its structure, which is caused primarily by degradation of hemicellulose. The changes are as high as the temperature is increased [50].

3.2.4 Different Particles of Wood for WPC

Different types (shapes) of filler particles are used for WPC production. The choice of wood source depends on desired properties of final products. Wood particles differ in size, shape and hence influence the properties of composites. Different kinds of wood elements are showed in Fig. 3.7.

Cellulose fibers are used in composites because of good reinforcement. Sometimes white color of fibers could be an advantage for special applications.

However, WF is used as reinforcement rather than separated wood fibers. Isolation process of wood fibers is more expensive than get WF. [51]



Fig. 3.7: Basic wood elements (largest → smallest) [52]

3.3 Polypropylene

Polypropylene (PP) is a linear polymer consisting of only two elements – carbon and hydrogen; and together with polyethylene or poly(1-butene) it is a part of the polyolefins or saturated polymers. The PP possesses an excellent resistance to organic solvents. PP generally has higher tensile, flexural, and compressive strength and higher moduli than PE. This is due to the steric interaction of the pendant methyl groups, which can result in a more rigid and stiff polymer chain than in PE. [53]

3.3.1 Synthesis

In 1869, the French chemist Marcellin Pierre Berthelot performed the first experiment of PP polymerization with sulfuric acid. The result of this experiment was viscous oil, however did not find utilization in industry. The next important step in evolution of PP was the year 1954, when Giulio Natta used organometallic catalyst based on titanium and aluminum to produce semi-crystalline polymer [54]. Further development of catalysts for PP polymerization (in the 1950's) made the production of stereospecific PP easier and led to the growing annual production that remains until today. [53]

Catalysts are substances that decrease activation energy of particular reaction and make reaction possible to run under given conditions, whilst their composition remains untouched. [53] Ziegler-Natta or metallocene catalysts are used for preparation of PP. Ziegler-Natta catalysts are the most common commercial catalysts. Karl Ziegler and Giulio Natta received the Nobel Prize in 1963 for the development of polyolefin polymerization catalysts with high yield and high degree of stereospecificity. Metallocene catalysts have recently been developed for industrial use, and metallocene-produced PP is now available. [53]

3.3.2 Structure of Polypropylene

The polymerization reaction is highly stereospecific. Propylene molecules are connected to the main polymer chain, increasing the chain length, and not to one of the methyl groups attached to alternating carbon atoms (the pendant methyl groups), which would result in branching [53]. Polymerization of the non-symmetrical propylene molecules can lead to three possible sequences (Fig. 3.8): head-to-tail, tail-to-tail or head-to-head [53, 54].

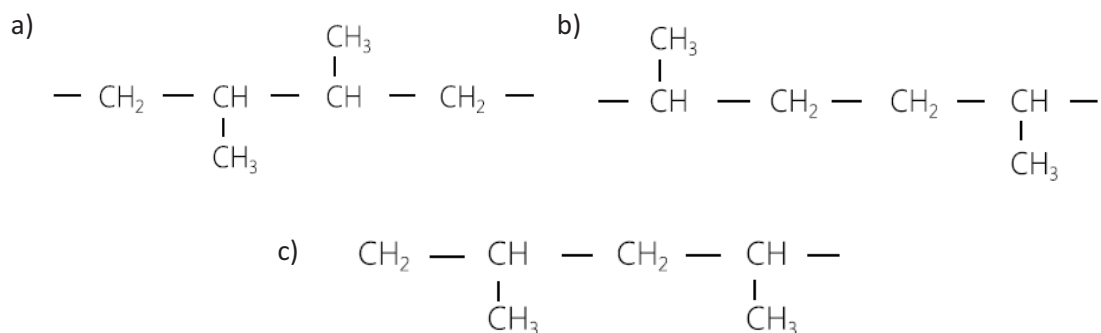
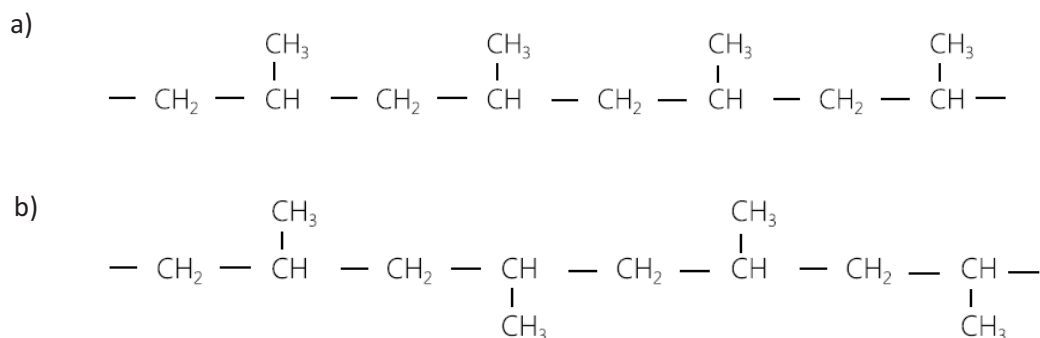


Fig. 3.8: The orientation of the pendant methyl groups in PP: a) tail-to-tail, b) head-to-head, c) head-to-tail [55]

Head-to-tail addition results in a PP chain with pendant methyl groups attached to alternating carbons; in tail-to-tail or head-to-head addition, this alternating arrangement is disrupted. Occasional tail-to-tail or head-to-tail additions of PP to the growing polymer chain disrupt the crystalline structure and lower the melting point of the polymer; formulations in which this occurs are used in thermoforming or blow molding. [53]

Three different configurations of PP can be obtained by polymerization of non-symmetric molecule. PP can be isotactic, syndiotactic, or atactic (Fig. 3.9), depending on the orientation of the pendant methyl groups attached to alternate carbon atoms. [53, 55, 56]



c)

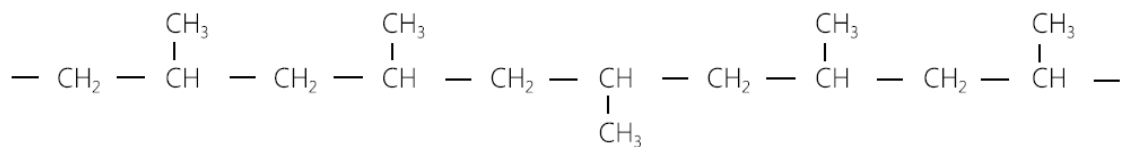


Fig. 3.9: Stereochemical configurations of PP: a) isotactic, b) syndiotactic, c) atactic (random) [53]

The structure and stereochemistry of PP affect its properties, because each of this structure is a part of new produced PP and their relative ratio influences the condition of polymerization. From the practical point of view, it is important to get the highest ratio of isotactic PP (higher than 90 %) and equally the lowest ratio of atactic PP, since this is source of decrease in mechanical properties. [53]

The most common commercial form of PP is isotactic polypropylene (iPP) in which all pendant methyl groups are in the same configuration and on the same side of the polymer chain. Due to this regular arrangement, iPP achieves high degree of crystallinity. [53, 56]

The syndiotactic PP consist of mers with alternating pendant methyl groups on opposite sides of the polymer backbone, with exactly opposite configurations relative to the polymer chain [53, 56]. In atactic PP, opposite methyl groups have a random orientation with respect to the polymer backbone.

Amounts of isotactic, atactic, and syndiotactic parts are determined by the catalyst used and the polymerization conditions. PP is predominantly isotactic, they however have small amount of atactic polymer. New metallocene catalysts allow other stereochemical configurations, such as hemi-isotactic PP. In this configuration, opposite methyl groups are on the same side of the PP chain, as in iPP; however, other methyl groups are inserted at regular intervals on the pendant side of the chain. [53, 56]

3.3.3 Isotactic Polypropylene

iPP usually achieves high crystallinity, leading to good mechanical properties, especially stiffness and tensile strength [53]. The conformation of chain of iPP is a helix, which has three units and can be right-handed or left-handed with period of 0.65 nm. As written above, methyl groups are always on the same side along the axis of the main chain and this configuration is caused of four different insertions of helix in iPP (these are related to axis) in crystalline state. [53, 56, 57] The crystal lattice of iPP is shown in Fig. 3.10.

iPP is polymorphic material which crystallizes into several crystallographic forms. These differ in crystallographic lattice: α form is monoclinic, β form is trigonal and triclinic γ form, the last crystallographic modification is so-called mesomorphic (smectic) form, which consist of rather small irregular crystallites. The occurrence of particular forms depends on tacticity and conditions given during crystallization such as temperature, pressure and rate of cooling. [56–58]

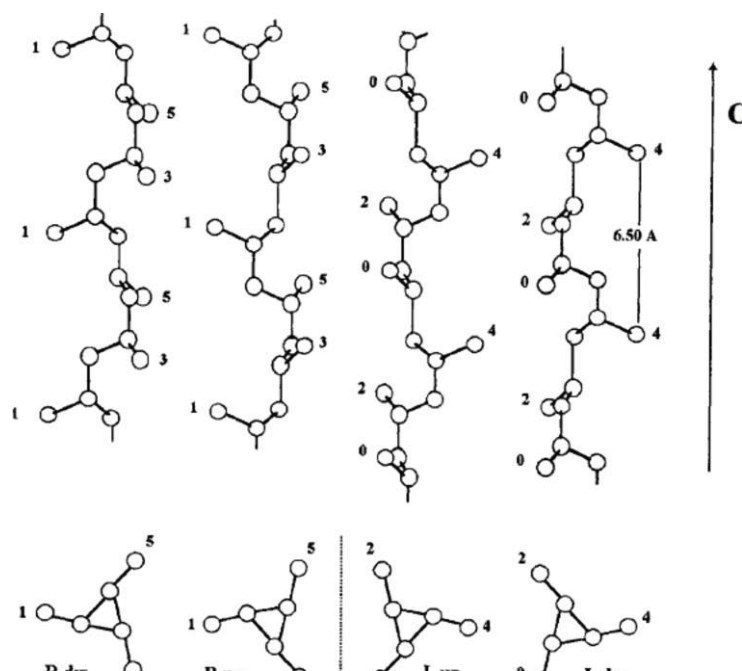


Fig. 3.10: *iPP* chain in the crystal lattice – the four possible insertions [57]

α form

α form is the predominant structure of *iPP* and the most important modification for practical purposes [57, 59]. The α form in *iPP* (α -*iPP*) is characterized by thermodynamic stability and has good mechanical and other working characteristics. The α form is obtained from the melt cooling or solution crystallization at the atmospheric or slightly increased pressure [59].

This crystallographic modification consists of four helices, which create monoclinic lattice with dimensions: $a = 0.666 \text{ nm}$, $b = 2.078 \text{ nm}$, $c = 0.6495 \text{ nm}$ and angles $\alpha = \gamma = 90^\circ$, $\beta = 99.62^\circ$. The density of α form is 0.946 g.cm^{-3} [56, 57, 60].