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IMPROVEMENTS IN WOOD THERMOPLASTIC MATRIX COMPOSITE MATERIALS PROPERTIES BY PHYSICAL AND CHEMICAL TREATMENTS

Abstract: *This paper presents a short overview of the developments made in the field of wood thermoplastic composites in terms of surface treatment, flammability, matrix/reinforcement model, properties and application of recycled polymer matrices. The usage of lignocellulosic fibers as reinforcement in composite materials demands well formed interface between the fiber and the matrix. Because of the different nature of reinforcement and matrix components some physical and chemical treatment methods which improve the fiber matrix adhesion were introduced, as well as the improvements of lignocellulosic fibers and thermoplastic polymer matrix based composites flammability characteristics. These physical and chemical treatments influence the hydrophilic character of the lignocellulosic fibers, and therefore change their physical and mechanical properties.*

Keywords: *bio-composites, wood thermoplastic composites, recycled polymer matrices*

1. Introduction

Wood, as a natural polymer matrix composite, is the oldest material of this type. Constitutive components of wood are lignin with hemicelluloses as a soft polymer matrix, and rigid cellulosic microfibrils as reinforcement, so called lignocellulosic fibers (Rong *et al*., 2011). The properties of wood reinforcing fibers depends on the type of plants, as well as the parts of a plant, because each vegetal creation has its own crystalline organization (Bledzki and Gassan, 1999). The application of lignocellulosic fibers as a reinforcement in polymer matrix composites has received increased attention. From the all lignocellulosic fibres, wood fiber is the most broadly used as composite materials reinforcement. Generally known lignocellulosic composites are laminated lumber, plywood, fiberboard, particleboard and wood plastic composite materials (WPCs) (Rowell, 1990). A large amount of wood waste in different form such as wood pulp, fibers or flour has been generated in wood industry. This wood waste forms are very suitable as a reinforcement for thermoplastic polymer matrices (Woodhams *et al*., 1984). On the other hand, incompatibility between non-polar hydrophobic thermoplastic matrices and polar hydrophilic wood reinforcement creates problems during the production of composites and results with their law mechanical properties (Yeh and Gupta,

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2008). Due to poor adhesion between the polar wood and the non-polar polymer, increasing amount of wood reinforcement causes reduction in composite strength (Klyosov, 2007). In order to overcome this problem, a lot of research has been done (Bledzki and Gassan, 1999; Satyanarayana *et al*., 2009; Adekomaya *et al*., 2016). Exposure to UV radiation and humidity also cause the reduction of WPC mechanical properties due to reduced fiber/matrix adhesion properties, lignin degradation and polymer chain scission, so changes occurring during accelerated weathering also were researched (Beg and Pickering, 2008; Stark and Matuana, 2003; Matuana and Kamdem, 2002; Matuana *et al*., 2001). As a matrix materials in WPC virgin but also recycled polymers have been used (Yeh *et al*., 2009; Adhikary *et al*., 2008; Augier *et al*., 2007). The most used thermoplastic polymers as a matrix in wood plastic composite materials are polyethylene, polypropylene, poly vinyl chloride, polystyrene and acrylonitrile-butadiene-styrene (Bledzki and Gassan, 1999; Yeh *et al*., 2009).

Because of superior strength/weight and stiffness/weight ratios of WPCs, their use in automotive industries is increasing. Automotive components, such as dashboards, door panels, seats, and cabin linings were made from WPCs (Ashori, 2008). Currently, aspirations of using WPCs for car parts includes replacements glass fiber reinforced composites and steels (Bismarck *et al.*, 2006).

2. Surface treatment

The surface structure and energy of the wood reinforcement can be changed by using different methods of physical and chemical surface treatment. These changes influence the mechanical bondings fiber/matrix, leading to different interface in composite material and different mechanical properties. The cellulose fibers treatment with oxygen plasma increased the free surface energy with increasing treatment time or level of corona treatment, which leads to an improved wettability of composite materials (Belgacem *et al*., 1994; Sakata *et al*., 1993). Physical treatments also include thermotreatment, stretching and calandering processes. Chemical modification includes delignification pretreatment, fiber surface modification and coupling agents' application (Bledzki and Gassan, 1999).

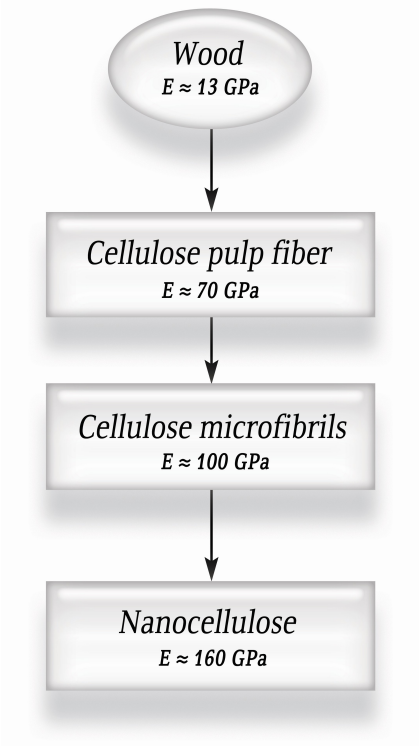

Figure 1. Levels of wood structure

Due to complex wood composition, modifications can be applied on the each level of structure observation, Figure 1.

2.1. Delignification

Removal of lignin from wood fibers increases fiber/matrix adhesion due to better physical bonding between cellulose fiber and thermoplastic matrix, as it has been shown in Figure 2 (Mai *et al*., 1983; Beg and Pickering, 2008).

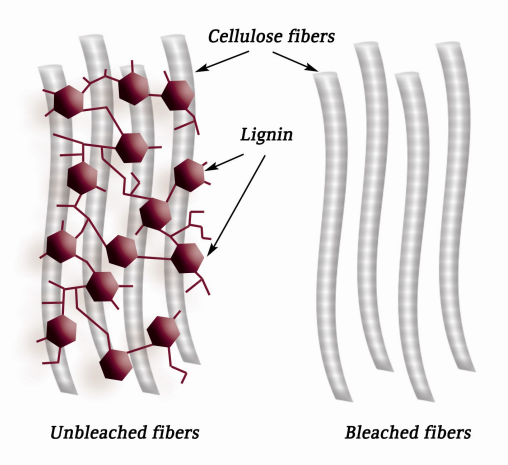

Figure 2. Schematic representation of the removal of lignin from wood fibers

Lignin and hemicelluloses are the most responsible component for ultraviolet degradation of wood (Nevell and Zeronian, 1985). Beg and Pickering (2008), investigated moisture/ultraviolet (UV) weathering performance of unbleached and bleached 40 wt% wood fiber reinforced polypropylene (PP) composites, with 3 wt% of a maleated polypropylene (MAPP) coupling agent. Initially, bleached fiber composites showed better mechanical properties, but after accelerated weathering, extent of the mechanical properties reduction was almost the same for both bleached and unbleached wood fiber composites. The changes occurred during accelerated weathering were registrated with differential X-ray diffraction, thermogravimetric analysis, scanning calorimetry and scanning electron microscopy. For long-term application of PP composites authors recommended usage of PP UV stabilizer.

2.2. Coupling agents and fiber surface modification

Interfacial adhesion in WPC can be improved by the chemical modification with the introduction of a coupling agent. Often this coupling agent is a functionalized polymer. As functionalized polyolefin composite matrix for improving interfacial adhesion, prevent debonding and the formation of voids into the composite materials, maleated polypropylene (MAPP) or polyethylene (MAPE) has been used (Keener *et al*., 2004; Li and Matuana, 2003; Myers *et al*., 1990; Kazayawoko *et al*., 1999; Qiu *et al*., 2003; Kazayawoko *et al*., 1997; Ndiaye *et al*., 2011; Hristov *et al*., 2004; Lu *et al*., 2005; Bledzki *et al*., 2002; Beg and Pickering, 2008). The surface of wood reinforcement contains the–OH groups which form chemical bond with maleic anhydride groups. Result of this formation is improved interfacial bonding. Schematic representation of the modification of interface by maleated polypropylene in wood/PP composite material is shown in Figure 3. For modification of wood reinforcement the other anhydrides, such as succinic or phthalic, also were used (Matsuda, 1987; Zhang *et al*., 1994; Gellerstedt and Gatenholm, 1999; Kokta *et al*., 1990), but maleic shows the best improvement in mechanical properties.

Beside anhydrides, in order to enhance interfacial adhesion in wood composites, poly[methylene(polyphenyl isocyanate)] (Maldas *et al*., 1989), copper amine (Jiang *et al*., 2003; Kamdem *et al*., 2004), chromated copper arsenate (Stilwell *et al*., 2003) and silane (Kokta *et al*., 1990; Bengtsson and Oksman, 2006), were also used as chemical coupling agents.

Improved flammability of WPC materials is of the great importance for thermal insulators and automotive constitutive elements (Ashori, 2008). Commonly the composites based on polypropylene matrix and wood fiber reinforcement were used for this purposes and many studies of flammability of iPP composites with various content of long cellulose fibers was conducted (Borysiak *et al*., 2006; Helwig and Paukszta, 2000; Lv *et al*., 2005; Bras *et al*., 2005). There are two methods for improvements of WPC flammability with retardant agents: during the manufacturing process and during the finishing process

(Kim and Pal, 2010; Kozlowski and Helwig, 1998). Typically additive flame retardants are minerals (aluminum hydroxide, magnesium hydroxide, red phosphorus or borates), but modification of organohalogens and organophosphorus compounds also results of significant improving in flammability (Sain *et al*., 2004; Kozlowski and Wladyka-Przybylak, 2000; Anna *et al*., 2003). Baysal *et al*. (2007) used boric acid and borax mixture for impregnation of pine wood reinforcement/vinyl copolymers. Tests show improvements in antiswelling efficiency, reduced water absorption, modulus of elasticity, resistance against decay caused by fungi and decrease in flammability.

Dányádi *et al*. (2010), researched influence of surface modification on interfacial interactions in PP/wood composites by addition of a MAPP, benzylation as chemical modification of the wood surface and application of surfactants. The addition of a maleated polymer improve interfacial adhesion of PP/wood composites, but does not influence homogeneity, viscosity and water absorption regardless of coupling agent amount. Homogeneity was improved by surfactants, and water absorption decreasing was obtained by chemical modification of wood by benzylation.

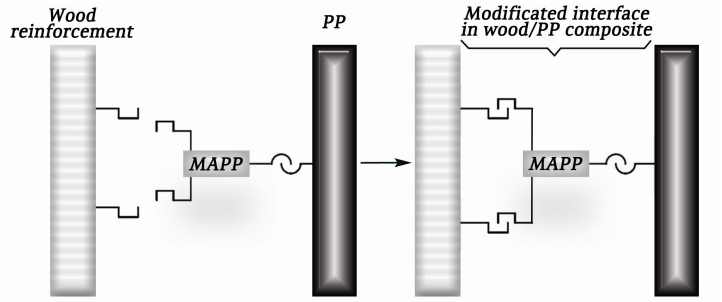

Figure 3. Schematic representation of the interface modification in wood/PP composite material with functionalized polymer coupling agents (MAPP)

Previous research of Dányádi *et al*. (2007) reported influence of MAPP different molecular weights and functionality on interfacial adhesion of PP/wood composites with wood content from 0 to 70 wt%. They proved that MAPP with the larger molecular weight and smaller functionality provide better improvement of composite strength. On the other hand, MAPP with the smaller molecular weight reduces viscosity and improves processability of WPC. The upgrading of WPC processability is of the great importance because of increased production of different components for the civil and automotive industry, packaging or furniture (Bledzki and Gassan, 1999; Adekomaya *et al*., 2016; Bledzki *et al*., 2005; Jacob, 2006; Bledzki *et al*., 2006).

Resent research (Xu *et al*., 2014) includes application of chitosan as a coupling agent in wood/PVC composites. Beside its biological activities, Chitosan owns excellent mechanical, thermal and anti-bacterial properties (Amri *et al*., 2013; Lu *et al*., 2010; Martinez-Camacho *et al*., 2010; Cheung *et al*., 2007; Vasile *et al*., 2013). It has similar function as the chemical coupling agents with amino-groups because of consisting amino-polysaccharide, Figure 4. The big advantages of chitosan are low price and environmentally friendly characteristics which makes it suitable for the production of biocomposite materials.

Xu *et al*, (2014) investigated effects of chitosan on interfacial adhesion and on the thermal and rheological properties of wood flour/polyvinyl chloride composites. They reveal optimal amount and particle size of

chitosan for better heat resistance capacity, glass transition temperature and thermal stability of analyzed wood composites. It was proved that low or high content of chitosan resulting in the low vicat softening temperature which value is the highest when the amount of chitosan achieves an optimal value of 30 phr. The vicat softening temperature of wood/PVC composites with chitosan as coupling agents were compared with the same composite with silane as a popular chemical coupling agent. The results proved the better heat resistance capability of wood/PVC composites with chitosan coupling agent. Xu *et al*. (2014) researched effects of particle sizes of chitosan and prove that smaller particle size provide the better interfacial compatibility.

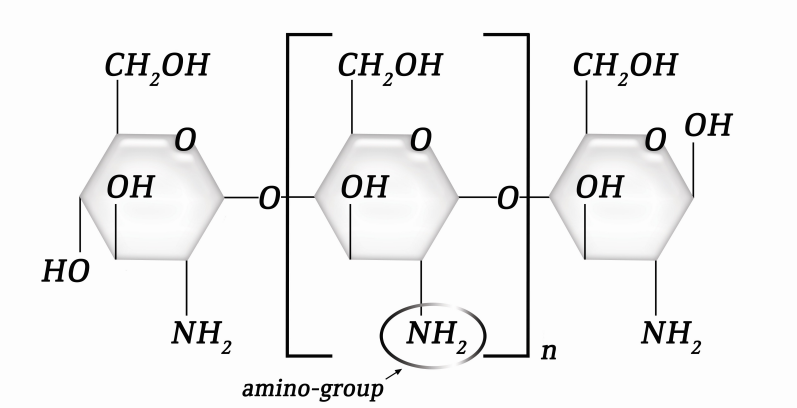

Figure 4. Chemical structure of chitosan

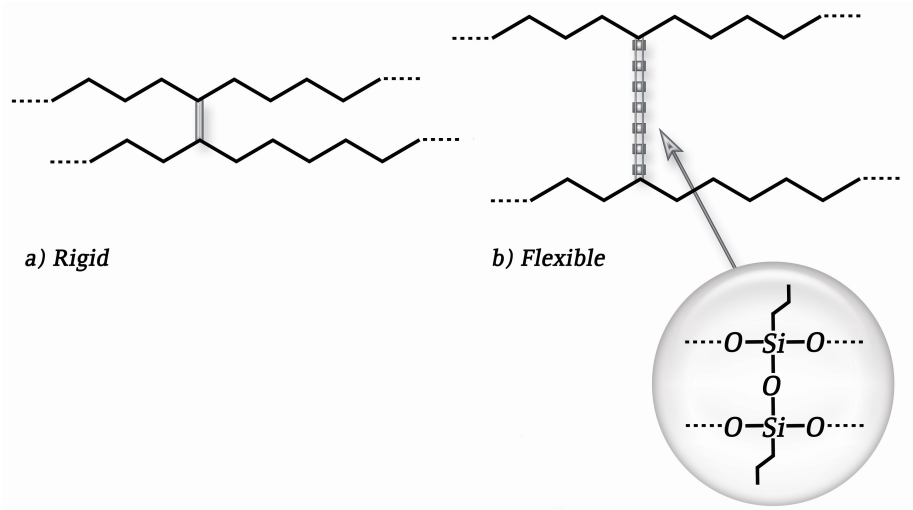

Figure 5. Chemical bonds in PE crosslinked a) by peroxide or radiation and b) by silane technology

Beside the most common used coupling agents functionalized polymers MAPP and MAPE, the silanes are also widely used (Oksman and Clemons, 1998; Kokta *et al*., 1989; Raj *et al*., 1989). Silanes are monomeric silicon compounds with four substituent groups attached to the silicon atom. These substituent groups can be very

different in composition and reactivity (nonreactive, inorganically or organically reactive). Vinyl silanes can be grafted onto the polyethylene chains giving crosslinked polyethylene. While the C-C bond obtained in PE crosslinked by peroxide or radiation is rigid, structure of PE crosslinked by silane technology contains flexible bonds, Figure 5. In this manner used polyethylene as matrix materials significantly improves creep properties of composite with wood reinforcement (Kokta *et al*., 1989; Kokta *et al*., 1989). Content of wood reinforcement in WPC with silane grafted HDPE matrix could be high up to the point when there are no free silanol groups which could further react with hydroxyl groups in cellulose fibers (Bengtsson *et al*., 2005; Park and Balatinecz, 1998). Bengtsson and Oksman (2006) investigated the use of silane technology in crosslinking PE/wood flour composites. Softwood from spruce and pine was used as wood reinforcement. The results show significantly higher flexural strength and elongation at break in the silane crosslinked composites compared with non-crosslinked ones. Improved adhesion between the wood reinforcement and crosslinked PE and strengthening of the matrix upon crosslinking cause toughness and impact strength improvements of the composite materials. Disadvantage of such prepared WPC is the lower flexural modulus in the crosslinked samples than in the noncrosslinked ones. The authors explain the lower flexural modulus as a consequence of a lower crystallinity in the crosslinked composites and plastification of non-reacted silane. The proved lower creep in the crosslinked composites was interpreted with reduced viscous flow due to crosslinking and increased adhesion between wood reinforcement and thermoplastic PE matrix.

In order to increase adhesion and interface properties of wood fibers and non-polar thermoplastics such as, HDPE, PP and PVC, a pretreatment of fibers was often applied. For this purpose a lot of methods and the different treatments have been researched (Shukla *et al*., 1993; Liao *et al*., 1997). The organic carboxylic acids (e.g. stearic acid, acetic anhydride) also have been applied for surface modification (Mahlberg *et al*., 2001; Zafeiropoulos *et al*., 2002).

Zheng *et al*. (2007) investigated the effect of benzoic acid surface modification on the mechanical properties of the PVC matrix composites reinforced with lignocellulosic fibers. They proved that treatment with benzoic acid provides 37% the better tensile strength of the composite compared to the tensile strength of untreated composite. The lignocellulosic fiber treatment with benzoic acid significantly improved dispersion of the fiber in PVC thermoplastic matrix which is supported by SEM micrographs of impact fracture testing composites materials.

An another example of dual modification in WPC has been given by Wang *et al*. (2015). They improved the interfacial adhesion through modifying both composite components, thermoplastic matrix (PP) and bamboo wood fiber. In order to establish strong interfacial interaction between polar reinforcement and non-polar matrix, MAPP was used as a coupling agent and bamboo cellulose fiber was oxidized with 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO). It was proved that reactive hydroxyl groups on the fiber surface created by oxidation with TEMPO successfully bonded with MAPP modified PP. It was supported by FTIR, XRD and TGA analysis. Tensile strength of dual modified WPC cellulose fiber/PP based on 50% of fiber content is significantly improved.

2.2. Water absorption

Water has a adverse influence on the mechanical properties of WPC (Stark and Matuana, 2004). In contact with water and moisture, reaction of oxidation take place on the wood fiber surfaces and causes swelling of the WPC. Degradation of lignin or thermoplastic matrix in WPC during weathering make cellulosic fibers unprotected and cause moisture absorption

inside the composite material (Stark, 2006).

Chemical treatments can increase the interface adhesion between the polar fiber and non-polar matrix, but also can decrease the water absorption of hydrophilic wood reinforcement. As mentioned above, bleached wood fiber reinforced composites containing MAPP, shows better mechanical properties after accelerated weathering than the unbleached one (Beg and Pickering, 2008). Generally, the main disadvantage of wood fibre/thermoplastic polymer composite materials is their hydrophilic nature. Due to using of wood fibre reinforced composites in outdoor applications demands their greater environmental and dimensional stability, study of their mechanical properties under the influence of weathering attracted great attention (Beg and Pickering, 2008; Cantero *et al*., 2003).

Mechanical properties before and after accelerated weathering of wood reinforcement/thermoplastic LLDPE-g-MAPP matrix was investigated by Kallakas *et al*. (2015). Three different wood flour fractions sizes from birch and bleached-chemi-thermo-mechanical aspen pulp reinforcement surface were treated with two coupling agents, 3-aminopropyltriethoxysilane (APTES) and polyvinyalcohol (PVA). The best tests results were obtained with composites made of APTES modified wood flour and LLDPE-g-MAPP. Increasing the wood flour fractions size in the composites increases the amount of absorbed water as well as swelling. Consequently, flexural modulus and strength, and deflection of tested WPC decreased. Damages on the cross-section of WPC after weathering tests were supported by SEM analysis.

Butylina *et al*. (2012), studied softwood/PP composites behavior exposed a long-term weathering to Finnish climatic conditions. For analyzing the weathering caused degradation of the composites a combination of SEM, FTIR spectroscopy, colorimetric measurements and DSC were used. It is proved that the composite with a higher polypropylene content and lubricant was less damaged by weathering. Impact strength of analyzed WPC was determinated by Charpy test method. The results reveal a decrease of impact strength for composites with higher water absorption after weathering.

Effect of wood species and particle size on water absorption in WPC with HDPE matrix and MAPP as coupling agent, were analyze by (Dorostkar *et al*., 2014). Results showed decreased water absorption percent with increasing reinforcement particle size, but significant differences of water absorption property between different species was not observed.

3. Recycled polymer matrices

Products obtained from recycled thermoplastic polymers include also matrices in WPC. The most common recycled polymers are polypropylene, polyvinyl chloride, *acrylonitrile butadiene styrene* (ABS), *high-density polyethylene* (*HDPE*), etc. Pattanakul *et al*. (1991) investigate properties of the recycled HDPE from used milk bottles and proved that the properties of the recycled and virgin polymer does not have difference of great scale. On the other hand, wood fibers and flour from industry waste are very suitable as reinforcement for thermoplastic polymer matrices, giving composite materials for automotive components, furniture, enterior design, packaging and many other commercial products. Adhikary *et al*. (2008) used sawdust of pine softwood and recycled or virgin HDPE with MAPP coupling agent for manufacturing composite samples. Results show that the content of wood reinforcement significantly influences water absorption and swelling of WPC. Samples prepared with coupling agents MAPP showed improved characteristics. Only 3-5wt% of MAPP increase amount of optimal wood reinforcement from 30wt% to 50wt% for achievement equivalent stability properties. Improved interfacial bonding of composite

with modified HDPE matrix is observed by SEM images of the fracture surfaces of WPC. Authors concluded that dimensional stability and mechanical properties of composites can be achieved by increasing the polymer content or by addition of coupling agents.

Ashori and Nourbakhsh (2009) compared properties of WPCs with recycled HDPE and recycled PP. In both case reinforcement was obtained from old newspaper and it was used in different percentage. For improvement of reinforcement/matrices interface MAPP was used as coupling agent. Results report that WPC with recycled HDPE achieved moderately superior mechanical properties compared with composite with recycled PP. Also, composites made with low content of reinforcement without coupling agent show lower mechanical properties. Less water absorption, dimensional stability and good mechanical properties can be obtained using MAPP as coupling agents in 2–4 wt%. The similar approach was done with recycled and virgin ABS making composites with maple wood flour as reinforcement (Yeh *et al*., 2009). The coupling agents were not used.

Currently, recycling of WPC waste attracts attention due to economy and environment protecting reasons. According to the European Guideline 2000/53/EG administered by the European Commission, means of transport have to be produced with 95% recyclable materials consisting re-produced WPCs (Ashori *et al*., 2008). Petchwattana *et al*. (2012), studied changes in the mechanical and physical properties upon closed-loop recycling and reprocessing of wood reinforcement/PVC matrix composite materials. The composite were produced by mixing of WPC scrap and WPC freshfeed. Based on the mechanical properties appropriate mixing ratio of the WPC scrap: WPC freshfeed at 30:70 was established by maximizing the use of WPC scrap. Due to chain scission of PVC melted during each re-processing pass a drop in the flexural strength and flexural modulus was observed. Implementation of recycled WPC materials in the production of new constitutive parts and improvement of their properties is still developing.

5. Conclusions

The main disadvantage of lignocellulosic fibers is their strong polar character. Contrary, thermoplastic polymers has non-polar character which creates incompatibility with lignocellulosic fibers. To overcome this problem many physical and chemical surface treatments were developed. Application of coupling agent can significantly increase the interface adhesion of polar lignocellulosic fiber with thermoplastic matrices, and also decrease the water absorption of composite materials. The most commonly used coupling agents with the high improvements of WPC properties are maleated polypropylene (MAPP), chitosan and silane. Environmentally friendly characteristic is the big advantage of chitosan which makes it suitable for the production of bio-composite materials. Lignocellulosic fibers pretreatment is preferable to improve interfacial adhesion and decrease water absorption. For this purpose different surface modification were studied, including the oldest one - delignification. Organic carboxylic acids, benzoic acid, and 2,2,6,6-tetramethylpiperidine-1-oxy radical show very favorable results. For cellulosic fiber lignin and thermoplastic matrix in WPC have protecting role, so their degradation cause serious damage in WPC. Due to requirements for outdoor application of WPC many researches focused on their accelerated weathering. Bleached wood fiber reinforced composites containing MAPP, show good mechanical properties after accelerated weathering. The good results also were obtained by using 3-aminopropyltriethoxysilane (APTES) as coupling agents.

Recycling of thermoplastic polymers and their composites attract attention due to enviroment protection requirements. As the most common recycled matrices are

polypropylene, polyvinyl chloride, *acrylonitrile butadiene styrene* (ABS) and *high-density polyethylene* (*HDPE*). It is proved that the properties of the recycled and virgin HDPE does not have difference of great scale. Mechanical properties of composites with recycled polymer matrices can be improved by using coupling agents.

WPC waste can be included in re-processing with maximum of 30%. Application possibility of recycled WPC materials and improvement of their properties is still developing.

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