

Polyolefin Composites with Natural Fibers and Wood-Modification of the Fiber/Filler–Matrix Interaction

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ABSTRACT: Numerous strategies to improve the fiber–matrix interaction in natural fiber composites (NFCs) and wood polymer composites (WPCs) have been proposed and investigated. We have reviewed literature on polyolefin-based NFCs and WPCs to get an overview of the current state of the art of compatibilization methods. Those are classified in two categories here, namely fiber-based strategies and matrix-based strategies. Although this issue has been covered by several reviews before, as yet no work exists that is focused on polyolefin-based NFCs and WPCs. Furthermore, a ranking of the compatibilization methods based on their effects on material properties such as tensile/flexural strength and modulus, impact strength and water absorption, allows for an assessment of the efficiency of the various methods. As to the fiber-based strategies, silanes, maleated polyolefins (MA-POs), mercerization and acetylation are most thoroughly investigated. Silanes are most effective judged by achievable material property improvements, allowing for increases in tensile and flexural strength of more than 100%. Among the matrix-based strategies, MA-POs and isocyanates are most prominent in the literature. The first class enables the more significant material improvements, with reported increases of tensile and flexural strength of 132% and 85%, respectively. While strengths can be enhanced by many compatibilization methods, moduli, and impact strength (notched in particular) are in most cases improved to a lesser degree or even reduced. Especially, the last point calls for further attention, because impact strength is still a weak point of NFCs and WPCs. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 127: 1–17, 2013

KEYWORDS: biomaterials; compatibilization; composites; mechanical properties; polyolefins

Received 12 July 2011; accepted 25 January 2012; published online 25 April 2012

DOI: 10.1002/app.36935

INTRODUCTION

Natural fiber composites (NFCs) and wood polymer composites (WPCs) based on polyolefins (polyethylene, PE; polypropylene, PP) have gained increasing interest over the past two decades, both in the scientific community and in industry. The main driving forces behind this have been discussed in detail by several authors before.^{1–3}

Probably, the most important drawback in polyolefin NFCs and WPCs, and the main obstacle to overcome when their material properties should be improved, is the chemical incompatibility between hydrophilic natural fibers or wood and the hydrophobic thermoplastic matrices. Numerous strategies to improve the interaction at the fiber–matrix interface have been developed and published, with varying success.

Incompatibility at the interface results in reduced adhesion. This limits stress transfer via the interface, meaning that the

reinforcement potential of natural fibers or wood particles cannot be exploited to the full extent, especially for short fibers and particles. This situation is expressed in the concept of critical fiber length. In an ideal composite consisting of a cylinder of matrix material reinforced by a single short fiber, a force oriented parallel to that fiber results in strain of the composite (Figure 1). Force, and thus strain can be increased until the fiber fracture stress σ_{ff} is reached. At this point, a force balance in the fiber can be formulated as follows.⁴

1. Tensile force in the fiber: $F_t = \sigma_{\text{ff}} (\pi \times D^2/4)$
2. Shear force at the interface: $F_s = \tau_i (\pi \times D \times l_c/2)$

D is the fiber diameter (cylindrical fiber) and l_c is the “critical fiber length”. If the actual fiber length l is below l_c , the interface fails before the fiber, resulting in debonding and fiber pull out (see Figure 2). If l is above l_c , σ_{ff} is reached and the fiber is fractured. If this is the case, the reinforcement potential of the

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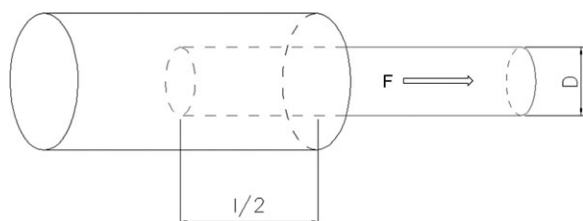


Figure 1. Fiber embedded in a cylinder of matrix material. Idealized composite for illustrating the concept of critical fiber length.

fiber has been exploited to the full extent. From this, two strategies to improve the performance of a given composite system can be deduced:

1. Increasing the aspect ratio l/D of the fibers, to approach or exceed l_c
2. Increasing the capability for stress transfer at the interface (fiber–matrix interaction), and thus τ_i .

For discontinuous, short fiber-reinforced composites, strategy 1 is often constricted for reasons connected to processing. Fiber breakage, resulting from compounding or other procedures, which involve agitation of the compound melt, decreases original aspect ratios inevitably. Furthermore, increased fiber length can go along with a reduction in melt flow properties of the material.^{5–7} Therefore, strategy 2 is most promising in many cases. Applying the concept of critical fiber length to NFCs and WPCs, it should not be forgotten that neither natural fibers nor wood particles approximate ideal cylindrical fibers very well. Both do usually have a rough surface, meaning that besides adhesion or chemical coupling, mechanical interlocking contributes to stress transfer at the interface, as well.^{8–11} Furthermore, particularly wood particles are compressed during processing. Thereby, original dimensions are altered, making geometrical description a difficult task. Nevertheless, an investigation on the influence of aspect ratio and interfacial adhesion on the mechanical properties of NFCs and WPCs by Renner et al. has shown the principal applicability of this concept to such composite materials.¹²

For polyolefin NFCs and WPCs, the hydrophilic properties of the reinforcement fibers or particles are an additional reason to attempt improvement of the fiber–matrix interaction (compatibilization). Potentially, the hydrophobic matrices can protect the reinforcements from humidity. However, this potential can only be fulfilled if the fibers or particles are dispersed evenly throughout the matrix, and if they are covered with matrix polymer most tightly. A gap between the matrix and reinforcement, as it can often be observed in uncompatibilized NFCs or WPCs, acts like a pathway for humidity into the material.^{13,14} Absorbed moisture leads to dimensional changes, which is problematic for almost all applications. Furthermore, it causes a reduction of mechanical performance,^{15–18} and of the product lifetime, especially in combination with weathering.^{19–21}

The fiber–matrix interaction can be improved either via the fiber, usually by modifying its surface, or via the matrix, usually by employing additives called coupling agents (Figure 3). Furthermore, combinations of those two approaches, meaning usage of pretreated fibers/fillers together with matrix-based coupling agents, have been reported, also.^{22–26} In this review, we are summarizing literature dealing with compatibilization in polyolefin-based NFCs and WPCs. Only discontinuous, randomly oriented (except for possible alignment effects from processing) fiber-reinforced composites have been taken into account, manufactured either by injection or by compression molding, and in one case, extrusion.²⁷ As to the effects of compatibilization strategies on mechanical properties, these are comparable under the premise that fiber–matrix interaction is equally important in specimens produced by those different processes, and controlled by the same parameters.

We have only taken papers into account which give material property data as influenced by a certain compatibilization approach. This allows for an assessment of the effects of the fiber–matrix interaction modification applied on a level close to actual application. The different strategies described in these articles are summarized shortly, to explain how the compatibilization is meant to work from the chemist's viewpoint. As a measure of the

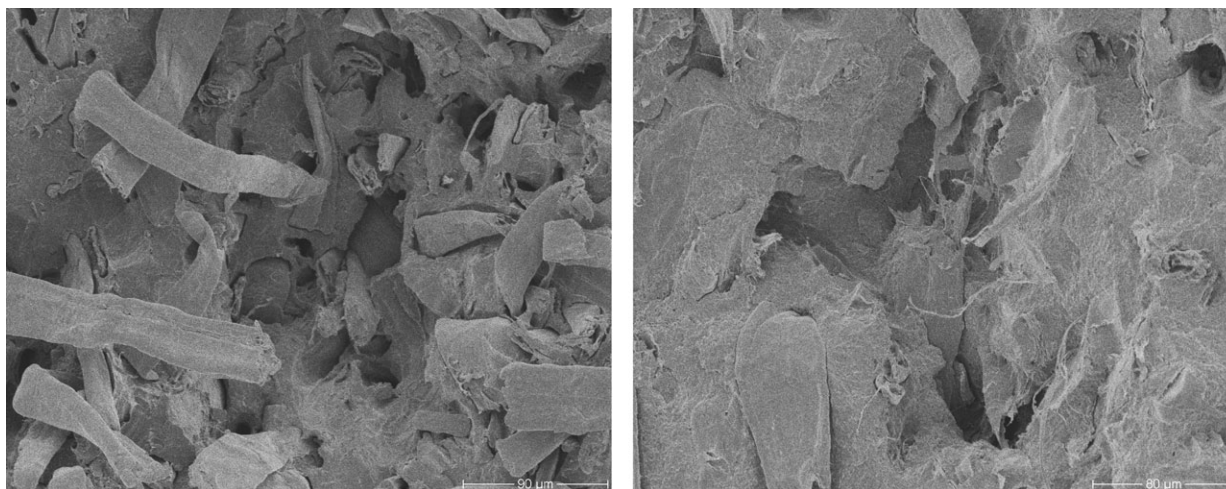


Figure 2. SEM-image of PP-composite fracture surfaces. Left: uncompatibilized, showing fiber pull out; Right: compatibilized, showing less fiber pull out [unpublished data of the first author].

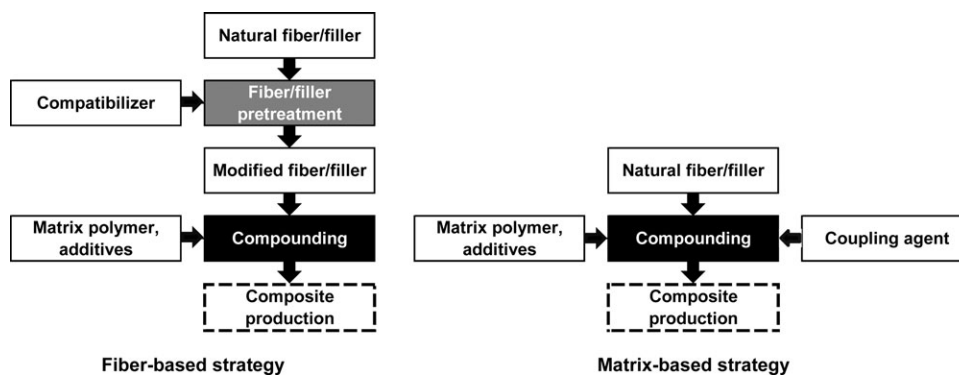


Figure 3. Schematic representation of fiber-based and matrix-based interface modification strategies.

effectiveness of the various methods from the material scientist's viewpoint, their influence on tensile and flexural properties, as well as impact strength and water absorption are compared. In some of the papers taken into account, results are presented only in the form of diagrams, and not printed as numbers (in the text or in tables). In this case, the effects achieved were estimated from these diagrams. For the most important modification methods, the data available were summarized in the form of bar charts. Finally, a short summary and discussion of the most efficient methods presented is given. As appendix, a table containing the most relevant information on the papers included in this overview is presented, as well. Concluding this introduction, it should not be concealed that several reviews covering modification of the interfacial interaction in natural fiber/filler-reinforced composites exist already.^{1–3,9,28–31} However, none of them gives a comprehensive overview of compatibilization strategies in polyolefinic NFCs and WPCs, and an assessment of their effects based on their influence of material properties.

FIBER-BASED STRATEGIES

Except for heat,²⁴ enzymatic,³² and special forms of maleated polyolefin (MA-PO),^{33,34} and stearic acid,³⁵ treatment, fiber-based methods usually rely on modification of the fiber in organic or aqueous solvents. Of course, this is problematic because such methods are relatively elaborate, and the usage of large amounts of particularly organic solvents is inappropriate for both economic and ecological considerations. Most common are silane treatments,^{22,27,34,36–46} followed by maleated polyolefins (MA-PE, MA-PP), which can be applied as an organic solution,^{17,39,47,48} as a melt, employing a thermokinetic mixer³³ or a roll mill,³⁴ or as an emulsion.^{38,49} Mercerization, or treatment with NaOH, is sometimes employed to activate the fiber surface for subsequent modification steps,^{11,36,42,44,46} but can also act as the modification itself.^{23,36,40,44,48,50,51} Other fiber surface treatments included are acetylation^{26,52,53} and maleic anhydride (MA) treatment.^{39,48,54} Several other treatments have been investigated by various researchers, and are covered in “Other Fiber-Based Strategies” section.

Silane Treatment of Fibers/Fillers

Silanes have been used as coupling agents in glass fiber-reinforced polymers for many years,^{5,55,56} which might explain why they are among the most common fiber-based compatibilization strategies. Initially, silane coupling agents have been developed

in the 1940s, and a large variety of types for different applications is available today.⁵⁷ All those molecules share the same basic structure (Figure 4).

The R' group is usually hydrolyzed during the fiber pretreatment. The OH-groups formed thereby are meant to interact with those on the cellulose of the fiber/filler, either via ether-bonds, or hydrogen bridges. Furthermore, the silane molecules themselves can crosslink through such interactions, forming a network on the fiber/filler surface. The functional group R is the part of the coupling agent which is meant to interact with the matrix. By choosing a silane with the right R group, compatibility with different sorts of polymers can be tuned. By those mechanisms, composite mechanical properties should be improved by enhanced fiber–matrix interaction, and possibly also better dispersion of the fiber/filler throughout the matrix.

The fiber/filler pretreatment conditions are, of course, also adapted to silane chemical structure. Depending on this, application is performed in organic-based solvents, such as acetone/acetic acid,⁴⁴ carbon tetrachloride,³⁴ methanol/water,^{36,42} ethanol/water,^{25,37,46} or ethanol,⁴¹ and water-based solvents,^{22,38–40,45} respectively. A NaOH pretreatment of the fiber/filler can be done prior to the silane one.^{36,42,46} Furthermore, initiators such as benzoyl chloride³⁴ or dicumyl peroxide (DCP)³⁶ are sometimes added. In any case, the solvents have to be removed after the treatment, and the fibers/fillers dried. Grubbstrom et al., in contrast to others, use a silane-peroxide solution which is added in a direct extrusion process.²⁷ Usually, a heat treatment, which can coincide with a drying step, is performed after the silane application, to promote chemical coupling. Mohanty et al. use a water-based silane/MA-PP emulsion in combination with a powder PP-based compression molding process.³⁸ Two groups combine the fiber-based silane approach with a matrix-based one, employing maleated styrene-ethylene-butylene-styrene²² and MA-PP, respectively.²⁵ Furthermore, a study conducted by



Figure 4. Silane basic structure.⁵⁸ [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

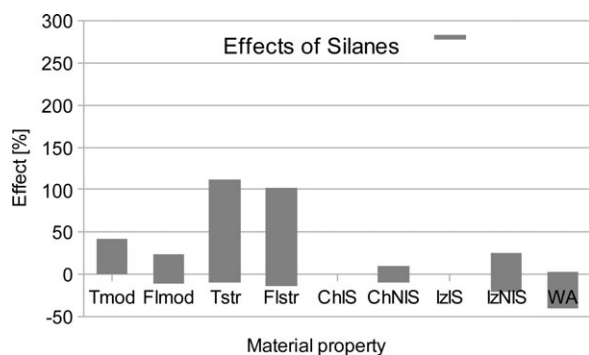


Figure 5. Effects of silane coupling agents on the properties of NFCs and WPCs.

Arbelaz et al. has shown that simple addition of a silane to the matrix rather than a fiber pretreatment can be sufficient for improving interfacial adhesion in a PP-30% flax system (“Other Matrix-Based Strategies” section).⁴⁸

Most of the groups working with silane coupling agents achieve an increase in tensile and flexural strength, respectively, ranging up to above 100%,²⁷ flexural, LDPE-50% wood,³⁴ tensile, HDPE-40% wood]. Four groups find reductions of approximately 10% in flexural^{38,39} and tensile strength,^{43,44} respectively, as a result of the fiber pretreatments applied. The effects of the treatment on stiffness are generally smaller, with a maximum increase in Young’s modulus of $\sim 40\%$,³⁷ (PP-30% wood) and in flexural modulus of 74%,⁴⁵ (PP-20% kenaf). The silane solution/MA-PP emulsion increases flexural strength by $\sim 30\%$, and flexural modulus by $\sim 60\%$,³⁸ PP-40% kenaf. The influence of silane pretreatments on impact strength (IS) is ambiguous. Most researchers observe modest effects between approximately -20% and $+25\%$ for notched Charpy or Izod measurements.^{22,40,42,45} Colom et al., on the other hand, find unnotched Izod IS increased by 290% by their silane pretreatment,³⁴ (HDPE-40% wood). Water absorption (WA) was measured by two groups, only. While Bettini et al. report a minimal increase of approximately 3% for their treatment after 1 year of submersion,²⁵ (PP-20% wood), Lee et al. find WA reduced by 40% for a 24 hr test,⁴² (PP-30% and 50% bamboo, respectively).

The results (Figure 5) do not allow an interpretation as to which silane types are the most effective ones. In general, most of the silane pretreatments applied lead to improvements in material tensile and flexural strength, while for stiffness and impact strength, the situation is not so clear. For the latter, interpretations are hindered by the large variety of methods for determination (Charpy, Izod, notched/unnotched, instrumented, etc.).

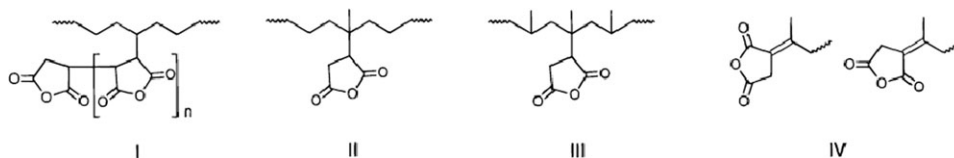


Figure 6. Structures that can arise in radical initiated grafting of maleic anhydride onto polyolefins. I, MA oligomers as found in HDPE and LDPE; II and III, MA grafted to tertiary carbons in PP and copolymers; IV, Terminal structure resulting from PP chain scission [Reprinted with permission from Ref. 68 by the courtesy of ACS Publications].

For water absorption, the results existing are too few to draw a conclusion. The application of silanes is relatively elaborate, but the fact that water-based solutions are sufficient for some types is encouraging. Generally, silane coupling agents, especially the water-soluble ones, do definitely have some potential as modifiers for the fiber–matrix interaction in NFCs and WPCs.

Maleic Anhydride Grafted Polyolefins (Applied to Fiber)

MA-POs are another well-known class of coupling agents which have proven efficient compatibilizers in conventional composites, like PP-glass fiber compounds, already.^{59,60} Maleic anhydride can be grafted onto polyolefins by radical initiated grafting. This can be performed either in the molten state^{61,62} (usually as reactive extrusion), in solid state^{63–65} or in solution,^{66,67} of which only the first two processes are of commercial relevance. In any case, initiators, usually peroxides, are needed to start the grafting reaction. In melt and solution processes, tertiary carbon atoms in the PO chain are the preferred acceptors of MA moieties. However, functionalization does also occur on secondary carbons in $(CH_2)_m$ sequences with $m > 3$. In longer propylene sequences, chain scission can lead to a structure where the anhydride is attached to the chain terminus via a double bond (Figure 6). Side reactions, like homopolymerization of the MA monomer, chain scission in PP, and crosslinking in PE, respectively, are inevitable.^{62,68} In the case of MA-PE, an actual copolymerization approach (in contrast to grafting), resulting in a product showing superior properties, was presented 2009 by Decodts from Dupont.⁶⁹ To our knowledge, no attempts to copolymerize maleic anhydride with propylene have been published yet.

Particularly in reactive extrusion, the side reactions lead to a tradeoff between two parameters: For MA-PP, increasing the graft level usually leads to a reduction in molecular weight of the base polymer.⁶¹ For MA-PE, on the other hand, achieving high MA contents is often connected to high gel contents resulting from crosslinking.⁶⁶ Solid-state grafting, on the other hand, allows for a widely mutually independent adjustment of graft level and molecular weight.^{63,70} However, at least for PP, there are still crosslinking and degradation reactions, respectively, depending on the process temperature.⁶⁵ Although increased graft level should increase interaction with a hydrophilic fiber/filler, decreased molecular weight might decrease interaction of the coupling agent polymer backbone with the matrix polymer. Therefore, the right balance between maleic anhydride content and backbone polymer chain length is supposed to be very important for MA-POs to be efficient compatibilizers.^{71,72}

The actual mechanism of chemical interaction at the interface that MA-POs promote has been investigated by several researchers. In most cases, Fourier transformed infrared spectroscopy (FTIR) analysis is applied to natural fibers or fillers, which have either been pretreated with coupling agents or re-extracted from composites, usually with xylene. Biagiotti et al. investigated MA-PP-treated flax fibers by FTIR, and report a novel peak at 1740 cm^{-1} representing an ester group.³⁹ Kazayawoko et al. modified bleached Kraft pulp and thermomechanical pulp (TMP) fibers with MA-PP. The group detected ester linkages by FTIR for the first, but not the second fiber type.³³ Employing the extraction approach, Lu et al. found signals between 1650 and 1800 cm^{-1} indicating the existence of ester bonds between wood surface OH-groups and MA-PE.⁷³ These findings are backed by electron spectroscopy for chemical analysis results. Nourbakhsh et al. reported signals in the same wavelength range in PP/wood composites compatibilized with MA-PP, but did not interpret them as a result of covalent bonding at the interface.⁷⁴ Paunikallio et al. also report detection of ester linkages between viscose and MA-PP on fibers extracted from the composites prepared.⁷⁵ Wang et al. investigated the influence of several PE-based compatibilizers on HDPE-wood composites and did also find evidence for ester bonds between the MA moieties of the coupling agents and the re-extracted filler.⁷⁶ In a similar study, Lai et al. identified increased absorption bands in the carbonyl region that might indicate the formation of covalent linkages at the interface.⁷⁷ Both the pretreatment and the re-extraction approach are representative of the interfacial features of a real composite only to a limited degree. For the former, despite giving similar improvements in mechanical properties in composites as matrix-based MA-PO deployment,¹⁷ it is not likely that the chemical structures formed at the fiber/filler surface during solution treatment remain unchanged in the melt during compounding. For the latter, it is just the other way round: the chemical structures formed in the melt during compounding will most likely be altered upon extraction of the fiber/filler from the compound in hot xylene (or another solvent).

Harper employed another approach for investigating chemical structures at the interface in his dissertation. He subjected $40\text{-}\mu\text{m}$ thin hot stage film specimens to FTIR microscopy. Based on this method, Harper could not confirm covalent bonding between MA-PP and wood. This was because the absorption bands that would result from potential ester bonds largely overlap with those from aliphatic esters in lignin at 1745 cm^{-1} , thus impeding spectra interpretation.⁷² Of course, this affects all FTIR-based methods and thus hinders conclusive verification of the formation of covalent linkages based on such results. Summing up these findings, it can be said that most FTIR data available suggests the existence of covalent linkages in the form of ester bonds between the MA moieties of grafted polyolefin coupling agents and the OH-groups on the surface of lignocellulosic fibers/fillers. Furthermore, the formation of those bonds seems to be independent of the way of deployment of the coupling agent (fiber/filler pretreatment or incorporation as additive during compounding, see “Maleic Anhydride Grafted Polyolefins as Matrix Additives” section). However, the fact that

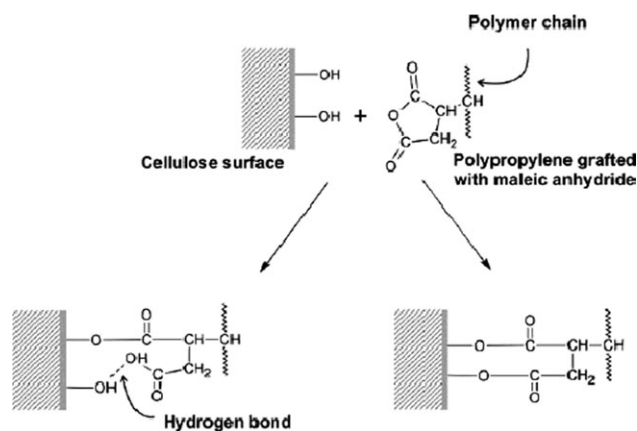


Figure 7. Assumed coupling reactions of MA-PP with OH-groups of cellulose at the fiber/filler surface. The MA moiety undergoes esterification with OH-groups on the surface, or interacts via hydrogen bridges [Reprinted with permission from Ref. 25 by the courtesy of John Wiley and Sons].

the absorption bands of the suggested ester linkages would partly overlap with those of existing aliphatic lignin esters demands scrutiny when dealing with FTIR investigations of the interface. Besides the possible covalent linkages, hydrogen bridges might also contribute to interaction (Figure 7).²⁵ The polymer backbone is meant to interact with the matrix by chain entanglement and possibly cocrystallization, which, however, might be hindered by high MA graft levels.^{61,71,72,76,78} By the mechanisms summarized above, MA-POs should increase composite mechanical properties by improving the interfacial shear strength and possibly also fiber/filler dispersion.

Pretreatment of fibers/fillers is often performed employing an organic solution of the MA-PO coupling agent. The solvent can be either boiling xylene^{17,39,48} or hot toluene.⁴⁷ In any case, it has to be removed again from the fibers/fillers before composite processing. Furthermore, melt-based pretreatments can be performed in a roll-mill³⁴ or in a thermokinetic mixer.³³ Two groups use MA-PO emulsions for fiber pretreatment.^{38,49}

All groups found increases in tensile strength upon fiber/filler MA-PO pretreatment, reaching from $\sim 15\%$ ³⁴ (HDPE-40% wood) to 40% ⁴⁸ (PP-30% flax). For flexural strength, Biagiotti et al. detected a minimal negative effect of their MA-PP pretreatment in a PP-30% flax system.³⁹ All other groups found flexural strength enhanced upon their MA-PO pretreatments, with increases ranging from 15% ³⁸ (PP-40% kenaf) to $\sim 70\%$ ⁴⁷ (PP-30% jute). For tensile modulus, two groups report modest effects between zero and $\sim 6\%$ increase.^{33,34} On the other hand, Biagiotti et al. and Arbelaiz et al. report 17% and 37% increase, respectively, upon MA-PP pretreatments of the fiber in a PP-30% flax system.^{17,39} As regards flexural modulus, the effects of MA-PO pretreatments found range from approximately -10% ⁷⁹ (PP-30% flax) to approximately $+10\%$ ¹⁷ (PP-30% flax), while the silane solution/MA-PP emulsion pretreatment of Mohanty et al. increases this property by $\sim 60\%$ ³⁸ (PP-40% kenaf). The effect of MA-PO fiber pretreatments on Izod impact strength was investigated by two groups. While Colom et al. found

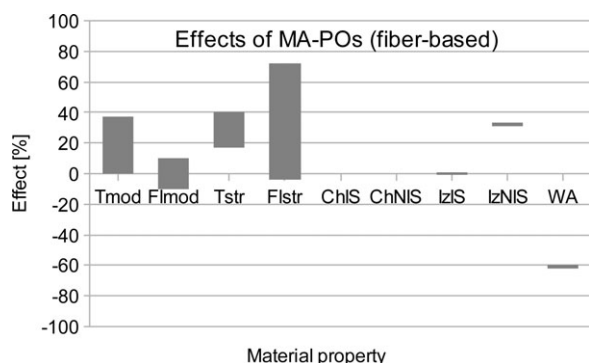


Figure 8. Effects of fiber-based MA-PO treatments on the properties of NFCs and WPCs.

unnotched IS in their HDPE-40% wood system unchanged, Mohanty et al. report an increase of notched IS by $\sim 30\%$ for their PP-30% jute system. This group also found water absorption in a 24 hr immersion test reduced by $\sim 60\%$ as a result of their MA-PP fiber pretreatment.

As to the effects of MA-PO pretreatments on material properties (Figure 8), the situation is similar to silane pretreatments: tensile and flexural strength can definitely be improved via this approach, while effects on stiffness are smaller. As regards impact strength and water absorption, too few results exist to draw conclusions. The same is true for the method of application of the MA-POs: solution-based, emulsion-based, and melt-based pretreatments can be effective, but the data available to date do not allow a rating as to which method brings about the best properties.

Mercurization of Fibers/Fillers

Mercurization or treatment with strong alkali bases was developed as a method for cotton fiber modification by John Mercer in 1850. It causes swelling of the cell walls, along with longitudinal shrinkage and an increase of the amount of cellulose-II at the expense of cellulose-I. Furthermore, it renders treated fibers a more circular cross section.⁸⁰ Applied to lignocellulosic natural fibers, mercurization also reduces the lignin- and hemicellulose-content, which in turn can improve tensile properties.⁸¹ For flax and jute fibers, improvements of 15%–40% in Young's modulus and tensile strength as a result of mercurization have been reported.⁸² Goda et al. applied mercurization to ramie fibers. They report an increase in tensile strength of the fibers of 4%–18%, along with a twofold to threefold increase in strain

at break. This was accompanied by a reduction of tensile modulus.⁸³ Tripathy et al., on the other hand, found a reduction in tensile strength of $\sim 25\%$ upon NaOH treatment of jute fibers. By making cellulose at the fiber surface more easily accessible, mercurization can be applied as a form of activation for subsequent modification steps,^{36,42,46} or in combination with matrix-based compatibilization strategies.^{23,46}

Fibrillation, meaning a splitting of fiber bundles into filaments, increases the surface available for fiber–matrix interaction, and also the aspect ratio, thus potentially improving the material properties of composites (Figure 9).^{11,82} Mercurization also tends to increase the fiber surface roughness. This in turn improves the potential for stress transfer through mechanical interlocking at the fiber–matrix interface.^{36,85,86} Summing up all these mechanisms, it can be said that fiber/filler mercurization can potentially influence composite mechanical properties not only via fiber–matrix interaction but also via changing the fiber properties themselves.

Mercurization is usually performed applying aqueous solutions of NaOH, at reaction times of 30 min up to 3 hr. Theoretically, other alkali types can be used as well, but sodium atoms have been shown to provide the optimal diameter for cellulose swelling, meaning that the treatment with NaOH is most efficient.³¹ In any case, excess alkali has to be removed by washing the modified fibers/fillers subsequently, followed by a drying step.

Effects of natural fiber mercurization on the tensile strength of the resulting NFCs as reported in the literature reach from -4% to $+50\%$ ^{44,51} (PE-20% TMP; LDPE-30% sisal), those on Young's modulus from -27% to $+46\%$ ^{51,87} (PP-20% sisal) (Figure 10). Valadez-Gonzalez et al. investigated HDPE-23% henequen composites. They report tensile strength unchanged for mercurization alone, while in combination with a subsequent xylene-based HDPE solution treatment, this property is increased by 10%. Combining NaOH with silane treatment, tensile strength is enhanced by $\sim 30\%$.³⁶ Herrera-Franco and Valadez-Gonzalez have investigated the same composite system. For a NaOH/silane pretreatment, they report increases of tensile and flexural strength of $+30\%$ and $+10\%$, respectively. Silane pretreatment alone yielded only half the effect on tensile, but twice the effect on flexural strength.¹¹ Combining NaOH fiber pretreatment with matrix modification by MA-PP addition, Solimani et al. achieved considerable improvements in mechanical properties in their PP-30% flax system. In fact, while tensile and flexural strength are increased by 50% and 20%,

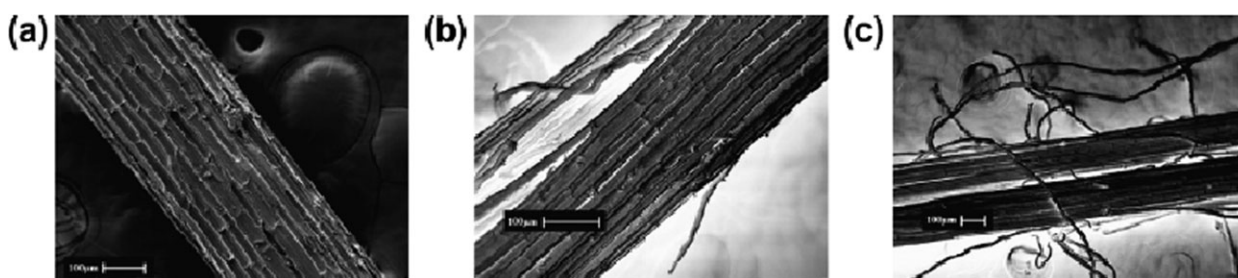


Figure 9. SEM images of sisal fibers: (a) untreated, (b) mercurized, (c) mercurized under tension. Fibrillation as a result of the treatment can be seen in (b) and (c) [Reprinted with permission from Ref. ⁸⁴ by the courtesy of Elsevier].

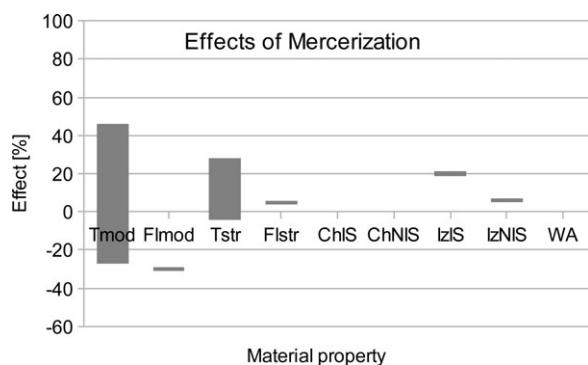


Figure 10. Effects of mercerization on the properties of NFCs and WPCs.

respectively, the respective stiffness values are improved by $\sim 20\%$. Also, tensile impact strength is enhanced by $\sim 50\%$, and water absorption upon 24 hr immersion is reduced by $\sim 25\%$. Without the NaOH fiber pretreatment, addition of MA-PP is far less efficient (tensile/flexural strength $+30\%/+15\%$, respectively, moduli $+10\%/+20\%$, IS none, WA 24 hr -20%).²³ Employing a similar compatibilization approach, Farsi achieved improvements in tensile and flexural strength of 20% and 30%, respectively, while notched Izod IS was reduced by $\sim 10\%$. With MA-PP alone, strengths of the PP-40% wood composite were increased to a lesser degree, while the negative effect on IS was avoided.⁴⁶

The material property improvements in NFCs and WPCs achieved by fiber/filler mercerization (Figure 10) are far less pronounced than those resulting from silane and MA-PO pretreatments, respectively. However, there is not enough data yet to disqualify this compatibilization strategy for natural fiber/filler-reinforced polyolefins. In any case, NaOH pretreatment might be a useful “activation step” in combination with other fiber- or matrix-based approaches.^{11,23,36,42,46}

Acetylation of Fibers/Fillers

Acetylation as a method for solid wood modification is known since 1946.⁸⁸ This treatment can improve wood durability and dimensional stability due to its anti-shrink effect. A partial replacement of OH-groups in the wood by the more bulky and less hydrophilic acetate groups results in a permanently swollen state of the material.⁸⁹ Of course, for reasons of increased surface/volume ratio, this modification can be applied to wood fibers or particles even more easily. Thus, the permeability of the material for liquids is far less important than is the case for solid wood.⁹⁰

Acetylation is usually performed using acetic anhydride, acetyl chloride, or thioacetic acid and keten (plus, e.g., suitable solvents, catalysts, and swelling agents), of which only the first approach is being applied in larger scale up to commercial

industrial production as yet.⁹¹ As a side product of the acetic anhydride reaction with wood OH-groups, acetic acid accumulates, causing unpleasant odor, and potentially cellulose degradation in the modified wood (Figure 11). This problem can only partially be solved by extraction of the byproduct. A more recent acetylation method is based on isopropenyl acetate (Figure 12). This approach allows for selective reactions under mild conditions. Acetone which is formed as a side product can be removed with relative ease.⁹² A patent covering this procedure has been granted to Wacker Chemie and Wood K plus in 2006.⁹³

Tronc et al. have modified blue agave fibers by acetylation with acetic anhydride in octanoic acid. After extraction of acetic acid with acetone and removal of the solvent, the fibers were characterized employing FTIR and NMR. Peaks at 1750 cm^{-1} and 172 ppm, respectively, provided indication for a successful modification.⁵² Bledzki et al. have acetylated flax fibers in a toluene solution of acetic anhydride. Afterwards, chemical characterization was performed, including a determination of the degree of acetylation by saponification.²⁶ Besides applying acetylation directly to fibers or fillers, industrially treated solid wood can be machined (milled) to particles. Grüneberg et al. have used commercially available modified woods (besides in their study). However, this approach leads to limited comparability of the results, because the different treatments affect milling behavior and thus particle size distributions.⁵³

Tronc et al. have produced compression molded HDPE composites with 40% treated and untreated fibers. They report a slight reduction of tensile modulus, along with an increase in unnotched Izod IS of $\sim 15\%$ upon acetylation. Bledzki et al. have investigated injection-molded PP composites with 30% flax fibers. They report tensile and flexural moduli increased by 20% and 5%, respectively, as a result of fiber acetylation. The respective strengths were found increased by 15% and 10%, while notched Charpy IS was reduced by $\sim 10\%$. In combination with matrix-based compatibilization by MA-PP addition (“Maleic Anhydride Grafted Polyolefins as Matrix Additives” section), tensile and flexural strength could be further improved, while IS was further reduced. Grüneberg et al. have prepared PP-based WPCs (60% wood content) using particles made from commercial treated and untreated wood. They did not find an influence on tensile properties as a result of using acetylated particles, but unnotched Charpy IS was reduced by $\sim 25\%$. On the other hand, water absorption upon 14 days of immersion was reduced by 50%. Summarizing these results (Figure 13), it has to be said that there is not enough data at the moment to come to a concluding statement on the effectiveness of acetylation for the improvement of NFCs and WPCs. However, the method seems to have some potential and has the benefit of already being applied industrially to solid wood.



Figure 11. Reaction of wood OH-groups with acetic anhydride; Acetic acid is formed as side product.

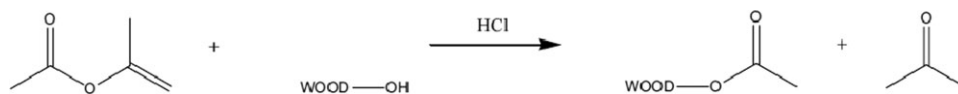


Figure 12. Reaction of wood OH-groups with isopropenyl acetate; acetone is formed as side product.

Maleic Anhydride Treatment of Fibers/Fillers

In efforts to increase chemical compatibility between natural fibers/fillers and polyolefins, maleic anhydride (MA) can be applied. The objective of this approach is to produce ester bonds between MA and OH-groups on the fiber/filler surface, thus reducing its hydrophilicity. Fiber/filler pretreatment with MA is usually performed applying an organic solution of the chemical to the reinforcement. The solvent can be acetone^{39,48} or xylene,⁹⁴ for example. By employing FT-IR analysis, Biagiotti et al. found indications for such an esterification reaction upon MA treatment of flax pulps (more intense peak at 1735 cm^{-1}). This group also reports reduced surface polarity of treated flax fibers, as determined by contact angle measurements.³⁹

As to the influence of MA-pretreatments on mechanical properties, relatively modest effects are reported in the literature. For tensile and flexural strength, Biagiotti et al. found results between -8% and $+12\%$ for a PP-30% flax system. Tensile and flexural moduli are reported to increase by approximately 10% – 15% upon MA-pretreatment of the reinforcement constituent.³⁹ Investigating the same composite system, Arbelaz et al. have reported effects of MA-pretreatments on tensile and flexural properties in the same range.⁴⁸ Deploying MA via the matrix rather than via the fiber, significantly higher improvements were achieved (“Other Matrix-Based Strategies”). Effects similar to those reported for PP-30% flax have been detected by Nunez et al. in a PP-50% wood system. For impact strength, the group reports notched Izod IS reduced by 20% as a result of their MA-pretreatment.⁵⁴

Other Fiber-Based Strategies

Other strategies reported in the literature which are aimed at improving the fiber–matrix interaction employ a paper wet-strength additive,⁹⁵ stearic acid,^{35,43} acrylic acid and benzoyl chloride,^{35,46,50} potassium permanganate and toluene-2,4-diisocyanate (TDI, KMnO_4),^{51,87} polymethylene (polyphenyl isocyanate) (PMPPIC)⁸⁷ and polymeric methylene diphenyl diisocyanate (PMDI).⁹⁶ Furthermore, *m*-phenylene bismaleimide (mPBM),⁹⁷ bleaching (sodium hypochlorite treatment),²³ octanoyl chloride,⁹⁸ *O*-hydroxybenzene diazonium salt (HBDa)⁹⁹ heat treatment,²⁴ or enzymes³² have been applied.

Geng et al. have investigated the suitability of the paper-wet-strength additive Kymene 557H as a compatibilizer in a HDPE-40% wood system. Various pretreatment regimes were tested. Combining fiber pretreatment with addition of stearic anhydride to the matrix, tensile strength, and stiffness could be improved by 35% .⁹⁵

In a PP-25% flax system, fiber pretreatment with stearic acid did not influence tensile strength, but reduced both tensile and flexural stiffness by $\sim 10\%$.⁴³ Similar results were achieved by Danyadi et al. for a PP-20% wood system.³⁵ Acrylic acid (AA) and benzoyl chloride (BC) have been tested as compatibilizers

in a PP-40% wood composite by Farsi⁴⁶ and Gashemi and Farsi.⁵⁰ Only minor changes upon pretreatments were reported by Farsi (Increases in strength between 10% and 20% , decreases in Izod IS around 15%). The latter group, however, found tensile modulus and unnotched Izod IS enhanced by 40% and 25% , respectively, upon AA pretreatment, while the BC pretreatment was less effective. As a result of filler pretreatment with BC, Danyadi et al. reported tensile properties of a PP-20% wood composite reduced by 20% , while WA upon 500 hr of immersion was reduced by 85% .³⁵

KMnO_4 has been employed as a sisal fiber pretreatment agent by Joseph et al., for both LDPE-30% fiber⁵¹ and PP-20% fiber⁸⁷ as composite systems. While for the first system, considerable improvements in tensile properties were achieved (tensile strength/modulus $+48\%/+85\%$), the results for the latter system were less encouraging (tensile strength/modulus $+10\%/−27\%$).

The same group has also employed TDI as a compatibilizer to improve the properties of the polyolefin-sisal composites mentioned earlier. As for KMnO_4 , while for the LDPE-based system, considerable improvements were achieved (tensile strength/modulus $+33\%/+57\%$), the approach was less successful for the PP-based system (tensile strength/modulus $+9\%/−74\%$).

PMPPIC was tested as a fiber-based compatibilizer by Joseph et al., the results being published in the paper cited already.⁸⁷ Pretreatment of the sisal fibers improved tensile strength of the resulting PP composites by 10% , but reduced the respective modulus value by 40% . Pretreatment of a wood filler with PMDI was performed by Geng et al.⁹⁶ In the resulting HDPE composites with 40% filler content, tensile properties were found increased by 25% . However, simple addition of the PMDI in the compounding step was even more effective (Isocyanate-Functionalized Polymers as Additives).

Sain and Kokta have pretreated chemithermomechanical pulp (CTMP) with mPBM. PP composites with $35\text{ m}\%$ fibers were

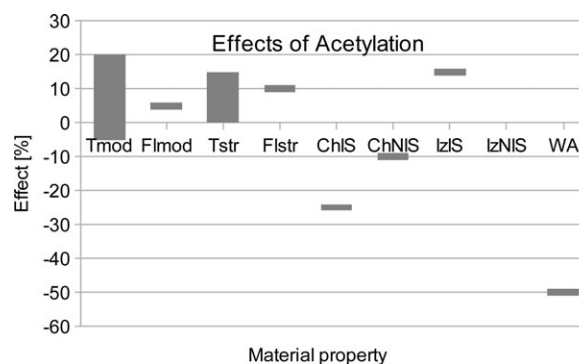


Figure 13. Effects of fiber/filler acetylation on the properties of NFCs and WPCs.

prepared by melt compounding and compression molding. The authors report an increase in tensile strength and modulus of 77% and 20%, respectively. On the other hand, unnotched Charpy IS was reduced by $\sim 20\%$.⁹⁷

Soleimani et al. have, besides mercerization, also investigated bleaching (meaning a sodium hypochlorite treatment) as a method for flax fiber modification. In PP composites containing 30% fibers, significant improvements in material properties were found. Tensile and flexural strength were improved by 50% and 20%, respectively. The corresponding moduli were increased upon the bleaching by 25% and 30%, respectively. Furthermore, IS as determined by a tensile test was increased by 50%, and water absorption upon 24 hr of immersion was reduced by $\sim 25\%$.²³

Zhang et al. have investigated PP-based WPCs with 60% wood content. The wood particles were treated with octanoyl chloride (C_8Cl), employing DMF and chloroform as solvents, respectively. For both treatments, flexural properties of compression molded specimens decreased significantly compared with WPCs containing untreated wood. Nevertheless, water absorption upon 24 h of immersion was reduced by 80% and 60%, respectively.⁹⁸

Islam has employed an *o*-hydroxybenzene diazonium salt pretreatment to render coir fibers a higher compatibility with PP. In composites with 25% coir fibers, this led to improvements in mechanical properties of up to 15% (tensile strength). WA, on the other hand, could be reduced by 25%.⁹⁹

Kaboorani et al. have assessed the feasibility of using heat-treated wood for HDPE-based WPC production (25/50% wood content). Wood particles were treated at different temperatures (175°C–205°C) and compounded with HDPE, specimens were prepared by injection molding. While tensile strength could be slightly increased, Young's modulus was reduced (both by $\sim 5\%$) for the WPCs containing 50% wood particles. In combination with MA-PP, strength could be increased by 50%, while the modulus was further reduced. Heat treatment at 175°C proved most favorably, judged by the properties of the resulting composites.²⁴

Bledzki et al. have investigated two enzyme-based modification methods as applied to abaca fibers. PP-compounds with 30% of the treated or untreated fibers were produced in a heat-cooling mixer system, and specimens prepared by injection molding. The objective of the treatments applied was twofold. First, the fiber bundles should be separated to individual fibers, so that their higher strength might be exploited. Furthermore, such a mainly longitudinal separation would also increase the aspect ratio of the reinforcement. Second, a removal of undesired, loosely bonded substances on the fiber surface (like fats and waxes) should also improve the fiber–matrix interaction. Thus, the treatments would enhance composite mechanical properties both by improving the fiber–matrix interaction and fiber aspect ratio. Two approaches to the desired modification were tested: In the first, fibers were collected from elephant dung, washed and dried. Thus, the natural digestive system (NDS) of the animals was used as a “reactor.” In the second approach, an enzyme mixture called “fungamix” was applied as an aqueous

solution. With both treatments, material properties of the PP-30% abaca composites could be improved significantly. For the NDS approach, tensile and flexural strength were increased by $\sim 5\%$ – 10% , while notched Charpy IS was enhanced by $\sim 15\%$. With the fungamix enzyme, tensile, and flexural strength could be improved by 45% and 35%, respectively, along with an increase of notched Charpy IS by $\sim 25\%$. For both treatments, water absorption upon 90d of exposure to 95% rh was reduced by $\sim 45\%$.³²

MATRIX-BASED STRATEGIES

Matrix-based strategies for improving the fiber–matrix interaction in NFCs and WPCs rely on so-called coupling agents (CAs), which are simply added during the compounding step in composite production. In most cases, these coupling agents are functionalized polymers, with a backbone that should be compatible with the matrix, and functional groups grafted to this backbone that can interact with the reinforcements. Compatibility with the matrix is often achieved by using polymers as backbone that are similar to or identical with the matrix material. Interaction with hydrophilic reinforcements (like natural fibers/fillers), on the other hand, is based on covalent or noncovalent bonds (e.g., hydrogen bridges) between the functional groups of the coupling agent and on the fiber/filler surface (like OH-groups).

The by far most important group among these CAs, judged by the abundance in the literature, are polymers with grafted maleic anhydride (MA) groups. In 41 studies included in this overview, the effect of such MA-CAs on material properties of NFCs or WPCs is investigated.^{17,22–26,29,32,40,43,45,48,54,61,71,77,95,97,98,100–123}

Most of the functionalized polymers reported on in these works are MA-POs. Only one of the MA-CAs being investigated is based on a backbone polymer other than a polyolefin, namely styrene-ethylene-butylene-styrene (SEBS).^{22,77,122} Besides the maleic anhydride grafted polymers, other functionalized polyolefins which have been investigated are oxidized PE,^{61,109} carboxylated PE,¹⁰⁸ acrylic acid functionalized PE,¹⁰⁰ N-vinylformamide-grafted PP (VFPP),²⁹ vinyltriethoxysilane functionalized PP (VTES-PP), and *m*-isopropenyl-*a,a*-dimethylbenzyl-isocyanate grafted PP (*m*-TMI-PP).¹²⁴

Other chemicals that have been tested for applicability as coupling agents in polyolefinic NFCs or WPCs are a silane,⁴⁸ maleic anhydride,^{48,87} and various isocyanate-functionalized polymers, like polymethylene (polyphenyl isocyanate) (PMPPIC),^{115,125} polymeric methylene diphenyl diisocyanate (PMDI),^{29,96} and polybutadiene isocyanate (PBNCO).^{114,118} Furthermore, investigations on stearic acid,^{96,101} and a so-called titanium CA¹⁰⁸ are reported on in the literature.

Maleic Anhydride Grafted Polyolefins as Matrix Additives

The basics on MA-POs have been given above already. A great advantage of these CAs is that a (relatively laborious) pretreatment of the fibers/fillers, as explained earlier, can be avoided, while still achieving compatibilization that leads to improved material properties. Arbelaz et al. have shown for a PP-30% flax system that similar increases in tensile and flexural properties are achieved, whether the natural fibers are pretreated with

MA-PP, or this CA is just incorporated during the compounding step as an additive.^{17,48} Almost all of the groups (whose articles are included in this review) applying the latter way of deployment achieve significant improvements in material properties, particularly tensile and flexural strength. Only Nourbakhsh et al. use MA-PP in combination with a peroxide as initiator,¹¹⁹ but judged by the results of the other groups, this is not required for achieving compatibilization at the interface. Mostly FTIR-based evidence suggests that the mechanisms of chemical interaction at the interface promoted by MA-POs are independent of the way of deployment of the coupling agents. Thus, interaction with the fiber is based on ester bonds and hydrogen bridges, while interaction with the matrix originates from backbone chain entanglements and possibly co-crystallization with the matrix polymer.

With only one exception,⁵⁴ (PP-50% wood with MA-grafted PP copolymer, flexural strength -6%), all of the researchers employing MA-PO CAs achieve significant increases in tensile and flexural strengths of the NFCs and WPCs investigated. For the first property, increases range from below 10% ,²⁵ (PP-20% wood; 118, PP-30% bagasse) to above 100% ,^{61,100,102,109,115,125} (HDPE-50% wood; HDPE-40% wood; PP-60% jute; HDPE-50% wood; PP-50% wood; HDPE-40% nut shell flour). For the latter property, the range of increases achieved is narrower, reaching from $\sim 10\%$ ¹¹⁰ (PP-20% wood) to $\sim 70\%$,¹⁰⁰ (HDPE-40% wood). As regards stiffness, the effects of MA-PO compatibilization are less pronounced, reaching from -20% ¹⁰⁰ to $+80\%$ ¹¹⁵ for Young's moduli, and from -25% ,¹¹¹ (PP-40% roselle) to $+65\%$,⁴⁵ (PP-20% kenaf) for flexural moduli, respectively. As mentioned for other strategies above, the effects of maleic anhydride-grafted polyolefins on impact properties are ambiguous. Unnotched Charpy IS is usually reported to be improved upon MA-PO addition, with increases of up to 60% ,¹⁰⁴ (PP-50% wood). For notched Charpy specimens, the effects are less pronounced, with reported increases of up to 16% ,¹⁰⁸ (rHDPE-30% bagasse). More than 75% of the authors cited here rely on Izod IS measurements. For unnotched Izod IS, effects of MA-PO addition between -20% ¹¹¹ and $+280\%$ ⁶¹ are observed. For notched Izod IS, on the other hand, effects between -27% ,⁴⁰ (PP-40% wood) and $+30\%$ are reported¹¹⁹ (PP-40% wood). Soleimani et al. employed a tensile impact test.²³ They report IS unchanged upon MA-PP addition alone, while in combination with a fiber pretreatment by bleaching and mercerization, respectively, an increase is achieved (see earlier sections). Nine of the groups dealing with MA-POs have investigated water absorption as influenced by the coupling agent addition.^{23,25,29,32,98,102,106,113,121} Except for one group,²⁵ (PP-20% wood, 1 year immersion), which did not find an improvement, all of them report a reduction in WA, reaching from -20% ,²³ (PP-30% flax) to -55% ,^{98,113} (PP-50% bamboo; PP-60% wood) as measured after 24 hr of immersion.

Judged by the effects on material properties (Figure 14), the usage of MA-PO coupling agents is an effective strategy for compatibilization in NFCs and WPCs. Comparing these results of simple CA addition with those achieved by fiber/filler pretreatment (Figure 8), it becomes obvious that the latter, more laborious approach does not necessarily lead to more pro-

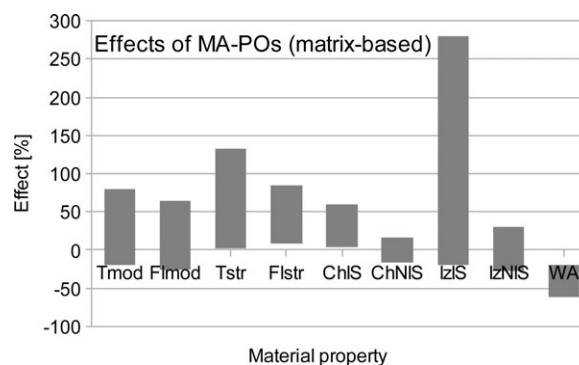


Figure 14. Effects of MA-POs (as applied as additives in compounding) on material properties of NFCs and WPCs.

nounced improvements. While for tensile and flexural properties, the picture is clear, the situation is more complex for impact properties. For both Charpy and Izod measurements, it looks like improved fiber–matrix adhesion through MA-POs has a positive influence on unnotched IS, while notched IS is ambiguously affected. Similar results have been reported for cellulose-reinforced polylactic acid (PLA) and polyhydroxybutyrate (PHB) by Erdmann and Ganster.¹²⁶ As regards water absorption, it seems obvious that this unwanted characteristic of NFCs and WPCs can be diminished employing MA-POs.

Other Functionalized Polyolefins as Additives

Polyolefins bearing functional groups (other than maleic anhydride), which can interact with OH-groups (or other functional groups) on the natural fiber or wood particle surface have been investigated by several researchers.

Keener et al. and Lu et al. have compared several functionalized polyolefin coupling agents, among them oxidized PE (containing functional groups like carboxyl, ketone, ester) in PE-50% wood and PE-50% TMP systems, respectively.^{61,109} While the first group found only minimal improvements in tensile strength resulting from oxidized PE usage, the latter group found the same material property increased by $\sim 110\%$.

Lei et al. have investigated recycled HDPE-based composites reinforced with bagasse fibers (30% fiber content). They found tensile strength improved by $\sim 15\%$ as a result of adding a carboxylated PE coupling agent in the compounding step. Notched Izod IS was not affected.¹⁰⁸

Acrylic acid functionalized PE was investigated for its effect as a compatibilizer in a HDPE-40% wood system by Li and Matuana. The group found tensile and flexural strength improved by $\sim 17\%$ upon employing this coupling agent. The Young's modulus, on the other hand, was slightly reduced, while flexural modulus was not affected.¹⁰⁰

N-vinylformamide grafted PP (VF-PP) was tested as a compatibilizer in a PP-40% wood system by Zhang et al. With this coupling agent alone, flexural strength and modulus could be improved by 10% and 20% , respectively. In combination with polymeric methylene diphenyl diisocyanate (PMDI), the respective increases were 45% and 40% , while water absorption upon 20d of immersion could be reduced by $\sim 40\%$. Thus, this

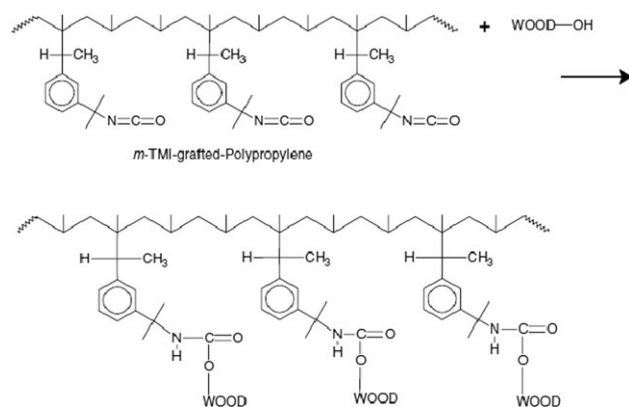


Figure 15. Presumed reaction of an isocyanate coupling agent with wood OH-groups. [Reprinted with permission from Ref. ¹²⁴ by the courtesy of Elsevier].

approach was comparable with MA-PP in terms of mechanical property improvements, while bringing about superior water absorption properties (MA-PP: 30% reduction).²⁹

Nachtigall et al. modified PP with MA and vinyl-triethoxysilane (VTES), respectively. Those coupling agents were then tested in a PP-30% wood system. While with MA-PP, a tensile strength increase of 50% was achieved, this increase was even 80% employing the novel VTES-PP. For water absorption in a 24 hr submersion-test as well, VTES-PP was superior, reducing the amount of absorbed moisture by 65% compared with 15% for MA-PP.¹²¹

Karmarkar et al. also produced a novel modified PP coupling agent by grafting *m*-isopropenyl-*a,a*-dimethylbenzyl-isocyanate (mTMI) onto PP. They investigated the effect of this copolymer on a PP-bleached Kraft pulp system with up to 50% fiber content. At maximum reinforcement level, an increase in tensile and flexural strength of 45% and 85% was achieved, respectively. Tensile modulus was improved by $\sim 35\%$, while the effects on Izod IS were small.¹²⁴

Glycidyl methacrylate (GMA)-grafted PP was tested as a coupling agent in a PP-20% hemp system by Pracella et al.¹²⁷ While the effect on tensile strength was negligible, the respective modulus could be improved by $\sim 5\%$. The same group also grafted GMA directly to hemp fibers, but did not determine mechanical properties of the resulting PP composites.

Isocyanate-Functionalized Polymers as Additives

Different authors have tested various isocyanate-functionalized polymers for their applicability as coupling agents in NFCs and WPCs. The objective behind this approach is a presumed addition reaction of the isocyanate group with OH-groups on the wood surface (Figure 15). The backbone of the functionalized molecule is meant to interact with the matrix polymer, thus increasing interfacial adhesion.

Polymethylene (polyphenyl isocyanate) (PMPPIC) has been investigated as a compatibilizer by Raj et al.¹²⁵ and Pickering and Ji.¹¹⁵ The first group worked with a PP-40% nut shell flour system and found tensile strength increased by 120% upon coupling agent addition. Unnotched Izod IS was improved by

$\sim 10\%$. Pickering and Ji investigated a PP-TMP system with 0%–50% filler content. At the highest filler level, only modest improvements were achieved using PMPPIC alone. In combination with MA-PP, on the other hand, tensile strength could be increased by $\sim 115\%$, and the respective modulus by $\sim 85\%$. However, these effects are similar in magnitude to those caused by MA-PP addition alone.

Polybutadiene isocyanate (PBNCO) was tested as a compatibilizer in PP-based composites by Nourbakhsh et al.¹¹⁴ and Ashori and Nourbakhsh.¹¹⁸ The first group worked with 30% TMP as reinforcement. With a combination of MA-PP and PBNCO coupling agents, tensile strength was increased by $\sim 40\%$, and unnotched Charpy IS by $\sim 115\%$. With MA-PP alone, approximately half of these effects could be realized. The second group used bagasse fibers as reinforcement. At a loading of 30%, only minimal improvements in tensile properties could be achieved. However, notched Izod IS could be improved by $\sim 80\%$, as compared with an increase of $\sim 45\%$ resulting from MA-PP addition.

Zhang et al. have tested polymeric methylene diphenyl diisocyanate (PMDI) as a compatibilizer for a PP-40% wood system.²⁹ With this compatibilizer alone, flexural strength and modulus could be increased by $\sim 15\%$ and 25% , respectively. In combination with VF-PP, the improvements were even more pronounced (see “Other Functionalized Polyolefins as Additives” section). PMDI was also reported an efficient compatibilizer by Geng et al.⁹⁶ In a HDPE-40% wood system, tensile strength and modulus were increased by 60% and 30%, respectively, while WA upon 30hd of immersion was reduced by 60%. These material property enhancements exceeded those achieved by compatibilization with MA-PE, and further improvements were possible by combining the PMDI approach with addition of stearic acid to the compound.

Judged by the achievable improvements in mechanical properties (Figure 16), isocyanate functionalized polymers are less effective compatibilizers for NFCs and WPCs than MA-POs. What seems to be promising, though, is the fact that those two classes of coupling agents can be combined, with effects at least partly adding up. Furthermore, PBNCO seems to be an efficient toughening agent in NFCs.

Other Matrix-Based Strategies

In comparison with a fiber pretreatment method, Arbelaiz et al. have also employed vinyltrimethoxy-silane (VTMS; DCP as initiator) as an additive in compounding of a PP-30% flax composite. Both tensile and flexural strength were improved by $\sim 60\%$, and the respective moduli by $\sim 30\%$. In contrast to this, and quite surprisingly, a fiber pretreatment with VTMS did not result in significant improvements of composite mechanical properties.⁴⁸

Maleic anhydride as an additive coupling agent has been tested by Joseph et al. in a PP-20% sisal system,⁸⁷ and by Arbelaiz et al. in a PP-30% flax system, employing DCP as a radical initiator.⁴⁸ While the first group reports an increase in tensile strength of 15%, accompanied by a decrease of the respective modulus value by 60%, the second group finds significant improvements upon DCP/MA addition to the matrix polymer. This might be explained by actual radical initiated grafting of MA

onto PP, resulting in in situ formation of MAPP in the melt. In fact, tensile and flexural strength are increased by 70%–80%, while the respective moduli are enhanced by 30%–35%.

Wu et al. have investigated the effects of MA-grafted styrene-ethylene-butylene-styrene copolymer (MA-SEBS) on a PP-10% wood system. While the effects of the compatibilizer on tensile properties were minimal, notched Charpy impact strength was increased by ~ 74%. Since this increase is significantly more pronounced than that which can be achieved by addition of MA-SEBS to neat PP (without a wood filler), the authors attribute the reported effect to “synergistic toughening.” Furthermore, in combination with vinyl-trimethoxy silane, IS could even be doubled.²² Lai et al. tested MA-SEBS in a HDPE-30% wood system. While tensile strength was increased by ~ 5%, notched Izod IS was improved by ~ 20%. The Young’s modulus, however, was reduced by 30%.⁷⁷ Nitz et al. investigated the effects of MA coupling agents on a PP-30% wood system. With MA-SEBS, tensile strength was increased by 41%, while the respective modulus value fell by 12%. This was accompanied by an increase of notched Izod IS of 31%, which could not be achieved by employing MA-PP instead.¹²² These results show that IS values can be improved with MA-SEBS, but at the expense of stiffness (Figure 17).

Stearic acid (SA) was incorporated in PP-wood composites by Stark, with the objective to improve filler dispersion and thus mechanical properties. Nevertheless, the group reports tensile and flexural properties to be slightly reduced upon SA addition to a PP-40% wood system. Only unnotched Izod impact strength could be increased by ~ 7%.¹⁰¹ Geng et al. also reported minimal reductions of tensile strength upon addition of SA to a HDPE-40% wood system. However, WA after 24h of immersion could be reduced by 25%.⁹⁶

Cellulose palmitate was used to modify the interfacial interaction in PP-20% wood composites by Danyadi et al.³⁵ The group reported a reduction of the tensile properties of ~ 10% as a result of adding the surfactant to the compound. Also, WA increased by ~ 20%.

Lei et al. have tested a so-called titanium-derived mixture (TDM) for applicability as a coupling agent in recycled HDPE-30% bagasse composites. No explanation for a potential mechanism of interfacial coupling promoted by this CA is given. The researchers found tensile strength improved by 5%, and notched Izod IS increased by 12% as a result of TDM addition.¹⁰⁸

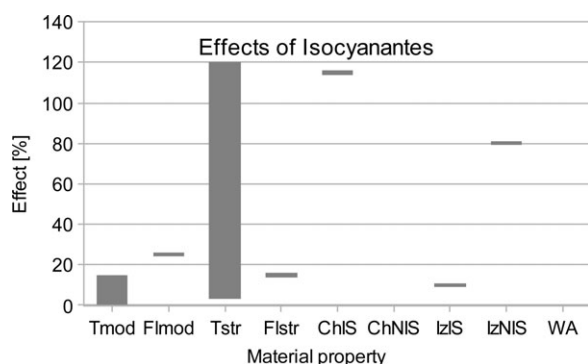


Figure 16. Effects of isocyanates on the properties of NFCs and WPCs.

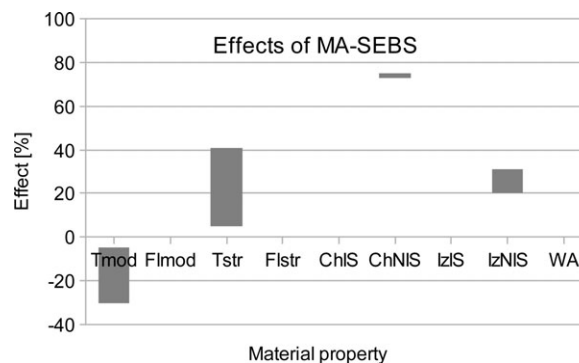


Figure 17. Effects of MA-SEBS on the properties of WPCs.

CONCLUSIONS

Of the various fiber-based interface modification strategies presented in “Fiber-Based Strategies” section, silanes, MA-POs (as applied to the fiber), mercerization (often just as a pretreatment for other matrix-based strategies) and acetylation are most thoroughly investigated and have proven efficient in polyolefin-based NFCs and WPCs. However, less common strategies like enzymatic treatment and modification with *m*-phenylene bismaleimide seem to hold some potential also. Mercerization of the fiber/filler alone does not greatly improve the mechanical properties of NFCs and WPCs. Nevertheless, there is some evidence for it improving the effectiveness of subsequent silane treatments, and of MA-PP as a matrix-based compatibilizer. In general, fiber-based strategies require a pretreatment step of the fiber/filler before composite production. Thinking of potential industrial application, this is a serious drawback, particularly given the fact that cost pressure considerations are a major driving force of NFC and WPC development. Especially treatments that require organic solvents might probably neither be economically justifiable, nor ecologically acceptable.

As regards matrix-based strategies, MA-POs are the predominant form of coupling agents for polyolefin-based NFCs and WPCs, judged by the abundance of references in the literature. Maleic anhydride functionalized polyolefins are proven to increase tensile and flexural strength and reduce water absorption. In many studies, the respective moduli have also been found improved, albeit in most cases to a lesser degree. For IS, the results are ambiguous. As to the form of MA-PO application, two studies indicate that fiber pretreatment does not result in higher improvements compared with simple addition of the coupling agent in the compounding step (earlier sections). This is supported by the abundance of data generated by other researchers employing either the fiber- or the matrix-based approach. Among the differently functionalized polyolefins, especially oxidized PE, VTES-PP, and mTMI-PP seem to hold some potential for NFC and WPC material property improvement (mentioned earlier). Of the CA-types not based on polyolefins, particularly polymers bearing isocyanate-groups are promising. Apparently, some of those can be applied in combination with MA-POs. Furthermore, PBNCO seems to be an efficient impact modifier in NFCs (mentioned in previous sections).

To date, there are several efficient coupling agents available for improving tensile and flexural strength, and reducing the water absorption of NFCs and WPCs. As regards stiffness, material property data of many studies shows that, in contrary to strength, it can be improved by introducing fibers/fillers even without providing good interfacial interaction. This is because tensile and flexural moduli are measured at low strains, when stress transfer via the interface is less crucial than in the nonlinear regime of the stress/strain curve, where finally breakage occurs. The relatively small effects that interface modifications in composites take on these properties can also be accounted to this phenomenon. As regards the main weak point of NFCs and

WPCs, namely the relatively low impact strength, improvement by interface modification seems to be a difficult task. Although many researchers report IS increased as a result of their compatibilization approach, especially notched impact strength is also found reduced in several cases. In NFCs, fiber pull-out seems to be an important mechanism for energy dissipation, which is partly suppressed by improved interfacial interaction [unpublished data of the first author]. However, some of the data reviewed here is contradicting this hypothesis. This ambiguity deserves increased scientific attention to finally develop coupling agents which should reliably improve IS along with the other material properties of interest.

APPENDIX

Table A1. Composites/Modifications Covered

Reference	Spec.	Fiber/Filler	Matrix	Fiber Modification
11	CM	20% Henequen	HDPE	NaOH, silane (2-methoxy-ethoxy)
17	IM	30% Flax	PP	MA-PP
22	IM	10% Wood	PP	Silane (vinyl-trimethoxy), MA-SEBS (matrix)
23	CM	30% Flax	PP	Bleaching, NaOH, MA-PP (matrix)
24	IM	50% Wood	HDPE	Heat treatment (175°C), MA-PP (matrix)
25	IM	20% Wood	PP	Silane (γ -aminopropyl-triethoxy), MA-PP (matrix)
26	IM	30% Flax	PP	Acetylation, MA-PP (matrix)
27	rEX	50% Wood	LDPE	Silane (vinyl-trimethoxy)/DCP
32	IM	30% Abaca	PP	Fungamix enzyme, natural digestive system (elephant)
33	IM	30% TMP, BKP	PP	MA-PP (thermokinetic treatment)
34	CM	40% Wood	HDPE	MA-PE, silane (γ -methacryloxypropyl-trimethoxy)
35	CM	20% Wood	PP	Stearic acid, benzoyl chloride
36	IM	20% Henequen	HDPE	NaOH, HDPE, silane (vinyltris (2-methoxy-ethoxy))
37	IM	30% Wood	PP	Silane (aminopropyl-trialkoxo)
38	CM	40% Kenaf, hemp, flax, sisal	PP	MA-PP, silane (aminoethyl-aminopropyl-trimethoxy), silane (aminoethyl-aminopropyl-trimethoxy)
39	IM	30% Flax	PP	MA, MA-PP, silane (vinyl-trimethoxy)
40	IM	40% Wood	PP	NaOH, silane (vinyltris (2-methoxy-ethoxy))
41	IM	50% Wood	HDPE	Silane (allylester), silane (epoxy)
42	IM	30/50% Bamboo	PP	NaOH/silane (tetramethoxy ortho)
43	IM	25% Flax	PP	Silane (vinyl-trimethoxy), silane (glycidyl-propyl-trimethoxy), stearic acid
44	IM	20% TMP	PE	NaOH, silane (dichloro-diethyl)
45	IM	20% Kenaf	PP	Silane (aminoethyl-aminopropyl-trimethoxy)
46	IM	40% Wood	PP	NaOH/silane (triethoxy vinyl), NaOH, benzoyl chloride, acrylic acid, MA-PP (matrix)
47	CM	30% Jute	PP	MA-PP
48	IM	30% Flax	PP	NaOH, MA, MA-PP
49	CM	55% TMP	rHDPE	MA-PE
50	IM	40% Wood	PP	NaOH, AA, Benzoyl chloride
51	IM	30% Sisal	LDPE	TDI, DCP, $KMnO_4$
52	CM	40% Blue agave fiber	HDPE	Acetylation
53	IM	60% Wood	PP	Acetylation, furfurylation (from com. solid wood)
54	IM	50% Wood	PP	MA
87	CM	20% Sisal	PP	PMPPIC, TDI, $KMnO_4$
97	CM	35% CTMP	PP	<i>m</i> -phenylene bismaleimide
95	CM	40% Wood	HDPE	Paper wet-strength additive, stearic acid (matrix), MA-PE (matrix)

TABLE AI. Continued

Reference	Spec.	Fiber/Filler	Matrix	Fiber Modification
96	CM	40% Wood	HDPE	PMDI
98	IM	60% Wood	PP	C8-chloride/CHCl ₃ , C8-chloride/DMF
99	IM	25% Coir	PP	O-hydroxybenzene diazonium salt
Reference	Spec.	Fiber/Filler	Matrix	Matrix Modification
17	IM	30% Flax	PP	MA-PP
22	IM	10% Wood	PP	MA-SEBS
23	CM	30% Flax	PP	MA-PP
24	IM	50% Wood	HDPE	MA-PP
25	IM	20% Wood	PP	MA-PP
29	CM	40% Wood	PP	MA-PP, PMDI, VF-PP
32	IM	30% Abaca	PP	MA-PP
35	CM	20% Wood	PP	MA-PP, cellulose palmitate
40	IM	40% Wood	PP	MA-PP
46	IM	40% Wood	PP	MA-PP
48	IM	30% Flax	PP	Silane (vinyl-trimethoxy) / DCP, MA / DCP, MA-PP
54	IM	50% Wood	PP	MA-PP copolymer
61	IM	30% Flax	PP	MA-PP, MA-PE, oxPE
71	IM	30% Flax	PP	MA-PP
77	IM	30% Wood	HDPE	MA-HDPE, MA-LLDPE, MA-PP, MA-SEBS
87	CM	20% Sisal	PP	MA
96	CM	40% Wood	HDPE	MA-PE, PMDI, stearic acid
97	CM	35% Wood	PP	MA-PP
98	IM	60% Wood	PP	MA-PP
100	IM	40% Wood	HDPE	AA-HDPE, MA-HDPE, MA-LLDPE, MA-PP
101	IM	40% Wood	PP	MA-PP, stearic acid
102	IM	30/60% Jute	PP	MA-PP
103	IM	50% Kenaf	PP	MA-PP
104	IM	50% Wood	PP	MA-PP
105	IM	40% Palm fiber	PP	MA-PP
106	CM	30/60% Wood	PP	MA-PP wax
107	IM	30% Wood	PP	MA-PP
108	CM	30% Bagasse	rHDPE	MA-PE, carbPE, titanium CA
109	CM	50% Wood	HDPE	MA-PE, oxPE
110	IM	20/40% Wood, 20/40% Wood fiber	PP	MA-PP
111	IM	40% Roselle fibers	PP	MA-PP
112	IM	30% Lyocell fibers	PP	MA-PP
113	IM	30/50% Bamboo	PP	MA-PP
114	CM	30% TMP	PP	MA-PP, PBNCO
115	IM	50% TMP	PP	MA-PP, PMPPIC
116	CM	50% Kraft pulp, sulfite pulp	PP	MA-PP
117	IM	20% Curaua	PP	MA-PP
118	CM	30% Bagasse	PP	MA-PP, PBNCO
119	IM	40/60% Wood	PP	MA-PP/DCP
120	IM	50% Wood	HDPE	MA-PE
121	CM	30% Wood	PP	MA-PP, VTES-PP
122	IM	30% Wood	PP	MA-PP, MA-SEBS
124	IM	50% Bleached Kraft pulp	PP	mTMI-PP
125	CM	40% Nut shell flour	HDPE	PMPPIC
127	CM	20% Hemp	PP	GMA-PP

REFERENCES

- Mohanty, A. K.; Misra, M.; Hinrichsen, G. *Macromol. Mater. Eng.* **2000**, 276/277, 1.
- Bledzki, A. K.; Reihmane, S.; Gassan, J. *Polymer Plast. Tech. Eng.* **1998**, 37, 451.
- Saheb, D. N.; Jog, J. P. *Adv. Polym. Tech.* **1999**, 18, 351.
- Matthews, F. L.; Rawlings, R. D. *Composite Materials: Engineering and Science*. CRC Press: Woodhead Publishing Limited, Cambridge, UK, **1999**; p 296.
- Campbell, F. C. *Manufacturing Processes for Advanced Composites*. Elsevier Ltd., **2004**; p 41, 420.
- Barbosa, S. E.; Kenny, J. M. *Polym. Eng. Science* **2000**, 40, 11.
- Czarnecki, L.; White, J. L. *J. Appl. Polym. Sci.* **1980**, 25, 1217.
- Bogoeva Gaceva, G.; Avella, M.; Malinconico, M.; Buzarovska, A.; Grozdanov, A.; Gentile, G.; Errico, M. E. *Polym. Compos.* **2007**, 28, 98.
- George, J.; Sreekala, M. S.; Thomas, S. *Polym. Eng. Sci.* **2001**, 41, 1471.
- Kalaprasad, G.; Bejoy, F.; Selvin, T.; Kumar, C. R.; Pavithran, C.; Groeninckx, G.; Thomas, S. *Polym. Int.* **2004**, 53, 1624.
- Herrera-Franco, P. J.; -Gonzalez, A. *Compos. B* **2005**, 36, 597.
- Renner, K.; Kenyo, C.; Moczo, J.; Pukanszky, B. *Compos. A* **2010**, 41, 1653.
- Klyosov, A. A. *Wood-Plastic Composites*. John Wiley & Sons, Inc., Hoboken, NJ, **2007**; p 383.
- Espert, A.; Vilaplana, F.; Karlsson, S. *Compos. A* **2004**, 35, 1267.
- Svoboda, M. A. *Werkstoffe aus nachwachsenden Rohstoffen*. Thesis/Dissertation; Montanuniversität Leoben, **2003**; p 145.
- Viksne, A.; Bledzki, A. K.; Rence, L.; Berzina, R. *Mech. Compos. Mater.* **2006**, 42, 73.
- Arbelaiz, A.; Fernandez, B.; Ramos, J. A.; Retegi, A.; Llano-Ponte, R.; Mondragon, I. *Compos. Sci. Technol.* **2005**, 65, 1582.
- Chow, C. P. L.; Xing, X. S.; Li, R. K. Y. *Compos. Sci. Technol.* **2007**, 67, 306.
- Schirp, A.; Köhler, B.; Wittenberg, K. *Veränderung der Farbe und mechanisch-physikalischer Eigenschaften von Wood-Plastic-Composites auf Polyolefinbasis nach QUV-Schnellbewitterung und Wasserlagerung - Teil 2: Veränderung mechanisch-physikalischer Eigenschaften*. Holztechnologie **2010**; 02/2010.
- Bajwa, S. G.; Bajwa, D. S.; Anthony, A. S. *J. Thermoplast. Compos. Mater.* **2009**, 22, 227.
- Lopez, J. L.; Sain, M.; Cooper, P. *J. Appl. Polym. Sci.* **2006**, 99, 2570.
- Wu, J.; Yu, D.; Chan, C.-M.; Kim, J.; Mai Y-W. *J. Appl. Polym. Sci.* **2000**, 76, 1000.
- Soleimani, M.; Tabil I, Panigrahi, S.; Opoku, A. *J. Polym. Environ.* **2008**, 16, 74.
- Kaboorani, A.; Faezipour, M.; Ebrahimi, G. *J. Reinf. Plast. Compos.* **2008**, 27, 1689.
- Bettini, S. H. P.; Bonse, B. C.; Melo, E. A.; Munoz, P. A. R. *Polym. Eng. Sci.* **2010**, 50, 978.
- Bledzki, A. K.; Mamun, A. A.; Lucka-Gabor, M.; Gutowski, V. S. *Express Polym. Lett.* **2008**, 2, 413.
- Grubbstrom, G.; Holmgren, A.; Oksman, K. *Compos. A* **2010**, 41, 678.
- Bledzki, A. K.; Reihmane, S.; Gassan, J. *J. Appl. Polym. Sci.* **1996**, 59, 1329.
- Zhang, C.; Li, K.; Simonsen, J. *J. Adhes. Sci. Technol.* **2004**, 18, 1603.
- Li, X.; Tabil, L. G.; Panigrahi, S. *J. Polym. Environ.* **2007**, 15, 25.
- Maya, J. J.; Anandjiwala, R. D. *Polym. Compos.* **2007**, 29, 187.
- Bledzki, A. K.; Mamun, A. A.; Jaszkievicz, A.; Erdmann, K. *Compos. Sci. Technol.* **2010**, 70, 854.
- Kazayawoko, M.; Balatinez, J. J.; Matuana, L. M. *J. Mater. Sci.* **1999**, 34, 6189.
- Colom, X.; Carrasco, F.; Pagès, P.; Canavate, J. *Compos. Sci. Technol.* **2003**, 63, 161.
- Danyadi, L.; Móczó, J.; Pukánszky, B. *Compos. A* **2010**, 41, 199.
- Valadez-Gonzalez, A.; Cervantes-Uc, J. M.; Olayo, R.; Herrera-Franco, P. J. *Compos. B* **1999**, 30, 309.
- Gironès, J.; Méndez, J. A.; Boufi, S.; Vilaseca, F.; Mutjé, P. *J. Appl. Polym. Sci.* **2007**, 103, 3706.
- Mohanty, A. K.; Drzal, L. T.; Misra, M. *J. Mater. Sci. Lett.* **2002**, 21, 1885.
- Biagiotti, J.; Puglia, D.; Torre, L.; Kenny, J. M. *Polym. Compos.* **2004**, 25, 470.
- Ichazo, M. N.; Albano, C.; Gonzalez, J.; Perera, R.; Candal, M. V. *Compos. Struct.* **2001**, 54, 207.
- Xiong, C.; Qi, R. R.; Wang, Y. L. *J. Appl. Polym. Sci.* **2009**, 114, 1160.
- Lee, S. Y.; Chun, S. J.; Doh, G. H.; Kang, I. A.; Lee, S.; Paik, K. H. *J. Compos. Mater.* **2009**, 43, 1639.
- Hornsby, P. R.; Hinrichsen, E.; Tarverdi, K. *J. Mater. Sci.* **1997**, 32, 1009.
- Pickering, K. L.; Abdalla, A.; Ji, C.; McDonald, A. G.; Franch, R. A. *Compos. A* **2003**, 34, 915.
- Karnani, R.; Krishnan, M.; Narayan, R. *Polym. Eng. Sci.* **1997**, 37, 476.
- Farsi, M. *J. Reinf. Plast. Compos.* **2010**, 29, 3587.
- Mohanty, S.; Nayak, S. K.; Verma, S. K.; Tripathy, S. S. *J. Reinf. Plast. Compos.* **2006**, 23, 625.
- Arbelaiz, A.; Fernandez, B.; Cantero, G.; Llano-Ponte, R.; Valea, A.; Mondragon, I. *Compos. Part A: Appl. Sci. Manufact.* **2005**, 36, 1637.
- Nourbakhsh, A.; Ashori, A. *J. Compos. Mater.* **2009**, 43, 877.
- Ghasemi, I.; Farsi, M. *Iranian Polym. J.* **2010**, 19, 811.
- Joseph, K.; Thomas, S.; Pavithran, C. *Polymer* **1996**, 37, 5139.

52. Tronc, E.; Hernandez Escobar, C. A.; Ibarra-Gomez, R.; Estrada-Monje, A.; Navarrete-Bolanos, J.; Zaragoza-Contreras, E. A. *Carbohydr. Polym.* **2007**, *67*, 245.
53. Grüneberg, T.; Krause, A.; Militz, H.; Mai, C.; Steuernagel, L. Chemical wood modification as improvement of selected properties of Wood Polymer Composites (WPC). In 8th International Symposium "Materials made of Renewable Resources," Erfurt, Germany, **2010**.
54. Nunez, A. J.; Sturm, P. C.; Kenny, J. M.; Aranguren, M. I.; Marcovich, N. E.; Reboledo, M. M. *J. Appl. Polym. Sci.* **2003**, *88*, 1420.
55. Yue, C. Y.; Cheung, W. L. *J. Mater. Sci.* **1991**, *26*, 870.
56. Drown, E. K.; Almoussawi, H.; Drzal, L. T. *J. Adhes. Sci. Technol.* **1991**, *5*, 865.
57. Comyn, J. In *Structural Adhesives: Developments in Resins and Primers*; Kinloch, A. J., Ed. Springer, **1986**, p. 269.
58. Datasheet; Silane Coupling Agents. Dow Corning, **2009**.
59. Xanthos, M. *Polym. Eng. Sci.* **1988**, *28*, 1392.
60. Roberts, D. H.; Constable, R. C.; Thiruvengada, S. *Polym. Eng. Sci.* **1997**, *37*, 1421.
61. Keener, T. J.; Stuart, R. K.; Brown, T. K. *Compos. A* **2004**, *35*, 357.
62. Moad, G. *Progr. Polym. Sci.* **1999**, *24*, 81.
63. Khunova, V.; Zamorsky, Z. *Polym. Plast. Tech. Eng.* **1993**, *32*, 289.
64. Rengarajan, R.; Vicic, M.; Lee, S. *J. Appl. Polym. Sci.* **1990**, *39*, 1783.
65. Rätzsch, M.; Arnold, M.; Borsig, E.; Bucka, H.; Reichelt, N. *Progr. Polym. Sci.* **2002**, *27*, 1195.
66. Huang, L. P.; Zhou, X. P.; Cui, W.; Xie, X. L.; Tong, S. Y. *Polym. Eng. Sci.* **2009**, *49*, 673.
67. Garcia-Martinez, J. M.; Laguna, O.; Collar, E. P. *J. Appl. Polym. Sci.* **1998**, *68*, 483.
68. Heinen, W.; Rosenmoller, C. H.; Wenzel, C. B.; De Groot, H. J. M.; Lugtenburg, J.; Van Duin, M. *Macromolecules* **1996**, *29*, 1151.
69. Decodts, M. Influence of Anhydride- Functional Coupling Agents on the Mechanical Properties of Polyolefin based Wood Polymer Composites. In 4th Wood Fibre Polymer Composites International Symposium, Bordeaux, France, **2009**.
70. Rapptel, I.; Haeußler, A. Effektive Haftvermittler für Holz und andere Naturfaserverbunde. Unpublished work; Kometra GmbH **2005**.
71. Snijder, M. H. B.; Bos, H. L. *Compos. Interfaces* **2000**, *7*, 69.
72. Harper, D. P. A thermodynamic, spectroscopic, and mechanical characterization of the wood-polypropylene interphase. Thesis/Dissertation. Department of Civil and Environmental Engineering, Washington State University, **2003**; Chapter 3.
73. Lu, J. Z.; Negulescu, I. I.; Wu, Q. *Compos. Interfaces* **2005**, *12*, 125.
74. Nourbakhsh, A.; Ashori, A. *Polym. Compos.* **2008**, *29*, 569.
75. Paunikallio, T.; Kasanen, J.; Suvanto, M.; Pakkanen, T. T. *J. Appl. Polym. Sci.* **2003**, *87*, 1895.
76. Wang, Y.; Yeh, F. C.; Lai, S. M.; Chan, H. C.; Shen, H. F. *Polym. Eng. Sci.* **2003**, *43*, 933.
77. Lai, S. M.; Yeh, F. C.; Wang, Y.; Chan, H. C.; Shen, H. F. *J. Appl. Polym. Sci.* **2003**, *87*, 487.
78. Duvall, J.; Sellitti, C.; Myers, C.; Hiltner, A.; Baer, E. *J. Appl. Polym. Sci.* **1994**, *52*, 207.
79. Cantero, G.; Arbelaiz, A.; Llano-Ponte, R.; Mondragon, I. *Compos. Sci. Technol.* **2003**, *63*, 1247.
80. Carr, C. M. *Chemistry of the Textiles Industry*. Springer, The Netherlands, **1995**; p 275.
81. Bledzki, A. K.; Gassan, J. *J. Appl. Polym. Sci.* **2008**, *71*, 623.
82. Thwe, M. M.; Liao, K. *Plast. Rubber Compos.* **2002**, *31*, 422.
83. Goda, K.; Sreekala, M. S.; Gomes, A.; Kaji, T.; Ohgi, J. *Compos. A* **2006**, *37*, 2213.
84. Kim, J. T.; Netravali, A. N. *Compos. A* **2010**, *41*, 1245.
85. Gassan, J.; Mildner, I.; Bledzki, A. K. *Compos. Interfaces* **2001**, *8*, 443.
86. Vazquez, A.; Dominguez, V. A.; Kenny, J. M. *J. Thermoplast. Compos. Mater.* **1999**, *12*, 477.
87. Joseph, P. V.; Joseph, K.; Thomas, S. *Compos. Sci. Technol.* **1999**, *59*, 1625.
88. Dreher, W. A.; Goldstein, I. S.; Cramer, G. R. *Forest Prod. J.* **1964**, *2*, 66.
89. Clermont, L. P.; Bender, F. *Forest Prod. J.* **1957**, *5*, 167.
90. Beckers, E. P. J.; Militz, H. Acetylation of solid wood—Initial trials on lab and semi industrial scale. In Second Pacific Rim Bio-Based Composites Symposium, Vancouver, BC, Canada, **1994**.
91. Accsys Technologies PLC. Accoya product presentation. Accsys Technologies **2010**; http://www.accoya.com/pdf/Web_PDF_brochure.pdf
92. Putz, R. Modifizierte Holzspäne für höherwertige Holz-Kunststoff-Verbundwerkstoffe. Bundesministerium für Verkehr, Innovation und Technologie; **2006**.
93. Tanczos, I.; Putz, R.; Stadlbauer, W.; Schmidt, H.; Bruestle, B.; Kitzmueller, M. WO/2006/072119. **2006**.
94. Nunez, A. J.; Kenny, J. M.; Reboledo, M. M.; Aranguren, M. I.; Marcovich, N. E. *Polym. Eng. Sci.* **2002**, *42*, 733.
95. Geng, Y.; Li, K.; Simonsen, J. *J. Appl. Polym. Sci.* **2004**, *91*, 3667.
96. Geng, Y.; Li, K.; Simonsen, J. *J. Adhes. Sci. Technol.* **2005**, *19*, 987.
97. Sain, M.; Kokta, B. V. *Polym. Plast. Technol. Eng.* **1994**, *33*, 89.
98. Zhang, Y.; Toghiani, H.; Zhang, J.; Xue, Y.; Pittman, C. U. *J. Mater. Sci.* **2009**, *44*, 2143.
99. Islam, M. Physico-mechanical properties of chemically treated coir reinforced polypropylene composites. *Compos. A* **2010**, *41*, 192.
100. Li, Q.; Matuana, L. M. *J. Thermoplast. Compos. Mater.* **2003**, *16*, 551.
101. Stark, N. M. *Forest Prod. J.* **1999**, *49*, 39.

102. Rana, A. K.; Mandal, A.; Mitra, B. C.; Jacobson, R.; Rowell, R. M.; Banerjee, A. N. *J. Appl. Polym. Sci.* **1998**, *69*, 329.
103. Sanadi, A. R.; Caulfield, D. F.; Stark, N. M.; Clemons, C. M. Thermal and mechanical analysis of lignocellulosic polypropylene composites. In *The Fifth International Conference on Woodfiber-Plastic Composites*, Madison, Wisconsin, **1999**.
104. Bledzki, A. K.; Faruk, O. *Appl. Compos. Mater.* **2003**, *10*, 365.
105. Kahraman, R.; Abbasi, S.; Abu-Shark, B. F. Influence of epolene as a coupling agent on the mechanical behaviour of palm fibre PP composites. *Int. J. Polym. Mater.* **2005**, *54*, 483.
106. La Mantia, F. P.; Morreale, M. *Compos. Interfaces* **2007**, *14*, 685.
107. Sombatsompop, N.; Yotinwattanakumtorn, C.; Thongpin, C. *J. Appl. Polym. Sci.* **2005**, *97*, 475.
108. Lei, Y.; Wu, Q.; Yao, F.; Xu, Y. *Compos. A* **2007**, *38*, 1664.
109. Lu, J. Z.; Wu, Q.; Negulescu, I. I. *J. Appl. Polym. Sci.* **2004**, *96*, 93.
110. Stark, N. M.; Rowlands, R. E. *Wood Fiber Sci.* **2003**, *35*, 167.
111. Junkasem, J.; Menges, J.; Supaphol, P. *J. Appl. Polym. Sci.* **2006**, *101*, 3291.
112. Borja, Y.; Rieß, G.; Lederer, K. *J. Appl. Polym. Sci.* **2006**, *101*, 364.
113. Lee, S. Y.; Kang, I. A.; Park, B. S.; Doh, G. H.; Park, B. D. *J. Reinf. Plast. Compos.* **2009**, *28*, 2589.
114. Nourbakhsh, A.; Kokta, B. V.; Ashori, A.; Jahan-Latibari, A. *J. Reinf. Plast. Compos.* **2008**, *27*, 1679.
115. Pickering, K. L.; Ji, C. *J. Reinf. Plast. Compos.* **2004**, *23*, 2011.
116. Bengtsson, M.; Baillif, M. L.; Oksman, K. *Compos. A* **2007**, *38*, 1922.
117. Spinace, M. A. S.; Feroseli, K. K. G.; De Paoli, M. A. *J. Appl. Polym. Sci.* **2009**, *112*, 3686.
118. Ashori, A.; Nourbakhsh, A. *J. Appl. Polym. Sci.* **2009**, *111*, 1684.
119. Nourbakhsh, A.; Karegarfard, A.; Ashori, A. *J. Thermoplast. Compos. Mater.* **2010**, *23*, 169.
120. Huang, H. X.; Zhang, J. J. *J. Appl. Polym. Sci.* **2009**, *111*, 2806.
121. Nachtigall, S.; Cerveira, G. S.; Rosa, S. M. L. *Polym. Test* **2007**, *26*, 619.
122. Nitz, H. J.; Reichert, P.; Mülhaupt, R. *Macromol. Mater. Eng.* **2000**, *276–277*, 51.
123. Feng, D.; Caulfield, D. F.; Sanadi, A. R. *Polym. Compos.* **2001**, *22*, 506.
124. Karmarkar, A.; Chauhan, S. S.; Modak, J. M.; Chanda, M. *Compos. A* **2007**, *38*, 227.
125. Raj, R. G.; Kokta, B. V.; Nizio, J. D. *J. Appl. Polym. Sci.* **1992**, *45*, 91.
126. Erdmann, J.; Ganster, J. Tailor-made PLA and PHB based cellulose fibre composites through coupling or anti-coupling agents. In *8th International Symposium "Materials made of Renewable Resources"*; Erfurt, Germany, **2010**.
127. Pracella, M.; Chionna, D.; Anguillesi, I.; Kulinski, Z.; Piorowska, E. Functionalization, compatibilization and properties of polypropylene composites with hemp fibres. *Compos. Sci. Technol.* **2006**, *66*, 2218.