

Polypropylene-Based Wood Polymer Composites—Effect of a Maleated Polypropylene Coupling Agent Under Dry and Wet Conditions

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ABSTRACT: Polypropylene (PP)-based wood polymer composites with 40 and 60 m % wood content, respectively, have been prepared, employing two different wood types and 0.0–20.0% (based on wood content) of a maleated polypropylene (MA-PP) coupling agent (CA). The main objective of this research was to find out if the optimum CA content is dependent on wood filler particle size. Tensile and flexural properties, as well as impact strength, heat deflection temperature, and water absorption served as indicator properties for the CA influence. For all properties, there is an optimum or the onset of a plateau occurring between 8.0 and 13.0 m % MA-PP content. Flexural properties were determined after 28 days of water submersion as well, for both wet and redried specimens, revealing that the mechanical properties can be restored to a large extent in sufficiently coupled compounds. A dependence of the MA-PP content optimum on particle size was not detected. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3687–3695, 2013

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INTRODUCTION

In a previous study, the influence of maleated polypropylene (MA-PP; Table I) coupling agent (CA) flow properties, expressed by the melt flow rate (MFR), and graft level on their capability for compatibilization in PP-based WPCs with 40 and 60 m % wood content, respectively, was investigated. In this work, the influence of CA content was studied, as well, and for most properties, the positive effect was found to level off between about 5% and 10% (based on wood content).¹

Effect of Particle Size

In the current article, we have focused on one CA type which has shown good overall properties in previous investigations. For this type, we wanted to determine optimum contents more accurately than before, to finally find out if this optimum was dependent on the particle size of the wood filler.

Assuming that MA-PPs are active at the interface in WPCs, increasing the interface area by reducing the filler particle size at a given wood content should also increase the amount of CA required for achieving optimal properties. Thus, when using a coarser wood type, lower CA content optima should be found (Figure 1). This working hypothesis shall be called the “particle size hypothesis” throughout this article.

Effect of Water Absorption

As discussed in an earlier publication, water absorption (WA) is a feature of WPCs and NFCs that distinguishes them from conventional PP composites (like talc or glass fiber filled PP).² Thus, the second objective of this current work was to find out more about the influence of WA and redrying of the material on the flexural properties of WPCs. Again, CA content and wood filler particle size were considered as factors in these tests.

With regard to the literature reporting on optimal contents of CAs in NFCs and WPCs, the relevant papers known to the authors have been quoted in the publication cited already above. There is a considerable amount of published data available, as well, regarding the influence of WA on the mechanical properties of NFCs and WPCs.

Svoboda has investigated extruded WPCs with high filler content (70 m % wood) in his PhD thesis.³ He found that the tensile properties (strength and modulus) are reduced by up to 55% when the material has absorbed more than 10% moisture upon water immersion.

Lin et al. investigated WA and its effect on mechanical properties of PP-based WPCs as a function of wood content and wood pretreatment. Interestingly, tensile strength increased upon WA at wood contents below 30%, while it decreased at

Table I. Abbreviations Used in the Text

Abbreviation	Explanation
NFC	Natural fiber composite, meaning a fiber/matrix composite that contains natural fibers or wood based cellulose fibers
WPC	Wood polymer composite, meaning a filler/matrix composite that contains wood particles
M_p	Melting point (°C)
M_n	Number-average molecular weight (kDa)
M_w	Mass-average molecular weight (kDa)
IS/NIS	Impact strength/notched impact strength
WA xd	Water absorption for x days
PP-(x%)y	Polypropylene reinforced with y (x % of y)
SEM	Scanning electron microscopy
IM	Injection molding
MA-PP	Maleic anhydride grafted polypropylene
Flmod/Flstr	Flexural modulus/strength
Tmod/Tstr	Tensile modulus/strength

wood contents above 30%. Flexural properties decreased upon WA irrespective of the wood content.⁴

Bledzki et al. studied the influence of various compounding methods [twin screw extruder (TSE), kneader, high speed mixer] on the material properties of PP-based WPCs with 50% wood content. Furthermore, tensile and flexural properties were compared employing dry specimens and specimens subjected to a 24 h water treatment at 90°C. While strength values were reduced by approximately one fourth to one third, moduli were reduced by more than 50% in most cases.⁵

In another publication, Bledzki et al. compared the performance of various WPCs with that of medium density fiberboard (MDF) and solid wood. While the latter materials showed higher tensile and flexural properties in a dry state, their WA upon 28d of submersion was significantly higher compared to the WPCs. Also, while MDF and solid wood lost approximately 90% and 50% of their flexural strength, respectively, a PP-based WPC with 55% wood content showed reductions in flexural strength of less than 10% resulting from the submersion.⁶

van den Oever et al. investigated PP composites reinforced with 50% jute fibers. WA trials were performed employing seawater with 3.5% salt content. Upon 150d of immersion, flexural modulus had dropped by about 30%, and flexural strength by about 40%.⁷

Cantero et al. investigated PP-based WPCs with wood contents up to 50%. The effects of hygrothermal exposure (storage at 95% relative humidity during temperature cycling from -15°C to 55°C) on flexural properties were determined. Upon 30d of exposure, WPCs with 40% wood content lost about one third of their strength and half of their stiffness.⁸

Joseph et al. prepared PP-sisal composites with fiber contents of up to 30%. The group tested various fiber pretreatments, also studying their effect on mechanical properties before and

after exposure to boiling water for 7 h. At 30% fiber content, reductions in flexural modulus between 20% and 30% were observed, depending on pretreatment.⁹

Chow et al. investigated composites of similar composition, also covering the effects of a hot water treatment on tensile and impact properties. After 100 h of immersion time, stiffness and strength of a PP-based 30% sisal composite were reduced by almost 50%. As to Izod IS, the first 30–70 h of the hot water treatment resulted in an increase of the respective property values, probably due to plasticization effects. Toward the end of the immersion period, however, IS of the PP-30% sisal composite saw a decline of roughly 30%.¹⁰

Beg and Pickering studied the effects of water immersion on PP-40% Kraft pulp composites. For a 238d treatment at 30°C, Young's modulus and tensile strength were reduced by approximately 50% and 25%, respectively. Notched Charpy IS, however, was increased by 85% by this treatment, which the authors explained by absorbed H₂O acting as a plasticizer. An increase of the water temperature to 50°C and finally 70°C increased the negative effects on tensile properties and reduced the positive effect on NIS.¹¹

Effect of Redrying

The literature cited above (a more comprehensive overview of which is beyond the scope of this work) shows the significant effects of WA on mechanical material performance in NFCs and WPCs. Of course, the question as to which extent original properties can be recovered by material redrying is of practical relevance. Despite the large number of publications available on WA, the effects of redrying have not yet been investigated comprehensively. In fact, only two papers known to us cover this issue.

Panthapulakkal and Sain have investigated PP-hemp/glass hybrid composites, with a fixed total fiber content of 40%. Submersion in distilled water at various temperatures revealed a

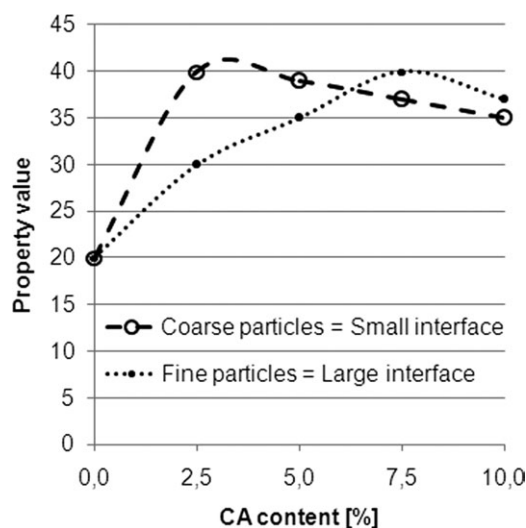


Figure 1. Schematic representation of the expected influence of particle size on CA optimum contents.

Fickian mode of diffusion for all materials tested. Tensile properties of the composites were tested before and after submersion until saturation, both in wet and in redried state. For PP-40% hemp, 65% of the original strength, but only 44% of the original modulus were retained. Redrying raised these figures to 78% and 66%, respectively. The authors interpret the incomplete recovery as an indication that water does not simply act as a plasticizer in the NFCs, but rather irreparably damages the fiber and its interface with the matrix.¹²

Taib et al. prepared composites from PP and steam exploded *Acacia mangium* fibers with 40% fiber content and 0–20% MA-PP (based on wood content) as CA. Tensile properties were determined before and after 3 months of water submersion, and again after redrying wet specimens. While the reductions in stiffness resulting from WA were around 50%, and almost independent of MA-PP content, the reductions in strength increased with MA-PP content. Thus, the beneficial effect of increasing CA content was eliminated by the water submersion treatment. In the absence of a MA-PP, redrying led to a recovery of modulus and strength by only 78% and 88%, respectively. In the presence of a CA, however, more than 90% of the tensile properties could be recovered.¹³ The interpretation of those results given in this article is similar as in Ref. 12.

Objective of this Current Work

As discussed above, the influence of particle size on WPC mechanical properties and CA content optima is of great relevance and has only scarcely been investigated as yet. Furthermore, relatively few papers on WPC WA-redrying studies are available to date. Thus, the objective of this study is twofold:

1. Investigation of the effect of wood filler particle size on WPC mechanical properties, WA, and MA-PP optimum contents.
2. Investigation of the effects of WA and redrying on WPC flexural properties as functions of wood filler particle size and content.

MATERIALS AND METHODS

Materials

All compounds subject to this study are based on the isotactic homopolymer PP grade HD120MO by Borealis. This type has an MFR_{230°C/2.16 kg} of 8.0 g/10 min, corresponding to a M_w of 370 kDa. As CA, Scona TPPP 8112 FA by BYK Altana (formerly Kometra AG) has been used. This MA-PP is based on a PP homopolymer, has a M_w of 73 kDa, and a MA graft level of 1.5% (as stated in the supplied datasheet).

As wood fillers, Lignocel® S 150 TR and BK 40/90 by J. Rettenmaier & Söhne (Rosenberg, Germany) were used. These types are made from softwood, of which approximately 90% is spruce. The mean particle sizes are 108 μm and 323 μm , respectively, and the average aspect ratio is 1.8–1.9 for both types. Figure 2 shows the sieve analysis results for both wood types. The fillers were used for compounding only at moisture contents around 6.0%. Assuming that within the WPC compounds, the wood fillers are found as spherical particles with identical densities, the finer wood type would, at identical filler contents, produce a filler/matrix interface three times as large as the coarser wood type.

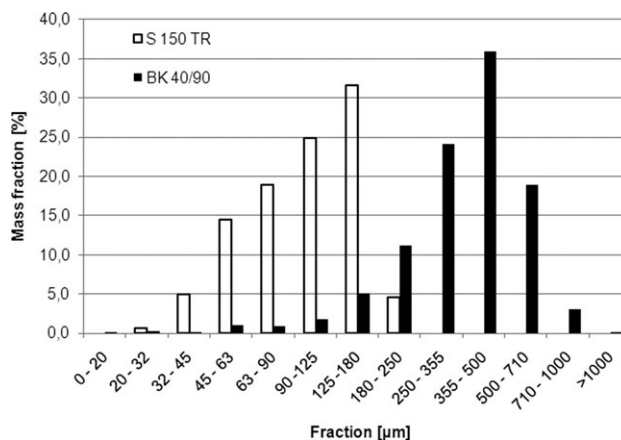


Figure 2. Sieve analysis results and particle size distribution for the two wood types used.

Methods

Wood Particle Characterization. Wood particles were subjected to sieve analysis according to DIN 66165, employing a Fritsch Analysette 3 equipment. The data recorded thereby were fitted with Gauss curves using Origin software in order to determine the mean particle size.

Particle L/d ratios were determined by a method developed at Wood K plus. Samples of 10–15 mg were separated via sieves and spread on a black sheet of paper. Next, the particles were fixed on the paper with a sheet of adhesive film. The samples thus prepared were scanned with a resolution of 2000 dpi. The resulting images were processed with ImageJ software. The dimensions of the particles were determined as Feret's diameters. This analysis method constructs tangents on the circumferential line of an object. The highest and lowest distances normal to two tangents each are taken as length and diameter, respectively.

Compounding and Specimen Preparation. Compounding of formulations according to Table II was performed on a *battenfeld-cincinnati* Fiberex K38 conical counter-rotating TSE, coupled to an *Erema* KG80 Hot die face pelletizing system. The temperature profile was set to 220/210/170/170/180°C from the hopper to the die; the pelletizer head was run at 175°C. The extruder was run with an output of 15 kg/h, at 17 revolutions/min. The raw materials (PP, MA-PP, and wood particles) were fed via *Motan-Colortronic* gravimetric dosing scales.

Shouldered bar-like specimens according to ISO 294, type A were prepared on an *Engel* VC 330/80 IM machine. The temperature profile was set to 160/175/190/190/190°C from the hopper to the die. All compounds were dried to a moisture content of <0.5% before IM. The specimens were stored in sealed low density polyethylene (LDPE) bags at room temperature for 1 week before being employed for material characterization.

Mechanical Characterization. Flexural properties were determined on a *Messphysik* Beta 20-10 universal testing machine equipped with a 1 kN load cell, according to ISO 178, at a loading rate of 3 mm/min. Tensile properties were determined on the same testing machine according to ISO 527. Tensile modulus and strength were determined at loading rates of 1 and 5 mm/min, respectively. For both flexural and tensile property determination, at least five specimens each were employed. Charpy IS was determined

Table II. Compounds Prepared and Measurements Performed on the Respective Specimens. Mechanical Properties Were Determined 1 Week After IM as Described Above. Flexural Properties Were Determined in Wet and Redried States, After 28d of Submersion

Compounds			WA 28d		
Wood type	Wood content (%)	CA	Mechanical properties	Flexural properties	Flexural properties redried
		content (% wood)			
S 150 TR	40	0	×	×	×
		5	×	×	×
		10	×	×	×
		15	×	×	×
		20	×		
	60	0	×	×	×
		5	×	×	×
		10	×	×	×
		15	×	×	×
		20	×		
BK 40/90	40	0	×	×	×
		5	×	×	×
		10	×	×	×
		15	×	×	×
		20	×		
	60	0	×	×	×
		5	×	×	×
		10	×	×	×
		15	×	×	×
		20	×		

according to ISO 179, on a Zwick 5113 equipment. At least 10 unnotched specimens each were employed (1 fU). Heat deflection temperature was determined according to ISO 75, in mode A (HDT-A), using three specimens each. The set of data generated by the methods described above is referred to as “mechanical properties” below.

Density and WA. Density of the composites was determined by a buoyancy method, employing a Sartorius analytical scale, and following ISO 1183-1.

WA of the various compounds was measured upon immersion of bars of 80 mm × 10 mm × 4 mm (cut from ISO 294, type A specimens) in distilled water. WA (%) was determined as specimen weight gain, measured on a Sartorius analytical scale.

For determining the flexural strength of wet specimens, specimens were taken out of the water, wiped with cleaning paper, put in sealed plastic bags, and measured immediately afterward. Redrying of specimens was performed at 80°C in a drier (Binder), until constant weight was reached.

RESULTS AND DISCUSSION

Effects of MA-PP Content and Wood Type in Dry State

In the following, mechanical properties measured in the dry state are discussed. Flexural properties, showing basically the

same trends as the tensile properties, will be covered within the next section, when describing the effects of WA.

Tensile Properties. Figure 3(a,b) shows the dependency of WPC tensile properties on wood type, wood content, and MA-PP content. As expected, the influence of coupling on stiffness is relatively small at low wood contents, irrespective of the filler type. This is not surprising, since modulus is measured at very low strains (0.05–0.25% according to ISO 527), when interfacial adhesion is of limited importance. However, the effect of the CA becomes more significant at the higher wood content. This probably reflects the fact that stress transfer via the fiber/matrix interface gains more importance at higher filler contents. For both filler types, 10% MA-PP is sufficient for achieving optimal stiffness. Contents above 15% lead to modulus reductions. This is probably a result of excess MA-PP diluting the matrix polymer, which might also negatively affect PP crystallization.

Interestingly, significantly higher modulus values are achievable with the finer wood type S 150 TR. Effects of particle size on WPC mechanical properties have been studied before.^{14–19} Khalil et al. have investigated PP-based WPCs prepared with wood fillers of 100, 212, and 300 μm mean particle size, respectively, and report a similar trend for the Young's modulus. The group interprets this effect as a result of better particle dispersion with decreasing particle size.¹⁹ However, this interpretation is in contradiction with mixing-energy based considerations. In fact, dispersing smaller particles in a polymer melt requires more energy for interface generation compared to dispersing coarser ones. Thus, homogeneity is more easily achieved in the latter case. The other papers cited above do not report clear correlations between particle size and stiffness.

In this context, the density of the composites tested becomes especially relevant. The two different wood fillers employed might also be compressed to a different extent during processing. This in turn might explain the effects of particle size on mechanical properties that were observed in this study. However, the measurements performed show that composite densities are a function of the wood content only, while the filler particle size does not have a significant influence. For WPCs with 40% wood, values of $1.065 \pm 0.005 \text{ g/cm}^3$ are obtained, while WPCs with 60% wood show a density of $1.165 \pm 0.004 \text{ g/cm}^3$.

As discussed above, the density hypothesis can be rejected as an explanation for the influence of particle size on stiffness observed in our study. Hence, this effect is most likely based on differences in mechanical properties between the two filler types themselves. The smaller particles should consist of a lower number of cells and thus contain less voids and defects compared to the larger particles. Therefore, the former might bring about higher inherent mechanical properties.

As to tensile strength, the influence of the MA-PP content is far more significant. The effect of CA addition levels off at around 10% for both filler types and contents. Again, a significant difference between the two wood types can be detected only at the higher level. Analogous to the results for stiffness, higher strength values are achieved with the finer S 150 TR type. This might be attributed to a higher likelihood of the larger particles

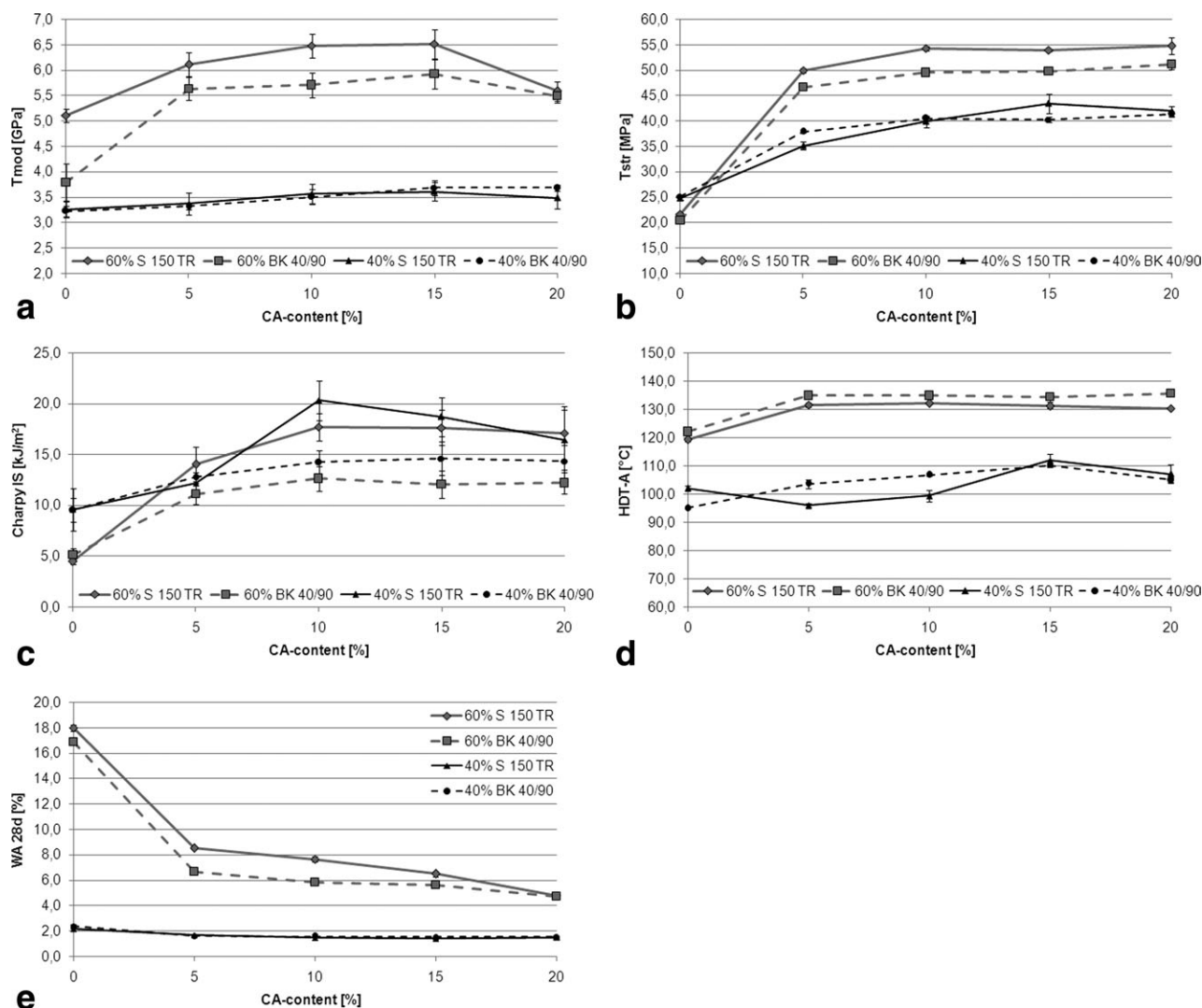


Figure 3. (a) Tensile modulus (T_{mod}) as a function of wood type, wood content, and MA-PP content. (b) Tensile strength (T_{str}) as a function of wood type, wood content, and MA-PP content. (c) Unnotched Charpy IS as a function of wood type, wood content, and MA-PP content. (d) Heat deflection temperature determined in mode A as a function of wood type, wood content, and MA-PP content. (e) WA determined as weight gain after 28d of submersion as a function of wood type, wood content, and MA-PP content. (f) Flexural modulus of WPCs with 40% and 60% wood content, respectively, before (dry) and after (28d) 28d of submersion in distilled water, and after 28d of submersion and subsequent redrying to constant weight (redr.). Moduli are given for S 150 TR (left) and BK 40/90 (right) as functions of MA-PP content. (g) Effect of 28d of WA on the flexural stiffness of WPCs with 60% wood content as a function of the MA-PP content, measured on wet and redried specimens. (h) Flexural strength of WPCs with 40% and 60% wood content, respectively, before (dry) and after (28d) 28d of submersion in distilled water, and after 28d of submersion and subsequent redrying to constant weight (redr.). Moduli are given for S 150 TR (left) and BK 40/90 (right) as functions of MA-PP content. (i) Effect of 28d of WA on the flexural strength of WPCs with 60% wood content as a function of the MA-PP content, measured on wet and redried specimens.

touching one another (especially at the higher filler level), which would in turn reduce their reinforcement contribution. Khalil et al.,¹⁹ Nourbakhsh et al.,¹⁷ and Myers et al.¹⁸ have reported similar effects of wood particle size on tensile strength of PP-based WPCs with filler contents of up to 55%.

Impact Properties. Referring to Figure 3(c), it becomes obvious that the dependency of IS on wood type, wood content, and MA-PP content is complex. At both filler levels, the finer wood type S 150 TR delivers the better performance. Interestingly, this superiority shows only in the presence of MA-PP. Without coupling, BK 40/90 and S 150 TR bring about approximately the

same IS values at both filler contents. At MA-PP contents of 10% and higher, WPC compounds with the finer wood type show a better performance compared to those with the coarser wood type. Thus, coupling seems to be more effective with the former filler type. Surprisingly, the compound with 60% S 150 TR even exceeds that with only 40% BK 40/90. All WPCs show an IS plateau from 10% MA-PP content onward, except the best performing type with 40% S 150 TR, which shows an optimum at this CA content.

It is well known that finer fillers usually lead to higher impact properties in PP composites,²⁰ and this has been shown to also

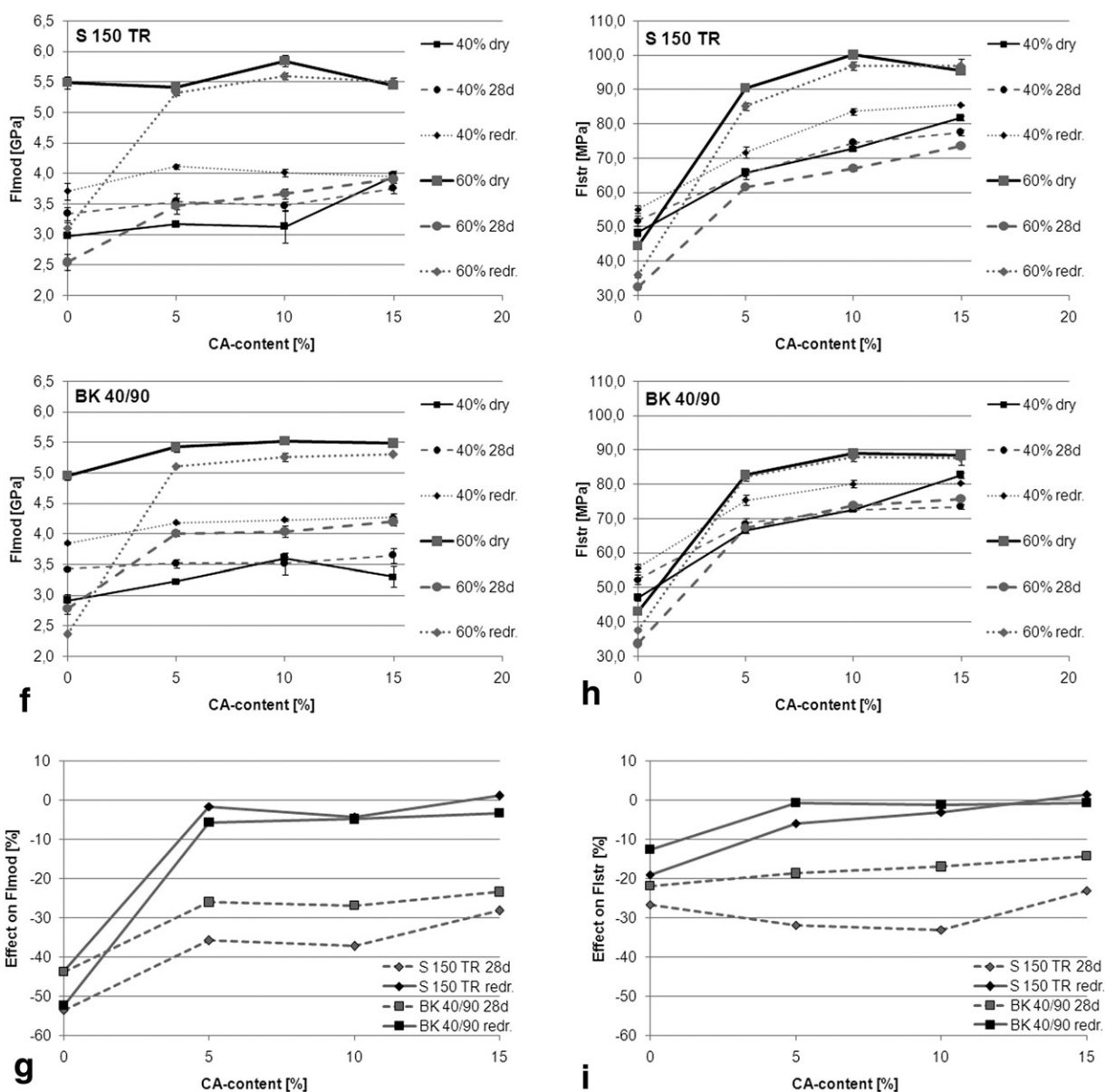


Figure 3. Continued.

hold true for at least the IS of WPCs.^{14,16,19} This phenomenon can be explained by fracture mechanics based considerations. Crack initiation leading to fracture upon impact loading occurs at defects in the specimen. Filler particles, especially when chemically incompatible with the matrix, may act as such defects. The larger the defect size, the lower is the force required for crack initiation, which dominates the fracture process in unnotched specimens. What is surprising is that this effect seems to come into play only in the presence of a CA, which is in contrast to the findings of Stark et al., who observed it also in the absence of such an additive.^{14,16}

Besides filler particles acting as defects, other effects come into play under impact loading. For example, wood particle compression during processing might also have an influence. It is well known that, for example, softwood has a density of approx-

imately 1.3 g/cm^3 as a constituent of injection molded WPCs, while the respective solid wood shows densities around 0.5 g/cm^3 .² The compression obviously taking place probably also causes defects within the particles and might affect their mechanical properties. Consequently, larger wood particles in compounds might fracture more likely than smaller ones under load. Furthermore, as reported by Dubnikova et al.²¹ and Zhuk et al.,²² decreasing particle size usually goes along with increasing debonding stress. This effect might partly compensate the influence of compression during processing on inherent particle strength.

All the phenomena mentioned above should play a role in both coupled and uncoupled compounds. Thus, they cannot explain the fact that for the WPCs subject to this study, the effect of wood particle size on IS is significant only in the presence of

MA-PP. However, a potential explanation could be based on micro-inhomogeneities occurring in the absence of a CA. As discussed in “Tensile properties” section, smaller particles require more energy input for homogeneous dispersion during compounding. By increasing the compatibility at the interface, a MA-PP can also improve homogeneity. It is possible that our compounding approach was not sufficient for completely dispersing the finer particles in the absence of a CA. Thus, the resulting micro-inhomogeneities might have eliminated the advantage of the S 150 TR wood type in formulations without MA-PP.

Adding 10% MA-PP improves the IS of PP–40% S 150 TR by 117%, compared to 49% for the IS of PP–40% BK 40/90. At the higher filler content, it is 296% compared to 147%. Thus, a comparable level of coupling has about twice the effect on WPCs with the finer wood type compared to those prepared with the coarser wood type. Adding more than 10% MA-PP does not further improve the impact performance for any formulation. As mentioned above, we had hypothesized that finer particles, producing a larger filler/matrix interface at constant filler constants, would require higher CA contents for achieving optimum properties. Judged from the mechanical testing results, this assumption is to be rejected.

Heat Deflection Temperature. Figure 3(d) shows that the HDT-A of WPCs is controlled by wood content rather than wood type and MA-PP content. At the higher filler level, the results obtained are easy to interpret: While some coupling seems necessary, from 5% MA-PP content onward, no further significant changes are observed. Over the whole CA content range, slightly higher HDT-A values are achieved with the coarser wood type BK 40/90. Larger mean particle size fillers bringing about higher HDT values have been observed in other, as yet unpublished studies several times. At the lower filler level, however, the effects of WPC formulation on HDT-A are more complex. Surprisingly, higher MA-PP contents, namely, around 15%, are required for achieving optimum performance with both fillers. Furthermore, the fact that the finer wood type S 150 TR delivers higher HDT-A values over part of the CA content range contradicts the above finding on the higher wood content level. However, the variations in performance observed are small and should thus not be over-interpreted.

To our knowledge, no other published study has dealt systematically with the effects of compound formulation on WPC heat deflection performance as yet. This is surprising given that HDT values are important criteria for many technical applications.

Water Absorption. Figure 3(e) shows that increasing the wood content from 40% to 60% leads to a dramatic increase in WA. Most probably, a threshold level above which the wood particles contact on another and form physical networks within the specimens lies within this range.²³ At the lower filler content, adding 5% MA-PP leads to a reduction of WA by approximately 0.5%, and further increasing the CA content does not lead to further improvements. At the higher filler content, adding 5% MA-PP to the uncoupled compound reduces WA by more than 50%. Further increases in CA content lead to further gradual

reductions in WA. Generally, lower WA values are obtained with the coarser wood type BK 40/90. However, at higher MA-PP contents, a similar performance can be achieved with S 150 TR.

The dependency of WA on filler particle size and CA content is unique among all composite properties tested. The curves shown in Figure 3(e) are the only ones which seem to at least partly corroborate the “particle size hypothesis” presented in “Effect of particle size” section. However, no clear plateaus or optima have been detected within the CA content range covered. Furthermore, the differences in performance between the two wood types employed are relatively small. Thus, the WA data obtained can by no means serve as a proof for the “particle size hypothesis.”

Khalil et al. have investigated composites prepared from recycled PP and three different types of wood fillers with mean particles sizes of 100, 212, and 300 μm , respectively. Wood contents of up to 50% were studied; however, no CAs were used.¹⁹ The group reported an increase in WPC WA with increasing particle size. A “better fiber/matrix interaction” is ascribed to the smaller particles. While this interpretation may raise some doubts, the fact remains that the data presented are in contradiction to our results. A potential explanation for this discrepancy might be neglected differences in fiber aspect ratios. Furthermore, the Soxhlet extraction procedure that was applied to the fillers before compounding might change their WA behavior compared to the fillers used in our work. To our knowledge, no other published study deals with the effects of wood filler particle size on WPC WA.

Effects of MA-PP Content and Wood Type in Wet State

Figure 3(f) shows that WA upon submersion for 28d has significant effects on WPC flexural stiffness. At the lower filler content level, a positive effect is observed for both wood types. Given the fact that weight gain after 28d is around 2% and thus relatively small for these composites [Figure 3(e)], this result is probably not accounted for by absorbed moisture after all. Rather, ongoing crystallization in the specimens during the submersion phase might explain increased moduli. When the specimens are re-dried to constant weight at 80°C, stiffness increases even further, probably also because of crystallinity being increased by this treatment. The effects of MA-PP content are relatively small on the lower filler content level.

For WPCs with the higher filler content employed, WA leads to drastic reductions in stiffness, ranging from 53% to 28% for S 150 TR and from 44% to 23% for BK 40/90 [Figure 3(f,g)]. For each filler type, the negative effect decreases with increasing CA content. Apparently, a CA content of 5% is sufficient to significantly reduce the negative effect of the submersion treatment, especially for redried specimens, for which almost original property values are achieved (meaning net effects close to 0%). While the effect of drying is relatively small in the absence of an MA-PP, it improves stiffness by 20–35% at CA contents from 5% onward. Thus, it can be concluded that WA leads to irreversible effects (damage) of the composites in the absence of CAs, while original properties can almost be restored when a CA has been added to the formulation. The latter is probably a result of the different absolute amounts of absorbed water for

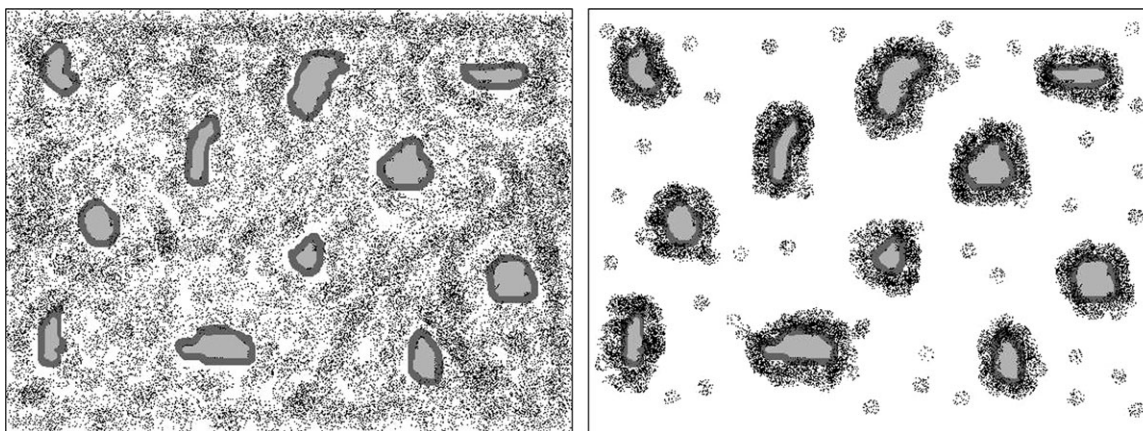


Figure 4. Composite cross sections to illustrate possible CA distribution patterns. The fillers/fibers are shown in black, the interphase in gray, and the matrix in white, while CA molecules are represented by red dots. Left: CA distributed randomly throughout the matrix; Right: CA accumulated in the interphase.

formulations with and without MA-PP. Above a certain WA threshold, the wood particles themselves and/or their interface with the matrix seem to be damaged irreparably.

Figure 3(h) shows that the effects of WA on flexural strength are much smaller than those that the submersion treatment induces in terms of stiffness. On the lower filler content level, strengths are almost unchanged as measured on wet specimens and are even increased in case of the redried specimens. Most probably, this is an effect of the drying process analogous to annealing. At the higher filler content level, strengths are significantly reduced but can almost completely be restored by specimen redrying.

Figure 3(i) shows even more clearly that WPCs with 60% wood content and MA-PP contents above 5% almost completely regain their flexural strength upon redrying. As to the wet specimens, a linear dependency of effect on CA content is found for the BK 40/90 wood type, while for the finer filler S 150 TR, the dependency is more complex. The detrimental effect of absorbed moisture is more pronounced here compared to the coarser filler type. This might be explained by higher absolute amounts of WA for S 150 TR, particularly at MA-PP contents between 5% and 15% [Figure 3(e)]. An interpretation thereof is given in “Water absorption” section. Total losses in strength are between 14% and 33%. As for stiffness, the fact that only 5% MA-PP are sufficient for almost complete recovery of strength after redrying indicates that irreparable damage occurs above a certain absolute WA threshold. Judging from the WA data presented in Figure 3(e), this threshold must be somewhere between 9% and 17% weight gain.

Comparing Figure 3(g,i), it becomes obvious that WA has a far more pronounced effect on stiffness than on strength. This is in accordance with several of the previous studies cited above.^{5,8,11,13} It is well known that increasing the moisture content has negative effects on solid wood tensile properties.^{24,25} Most probably, filler particles in WPCs absorbing water exhibit similar tendencies. Regarding stiffness, the softening of the reinforcement is more or less directly imparted to the composite

via the “rule of mixtures.” As to the effects of moisture on ultimate strength, the situation is more complex, because several mechanisms come into play. Besides the supposed reduction of particle strength, absorbed water might also interfere with wood-OH-MA-PP interactions or linkages, reducing interfacial adhesion. On the other hand, swelling of the filler particles would increase the contribution of mechanical interlocking to stress transfer at the interface. The fact that absorbed moisture reduces moduli more than strength indicates that under these conditions, it is the reinforcement potential of the particles themselves that suffers rather than the stress transfer via the particle/matrix interface.

CONCLUSION

With all formulations tested, for most properties a plateau is reached at a CA content of 5% (relative to the wood content). Tensile strength and IS can be further improved when the MA-PP content is increased to 10%. The most significant reduction in WA is achieved by increasing the MA-PP content from 0% to 5%. However, when it is further increased to 20%, representing the upper limit of the content range tested, further gradual reductions of WA are seen.

Clear optimum CA contents as a function of wood filler particle size were not detected. Despite producing larger fiber/matrix interfaces (at constant gravimetric/volumetric filler contents, assuming that the particles are homogeneously distributed and not forming agglomerates), smaller particles do not require higher amounts of MA-PP to fully contribute to composite strength. This in turn is an indication that the CA is rather distributed randomly throughout the matrix than accumulated in the interphase. In this case, at a given content level the CA concentration in the interphase would be independent of the filler/matrix interface area (Figure 4).

As regards the effects of WPC WA on flexural properties, only the composites with 60% filler content are significantly affected. For those, 28d of submersion leads to reductions in stiffness of approximately 50%, while strength is reduced by about one third. While in the absence of MA-PP, redrying has only small

positive effects, it leads to almost complete restoration of composite properties at CA contents of 5% and higher.

REFERENCES

1. Sobczak, L.; Welsch, R.; Brüggemann, O.; Haider, A. J. *Thermoplast. Compos. Mater.* **2012**. Published online before print June 11, 2012, DOI: 10.1177/0892705712447806.
2. Sobczak, L.; Lang, R. W.; Haider, A. *Compos. Sci. Technol.* **2012**, *72*, 550.
3. Svoboda, M. A. Werkstoffe aus nachwachsenden Rohstoffen. Thesis/Dissertation; Montanuniversität Leoben; **2003**.
4. Lin, Q.; Zhou, X.; Dai, G. J. *Appl. Polym. Sci.* **2002**, *85*, 2824.
5. Bledzki, A. K.; Letman, M.; Viksne, A.; Rence, L. *Compos. Part A: Appl. Sci. Manuf.* **2005**, *36*, 789.
6. Bledzki, A. K.; Gassan, J.; Theis, S. *Mech. Compos. Mater.* **1998**, *34*, 563.
7. van den Oever, M. J. A.; Snijder, M. H. B. *J. Appl. Polym. Sci.* **2008**, *110*, 1009.
8. Cantero, G.; Arbelaiz, A.; Mugika, F.; Valea, A.; Mondragon, I. J. *Reinf. Plast. Compos.* **2003**, *22*, 37.
9. Joseph, P. V.; Rabello, M. S.; Mattoso, L. H. C.; Joseph, K.; Thomas, S. *Compos. Sci. Technol.* **2002**, *62*, 1357.
10. Chow, C. P. L.; Xing, X. S.; Li, R. K. Y. *Compos. Sci. Technol.* **2007**, *67*, 306.
11. Beg, M. D. H.; Pickering, K. L. *Compos. Part A* **2008**, *39*, 1748.
12. Panthapulakkal, S.; Sain, M. J. *Compos. Mater.* **2007**, *41*:1871.
13. Taib, R.; Ishak, Z. A.; Rozman, H. D.; Glasser, W. G. *J. Thermoplast. Compos. Mater.* **2006**, *19*, 475.
14. Stark, N. M.; Rowlands, R. E. *Wood Fiber Sci.* **2003**, *35*, 167.
15. Bledzki, A. K.; Faruk, O. *Appl. Compos. Mater.* **2003**; *10*, 365.
16. Stark, N. M.; Berger, M. J. The Fourth International Conference on Woodfiber-Plastic Composites, Madison, Wisconsin; USDA Forest Service, Washington, DC; **1998**.
17. Nourbakhsh, A.; Karegarfard, A.; Ashori, A. J. *Thermoplast. Compos. Mater.* **2010**, *23*, 169.
18. Myers, G. E.; Chahyadi, I. S.; Coberly, C. A.; Ermer, D. S. *Int. J. Polym. Mater.* **1991**, *15*, 21.
19. Khalil, H.; Shahnaz, S. B.; Ratnam, M. M.; Ahmad, F.; Fuaad, N. A. *J. Reinf. Plast. Compos.* **2006**, *25*, 1291.
20. Jilken, L.; Malhammar, G.; Selden, R. *Polym. Test.* **1991**, *10*, 329.
21. Dubnikova, I. L.; Berezina, S. M.; Antonov, A. V. *J. Appl. Polym. Sci.* **2004**, *94*, 1917.
22. Zhuk, A. V.; Knunyants, N. N.; Oshmyan, V. G.; Topolkar-aev, V. A.; Berlin, A. A. *J. Mater. Sci.* **1993**, *28*, 4595.
23. Wang, W.; Sain, M.; Cooper, P. A. *Compos. Sci. Technol.* **2006**, *66*, 379.
24. Östman, B. A. L. *Wood Sci. Technol.* **1985**, *19*, 103.
25. Lenth, C.; Sargent, R. *Drying Technol.* **2008**, *26*, 1112.