

INFLUENCE OF FLOWABILITY AND MAH-CONTENT OF MALEATED POLYOLEFINES ON RHEOLOGICAL AND MECHANICAL INTERACTION EFFECTS OF WOOD FILLERS IN POLYOLEFINES

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ABSTRACT

Wood plastic composite (WPC) is an important representative of the group of natural fibre reinforced plastics. In order to bond the polar wood fibres chemically to the nonpolar polymer matrix, coupling agents are used. The most important group of coupling agents for WPC are maleated polyolefins in which the backbone polymer as well as the maleic anhydride content (MAH-content) can be varied.

In this study, the influence of the flowability and the MAH-content of coupling agents on rheological and mechanical interaction effects of wood fillers in different WPC formulations have been investigated. It has been shown that the MAH-content as well as the flowability of coupling agents is in terms of rheological interaction effects of negligible influence. Furthermore, it was found that mechanical interactions are significantly influenced by coupling agents. In this context, the flowability of the coupling agent is of greater importance than the MAH-content.

1. INTRODUCTION

Natural fibre reinforced plastic have constantly high growth rates in the global market for years. Wood plastic composite (WPC) is an important representative of this class of materials. WPC consists of a thermoplastic matrix polymer which is filled with wood flour and additives that improve the processability and the product properties. A challenge in processing and application of WPC is the incompatibility of the polar wood fibres and the non-polar polymer matrix. This incompatibility generally results in poor fibre wetting and weak fibre-matrix adhesion [1, 2]. This lack of adhesion prevents efficient stress transfers [3]. There are several ways to improve the fibre-matrix adhesion. Fibre surfaces can be treated using physical, physico-chemical or chemical methods depending on the polymer matrices to be used [4]. One approach to improve adhesion between the wood fibres and polymer matrix is by adding a block copolymer compatibilizer [2, 5], which is able to form covalent bonds between the anhydride groups of the coupling agent and the hydroxyl groups of the wood particles. The formation of covalent bonds is one of the reasons for strength improvement. Entanglements between the polymeric backbone of the coupling agent and the matrix polymer can be created, which acts as physical cross-links [6]. When stress is applied, it can be transmitted to the fibre through these physical cross-links [6].

The most important group of coupling agents for WPC are maleated polyolefins in which the backbone polymer as well as the maleic anhydride content (MAH-content) can be varied. The

effectiveness of a coupling agent is determined by its ability to form covalent bonds and physical cross-links. A high number of covalent and hydrogen bonds with the wood filler can be achieved by high functionalization with maleic anhydride groups of the adhesion promoter. A high entanglement density and a high number of physical cross-links between the matrix polymer and the coupling agent can be achieved by a high molecular weight of the coupling agent. However, a high molecular weight is associated with a low diffusion rate of the coupling agent within the wood-filled polymer melt. If the diffusion rate is too low, only a small amount of the coupling agent might form chemical bonds with the wood particles.

Several studies have been published in which a better dispersion of the fibres in the polymeric matrix was achieved [1, 6, 7]. The reason for this is a good wetting of the fibres by the coupling agent, which is affected by its diffusion rate. A better dispersion of the fibres results in more interparticular interactions. In earlier studies, the rheological effect of interparticular interactions have been investigated [8, 9, 10]. According to this, the intensity of interparticular interactions can be expressed by the *interaction exponent* (χ). The *generalized interaction function* is used in order to describe the interaction exponent as a function of the consistency (K_c), taking into account the transition from negligible interparticle interactions to the domain of non-negligible interparticle interactions as shown in Eq.(1):

$$\chi = \frac{n_c}{n_0} = f(K_c) = \frac{1}{\left(1 + \left(\lambda \cdot \ln\left(\frac{K_c}{K_0}\right)\right)^a\right)^{\frac{b}{a}}} \quad (1)$$

χ	interaction exponent	[-]
n_c	flow index (suspension)	[-]
n_0	flow index (matrix polymer)	[-]
K_c	consistency (suspension)	[Pa s ⁿ]
K_0	consistency (matrix polymer)	[Pa s ⁿ]
λ, a, b	model parameter	[-]

The aim of this study is to investigate the impact of the flowability and the MAH-content of different coupling agents on the dispersibility of the wood fibres in polyolefin melts and thus on rheological interparticular interaction effects. Furthermore, it is investigated to which extent of the flowability and the MAH-content of different coupling agents influence the formation of chemical bonds and physical cross-links and thus the ability of interfacial stress transfer.

2. MATERIALS AND METHODS

In this study two different types of matrix polymers were used. On one hand low-density polyethylene (LDEP, Lupolen 2420 K), which is a highly branched polymer with strongly exhibited shear thinning flow behaviour and on the other hand polypropylene (PP, Moplen HP 501L), which is a homopolymer with linear structure. The softwood fibres Lignocel® BK 40/90 was used as filler (Fig. 1). In order to characterize the filler with respect to its particle size distribution, a particle size analysis was carried out by laser diffraction using Mastersizer 3000 (Malvern Instruments GmbH), which led to the following results: $d_{10} = 261.974 \mu\text{m}$, $d_{50} = 526.834 \mu\text{m}$, $d_{90} = 1167.567 \mu\text{m}$. The geometry of the filler particles were characterized by transmitted light microscopy using VHX 2000D (Keyence Microscopes). In order to improve the interfacial adhesion between the polar wood fibres and the nonpolar

matrix polymer, three different coupling agents (CA) have been used in this study: (1) SCONA TSPE 1112, a linear low density polyethylene (LLDPE) grafted with MAH, (2) SCONA TPPP 8112, and (3) SCONA TPPP 2112 which are both polypropylene (PP) grafted with MAH. The melt flow rates (MFR) and the MAH-contents of the coupling agents are listed in Table (1).

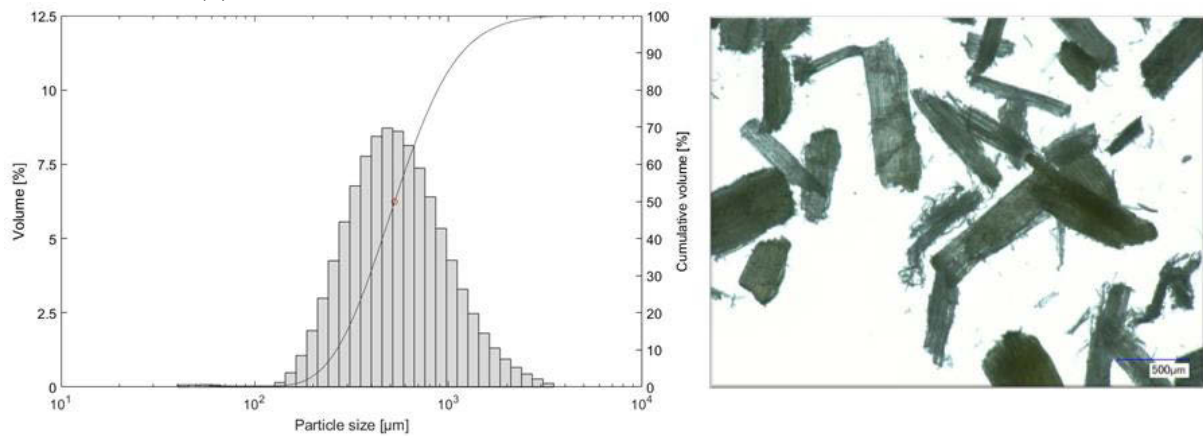


Figure 1 left: Particle size distribution of the wood fibres, right: transmitted light microscopy of the wood fibres, magnification: 100x

Table 1 MFR and MAH-content of the coupling agents used in this study

	melt flow rate (MFR)	MAH-content
	[g/10 min]	[wt.%]
SCONA TSPE 1112	> 5 (190 °C, 5 kg)	2
SCONA TPPP 8112	> 80 (190 °C, 2.16 kg)	1.4
SCONA TPPP 2112	2 – 7 (190 °C, 2.16 kg)	0.9 – 1.2

Figure 2 shows comparatively the rheological properties of coupling agents and matrix polymers which are used in this study. While the flow properties of the PE-based coupling agent TSPE 1112 are quite similar to the matrix polymer, the PP-based coupling agents show significant differences in flow behaviour. Due to its lower molecular weight, TPPP 8112 exhibit a significantly higher flowability compared to TPPP 2112. The flow characteristics of TPPP 2112 and the PP matrix are almost identical.

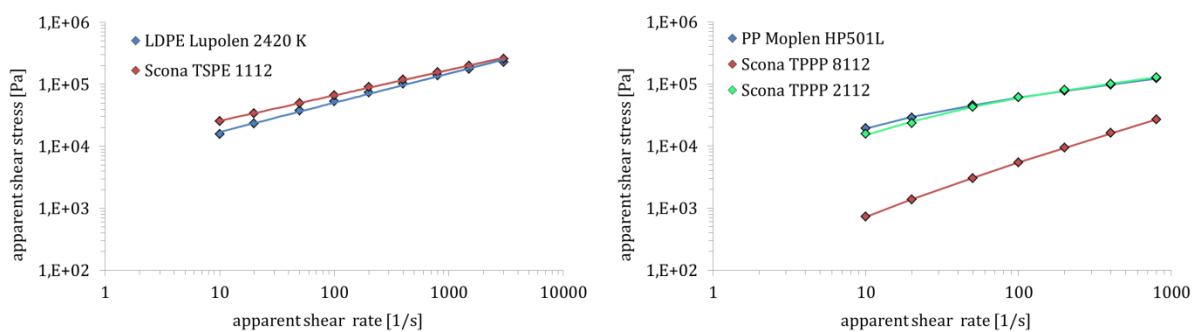


Figure 2 Flow functions of matrix polymers and coupling agents, left: PE-based, right: PP-based

The preparations of all formulations were carried out by compounding on the co-rotating twin screw extruder, with a melt temperature of 190 °C. In order to investigate the influence of the flowability and the MAH content of the coupling agents on rheological interaction effects of the wood particles, the flow behaviour of the WPC melts was analysed by means of high pressure capillary rheometry, Smart RHEO 5000 twin bore (CEAST, Instron®) using a round

die with a diameter of 2 mm and a length of 40 mm. In order to obtain conclusions on mechanical interaction effects of the wood particles, tensile tests were carried out on standard test specimens. All tension tests were performed by using an electrodynamically testing machine (ElectroPuls™ E3000, Instron®).

3. RESULTS AND DISCUSSION

3.1 Influence of coupling agent on rheological interaction effects of wood fillers

3.1.1 LDPE-based WPC

Figure 3 shows the viscosity functions of wood fibres (WF) filled LDPE. On the left, without the use of coupling agents and on the right, with a constant mass content of 2 wt.% TSPE 1112. Figure 3 clearly shows that the flow behaviour of the WPC melts is hardly affected by the use of coupling agents. All viscosity functions exhibit shear thinning flow behaviour. The flow behaviour of the LDPE-based WPC melts is highly influenced by the wood fillers. Due to their fibrous structure, these particles have a great tendency to interact with one another.

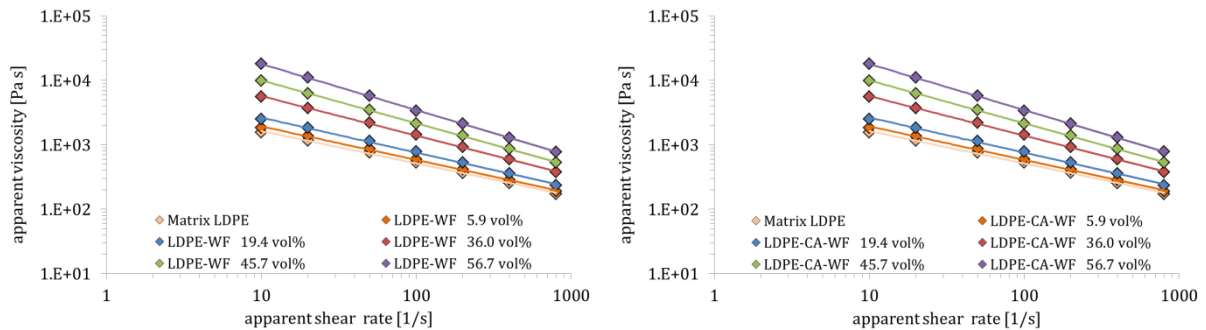


Figure 3 Viscosity functions of LDPE-based WPC, left: without coupling agent, right: with 2 wt.% TSPE 1112

As mentioned above, the rheological effect of interparticular interactions can be mathematically described by Eq.(1). Based on the measured data for LDPE-based WPC without coupling agent, the following values for the empirical model parameters have been found, $\lambda = 0.056$, $a = 1.219$, $b = 6.598$.

Figure 4 clearly shows that the pairs of values (consistency (K) / interaction exponent (χ)) of LDPE-based WPC with the use of coupling agent are almost similar to the interaction function of LDPE-based WPC without coupling agent. Hence, the characteristic of interparticle interactions is not affected by the use of the coupling agent TSPE 1112.

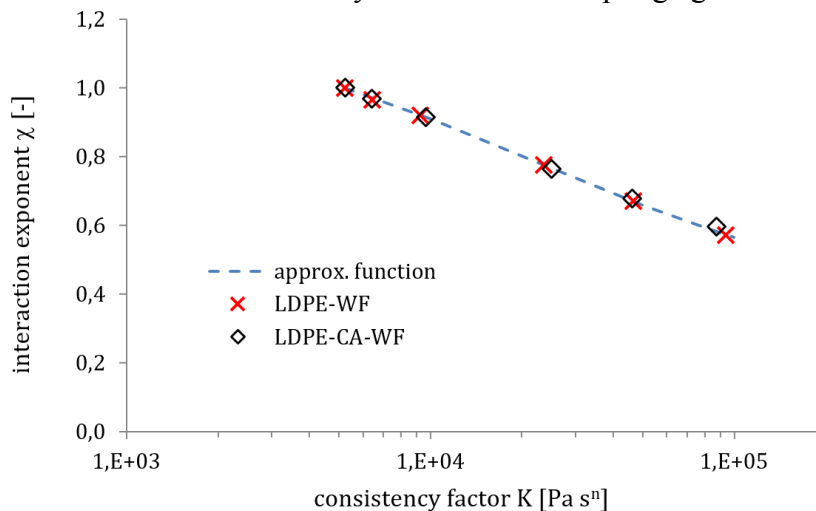


Figure 4 Interaction function LDPE-based WPC

3.1.2 PP-based WPC

Figure 5 shows the viscosity functions of PP-based WPC. On the left, without the use of coupling agents and on the right, with a constant mass content of 2 wt.% TPPP 8112. Similar to the LDPE-based WPC, the flow behaviour of the wood fibres filled PP melt is only slightly influenced by the use of coupling agents.

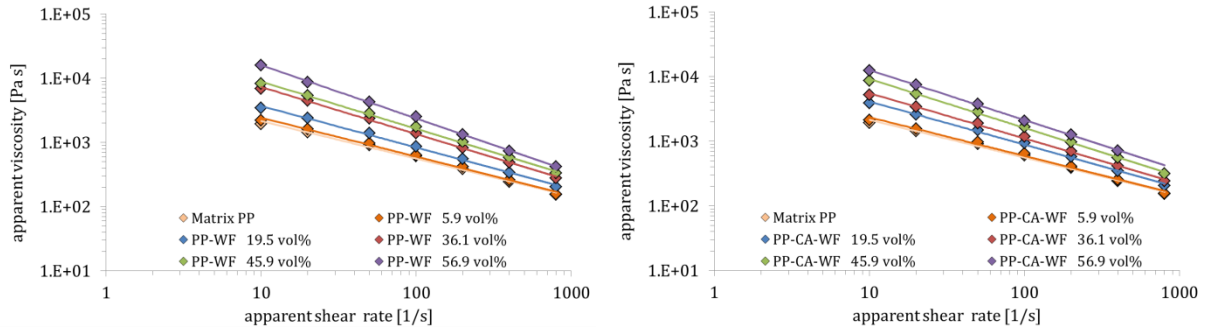


Figure 5 Viscosity functions of PP-based WPC, left: without coupling agent, right: with 2 wt.% TPPP 8112

According to Eq. (1), the following parameters have been found on the basis of the measured data for PP-based WPC, $\lambda = 0.012$, $a = 1.253$, $b = 86.254$.

Also the pairs of values (consistency (K) / interaction exponent (χ)) of PP-based WPC with the use of coupling agent are almost similar to the interaction function of PP-based WPC without coupling agent (Fig. 6). Consequently, it can also be concluded for the wood fibres filled PP that the coupling agent TPPP 8112 has almost no influence on the characteristic of interparticle interactions.

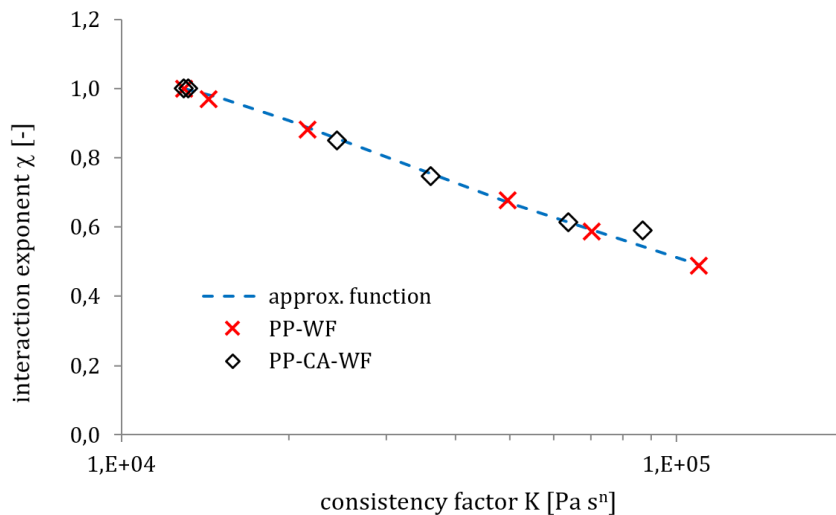


Figure 6 Interaction function PP-based WPC

In order to investigate the influence of the flowability and the MAH-content of the coupling agents on rheological interaction effects of the wood particles within the WPC melt, another coupling agent (TPPP 2112), whose flow properties are very similar to those of the matrix polymer, were used in addition to the low-viscosity coupling agent (TPPP 8112). Although the viscosity function of TPPP 8112 is significantly lower in comparison to the viscosity functions of TPPP 2112 and the matrix polymer PP (Fig. 2), the viscosity function of the WPC is not affected (Fig. 7), independent of the coupling agent content.

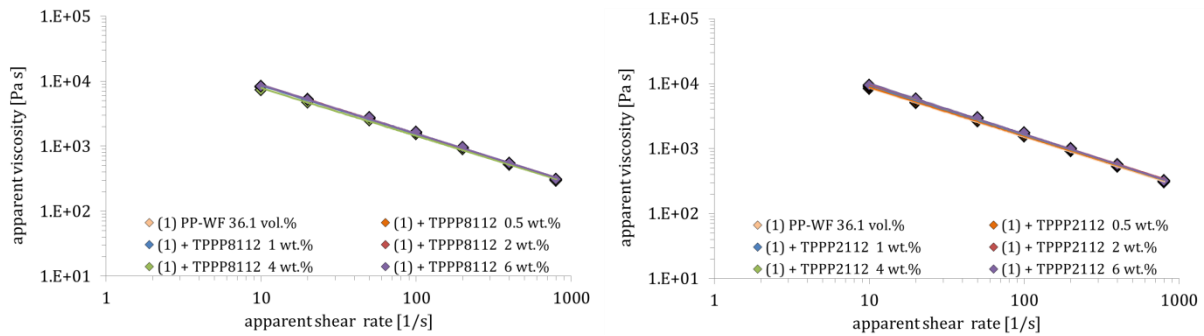


Figure 7 Viscosity functions of PP filled with 36.1 vol.% wood flour and with variation of the coupling agent content, left: TPPP 8112, right: TPPP 2112

Obviously, the low-viscosity coupling agent (TPPP 8112) does not act like an inner lubricant. This is apparently due to the immobilization of the coupling agent by esterification of the anhydride groups of the coupling agent on the hydroxyl groups of the wood particles during compounding. Therefore, it can be concluded that both the MAH-content and the flowability of coupling agents are in terms of rheological interaction effects of negligible influence.

3.2 Influence of coupling agent on mechanical interaction effects of wood fillers

3.2.1 Variation of wood content at a constant amount of coupling agent

The mechanical properties of all different WPC formulations were characterized by tensile tests and compared with one another. For both the LDPE-based WPC and the PP-based WPC, the tensile modulus increases with increasing volume content of the wood fillers (Fig. 8). This can be attributed to the significantly higher Young's modulus of the wood fibres. Furthermore, the addition of coupling agents leads to better stress transfer from the polymer matrix to the wood fibres.

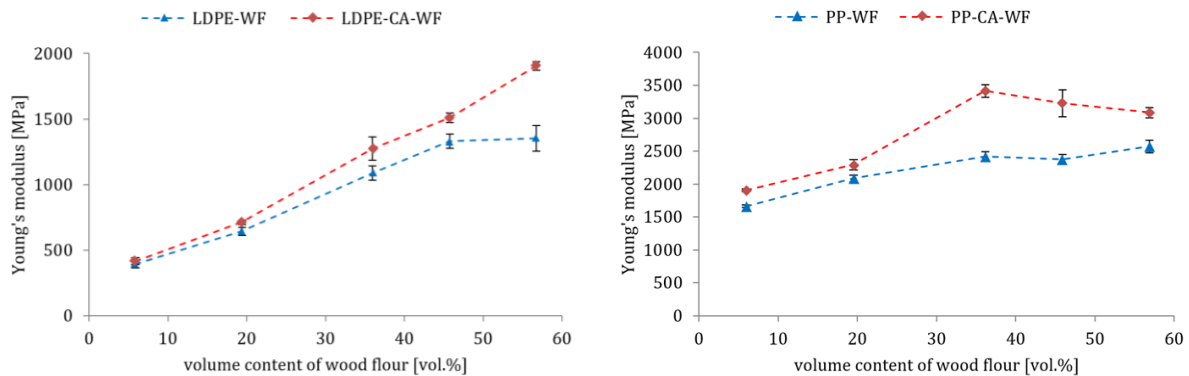


Figure 8 Young's modulus versus volume content of wood flour, left: LDPE-based WPC, right: PP-based WPC

Figure 9 shows that the tensile strength of the wood filled polyolefines decreases without the use of coupling agents. When 2 wt.% coupling agent is added, the tensile strength increases for both the LDPE-based WPC and the PP-based WPC. At a volumetric wood filler content of approximately 36 vol.% a maximum in tensile strength is achieved. This indicates an optimal wetting of the wood fibres by the coupling agent, which is a prerequisite for a good stress transfer between polymer and wood fillers.

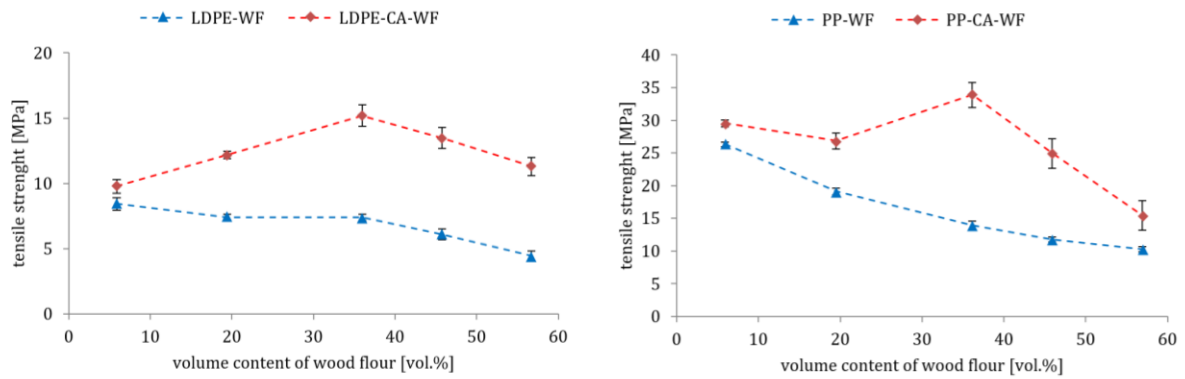


Figure 9 Tensile strength versus volume content of wood flour, left: LDPE-based WPC, right: PP-based WPC

The elongation at break is shown in Figure 10. A decrease in fracture strain with increasing volume content of wood has been observed for LDPE-based WPC as well as for PP-based WPC.

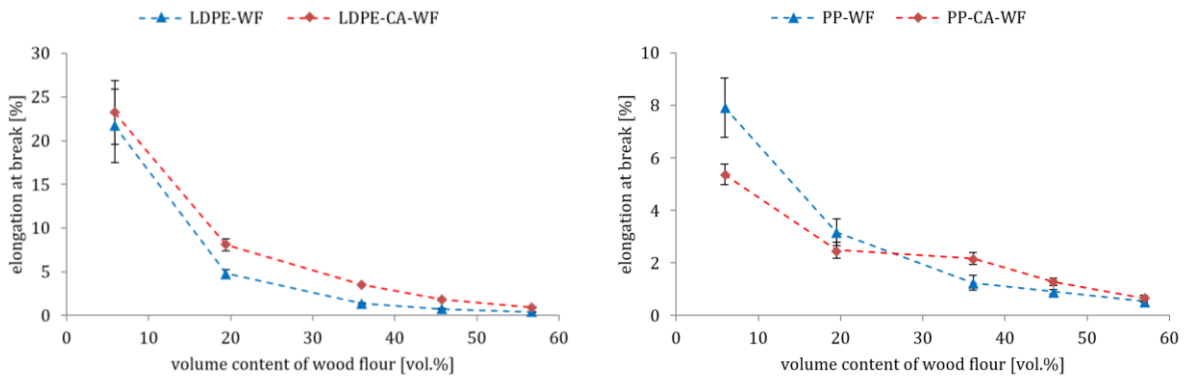


Figure 10 Elongation at break versus volume content of wood flour, left: LDPE-based WPC, right: PP-based

The characteristic decline in fracture strain for particle filled polymer compounds is well known and is hardly influenced by the use of coupling agents. This is caused by local strain increases, the so-called “strain-expansion”, which occurs in the polymer matrix between the filler particles perpendicular to the direction of loading [11, 12]. Strain-expansions are the result of stress concentrations which are caused by differences in stiffness between wood filler and matrix polymer, notch effects on the interface between filler particle and polymer as well as on small pores within the compound.

Figure 11 and 12 illustrate exemplarily the fracture-mechanical material behaviour of LDPE filled with approx. 6 vol.% wood flour. The images were taken by means of transmitted light microscopy at approx. 30 μm thin microtome samples. Notch effects which lead to strain-expansions are clearly recognisable, for example Fig. 11 (a.) or Fig. 12 (c.). Furthermore, the differences in stress transfer at the interface between wood particles and polymeric matrix are well noticeable. Figure 11 (b.) shows the poor interfacial adhesion between wood filler and LDPE, whereas Figure 12 (d.) clearly shows that the crack runs straight through the wood fibres. This is due to chemical bonding of the coupling agent to the filler, which allows a higher interfacial stress transfer.

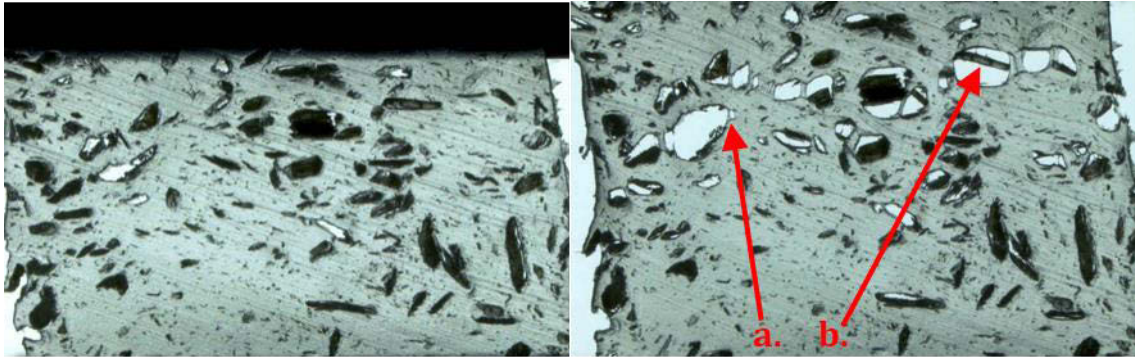


Figure 11 LDPE filled with approx. 6 vol.% wood flour, uncompatibilized, left: unloaded sample, right: elongated sample

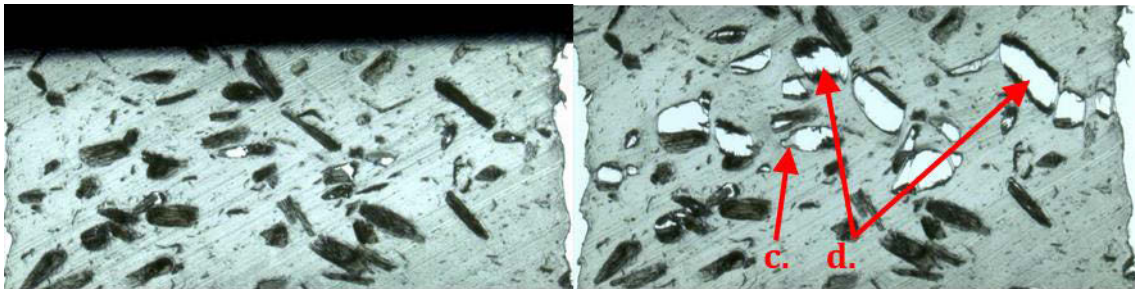


Figure 12 LDPE filled with approx. 6 vol.% wood flour, compatibilized with 2 wt.% coupling agent, left: unloaded sample, right: elongated sample

3.2.2 Variation of type and content of coupling agent at PP filled with 36.1 vol.% wood flour

In order to investigate the influence of the flowability and the MAH-content of the coupling agents on mechanical interaction effects, both PP-based coupling agents (TPPP 2112 and TPPP 8112) were used in different concentrations. Despite the negligible influence of the coupling agents on the flow behaviour of WPC, the mechanical properties can be significantly improved. The change in Young's modulus and tensile strength with the mass content of the coupling agents is shown in Figure 13, whereas the elongation at break is shown in Figure 14.

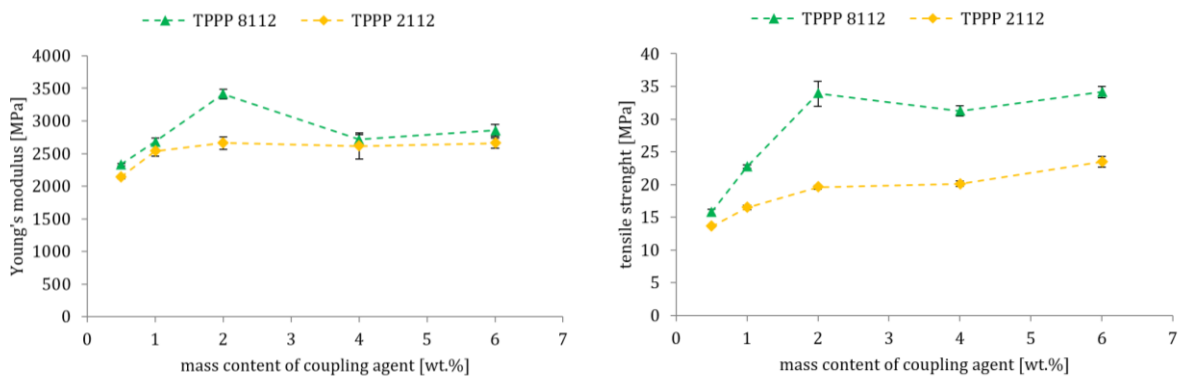


Figure 13 Comparison of TPPP 8112 and TPPP 2112, left: Young's modulus versus mass content of coupling agents, right: tensile strength versus mass content of coupling agents

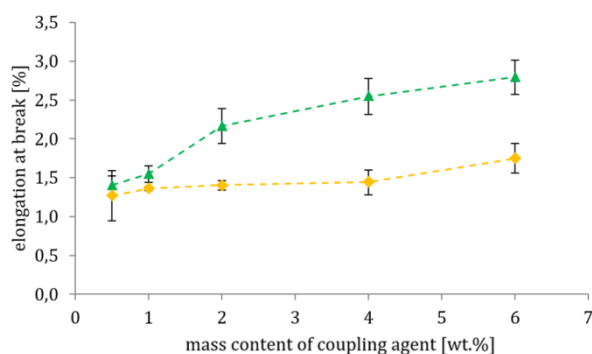


Figure 14 Comparison of TPPP 8112 and TPPP 2112, elongation at break versus mass content of coupling agents

The results clearly show that the low-viscosity coupling agent (TPPP 8112) has a greater impact on the mechanical properties. The maximum tensile strength can be achieved at significantly lower concentrations by using the more flowable coupling agent. Thus, the flowability of the coupling agent has a considerable influence on its effectiveness. The reason for this is a higher diffusion rate within the WPC melt, which is decisively influenced by the molecular weight of the backbone polymer. The higher the diffusion rate, the more esterification of the anhydride groups of the coupling agent on the hydroxyl groups of the wood particles can occur during compounding.

With regard to the influence of the MAH-content on mechanical interaction effects, both coupling agents show different results. In the case of the low-viscosity coupling agent (TPPP 8112), the tensile strength reaches a maximum at a mass content of 2 wt.%, which cannot be increased by increasing its mass content. Due to the high diffusion rate, TPPP 8112 can obviously wet the wood particles optimally at a mass content of 2 wt.% and form covalent and hydrogen bonds. As a result of the slower diffusion rate of the coupling agent TPPP 2112, the wood fibres cannot be optimally wetted even at the highest mass content of 6 wt.%. This leads to a lack of interfacial stress transfer and a lower tensile strength.

4. CONCLUSION

In this study, the influence of the flowability and the MAH-content of maleated polyolefins as coupling agents rheological and mechanical interaction effects in different WPC formulations have been investigated. On the basis of the results, the following conclusions can be drawn.

The flow behaviour of wood filled polyolefin melts is strongly influenced by interparticular interaction effects. The generalized interaction function can also be used to describe interparticular interaction effects of filled polyolefin melts when adding coupling agents. Both MAH-content and flowability of coupling agents are in terms of rheological interaction effects of negligible influence.

The mechanical properties of WPC are significantly improved by the use of coupling agents, which are able to form covalent and hydrogen bonds between the anhydride groups of the coupling agent and the hydroxyl groups of the wood particles. Compared to the MAH content, the flowability of the coupling agent has a greater effect on the mechanical interaction effects.

REFERENCES

- [1] H. Sojoudiasli, M.-C. Heuzey, and P. J. Carreau, "Rheological, morphological and mechanical properties of flax fiber polypropylene composites: influence of compatibilizers", *Cellulose* (2014) 21:3797–3812, Springer, Dordrecht, 2014

- [2] M. Kaseem, et al., “Material Properties of Polyethylene/Wood Composites: A Review of Recent Works”, *Polymer Science, Ser. A*, 2015, Vol. 57, No. 6, pp. 689–703, Pleiades Publishing, Ltd., 2015.
- [3] M. H. Schneider and K. I. Brebner, “Wood-polymer combinations: The chemical modification of wood by alkoxysilane coupling agents”, *Wood Sci. Technol.* 19:67-73, Springer, 1985
- [4] C. Miao, and W. Y. Hamad, “Cellulose reinforced polymer composites and nanocomposites: a critical review”, *Cellulose* (2013) 20:2221–2262, Springer, Dordrecht, 2013
- [5] K. Oksman, “Improved interaction between wood and polymers in wood/polymer composites”, *Wood Science and Technology* 30 (1996) 197-205, Springer, 1996
- [6] A. Arbelaiz, et al., “Mechanical properties of short flax fibre bundle/polypropylene composites: Influence of matrix/fibre modification, fibre content, water uptake and recycling”, *Composites Science and Technology* 65 (2005) 1582–1592, Elsevier Ltd., 2005
- [7] A. K. Rana, et al., “Short Jute Fiber-Reinforced Polypropylene Composites: Effect of Compatibilizer”, *Journal of Applied Polymer Science*, Vol. 69, 329-338 (1998), John Wiley & Sons. Inc., 1998
- [8] H. Hansmann, N. Laufer und S. Kühn, “Investigation on the Flow Behavior of WPC Melts”, A. K. Bledzki und V. E. Sperber, Hrsg., München: Hanser, 2012, pp. A6-1 - A6-11
- [9] N. Laufer, H. Hansmann, M. Koch, “High Pressure Capillary Rheometer on Wood Plastic Composites with Variation of Wood Content and Matrix Polymer”, 58th Internationale Wissenschaftliche Kolloquium, Ilmenau 2014
- [10] N. Laufer, H. Hansmann, M. Koch, “Rheological Characterisation of the Flow Behaviour of Wood Plastic Composites in Consideration of Different Volume Fractions of Wood”, 2nd International Conference on Rheology and Modeling of Materials, Miskolc-Lillafüred, 2015
- [11] G. W. Ehrenstein, *Polymer Werkstoffe*, 2. Aufl., Hanser Verlag, München, 1999
- [12] K.J. Strack, “Crack-toughened epoxies for room-temperature applications”, MOTORLESS FLIGHT RESEARCH, National Technical Information Service, Springfield, 1973

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