SURFACE MODIFICATION OF FILLERS AND REINFORCEMENTS FOR IMPROVED PERFORMANCE IN POLYPROPYLENE COMPOUNDS

Christoph Burgstaller
Transfercenter für Kunststofftechnik GmbH, Franz-Fritsch-Strasse 11, 4600 Wels, Austria

Abstract

Using fillers like calcium carbonate or talc and reinforcements like glass fibers in polyolefins is a straight forward approach to tailor materials properties. In such composites, the interfacial interaction between the reinforcement and the matrix is within a selected formulation the dominating effect in regard to composite properties.

Therefore, the aim of this work was to investigate the influence of chemical modification of the reinforcement surface on the interfacial interaction for three different cases, i.e. for talc, glass fibres and wood particles. Surface modifications were carried out with the addition of different silanes or other reactive chemical compounds onto the reinforcement by means of a high speed mixer for talc particles as well as for the wood. As glass fibres exhibiting different surface treatments we used differently sized industrial grades. From these materials, compounds with polypropylene as well as a compatibilizer were produced by means of a co-rotating twin screw extruder. These compounds were injection moulded to retrieve universal test specimen, which were characterised for tensile and impact properties, as well as for composite density and morphology.

We found, that the right surface treatment can greatly enhance the mechanical properties. In case of the glass fibres, the differences a most pronounced due to the highest reinforcing potential of the fibres due to their high aspect ratio. In case of talc, we also could improve the mechanical properties in regard to the silane used. The differences in the mechanical properties here can be correlated with the chemical composition of the respective silanes. In case of the wood particles, also some improvements were found with the surface treatments, mostly due to the fact that the accessibility of reactive sites was much higher due to the treatment. In conclusion these results show that surface modification is a promising route to improve the properties of such composites, but one has to keep the different mechanisms at the interface in mind.

Introduction

Using fillers and reinforcements to tailor materials properties of thermoplastic polymers is a widespread approach. Such materials can be found in applications like pipes and profiles, in automotive as well as in technical parts, just to name some examples. A parameter often discussed for the effectiveness of such reinforcements is the aspect ratio, which is calculated from the length and diameter of the reinforcements. The higher the aspect ratio, the better the typical reinforcing capability is [1]. This was shown in literature several time for glass fibres, for example by Thomason et al. [2-4]. They found, besides the effect of the fiber content, that, the longer the fibers – which gives, in combination with the constant fiber diameter higher aspect ratios – the better the reinforcing properties are.

But the aspect ratio is not the sole parameter, for a given formulation, which influences the properties. The interaction at the interface (or the composition of the interphase region) between fiber (or reinforcement) and matrix is determining the load transfer from the matrix to the reinforcement, thus determining the final properties of the composite. These interactions can be investigated by direct methods, like single fiber pull out or microdebond tests [5-6], but limited to fibers, due to the necessary sample size to manipulate such. To assess the interfacial interactions for fillers, direct methods are very often not available, but indirect evaluation via the application of micromechanical models is available, as was shown by Pukanszky et al. [7].

Anyway, the effect of surface pre-treatment of fillers and reinforcements is very often considered to tailor composite properties. Advantages like higher strength or stiffness without increasing the reinforcement content, which has positive effects in regard to composite density, but also in abrasion and flowability properties, are of great interest for industrial applications. Therefore, the aim of this work was to investigate the effects of surface modification for different reinforcements to evaluate the effects found in correlation.

This paper was presented at the 2016 SPE Polyolefins Conference in Houston, TX, USA.

Materials & Methods

The materials used in this study were two polypropylene homopolymers with a melt flow rate at 230°C and 2.16 kg piston weight of 8 and 55 g/10min, respectively. The polypropylene with the lower MFR was used for the set of experiments with talc, and the other grade was used for investigations with glass fibers and wood particles.

As reinforcements softwood particles with an average particle size of about 450 µm were used as well as talc particles with an average particle size d_{50} of 3.8 µm and d_{98} of 15 µm. These reinforcements were used as delivered as well as pre-treated in a high speed mixer, as described below. The glass fibers used here were two industrial grades with different silane sizings, where one grade is treated with an amino based silane and the other with an epoxy based silane. As a compatibilizer, maleic anhydride grafted polypropylene (MAPP, with a graft level of about 1.4%) was used for all formulations except noted otherwise.

As chemical agents for wood surface modification, maleic anhydride, ε-Caprolactone and ε-Caprolactame (all of reagent grade) were used. The wood particles were pre-treated with 3 % of the chemical agent per hundred parts of wood (by weight) at a sheath temperature of 200°C and a rotational frequency of 5 Hz in a high speed mixer (Diosna, 5000 cm³ volume). The base formulation for the compounds was 40 wt% of wood particles (treated and untreated), 4 wt% of compatibilizer and 56 wt% of polypropylene. The wood content of 40 wt% was chosen due to the fact, that at this level possible effects from the interface should give a pronounced effect and on the other hand, the matrix fraction is high enough to have sufficient wetting of the wood particles.

Talc was pre-treated with different silanes, i.e. amino, epoxy, vinyl and mercapto based. The chemical structures are given in Fig. 5. From the silanes, 1% w/w in relation to the talc was used. These were brought together with water (1:1) and acetic acid as a catalyst into the high speed mixer, to treat the talc particles at 15 Hz rotation speed and a sheath temperature of 150°C. Afterwards, the talc was dried in a hot air cabinet at 150°C for an hour to ensure proper reaction between the silanes and the talc surface. The base formulation was 30 wt% of talc, 3 wt% of MAPP and 67 wt% of polypropylene.

The different compounds were produced using a co-rotating twin screw extruder (Thermo Prism TSE 24HC) with 24 mm screw diameter and L/D ratio of 28, equipped with a gravimetric dosing system. The throughput was kept constant at 8 kg/h, as well as the maximum barrel temperature was set to 200 °C. The melt strands were cooled by a water bath, cut to granules by means of a strand cutter and dried at 80°C for at least 4 h. Subsequent injection molding was carried out on a conventional injection molding machine to yield universal test specimen (in accordance to ISO-3167, specimen geometry according to ISO-527). Melt flow rate (in accordance to ISO-1133) was determined (for the talc compounds only) at 230 °C and 2.16 kg piston weight by means of a Zwick-Roell 4106 test device. The universal test specimens were stored at 50% r.h. and 23 °C for at least 88 h prior to testing. Tensile testing for elastic modulus and tensile strength in accordance to ISO-527 was carried out on a universal testing machine (Zwick Roell Z020) with a crosshead speed of 1 mm/min for the acquisition of the elastic modulus and afterwards with 5 mm/min until the break of the samples. Analysis of selected fracture surfaces from tensile tests were carried out by means of scanning electron microscopy (*Vega II Tescan*) after sputtering the samples surfaces with gold.

Results & Discussion

Influence of surface treatment of glass fibers on composite properties

As can be seen in Fig. 1, the mechanical properties increase with increasing glass fiber content in polypropylene. With the amino sizing, which is able to interact with the MAPP, i.e. with the maleic anhydride group, one gets significantly higher elastic modulus as well as tensile strength. With the epoxy sizing, this interaction, e.g. via covalent or hydrogen bonding, is not possible, therefore both investigated properties are lower than for the amino sized glass fibers. A possible reaction scheme for this is proposed in Fig. 2. One has to admit that, for a more detailed evaluation, also residual fiber lengths in the composite should be determined. In that case, due to the comparable processing routes, we did not investigate this in detail.

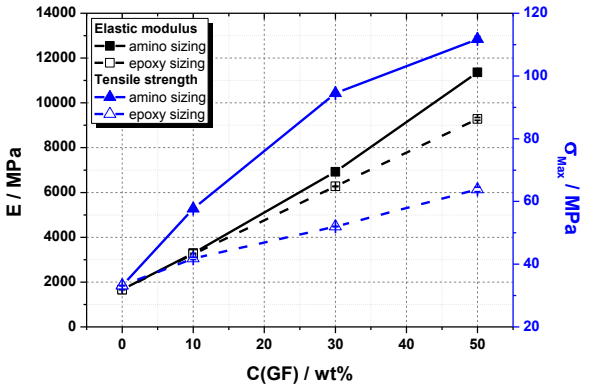

Figure 1. Elastic modulus (E) and tensile strengths (σ_{Max}) of composites containing glass fibers with different sizings in polypropylene with 3 wt% MAPP

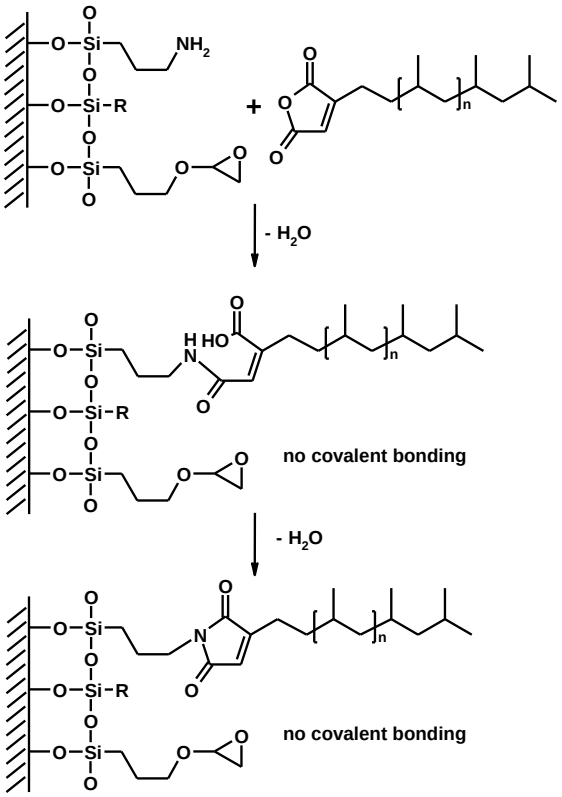

Figure 2. Proposed reaction scheme between MAPP and the different silane surface treatments

Influence of surface treatment of talc particles on composite properties

In case of the treated talc, one can see two main differences in regard to the glass fibers. As shown in Fig. 3., the differences between the different treatments are much smaller than for the fibers, which is due to the smaller aspect ratios. Furthermore, the differences between the different treatments correlate with the silane used for such. In case of the amino and mercapto based treatments, there is possible interaction through covalent or hydrogen bonding, as proposed in Fig. 5. In case of the epoxy sizing, an interaction is only possible after hydrolysis of the oxiran ring, therefore providing hydroxyl groups, which can react with the anhydride of the MAPP. In case of the vinyl based silane, no reaction will occur without the presence of a radical generator, activating the double bond. Therefore, there are only some Van-der-Waals interactions possible between the talc surface and the polypropylene in the latter case, thus resulting in weak bonding. This is also reflected by the order of the mechanical properties, where the treatments with the higher degree of interaction yield higher mechanical properties. These findings are supported by the data found for the MFR (Fig. 4.), where lower MFR values indicate better interaction

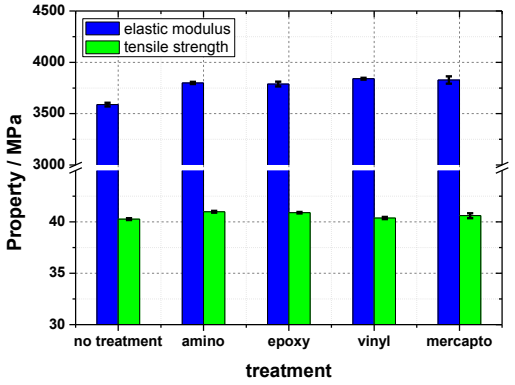

Figure 3. Mechanical properties of composites with 30 wt% of differently treated talc and 3 wt% of compatibilizer in polypropylene

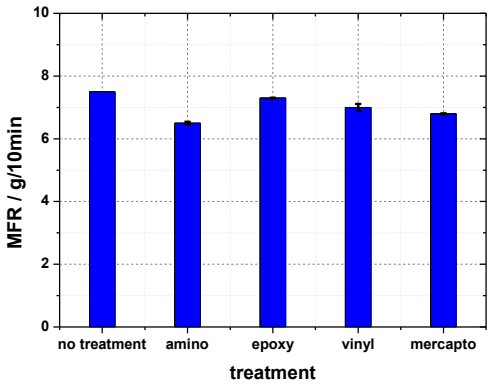

Figure 4. Melt flow rate of compounds with 30 wt% of differently treated talc and 3 wt% of compatibilizer in polypropylene

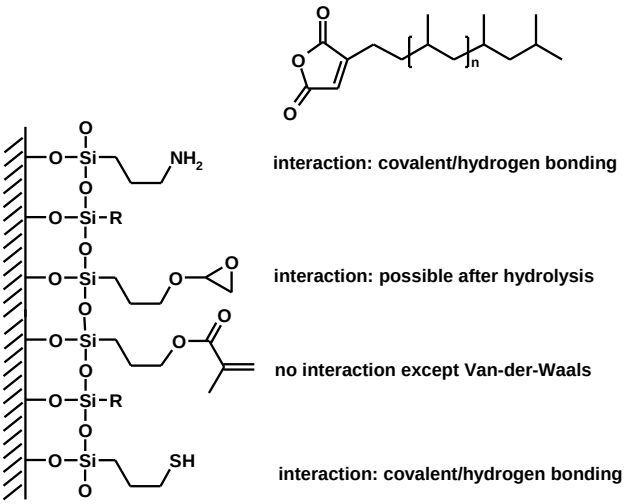

Figure 5. Interaction chart for the different applied silanes (left, from top to bottom: amino, epoxy, vinyl and mercapto based) and MAPP (top right)

Influence of surface treatment of wood particles on composite properties

In case of the treated wood particles, one can see that the addition of MAPP to the neat formulation improves elastic modulus as well as tensile strength due to the promotion of adhesion between the maleic anhydride group of the MAPP and the wood surface (Fig. 6). Furthermore, the addition of the other chemical compounds, further improve the tensile strength, while the elastic modulus can be considered nearly unchanged. Here again we can see that the molecular structure has a pronounced influence on the interaction at the interface, as proposed in Fig 7. In that case, the additional improvement is believed to originate from reduced steric hindrance due to the reactive end groups of the surface treatment being easier accessible than the untreated wood surface itself. This is also reported somewhere else in detail [8].

The simultaneous improvement in stress and strain is not typical, but, as can also be seen in more detail in the stress-strain-curves for the different composites in Fig. 8, is not due to some errors in the evaluation of the data. As a hypothesis for this effect, one can think of the chemical treatment as a covalent linkage between the MAPP and the wood particle surface, which helps overcome some steric hindrance in the process of the MAPP interacting with the wood surface. Therefore, the composites can be strained further, because due to the increased connection points higher stresses are transferred, thus resulting in increased stress and strain. An indication for such a mechanism can be found in the SEM micrographs from composite fracture surfaces in Fig. 9, where some indications for increased interaction can be interpreted from the fracture morphology.

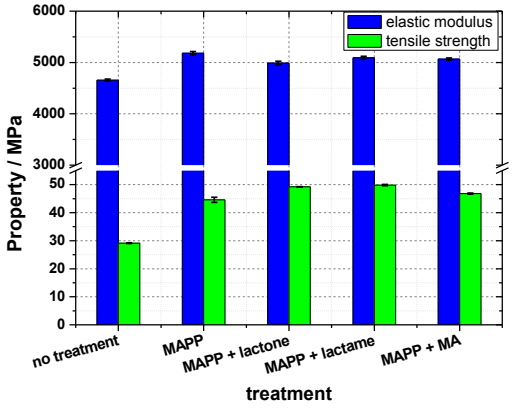

Figure 6: Mechanical properties of wood plastic composites with 40 wt% of differently treated wood, 4 wt% of MAPP and 56 wt% of polypropylene

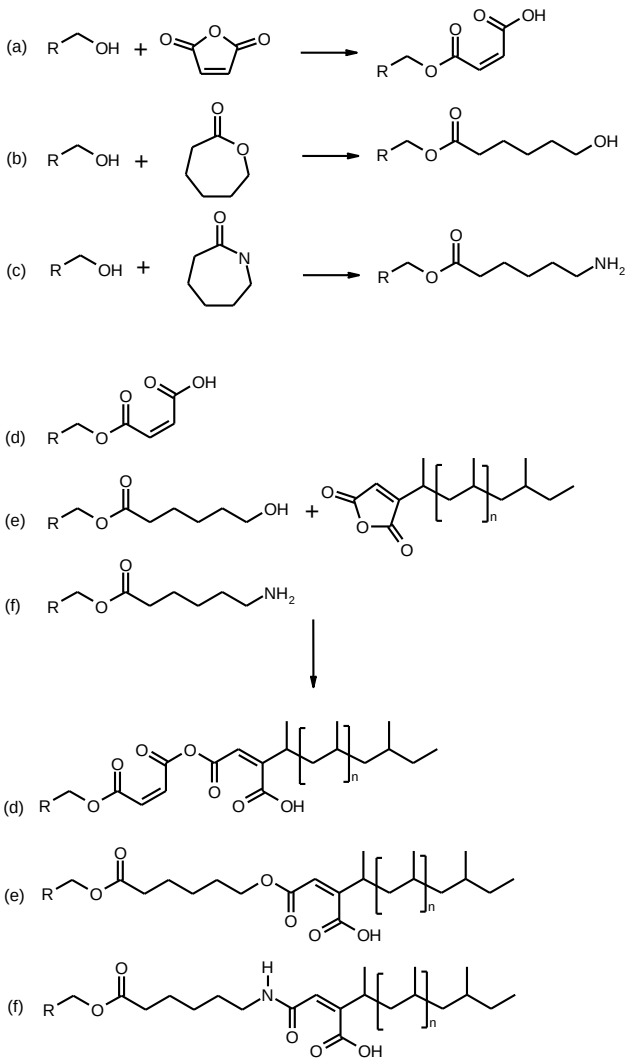

Figure 7: Proposed reactions between chemical modification agents and wood surface (a – c) and between chemically modified wood surface and compatibilizer (d – f) [8]

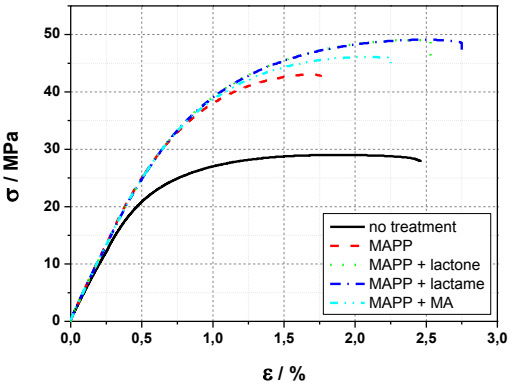

Figure 8: Stress-strain-curves of wood plastic composites with 40 wt% of differently treated wood, 4 wt% of MAPP and 56 wt% of polypropylene

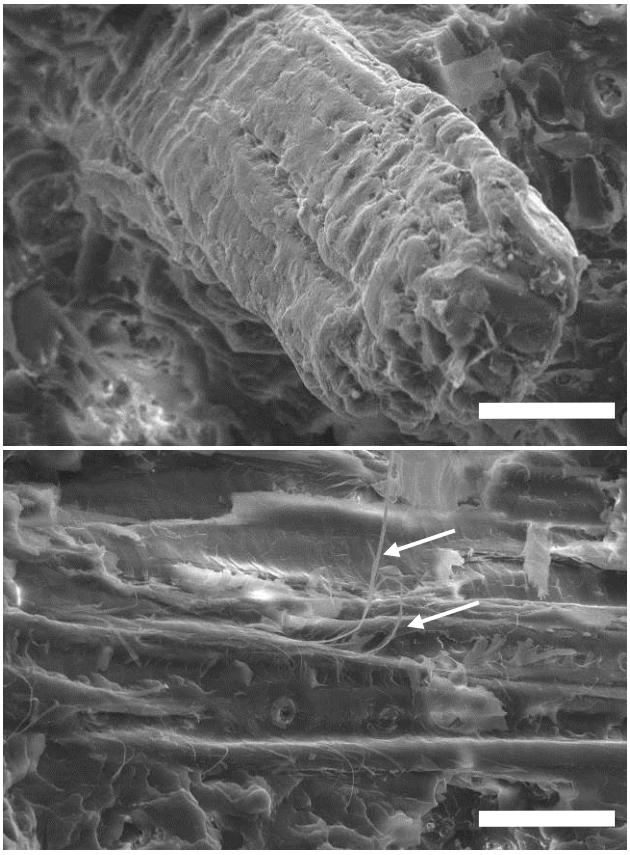

Figure 9: SEM micrographs of the fracture surface of the composites with MAPP (top) and the one with MAPP and ε-Caprolactone (scale bar represents 50 µm, arrows indicate polymer residues attached to the wood) [8]

Conclusions

In this paper, the effects of surface treatment on different composites were investigated. We found, that with a proper treatment, i.e. a surface treatment where chemical compatibility and therefore interaction is provided, one can improve the mechanical properties of the composites. The height of the improvement is also influenced by the aspect ratio of the reinforcement, i.e. glass fibers show the highest improvement due to an improved interfacial interaction, followed by wood particles (which are coarser than talc, but also exhibit higher aspect ratios) and the fine talc platelets.

As conclusion, we can see that the composition and structure of the interface is of great influence on the composite properties, as often reported in literature. The effectiveness of the improvement will determine industrial sustainability, anyhow the surface treatments work, and should be applied in cases with sufficient aspect ratios to harness these effects.

Acknowledgements

The author wants to thank Keyan Liu, MSc, for carrying out some part of the lab work on surface treated talc composites. Furthermore, the author is grateful for the funding provided by the Upper Austrian government for parts of this work.

References

1. W.D. Callister, Ed, Materials Science and Engineering – An Introduction, Chapter 16, John Wiley and Sons (2007)
2. J.L. Thomason, M.A. Vlug, *Composites Part A: Applied Science and Manufacturing* **27**, 477 (1996)
3. J.L. Thomason, M.A. Vlug, G. Schipper H.G.L.T. Krikor, *Composites Part A: Applied Science and Manufacturing* **27**, 1075 (1996)
4. J.L. Thomason, M.A. Vlug, *Composites Part A: Applied Science and Manufacturing* **28**, 277 (1997)
5. A. Kelly and W.R. Tyson, *Journal of the Mechanics and Physics of Solids* **13**, 329 (1965)
6. C. Burgstaller, *Int. J. Materials and Product Technology* **36**, 11 (2009)
7. L. Danyadi, K. Renner, J. Moczo, B. Pukanszky, *Polymer Engineering and Science* **47**, 1246 (2007)
8. C. Burgstaller, B. Priller, W. Stadlbauer, "Improving interfacial adhesion in wood plastic composites" *ANTEC 2011 - Proceedings of the 69th Annual Technical Conference & Exhibition*, Boston, MA, May 1-5. Society of Plastics Engineers, pp. 616-621

Key Words: Glass fiber, polypropylene, talc, wood plastic composites, chemical modification, surface treatment, mechanical properties