

# Interlaminar interaction in paper thermoplastic laminate composites

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**Abstract.** Bio-based composites are a research topic since several decades, which aims for sustainable and durable materials. In the scope of this research, many different sources for bio-based reinforcements have been investigated. Typical issues associated with the use of such are property variations due to cultivation area and climate, besides the influences of the type, pre-treatment and fibre geometry. Another issue can be the availability of such natural fibres. Due to these reasons, we started using paper sheets as reinforcements in laminate composites with thermoplastic materials. In preliminary studies with polypropylene composites, we found good mechanical properties, even higher than could be expected by estimating the composite properties from the constituents by applying simple rule of mixtures type models. We suspect, besides some effect of paper compaction, interlaminar effects to be the reason for this. Therefore, the aim of this work is to investigate the effects of the interfacial interaction on the different paper laminate properties due to different matrix polymers. For this work, we used polypropylene, polyamide 6 and 12 as well as polystyrene. Composites were produced via compression moulding and samples for mechanical testing and density evaluation were cut from the moulded plates. The results from mechanical tests show, that there is a reinforcing effect, regardless of matrix polymer used. Simple rule of mixtures evaluations show, that the different matrices exhibit different degrees of interaction, based on their chemical structure. In addition, also influences due to processing were found.

## 1. Introduction

Bio-based composites are in the focus of researchers since several decades. Different reinforcements, like natural fibres from stems, leaves or seeds of different plants as well as agricultural by-products like rice husks or wheat straw have been investigated for their potential to reinforce plastic matrices. [1, 2] The reinforcements have been investigated either as short cut fibres or powders or as semi-finished products, like fabrics or fleeces. Although natural reinforcements are bio-based, require less energy input than man-made fibres and are widespread, there are some problems associated to them due to their natural basis. These are property variations due to cultivation area and climate, besides the influences of the type, pre-treatment and fibre geometry [3]. Another factor is the availability, also throughout the year, of specific fibre types and qualities, which limits their applicability.



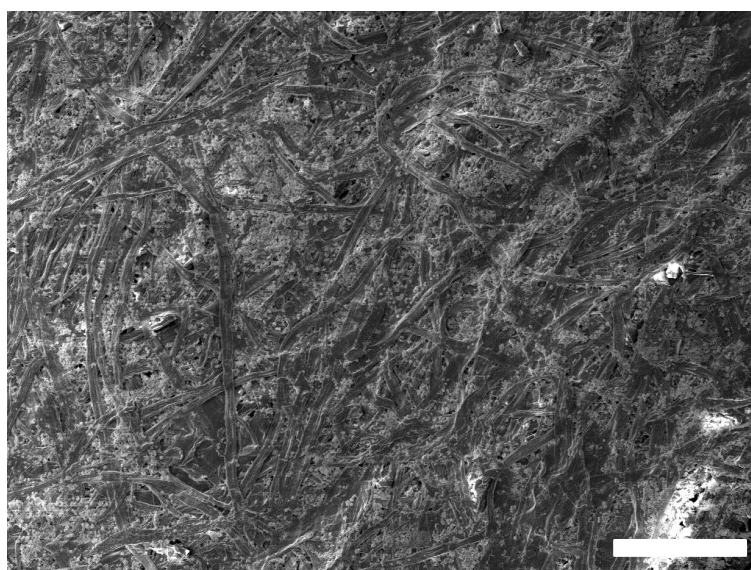
Therefore, we started using paper sheets as reinforcements in laminate composites with thermoplastic materials, i.e. polypropylene [4]. In the course of this research we found interesting properties for polypropylene paper laminates with a paper volume fraction of approximately 50 vol.-% of 6 GPa elastic modulus and 70 MPa tensile strength. Furthermore, when modelling these composite properties from the constituent properties via simple rule of mixture type models, we found an increase in constituent properties in the composite, which cannot be attributed solely to the paper compaction [5].

Therefore, the aim of this work is to investigate the effects of the interfacial interaction on the different paper laminate properties due to different matrix polymers. This approach was chosen because the characterisation of the interaction between paper fibres and a matrix is rather complicated. Typical micromechanical approaches, like single fibre pull-out or microdebond tests, are inapplicable due to the short fibre length (below several millimetres) of the single paper fibres, and tests like determining interlaminar shear strength with short beam bending tests or peel off tests are not applicable, as these do not show the required failure modes due to the thermoplastic matrix.

## 2. Materials and Methods

In this work a standard copy paper (Xerox Transit 80 g/m<sup>2</sup> from Kraft pulp fibres from softwood and apparent density of 0.816 g cm<sup>-3</sup>) with a thickness of 98 µm was used. A SEM micrograph (taken with a Vega Tescan scanning electron microscope at the University of Applied Sciences in Wels, after sputtering the samples with gold) depicting the paper surface, showing the fibre orientation as well as some inorganic filler can be found in figure 1. Any further information about the constituents is proprietary information with the paper producer and is not available for publication.

For laminate fabrication, the different polymers (table 1), i.e. polypropylene (PP), polyamide 6 (PA6), polyamide 12 (PA12) and polystyrene (PS), were produced into films by means of a flat film extrusion line (P/M Plastic Maschinenbau, 35 mm screw diameter, screw length over screw diameter (L/D) ratio of 18). Typical film thicknesses produced were 140 and 100 µm, and also 250 µm for the PS films. In case of the PP, a compatibilizer (5 wt.-% Scona TPPP 8112) was used in all the formulations to increase the interaction between the matrix and the paper fibres and is therefore not noted further.

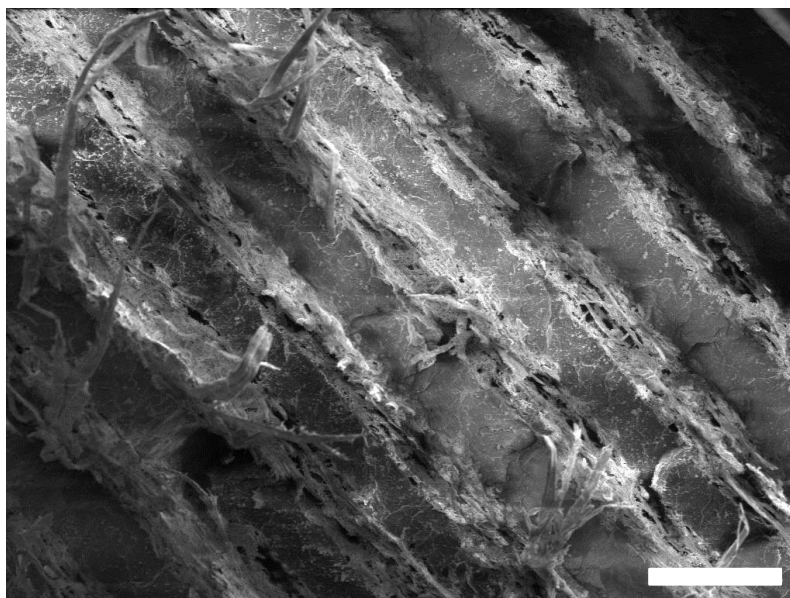


**Figure 1.** SEM micrograph of paper surface of the copy paper used in this study (scale bar represents 200 µm)

**Table 1.** Polymers used in this study and their properties

Polymer	Density (gcm <sup>-3</sup> )	T <sub>(Processing)</sub> (°C)	Melt volume flow rate (cm <sup>3</sup> 10 <sup>-1</sup> min <sup>-1</sup> )
PP	0.905	210	9 (230°C, 2.16 kg)
PA6	1.140	230	40 (250°C, 2.16 kg)
PA12	1.010	210	--
PS	1.040	210	12 (200°C, 5 kg)

The laminates were produced by stacking the pre-cut films and paper sheets, the latter all oriented in machine direction, in a pre-heated steel mould with 10x10 cm<sup>2</sup> free volume and subjecting the whole setup to 50 bar for 5 min at the respective processing temperature for each matrix polymer, given in table 1. For composite build up, the outer layers always were polymer layers, so the stacking sequence starts and ends with a film sheet. To achieve the different volume fractions, films with different film thickness, i.e. 100, 140 and 250 µm were used. Additionally, for volume fractions of 20 vol.-% and below, the films were used double to increase the polymer volume fraction. The calculated paper content was checked by optical microscopy and was used for all the comparisons in this paper. An example for such a cross-section is given in figure 2, where the polymer layers can be distinguished from the paper layers, as well as the remaining porosity in the paper can be seen.



**Figure 2.** SEM micrograph of cross-layer fracture surface of the composite consisting from 50 vol.-% of copy paper in polypropylene (scale bar represents 200 µm)

Different specimens were milled from the laminates by means of a Coesfeld CPM 3020 mould cutter. Tensile testing was carried out on a Zwick-Roell Z020 20 kN universal testing machine, in accordance with ISO 527-2 (on specimens type 1BA) with three replicates per series with a loading rate of 1 mm min<sup>-1</sup> for determining elastic modulus and after that 5 mm min<sup>-1</sup> until the break of the samples. Flexural testing was performed by a Zwick-Roell ZMART.PRO 10 kN universal testing machine, according to ISO 178, on three replicates with sample dimensions 75 x 10 x 3.5 mm<sup>3</sup>, and a loading rate of 1 mm min<sup>-1</sup> for determining elastic modulus and after that 2 mm min<sup>-1</sup> until the break

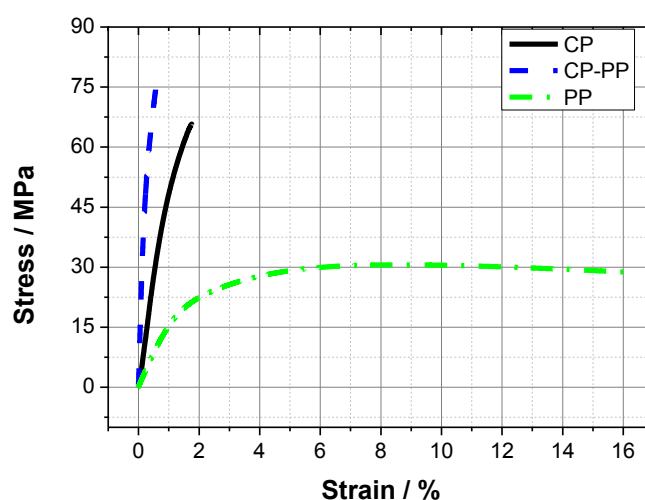
of the samples. The interlaminar shear strength (ILSS) was determined by an unnotched Charpy flatwise impact strength measurement, carried out by a Zwick-Roell 5113.300 impact pendulum, according to ISO 179-1/3fn. Five replicates of type 3 specimens with dimensions of 45.5 x 10 x 3.5 mm<sup>3</sup> and a pendulum with 5 J impact energy were applied. The density of the samples was measured with a Sartorius YDK 01LP density determination kit on an analytical balance (Sartorius AX 224), according to ISO 1183-1, where ethanol was the immersion liquid. The density of the latter was determined before the measurement with the help of a standardised volume glass immersion body.

### 3. Results and Discussion

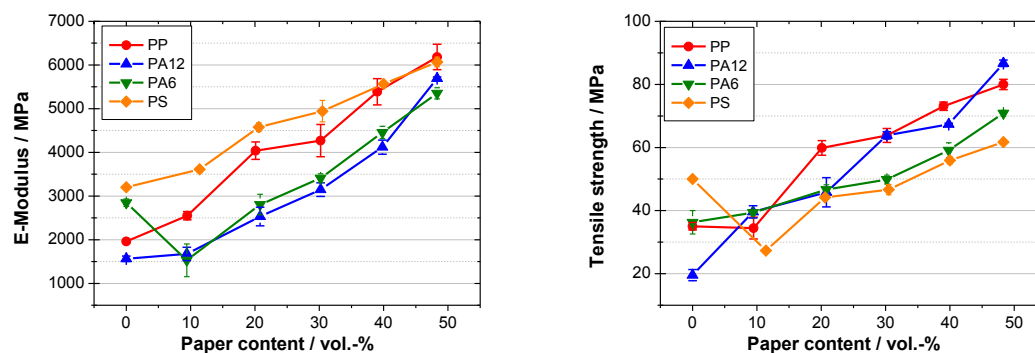
Reinforcing polymers with paper leads to increased mechanical tensile and flexural properties. An example for the stress strain curves of paper, polymer and the composite are given in figure 3, where a synergistic reinforcement effect can be seen at the first glance. In our opinion this is due to the fact that the paper strength accounts for paper fibre interaction mainly, while in the case of the composites, the fibre properties itself are – at least partially – harnessed, thus resulting in increased composite properties.

As shown in figure 4, the elastic modulus of the different composites is increasing with increasing paper content. The initial decrease of the elastic modulus in case of the PA6 based composites is suspected to arise from moisture uptake of the PA6 from the ambient air, which therefore reduces the elastic modulus of PA6 [6]. Nevertheless, there is a reinforcement effect visible for all investigated polymer matrices. The same is true for the tensile strength (figure 4), where also an increase with increasing paper content can be found. In case of the PS based composites, the sharp decrease through the addition of the paper is due to the fact that the pure polystyrene strains to about 1.4 % for the tensile strength, but the composite with 10 vol.-% of paper strains only to 0.86 %. Taking this into account for the neat PS, i.e. using the stress value at the reduced strain, one yields approx. 24 MPa, which is in good accordance with the trend of tensile strengths of the PS based composites.

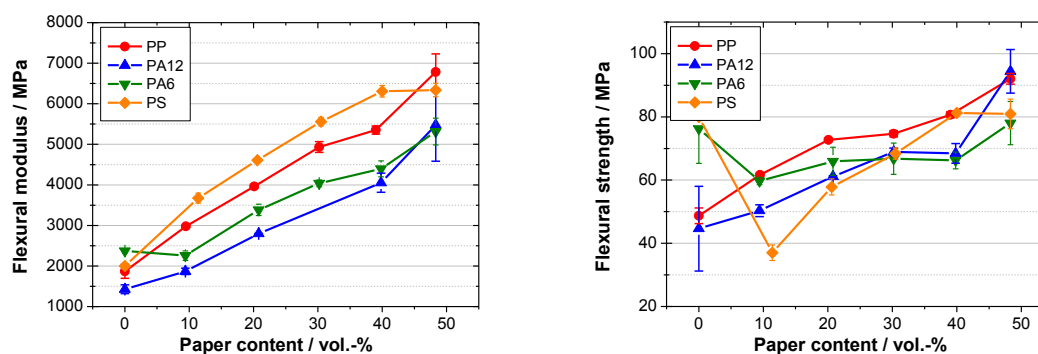
In case of the flexural tests, we can find similar results for flexural modulus and flexural strength (figure 5). For the moduli, the data are slightly different from the ones from tensile testing, but exhibit the same trends. The flexural strength data also show the same trends, with the exception that besides the neat PS also the neat PA6 shows higher flexural strength than the respective composites with 10 vol.-%, which again can be explained by the limited strain applied in the composites in comparison to the unreinforced materials.



**Figure 3.** Stress strain curves for polypropylene film (PP), copy paper (CP) and the composite with 50 vol.-% of copy paper in polypropylene (CP-PP)



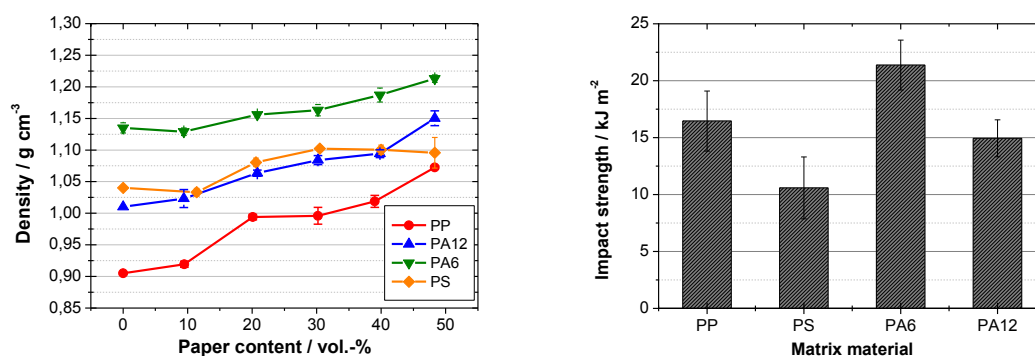
**Figure 4.** Elastic modulus from tensile tests (left) and tensile strength (right) vs. paper content of the composites with paper and different matrix polymers



**Figure 5.** Flexural modulus (left) and flexural strength (right) vs. paper content of the composites with paper and different matrix polymers

The composites density (figure 6) shows an increase in density with an increase in paper content. This may not seem surprising at a first glance, but the paper itself exhibits a density of  $1.03 \text{ g cm}^{-3}$ , which is surpassed rather quickly by the different composites. There are different reasons for this behaviour. First, the density of the paper is product from the density of the cellulose fibres and the pores in the paper (neglecting here the influences of inorganic fillers, which are also present in most paper grades). The pores also are either within the cellulose fibres (the lumen) or between, which are the pores of the paper. These pores can be compacted (the lumen) or filled with the matrix, which then gives a higher apparent density of the paper in the composite. The effectiveness of the compaction is depending mainly on the applied pressure in the fabrication (besides the compressibility of the matrix), while the pore filling is a parameter which can be related to the interlaminar interaction between the different matrices and the paper. As a first evaluation for this, a linear fit for extrapolating the paper density was applied. The authors are aware that this is only a very crude evaluation, but due to the aforementioned problematics of determining paper fibre interactions with polymer matrices, this seems to be a first indication of how well a matrix can interact with a given paper. We find values (all of them in  $\text{g cm}^{-3}$ ) of 1.29 (PA6), 1.27 (PA12), 1.23 (PP) and 1.18 (PS). Comparing these to the data from ILSS testing (the short beam Charpy impact tests, where a fractured sample from these tests is shown in figure 7), these seem to be in reasonable accordance due to the similar ordering of the values found in ILSS. In case of the ILSS, also PA6 exhibits the highest values and PS the lowest. The difference in the order between PP and PA12 can be due to the fact, that the density evaluation is a simplified method giving averaged value. Also, there is some influence of the impact test itself on the ILSS data, as can be seen from the fractured specimen in figure 7. There is a large delamination

visible, but also some laminate fractures in the middle of the specimen. This means that with the ILSS data, always some influence of the matrix impact strength can also be found.

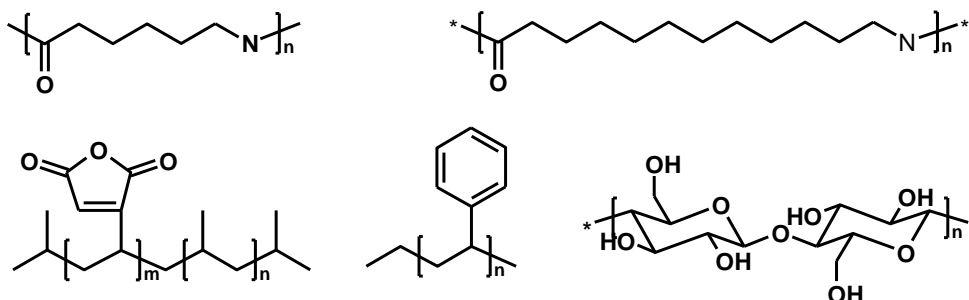


**Figure 6.** Composite density vs. paper content (left) and impact strength from ILSS testing of composites with 40 vol.-% paper vs. matrix material (left) of the composites with paper and different matrix polymers



**Figure 7.** Exemplary fractured test specimen from ILSS impact testing exhibiting laminar failure (scale bar represent 5 mm)

Putting these data into perspective with the results from tensile strength (figure 1), where interlaminar interaction should play an important role, one finds some differences. Using again a linear fitting approach for the tensile strength, thus being a simplified application of a rule-of-mixtures, where the constituents properties add up to the composites properties in relation to their volume fractions, one can use the slope of these fits as a measure for the reinforcing effect. Again, we decided here to not take porosity into account as a separate factor, due to a current lack of proper analysis of that in the investigated composite system, but leave that summarized in the paper contribution. The slopes calculated from the tensile strength vs. the paper volume fraction show, that PA12 exhibits the greatest reinforcing effect, followed by PP, PS and PA6 in that order. With the exception of PA6, one could expect that from the ILSS and density data. Also the chemical structures of the constituents (figure 8) can give some explanation for that. Putting PA6 aside, the chemical structure of PA12, with the amide groups in the chain, will be capable of forming chemical bonds (hydrogen and covalent bonds at the chain ends), as can the PP with the help of the maleic anhydride grafted chains added into the material due to the compatibilizer. The chemical structure of PS can only form polar bonds due to the nucleophilic nature of the benzene rings in the structure.



**Figure 8.** Schematic chemical structures of the used polymers and cellulose; top: left – PA6, right – PA12; bottom: left – PP grafted with maleic anhydride, middle – PS, right - cellulose

Following this logic, PA6 should be even better, due to the fact that it exhibits roughly double as much amide bonds as PA12 does for a comparable chain length. On the other hand, PA6 is more susceptible to water uptake – and therefore hydrolysis – as PA12 [6]. Another factor is, that the melting point for PA6 is about 220 °C, and a processing temperature at 230 °C means that the material is relatively viscous. The ILSS results show a good impregnation of the paper, so another factor can be the degradation of the paper itself. Cellulose degradation starts around 250 °C, but other paper components, like starch-based coatings (which are applied to increase printability [7]), degrade earlier. Therefore, the significantly higher processing temperature of PA6 can play a role, which would explain our findings to some extent.

A last simple use of our rule-of-mixtures fitting, i.e. using the volume fractions weighed constituents properties in order to estimate the respective composite property, is to predict the tensile strength of the paper by extrapolating to 100 vol.-% with the linear fits. Again, this is only a rough estimation, but should give us some more insight on the mechanisms effective in the composites. Here we yield 139 and 130 MPa for PA12 and PP, respectively, while about 106 MPa for the other two matrix polymers. The copy paper itself exhibits about 62 MPa from mechanical testing. Similar predictions for the elastic modulus of the paper yield around 10,400 MPa for all matrices except PA6, where about 9,200 MPa are yielded, while the neat paper shows an elastic modulus of about 5,400 MPa. The fact that the estimated data here is in a much closer range than for the tensile strength shows two things – first, at the lower strain levels where the elastic modulus is measured, the interlaminar adhesion plays a lesser role than at the higher strains where tensile strength is determined, and second, with the exception of PA6, all the matrices exhibit very comparable data, therefore this interaction can be attributed to the paper and its surface structure. The fact that PA6 shows lower values here may again be due to the higher processing temperature and therefore some degradation of the paper surface, as discussed above. Also, all of this shows, that the composites are utilizing not only the properties of the constituents, but also, due to the interaction at the interfaces, utilizing the properties of at least a portion the single fibres.

#### 4. Conclusions

In the scope of this work, we investigated the properties of composites built up as laminates from paper and different thermoplastic polymer matrices. We found, that all the composites show increasing properties with increasing paper content, but also the properties of the matrix play an important role. The chemical structure as well as the processing exhibits influences on the composite properties. Using simple rule of mixture type models to evaluate the composites show, that the pores in the paper are filled or compacted, and that the apparent paper properties in the composites are significantly higher, i.e. about double, than the properties of the neat paper. These results show, that due to the interaction between the constituents, the paper fibres themselves and not only the paper layers are – at least to some extent – utilized for their properties.

Further investigations will deal, besides other polymer matrices to widen the view for the simple modelling applied here, with detailed investigations on the interaction between the matrix and the fibres, to further understand the mechanisms in such layered composites, and therefore getting the tools to improve their performance further towards industrial applicability.

## References

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