USING PAPER AS REINFORCEMENT MATERIAL IN THERMOPLASTIC COMPOSITES: LAMINATE FABRICATION AND CHARACTERIZATION

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Keywords: Thermoplastics, Laminates, Bio-Composites, Mechanical properties, SEM analysis

Abstract

Composite laminates, consisting of copy paper sheets and four different thermoplastic matrices were produced and characterized in this work. The laminates were fabricated by manual stacking and subsequent hot pressing with paper contents between 0 to 50 vol.%. The mechanical properties, obtained by tensile and flexural testing, were compared to polypropylene laminates, reinforced with plain weave glass fiber mats. Further investigations on the composite's interface were carried out by interlaminar shear strength measurements and SEM analysis, as well as density determinations. By comparing the specific properties of the paper laminates to the glass fiber reinforced composites, comparative results were obtained pointing out a high potential for standard copy paper as environmentally friendly reinforcement material.

1. Introduction

Fiber reinforced polymers are suitable materials for several applications, e.g. in the field of automotive, aerospace, packaging, furnishing or sports industry, due to their good mechanical property profile and low density. However, considering the limited recycling options for composite materials and the high energy demand during the production of conventional reinforcement fibers, the search for alternatives is of high interest [1, 2]. One way to enhance the recyclability of composite materials is the substitution of the synthetic reinforcement, e.g. glass fibers, by naturally grown plant fibers. In combination with a thermoplastic matrix, the opportunities for material separation, reuse and thermal energy recycling can be drastically improved. Natural fibers have suitable mechanical properties, low density, low health risk and almost no abrasiveness to plastic processing machines. Additionally, their low price and wide distribution make them an attractive option for synthetic fiber replacement. Drawbacks of natural fibers are their high water uptake, low fiber matrix adhesion and the varying fiber quality, which hampers the production of high volumes of fiber material with the same properties. The final characteristics of naturally grown fibers strongly depend on environmental influences, such as weather, climate, harvesting season or soil properties [3–6]. This problem can be circumvented by the use of refined natural fibers, i.e. pulp and paper fibers, for composite production. Paper fibers are of constant quality, as they are derived from a defined type of wood and unfavorable plant components are removed by chemical and mechanical processes. Furthermore, paper sizing agents support the interfacial bonding and can act as a compatibilizer for some thermoplastic matrices [7, 8].

Excerpt from ISBN 978-3-00-053387-7

In this work standard copy paper was used to reinforce four different thermoplastic polymers: Polyproyplene (PP), Polyaminde (PA6 and PA12) and Polystyrene (PS). Most studies, found in literature on the topic of paper reinforcement in thermoplastics, deal with ground paper fibers and injection molded composites [9–12]. Frequently, this method results in poor fiber dispersion and agglomeration of the hydrophilic fibers in the polymer matrix. By using whole paper sheets for composite production this aspect can be disregarded. However, an efficient interfacial adhesion between the polymer and the paper layers is crucial in order to prevent delamination effects.

The aim of this work was to study the influence of the matrix material on the mechanical properties and interfacial adhesion of the paper composites. In order to do so tensile, flexural and density tests were carried out. The interface properties were investigated by charpy impact measurements for determining the interlaminar shear strength (ILSS) and electron microscopy (SEM) analysis. The mechanical properties and the specific properties were compared to PP laminates, reinforced with plain weave glass fiber mats, which find wide usage in a variety of lightweight applications. Therefore, searching for sustainable material combinations with comparable property profiles was a further aim of this study.

2. Methods and Materials

The following polymers were used for laminate fabrication: PP HD120MO (density 905 kg/m^3, MVR 9 cm³/10min at 230 °C and 2.16 kg), PA6 Durethan B 30 S (density 1140 kg/m³, MVR 110 cm³/10min at 260 °C and 5 kg), PA12 Grilamid L16 LM (density 1010 kg/m³) and PS Empera 124N (density 1040 kg/m³, MVR 12 cm³/10min at 200 °C and 5 kg). The polypropylene samples were produced with the addition of 5 wt% of Scona TPPP 8112 GA (maleic anhydride grafted PP, MAPP) as a coupling agent, which were added to the polymer before flat film extrusion. A standard office paper type (CP) was used as reinforcement (copy paper Xerox Transit 80 g/m²) with a thickness of 98 µm. For comparison, PP laminates reinforced with plain weave glass fibers (GF) were produced and tested as well. The weave was obtained by R&G Faserverbundwerkstoffe GmbH (Aero glass fabric 280 g/m², thickness of 260 µm,).

The laminates were produced by a manual film-stacking method of the material layers in a pre-heated steel mold and hot pressing with a Wickert WLP 80/4/3 press (210 °C, 50 bar for 5 min). The final thickness of the samples was adjusted to 3.5 mm by a spacer frame. Specimen for tensile (in the style of 1BA type specimen), flexural (bar with 75 x 10 x 3.5 mm³ dimensions) and charpy impact testing were cut from the laminates with a Coesfeld CPM 3020 mold cutter.

Tensile testing was carried out on a Zwick-Roell Z020 20 kN universal testing machine, in accordance with ISO 527-2. Flexural testing was performed by a Zwick-Roell ZMART.PRO 10 kN universal testing machine, according to ISO 178. The interlaminar shear strength 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. Type 3 specimens with dimensions of 45.5 x 10 x 3.5 mm³ and a pendulum with 5 J impact energy were applied. When composite laminates are tested according to the described method, the failure mode of the tested charpy specimens is shear induced, which leads to delamination of the specimens after impact. Therefore, the obtained impact strength is also an indication for the interlaminar shear strength of the laminates. 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. The samples were weighted in the dry state and immersed in ethanol, which was temperature corrected.

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3. Results and Discussion

3.1. Mechanical Properties

Composite laminates with paper contents between 0 and 50 vol.-% were prepared with four different thermoplastic matrices (PP, PA12, PA6 and PS). For a comparison of the mechanical properties, plain weave glass fiber (GF) reinforced PP laminates were fabricated the same way as the paper composites. In Figure 1, the results of tensile and flexural testing are depicted. In general, all properties increase with increasing reinforcement content in a more or less linear way. Regarding the paper composite, the highest mechanical properties were obtained by a paper content of app. 50 vol.-%. The PS and the PP laminates exhibit the highest values for Young's modulus and the flexural modulus, for high paper contents. Moduli of 6-7 GPa were obtained in combination with these matrix materials. All laminates, built up from PA polymers showed significantly lower moduli than the PP and PS samples. Regarding the high initial modulus of PA6 without reinforcement material and the more hydrophilic nature of the PA polymer, this result is surprising. It is assumed that the applied paper sizing agents reduce the compatibility between paper surface and PA, leading to a drop of mechanical properties with the insertion of paper layers into the polymer. The black dashed line in the graphs refers to the GF reinforced PP samples. In comparison, the paper composites exhibited similar moduli to the GF composites, pointing out the high potential of the paper laminates.

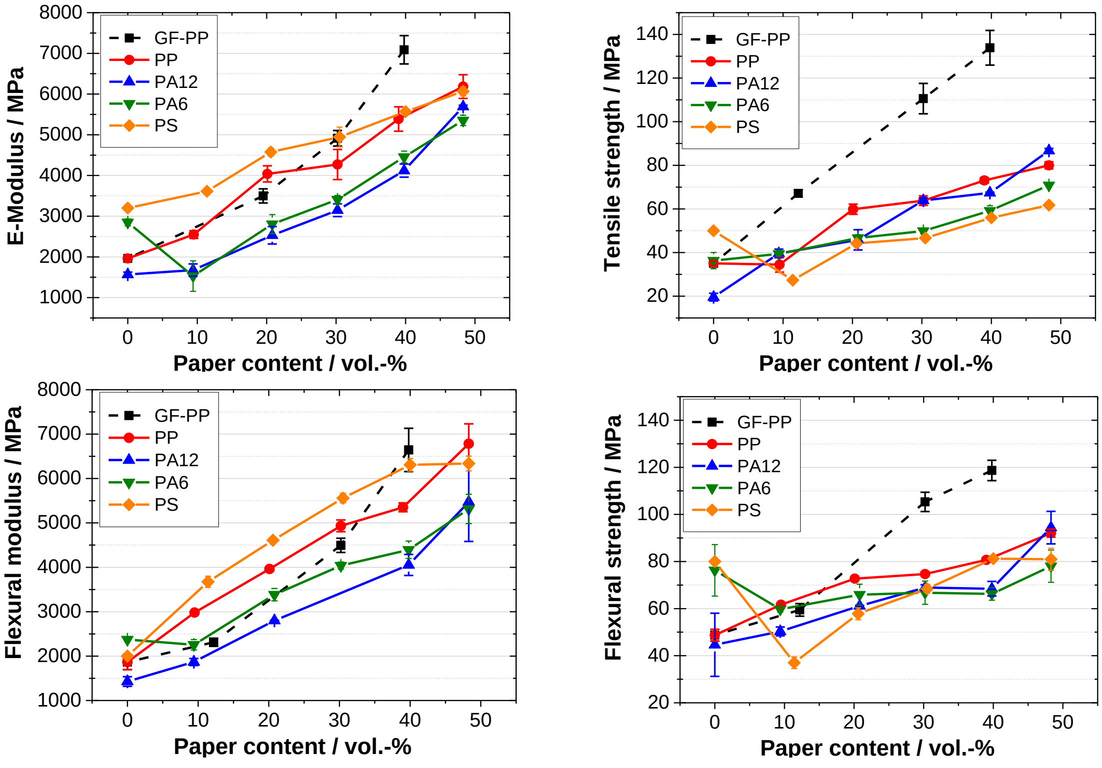

Figure 1. Tensile and flexural properties of the paper composites with varying matrix materials and paper content in comparison with glass fiber reinforced PP (black dashed line).

Considering the tensile strength and the flexural strength of the laminates, the GF-PP samples show higher values than the paper samples, indicating a limitation in the field of applications. However, glass fibers have a higher density than paper, which leads to comparable results when the specific properties are regarded. Additionally, as paper is a rather thin material, it is possible to fabricate laminates with a high number of material layers, evenly distributed in the polymer matrix. In

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preliminary works, the usage of thin polymer films and thin paper sheets was found to be advantageous concerning the mechanical properties [13, 14]. The highest strength values were obtained for the PP and PA12 composites with a tensile strength of approx. 90 MPa at a paper content of 50 vol.-%. PS laminates showed comparatively low tensile strengths, in contradiction to the flexural moduli, which was associated with compatibility issues, similar to the PA6 composites. At high stress values, the influence of interfacial adhesion and fiber embedding becomes more important explaining the low strength values obtained by PS laminates. The interface properties have an important influence on the structure and mechanics of the composites and vary significantly between the different matrix materials. In order to obtain further knowledge about the interfacial region, ILSS tests and SEM analysis were carried out.

3.2. Charpy impact measurements for determining ILSS

An efficient adhesion at the interface between the paper fibers and the polymer matrix is crucial in order to guarantee an efficient stress-strain transfer from the matrix to the reinforcement resulting in high mechanical properties. Also the extent of fiber embedding has an important influence on the performance of the composite. As could be observed by mechanical testing and SEM analysis, the interfacial properties vary significantly for the different material combinations. The ILSS was measured by a flatwise charpy impact test. By applying test specimen of type 3 for this measurement, a shear induced failure of the test specimen is observed. Therefore, the obtained values for impact strength can be used for determining the ILSS [15]. A standard 3-point short beam test could not be applied due to the lack of rigidity of the materials, which shifts the mode of failure from shear to flexural.

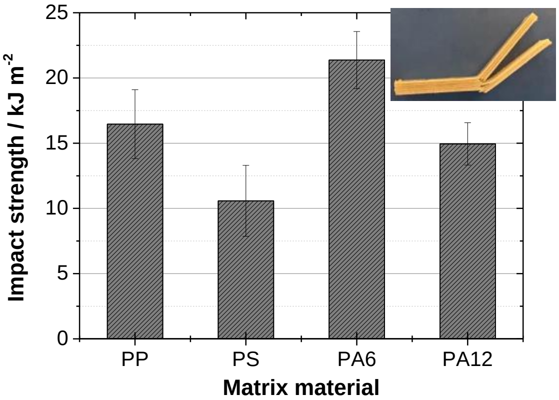

Figure 2. Result of flatwise charpy impat tests of paper composites with different matrix materials and picture of a tested CP-PP specimen in the right corner.

In Figure 2, the results of the charpy impact testing and a picture of a tested CP-PP specimen are depicted. The test specimen clearly shows delamination upon impact testing. It is assumed that high values for ILSS are derived from strong interactions on the interface and also lead to high tensile and flexural strength. The PP and PA12 laminates gave similar results concerning tensile strength values and also the ILSS results are in the same range. In comparison, the PS laminates exhibited high stiffness at tensile testing, due to the more rigid matrix material. However the tensile strength values were significantly lower for this laminate type, indicating reduced interfacial properties. The ILSS measurement agrees with this result, revealing a smaller value for the impact strength of only 10.5 kJ/m². Additionally, a high degree of paper fiber pull outs was observed by SEM analysis of the PS laminates, supporting the assumption of weak bonding. A surprising result was obtained by the

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ILSS measurement of the PA6 laminate. With 21 kJ/m² it represents the highest value for ILSS of all tested composites. This result is not consistent with the data obtained from tensile and flexural testing, which gave the lowest results for this composite type. Hence, an inefficient interfacial adhesion was assumed being not confirmed by the ILSS measurement. It is possible that the relatively high charpy impact strength of the matrix material influences the values of the ILSS measurement leading to unexpected high results. Furthermore, the interfacial region exhibited several fiber pull outs, as could be observed at the SEM analysis supporting the theory.

3.3. SEM analysis

In order to obtain additional information in particular about the paper fiber embedding and the impregnation of the whole paper layers, SEM analysis of the laminate interfaces was carried out (Figure 3).The cryo-fractured surfaces of the paper laminates with the four different matrix materials were investigated and compared by means of paper fiber pull outs as indication for weak fiber matrix adhesion. In picture a, the fracture surface of the PP laminate is depicted. For this material combination, no fiber pull outs were observed, indicating high interactions between the paper layers and the polymer matrix. In contrast, picture b shows several pull outs at the interfaces of the PS laminate. The reduced fiber-matrix adhesion was also observed by mechanical testing, considering the low values for tensile strength and ILSS. Similar results were obtained for the PA6 laminate (picture c) displaying a high degree of fiber pull outs. Also tensile and flexural testing resulted in comparatively low properties resulting from the less efficient stress-strain transfer between the material layers. Picture d shows a PA12 laminate with a moderate degree of pull outs. The PA12 composites gave the highest strength values, together with the PP laminates at high paper contents. This result is supported by SEM analysis and ILSS measurement revealing an efficient fiber matrix adhesion as well.

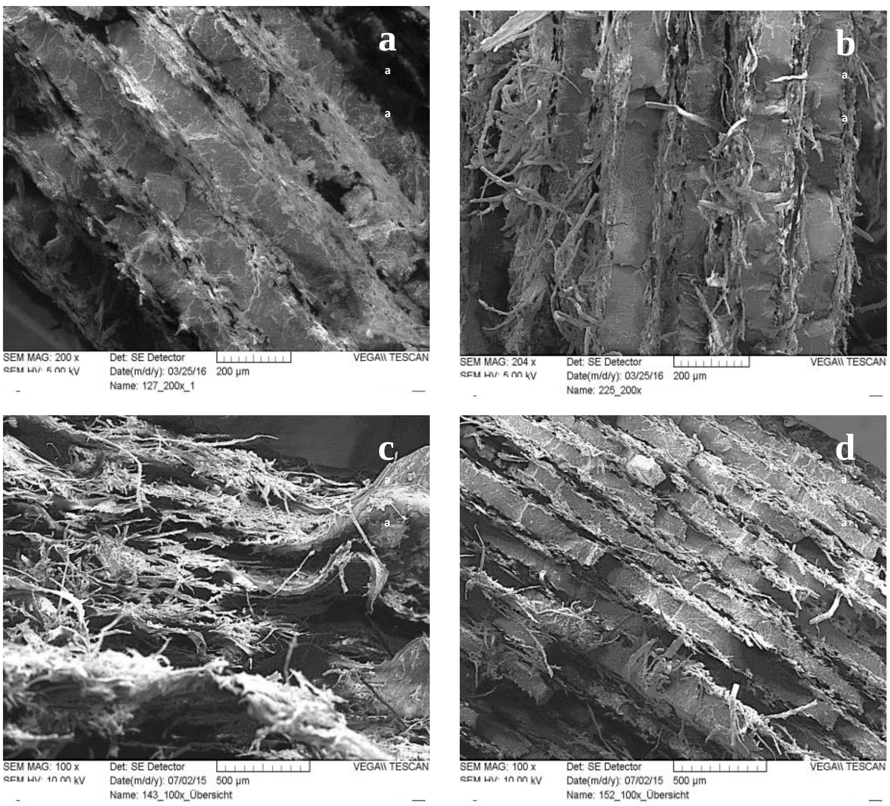

Figure 3. SEM analysis of composite interfaces: matrix materials a – PP, b – PS, c – PA6, d – PA12, all reinforced with copy paper sheets.

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PA6 and PA12 were expected to produce comparable results concerning the fiber matrix adhesion, due to the similar chemical buildup of their polymer chains and hydrophilic nature. However, regarding the results of mechanical testing and the SEM analysis, obvious differences were observed. Even though the mechanical properties of PA6 are superior to the ones of PA12, the laminates with the respective matrix material show opposite results. It is assumed that the low melting temperature of PA12 at 178 °C is beneficial regarding the fiber impregnation and interfacial bonding resulting in improved mechanical properties. On the contrary, the melting temperature of the applied PA6 type is significantly higher (222°C). Considering that cellulose starts degrading at 240°C, the process temperature for laminate fabrication is limited to 200 – 230 °C. It is assumed that the processing of PA6 marginally above its melting point has a negative effect on the impregnation and further on the interfacial properties of the laminates.

3.4. Composite Density and Specific Properties

For several industrial applications, e.g. in the field of automotive, lightweight construction, packaging or transport, low density materials with high mechanical properties are of high importance in order to reduce weight and/or costs. Polymers are materials of low density, however in order to obtain the necessary property profile, they are frequently reinforcing with synthetic fibers, such as glass or carbon fibers, increasing the materials density significantly with increasing filler content. In Figure 4, a comparison of the densities of the paper and GF laminates is depicted. The density of the GF-PP test series increases in a linear way with increasing filler content and shows the highest slop of the study. A direct comparison was made with the paper reinforced PP laminates, which also show a density increase with increasing paper content. However the slope is significantly smaller, revealing less influence of the filler content on the final composite's density. The other three thermoplastics used in this study have higher densities than PP, however, above filler contents of 30 vol.-%, they all show lower densities than the respective GF-PP laminates. The density changes of the PA6 and PS laminates with increasing paper content are less pronounced, due to the fact that the density of compacted paper is similar to the polymer densities. According to this, composites with high filler contents can be fabricated without being forced to make too many trade-offs regarding the final material's density and weight.

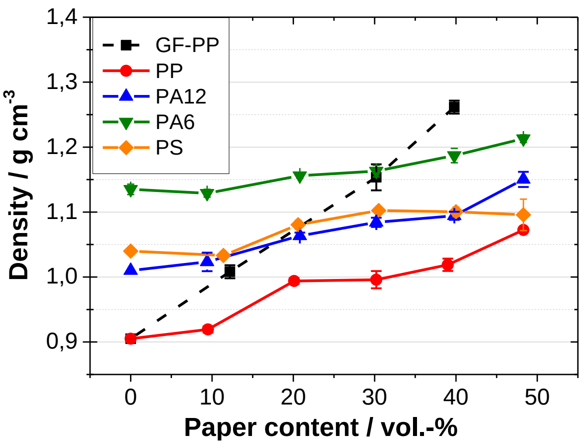

Figure 4. Densities of paper composites with different polymer matrices in comparison with glass fiber reinforced PP (black dashed line).

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One way to evaluate material's performance is to compare the specific properties (property divided by density). In Table 1, the specific properties of the GF reinforced PP laminate are compared to the paper laminates with different composite matrices. It has to be taken into account that the filler content of the GF composite was 40 vol.-%, while the paper content of the laminates was up to 48 vol.-%, as the highest obtained properties were used for the comparison. Concerning the elastic and flexural modulus, all paper laminates show comparable results to the GF reinforced composite. The paper-PP laminate does even exceed the one reinforced with GF in its specific properties. Tensile and flexural strength of the paper composites are somewhat lower than the GF composite, however especially for the PP and PA12 composites, the results are well within range.

Table 1. Specific tensile and flexural properties of paper and glass fiber composites.

	Specific properties ((MPa*cm³)/g)			
	Elastic modulus	Flexural modulus	Tensile strength	Flexural strength
GF-PP	5618	5266	106	94
CP-PP	5767	6325	75	86
CP-PA12	4947	4760	75	82
CP-PA6	4412	4381	58	64
CP-PS	5166	5362	53	70

4. Conclusions

Thermoplastic composite laminates were fabricated with copy paper as reinforcement by hot pressing and compared to GF reinforced PP laminates. Especially for PP and PA12 paper laminates, high tensile and flexural properties were measured. When the specific properties were regarded, even higher results for the moduli were obtained. Further investigations on the material interfaces were carried out, in order to obtain more information about the influence of material choice on the mechanical properties. Paper composites, which had PP and PA12 as polymer matrices, exhibited the best results concerning modulus, strength, ILSS and degree of fiber embedding. As a result of this study, the fabricated low-density thermoplastic-paper composites could compete with plain weave glass fiber reinforced PP, particularly at low stress values. This demonstrates the high potential of standard copy paper as sustainable reinforcement material. By applying cellulose based paper sheets as reinforcement in thermoplastic polymers, composite materials with a good mechanical property profile and improved recyclability could be produced.

Acknowledgments

The authors are grateful for financial support of the research work from the Austrian Research Promotion Agency (FFG) for funding the project "Structural Paper-Thermoplastic Composites" in the scheme of "Industry-orientated Dissertation".

Excerpt from ISBN 978-3-00-053387-7

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