BIOBASED AND BIOINSPIRED: INTERFACE MODIFICATION IN CELLULOSE/POLYOLEFIN COMPOSITES BY PHOTO- INITIALIZED THIN LAYER DEPOSITION

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Abstract
This study aims to improve fibre-matrix adhesion between naturally hydrophilic regenerated cellulose fibres and hydrophobic polyolefinic matrices. Materials that are interesting for a wide range of applications such as consumer electronics or conveyor belts. As an alternative approach to conventional bonding agents, deposition of thin hydrophobic layers on the fibre surface is investigated. The formation of thin layers is attained by UV-induced photo-polymerization of a hydrophobic monomer. In dependency on different process parameters, thin layers are visible on treated cellulose fibres. Fibre pull-out tests indicate a higher fibre-matrix adhesion of processed fibres and compression moulded composites with treated fabrics show an increasing apparent interlaminar shear strength. Due to better fibre-matrix adhesion the impact strength could be enhanced and matches properties of glass-fibre reinforced polypropylene composites.

1. Introduction

In times of climate change and a foreseeable end of fossil resources, there is a growing demand for sustainable materials. Facing those difficulties, bio-based cellulose fibre reinforced composites are a promising solution due to their renewability and good mechanical properties. Besides natural fibres like flax or hemp, there is an increasing interest in regenerated cellulose fibres since these endless fibres offer homogeneous mechanical properties. Recent studies show, that regenerated cellulose fibres embedded in a thermoset matrix have mechanical properties that can match glass-fibre reinforced composites [1,2]. However there are applications, were low-cost thermoplastic matrices like polyolefins are preferred for composite manufacturing by compression moulding. For instance in casings for consumer electronics, suitcases or conveyor belts in the food industry.

The main problem in combining those components is a difference in surface properties. Embedding highly hydrophilic cellulose fibres into a hydrophobic polyolefin matrix leads to poor fibre-matrix adhesion that is essential for the transfer of stress between fibre and matrix and therefore for the mechanical properties. A common approach to enhance fibre-matrix adhesion between polyolefins and cellulose fibres is the usage of bonding agents such as polypropylene grafted with maleic anhydride (MAPP) [3,4]. Nevertheless these bonding agents are not permitted for applications in the food industry. Therefore the aim of this study is to find a way of enhancing fibre-matrix adhesion between

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regenerated cellulose fibres and a polyolefinic matrix without bonding agents. Several attempts have been made by modifying the fibre surface of cellulose fibres by physical, chemical or enzymatic treatment [5,6]. Recent studies showed that fibre surfaces can be modified by UV-light induced graft-co-polymerization as well as homo-polymerization of thin layers on the fibre surface [7-10]. This process can be described as following: Fibres are treated with a solution containing a highly UV-absorbing monomer. Under UV-radiation radicals are generated on the fibre surface as well as in the monomer solution. Depending on the ratio of absorbances in the relevant UV spectral range, cross-linking of a thin polymer layer might initiate on the fibre surface (co-polymerization or "grafting from") or in the bulk of the monomer solution (homo-polymerization or "grafting onto"). This process was successfully established for polyethyleneterephthalate and polypropylene fibres resulting in a mechanically modified fibre surface [9,10].

Given this background, the idea of this work is to establish thin hydrophobic layers by UV-induced photo-polymerization on regenerated cellulose fibres to improve fibre-matrix adhesion.

In contrast to conventional methods, thin layers offer the opportunity to achieve a gradual stiffness transition from the fibre to the matrix. This design-principle can be found in a variety of plant structures, where a graded transition of mechanical properties between the interfaces of fibres, fibrils and the surrounding matrix is vital to ensure good damping properties [11].

2. Materials and methods

2.2. Materials

To represent a process that is close to time and cost requirements of the composite industry, regenerated cellulose fibres were treated within the fabric (Cordenka® T1812, plain weave, 295 g/cm², Cordenka GmbH & Co. KG, Oldenburg, Germany). As a representative polyolefinic polymer a common polypropylene (Adstif HA840R, LyondellBasell Industries, Rotterdam, NL) was chosen.

2.3. Fibre treatment

In a first step the regenerated cellulose fibre fabrics were immersed into a solution of the reactive monomer Pentaerythritol triacrylate (PETA) in isopropanol. In a second step the fabrics were dried and subsequently irradiated with broadband UV (UVACUBE 2000 Hg lamp, Dr. Hönle, München, Germany). This process was completed by extraction in isopropanol to remove redundant monomers. As relevant process parameters, monomer concentrations as well as UV-exposure time were varied. Based on preliminary tests, monomer concentrations between 1 % and 5 % were chosen. UV-exposure time was varied between 1 min and 20 min.

2.4. Fibre pull-out

The effect of the fibre treatment on fibre-matrix adhesion was investigated by fibre pull-out tests as shown in figure 1A. Therefore single fibres were separated from the treated fabric and fixed between two polypropylene sheets. After compression moulding (temperature: 180 °C, pressure: 0.13 - 0.16 N/mm², time: 5 min), samples for tensile testing with parallel embedded fibres were cut out of the 300 – 400 µm thick sheets. Before testing all samples were conditioned for at least 18 h at 23 °C and 50 % relative humidity. Tensile samples were loaded axially with a universal testing machine (Type Z020, Zwick/Roell GmbH, Ulm, Germany). Manually closable clamps (Type 8133, 1 kN, Zwick Roell GmbH) were used and data was recorded with a 500 N load cell. The clamping length was set to 10 mm and the testing speed to 2 mm/min. Every sample was tested until fracture. The fractured surface was analyzed using a polarization microscope (Bresser Science ADL-601P, Bresser GmbH, Rhede, Germany with Bresser Microcam 9.0 MP) by measuring the length of the pulled out fibres (fibre pull-out length) (Fig. 1B). Assuming the same diameter and tensile strength for every tested fibre, the fibre

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pull-out lengths were compared directly as an indicator for fibre-matrix adhesion. A poor fibre-matrix adhesion should lead to a long fibre pull-out length and vice versa. Since pull-out lengths scatter broadly, 10 - 20 tensile samples were tested for every process specification in fibre treatment, containing 83 - 127 fibres.

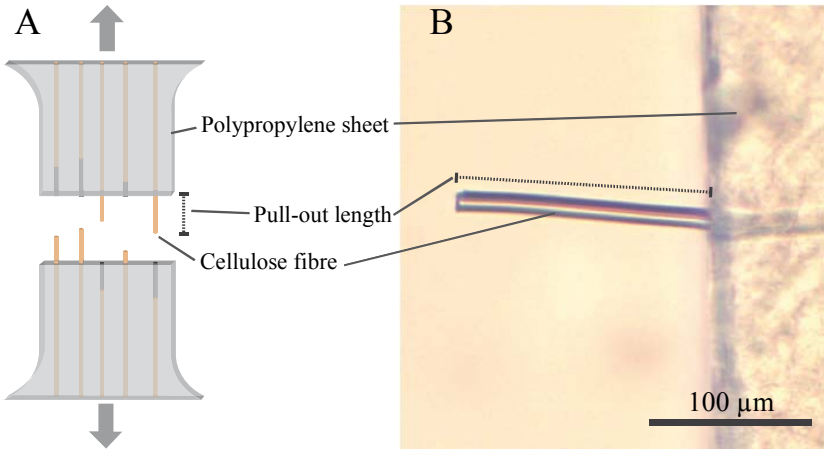

Figure 1. Schematic illustration of fibre pull-out tests (A). Fracture surface of a specimen with a fibre pulled out during tensile testing (B).

2.5. Composite manufacturing

To investigate the fibre treatment on the properties in composite materials, small plates were manufactured by compression moulding (Fig. 2A). Therefore 11 to 12 fabric layers (0°/90°) were stacked with polypropylene in between and pressed in a small mould especially designed for an instron universal testing machine (Type Z020, Zwick/Roell GmbH, Ulm, Germany). To achieve a good impregnation of the fabrics, press temperature was set to 210 °C. A pressure of 0.16 N/mm² was applied for 5 min and then raised to 0.8 N/mm² for another 5 min. The composite structures were cured by cold pressing between aluminium plates and had a final thickness of about 4 mm with a fibre volume content betwenn 55 % and 65 %.

2.6. Interlaminar shear strength

Interlaminar shear properties in composite materials were tested by double notched tensile testing according to DIN 65148 (Fig. 2B). Since the manufactured composite plates were 80 mm in width and length, the required specimen length had to be adjusted. By measuring the maximum force during shearing divided by the shear plane, the apparent interfacial shear strength was calculated. Five specimens were tested for each series of experiment.

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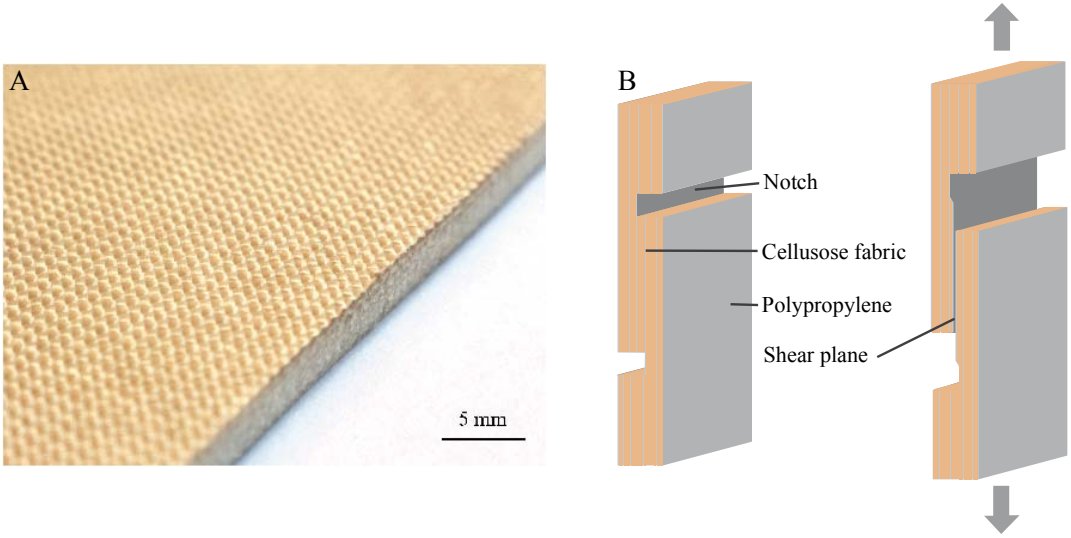

Figure 2. Composite plate made of cellulose fibres in a polypropylene matrix by compression moulding (A). Schematic illustration of double notched tensile testing (B).

2.7. Impact properties

Fibre-matrix adhesion as determined by fibre pull-out (single fibres) and double notched tensile testing (composite) is important for the impact properties of a composite. Therefore unnotched charpy-impact experiments were carried out according to DIN EN ISO 179-1 with a 4 J hammer and a support distance of 62 mm (Zwick 5102, Zwick/Roell GmbH, Ulm, DE).

For all three described experiments untreated fabrics/fibres were compared with different treated samples. Before testing all samples were conditioned for at least 18 h at 23 °C and 50 % relative humidity.

2.8 Statistics

Statistical analysis for a small number of samples (e.g. charpy-impact and interlaminar shear experiments) was done in Excel (Version 2010, Microsoft Cooperation, Redmond, USA). Statistical analysis for fibre-pull out experiments and graphic preparation were done in R (Version 3.1.2, The R Foundation for Statistical Computing).

3. Results and discussion

After fibre treatment by photo-polymerization processes, the deposition of thin polymer layers on the cellulose fibre surfaces was confirmed in SEM analyses (data not shown). An UV-exposure time of five minutes was found to be sufficient for thin layer deposition. Figure 3 shows fibre pull-out lengths in dependency on the monomer concentration. Whereas no improvement of fibre-matrix adhesion could be achieved with a low monomer concentration of 1 % PETA, a higher monomer concentration of 5 % PETA leads to a significant (U-test, $\alpha = 0.05$) decrease of fibre pull-out length and therefore increase of fibre-matrix adhesion. During preparation of single fibres for fibre pull-out testing, fibres are taken randomly from the inner and the outer region of a yarn. For this reason, the wide scattering of fibre pull-out lengths could be due to uneven deposition of thin layers within the fabric.

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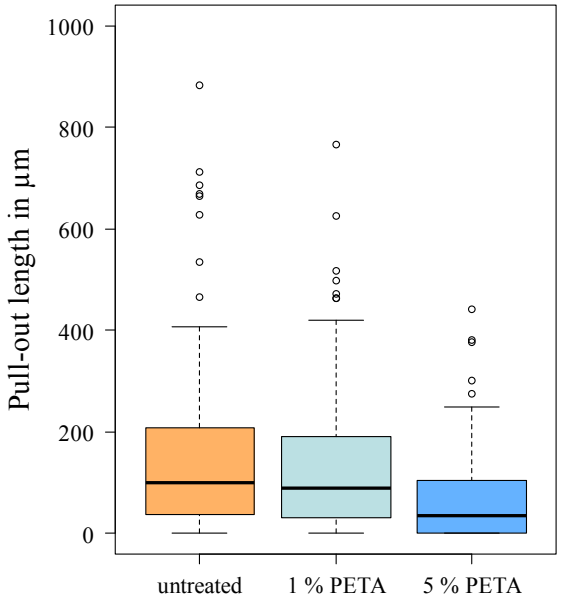

Figure 3. Boxplots for fibre pull-out lengths of untreated regenerated cellulose fibres and the same fibres treated by a photo-polymerization process with different monomer concentrations of PETA. Pull-out lengths over 1000 µm are not included in this figure. The boxplot shows the median within a box between the first and third quartiles. Whiskers indicate lowest and highest values within 1.5 % of the interquartile range. Outliers are plotted as single dots.

Contrary to the influence of a low monomer concentration on fibre-matrix adhesion measured on single fibres, the apparent interlaminar shear strength in a composite structure made of treated fabrics increases significantly (U-Test) also for low monomer concentrations (Fig. 4). As the local concentration of absorbing monomer is vital for the resulting layer formation, it is reasonable to assume that photo-polymerization processes are mainly initiated on the outer surface of the multifilament yarn and to a lesser degree in the yarn capillaries, where monomer concentration is strongly dependent on the penetration of the monomer solution during immersion and might therefore be reduced. Accordingly, a greater number of fibres can be expected to be unmodified in case of the low PETA concentration, and a low fibre-matrix adhesion is observed when measuring single fibres. In contrast, the fibre-matrix adhesion, represented by the apparent interlaminar shear strength within a composite made of treated fabrics, seems to depend mostly on shear resistance between the fabric layers. For this reason a thin layer deposition with a low monomer concentration on the yarn surface and therefore on the interphase between fabrics seems to be sufficient to improve the apparent interlaminar shear strength.

A similar and also significant (U-Test) trend is obvious regarding the impact properties of composite materials made of treated regenerated cellulose fibres. Thin layer deposition leads to higher charpy impact strength of composites made of regenerated cellulose fibres and polypropylene. Starting with a good fibre-matrix adhesion and improving it even further should lead to decreasing impact strength because energy absorbing mechanisms, such as fibre pull-out and debonding, are malfunctioning with a perfect adhesion [12,13]. In contrast, a poor or non-existent adhesion results in low impact strengths, due to a lack of stress transfer between fibre and matrix. Given this starting position, an improvement of fibre-matrix adhesion leads to better impact strengths, which could be observed in this study.

Charpy impact strength of random glass-fibre fleece reinforced polypropylene summarized by Wambua et al. [14] is about 54 kJ/m². Similar values were reported by Thomason and Vlug [12] for short-fibre reinforced polypropylene. Even if a direct comparison with results determinded within this study is limited because fabrics made of endless fibres were investigated, it is obvious that impact

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properties of cellulose fibres, treated in a thin layer deposition process, can match those of glass-fibres within a polypropylene matrix.

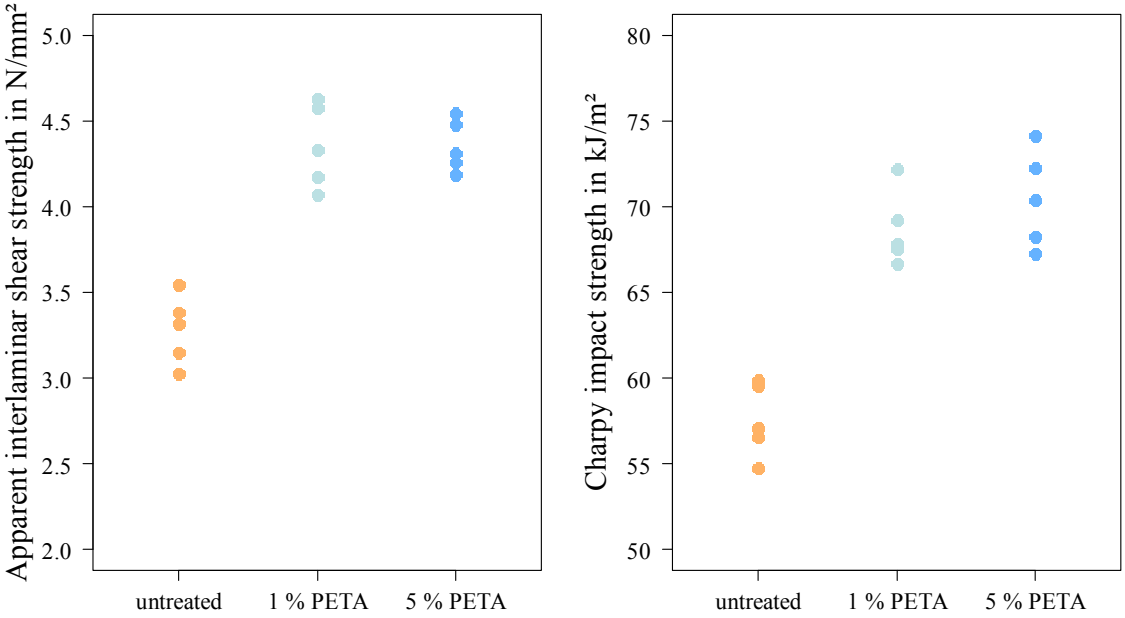

Figure 4. Apparent interlaminar shear strength and charpy impact strength of composite samples made of untreated fabrics in comparison to composites made of treated fabrics using either a 1 % monomer concentration of the reactive polymer PETA or a 5 % monomer concentration. Five samples were tested for each series.

4. Conclusions

By using photo-polymerization processes, thin layers can be deposited on regenerated cellulose fibres. The hydrophobic surface properties of these layers result in a higher fibre-matrix adhesion, if treated fibres are embedded in a polyolefinic matrix such as polypropylene. Improved fibre-matrix adhesion leads to better impact properties of composite materials. Future work will focus on the bio-inspired aspect of gradual stiffness transition between fibre and matrix, by nanoindentation experiments and the evaluation of composite damping properties. Optimized composites are promising for application in consumer electronics or conveyor belts in the food industry.

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