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Sustainable wood-plastic composites from bio-based polyamide 11 and chemically modified beech fibers

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ABSTRACT

Wood-plastic composites from bio-based polymers and wood fibers (bio-WPC) provide an improved sustainability and carbon footprint compared to conventional composites. Actually, the implementation of this approach into industrial applications is hindered by the missing knowledge on the mechanical and thermo-mechanical properties of such bio-WPC. In this study, the properties of a bio-WPC from bio-based polyamide 11 (PA 11) and chemically modified beech fibers were investigated. The chemical modification of the beech fibers by an alkaline treatment with an aqueous solution of sodium hydroxide (NaOH) was done to support the melt processing and adhesion to the PA 11 matrix. Analysis of the modified fibers by Thermogravimetric Analysis (TGA) proved an increased thermal stability, as identified by an increase of the extrapolated TGA onset temperature from 290 to 330 °C. This improvement resulted from hemicellulose removal, as confirmed through Attenuated Total Reflection Infrared Spectroscopy (ATR-FTIR). Consequently, mechanical and thermo-mechanical analysis of the processed bio-WPC showed an increase in elastic modulus and storage modulus of the composites by the chemical treatment of the fibers. This effect was attributed to an increased number of hydrogen bonds between the modified beech fibers and the PA 11 matrix. The overall mechanical properties of the investigated bio-WPCs support their use as sustainable construction material for technical applications.

1. Introduction

Wood-plastic composites (WPC) have been used as construction materials for many years due to their beneficial properties in comparison to synthetic fiber composites, like decreased density and lower costs [1]. The raw materials used to process WPC are mainly polyolefin thermoplastics, such as polyethylene (PE), polypropylene (PP) or polyvinylchloride (PVC), and wood flour or fibers mainly from softwood like spruce or pine [2–4]. Typical applications include extruded decking and profiles in the building and construction sector and also complex interior parts for automotive applications, produced by injection molding [5,6]. The next generation of these materials is based on the implementation of biogenic matrix polymers and thus being processed from completely regenerative raw materials [7]. The idea behind the approach of such completely biogenic wood-plastic composites (bio-WPC) is that the amount of CO_2 generated by the processing of the composite material is partially or completely compensated by the CO_2 consumed in the growth phase of the plants used as raw materials [8]. Thus, construction materials with a significantly improved sustainability and carbon footprint could be produced. Despite the ecological advantages, economic interests like decreased dependency in fossil resources and the support of the development of new and sustainable technologies are also addressed with this approach.

Biopolymers can be divided into biodegradables and non-biodegradables, the latter being of particular interest for the use as matrix polymers in technical composite materials since they can be seen as drop-in solutions for already existing conventional plastics [9]. In recent years, bio-based polyethylene from sugar cane and bio-based polyamides from castor oil have become commercially available and represent the most interesting alternatives to their fossil-based counterparts [10]. The main obstacle in producing WPC based on polyamides is their relatively high melting temperature which promotes thermal degradation of the wood fibers during processing. Despite this, conventional polyamide 6 (PA 6) has been studied as matrix material for natural fiber-reinforced composites because of its beneficial thermo-mechanical properties [11–18]. Bio-based polyamides, like polyamide 11 (PA 11), polyamide 10.10 (PA 10.10) and polyamide 6.10 (PA 6.10), have generally lower melting temperatures than conventional PA 6 [19]. This enables the melt processing of wood fiber reinforced composites before the start of thermal degradation of the wood fibers, which has been reported to be at around 220 °C [20]. Accordingly, there is a

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great potential to develop sophisticated and sustainable bio-WPCs with these bio-based polyamides. However, actual market prices of bio-based polyamides are up to five times higher than conventional PA 6 due to lower production capacities [21].

The chemical modification of wood fibers has been studied in the past mainly to improve their adhesion to thermoplastic polymers or coupling agents and in consequence to improve the mechanical properties of the subsequently processed wood-plastic composites. One widely used chemical treatment is mercerization, an alkaline treatment with aqueous sodium hydroxide (NaOH) [22]. The main effect is the disruption of the hydrogen bonds on the fiber surface, leading to a higher roughness of the surface by removal of certain amounts of lignin, waxes, oils and hemicelluloses. In consequence, this increases the amount of hydroxyl groups on the fiber surface and improves wetting and adhesion with thermoplastic polymers. Additionally, the thermal stability of the wood fibers can be enhanced. Improvement of the thermal stability of wood fibers can also be done by physical modification techniques, especially by heat treatment [23]. The general mechanism of both treatments is the selective decomposition of the hemicellulose components, which display the least thermally stable components of wood fibers.

Although non-biodegradable biopolymers, such as bio-based polyamides, are gradually entering the market, there is no extensive knowledge about their potential as matrix polymers in composite materials for technical applications. There is a multitude of studies available on wood-plastic composites based on conventional polyolefins, but only a few studies discuss the approach of bio-WPC from non-biodegradable biopolymers as sustainable composite materials for technical applications. Furthermore, the mechanism of improving the thermal stability of wood fibers by chemical modification is already discussed but not systematically applied to process wood-plastic composites from highly melting polymers like polyamides in literature. In this study, the processing and the resulting properties of a bio-WPC from bio-based polyamide 11 (PA 11) and chemically modified pulped beech fibers were therefore investigated. In the first part, modification of the morphology and the thermal stability of the beech fibers was done by an alkaline treatment to improve the processability with the PA 11. In the second part, characterization of the morphological, mechanical and thermo-mechanical properties of the subsequently processed bio-WPC was done. The goal of these investigations was to quantify the potential of bio-WPCs based on bio-polyamides and further to support their implementation as sustainable drop-in materials for conventional WPCs in already existing technical applications.

2. Materials and methods

2.1. Materials

2.1.1. Bio-based polyamide 11

The matrix polymer used to produce the bio-WPC was a bio-based polyamide 11 (PA 11, Rilsan BESNO TL) from Arkema Company. The raw material for this polymer is castor oil, which can be converted into 11-aminoundecanoic acid and subsequently polycondensed into PA 11 with a bio-based carbon content of >98%. The melting temperature of the used grade is 186 °C and the density is 1.02 g/cm^3. The material was used as delivered in spherical pellet form and dried at 80 °C for 8 h before processing.

2.1.2. Chemically modified beech fibers

The beech fibers (BF) used to process the bio-WPC were derived by a thermo-mechanical pulping process from beech wood (Fagus sylvatica). In the first step, a hydro-thermal pretreatment of the beech wood chips was done at 80 °C. Secondly, the pretreated wood chips were transported into a digester, where they were plasticized over 4 min at a temperature of 170 °C and a pressure of 9 bar. Given this, the plasticized wood material was conveyed into a twin disk refiner with a gap of 0.1 mm. Finally, the obtained beech fibers were dried at 80 to 100 °C to a water content of approximately 6.5% as measured with the Soxhlet method. The chemical modification of the beech fibers was done separately after the pulping process with an alkaline treatment (mercerization). For this, the fibers were soaked in distilled water and then washed in an aqueous solution of sodium hydroxide (NaOH) with a concentration of 10 g/l at room temperature for 60 min. Afterwards, the fibers were removed and washed again with distilled water until pH 7 was achieved. Drying of the modified beech fibers (BF_{mod}) was done at 100 °C for 5 h in a convection oven to a moisture content of approximately 2.8% as measured with the Soxhlet method.

2.2. Methods

2.2.1. Attenuated total reflection infrared spectroscopy (ATR-FTIR) of beech fibers

The ATR-FTIR measurements were conducted with a Bruker Equinox 55 device with an ATR unit. The unit is equipped with a diamond ATR crystal with a total measurement area of 4 mm^2. The measuring chamber was continuously purged with gaseous N_2. For data collection and processing, the software OPUS 6.5 was used. All spectra were collected over the wave number span of 650–4000 cm^{-1} at a resolution of 4 cm^{-1}. Before the specimen measurement, a reference spectrum of the gaseous environment was collected. Then, compacted pellets of the wood fibers were placed onto the ATR crystal and secured with a screw. For each sample, three spectra were collected and converted into a mean spectrum. The baselines of the spectra were corrected using the concave rubber band method with 10 iterations.

2.2.2. Thermogravimetric analysis (TGA) of beech fibers

The characterization of the thermal stability of the beech fibers was done by TGA with a Netzsch STA 449 F1 device. Compacted pellets of approximately 4.5 mg of wood fibers encased in aluminum pans were placed into the device and the weight loss from room temperature to 600 °C was measured in dynamic mode with a heating rate of 10 K/min. During the measurements, the measuring chamber was continuously purged with gaseous N_2. Analysis of the obtained data was done with the software Proteus Analysis.

2.2.3. Preparation of bio-WPC and test specimens

The preparation of the bio-WPC was carried out by discontinuous mixing in a two-roll internal mixer (PolyLab, Thermo Scientific). Compounds of the PA 11 and the modified as well as the unmodified beech fibers were processed with fiber contents of 30, 40 and 50 wt.%. The processing conditions were kept constant for all the composites at 196 °C melt temperature and 50 rpm rotation speed. After 3 min melting of the PA 11, the beech fibers were added and the components were mixed for 5 min. Subsequently, the composites were removed from the mixing chamber and directly injection molded into standard test specimens by a lab scale plunger injection molding machine (MiniJet, Thermo Scientific). Processing parameters for the preparation of the test specimens were kept constant at 220 °C melting temperature, 110 °C mold temperature, 3.5 min melting time, 900 bar injection pressure and 460 bar hold pressure. The processed test specimens were immediately sealed in multilayered aluminum foil to prevent water uptake (fresh as-molded).

2.2.4. Morphological characterization of beech fibers and bio-WPC

The morphological properties of the beech fibers were determined by manual statistical analysis of the length and width of the unmodified and modified fibers. For this, random fiber samples were individually arranged between two transparent polypropylene films and optical scans were made. Picture analysis was subsequently done manually with an evaluation program (CellF) for approximately 2500 single fibers. In result, the average fiber length and fiber width were obtained. Additionally, the surfaces of the unmodified and modified beech fibers as well as the fracture surfaces of Charpy notched impact test specimens