Tailor-made PLA and PHB based cellulose fibre composites through coupling or anti-coupling agents

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Abstract

The mechanical properties such as tensile strength and impact strength of fibre reinforced materials are adjustable by modifying the fibre-matrix interface. The present contribution deals with polylactic acid (PLA) and polyhydroxybutyrate (PHB) reinforced with 20 wt% cellulose man made fibres (rayon, tyre cord yarn). By incorporating additives the fibre-matrix adhesion is varied between strong and weak. The composites were characterized mechanically and structurally using data from the tensile test, impact penetration test and Charpy notched/unnotched impact test, or using scanning electron microscope (SEM) fracturing analysis.

When hexamethylene diisocyanate (HMDI) is used for reactive compounding an excellent fibre-matrix adhesion with a strong interface is achieved. This is obvious from scanning electron microscopy fracture micrographs. In the case of PHB with 20 wt% fibre content the tensile strength can be improved by 50% from 36 to 54 MPa by addition of 1 wt% HMDI. By contrast, with maleated polypropylene (MAH-g-PP) the fibre-matrix adhesion can be reduced as far as possible. In this case a frictional mechanism is activated for absorbing fracture energy. For PLA with 20 wt% fibre content and 3 wt% MAH-g-PP, Charpy notched impact strength can be improved by about 200% from 8 to 26 kJ/m².

Keywords: PLA, PHB, cellulose fibre, fibre-matrix adhesion, fibre-matrix interface, mechanical properties, improved impact properties, improved tensile strength

1 Introduction

Bio-based and biodegradable polymers like polylactide (PLA) and polyhydroxybutyrate (PHB) are becoming increasingly more prevalent as ecological alternatives to polymers made from fossil resources. Therefore one of the aims of applied research is to discover technical applications for these biopolymers in, for example, the automotive industry (for door panels or dash boards) as a replacement for established petroleum-based materials such as polymer blends made from PC and ABS, as well as short glass fibre reinforced polypropylene (PP/GF). However, the high material requirements in this industry are only partially met by native PLA. In order to improve in particular the mechanical properties, bio-based cellulose reinforcing fibres like cellulose rayon can be incorporated into the PLA matrix. In such a way, the composite remains completely bio-based¹. A continued improvement of PLA composites can be achieved through modifying the fibre-matrix interface. In this case the mechanical properties can be varied in a wide range and are adjustable for different applications.
1.1 Experimental

Materials

Table 1: Matrix polymers, fibres and additives used in this study

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Trade Name</th>
<th>Producer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-D,L-lactide</td>
<td>PLA</td>
<td>NatureWorks® PLA-7000 D</td>
<td>Cargill Dow</td>
</tr>
<tr>
<td>Polyhydroxybutyrate</td>
<td>PHB</td>
<td>Biomer® P 226</td>
<td>Biomer</td>
</tr>
<tr>
<td>Cellulose fibre</td>
<td>CF</td>
<td>Cordenka® RT 700</td>
<td>Cordenka GmbH</td>
</tr>
<tr>
<td>a) continuous filaments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b) cut fibres, 4 mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maleic acid anhydride grafted</td>
<td>MAH-g-PP</td>
<td>Fusabond® MD353D</td>
<td>Du Pont</td>
</tr>
<tr>
<td>polypropylene</td>
<td>HMDI</td>
<td>MERCK Schuchardt GmbH</td>
<td></td>
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<tr>
<td>Hexamethylene diisocyanate</td>
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Compounding and Sample Preparation

PLA, PHB and the cellulose man-made fibres were dried overnight under vacuum at 50°C and 100°C, respectively until moisture levels reached 0.025 wt% and 0.1 wt%.

Small scale compounding (200 g)

Compounding was performed with a Brabender W 350 kneader at approx. 180°C for 5 min. Additives like anti-coupling agent MAH-g-PP (3 wt.%) and coupling agent HMDI (1 wt.%) were added after one minute.

Enlargement scale compounding (5 kg)

A pultrusions technique was applied with a conventional co-rotating twin screw extruder (Haake Rheocord 9000 PTW 25) equipped with a coating die assembly to cover a number of continuous cellulose fibre filament tows with the molten anti-coupling agent mixture. The maximum temperature of the extruder and the die were 170°C. The coated filament tows were cooled with water and cut into pellets which were dried overnight at 50°C in the presence of P₂O₅. In a second step, the pellets were extruded with the same extruder under the same conditions to homogenise the fibre-matrix mixture. After cooling the tread was cut into final pellets of defined lengths between 3 and 5 mm.

Injection moulding

Standard test specimens were prepared according to DIN EN ISO 527-2 (tensile test) and DIN EN ISO 179 (Charpy impact test) using an injection moulding machine Allrounder 270 M 500-90, Arburg for enlargement scale and HAAKE „MiniJet“ for small scale.

Characterisation

The mechanical properties tensile strength σₘ, tensile E-Modulus (E) and elongation at break εₜ have been determined with a universal testing machine Zwick 1445 at 50 % relative humidity and 23°C.

Charpy notched impact strength a₀CN and Charpy unnotched impact strength a₀ were measured with a Ohst Co. Charpy tester using a 1 J and 4 J hammer respectively, at 23°C and -18°C, 50 % humidity.

The specific values maximum force Fₘ, absorbed Energy Eₘ and loss to stored energy ratio (damping factor Δ) from the impact penetration test have been determined with an falling weight of 130 J (13.65 kg, 4.43 m/s) according to DIN EN ISO 6603-2.

Fracture surfaces from tensile experiments were analysed with a scanning electron microscope Jeol JSM 6330 at 5 kV acceleration voltage.
1.2 Results and Discussion (Small scale compounding)

Mechanical Properties

**Strong fibre-matrix interface**

The coupling agent HMDI has two highly reactive isocyanate end groups and is capable to react with the hydroxyl groups of the cellulose surface chains on the one hand, and with the hydroxyl or carboxyl groups at the PLA or PHB chain ends on the other, forming covalent urethane or amide bonds. By this grafting reaction of PLA or PHB onto cellulose the latter becomes more compatible with the PLA or PHB matrix and the wetting of the fibre is improved \(^2,^3\). Entanglements are possible, allowing an interface layer between fibre and matrix to be developed which guarantees good adhesion. Tensile forces can be transferred better to the reinforcing fibres at higher elongations. However, in contrast to what would be expected, tensile strength is increased only moderately for PLA while modulus but also notched impact strength remain unchanged as seen in Fig. 1a. In the case of PHB with 20 wt% CF fibre content the tensile strength and unnotched Charpy impact strength is clearly improved by 50 % from 36 to 54 MPa and by 90 % from 30 to 55 kJ/m\(^2\) respectively, through addition of 1 wt% HMDI as seen in Fig. 1b.

![Fig. 1a: Influence of cellulose fibre (CF) reinforcement and improved fibre-matrix adhesion (through coupling agent HMDI) on the mechanical performance of PLA based composites](image1a)

![Fig. 1b: Influence of cellulose fibre (CF) reinforcement and improved fibre-matrix adhesion (through coupling agent HMDI) on the mechanical performance of PHB based composites](image1b)

**Weak fibre-matrix interface**

Reactions and bonding schemes between cellulose fibres and MAH-g-PP are described in the literature on polypropylene composites \(^2,^3\). By covalent bonding of MAH-g-PP through ester linkages to cellulose hydroxyl groups the fibre is made more hydrophobic and entanglements promote fibre-matrix adhesion.

![Fig. 2a: Influence of cellulose fibre (CF) reinforcement and decreased fibre-matrix adhesion (through anti-coupling agent MAH-g-PP) on the mechanical performance of PLA based composites](image2a)

![Fig. 2b: Influence of cellulose fibre (CF) reinforcement and decreased fibre-matrix adhesion (through anti-coupling agent MAH-g-PP) on the mechanical performance of PHB based composites](image2b)
In the present case there cannot be any interdiffusion (entanglements) between grafted PP and PLA or PHB due to their thermodynamic incompatibility. Therefore, forces, acting above 0.5% strain, cannot be transferred to the fibres. In this context, MAH-g-PP acts in cellulose fibre reinforced PLA or PHB systems as an anti-coupling agent. Tensile strength is not much higher than for unreinforced PLA or PHB (Fig. 2a, b). However, a frictional pull-out mechanism is activated as the energy absorbing process for impact loading (see Fig. 3a1, b1). Thus, notched Charpy impact strength is increased by 400% for 20 wt% CF fibre content. Stiffness, a property at very low strains, is not affected.

Structural Analysis

Fig. 3: SEM tensile fracture surface micrographs of a) PLA/CF and b) PHB/CF composites with varied quality of fibre-matrix adhesion

In the composites with MAH-g-PP an extreme fibre pull-out is observed with its typical cylindrical voids and long fibre ends (Fig. 3a1, 3b1). Moreover, gaps are visible between fibre and matrix (Fig. 2a1, 2b1). With increasing fibre-matrix adhesion the pull-out fibres become shorter (see Fig. 3b1, b2, b3). In cellulose fibre reinforced PLA and PHB composites with strong interface no pull-out fibres or cylindrical voids can be observed throughout the whole cross section and all fibre fractures are in the fracture plane (see Fig. 3a3, b3). There are no gaps between fibre and matrix material and the fibres are completely covered with matrix material.
1.3 Results and Discussion (Enlargement scale compounding)

Mechanical Properties

**Weak Fibre-Matrix Interface**

The additive MAH-g-PP acts as a very efficient impact modifier for cellulose fibre PLA based composites. This is shown from testing the notches Charpy impact specimens (Fig. 2b) which were prepared from small scale compounding. Because of the great potential of the anti-coupled PLA/CF system an upscaling to enlargement scale compounding were done. From impact penetration test we observed a significant improvement of absorbed energy $E_A$ due to the extreme fibre pull-out mechanism during deformation (Fig. 4a). This increase of loss energy resulted in a higher damping factor. For PLA with 20 wt% fibre content and 3 wt% MAH-g-PP, all specific values from Charpy impact strength can be improved significantly, such as $a_{CN}$ by 220 % from 8 to 26 kJ/m², while the composite stiffness remains unchanged on a high level (Fig. 4b). Through cellulose man-made fibre reinforcement and the use of the anti-coupling agent MAH-g-PP it is possible to generate bio-based PLA composites with mechanical properties above the level of PP/GF (Fig. 4b).

![Fig. 4a: Influence of cellulose fibre (CF) reinforcement and decreased fibre-matrix adhesion (through anti-coupling agent MAH-g-PP) on the impact properties from impact penetration test of PLA based composites](image)

![Fig. 4b: Influence of cellulose fibre reinforcement and decreased fibre-matrix adhesion (anti-coupling agent MAH-g-PP) on the mechanical performance of PLA based composites in comparison with conventional PP/GF composites](image)

**2 Summary**

- HMDI is suited as an efficient coupling agent in cellulose fibre reinforced PLA and PHB composites
- MAH-g-PP acts as a very efficient impact modifier, by activating an energy absorbing pull-out mechanism, without degreasing the composite stiffness
- Improved fibre-matrix adhesion leads to moderate improvements in strength
- Composite stiffness is independent of fibre-matrix adhesion

**3 References**