

COTTON FIBRE-REINFORCED COMPOSITES FOR INJECTION MOULDING AND 3D PRINTING

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A fast developing and demanding industry on the one hand and a growing concern for sustainable solutions on the other hand, are a major challenge in current material development. Cellulose fibre-reinforced composites offer an opportunity to face this challenge. Due to their good mechanical properties, natural fibres like flax or hemp are often discussed within this context. However coarse fibre bundles and impurities limit the applicability, for example in micro-injection moulding or in thermoplastic Fused Deposition Modelling (FDM) techniques. Against this background there is a growing interest for cotton fibre-reinforced composites due to high availability and relatively low prices for cotton noils or cotton combings, as well as good processability and mechanical properties. The aim of this study was to develop cotton fibre-reinforced composites for the wide spread injection moulding process and the upcoming 3D printing process by FDM. To meet the requirements of each process, cotton fibres and cotton noils with bio-based thermoplastic matrices, varying the fibre content. An optimised compounding system for the processing of natural fibres was used to produce pellets for injection moulding. In addition those pellets were used to produce thermoplastic wires for FDM. The new materials were characterised by tensile and impact testing. High and adjustable mechanical properties are promising for industrial application and offer the chance for cotton fibres to break into new markets.

As we can't imagine a modern textile industry without cotton fibres, we can't imagine our everyday life without polymers. The worldwide production of polymers is still rising and the amount of different applications for those materials is growing. New applications require materials with improved property profiles. Therefore there is an increasing demand for fibre-reinforced polymers, which offer superior mechanical

properties. On the same time there is a widespread consciousness about environmental problems caused by polymers like the pollution of oceans and landscape by waste and micro-plastic. Another concern is the use of fossil based materials like mineral oil for polymer production with regard to climate change and limited resource capacities.

One approach to face those difficulties is the use of natural fibre-reinforced composites (NFC). These materials can offer mass specific mechanical stiffness values in the same range as glass fibre reinforced composites (Herrmann et al. 1998, Saheb & Jog 1999, Wambua et al. 2003). Using polymers made of natural resources like polylactic acid (PLA), these materials are 100 % bio-based and, depending on the polymer, also biodegradable. Due to high strength and stiffness, bast fibres like flax and hemp are often used for NFC, for example in door panels and other interior parts in the automotive industry (Karus et al. 2004). However coarse fibre bundles and impurities limit the applicability of bast fibres for production techniques like micro-injection moulding and FDM with high requirements towards fibre fineness.

Against this background there is a growing interest for cotton fibre-reinforced composites due to high availability and prices of around 1.5 € - 1.6 € per kg. A major advantage of cotton fibres compared to bast fibres is the fibre fineness. Whereas flax fibres or flax fibre bundles have a thickness of about 40 – 620 µm, cotton fibres have a thickness of about 12 - 38 µm (Müssig 2010, table 13.6.) Especially in short fibre-reinforced thermoplastic polymers, the fibre thickness is of great interest. A widespread production technique for short fibre-reinforced thermoplastic materials is the injection moulding process, where the material in form of pellets is molten at a certain temperature and injected as a viscous fluid into a tool. The processable fibre thickness within this process is limited by the dimensions of the moulded structure. Thin fibres offer the opportunity to produce thin parts.

Another innovative process where fibre thickness is of great interest is the 3D-printing process by FDM. Here the material in form of a thermoplastic wire is molten and printed by a nozzle. Since those nozzles have a small diameter, thick fibres would clog up the nozzle.

The interest in additive manufacturing technologies like FDM has rapidly increased during the last years close connected to the digital industrial revolution. Due to the ability to build complex and customised parts without the need for an expensive mould, FDM has developed from a niche technology towards a well approved manufacturing process in the industry and private sector. Since the massive rise in FDM usage, bio-based polymers such as polylactide (PLA) plays a major role due to their low melting point and good processability. Taking the chance to implement sustainable materials into an upcoming manufacturing technology, other bio-based materials like wood fibre-reinforced polymers appeared on the market. However most

of the research concentrated on the usage of wood powders to create a wood-like looking and surface feeling of printed products (Michels 2017). To extend the number of possible applications for bio-based materials in FDM, it is necessary to improve the mechanical properties such as Young's modulus, strength or impact resistance, depending on the later application of the manufactured parts.

Within this context cotton fibre-reinforced compounds were developed and tested within our research programme to fulfil the high process requirements of injection moulding and FDM and to optimize material properties.

Materials & Methods

Materials

Cotton fibres and cotton noils were purchased from W. Buckmann Speditionsges.mbH Bremen (Germany). As a biobased polymer PLA was chosen because of a good availability, biodegradability and a proven processability in injection moulding and FDM processes. For injection moulding compounds PLA3251D (NatureWorks LLC, Minnetonka, USA) was used and for FDM Compounds (PLA4043D (NatureWorks LLC, Minnetonka, USA). Since PLA is known to be relatively stiff and brittle, biobased impact modifier were added to some compounds to enhance impact strength. Here again two different sorts were used: Naturegran 11bz10071 (Linotech GmbH & Co.KG, Forst, Germany) for injection moulding compounds and Naturegran 11bz10091 (Linotech GmbH & Co.KG, Forst, Germany) for FDM compounds.

Processing

For the compounding process ("mixing" of fibre and polymer to pellets for further processing) an innovative method developed within a cooperation of 3N Kompetenzzentrum Niedersachsen Netzwerk Nachwachsende Rohstoffe und Bioökonomie e. V. (Werlte, Germany), Hochschule Bremen and Linotech GmbH & Co.KG (Forst, Germany) was used. Within this process natural fibres can be processed directly after drying without further processing. Compared to other methods, the mechanical damage to the fibres during processing is relatively low. For further information see Müssig (2013). To create a broad range of material properties, compounds with varying fibre mass content were produced. Pellets were injection moulded into standardised tensile bars (Figure 1) according to DIN EN ISO 527-2.



Figure 1: Pellets and injection moulded standard tensile testing bars made of cotton fibre-reinforced bio-based polymers.

For the FDM process the cotton fibre-reinforced pellets were molten into thermoplastic wires with a standardised thickness of 2.85 mm. A standard FDM-printer (Orcabot 0.43, Mendel Parts, Netherlands) was used to print tensile samples according to DIN EN ISO 527-2. Commercially available thermoplastic wires were printed with the same procedure for comparison. Low- and high price wood fibre-filled thermoplastic wires were chosen, as well as a conventional acrylonitrile butadiene styrene (ABS) thermoplastic wire. In the FDM process the molten polymer is layed in lines. The pattern of those lines is affecting the mechanical properties of the printed object. Therefore the polymer was layed down in a standardized pattern with an orientation of $\pm 45^\circ$ towards the loading direction to ensure comparability (Figure 2). The printing temperature was adapted to the polymer within the thermoplastic wire.



Figure 2: Tensile bar printed with a cotton fibre-reinforced thermoplastic wire.

Characterisation

Mechanical properties like Young's modulus, strength and elongation at break were characterised in tensile testing according to DIN EN ISO 527-4. Tensile bars were clamped into an universal testing machine (Z020, Zwick Roell GmbH & Co. KG, Ulm Germany) and loaded with a speed of 2 mm min^{-1} . Before testing the specimens were conditioned at $23 \text{ }^\circ\text{C}$ and 50 % relative humidity for at least 18 h. The elongation was measured optically with a videoextensometer and the Young's modulus was calculated between 0.05 % and 0.25 % elongation. The unnotched Charpy impact strength was measured 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). Fracture surfaces of tested samples and fibres were analysed using a scanning electron microscope (JSM-6510, Joel GmbH, Freising).

Results and Discussion

Injection moulding: The mechanical properties of cotton fibre-reinforced PLA in dependence on the cotton fibre content are shown in figure 3. Even with a low fibre content of 20 % (all fibre contents within this study were calculated based on mass) the Young's modulus is increased by around 100 % to 7113 MPa (SD = 462 MPa, $n = 7$) compared to the pure PLA. With rising fibre content the Young's modulus increases to 10425 MPa (SD = 764 MPa, $n = 7$) for 40 %. A similar effect can be observed regarding the tensile strength. With rising fibre content the strength increased to 79 MPa (SD = 1.6 MPa, $n = 7$) for 40 %. The elongation at break decreased with rising fibre content and increasing Young's modulus, a common effect observed in fibre-reinforced composites. Whereas a low fibre content of 20 % does not affect the impact strength, the impact strength decreases with higher fibre contents compared to the pure polymer.

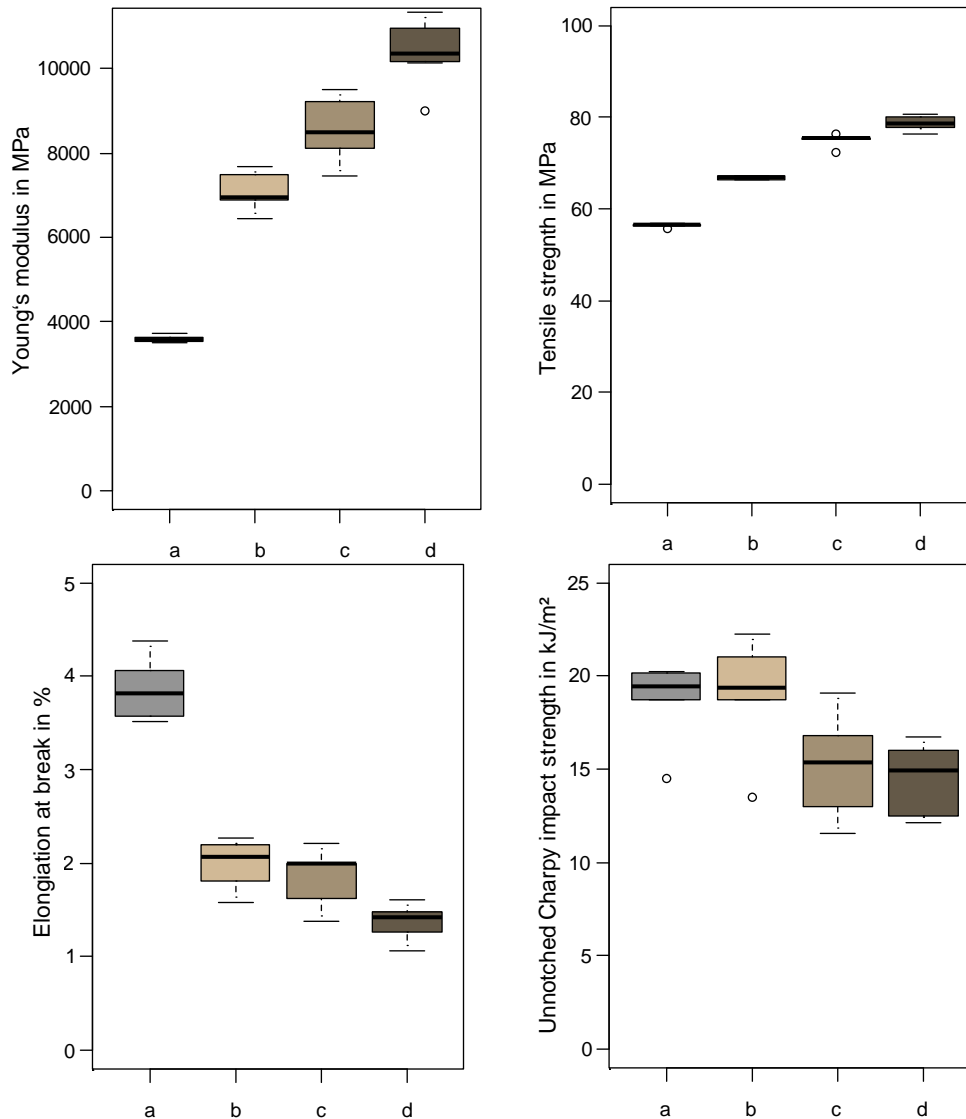


Figure 3: Tensile and impact properties of cotton fibre reinforced PLA samples for different fibre mass contents: a) pure polymer, b) 20 % cotton fibre, c) 30 % cotton fibre, d) 40 % cotton fibre. The boxplot shows the median within a box between the first and third quartiles. Whiskers indicate lowest and highest values within 1.5 times the interquartile range. Outliers are plotted as single dots. Seven samples were tested for each test serie.

Graupner (2008) reported an Young's modulus of 5230 MPa and a tensile strength of 45 MPa for cotton fibre reinforced PLA samples with a fibre mass content of 40 %. The results obtained in this study are considerably higher.

Since then, compounds reinforced with bast fibres like flax and hemp were known for their high strength and stiffness. Oksman et al. (2003) reported a tensile strength of about 50 MPa for flax fibre reinforced PLA with a fibre content of 40 % and Young's modulus of about 8000 MPa. Bax & Müssig (2008) reported a tensile strength of 54

MPa and Young's modulus of 6300 MPa for flax fibre reinforced PLA with a similar fibre mass content. The cotton fibre compounds developed within this project can easily compete regarding strength and stiffness.

Another interesting comparison is towards glass fibre reinforced composites. Huda et al. (2006) reported a tensile strength of 80 MPa and Young's modulus of 6700 MPa for glass fibre-reinforced PLA with a fibre content of 30 %. With cotton fibres a tensile strength of 75 MPa (SD = 1.3 MPa, n = 7) and Young's modulus of 8600 MPa (SD = 769 MPa, n = 7) is achieved for 30 %.

There are different reasons that come into consideration regarding the high observed mechanical properties. The new compounding method used within this study was developed to minimise fibre damage during processing (Müssig 2013). For this reason it can be assumed that the innovative compounding process is an important factor regarding the good mechanical properties. Another important factor for the properties of fibre-reinforced composites is the adhesion between fibres and polymer (matrix). Therefore current investigations focus on the characterisation of fibre-matrix adhesion with single fibres embedded in different polymer blends.

To sum up: the new compounds made of cotton fibres can compete with a wide range of conventional materials in terms of strength and stiffness and are therefore interesting to a wide range of applications.

Composite materials with high stiffness and high fibre-matrix adhesion often show relatively low impact strength, as could be observed within this study. Most important mechanisms to absorb energy in fibre-reinforced composites are the capability for plastic deformation, debonding mechanisms, fibre breakage and energy absorption by friction during fibre pull-out. Therefore the relatively low impact strength of cotton fibre-reinforced PLA could be explained by the brittle nature of PLA within compounds tested in this study.

To increase the deformation capability and therefore the impact strength of the polymer, an impact modifier was added to the PLA. Figure 4 shows the mechanical properties for a compound with 20 % cotton fibre content, impact modified (f) and without modification (b). It is obvious, that adding an impact modifier leads to a distinctly lower Young's modulus and lower tensile strength. At the same time the impact modifier proves its function by increasing the impact strength values. Regarding the relatively high decrease in stiffness and strength compared to a small increase in impact strength, one could doubt the sense of adding an impact modifier. However, the impact modifier used within this study distinctly increases the heat deflection temperature of the composite material, which is important for a wide range of applications.

Due to high amounts of energy, pesticides and water needed for cotton fibre cultivation, the environmental impact is relatively high (Broeren et al. 2017). Therefore the potential of cotton noils, as a by-product of the cotton fibre production, as reinforcement for PLA composites was investigated. The results are shown in figure 4 for series (e) and can be compared to the cotton fibre compound (f) with the same fibre content and polymer blend.

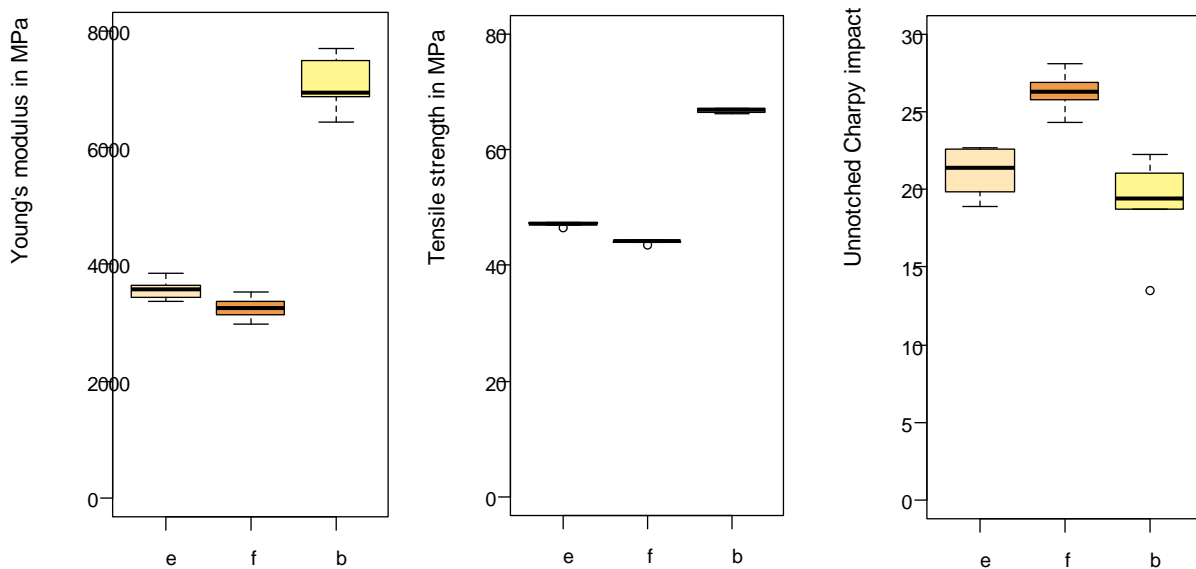


Figure 4: Tensile and impact properties of cotton fibre-reinforced PLA samples for a fibre mass content of 20 %: e) cotton noils in impact modified PLA, f) cotton fibres in impact modified PLA, b) cotton fibres in PLA. The boxplot shows the median within a box between the first and third quartiles. Whiskers indicate lowest and highest values within 1.5 times the interquartile range. Outliers are plotted as single dots. Seven samples were tested for each test series.

A significant increase in stiffness from 1996 MPa (SD = 38 MPa, n = 7) for the pure polymer to 3561 MPa (SD = 168 MPa, n = 7) for the cotton noil reinforced compound could be observed. The tensile strength increased from 38.25 MPa (SD = 0.81 MPa, n = 7) for the polymer to 47.17 MPa (SD = 0.33, n = 7) for the reinforced polymer. The tensile strength and stiffness of the cotton fibre-reinforced compound are in the same range and even a bit lower compared to the cotton noil-reinforced compound (figure 4).

SEM pictures of the cotton fibres and noils used as reinforcement indicate a difference in the maturity and thickness (Figure 5). The apparent lower maturity of cotton noils seems to have no negative effect on the composite properties. Contrary, the fine fibres and lower content of impurities, compared to cotton fibres, result in good mechanical properties.

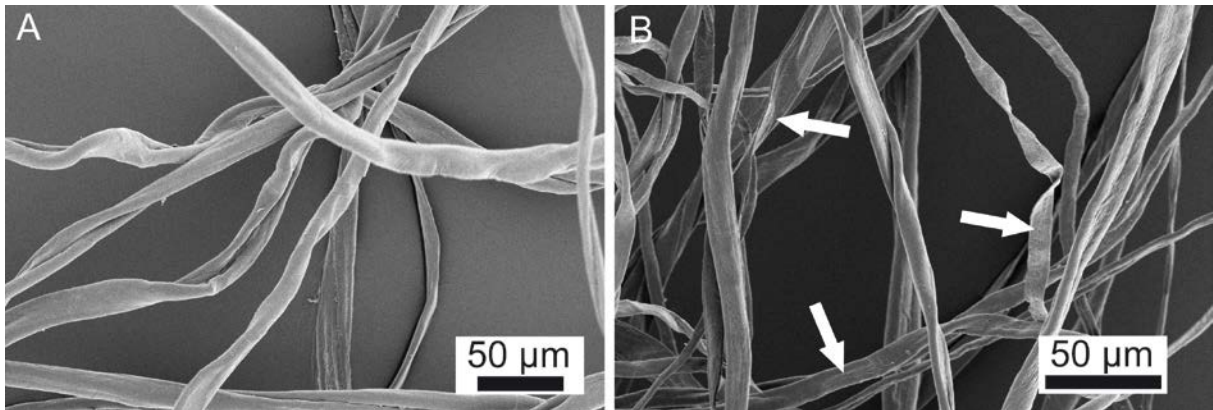


Figure 5: SEM pictures of cotton fibres (A) and cotton noils (B). Arrows indicate fibres with low maturity.

Figure 6 shows the fracture surface of a cotton noil-reinforced impact sample. The fibres protruding from the polymer, indicate a comparably low fibre-matrix adhesion. Current investigations focus on the characterisation of fibre-matrix adhesion in dependence on the fibre (cotton fibre vs. cotton noil) and the polymer (PLA with vs. without impact modifier).

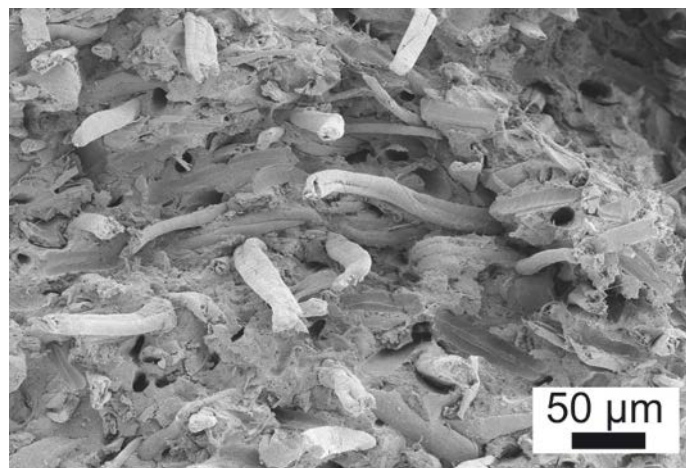


Figure 6: Fracture surface of cotton noil reinforced impact modified PLA.

The prospect of using cotton noils as reinforcement in bio-based composites with high mechanical properties is encouraging, due to relatively low prices and higher sustainability due to the usage of a side product.

3D-Printing: The cotton fibre thermoplastic wires showed a high enough flexibility to be rolled up and processed. The results from tensile testing of the 3d printed tensile bars are shown in figure 7. The Young's modulus of 3233 MPa (SD = 41 MPa, n = 5) and tensile strength of 41 MPa (SD = 1 MPa, n = 5) are distinctly higher compared to all tested commercially available thermoplastic 3D printing wires. This indicates that the high values achieved with cotton fibre-reinforced injection moulding compounds are as well evident in the FDM-process.

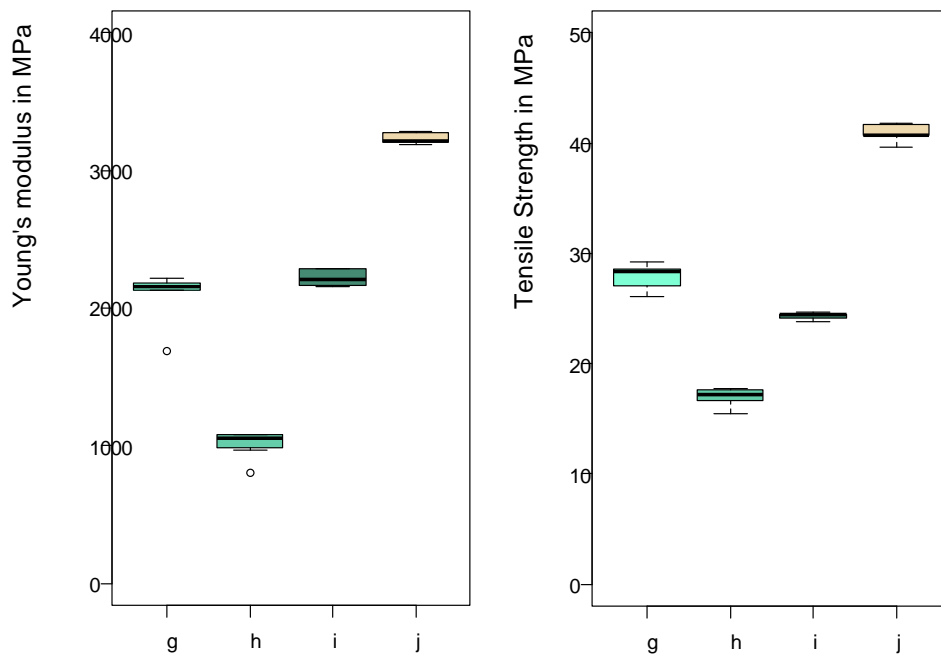


Figure 7: Results from tensile testing with FDM tensile samples printed with different thermoplastic wires: g) Wires made of ABS (n = 5). h) Low price wood fibre-filled wire(n = 7). i) High price wood fibre-filled wire (n = 5). j) Cotton fibre-reinforced wire based on an impact modified PLA with a fibre content of 10 % (n = 5). The boxplot shows the median within a box between the first and third quartiles. Whiskers indicate lowest and highest values within 1.5 times the interquartile range. Outliers are plotted as single dots.

The obtained results show, that cotton fibre reinforced 3D printing wires are a promising alternative for bio-based FDM-materials combining a natural appearance with high mechanical properties. Further work will focus on the processability of cotton fibre-reinforced wires on different printing systems as well as the usage of cotton noils as a sustainable alternative.

Conclusion and Outlook

A broad range of bio-based cotton fibre-reinforced compounds for injection moulding (and 3D printing by FDM) was developed and characterised. Cotton fibre-reinforced composites show extraordinary high tensile strength and stiffness and can compete with bast fibre as well as glass fibre-reinforced bio-based compounds. Further investigations will focus on the determination of fibre-matrix adhesion phenomena and the fibre damage during the production process for better comprehension of the observed properties. Bio-based composites with high mechanical properties are interesting for lightweight applications in the automotive industry, sports and leisure equipment or for consumer goods.

The usage of cotton noils as reinforcement leads to a promising improvement of mechanical properties. For further reduction of the environmental impact of cotton fibre production, further research will focus on the usage of recycled cotton fibres or cotton textile waste. Fibres from cotton textile waste have been recently used to reinforce polymers like low density polyethylene (LDPE) or polypropylene (PP), but the achieved mechanical properties were comparably low (Bakkal et al. 2012, Bodur et al. 2015, Petrucci et al. 2015). The new compounding process offers the opportunity to develop compounds using fibres from cotton waste with less fibre damage and therefore higher mechanical properties.

The cotton fibre-reinforced 3D printing wires for the FDM-process show promising properties compared to conventional thermoplastic wires. To implement these materials into a growing market, further research will focus on processability and further optimization of the compounds.

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