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Bio-based polyamides reinforced with cellulosic fibres – Processing and properties

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ABSTRACT

Bio-based polyamides with a melting point above 200 °C were used as the polymer matrix, and compounds with 15 wt% and 30 wt% man-made cellulose fibres were prepared. A new, single-step pultrusion process was developed, and composites prepared using this method were compared to those produced in a common two-step pultrusion process. After the compounding process was completed, specimens were further processed using an injection moulding process, and, subsequently, the thermomechanical properties were evaluated. The new single-step pultrusion process creates composites with a significantly higher tensile strength and notched impact strength than composites made using the two-step process. The increases in tensile strength and tensile stiffness were investigated in correlation with increasing fibre content. When compared with glass fibre reinforced bio-based polyamides, those reinforced with man-made cellulose fibres display both a higher notched impact strength and lightweight potential. What is also remarkable, the heat distortion temperature of such materials is close to the melting point, which is above 200 °C.

1. Introduction

Composites made of thermoplastic matrix materials and cellulosic fibres, or natural fibres, which are used for injection moulding applications, have been well known for more than one decade [1,2]. The most popular matrix materials for such composites are polypropylene and polyethylene, which both have a low heat distortion temperature. The bio content of these composites is equivalent to the amount of fibres they contain. However, these composites have two deficits, namely their dependency on crude oil, and their thermomechanical properties. The latter concerns their suitability for use in engineering parts such as those employed in the automobile industry [1,3]. In order to incorporate a higher amount of renewable raw material in the composite, and achieve higher thermomechanical properties, it is recommendable to use engineering thermoplastics made of renewable raw materials as matrix materials, i.e., bio-based polyamides [4–6]. At present, only a few studies exist which use bio-based polyamides as a matrix for composites reinforced with cellulosic fibres. Studies which use polyamides with a melting point over 200 °C are especially rare [7–15,17]. One of the earliest investigations was carried out by Klason et al. in 1984 [18].

Bio-based polyamides are only one example of the numerous engineering, thermoplastic matrix materials with a higher melting point which could also be reinforced with cellulosic fibres. The most common reinforcement for such polymers are glass fibres. An additional benefit of cellulosic fibres is the lightweight potential they possess in comparison to glass fibres. Also, the lower energy consumption during the manufacture of fibres is an advantage [19]. The main challenge of compounding engineering thermoplastics with cellulosic, or natural fibres, is to control the degree of thermal degradation in the fibres during processing, because cellulosic fibres contain thermally sensitive components [20–24]. In other studies, man-made cellulose fibres show high reinforcement potential in thermoplastic matrix materials, for example in polypropylene [25–27], or polylactic acid [28–30]. A benefit of these man-made fibres is their high cellulose content, and the constant quality in regards of their shape and mechanical properties in comparison to natural fibres from plants [31].

The aim of this study is to evaluate the properties of the bio-based polyamides reinforced with cellulose fibres which were prepared using two different compounding processes. First, a two-step pultrusion process that is well known from literature [28,31,26] was used to combine the endless man-made cellulosic fibres with the polymer's matrix. This process solves the challenge of metering, or feeding cellulosic fibres into a common compounding process without using a batch process. However, in the case of

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polyamides with a melting point above 200 °C, the two-step pultrusion process did not show such good results regarding the mechanical performance of the prepared composites [7]. In addition, the two-step process is not economical, and is very damaging for the sensitive fibres. For this reason, a single-step process was developed and used for the preparation of engineering thermoplastics reinforced with cellulosic fibres [6,17,35,36]. The mechanical performances of the composites produced using both processing methods were compared to each other.

2. Experimental

2.1. Materials

2.1.1. Matrix polymer

Two bio-based polyamides, PA 6.10 and PA 10.10 provided by Evonik Industries, were used as polymer matrixes. Both consist of castor oil, and have a bio content of approx. 62% (PA 6.10) and 100% (PA 10.10). The properties of PA 6.10 are similar to those of common, petro-based PA 6. PA 10.10 has a melting point of approx. 200 °C. Its property profile ranges between those of PA 6 and PA 12 [33].

For reference purposes, a common, petro-based PA 6, Ultramid B27E, which was provided by the company BASF SE, was used as the polymer matrix. Table 1 shows selected properties of the investigated matrix polymers.

2.1.2. Fibres

Man-made cellulose fibres, Type 700 Super 3, provided by the company Cordenka GmbH, and glass fibres provided by the company Lanxess AG were used as reinforcement fibres. The endless cellulose fibres have a very high content of cellulose (>99%), and require no special treatment for polyamides. This is not the case for the studied glass fibres. The geometry of the cellulose fibres is similar to that of glass fibres (single filament with a diameter of approx. 12 μm). Table 2 shows important properties of the studied fibres.

2.2. Composite preparation

2.2.1. Compounding

The composites were prepared using two different compounding techniques for endless fibre strands. A two-step process (Fig. 2) according to [28,31,26], which is well known from literature, and a newly developed, single-step process created by Bledzki and Feldmann et al. [6,17,35,36] were used in this investigation. Composites based on PA 6.10, PA 10.10 and PA 6 with 15 wt% and 30 wt% man-made cellulose fibres were prepared. Additionally, composites with 30 wt% glass fibres were compounded to be used as control materials.

2.2.1.1. Two-step compounding method. In the first compounding step of the two-step technique (Fig. 1), the polymer matrix was mixed with the endless fibres. For this purpose, a coating die (220 °C PA 10.10 and 245 °C PA 6/PA 6.10) was used in front of the extruder (twin-screw extruder from the company Haake, Rheomex PTW 25/32, $L/D = 32$, $D = 25$ mm). After coating the material, the endless fibre–matrix-strand was pelletized into granules with a length of 15 mm. Then, the granules were dried at 80 °C using a dry air dryer (TORO-systems TR – Dry – Jet EASY 15) until their moisture content was below 0.1 wt%. Afterwards, the granules were mixed using a single-screw extruder (Schwabenthan Polytest 30P, $L/D = 25$, $D = 30$ mm) with a temperature profile ranging from 200 °C to 230 °C for PA 10.10 composites and from 215 °C to 250 °C for PA 6/PA 6.10 composites. Subsequently, the composites were once again pelletized into granules with a length of 3 mm. During the two processing steps, the cellulose fibres come in contact with the high temperature of the molten polymer for approximately 3–5 min.

Fig. 2 illustrates the prepared granules and their according lengths. The polymer surrounds the filament, and each filament is not impregnated. It is only after the second processing step has been completed that the fibres are dispersed, but shortened in the polymer matrix. Afterwards, the strand was pelletized into 3 mm long granules for injection moulding.

2.2.1.2. Single-step compounding method. The single-step compounding technique (Fig. 3) creates fibre-reinforced granules that are ready for injection moulding. Drying was carried out before the special extrusion die (220 °C PA 10.10 and 245 °C PA 6/PA 6.10) was used to impregnate the fibres with polymer matrix. Additionally, a cooling and compacting unit was employed to cool down, and consolidate the fibre strand immediately. After this processing step, the fibre strand was pelletized into granules with a length of 3 mm. The fibres were only subject to the high temperature of the molten polymer for approximately 2–3 s. Fig. 4 shows the granule that is ready for injection moulding.

2.2.2. Injection moulding

Typ 1A test specimens were prepared according to DIN EN ISO 527 using a Kloeckner Ferromatik FM 85 injection moulding machine with a clamping force of 850 kN, a screw rotation speed of 100 rpm, and a screw diameter of 40 mm. The temperature profile ranged from 190 °C to 225 °C for PA 10.10 composites, and from 200 °C to 240 °C for PA 6/PA 6.10 composites. The granules were dried with a dry air dryer (TORO-systems TR – Dry – Jet EASY 15) before processing. After drying, their moisture content was below 0.1 wt%.

2.3. Characterisation

All examinations were performed on samples in their dry state, using the single-step compounding method and injection moulding process. Samples for Charpy and tensile tests were prepared using both compounding techniques, so as to be able to compare the two different methods with each other.

2.3.1. Morphology

The morphology of all composites was investigated using the scanning electron microscope (SEM) MV2300 by CamScan Electron

Table 1
Water uptake, melting point, density, CO/NH-relation and bio-content of the studied matrix polymers [32,26].

Polymer	Bio-content (%)	Melting point (°C)	Density (g/cm^3)	CO/NH (-)	Water uptake (%)	
					23 °C, 50% r.F.	Saturated
PA 6.10 Vestamid Terra HS (Evonik Industries)	~62	220	1.07	7	1.4	3.3
PA 10.10 Vestamid Terra DS (Evonik Industries)	~100	200	1.04	9	1	1.8
PA 6 Ultramid B27E (BASF SE)	0	222	1.14	5	3	9–10