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Exploring the microstructure of natural fibre composites by confocal Raman imaging and image analysis

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ABSTRACT

We describe a combination of Confocal Raman Imaging (CRI) and quantitative image analysis to characterise biocomposite material microstructures. Both techniques offer lateral resolutions close to 1.3 μm and axial resolution of 13 μm, while simplifying sample preparation to hand-cutting without any surface preparation. Extruded and injected polycaprolactone/hemp fibre composites were used as demonstration biocomposites. A green macrobisphenol additive (bis-*O*-dihydroferuloyl-1,4-butanediol) was also used as a chemical probe to characterise the dispersion efficiency of additives, with a detection threshold of 2.3 wt% above which very local heterogeneity can be determined by this technique. CRI provided microstructure information for the entire binary structure formed by the fibre network. The fibre dispersion and orientation depend on their location in the matrix, and the specific surface of the fibres increases with the fibre content as aggregates start to develop. The technique also highlighted a possible core-skin effect in the injected composite.

1. Introduction

Over the last decade, new economic trends have opened wide markets for biocomposites. They are employed in many domains, such as the transportation, textile and building industries. Of major concern are the thermal and mechanical properties of fibre based composites, especially lignocellulosic fibre-reinforced polymers.

Biocomposites are usually made from a polymer matrix reinforced with natural fibres. Polycaprolactone (PCL) is a well-known polymer formed by the polymerisation of ε-caprolactone. While not biosourced, this polyester is biodegradable and exhibits some interesting properties, e.g., a hydrophilic polymeric matrix when blended with natural fibres. It can be processed at a low temperature, avoiding thermal degradation of the natural fibres during the process. From the Natural Fibre Composite (NFC) manufacturing point of view, many lignocellulosic fibres have been thoroughly studied to replace synthetic fibres in materials because they are more eco-friendly and possess interesting mechanical properties [1–3]. The environmental footprint is in favour of bio-based composites because of the energy and greenhouse gas release savings as compared with fossil-based materials [4,5]. This is supported by life cycle assessment, which encourages the development of fibre-based composites, such as with hemp [6,7]. In the case of hemp fibres, many studies have shown that they are well suited to composite production [8,9]. Other studies have demonstrated that even low grade hemp fibres containing woody pieces are still acceptable in terms of mechanical properties for composite production [10].

The thermal and mechanical properties of biocomposites are a major concern for their final use in various industries. Consequently, various standardised tests have been developed for their characterisation, such as tensile, fatigue, fracture, stress and impact tests. The mechanical properties of the composite can be isotropic or anisotropic when the short fibres are oriented or randomised. As reported by Nguyen Thi et al., there are strong correlations between the fibre dispersion/orientation and the mechanical properties of the composites [11]. In a composite, the microstructure is known to impact mechanical properties and depends on the fibre orientation, dispersion and distribution in

Abbreviations: BDF, bis-*O*-dihydroferuloyl-1,4-butanediol; CRI, Confocal Raman Imaging; PCL, polycaprolactone; NFC, Natural Fibre Composite.

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the matrix, as well as the type and composition of the fibres and their geometrical characteristics [7,12–14]. The microstructure can help modulate the efficiency of the stress transfer from the polymer matrix to the fibres. Additionally, the process used and its parameters can strongly affect the microstructure [15].

As a case study, injection-moulding processes have a strong influence on the dispersion and orientation of fibres in thermoplastic matrices. The fibres are mainly oriented along the flow direction in the centre when the melted compound is injected into the mould or are much more randomised when the melted material contacts the surface of the mould [15]. Therefore, there are different locations (named "core", "shell" and "skin") in the same composite material where the fibres have different orientations.

Experimentally, composite microstructures can be assessed by imaging techniques. Transmission electron microscopy (TEM) is well suited to nanoscale material analysis, but sample preparation may be complicated, and imaging large areas is not possible [16]. Scanning electron microscopy (SEM) can achieve surface analysis of areas from a hundred nanometres to a few millimetres, but the energy dispersive X-ray analysis (EDX) that is often coupled with SEM only permits elemental characterisation. Micro X-ray computed tomography (X-ray CT) is a very promising non-destructive technique for microstructure characterisation of large areas or volumes but with lower resolution than that of microscopy [17,18]. Confocal fluorescence microscopy allows microstructural characterisations of material with lower resolution than electronic microscopy but on larger areas (hundreds of micrometres). The material imaged must be autofluorescent or contain fluorescent probes of known properties (size, interactions with the matrix and the fibres) to perform relevant characterisations [19]. Overall, these techniques can yield structural information but few can examine chemical data and study the fibre dispersion and orientation in composite materials. Confocal Raman Imaging (CRI) is a powerful alternative that identifies the distribution of the components at a microscopic scale based on their chemical composition [20,21]. CRI is the combination of Raman spectroscopy, which analyses inelastic scattering of coherent monochromatic light produced by a laser, and confocal microscopy. In CRI, the Raman spectra are collected with high throughput; the entire Raman spectrum is collected for each pixel, providing a chemical map of the sample [22,23]. Some studies conducted by Raman imaging have demonstrated the interest in using Raman spectroscopy to investigate the orientation of cellulose fibrils or the dispersion of microfibrillated cellulose in a polylactic acid matrix [24,25]. The aim of this work was to investigate the relevancy of CRI for the characterisation of the natural fibre composites.

CRI was applied to characterise the microstructure of large areas of both the surface and the cross-section of composite specimens made of PCL reinforced with lignocellulosic hemp. To further assess the microstructures, the obtained qualitative CRI mappings were processed with several advanced image analysis methods allowing quantitative microstructure descriptions. The potential influence of the microstructure on the mechanical properties (Young's modulus and tensile strength) of the composites was discussed. Finally, for qualitative appraisal of the developed approach, two additional quality controls were performed: the determination of the CRI detection threshold and the putative interference of the natural autofluorescence of lignocellulosic fibre. The detection threshold was determined by quantifying the minimum detectable amount of a newly synthesised green macrobisphenol additive (BDF) using a panel of hemp-PCL composites formulated with a broad range of BDF. The autofluorescence interference of lignocellulosic fibre with CRI was benchmarked with confocal laser scanning microscopy as a reference method.

2. Experimental section

2.1. Materials

Composites were prepared with Capa™ 6800 polycaprolactone (PCL) provided by Perstorp (UK). PCL has a molecular weight of 80.000 g mol^{-1} and a melting point of 58–60 °C. Hemp bast fibres (Cannabis sativa, variety Fedora 17, monoicous plants) were supplied by Fibres Recherches Développement® (Troyes, France). They still contained some woody impurities and were chopped into 5 mm pieces prior to extrusion.

For the chemical probe, the synthesis of BDF was achieved using an innovative bioprocess involving green chemical-enzymatic reactions. The full synthesis is described elsewhere [26]. BDF is synthesised from ferulic acid derivatives and 1,4-butanediol. Its chemical structure, containing aromatic cycles, yields specific Raman bands as described hereafter and has been used to determine the detection threshold of the CRI technique.

2.2. Processing

The extrusion process was conducted on a Scamia single screw extruder (Scamex, France L = 218 mm and D = 17 mm; L/D = 12.8). The temperature of the three zones (feeder, conveyor and die) was set at 100 °C. A thermocouple located before the die indicated a value of 100 °C, corresponding to the temperature of the extruded matter. The screw profile contained only conveyor elements, and the screw speed was set at 25 rpm, giving an overall low shearing stress to the compounds. After the first extrusion process, the compounds were granulated ($\geqslant$5 mm) and reprocessed during a second extrusion process to ensure efficient mixing. A series of PCL compounds containing different ratios of BDF or pure hemp fibres were processed. All the compounds and composites prepared are shown in Table 1. The amount of each product is expressed in weight percentage (wt%). The compounds were formed into tensile test specimens (ISO 527-2-5 A) by injection moulding conducted on a bench scale DSM Xplore micro injection mould IM 12 (Geleen, The Netherlands). The melting temperature was set at 130 °C and the mould at 45 °C. The injection pressure was set at 1.6×10^3 kN m^{-2}.

2.3. Fibre content in compounds

To determine the exact fibre content in each composite, fibres were extracted from PCL by Soxhlet extraction. Two grams of each composite were processed into a Soxhlet over 24 h in a 50/50 chloroform/dichloromethane solution. Then, the remnant fibre fraction was dried and weighed.

2.4. Mechanical characterisation

Tensile tests were performed on a Desktop Universal Tester from Testwell, according to ISO 527-2-A standard recommendations. The tensile test specimens had a total length of 74.0 mm, a centre width of 4.1 mm and a thickness of 2.0 mm. The room temperature was 20 °C and the room humidity was 65% RH. The speed was set at 10 mm min^{-1} with a force of 2 kN. Ten specimens were tested for each formulation. The values given hereafter are mean values +/− the standard deviation σ.

2.5. Chemical mapping by CRI to discriminate PCL, hemp fibre and the BDF additive

Chemical mapping was conducted on an Alpha 300R confocal Raman microscope from Witec equipped with a TrueSurface®