Composites: Part A 69 (2015) 299–305

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa

Preparation and characterization of flax biocomposites made of seed mucilage reinforced by fibers

Florence Paynel [a], Andrey Pavlov [b], Laurent Colasse [a], Christophe Rihouey [a], Nadège Follain [a], Davy Duriatti [c], Laurent Bizet [d], Iain Allan [e], Laurent Lebrun [a], Stéphane Marais [a], Claudine Morvan [a,*]

[a] University of Rouen, UMR 6270 CNRS, FR 3038, 76821 Mont-Saint-Aignan Cedex, France
[b] Department of Oil and Fiber Crops, NI Vavilov Research Institute of Plant Industry, Saint-Petersburg, Russia
[c] LBN Flax Scutching Company, Le Bocasse, France
[d] University of Le Havre, LOMC UMR 6294 CNRS, 76058 Le Havre Cedex, France
[e] University of Brighton, School of Pharmacy, BN2 4AT Brighton, United Kingdom

ARTICLE INFO

Article history:
Received 31 March 2014
Received in revised form 12 November 2014
Accepted 14 November 2014
Available online 12 December 2014

Keywords:
Fabrics/textiles
Mechanical properties
Mechanical testing
Compression moulding

ABSTRACT

Natural biocomposites were prepared from flax fibers and mucilage polysaccharides extracted from flax seeds, as a matrix, in two steps: impregnation and compression molding. The ribbons were preimpregnated with water plasticized mucilage. Solid mucilage (30%, w/w) was added to the ribbon impregnated with 20% mucilage, and the composite was compression molded. The solidified mucilage was homogeneous and rigid (2 GPa) with an elastic deformation of approximately 1%. The mechanical properties of the composites were in the ranges of 7–10 GPa, 300–400 MPa and 4–5% for the modulus, maximal strength and strain, respectively. The two latter parameters were larger than the ones for the fiber. The experimental values of the modulus and strength were in accordance with the values computed using the rule of mixture, which indicated a good interface between the fibers and the matrix. This was confirmed visually with scanning electron microscopy. The water sorption behavior of the composites was intermediate between the mucilage and the fiber alone.

1. Introduction

Flax fibers reinforced epoxy, poly(propylene), poly(ester) and poly(urethane)-based materials that are actively used in the construction [1], automotive [2], sport and leisure [3] and packaging industries [4]. For sustainable development, eco-based resins and recyclable matrices are increasingly assayed [5–10]. Natural polyesters, such as poly(lactic acid) (PLA) [3], PLA and montmorillonite clay [11], poly(hydroxybutyrate) (PHB) [4], and poly(hydroxybutyrate)-co-hydroxyhexanoate (PHB-co-HHx) [12], and proteins, such as gluten [13] or soy protein [14], natural rubber [15], polysaccharides such as starch [16], tannin [17] and oil derived resin [18], are used as a matrix for natural fibers and for proposed bio-based polymers. The main drawback of most eco- or bio-based composites remains the disposal at end of their usefulness; the materials cannot be 100% composted so they must be crushed and recycled.

The most common and economical process for natural fibers includes the coextrusion of fibers, a thermoplastic matrix together with plasticizer and compatibilizer, and then thermocompression of the extruded compounds (*e.g.*, Oksman et al. [19]). To preserve the high tensile properties of the fibers, the first step of the process might be a "film stacking" as described by Stamboulis et al. [20] for flax fibers and a polypropylene matrix or an optimization for the manufacture of PLA/flax fiber biocomposites as described by Ouagne et al. [21]. Alternatively, "prepregs" were produced by laying a resin (PLA) emulsion on the surface of the fibers, which were oven-dried; next, the composites were manufactured by hot pressing [22]. For thermosetting resins, impregnation of the fibers might be conducted with the resin and/or compatibilizers and hardeners in a vacuum bagging, which are eventually stored at low temperature for some time. Then, with or without an autoclave cure, the composites were manufactured *via* a thermal forming [23].

Flax biomaterials were previously developed in our laboratory using mucilages extracted from seeds and nonwoven fibers [24,25]. Because mucilages were hygroscopic polysaccharides, cross-linkers such as glutaraldehyde [24] or epichlorohydrin [25] were added to improve the hydrolytic stability of the flax-based materials. Despite these additives, including glycerol as a plasticizer, the tensile properties of the materials were low because of the nonwoven fabric. The aim of the present study was to test the

* Corresponding author. Tel.: +33 2 35 14 66 94; fax: +33 2 35 14 67 04.
E-mail address: claudine.morvan@univ-rouen.fr (C. Morvan).

http://dx.doi.org/10.1016/j.compositesa.2014.11.021
1359-835X/

feasibility of developing an all-natural, biodegradable composite, using soluble mucilage [26] as the matrix and flax ribbon-fibers (unidirectional technical fibers) as reinforcement, with only water as a plasticizer and without addition of a cross-linker. The hypothesis was that the fibers and the matrix shared common chemical structures (Fig. 1); therefore, the interface might be improved by developing an impregnation step before the elaboration of the composite by compression molding. To some extent, such a model would mimic the composite nature of flax fiber as described by Gorskhova and Morvan [27]. Indeed, the cellulosic fibers that provide the rigidity and strength to flax stems are composed of oriented cellulose microfibrils embedded in a two-phase (pectins and hemicelluloses) matrix. In this paper, the tensile properties of mucilage-flax roving composites were compared with the properties of the fiber ribbon with the hard mucilage constituting the matrix material. The water vapor sorption properties were also examined.

2. Experimental approach

2.1. Flax ribbon fiber

The flax ribbon (500 g km^{-1}), provided by LBN Company (Le Bocasse, France) and designated as R, was a roving of dew-retted, scutched, hackled and combed fibers, according to the textile industry. As observed by optical and scanning electronic microscopy (SEM), the ribbon contained both elementary fibers and partially degraded bundles of fibers (Fig. 1a and b).

2.2. Production of mucilage

Water-soluble mucilage was extracted from seeds, as previously described [26]. Briefly, seeds were put in water (1:10 w:w) at 28 °C for 4 h (twice) and then left overnight. The successively extracted mucilages were filtrated as soon as they were collected, stored at 4 °C, and later, gathered. One portion of the mucilage solution was freeze-dried, and when needed, it was progressively hydrated in water (100 g L^{-1} at 4 °C) and further diluted for use in the impregnation of the fibers. A second portion of the mucilage solution was mixed with ethanol (1:3 v/v) to precipitate the polysaccharides that were collected after centrifugation (4 °C, 15 min, 5000 g) and freeze-dried. These mucilages primarily behaved as Newtonian solutions with an average intrinsic viscosity of approximately 1 g L^{-1} of polysaccharides (in 0.1 M LiCl), as determined with a capillary tube (Fica 5360/20/058). As indicators of mucilage acidity, the percentages of galacturonic acid were estimated to be 28% and 23% of the mass of the total sugars in the liquid and solid mucilage, respectively. These galacturonic acids were contained in the pectic rhamnogalacturonan (RGI) moieties (45 ± 3% of the total mass of mucilage). In addition to RGI, a few percent of a second pectic moiety, *i.e.*, homogalacturonan (HG), was detected (<5%). From the ratio of RGI to arabinoxylan (AX) moieties, which was close to unity, and the high percent of pectic moieties, it was expected that they would interact with the pectins of similar composition present at the surface of the fibers (Fig. 1; see [26] for the detailed chemical analyses of mucilage).

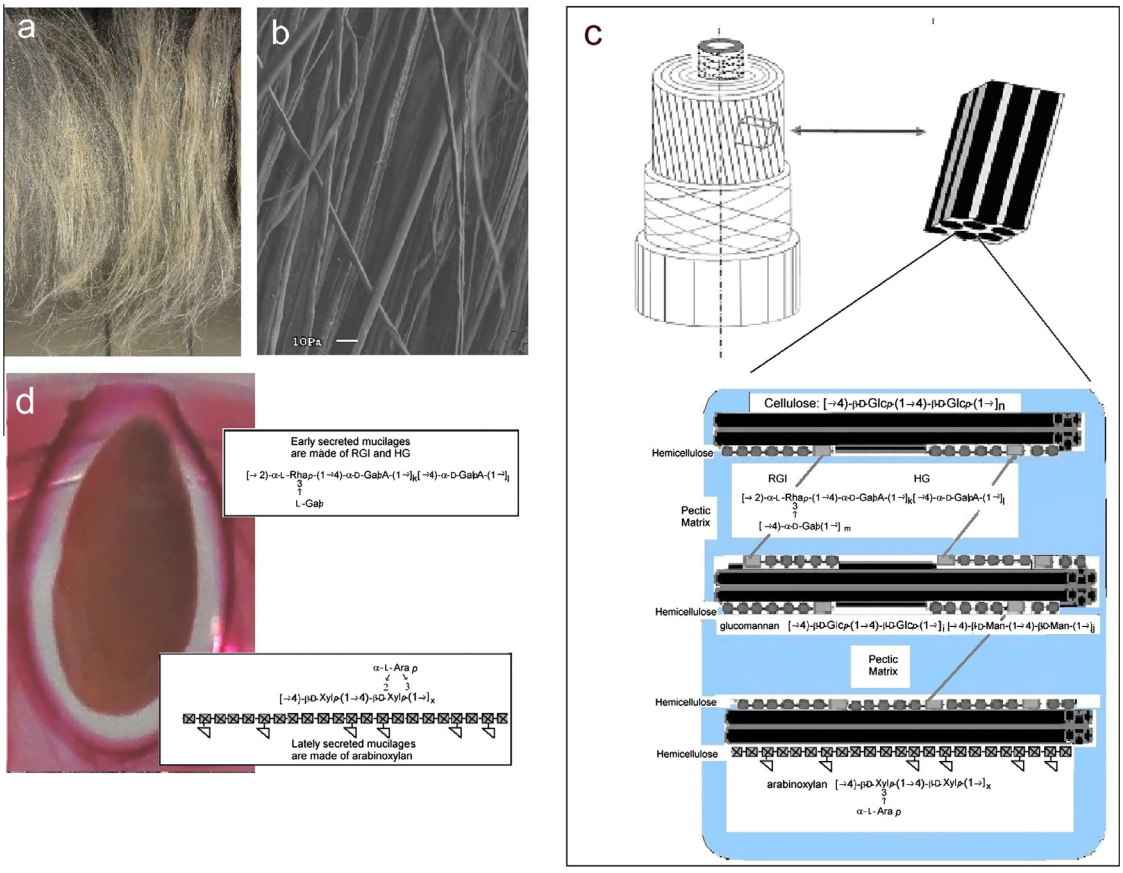

Fig. 1. Polysaccharide composition of flax fibers and mucilage. (a) Fiber ribbon photograph. (b) SEM of fiber ribbon. (c) Schematic representation of fiber cell wall with microfibrils embedded in a pectic matrix. Chemical composition from Gorshkovha and Morvan [23]. (d) Composition of seed and mucilage. Seeds were hydrated in ruthenium red, showing expansion of the pectic mucilage (stained in red). The structures of mucilage were inspired from Paynel et al. [21]. *Ara*, arabinose; *Gal*, galactose; *GalA*, galacturonic acid; *Glc*, glucose; *HG*, homogalacturonan; *Man*, mannose; *Rha*, rhamnose; *RGI*, rhamnogalacturonan of type I; *SEM*, scanning electronic microscopy; *Xyl*, xylose. *Scale bar* (b) 50 μm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)