Composites: Part A 78 (2015) 152–159

Contents lists available at ScienceDirect

Composites: Part A

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

Polysaccharidic binders for the conception of an insulating agro-composite

Narimane Mati-Baouche [a], Hélène de Baynast [a], Shengnan Sun [a], André Lebert [a], Emmanuel Petit [b], Philippe Michaud [a,*]

[a] Clermont Université, Université Blaise Pascal, Institut Pascal UMR CNRS 6602, Polytech Clermont Ferrand, 2 avenue Blaise Pascal, TSA 60026, CS 60026, 6318 Aubière cedex, France
[b] Laboratoire BIOPI, IUT d'Amiens (GB), Avenue des Facultés, le Bailly, 80025 Amiens Cedex, France

ARTICLE INFO

Article history:
Received 12 May 2015
Received in revised form 10 July 2015
Accepted 5 August 2015
Available online 14 August 2015

Keywords:
A. Biocomposite
A. Natural fibers
B. Adhesion
B. Thermal properties

ABSTRACT

The objective of this study is the formulation of a natural polysaccharidic binder for the conception of an insulating bio-based composite made with sunflower stalk particles. The formulation was performed using chitosan cross-linked with Genipin and mixed with alginate, guar gum and starch. A fractional factorial experimental design within 32 essays was established to find the formulation leading to composites with the best combination between good mechanical properties and limited amount of chitosan in the binder. Composites with a thermal conductivity (κ) of 0.07 W m^{-1} K^{-1} and a maximum tensile stress (σ_{max}) of 0.2 MPa were obtained with a total binder ratio of 5.5% (w/w). The results of this study show that the insulating bio-based composites evaluated have competitive mechanical and thermal performances compared with other eco-friendly insulating materials available on the market.

1. Introduction

The concept of "all green composite" is a recent and attractive research approach consisting in using mixtures of biopolymers and reinforcing fibers, both obtained from renewable resources [1]. Even if several industrial areas such as automobile industry, aeronautics and medicine have interest for this kind of composite, the building sector is probably where the demand is the most significant [2–4]. In this sector, European environmental legislation as well as consumer pressure have promoted the searching of new biosourced materials to improve the thermal insulation of existing buildings. The motivation includes cost, mechanical, thermal and acoustical performance enhancements of insulating materials but also their weight reduction and environment concerns [5]. Hence, bio-based insulator materials from by-products of agriculture are an interesting fossil carbon alternative to reduce thermal conductivity [6,7]. A material is considered as a thermal insulator when its thermal conductivity (κ) is lower than 0.1 W m^{-1} K^{-1}, some of them reaching 0.035 W m^{-1} K^{-1} [8]. Studies aimed at the development of bio-based insulating composites report that they have lower thermal conductivity, are cheaper, durable, lightweight and environmental friendly compared to conventional ones [9–17]. However, the binder (matrix) used in the insulating biocomposites is often mainly produced from petroleum-based polymers or from mineral resource (cement) [15,16]. These binders have questionable (or undesirable) environmental impact. Consequently, it is therefore desirable to introduce biopolymers in bio-based insulating agro-composites. As mentioned by Mati-Baouche et al. [13] and Binici et al. [18], there is a large potential for sunflower stems to be used in the conception of insulating composites. Sunflower is widely cultivated all over the world with a harvested area of 3.68 10^6 ha in 2010 in Europe [19]. Its stems are poorly valorized and usually burnt, used as natural fertilizer, for animal feed or for fuel production [19,20]. It has been estimated that each hectare of sunflower can produce up to 7 tons of dried biomass [21]. So the agglomeration of sunflower stalk particles with natural adhesives such as chitosan could lead to the conception of 100% bio-based insulating materials [13,22]. Chitosan is obtained industrially by deacetylation of chitin, which is the most abundant polysaccharide after cellulose [23–26]. It is a heteropolymer of β-(1,4)-linked 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose units. This polymer which is the sole cationic polysaccharide due to its positive charges (NH_3^+) at acidic pH (pH < 6.5) [23] has received attention as a functional non-toxic, antimicrobial, biocompatible and biodegradable macromolecule useable in the area of biomaterials and/or biosourced materials [22,24,25,27–31]. Mati-Baouche et al. have selected chitosan as a natural binder for the development of panels made with sunflower stalk aggregates [13]. Their mechanical and thermal performances

* Corresponding author. Tel.: +33 (0)473407425.
E-mail address: philippe.michaud@univ-bpclermont.fr (P. Michaud).

http://dx.doi.org/10.1016/j.compositesa.2015.08.006
1359-835X/

were competitive compared with those of bio-based insulators available on the market namely hemp concrete, coconut husk and date palm fibers insulation boards [10,32,33]. However, the use of chitosan binder is economically not viable (10 €/kg of chitosan) [22] compared to mineral binders such as cement (25 cents €/kg), even if the ratio binder/reinforcement is lower for composites made with chitosan. From an economical point of view the use of other cheaper biopolymers with adhesive properties such as starch (0.5 €/kg), guar gum (2 €/kg), and alginate (2 €/kg) could be an alternative to address this problem. Moreover, the environmental assessment of chitosan-based films caused higher environmental damage than polypropylene films in respiratory inorganics, land use, and minerals categories [34]. The environmental load is mostly related to the acetic acid used in the film manufacture and, in more significant way, to the hydrochloric acid employed during the raw material extraction [34]. So, to decrease its amount in insulating composites, chitosan was cross-linked with a natural cross-linker (Genipin) or an anionic polysaccharide (alginate) and interpenetrated networks were performed by incorporation of cheaper and adhesive biopolymers such as starch and guar gum.

2. Experimental

2.1. Raw materials

2.1.1. Preparation of binder solutions

Chitosan from shrimp shell deacetylated at 90% was supplied by France-Chitin (France) with the reference number 342. The polysaccharide was physico-chemically characterized in a previous study [35] and was solubilized at concentrations ranging between 1% and 4% (w/v) in acetic acid 1% (v/v) (Sigma–Aldrich, 98.9%) at room temperature (20 °C) for 2 h under stirring. As shown in Table 1, the ratios chitosan/sunflower stalk particles (reinforcement) tested were 1.09; 2.19; 3.28 and 4.38% (w/w). Genipin ($C_{11}H_{14}O_5$) (Sigma Aldrich, N° G4796) with a molecular weight of 226 Da was solubilized under continuous stirring at the concentration of 0.25% (w/v) in absolute ethanol (Sigma–Aldrich). Genipin is from *Gardenia* jasminoides Ellis [41]. The ratio Genipin/sunflower stalk particles used were 0.62×10^{-4} and 1.25×10^{-4}% (w/w). Hence, the ratios Genipin/chitosan tested in this study were: 14×10^{-4}; 18.9×10^{-4}; 28.5×10^{-4}; 38.1×10^{-4}; 56.8×10^{-4}; 105×10^{-4} and 114.6×10^{-4}% (w/w). Guar gum (Roper, GmbH) and sodium alginate (Sigma–Aldrich, N° 180947) were solubilized separately at concentrations ranging between 2% and 6% (w/v) in deionized water (20 °C) with stirring for 2 h. The ratios of guar gum/sunflower stalk particles and alginate/sunflower stalk particles tested were 1.46% and 2.92% (w/w). Corn starch (Sigma–Aldrich, N°S4126) was solubilized at concentrations ranging between 2% and 6% (w/v) in deionized water after heating under stirring during 15 min at 90 °C. The binder solution was used after cooling 1 h at room temperature (20 °C). The ratio starch/sunflower stalk particles tested were 1.46% and 2.92% (w/w).

The term "binder" defines the use of one polymer tested (i.e. chitosan, starch...) and it is expressed by percentage of its dry weight/reinforcement weight (% w/w). However the term "formulated binder" defines the formulation tested obtained by mixing chitosan, Genipin, starch, alginate and guar gum together, and is expressed by percentage of total binder dry weight/reinforcement weight (% w/w).

Table 1
Area of variations of the operating parameters.

Binders	Levels	% of binder/reinforcement (w/w)
Chitosan	4	4.38; 3.28; 2.19; 1.09
Alginate	2	2.92; 1.46
Starch	2	2.92; 1.46
Guar gum	2	2.92; 1.46
Genipin	2	1.25×10^{-4}; 0.62×10^{-4}

2.1.2. Molecular weight determination

The average molecular weights of chitosan, alginate and guar gum were determined by high pressure size exclusion chromatography (HPSEC) with online multi-angle laser light scattering (MALLS) filled with a K5 cell (50 μL) and two detectors: a He–Ne laser ($\lambda = 690$ nm) and a differential refractive index (DRI) as described previously [22]. The columns [OHPAK SB-G guard column, OHPAK SB806, 804 and 803 HQ columns (Shodex)] were eluted with 65 μM ammonium acetate (pH 4.5) at 0.7 mL min^{-1} for chitosan and 0.1 M sodium nitrate (pH 4.5) at 0.5 mL min^{-1} for alginate and guar gum. The solvent was filtered through a 0.45 μm filter. The samples were injected through a 100 μL full loop. The collected data were analyzed using the Astra 4.50 software package.

2.1.3. Sunflower stalk particles

The sunflower (reference LG5474) stalks used in this study were harvested in 2009 (Perrier, France) before to be stored in aerated bags in a shaded and ventilate site. Grinding of sunflower stalks was performed using a cutting mill SM 300 (Retsch) with a sieve of 20 mm mesh. The speed cut applied was 1000 rpm. The particles obtained were sieved at room temperature (20 °C) using Controlab sieve-tronic to obtain particles sizes between 3 and 5 mm. Fig. 1 shows some used particles composed of pith, which is the white and porous part and bark, corresponding to the brownish and lignocellulosic fraction of sunflower stem. These aggregates were stored at room temperature (20 °C) before use.

2.2. Bio-based composite preparation

Solutions containing neutral polysaccharides (starch and guar gum) were first mixed under stirring. After that, alginate (anionic polysaccharide) was added and put under stirring until the solution became homogenous. Then, chitosan and Genipin were added to the previous solution under continuous stirring for 10 min. Finally, the binder formulation was mixed with sunflower stalk particles at room temperature for 5 min. The ratio of the formulated binder/sunflower particles varied from 5% to 13% (w/w). Each type of mixture was prepared in polyvinylchloride (PVC) molds: 180 mm × 50 mm × 40 mm. Each set was compacted for 1 min at 20 °C at a compaction pressure of 32×10^{-3} MPa using weights. After drying 50 h at 50 °C in an oven, the resulting composites were cut with a band saw to obtain slender shapes of 180 mm × 24 mm × 12 mm for tensile mechanical characterization. Two composites with satisfied tensile mechanical performance were prepared in PVC mold of 180 mm × 50 mm × 120 mm for compressive measurements. Specimens obtained for compressive tests were cut to obtain dimensions of 80 mm × 50 mm × 50 mm before analysis and were stored at room temperature (20 °C). Fig. 2 shows the two composites obtained before their tensile and compressive analysis.

2.3. Mechanical characterization

Mechanical characterization was performed following the method described by Mati-Baouche et al. [35] using a tensile testing machine (Instron 5543) equipped with a load cell of 5 kN. The cross-head speed was equal to 5 mm min^{-1} and the specimen clamping length was 140 mm. Compressive tests were carried out with a Zwick–Roell testing machine equipped with a ±20 kN load cell. The tests were displacement-controlled with a cross-