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Improvement of the hydrolytic stability of new flax-based biocomposite materials

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ABSTRACT

New natural biocomposite materials were prepared from flax. Non-woven flax fibres material was chosen as a reinforcement and mucilage polysaccharides, extracted from flax seeds, were used as a matrix. Mucilages were extracted from two spring fibre-varieties, Aurore and Alizee. The matrix was crosslinked with epichlorohydrin ($T = 70\ ^{\circ}C$, $P = 50$ bar, 4 h) in order to improve the water stability of the biocomposite. Glycerol was added as plasticizer. The composite was optimised with Alizee-mucilage extracted at 40 °C and with epichlorohydrin 8% wt/wt. Swelling in liquid water and sorption of water vapour were the lowest (120% and 53% for 97% of relative humidity, respectively) due to the high protein content that crosslinked with epichlorohydrin. The best mechanical performances were obtained ($\sigma_B = 30$ MPa, $\varepsilon_B = 10\%$, $E = 450$ MPa) for the lowest crosslinker content (EP 4% wt/wt).

1. Introduction

Composite materials are usually made with an organic matrix (thermoset resins or thermoplastics) reinforced by carbon or glass fibres. For the sake of sustainable development, natural fibres such as flax, hemp, kenaf or jute are being tested as alternative reinforcements. Cellulosic fibres are low cost, eco-friendly and biodegradable. Moreover, they have low density and offer excellent mechanical properties. For examples, flax fibre for poly(propylene), poly(ester) and poly(urethane) reinforcement, are particularly attractive in automotive applications [1,2], construction and packaging industries. However, these composite materials are not completely biodegradable because the matrix used is synthetic.

One solution would be to prepare a natural, biodegradable composite made only from renewable resources. Several review articles have been published devoted to the preparation, processing, environmental issues and properties of biocomposites for a wide range of applications [3–5]. Various biodegradable polymers have been used for the matrix such as natural polyesters, e.g. poly(lactic acid) [6], poly(hydroxybutyrate) (PHB) [7], poly(hydroxybutyrate)-co-hydroxyhexanoate [8] or proteins such as gluten [9], soy protein [10], natural rubber [11], polysaccharides such as starch [12] or seeds mucilage [13]. Flax, hemp, jute, sisal and ramie, were the most common reinforced fibres cited. Nanoparticles such as whiskers could be added to improve the mechanical properties of natural composites [14]. Such "biocomposites" might be alternative materials to petroleum-based plastic biomedical, packaging or structural applications [2]. At the end of their lifetime, these materials could be crushed and composted. However, the development and the applications of such materials are limited because of their low strength and low water stability loading to premature hydrolytic ageing [15,16].

In a previous study, composites were performed using mucilages extracted from flax seeds (Aurore variety) reinforced by flax non-woven fibres [13]. An advantage was that the fibre and the matrix share a common chemical structure, which might improve their interfaces. While flax fibres are located in the stem, mucilages are present in the outermost cell layer of the seed coat. Mucilages are naturally secreted by the seeds upon hydration. Mucilages are very hygroscopic, being able to adsorb water more than 10 times their weight. In order to prepare biocomposite materials with non-woven fibres and mucilage as matrix, it is necessary to reduce its swelling rate, which was previously undertaken using glutaraldehyde as a mucilage crosslinker [13].

The aim of the present study was to test another crosslinker, e.g. epichlorohydrin, in order to possibly increase the water stability of the composite materials and to improve the cohesion between matrix and fibres. Importantly, we used two water-vapour sorption models in order to better understand the water sorption behaviour of such composites. We compared the characteristics of the mucilages originating from two spring fibre-flax varieties (Aurore and Alizee). Alizee was chosen in reference with the work of Roussière

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et al. [17] who used fibres from Alizee variety to reinforce poly(L-lactide acid) (PLLA) matrix and to prepare natural composites.

Mucilages were first extracted with water in 2 steps at two temperatures (20 °C and 40 °C), then precipitated and dried. The composition of each extract was analysed and compared. Epichlorohydrin (EP) and glycerol (25 g L^{-1}) were added in aqueous solutions of each extract. Epichlorohydrin was used as matrix crosslinker as previously explained. Glycerol was used as a plasticizer in order to reduce fragility and to increase the impact resistance of the composites. The moisture resistance of the composites was evaluated by swelling in liquid water and by water vapour sorption measurements. Tensile tests were also performed on the biocomposite materials according to the seed variety, the presence of EP crosslinker and glycerol.

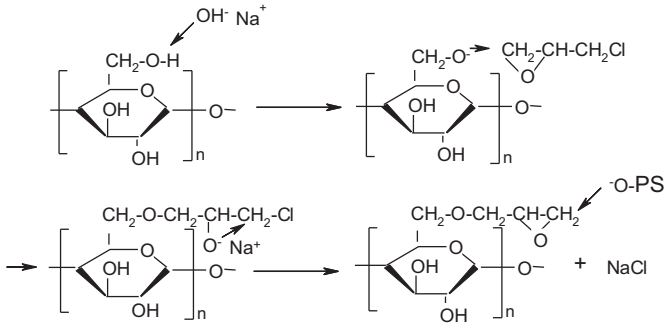

Fig. 1. Crosslinking polysaccharide (PS) with epichlorohydrin.

2. Experimental

2.1. Non-woven flax fibres material and flax seeds mucilages

The flax raw fibre material and the seeds were provided by the cooperative "Terre de lin" (Saint-Pierre-Le-Viger, France).

Flax fibres were extracted from Hermes, Diane and Agatha varieties, and mixed in non-woven tissue within the respective proportions of 70, 15, 15% wt. They consist of short fibres (14–24 mm in length; 17 mm on average) gathered in residual bundles of 5–20 elementary fibres attached together [18]. They were obtained from dew-retted stems that had been scutched. This process consists in eliminating the bark and the xylem in order to separate roughly the bundles of fibres, designated as technical fibres. Among them the long fibres had been removed for textile industry while the short ones (or tows) had been set aside for non-woven or technical uses. These tows were received in tow form without chemical treatment. The non-woven material obtained from fibres was prepared by the so-called "dry laying" technique at the "Ecole Industrielle de Rouen" (Rouen, France). The preparation and the characteristics of the non-woven have been previously detailed [18].

Mucilages were extracted from seeds coming from two spring fibre-flax varieties (Aurore and Alizee).

2.2. Chemicals

Epichlorohydrin (EP) and glycerol (Sigma Aldrich Co.) were used as crosslinker reagent and plasticizer, respectively.

2.3. Preparation of the biocomposite

Mucilages were extracted from seeds with water (45/200 wt/v) in 2 successive steps (2 h: 20 °C; 2 × 1 h: 40 °C). A third extraction was useless because the yields stayed low whatever the temperature of extraction. The extracted mucilages were filtrated through a Nylon flour filter under vacuum, then precipitated in ethanol (4 v/v) and dried in an oven (50 °C). They were designed as AU and AL for Aurore and Alizee mucilages, respectively.

The elaboration of the composites was investigated by preparing a 25 g L^{-1} mucilage solution in water of each extraction. Epichlorohydrin (4, 6, 8% based on wt of the dry mucilage) and NaOH 4.3 M (1% v/v the mucilage solution) were added to the solutions in order to crosslink the polysaccharides of the mucilage (Fig. 1) [19,20]. The solutions were stirred overnight. Glycerol (25% of the dry mucilage) was added as plasticizer in order to improve the flexibility of the mucilage. Discs of non-woven material were cut, dry weighted and swollen in water. Then, the wet non-woven discs were inserted between two equal volumes of mucilage solution in the 65/35 (dry mucilage/dry non-woven material) mass ratio. Plates were obtained after a complete evaporation of the solvent in an oven at 50 °C (average thickness: 2 mm). The crosslinking reaction was performed by thermal treatment in a hot press ($T = 70$ °C, $P = 50$ bar) for 2 or 4 h.

2.4. Characterisation of the mucilage

The composition of each extracted mucilage was analysed. The concentrations of the uronic acids and of the proteins were determined by colorimetric assays as previously described [13].

Viscosity measurements of mucilage samples were performed using a rotational (Couette type) viscosimeter (Low Shear 30 from Contraves, Zurich). The shear rate ranged between 0.20 and 20.4 s^{-1}. The measurements were performed at 25 °C on mucilage solution (1 g L^{-1} in NaCl 0.1 M) after clarification of the insoluble fraction. The viscosity values were estimated from the Newtonian plateau.

2.5. Characterisation of the biocomposite

The biocomposites were observed by Scanning Electron Microscopy (SEM) using a Jeol JSM 35 CF microscope. The samples were prepared either by fracturing under liquid nitrogen at −190 °C or by cutting with a scalpel blade, and then covered with a gold layer. The sections were observed to determine the homogeneity of mucilage dispersal, and the cohesion of the mucilage – fibre interface.

The efficiency of the crosslinking reaction was checked by FTIR measurements using the Nicolet Avatar 360 FTIR with ATR mode. The spectra of the composite samples were compared before and after crosslinking treatment.

Swelling measurements S_w in liquid water were also performed. Dry composites samples (constant weight m_d) were immersed in water at 25 °C. After 24 h, they were taken out of the solution and carefully wiped with absorbent paper before being weighed. The procedure was repeated several times until reaching a constant weight m_{eq}. The swelling in water was defined by Eq. (1).

$$S_w = \frac{m_{eq} - m_d}{m_d} \quad (1)$$

Water vapour sorption kinetics were studied on 20 mg biocomposite samples by using an automated electronic microbalance (Cahn D200 with a mass resolution of 0.1 μg) in an automated gravimetric dynamic vapour sorption system DVS1 Advantage (Surface Measurement Systems Ltd, London, UK). The temperature was controlled at 25 ± 0.1 °C. Water vapour activity (a_w) steps were applied on the sample previously dehydrated. The mass gain Δm of the sample was recorded as a function of time until equilibrium was