



Shape memory starch–clay bionanocomposites



Gildas Coativy^{a,b,c}, Nicolas Gautier^d, Bruno Pontoire^{b,c}, Alain Buléon^{b,c},
Denis Lourdin^{b,c,*}, Eric Leroy^{a,c}

^a LUNAM Université, CNRS, GEPEA, UMR 6144, CRTT, 37, Boulevard de l'Université, 44606 St Nazaire Cedex, France

^b UR1268 Biopolymères Interactions Assemblages, INRA, F-44300 Nantes, France

^c Structure Fédérative IBSM, INRA Nantes-Angers, Rue de la Géraudière, BP 71627, 44316 Nantes Cedex 3, France

^d Institut des Matériaux Jean Rouxel (IMN), Université de Nantes-CNRS, UMR 6502, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex, France

ARTICLE INFO

Article history:

Received 17 November 2013

Received in revised form 6 December 2013

Accepted 9 December 2013

Available online 17 December 2013

Keywords:

Shape memory

Starch

Clay

Bionanocomposite

Melt processing

ABSTRACT

1–10% starch/clay bionanocomposites with shape memory properties were obtained by melt processing. X-ray diffraction (XRD) and TEM evidenced the presence of a major fraction of clay tactoids, consisting of 4–5 stacked crystalline layers, with a thickness of 6.8 nm. A significant orientation of the nanoparticles induced by extrusion was also observed. Tensile tests performed above the glass transition of the materials showed that the presence of clay nanoparticles leads to higher elastic modulus and maximum stress, without significant loss in elongation at break which typically reached 100%. Samples submitted to a 50% elongation and cooled below the glass transition showed shape memory behavior. Like unreinforced starch, the bionanocomposites showed complete shape recovery in unconstrained conditions. In mechanically constrained conditions, the maximum recovered stress was significantly improved for the bionanocomposites compared to unreinforced starch, opening promising perspectives for the design of sensors and actuators.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Thermoplastic starch is a biobased and biodegradable plastic material that can be obtained from the melting of native starch granules extracted from a variety of widely available crops (Halley et al., 2008). Due to the chemical structure of the anhydroglucose repeating unit, the two starch constituting macromolecules (linear amylose and hyperbranched amylopectin) are highly hydrophilic. Starch is therefore subject to water uptake and plasticization by water molecules (Bizot et al., 1997). The estimated high glass transition temperature of dry amorphous starch, close to 315 °C, typically drops to 70 °C, when starch is stored at a relative humidity (RH) of 50%; and even below 25 °C if the RH is close to 100%. As a consequence, at 25 °C, the same amorphous starch matrix can either have a glass like rigid and fragile mechanical behavior, or a rubber like hyperelastic behavior, depending on moisture conditions. Such a high water sensitivity of thermomechanical properties tends to make thermoplastic starch poorly competitive for the replacement of petroleum-based commodity

thermoplastics (in applications) such as packaging(s). Even though the use of non-volatile plasticizers, such as glycerol, allows formulating soft materials by a “stabilization” of starch in the rubbery state, the increase of molecular mobility can favor the recrystallization of starch and a progressive embrittlement (Van Soest & Vliegthart, 1997). On the contrary, the moisture sensitivity of starch may be an advantage for the design of stimuli responsive functional materials. It has been recently shown that amorphous starch obtained by extrusion can acquire shape memory properties when subjected to adequate thermoforming treatment (Véchambre, Chaunier, & Lourdin, 2010). Such treatment involves a first heating of glassy amorphous starch above its glass transition temperature, in order to be able to subject it to a reversible large deformation in the rubbery state. By cooling the deformed material below its glass transition temperature, a glassy rigid temporary shape is then obtained. Such a thermoformed starch material is able to recover its initial shape if it enters the rubbery state, either by heating above its glass transition temperature, or by plasticization by water, thanks to moisture absorption.

The most promising applications of this new biobased material range from smart food products (Chaunier, Véchambre, & Lourdin, 2012) to biomedical devices since starch is edible and biocompatible. Nevertheless, the mechanical performances of starch in the rubbery state, which determine the ability to recover its shape in a constrained environment, limit the possibilities of using it as a stimuli-responsive actuator (Véchambre, Buleon, Chaunier, Gauthier, & Lourdin, 2011).

* Corresponding author at: UR1268 Biopolymères Interactions Assemblages, INRA, F-44300 Nantes, France.

E-mail addresses: gildas.coativy@univ-nantes.fr (G. Coativy), nicolas.gautier@cnrs-imn.fr (N. Gautier), bruno.pontoire@nantes.inra.fr (B. Pontoire), alain.buleon@nantes.inra.fr (A. Buléon), denis.lourdin@nantes.inra.fr (D. Lourdin), eric.leroy@univ-nantes.fr (E. Leroy).

Table 1
Composition of the extruded powder blends, average torque values during melt recirculation and calculated SME values.

Sample	Starch (%)	Water (%)	MMT (%)	SME (J/g)	Torque (N cm)
Starch	70	30	0.0	850 ± 100	98 ± 10
1% MMT	69.9	29.5	0.6	920 ± 100	112 ± 10
3% MMT	68.5	29.5	2.0	1200 ± 100	138 ± 10
5% MMT	67.3	29.5	3.2	1100 ± 100	130 ± 10
10% MMT	63.9	29.7	6.4	1050 ± 100	130 ± 10

One approach for overcoming such limitations is the introduction of clay nanoparticles to reinforce the material, which gave successful results in the case of shape memory polyurethane (Xu et al., 2010). In the present paper, we describe for the first time the elaboration and characterization of shape memory (starch/sodium montmorillonites) bionanocomposites by melt processing in presence of water, without additional plasticizer. We particularly studied the crystalline structure, the dispersion and the orientation of the clay tactoids and individual platelets, in the amorphous starch matrix, and their influence on large deformation mechanical behavior above the glass transition temperature and shape memory properties.

2. Experimental

2.1. Materials and formulations

Potato starch was purchased from Roquette frères (Lestrem, France) and sodium montmorillonites (MMT) from Sigma Aldrich. MMT powder consists of aggregates of clay tactoids, in which negatively charged monocrystalline platelets of 0.95 nm thickness are stacked, with sodium counter ions between the layers. According to the datasheet of the producer (Nanocor), the MMT have a cation exchange capacity of 1450 $\mu\text{equiv. g}^{-1}$. The individual clay platelets have a density of 2.6 and in-plane dimensions typically ranging from 100 to 130 nm. Such a structure is highly hygroscopic and subject to swelling in presence of water. The interlayer spacing (d_{001}) can be increased from 0.96 nm in the dry state, up to 2 nm when four layers of water are intercalated between the clay platelets of the tactoids (Norris, 1954). Since this phenomenon results in limited attractive forces between the crystalline layers, it was used to favor exfoliation during melt processing. Clays were first equilibrated at a water activity of 0.97, leading to a water content of 30% (wet basis (w.b.)) and to a basal spacing $d_{001} = 1.6$ nm. In parallel, starch was oven dried at 100 °C during 30 min, resulting in a water content of 8% (w.b.). Starch and MMT powders were then blended in a mortar and then rehydrated until reaching a global water content of 30% (w.b.), the day before extrusion. Such a procedure leads to an intimate mixing of powders before melt processing. The different used formulations are listed in Table 1: the weight contents of MMT were chosen to obtain bionanocomposites containing 1, 3, 5 and 10% of inorganic matter (dry basis (d.b.)).

2.2. Melt processing and sample preparation

The hydrated powder mixtures were melt-processed with a 7 cm³ microcompounder (Minilab, Thermo Haake). It is made up of a conical twin screw system with a backflow channel, which can be used as a batch mixing reactor given that the material can be recirculated rather than exiting through the die. Moreover, the conical twin screw system allows simulating the performance of a co-rotating or a counter rotating twin screw extruder. In all operations, the co-rotation operation was applied.

The hydrated powder mixtures were introduced in the microcompounder at 95 °C, with a screw speed of 100 rpm, and recirculated during 10 min before being extruded at lower screw

speed (10 rpm). The typical weight of the final extruded rods was 2 g (since the rest of the material stayed into the recirculating area), with a rectangular section of approximately 1 mm × 4 mm.

The torque signal was used to evaluate the specific mixing energy (SME), defined as follows:

$$\text{SME} = \int_0^t \frac{T \cdot 2\pi \cdot n}{M \cdot 60} dt$$

where T is the torque signal at time t , n is the screw speed (rpm) and M is the loaded mass (g).

These experimental conditions allowed a complete disruption of the native starch organization, in conditions combining a high shear rate and a long residence time, in order to obtain an efficient dispersion of the clay. Contrary to the typical extrusion temperature used for potato starch (DellaValle, Boch, Colonna, & Vergne, 1995), generally higher than 120 °C, the use of a temperature below 100 °C, allowed long residence times with low water evaporation during the process, and limited degradation of the macromolecules.

Several batches were produced for each formulation in order to have enough rods for the characterization of both the structure and the thermomechanical behavior of the materials after extrusion, and also for the molding of dogbone tensile test samples for the mechanical tests. In both cases, extruded rods were stored at 57% RH during two weeks before characterization or molding. Thermo-compression was performed at 130 °C using a mold sized to the section of the rod in order to avoid any orientation induced by the process. This temperature, significantly higher than the glass transition of the amorphous starch matrix, allowed erasing the thermal history of the samples, which were then stored again at 57% RH during two weeks before mechanical tests.

2.3. Water and clay contents

The amount of clay in extruded samples was checked by thermogravimetric analysis using a TGA 2050 (TA Instruments, DE). About 10 mg of material were heated with a temperature ramp of 10 °C/min under nitrogen atmosphere until 950 °C to destroy the organic part and keep the mineral part of the materials.

The samples were kept at 950 °C during 20 min. The water content of materials (extruded rods or molded tensile test specimens) was assessed by dehydration in an oven at 130 °C during at least 24 h, until an equilibrium constant weight was reached.

2.4. Morphology

Transmission electron microscopy was used to observe the morphology of the bionanocomposites, using an HNAR9000 LaB₆ TEM Microscope (Hitachi), with an accelerating voltage of 300 kV (maximum point to point resolution of 0.18 nm). Samples sections were prepared using a Leica UC7 ultramicrotome equipped with a diamond knife. The ultrathin sections of 100 nm thickness were cut at room temperature and under dry conditions and then transferred onto 300 mesh Cu grids coated with a lacey carbon film.

Download English Version:

<https://daneshyari.com/en/article/1385698>

Download Persian Version:

<https://daneshyari.com/article/1385698>

[Daneshyari.com](https://daneshyari.com)