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Reversible and irreversible changes in physical and mechanical properties of biocomposites during hydrothermal aging

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ABSTRACT

The use of biocomposites on a daily basis for industrial products brings to light the influence of environmental factors on the evolution of mechanical properties. This aging has a major influence in the lifetime of any product based on such materials. Among biobased composites, poly(lactic acid) reinforced with plant fibers are known to be sensitive to hydrothermal aging due to the intrinsic nature of their components. Although some papers studied the influence of temperature and water absorption on such materials, so far the difference between reversible and irreversible effects of aging has been hardly studied. This distinction is the purpose of this study. Poly(lactic acid) samples reinforced with various content of flax fibers (0%, 10%, and 30%) were immersed in water at different temperature (20, 35, and 50 °C) up to 51 days. The physical and chemical phenomena responsible for the changes in the mechanical properties of biocomposites were evaluated. It was observed that these changes were mainly reversible. However, irreversible effects of aging turned out to increase drastically with the amount of fiber and the aging temperature. While hydrolysis drastically deteriorated PLA for longer aging times, the lifetime of biocomposites was significantly extended (+230% at 50 °C from 0% to 10% in fiber content) by the presence of fibers which postponed the failure of PLA.

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1. Introduction

The growing demand for sustainable policies from public opinion drives industry toward the development of bio-based materials. In the field of thermoplastic composites, poly(lactic acid) reinforced with plant fibers meets a growing success for industrial application because of their good specific mechanical properties, availability, and similar processing properties than traditional polymers (Bocz et al., 2014). A limited number of products can already be found on the market targeting various fields of application such as automotive, mobile phones, or plant pots (Graupner et al., 2009; Summerscales and Grove, 2014). Such products are fully biodegradable and offer the advantage to be either recycled, composted or incinerated at their end of life (Le Moigne et al., 2014). However the intrinsic nature of these materials results in a high sensitivity to the presence of water and temperature (Le Duigou et al., 2009). Indeed several papers highlight the specific problems encountered in the presence of a hydrothermal environment (Islam et al., 2010) resulting in a decrease of mechanical properties. Though they do not rule out the idea of using such materials for outdoor applications (Cheung et al., 2009; Dittenber and GangaRao, 2012). As a result, the success of the commercial use of biobased composites lies in the control of the evolution of their mechanical properties in real-life conditions. This evolution of properties (physical and mechanical), which are the effects of aging, can be either temporary (reversible) or permanent (irreversible). In order to control aging, the first step consists in identifying the aging factors susceptible to result in a change of these properties. Among them, bacterial degradation, UV radiations and mechanical loadings are not negligible but temperature and humidity are the major causes for short-term aging (Kumar et al., 2010; van den Oever et al., 2010). The processes induced by the aging factors and their combination are well identified since they have been studied for years for usual polymers. However, their extension to biobased polymers requires additional research efforts because of the numerous processes at stake, their interactions, and the heterogeneity of both materials and aging processes. In addition to these difficulties, aging effects may be reversible, like plasticizing for instance, or, in most cases, irreversible (Mercier et al., 2008; Pochiraju et al., 2012; Weitsman, 2012). This distinction is essential to predict the evolution of properties, especially when aging factors are expected to evolve during the materials lifetime. Indeed, for any outdoor application, aging is cycled: day/night, sun/rain, seasons, indoor storage/outdoor use. In order to properly assess the sensitivity of materials to aging in

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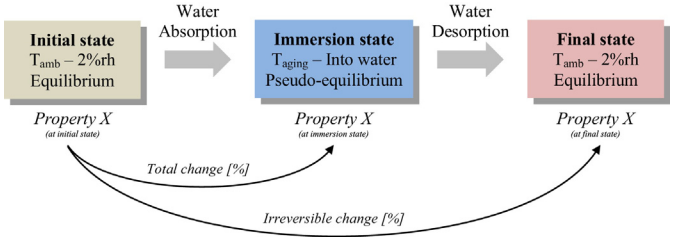

Fig. 1. Schematic representation of the methodology to evaluate the irreversible changes in the characterized properties during hydrothermal aging.

real-life conditions within a time period of several years, a complete understanding of the impact of both reversible and irreversible effects of aging is necessary. The purpose of this study is to assess the consequences of both the reversible and irreversible effects of a hydrothermal aging on the properties of a plant fiber reinforced poly(lactic acid) in order to offer new perspectives for predicting the lifetime of natural fibers reinforced composites.

2. Materials and methods

2.1. Methodology

Poly(lactic acid)/short flax fiber biocomposites have been selected for the present study. As described in Fig. 1, the analysis was decomposed into two steps:

1. Firstly the impact of hydrothermal aging was assessed on composites with various fiber contents. In this case, reversible and irreversible effects of aging occurred simultaneously, and only their combined effects were evaluated.
2. In a second step, materials were brought to the same hydrothermal conditions as before aging by removing water by desiccation. This procedure allowed the assessment of potential damage, and thus the distinction between reversible and irreversible effects of aging.

It is worth to mention that, in this study, the properties of the materials after an initial desiccation effected prior to aging constitutes the reference for the analysis of their changes. The total change of a property due to aging corresponds to the variation between its value after immersion and its reference value. Accordingly, the irreversible change of a property is defined by its variation at final desiccation. Then, the reversible part of a property is assessed from the difference between its total change and its irreversible change.

2.2. Materials

2.2.1. Poly(lactic acid) matrix

PLA Ingeo™ 7000D resin was obtained from NatureWorks® LLC (Blair, NE, USA). These granules were designed for injection stretch blow molded applications. This grade of PLA had a density of 1.24 g/cm^3, a glass transition temperature between 55 and 60 °C and a melting temperature between 155 and 165 °C (NatureWorks, 2005).

2.2.2. Flax fibers

The short flax fibers (*Linum usitatissimum*) FIBRA-S®6A used for this study were provided by Fibres Recherches Développement® (Troyes, France). According to the technical data sheet (FRD, 2011), fibers (bundles) were 6 mm long with a diameter of 260 ± 150 μm and their density was between 1.4 and 1.5 g/cm^3. Concerning quasi-static mechanical properties, Young's modulus of bundles was 36 ± 13 GPa, maximum stress was 750 ± 490 MPa and strain at break was 3.0 ± 1.9%.

2.3. Experimental techniques

2.3.1. Processing conditions

Various fiber weight contents were used: 0% (neat PLA) hereafter named PLA, 10% hereafter named PLA-F10, and 30% hereafter named PLA-F30. Polylactic acid granules and flax fibers were dried at 80 °C for at least 24 h and under vacuum at 120 °C for 4 h respectively. Composite granules were obtained with a corotative twin-screw extruder (Clextral BC21, screw length = 900 mm; temperature profile along the screw and at the die = 180 °C). After a second drying step under vacuum at 80 °C during 24 h, compounded granules were molded with an injection molding machine (Krauss Maffei KM50-180CX) into dog-bone samples according to the standard ISO 527-2 1BA. The temperature profile was increasing up to 200 °C and the mold was kept at 25 °C. After processing, samples were stored at room temperature and 2%rh (relative humidity) before characterization or aging. This equilibrium state constitutes the reference for evaluating the effects of aging on the materials.

2.3.2. Aging experiments

Three series of isothermal water immersion experiments were conducted for each material (PLA, PLA-F10 and PLA-F30) at 20 °C, 35 °C, and 50 °C. For each temperature and material, 10 samples were immersed in water, slightly wiped, characterized then re-immersed, up to 51 days. Afterward, samples were desiccated at room temperature and 2%rh until their mass reached an equilibrium. This desiccation was supposed not to imply other mechanisms than those previously caused by hydrothermal aging. This equilibrium state constitutes the final condition for evaluating the irreversible effects of aging.

2.3.3. Weight, volume, and density measurements

Samples mass was measured using a weighing scale Mettler-Toledo AT200 with a precision of 0.1 mg. Thickness and width were determined with a 1 μm-accurate palmer and length with a 10 μm-accurate caliper. A mean value performed on each sample was determined. The volume of the sample was approximately evaluated on the basis of dimensional measurements. As a result, the evaluation of density was based on water uptake and volume gain measurements. The reproducibility was evaluated on 10 measurements.

2.3.4. Scanning electron microscope observations

The morphology of the samples after several aging durations was analyzed using an environmental scanning electron microscope (ESEM) FEI™ Quanta 200 FEG. They were freeze-fractured in the middle part, and the surface was carbon-coated with Balzers CED030 sputter-coating device.

2.3.5. Size exclusion chromatography

The molecular mass of PLA was evaluated by size exclusion chromatography (SEC) with Optilab® rEX™ of Wyatt Technology (CIRAD, UMR 1208 (IATE), Université de Montpellier, France). 90 mg of each aged material was diluted in tetrahydrofuran stabilized with butylated hydroxytoluene, and then kept at 30 °C during 40 h in a water bath. After a 45 μm-filtration, each solution was injected in the column for measurement. The reproducibility was evaluated on 3 samples.

2.3.6. Differential scanning calorimetry

A Perkin-Elmer® Diamond DSC was used in order to assess the crystallinity of PLA. Samples mass ranged from 5 to 10 mg and ramp temperature was set at 10 °C/min. The enthalpy of a 100% crystalline PLA was assumed to be 93.7 J/g in order to determine crystallinity from thermograms (Garlotta, 2001).

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