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Modeling of nonlinear viscoelasticity-viscoplasticity of bio-based polymer composites

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Two different types of biodegradable polymers and polymer composites, namely Ecovio® reinforced by 30 wt% wood-flour, and flax/starch composites prepared elsewhere, were analyzed experimentally and theoretically. The monotonic loading, stress-relaxation and creep-recovery experiments revealed a highly nonlinear viscoelastic/viscoplastic response. This behavior was treated by a three-dimensional constitutive model, analytically presented in a previous work. The model presumes that the materials follow a nonlinear viscoelastic path, while later on viscoplasticity prevails. The combination of the transient network model, related to the viscoelasticity, with a plasticity theory, lead to a constitutive model, which was proved to be capable of describing the experimental data of stress-relaxation, monotonic loading and creep-recovery in a unified manner. Deviations, which were detected for the first material types, requiring new parameter values, were attributed to structural changes arising from creep-recovery experiment.

1. Introduction

Bio-based polymers, which are derived from natural resources such as corn starch and vegetable oils, have come forward as a potential replacement to resolve the environmental issues associated with petroleum-based polymers. Therefore, environmentally friendly biodegradable polymers have attracted a lot of attention in recent years for a variety of applications. To improve their thermal and mechanical resistance, these materials are often reinforced by an amount of either micro or nanosized fillers. To this trend, a lot of works have been focused on the preparation and study of biodegradable polymers based composites and nanocomposites [1,2]. On the other hand, it has been postulated that reinforcement with natural fibers, such as flax, hemp, kenaf is a convenient choice to achieve an acceptable enhancement of mechanical properties [3]. Especially wood polymer composites (WPC), although not as popular as composites with inorganic fillers, offer biodegradable materials, if a wood-flour is combined with a biodegradable polymer [4]. WPC's are materials with good properties, such as durability, excellent sound absorbing capacity, low density, high strength and modulus of elasticity [5]. A competitive advantage of WPC's is the low cost and availability of natural fibers. However, the quite low processing temperatures, and the strongly hydrophilic character of the natural fibers should also been accounted for.

In all cases, the afore mentioned polymer composites exhibit a strong time-dependent mechanical behavior, therefore these materials are treated as nonlinear elastic-viscoplastic ones [3,6–8].

A thermodynamically consistent theory of non-linear viscoelastic and viscoplastic materials was developed by Schapery [9]. This model considers the nonlinear viscoplastic response of materials as a particular case of nonlinear viscoelasticity, corresponding to infinite retardation times. Experimental methodology for complete material characterization in the framework of this model was presented by Ref. [10].

The time-dependent mechanical performance of flax fiber-reinforced thermoplastic starch matrix composite and neat starch is extensively analyzed in Ref. [3]. A detailed experimental study has been performed in terms of tensile experiments and tensile multiple step creep-recovery tests, for the matrix and the composite materials, with varying the relative humidity. The highly nonlinear response of these materials, attributed to the nonlinear viscoelasticity and viscoplasticity, were studied, whereas the viscoplastic strain could be successfully estimated by applying material models previously developed [11,12,6].

In a previous work [13], a new theory, describing the nonlinear viscoelastic/viscoplastic response of polymeric systems, under

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monotonic loading, and creep, has been introduced. The viscoelastic/viscoplastic response has been elaborated by the transient model [14] and the theory introduced by Drozdov [15]. In our approach [13], the nonlinearity has been accounted for by the introduction of a stress-dependent term in the Eyring-type equation, which expresses the rate of detachment of polymeric chains from their junctions. Concerning the viscoplastic response, a kinematic formulation, which separates the strain into elastic and plastic part, developed by Rubin in Ref. [16], has been employed. The functional form of the rate of plastic deformation, which has been analyzed in our previous work [17], has also been introduced in the above kinematic formulation. In this way, a 3-D constitutive equation has been derived, pertinent for an incompressible medium at small elastic and finite plastic deformation.

Despite the large number of relative works thus far, it is considered that studying the polymer's and polymer composites' inelastic behavior, namely creep-recovery, stress relaxation and monotonic loading in terms of a unified model remains still a very interesting topic.

The main objectives of the present work, given the growing interest in replacing non-renewable plastics and oil by competitive bio-based materials, is i) the experimental study of the time-dependent mechanical behavior of bio-based polymers and polymer composites and ii) the implementation of an integrated analysis, describing concurrently the nonlinear viscoelastic/viscoplastic response under monotonic loading, stress-relaxation and creep-recovery tests of these materials.

2. Materials

Two different material types were analyzed. The first one concerns a neat starch matrix and its composite with flax fibers at 20 wt%. The details of synthesis and processing are presented in Refs. [18,3].

In these works the highly nonlinear viscoelasticity of the materials is pointed out, as well as the strong effect of moisture content on the materials performance. Two different values of relative humidity were examined, namely 34 and 61%, for at least 2–3 weeks, as it is mentioned in Ref. [3]. Given that at a value of RH equal to 61% the effect of moisture is more intense, the experimental data of matrix and the composite, after conditioning at this RH value were selected for simulation. The second material group is based on the biodegradable commercial product Ecovio® supplied by BASF SE (Ludwigshafen, Germany). The selected grade Ecovio® L BX 8145 (EC), is basically a blend of poly(butylene adipate-terephthalate) copolyester (Ecoflex® F BX 7011), which is based on non-renewable resources, and Polylactic Acid (PLA) by NatureWorks. Because of the PLA content, Ecovio® L BX 8145 consists of 45% of renewable resources. The material in pellets form was dried at 75 °C for a minimum of 4 h prior to use in a desiccating dryer. Ecovio® was reinforced by 30 wt% wood-flour type Arbocel C100), whose basic raw material is raw cellulose and its average grain size is 70–150 μm.

Wood-flour has been dried for 24 h at 100 °C, due to its hydroscopic nature. Maleic anhydrite (2% w/w) was used as compatibilizer [19] to improve the polymer-filler interface interaction. The composites were prepared by a melt mixing procedure, analytically presented in Ref. [20].

3. Experimental

Ecovio® (EC) and its composite (ECWF) have been experimentally tested in stress-relaxation (Fig. 1), tensile monotonic loading (Fig. 2), and creep-recovery experiment at room temperature, at two different stress-levels, namely 2.5 and 4.5 MPa (Figs. 3 and 4).

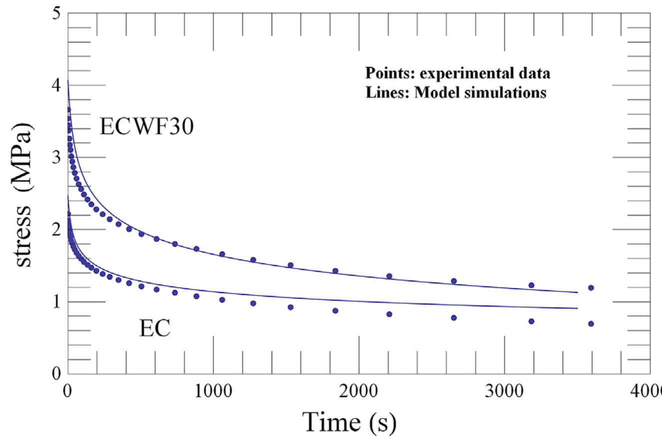

Fig. 1. Tensile Stress-relaxation curves of EC and ECWF at a strain equal to 0.006.

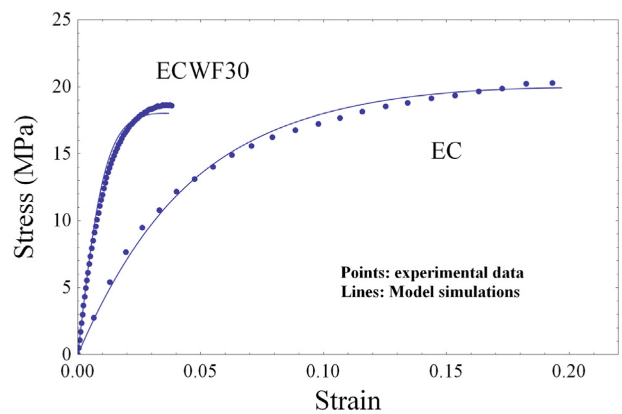

Fig. 2. Tensile stress-strain curves of EC and ECWF.

These stress levels are lower enough than the yield stress of the materials, which are approximately 12.5 and 16.5 MPa, for EC and ECWF correspondingly, as is shown from Fig. 2. Tensile measurements were performed at room temperature, at a strain rate equal to 4.1 10^{-4} s^{-1}, following the procedure presented in Ref. [20]. Stress-relaxation tests were performed at room temperature, at a strain value equal to 0.006, for both matrix and composite. Both creep and stress-relaxation tests have been performed with TA Q800, at a single cantilever beam mode of deformation, at room temperature.

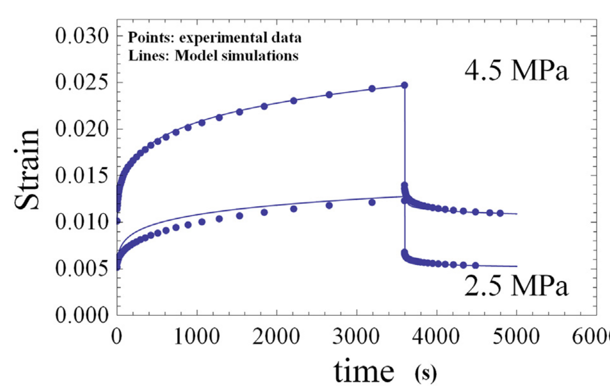

Fig. 3. Tensile creep-recovery curves of EC at two stress levels.