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The effect of surface treatment on the performance of flax/biodegradable composites

Panayiotis Georgiopoulos [a], Aggelos Christopoulos [a], Stefanos Koutsoumpis [b], Evagelia Kontou [a], *

[a] Mechanics Department, National Technical University of Athens, Iroon Polytechniou 9, Zografou, 15780, Athens, Greece
[b] Physics Department, National Technical University of Athens, Iroon Polytechniou 9, Zografou, 15780, Athens, Greece

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ABSTRACT

In the present study, three series of natural fiber-polymeric composite materials have been prepared and experimentally studied, in terms of Scanning Electron Microscopy, Differential Scanning Calorimetry, Tensile-Flexural testing, Dynamic mechanical analysis and Creep. The materials are unidirectional flax fiber composites, prepared with the "film stacking method", based on three types of biodegradable polymeric matrices. The addition of flax fibers with this method leads to a significant toughening of the polymers under investigation. In order to further improve the composites thermomechanical performance, three different surface treatments of flax fibers, namely silanization, plasticization and treatment with maleic anhydride, were employed. The effect of the fibers treatment on the mechanical properties of the composites has been comparatively studied and discussed. The surface treatment with maleic anhydride resulted to the highest Young's modulus increment, whereas silanization and plasticization improved both tensile and flexural properties. Similar effect was obtained for storage modulus increment, as well creep resistance of the composites with modified flax fibers.

1. Introduction

In recent years, due to the growing environmental awareness and the necessity for developing sustainable materials [1], there is a trend of replacing conventional fibers (glass, carbon), which are predominantly used as reinforcements in polymer matrices, with bio-fibers, i.e. fibers derived from natural sources such as plants, animals and minerals [2]. Low cost, low specific weight, flexibility in processing, competitive mechanical properties, recyclability, safer handling and working conditions but principally their contribution to the environmental issue, are the advantages of bio-fibers, in comparison with glass fibers, and the reason for the growing trend of using them [2–5]. However, there are compounding difficulties due to the inherent polar and hydrophilic nature of natural fibers, as a result of the strongly polarized hydroxyl groups of lignocellulose [6], and the non-polar features of most thermoplastics. This results to non-uniform dispersion of the fibers, while their high moisture absorption leads to bad adhesion with the matrix with the creation of voids at the interface [2]. Plant-based natural fibers consist of cellulose, hemicellulose, lignin, pectins and waxes. Their mechanical properties, thus, their reinforcing efficiency, depend on the content, nature and crystallinity of cellulose, and the angle of microfibrils [2–7]. Cellulose is a natural polymer, consisting of D-anhydroglucose ($C_6H_{11}O_5$) repeating units, joined by 1,4-β-D-glycosidic linkages at C_1 and C_4 position [8]. Among the various natural fibers, flax, kenaf, jute, hemp, coir, bamboo, ramie and sisal [4,9], are of particular interest.

In order to preserve the environmental advantages and the eco-efficiency of the natural fibers, biodegradable or recyclable polymers are considered as an ideal matrix for this kind of composites [10]. Biodegradability is an alternative eco-efficient solution for the end-of-life disposal of polymer products, if recyclability is not an option [11]. The so-called "green composites", by reinforcing biopolymers with natural fibers [12], due to their significant environmentally beneficial properties, create a new perspective for the composites technology. Construction, decoration, decks, roofs, auto-motive and soundproofing are some of the continuously increasing applications, or fields of application of biocomposites, exploiting their high stiffness and strength [2,3]. By using a biodegradable material as a matrix, the derived bio-composite is

* Corresponding author.
E-mail address: ekontou@central.ntua.gr (E. Kontou).

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totally biodegradable, thus, there is a new perspective by producing limited life-time polymer composites, designed to biodegrade after use. This kind of materials may find interesting applications as temporary structural material, mainly in agriculture and construction field [13]. Hydrophilic nature of most of the biodegradable polymers leads to the assumption of better interaction with natural fibers. Specifically for Poly-Lactic Acid (PLA), its polar structure is expected to provide improved adhesion of the fibers, thus, improved properties for the bio-composite [14]. This is not confirmed by Oksman et al. [15], as pull-outs and clean fiber surfaces were noticed in the fracture surface.

In recent years, material systems, based on a biodegradable matrix reinforced with flax fibers have been studied [11,13,15–23]. Polylactic acid (PLA) in particular, due to its competitive properties, has been examined as a matrix reinforced with kenaf fibers [24–26], bamboo fibers [27], hemp [28], jute [29,30] etc. The study of biodegradation procedure of a variety of composites, is focused on the special behavior exhibited by each specific matrix [11,25,27]. In a PLA/bamboo fiber composite, it was found that its degradability could be controlled by the amount of the compatibilizing agent, namely LDI (Lysine based diisocyanate). The degree of fibers adhesion on the matrix was effected by the LDI content that has been employed [27]. In a composite material, based on PLA and kenaf fibers, it was found that the biodegradation rate is increasing due to the presence of the fibers [25]. Another interesting topic is the role of plasticizers, employed for the compatibilization of PLA, and their absorption by the natural fibers [15].

Limited studies are reported, to our knowledge, for unidirectional natural fiber composites, regarding mostly polypropylene matrix [31–33] and epoxy resin [34–36]. Regarding biodegradable unidirectional natural fiber composites, studies have been made for PLA composites [24,33] and starch composites [22,37]. A major problem of the effectiveness of natural fiber/polymer composites is the incompatibility between hydrophilic fibers and hydrophobic matrix. This can lead to a poor fiber/matrix adhesion due to the presence of pendant hydroxyl and polar groups in the components. As a consequence, high moisture uptake takes place leading to a deterioration of the mechanical properties [3] Therefore, an important issue in studying polymer/natural fiber composites is the improvement of the fiber-matrix interaction, either by modifying the fiber's surface or by the matrix modification employing additives called coupling agents. Combination of the two approaches has been also reported [38]. In Ref. [39] five different chemical treatments were applied to examine their effect on the composites mechanical performance. Referring to chemical modification, it is meant as a chemical reaction between some constituents of the natural fiber and a chemical reagent, forming a covalent bond between them. This results in both, a better fiber dispersion, which is usually restricted due to the hydrogen bonding between fibers, and bond formation between fiber and polymer matrix [9].

The scope of this study is the evaluation of the effectiveness of three different biodegradable polymers as matrix materials for unidirectional flax fiber composites, prepared with the “film stacking method”, a procedure which has not been studied sufficiently so far. Previous work [40] has been focused on manufacturing unidirectional plant fiber reinforced composites, as well as on the use of a novel plant fiber yarn surface treatment method to enhance mechanical properties and fiber-matrix adhesion. Therefore, orientation of the fibers and less thermo-mechanical processing, as mixing is avoided, are considered to be the advantages of this method employed for the preparation of composites. In the majority of previous studies on these composites, the reinforced matrix is polypropylene, due to its low cost and thermal stability. The composites prepared in the present study, are essentially novel materials due to both, the matrix material and the unidirectional character of the fibers incorporated. In addition, three different methods improving the compatibility between matrix and fiber were applied, namely treatment of flax fibers with silane, plasticizer and maleic anhydride. Only few works have been previously done, to comparatively analyze the effect of similar fiber treatments on the thermomechanical performance on the materials. The thermal and mechanical properties of the prepared composites were comparatively investigated, providing information about the fibers/polymers efficiency to the mechanical enhancement, for each fiber's modification procedure employed.

2. Experimental part

2.1. Materials

Natural fiber polymer composites were prepared, based on three different types of polymer biodegradable matrices as follows. Poly-lactic Acid (PLA), which was supplied by NatureWorks LLC. The selected grade 2002D has a D content of 4.25%, a residual monomer content of 0.3% and a density of 1.24 g/cm^3. The material in pellets form was dried at 45 °C for a minimum of 8 h prior to use in a desiccating dryer. The second matrix under the commercial name Ecovio® was 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 PLA (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.

The third matrix employed has the commercial name Bionolle® 1001, and is based on Poly-butylene succinate, of an average density of 1.26 g/cm^3, kindly provided by Flexopack S.A. (Athens, Greece).

Very common technologies for natural fiber composite materials are resin transfer molding, vacuum injection molding, structural reacting injection molding, injection molding, and compression molding. Regarding PLA-natural fiber composites, their preparation usually involves a mixing of PLA matrix and fibers, after specific conditions of drying, and a hot pressing procedure [21]. Another type of manufacturing is the melt mixing procedure using a twin-screw extruder, or a solution mixing procedure, followed by a compression molding process hereafter, with the processing conditions being a subject of research [19,25].

In our work, unlike the most published works so far, the production procedure for natural fiber composites adopted, is quite similar to those for the production of conventional unidirectional laminate fiber composites. The three types of polymeric matrices examined, were prepared into thin films of an average thickness of 0.2 mm, by a hot press treatment. Hereafter, following the well-known film stacking method [16], alternating layers of polymeric film and flax fibers-tissue were placed and hot pressed for 6 h, at a pressure of 5 MPa, and at a temperature equal to 100 °C for Bionolle and 124 °C for Ecovio® and PLA. According to the followed procedure, the fiber breakage due to shear stresses imposed during the melt-mixing procedure, could be avoided, while an optimization of the fiber orientation could be achieved.

By this method, plates of unidirectional fiber polymer composites were prepared, at the same average weight fraction 22% and an average thickness of 1 mm. The corresponding volume fraction was calculated to be equal to 19.5%. The prepared composites are designated as BIONflax, ECflax and PLAflax, based on the three matrices, Bionolle®, Ecovio® and PLA, correspondingly. In addition, three different methods improving the compatibility of flax fibers with the matrix were employed. These methods are: A) silanization, where the flax fibers are immersed in a 2 wt% Vinyl-Triethoxy-