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Material Properties

Environmentally benign green composites based on epoxy resin/bacterial cellulose reinforced glass fiber: Fabrication and mechanical characteristics

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ABSTRACT

Bio-based bacterial cellulose (BC) epoxy composites were manufactured and their mechanical properties were examined. The BC was initially fabricated from Vietnamese nata de coco by means of alkaline pretreatment followed by solvent exchange. The obtained fibers were dispersed in epoxy resin (EP) by both mechanical stirring and ultrasonic techniques. The resulting blend was used as the matrix for glass-fiber (GF) composite fabrication using a prepreg method followed by multiple hot-press-curing steps. The morphology, mechanical characteristics and mode-I interlaminar fracture toughness of the fabricated composites were investigated. With a 0.3-wt% BC content, the mode-I interlaminar fracture toughness for both crack initiation and crack propagation were improved by 128.8% and 1110%, respectively. The fatigue life was dramatically extended by a factor of 12, relative to the unmodified composite. Scanning electron microscopy images revealed that the BC plays a vital role in increasing the interlaminar fracture toughness of a GF/EP composite via the mechanisms of crack reflection, debonding and fiber-bridging.

1. Introduction

As the growth of bio-based composites increases due to environmental concerns and the need to become more energy-efficient, researchers have paid more attention to the identification and use of renewable reinforcement materials for bio-based composite preparation. Among these, nano-sized cellulose fibers have been found to be a suitable reinforcing material because of their high mechanical strength, modulus and cost effectiveness. Furthermore, cellulose is the most abundant biological resource on Earth, and can be extracted either from plants by chemical treatment or synthesized from bacterial cells or sea animals. Bacterial cellulose (BC) nanofibers are secreted from the cell walls of some bacterial species such as *Acetobacter*, *Achromobacter* and *Aerobacter* [1]. Among these, *Acetobacter* is the most commonly used due to advantages such as its high cellulose yield and the chemical structure of the resulting cellulose fiber being suitable for a wide range of purposes. *Acetobacter* can be isolated from different sources such as juice [2], plants (including palm tree leaves) [3], and nata de coco [4]. The BC possesses the same chemical structure as the plant cellulose in which the main chain includes many glucose units linked via β 1–4 glucozit. They differ in their dimensions, however, as the BC's main chain contains about 2000–6000 units while the plant cellulose contains 13 000–14,000 units. Because of its high purity and low

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quantities of wax, lignin, hemicellulos, and pectin in comparision with plant cellulose, the bacterial cellulose exhibits high levels of crystalinity (up to 90%) [7]. In addition, the diameter of the BC ranges from a few to several tens of nanometers, while having a length of several micrometers [8] with a large surface area of about 37 $m^2 g^{-1}$ [9]. The Young's modulus of BC is estimated to be about 78–114 GPa [10,11]. In addition, the BC should be completely biodegradable, given its high water absorbency [12,13].

Numerous studies have focused on the fabrication of bio-based composite materials by using BC as a green reinforcement filler in materials such as polylactic acid (PLA) and poly (vinyl alcohol) (PVA) [5,6]. Luddee et al. [14] used BC of different particle sizes as a reinforcement filler for fabricating PLA biocomposites and stated that the tensile strength and elongation of a PLA/BC biocomposite decreased with increase in the BC particle size. However, in their study, surface of the BC was not treated with an organic compound. Gea et al. [15] prepared bio-nanocomposites via an in-situ growth process through the direct addition of PVA to an *Acetobacter xylinum*-inoculated medium and compared the results with composites made by impregnating BC gels with a PVA solution. Mechanical property tests showed that PVA in the BC acts as a plasticizer, interrupting the hydrogen bonding between the cellulose fibrils within the BC network. This resulted in a reduction in the Young's modulus and an increase in the toughness relative to pure BC sheet, especially for in-situ-grown samples, reporting that the mechanical properties of the PLA composites reinforced with surface-functionalized BC showed significant improvements when compared to unmodified PLA and BC-reinforced PLA. Quero et al. [16] showed that the Young's modulus and stress at failure of transparent, predominantly amorphous poly (L-lactic) acid (PLLA) films were found to increase by 100% and 315%, respectively, with an 18% volume fraction of BC fibers. Gabr et al. [17] showed that, for a BC fiber content of 0.5%, the initiation and propagation interlaminar fracture mode-I toughnesses were improved by 84% and 72%, respectively. The addition of 0.5% BC to the composite, modified with 10% liquid rubber, improved the storage modulus by 28% at 200 °C. Gindl et al. [18] fabricated and investigated the tensile properties of composites consisting of cellulose acetate butyrate reinforced with cellulose sheets synthesized from *Gluconacetobacter xylinus* by solvent evaporation casting. The composites contained 10 and 32 vol% cellulose, respectively. They exhibited a Young's modulus of 3.2 and 5.8 GPa, and a tensile strength of 52.6 and 128.9 MPa, respectively. Martins et al. [19] showed that, even with as little as 5% BC, there was a significant increase in both the modulus and tensile strength of the composite.

Concurrently, epoxy resin (EP) was successfully used as the matrix of composites for various industrial applications such as aircraft (half of the total weight of the Boeing 787 Dreamliner is epoxy-based composite), marine craft, and the chemical industry. However, given the intrinsic brittleness of EP after curing, as caused by its high crosslinking density, fiber-reinforced epoxy composites such as glass-fiber (GF) reinforced epoxy composite can be broken by even a low external impact energy. This problem can be solved by the introduction of nanoscale reinforcement material filler. Prusty et al. [20] found that the incorporation of 0.5-wt% graphene oxide into a glass fiber/epoxy composite exhibited a 21.1% improvement in flexural strength. On the other hand, Helmy and Hoa [21] indicated that the addition of clay enhances the resistance to mode-II crack propagation, and thus prolongs the fatigue life of glass/epoxy laminates. Withers et al. [22] used organo-modified surface nanoclay to reinforce an epoxy/glass-fiber composite and attained average improvements of 11.7% in ultimate tensile strength, 10.6% in tensile modulus, and 10.5% improvement in tensile ductility, relative to the mechanical properties obtained for the unmodified material. The results of tension–tension fatigue tests at a stress-ratio of ±0.9 and at 60 °C in air showed that the nanoclay-reinforced composite had a 7.9% greater fatigue strength and a fatigue life of more than a decade longer (1000% greater) than the unmodified composite when extrapolated to 10^9 cycles or a simulated 10-year cyclic life. Böger et al. [23] also demonstrated an increase in the fatigue life of GF/EP under mechanical loads by the incorporation of nanoparticles (both fumed silica and carbon nanotube (CNT)) in an epoxy matrix. Akinyede et al. [24] reported that the mode-I fracture toughness of epoxy/fiberglass composites was significantly improved by the inclusion of alumina nanoparticles as well as by the functionalization of alumina nanoparticles. With an increase in the high cycle fatigue strength of up to 250% for CNT-modified GF/EP [25], the introduction of CNT into the glass-fiber-reinforced epoxy composite increased the interlaminar shear strength by up to 33% [26]. Wichmann et al. [27] also showed that the interlaminar shear strengths of nanoparticle-modified composites were significantly improved (+16%) by adding only 0.3 wt% CNT.

In the present study, a suspension of BC in ethanol was initially fabricated and employed as a source of green filler, and its effects on the mechanical properties and morphology of glass-fiber-reinforced epoxy composites were investigated. The composite materials used for the mechanical testing were fabricated by using the prepreg method via multi-step hot-curing.

2. Experimental

2.1. Materials

Nata de coco (obtained from Dang Khoa Coconut Co. Ben Tre Province, Vietnam) with a dry content of 10 wt% was used as the BC source. Epoxy resin (EP, epoxy content = 22.63%, molecular weight ~383 g/mol, viscosity = 12–13 Pa·s, density = 1.16 g/cm^3 at 25 °C, Epikote 828) was supplied by Shell Chemical. The curing agent was 4, 4′-diaminodiphenylsulfone (DDS) with 97 wt% purity, purchased from Merck (Germany). Salicylic acid (HX, Sigma-Aldrich, USA) was used as an accelerator. The coupling agent was (3-glycidyloxypropyl) trimethoxysilane (Sigma-Aldrich). Woven Roving 400 type glass fiber (400 g/m^2) (China), NaOH, and ethanol (99 wt%) (China) were used as purchased.

2.2. Dispersion of BC in epoxy resin

First, a suspension of 20 wt% BC in ethanol was prepared from Vietnamese nata de coco by subjecting it to alkaline pre-treatment followed by a water-exchange process to replace the water in the nata de coco with ethanol. The nata de coco was then held in a 2.5 M NaOH solution for 8 h at room temperature to remove the bacterial cells, followed by washing with distilled water to achieve neutralization. The alkali-pretreated BC is shown in Fig. 1.

The alkali-pretreated nata de coco was well blended using a food mixer for 20 min to obtain a cellulosic pulp. In the next step, the water in the slurry was removed using a vacuum filter to produce a BC sheet containing approximately 80 wt% water and 20 wt% BC. Subsequently, the BC sheet was immersed in ethanol and blended using a food mixer for 20 min, after which it was filtered using a vacuum filter. This process was repeated three times to produce a 20 wt% BC suspension in ethanol. The obtained suspension was used for the preparation of both the EP/BC mixtures and bio-based composite materials.

In the next step, the suspension of BC in ethanol was dispersed in the epoxy resin using a high-speed (2000 rpm) mechanical stirrer at 70–80 °C for 5 h. Subsequently, the obtained mixtures were agitated by using ultrasonication for the required time. An ice bath was used in this step to prevent the evaporation of the ethanol.