EFFECT OF STARCH-BASED HYBRID ADDITIVE ON MECHANICAL AND THERMAL PROPERTIES OF EPOXY-BASED COMPOSITES

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Abstract

As industry shifts towards the use of renewable, sustainable materials, research focusing on green and biobased materials has expanded. One area of particular interest is the use of starch to create eco-friendly, bio-based additives for use in thermoset and thermoplastic composites. This study focuses on the evaluation of easily integratable, functionalized starch-based additives for use in epoxy resin and carbon fiber reinforced composites. Composite test panels with 0.1 and 0.5 wt% of these starch-based additives were created and the mechanical performance of the additive-enhanced carbon fiber reinforced composites was evaluated according to ASTM standards for tensile, interlaminar shear strength, and flexural properties. The results of this study showed that the bio-based functionalized starch additive can provide mechanical improvement where additive loading can be tailored for targeting specific properties. The findings also showed that easy, uniform, and stable dispersion can be achieved by introducing specifically advantageous functional groups to the starch structure in a scalable approach.

Introduction

There has been an increasing global interest in the study of renewable biobased polymers and composites made from natural resources resulting from the depletion of fossil fuels and the environmental effect of the mass production of plastic made from petroleum-based materials[1-3]. More than 300 million tons of plastic is manufactured each year for various applications, prompting initiatives to develop environmentally sustainable composites comprised of bio-based polymers[1-4]. Although there are a variety of renewable biobased polymers to choose from, they historically suffer from similar issues such as excessive water absorption[1], unstable thermal properties[3], inhomogeneity[1,3], poor mechanical performance[4], and low compatibility with matrices[2]. Addressing the issues in performance of biobased polymer composites is a necessary step towards creating materials with properties which can be comparable to composites already available in the market[1,3]. For example, one may seek to improve the mechanical properties of a biopolymer-based composite via the selection of additives able to promote interfacial interactions between the additive and matrix[4]. As such, numerous studies have been performed to identify methods for tailoring biopolymers with additives to create solutions capable of meeting the needs of modern engineering materials[4].

In the past decades, there have been numerous efforts to physically blend biobased additives with polymers that have led to poor mechanical properties due to incompatibility of their hydrophobic and hydrophilic characteristics[4]. As a result, functionalization of biobased polymers has been proven to be an effective method to add new desired properties for targeted applications without compromising other properties, particularly those relating to dispersibility and mechanical performance[5-8]. Chung et al showed that grafting poly lactic acid on lignin improved the miscibility with bioplastics and improved the mechanical performance including tensile strength (+16%) and strain (+9%) without sacrificing modulus[2]. Similarly, Thakur et al showed that grafting poly (butyl acrylate) on lignocellulose polymers decreased the moisture absorbance of the fibers and improved thermal, acid, and base resistance[9]. In addition, Zeng et al designed a biopolymer clay

composite adsorbent by introducing functionalized carboxymethyl chitosan matrix for the removal of mercury ions from aqueous solutions[10].

Some of the notable biopolymers that have received interest includes cellulose, chitosan, starch, natural rubber (NR), polyvinyl alcohol (PVA), polylactic acid (PLA), polyglycolic acid (PGA), polycaprolactone (PCL), polyhydroxy butyrate (PHB), and polybutylene succinate (PBS)[4]. Starch has been a promising candidate for biobased polymers due to its non-toxicity, renewability, and biodegradability[11-15]. Various forms of starches have been used within the textile industry as a sizing agent as well as in adhesives and binders in the paper industry[11]. In the medical world, starches have been used in the development of medicinal capsules thanks to their biodegradability and non-toxic nature. It was reported that starch blends accounted for 16.4% of the total global bio-plastic production in 2021[7]. However, in its natural form, it imposes severe limitations due to its weak material properties[4,7]. Specifically, starches tend to exhibit high brittleness, low strength and flexibility, and poor water resistance due to its hydrophilic nature[7,11-13]. Consequently, numerous strategies have been evaluated over the years to mitigate these issues.

Liu et al created a thermoplastic starch-based composite by a two-step melt blending extrusion with SiO_2 as a reinforcing agent. Both the tensile strength and elongation at break improved significantly, thereby proving that simple melt blending can have promising results in enhancing the properties of starch-based materials[8]. Moreover, Boudjema et al, prepared a biopolymer-based composite using a solution casting method with corn starch and cellulose fibers. The results showed a 92% improvement in elastic modulus and enhanced water resistance when compared to pure thermoplastic-starch films[14]. Similarly, Yu et al demonstrated the creation of starch-based high-density polyethylene (HDPE) composite fiber via a one-step reactive extrusion and melt spinning process. Results of the study showed that by grafting maleic anhydride (MA) to starch, there was an improved compatibility between starch and HDPE as the grafted MA provided better phase domains and promoted stronger interfacial adhesion of the materials through the introduction of covalent bonding mechanisms which led to an increase in the elongation at break[15].

The focus of this study is to create and evaluate an inexpensive, eco-friendly, bio-based functionalized starch additive for use in thermoset and thermoplastic composites. The functionalization of starch proves advantageous for mechanical enhancements in which additive loading can be tailored to target properties. Further research has demonstrated that uniform and stable dispersion can be achieved by introducing specific functional groups to the starch structure in an easily scalable chemical process. The mechanical performance of additive-enhanced carbon fiber reinforced composites was evaluated according to ASTM standards for tensile, interlaminar shear strength, and flexural properties using test panels containing 0.1 and 0.5 wt% of these additives.

Experimentation

Materials

The functionalized starch (herein called f-Starch) used in this study was supplied by MITO Material Solutions (Indianapolis, IN). For the matrix system used for the study, EPON 862 and EPIKURE Curing Agent W were purchased from Miller-Stephenson (Danbury, CT). A T700 12K 2x2 Twill 400 GSM carbon fiber was procured from Composite Envisions (Wausau, WI) for the production of fiber reinforced composites.

Sample Preparation

Particle Size Analysis

Samples for particle size analysis were initially prepared as a 1 wt% dispersion by first measuring 0.30 g of the functionalized starch powder inside a fume-hood which was then added to 30 g of water in a beaker. The mixture was mixed with a magnetic stirrer for 1 hour at 300 RPM at room temperature. When testing, the dispersion is further diluted to obtain the necessary transmission level. Care was taken to ensure the dispersion was adequately mixed prior to sampling, and multiple samples were taken to ensure the accuracy of the results.

Panel Fabrication

Plies of carbon fiber were cut from a 50-inch-wide roll using carbon fiber cutting scissors and the sets of plies (either 6 or 9 plies dependent on the thickness required for the testing being performed) were weighed. EPON 862 was measured and initially warmed to 70 °C to reduce the viscosity and aid in the dispersion of f-Starch into the resin. Dispersions were prepared at 0.1 wt% and 0.5 wt% of f-Starch with a handheld emulsifier and were processed for 5 minutes. The dispersion was then degassed, and the EPIKURE Curing Agent W was added and mixed again. The mixture was then degassed a second time and heated immediately prior to the hand lay-up process. Panels were laid-up by hand on a heated glass panel to ensure the resin remained thin and easily spreadable across the fiber plies. The uncured panels were then transferred to the first vacuum bag (breather and Teflon material is included on both the bottom and top sides of the panel to promote resin capture and flow). A second vacuum bag is applied for the purpose of consolidating the panel, and the panel was then cured in an oven at 180 °C for 2 hours.

Test Specimen Preparation

All composite panels were cut using a waterjet according to the respective ASTM testing specimen dimensions. Care was taken to ensure specimens were cut parallel to fiber alignment, and panels were processed quickly to avoid excessive water absorption. The specimens were then dried in a vacuum oven at 70 °C for 2 hours before being left to cool at room temperature. The specimens were then stored in sealed plastic bags until they were ready to be tested. 6-ply panels were used to produce tensile test specimens and 9-ply panels were used for ILSS and flexural testing specimens.

Characterization

Physical Testing

Thermogravimetric analysis was conducted on a TGA 550 from TA Instruments (New Castle, DE). Fourier Transform Infrared Spectroscopy was performed on a Nicolet™ iS20 FTIR Spectrometer from ThermoFisher Scientific (Waltham, MA).

Particle Size / Morphology Analysis

Particle size analysis was conducted using a Horiba LA-960S2 Laser Diffraction Particle Size Analyzer purchased from Daystar Scientific (Valparaiso, IN). For this study, particle size analysis was performed using distilled water for the dispersion medium. Particle morphology was examined using scanning electron microscopy (SEM) imaging. SEM was performed using a Hitachi TM4000 PLUS Series II SEM purchased from Angstrom Scientific Inc. (Ramsey, NJ).

Mechanical Testing

Mechanical testing was conducted on a 34TM-50 Universal Testing Machine from Instron

(Norwood, MA). Test methods were performed according to ASTM D638 for tensile strength and modulus, ASTM D7264 for flexural strength and modulus, and ASTM D2344 for interlaminar shear strength using the short beam shear method.

Results

Physical Testing

The FTIR spectra shown in Figure 1 provides evidence of the successful functionalization of the starch material through the decrease in -OH groups which can be observed in the spectra around 3399 cm^{-1}. Additionally, the f-Starch exhibits increased thermal stability and possesses approximately 14% residue at 800 °C compared to the 0.1% residue of the raw starch powder as seen in the TGA results presented below.

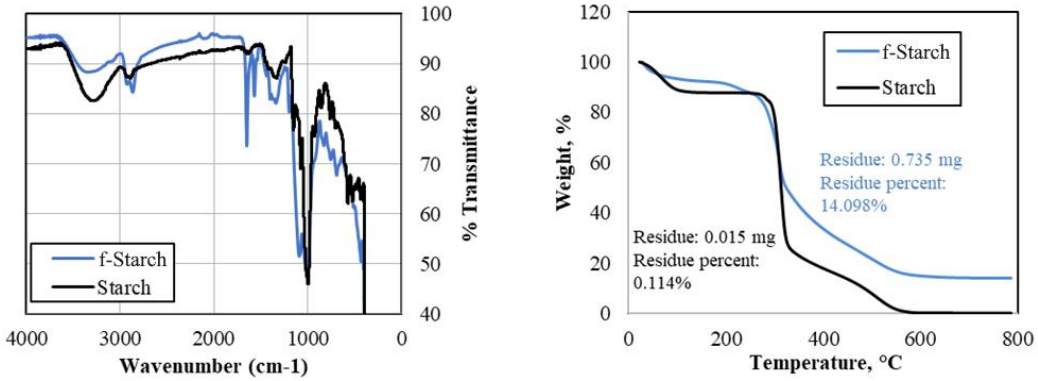

Figure 1: FTIR (left) and TGA (right) plots comparing f-Starch to the control starch.

f-Starch Particle Size Characterization

Three batches of f-Starch were evaluated via laser particle size diffraction, the results of which are depicted in the histogram in Figure 2. The f-Starch additive possesses a mainly unimodal distribution with particles on the low end of the micron scale. The SEM images provided in Figure 3 provide evidence that the f-Starch possesses consistent particle features with particle sizes consistent to the measurements obtained from laser particle size analysis.

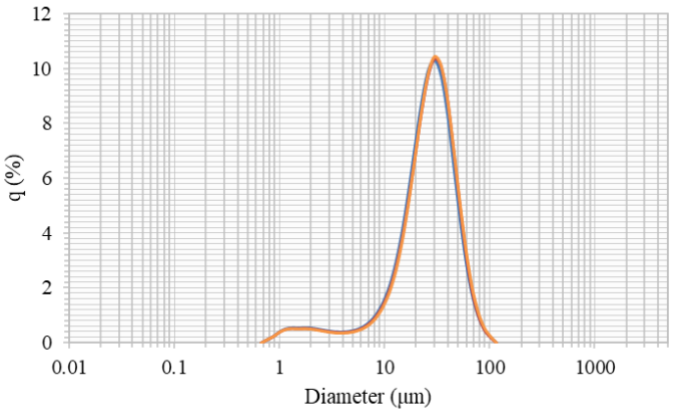

Figure 1: f-Starch particle size distribution histogram.

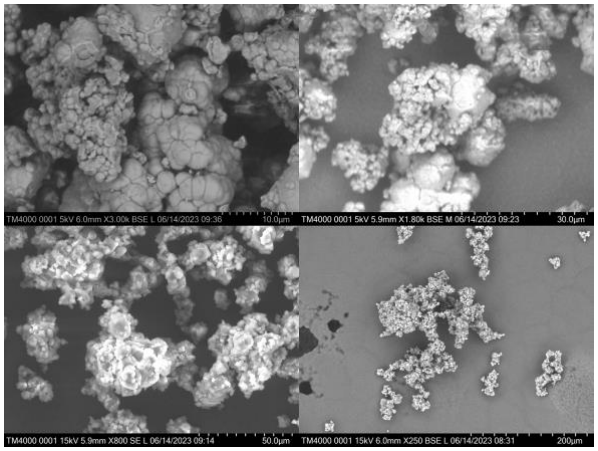

Figure 2: SEM images of f-Starch: top left: 3kX magnification; top right: 1.8kX magnification; bottom left: 800X magnification; bottom right: 250X magnification.

Mechanical Results

The mechanical testing results shown below have been normalized to the corresponding control panel's fiber volume content if needed and possible. Typically, when a nanofiller is added to a composite material, the modulus of the resulting material increases while the ultimate strength decreases. However, the addition of f-Starch at a loading of 0.1 wt% increased both the flexural and tensile strengths and moduli. There is a drop in flexural strength with the addition of 0.5% f-Starch. There is not a significant variation in the tensile strength and modulus between the two loadings of f-Starch. However, there is a substantial difference seen between the two loadings in interlaminar shear strength (ILSS). The ILSS of a composite sample can be an indication of how well the resin matrix is interacting with the fiber reinforcement. The addition of 0.1% and 0.5% f-Starch increased the interlaminar shear strength by 12.3% and 17.8%, respectively. This significant increase in ILSS indicates that the f-Starch is enhancing the bonding interaction between the epoxy resin and carbon fiber.

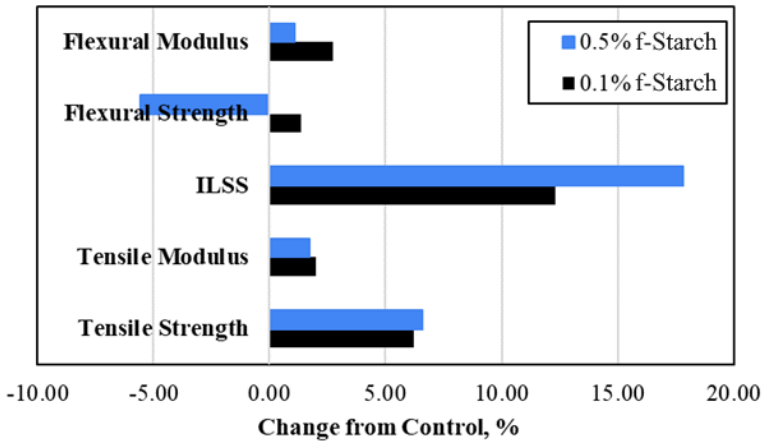

Figure 3: Percent change in composite properties from the addition of f-Starch at 0.1% and 0.5%

The mechanical data presented reveals that even at such small loadings of less than 1 percent by weight of resin, and while used in a composite panel made from high strength, standard modulus carbon fiber (T700 which is primarily used in high demanding structural applications

across multiple segments including in aerospace industries), and an epoxy Bis-F resin (EPON 862 which is formulated into products with applications similar to the T700 fibers), there is an observable level of engagement between the f-Starch, fiber, and resin that can be captured by mechanical tests performed here, with results indicating different degrees of performance improvement. To amplify this improvement, one must take a step further and incorporate these materials into lower grade carbon fiber and chopped (or chopped recycled) fiber in order to obtain a higher level of improvement. In addition to that, the impact resistance of the system can also be of interest as nanomaterials which have positive interaction with their surroundings, have shown higher influence on improving impact resistance of composites.

Summary and Next Steps

The results of this study showed that the bio-based functionalized starch additive provided a detectable and, in some cases, significant mechanical improvement. While the percent loading of f-Starch did not significantly affect tensile strength and modulus, there was still a 5-7% increase in tensile strength and a 3% increase in tensile modulus. Flexural and interlaminar shear properties were more sensitive to the loading of f-Starch. The findings also showed that easy, uniform, and stable dispersion can be achieved by introducing specifically advantageous functional groups to the starch structure. While these initial results are encouraging, further study of the f-starch additive is needed to fully understand the potential benefits it may provide to fiber reinforced composite materials. Future studies regarding the use of lower grade materials are planned, as well as an expansion of the characterization and testing methods beyond what has been presented in this work. Additional works are currently in progress, and results will be shared when possible in future presentations, conference proceedings, and publications.

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