



Completely self-assembled fiber composites



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ABSTRACT

Wheat gluten is hydrolyzed to low molecular weight proteins where some of the proteins self-assemble into high modulus fibers and the rest arrange around the fibers to form a polymer matrix so that the total material produces a fiber-reinforced polymer matrix composite. Self-assembly at 37 °C yields fiber composites with a modulus of 266 MPa. Self-assembly at 22 °C suppresses fiber formation resulting in polymer materials of much lower 20 MPa modulus. Fourier transform infrared (FTIR) spectroscopy results show both materials have similar β -sheet content of about 50% but the composites formed at 37 °C have increased hydrogen bonding. Hydrophobic interactions are also different in the 37 °C composite because it is hydrophobic interactions that drive self-assembly into large amyloid fibers. Scanning electron microscopy (SEM) shows that there is good interaction between the fiber and matrix because protein completely coats the fibers and no voids are observed at the fiber/polymer interface. Thermogravimetric analysis (TGA) shows that the 37 °C composite is more thermally stable at higher temperatures because of the increased intermolecular interactions and the presence of fibers.

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1. Introduction

A fiber-reinforced polymer composite consists of a continuous polymer matrix phase and a discontinuous fiber reinforcement phase. The matrix phase is usually present in higher volume fraction than the reinforcement phase although recent advances in composites, particularly with biobased fiber reinforcement, have used very high fiber contents [1,2]. In a typical polymer composite, the matrix is of low density and high toughness and the reinforcement is of higher density but high rigidity and strength. Combining the materials results in a composite that is more rigid and strong than the polymer itself and less dense and tougher than the reinforcement itself. Fibers can be short or long. Short fibers are amenable to mixing with the polymeric matrix on an extruder, making processing easier. Short fibers usually randomly orient in the matrix, unless the processing dictates otherwise, giving isotropic composite properties. Long fibers can be oriented in any direction to make anisotropic composites but cannot be processed on high volume equipment like extruders. Typical commercial fiber reinforcements include carbon and glass. Glass is economical but dense and carbon fiber vice versa. Glass and carbon are hydrophilic and most often are mixed with hydrophobic synthetic polymers

like polyolefins or epoxy to form a composite. Usually, a third component called a “compatibilizer” must be used to increase interactions between the fiber and polymer and yield a good fiber/polymer interface for efficient load transfer during use [3–9]. Neither carbon nor glass is considered sustainable and thus there has been interest in using natural fibers to reinforce polymer composites because they are of low density and high stiffness [6,10,11].

Traditional attempts to make more sustainable composites involve mixing natural fibers of lignocellulose or protein in a polymer matrix, which can be synthetic or biobased [6,12,13]. A lot of biopolymer matrices have poor mechanical properties and are prone to moisture absorption so forming a composite can improve mechanical properties and moisture resistance [12,14–16]. Natural fibers can vary in properties depending on how they are grown, which is not a problem with synthetic fibers [6,17]. Protein-based fiber composites have been studied including using poultry feather fiber as the reinforcing phase in polyolefin matrices and using lignocellulosic fibers in plasticized keratin, soy protein, or wheat gluten matrices [10,11,18–20]. Wheat gluten (WG) is an interesting natural material because of its abundance, low cost, good biodegradability, and non-toxicity [8,14,21,22]. Wheat gluten has good viscoelastic properties, reasonable tensile strength, is an excellent O₂ and CO₂ gas barrier, and has the ability to fully degrade in less than 50 days [14,21,23,24]. It is found that reinforcement with natural fibers significantly improves the mechanical

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properties of wheat gluten [17]. There are examples in the literature of wheat gluten being reinforced with a variety of natural fibers and fillers such as coconut fiber, hydroxyethyl cellulose, jute, nanoclay particles, hemp, and basalt [8,14,16,17,21–24]. Care has to be taken during the processing of temperature sensitive natural fibers and biopolymers to avoid degradation [6,25]. For this reason, the thermal processing used in synthetic composite manufacture may not be suitable for biobased composites [15,17]. WG has been processed using extrusion, compression molding, and solution casting but protein molecular weight decrease as a result of thermal degradation or solvent-induced hydrolysis can decrease mechanical properties [16,17,24].

Most fiber-reinforced polymer composites are considered “macrocomposites” by today’s standards because the fibers have a diameter, D , of 10–150 μm [3]. Nanocomposites are formed from nanometer-sized reinforcements and the typical one is nanoclay [26]. There is an emerging nanomaterial called an “amyloid” that exists as protofibrils ~2–4 nm high, 10–30 nm wide, and micrometers to millimeters long [27]. Amyloids are formed from the self-assembly of protein molecules [28–30]. Proteins unravel, straighten, and hydrogen bond to a nearby straightened protein to form a β -sheet. β -sheets can stack on top of one another and protein molecules can continue to add onto the ends of the growing β -sheets, elongating them into protofibrils where the β -sheets are oriented perpendicular to the protofibril axis [31]. While amyloids have been mostly studied in the context of neurodegenerative diseases, “functional” amyloids used to protect and proliferate life are a burgeoning field of study [32,33]. Functional amyloids include barnacle cement and fibrous hyphae used by bacteria and fungi to form biofilms and attach to surfaces [34,35]. The amyloid protofibril phase in these materials confers large increases in rigidity and toughness. Many different proteins have been shown to form amyloid fibrils [32]. Typical amyloid fibrils from a variety of proteins have moduli, E , of 2–4 GPa [36,37]. The fibril modulus is related to how much protein incorporates into the β -sheet [38]. Optimizing self-assembly conditions to incorporate more protein into β -sheets can yield amyloids with moduli higher than spider silk, i.e., E ~20–50 GPa [27]. Thus, there is substantial interest in producing amyloids for engineered materials like films, adhesives, and composites [39]. There are multiple research studies on using the nanometer-sized amyloid fibrils for nanocomposites. Some reports utilize the amyloid to produce “smart” nanocomposites that perform functions beyond load bearing or in specialized biomedical applications [40–42]. Others simply use the nanometer amyloid fibrils to provide reinforcement of commodity polymers such as cross-linked polydimethyl siloxane (PDMS) [43]. A 2 wt% amyloid nanocomposite shows equal reinforcement to a 2 wt% carbon nanotube (CNT) nanocomposite and both are about 50% higher in strength than the PDMS by itself. Increasing the amyloid content to 10 wt% and orienting the protofibrils along the deformation axis during testing results in a nanocomposite with 3 times the modulus of a 10 wt% CNT nanocomposite, which is still about 50% higher in modulus than the PDMS by itself. All of the nanocomposites maintain the 40% strain to break of the PDMS matrix, which is a good indication that the polymer matrix impact resistance is not degraded upon nanocomposite formation. Another report describes the lysozyme amyloid protofibril reinforcement of polylactic acid (PLA) at 1–5 wt% amyloid [44]. Modulus and strain to break increase dramatically as a function of amyloid content in the nanocomposites compared to the PLA matrix by itself with no change in breaking strength. It is found that the nanocomposites have higher glass transition temperature (T_g) but lower crystallinity. The amyloid suppresses crystallinity in the PLA phase and thus increases strain to break. As crystallinity is lost, load transfer is assumed by the amyloid protofibrils so the modulus increases and

breaking strength is maintained. Insulin amyloid protofibrils have been added to aqueous polyvinyl alcohol (PVOH) solutions and then the water evaporated. The resulting 0.6 wt% amyloid-PVOH nanocomposites are 15% stiffer than PVOH alone and again the PVOH crystallinity is suppressed with the addition of the amyloid [45].

It has been shown that self-assembly can continue beyond the protofibril stage all the way to the micrometer scale [46–52]. The final fibers are called “large amyloid fibers” with $D = 10$ – $20 \mu\text{m}$ and are similar in morphology and properties to natural protein fibers like silk. The key to hierarchical self-assembly of large amyloid fibers is to create mixtures of “template” and “adder” proteins that work cooperatively to overcome free energy barriers to self-assembly and allow protofibrils to further bundle into larger and larger structures. A very important feature of the “template and adder” process is that changing the adder protein sends the self-assembly down a different path resulting in large amyloid fibers of different shape, structure, and properties, which is related to the hydrophobicity and glutamine content of the adder protein. Hydrolysis of wheat gluten results in a mixture of template and adder proteins where the adder proteins have high glutamine (Q) content and produce compact protofibrils and round large amyloid fibers of $E = 2.5 \text{ GPa}$ [47].

Here, trypsin hydrolyzed wheat gluten produces lower molecular weight proteins where some proteins self-assemble into high rigidity large amyloid fibers and the rest arrange around the fibers to form a polymer matrix to produce a fully self-assembled fiber composite. Thus, this is the first report of fully self-assembled amyloid macrocomposites. It is hypothesized that a fully self-assembled fiber composite can overcome a lot of the problems of traditional sustainable biobased composites because: 1) a perfect interface exists in a self-reinforced composite because the fiber and matrix are made of the same material, 2) low temperature processing in water will not degrade the material, 3) self-assembled protein fibers can be produced *in vitro* with the same properties over and over again, 4) the composites would be of low density, and 5) the composites would mimic naturally-occurring composites formed through self-assembly processes, which have extraordinary strength, stiffness, and toughness [53]. In this study, self-assembled wheat gluten composites are formed and then characterized with 3-point bend (3PB) mechanical testing, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA).

2. Materials and methods

2.1. Hydrolyzed wheat gluten (WG)

Two solutions were prepared by dissolving 4 g of wheat gluten (MP Biomedicals, LLC, Solon, OH) in 160 ml of pure water and hydrolyzing with 60 mg of trypsin (Type I from bovine pancreas, Sigma–Aldrich, St. Louis, MO) at a 1:67 enzyme to substrate ratio (w/w). The solutions were maintained at 37 °C and pH 8 with 1 M NaOH for 24 h to hydrolyze the protein. The molecular composition of the hydrolysate has been characterized with fast protein liquid chromatography (FPLC) and sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) [54].

2.2. Formation of composite

After hydrolysis, one solution was maintained at 37 °C and the other maintained at 22 °C. The solutions were pipetted into rectangular 30 mm long \times 6 mm wide \times 6 mm thick silicone molds and then allowed to dry under a fume hood until the water level decreased significantly such that more solution could be pipetted

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