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Self-healing green composites based on soy protein and microfibrillated cellulose

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ABSTRACT

Self-healing soy protein isolate-microfibrillated cellulose (MFC-SPI) composites that incorporated poly(d,l-lactide-*co*-glycolide) microcapsules containing SPI (SPI-PLGA-MCs) as the healing agent were developed. SPI-PLGA-MCs prepared using a green solvent, ethyl acetate, had a protein loading of over 50%. Self-healing MFC-SPI (10 wt%) composites containing SPI-PLGA-MCs (15 wt%) had Young's modulus of about 970 MPa and strength of over 15 MPa whereas neat SPI resin had Young's modulus of 326 MPa and strength of about 8 MPa. The significantly higher tensile properties of composites compared to neat SPI resin was due to the inherent high tensile properties of MFC and excellent hydrogen bonding with SPI resin. Self-healing mechanism, i.e., healing agent (SPI) bridging the fracture surfaces of the microcracks, was observed through SEM imaging. Composites with no SPI-PLGA-MCs showed no self-healing whereas self-healing SPI composites showed 27% healing efficiency after 24 h healing. The self-healing efficiency was noticeably lower than 48% obtained earlier for self-healing SPI resin using the same SPI-PLGA-MCs. This was because the self-healing mechanism occurs only for the SPI resin component and not for the MFC fibrils. Self-healing of green composites can extend their useful life and make it easier for them to replace conventional composites derived from petroleum.

1. Introduction

Most fiber reinforced plastics or composites we use today are petroleum-derived. There are two major concerns with this scenario. First, the petroleum is estimated to last only 50–60 years and second, most of these polymers and fibers are non-degradable [1,2]. In the case of composites where fibers and resins may be chemically bonded and/or well mixed, it is almost impossible to recycle or reuse them in other applications. Most of them end up in landfills where they can last for many decades without degrading [2]. As a consequence, biodegradable green polymers and composites from economical and sustainable resources such as agricultural and food products have received significant attention in the past couple of decades. Moving towards green materials has also been a result of ecological awareness as well as future economic concerns [3]. Soy protein, which is one of the most commonly used natural resources for bio-based polymers and composites, offers a wide range of potential functional properties as an effective resin for green composites through the formation of numerous intermolecular bonds. The presence of polar amino acids such as carboxyl, amine and hydroxyl groups in soy protein can react with cross-linking agents or fibers to form covalent bonds and, thus, improve the mechanical properties of the composites [4].

Microfibrillated cellulose (MFC), which is obtained as a loose web-like structure of interconnected cellulose fibrils with diameters ranging from 10 nm to a few μm, is commonly used as the reinforcement for many biodegradable proteins and polysaccharides [1,5]. In many studies, the modulus of MFC sheet consisting of randomly oriented fibrillar network derived from softwood (pine and spruce trees) cellulose pulp has been estimated to be in the range of 29–36 GPa [6]. A single MFC fibril generated from lyocell fibers has been reported to have a value of about 98 GPa for the elastic modulus obtained using cantilever tip bending measurements by atomic force microscope [7]. Many researchers have reported significant increases in the fracture stress of bio-based composites after incorporating MFC [1,8,9]. For example, with the addition of 30 wt% MFC derived from bamboo, the fracture stress and Young's modulus were increased from 20.2 MPa to 59.3 MPa and from 596 MPa to 1816 MPa, respectively [10]. Nakagaito and Yano reported that phenolic composites

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containing 20 wt% MFC from kraft pulp to have Young's modulus of up to 370 MPa [11]. Patil and Netravali have reported that 40 wt% of MFC obtained from kraft pulp incorporated in mango seed starch increased fracture stress and Young's modulus from 16 MPa to 50 MPa and from 1347 MPa to 2407 MPa, respectively, compared to pure mango seed starch resin [1]. In the case of poly(lactic acid) (PLA) composites, the modulus tripled to 10 GPa as the MFC content in PLA composites increased from 10 to 70 wt% [12]. Furthermore, MFC has been reported to exhibit high interfacial bonding between the resin and fibers due to its high aspect ratio coupled with large number of hydroxyl groups on the surface [13].

Most composites, whether synthetic or natural, are subjected to harsh environments including high stress/strain, humidity or oxygen-rich conditions during their use. This exposure often leads to degradation of constituents and ultimate failure of the composites [14]. Microcracking is one of the most commonly observed deterioration phenomena during the use of composites. As these microcracks grow and combine composites fail catastrophically, significantly reducing their service life [15]. In order to tackle this problem, self-healing resins have been developed that increase the durability of the composites and, hence, offer longer service life [16,17]. While there are many self-healing systems, microcapsule (MC)-based system containing the healing agent/s have been shown to provide an effective healing in polymers and composites [18].

Many resins and composites using synthetic healing agents such as epoxy [19], dicyclopentadiene (DCPD) [20], 2-octylcyanoacrylate [21], glycidyl methacrylate [22,23], dibutylphthalate [24], encapsulated within microcapsules have demonstrated high levels of self-healing efficiencies [14,25]. For example, Kessler et al. were able to show the self-healing property of epoxy-woven glass fabric (193 g/m^2) composites that contained 20 wt% DCPD-loaded microcapsules in urea–formaldehyde shell and 5 wt% Grubb's catalyst by using width-tapered double cantilever beam test [26]. After 24 h of healing at room temperature (RT) and 80 °C, healing efficiencies were observed to be 45% and 80%, respectively [26]. Brown et al. studied the relationship between concentration of DCPD-loaded microcapsules from 5 to 25 wt% and Grubb's catalyst from 0 to 3 wt%. They found that at 2.5 wt% of Grubb's catalyst and over 20 wt % of microcapsules, epoxy resin showed the highest healing efficiency of over 90% after 10 h of healing time [27]. Yin et al. developed dual-microcapsule system (healing agent and hardeners) for self-healing epoxy composites, which consisted of epoxy-loaded urea–formaldehyde microcapsules (30–70 μm in diameter) as the healing agent and $CuBr_2$ and 2-methylimidazole (the complex of $CuBr_2$ and 2-methylimidazole)-loaded microcapsules as the latent hardener [28]. In this self-healing system, the epoxy composites were reinforced using woven glass fabric (27 vol%, 400 g/m^2). Self-healing epoxy composites containing epoxy MCs (10 wt%) and latent hardener MCs (2 wt%) exhibited over 100% recovery of its original fracture toughness after curing by hot pressing at 100 °C [28]. Brown et al. showed that epoxy resin containing 20 wt% of DCPD-loaded urea-formaldehyde microcapsules with 2.5 wt% of Grubb's catalyst could recover 127% of its fracture toughness [29]. Self-healing polydimethylsiloxane (PDMS) resin containing 12 wt% of PDMS-loaded microcapsules and 3.6 wt% of tin-catalyzed microcapsules showed 24% healing efficiency after 24 h at 50 °C [30].

While there are many self-healing studies of conventional polymers and composites, there have been almost no studies in microcapsule-based system for self-healing 'green' composites fabricated using sustainable resources. However, there are a few studies of self-healing of green polymers [31–36]. For example, self-healing soy protein isolate (SPI) based 'green' thermoset resin was developed using poly(d,l-lactide-*co*-glycolide) (PLGA) microcapsules containing SPI, as the crack healant [31,32]. In this case, the healing of the resin containing 15 wt% microcapsules and 12 wt % glutaraldehyde (GA) as the cross-linking agent was observed to occur by effectively bridging the two fracture surfaces and resulted in self-healing efficiency of up to 48% [31]. However, the SPI resin showed fracture strength of only 8 (±1) MPa and Young's modulus of 326 (±48) MPa which were not enough to meet desired mechanical properties for many durable applications [31]. It should be noted that the numbers in parentheses are standard deviations. Wertz et al. studied self-healing of poly(lactic acid) (PLA) films that contained 2.5 wt% of Grubb's catalyst and 7.5 wt% of DCPD-loaded microcapsules (31.5 μm diameter) showed increased fatigue toughness by up to 84% compared with virgin PLA films [33]. Self-healing vulcanized rubber using $CuCl_2$ as catalyst and vulcanized chloroprene rubber showed 100% recovery of their original tensile properties by rearranging disulfide linkages within the microcracks [34,35]. Self-healing behavior of blends of ethylene/methacrylic acid copolymer with 15–50 wt% of epoxidized natural rubber has also been investigated. In this case visual observation after ballistic puncture tests at entrance and exit regions of a bullet showed self-healed polymers [36].

As mentioned previously, our earlier study has shown excellent feasibility of obtaining green thermoset SPI based self-healing resin using protein-loaded microcapsules within PLGA shell [31]. In the present study, self-healing has been extended to SPI composites reinforced with MFC using PLGA microcapsules loaded with SPI containing microcapsules. Addition of MFC achieves higher mechanical properties for the MFC-SPI composites because of the inherent high strength of the MFC whereas the function of the SPI-loaded microcapsules is to self-heal or bridge the microcracks formed under stress. By bridging the microcracks the propagation of the microcracks can be fully arrested or slowed significantly. In addition, the microcapsules have been prepared using a green solvent, ethyl acetate, instead of dichloromethane which was used in the previous study. The self-healing MFC-SPI composites can offer longer service life and higher tensile properties which could be useful for many applications such as packaging, automotive, aerospace, biomaterials and civil engineering.

2. Experimental

2.1. Materials

SPI (PROFAM® 974) was donated by Archer Daniels Midland Co., Decatur, IL. MFC (Celish KY-100G) was obtained in the form of water-based paste containing fiber content of about 10 wt% from Daicel Corporation, Japan. PLGA with a copolymer ratio of 50:50 [lactide:glycolide (%)] (molecular weight 15–25 K) was purchased from Birmingham Polymers (Birmingham, AL, USA). Poly(vinyl alcohol) (PVA, average MW 31–50 K, 88% hydrolyzed), sodium hydroxide pellets (≥97.0%), hydrochloric acid (HCl) solution, sodium dodecyl sulfate (SDS), Rhodamine B, Bradford agent (in 45% methanol, 10% glacial acetic acid and DI water in the ratio of 5:4:1 with 0.1% Coomassie blue R-250), analytical glutaraldehyde (GA, 25 wt% in water) and ethyl acetate (≥99.8%) were purchased from Sigma Aldrich Chemical Co. (St. Louis, MO).

2.2. Preparation of SPI-PLGA microcapsules

The healing agent, SPI, was encapsulated in PLGA microcapsules (SPI-PLGA-MCs), following the water-in-oil-in-water double emulsion (w/o/w) procedure [31]. SPI solution was initially prepared by dissolving 10 g of SPI in 100 mL of distilled and deionized (DI) water with continuous magnetic stirring for 1 h. The pH of the mixture was adjusted to 11 ± 0.01, using 1 M NaOH solution. Ten mL SPI solution (10% w/v) was poured into a beaker along with 0.3 g of