Self-healing Green Composites Based on Soy Protein and Microfibrillated Cellulose

Joo Ran Kim and Anil N. Netravali

Fiber Science & Apparel Design

Cornell University, Ithaca, NY

Corresponding Author:

Dr. Anil Netravali
Fiber Science, College of Textiles
Human Ecology Building, Room 233
Ithaca, NY, 14805
Phone (607) 255-1875
Fax (607) 255-1875
e-mail: ann2@cornell.edu

Abstract

Self-healing soy protein-microfibrillated cellulose (MFC) 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 SPI-MFC (10wt%) composites containing SPI-PLGA-MCs (15wt%) 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.

Keywords: Self-healing green composites; Microcapsules; Soy protein isolate; Microfibrillated cellulose; green composites.

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 to 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 30wt% 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 containing 20wt% MFC from kraft pulp to have Young's modulus of up to 370 MPa.[11] Patil and Netravali have reported that 40wt% 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 70wt%.[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 20wt% DCPD-loaded microcapsules in urea-formaldehyde shell and 5wt% 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 25wt% and Grubb's catalyst from 0 to 3wt%. They found that at 2.5wt% of Grubb's catalyst and over 20wt% 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 ($30\text{--}70 \text{ }\mu\text{m}$ 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 (27vol%, 400 g/m^2). Self-healing epoxy composites containing epoxy MCs (10wt%) and latent hardener MCs (2wt%) 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 20wt% of DCPD-loaded urea-formaldehyde microcapsules with 2.5wt% of Grubb's catalyst could recover 127% of its fracture toughness.[29] Self-healing polydimethylsiloxane (PDMS) resin containing 12wt% of PDMS-loaded microcapsules and 3.6wt% 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 15wt% microcapsules and 12wt% 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 $8 (\pm 1)$ MPa and Young's modulus of $326 (\pm 48)$ 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 2.5wt% of Grubb's catalyst and 7.5wt% of DCPD-loaded microcapsules (31.5 μ m diameter) showed increased fatigue toughness by up to 84% compared virgin PLA films.[33] Self-healing vulcanized rubber using CuCl_2 as catalyst and vulcanized chloroprene rubber showed 100% recovery of its original tensile properties by rearranging disulfide linkages within the microcracks.[34, 35] Self-healing behavior of blends of ethylene/methacrylic acid copolymer with 15-50wt% 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 10wt% from Daicel Corporation, Japan. PLGA with a copolymer ratio of 50:50 [lactide:glycolide (%)] (molecular weight 15-25K) was purchased from Birmingham Polymers (Birmingham, AL, USA). Poly(vinyl alcohol) (PVA, average MW 31-50K, 88% hydrolyzed), sodium hydroxide pellets ($\geq 97.0\%$), 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, 25wt% in water) and ethyl acetate ($\geq 99.8\%$) 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 PLGA in 30 mL of ethyl acetate (1% w/v) solution. The combined solution of SPI and

PLGA/ethyl acetate were homogenized at 10,000 rpm for 10 min. After the mixing was complete, 5 g of PVA in 100 mL DI water solution (5% w/v) was prepared with heating at 80°C for 1 h and cooled to room temperature. This solution was added into the first water-in-oil (w/o) emulsion. The combined mixture, which consisted of three w/o/w phases of (SPI in water/ PLGA in ethyl acetate/ PVA in water), was homogenized for additional 5 min at 10,000 rpm in a homogenizer (VWR 250[®], VWR International Co., Radnor, PA). All samples were stirred at 300 rpm overnight at room temperature (RT) to allow ethyl acetate to evaporate and to obtain microcapsules. The microcapsules were collected after centrifugation at 5,000 rpm for 20 min. The obtained microcapsules were filtered, washed with DI water and freeze dried at -50°C for 6 h. Protein loading of SPI-PLGA-MCs was measured using the same protocol developed by Kim and Netravali.[31] Three replicates at three different times were carried out to make sure the procedure was reproducible as well as to calculate the average protein loading value and standard deviation.

2.3 Fabrication of self-healing SPI composites

SPI Powder was processed to make it suitable as a resin for green thermoset composite fabrication.[37] SPI powder was mixed with DI water in a beaker in 1:20 ratio. MFC, 10wt% of SPI, was added into the solution and homogenized at 10,000 rpm for 10 min and stirred for additional 12 h using a magnetic stirrer at 1,000 rpm. GA, 12wt% of SPI was added into the solution as a cross-linking agent and heated at 45°C for 30 min. SPI-PLGA-MCs, 15wt% of SPI, was added into the solution and stirred for 30 min at 300 rpm. This solution was poured into Teflon[®]-coated glass mold (15 cm x 15 cm) and pre-cured at 40°C for overnight. The dried sheet taken from the mold was cured in a hot press at 90°C and under a pressure of 0.43 MPa to

complete the SPI-GA cross-linking reaction.[31] The fully cured composite specimens were cut to the desired shape and size using a laser cutter for the self-healing tests.[31, 32] Figure 1 shows the schematic of the process for curing self-healing SPI-MFC composites containing SPI-PLGA-MCs and the laser cut specimen (extreme right) for the self-healing tests. All specimens including cured sheet were conditioned at $21 \pm 1^\circ\text{C}$ and $65 \pm 1\%$ for 72 h prior to any characterization.

Figure 1. Schematic of the process for curing self-healing SPI-MFC composites containing SPI-PLGA-MCs and the laser cut specimen (extreme right) for self-healing test.

2.4 Characterization of SPI-PLGA-MCs

Scanning electron microscopy (SEM, Tescan Mira3 FESEM, Kohoutovice, Czech Republic) was used for investigating fractured surfaces of SPI composites and morphology of SPI-PLGA-MCs. SPI-PLGA-MCs containing stained SPI with 0.5% rhodamine B (in w/o/w emulsion) were analyzed, in emulsion form, using a confocal laser scanning microscope (CLSM; Zeiss LSM710, Thornwood, NY). SPI composites containing stained SPI-PLGA-MCs were analyzed using a 514 nm excitation filter with 40x and 63x objective lenses.

2.5 Self-healing efficiency of SPI composites

The fracture toughness of SPI resin (SPI), SPI composite containing 10wt% MFC (SPI + MFC) and self-healing of SPI composites (SPI + MFC) as well as 15wt% SPI-PLGA-MCs (SPI

+ MFC + MC) was characterized at 0 h and after 24 h in accordance with ASTM E647-08.[33] For these tests following procedure was followed. After conditioning the specimens for 72 h, all specimens were tested at 0.3 mm/min displacement rate using Instron universal tester (Instron, Model 5566, Instron Co., Canton, MA). The displacement of clamps (grips) of Instron universal tester was set up to a distance of 10 mm until a significant crack was formed in the specimen to form two separate parts. After forming the crack the specimen was removed from Instron and the two parts were held together by realigning the crack. The specimen was kept in the conditioning room at 21°C and 65% RH for 24 h. After 24 h, healed specimens were placed, individually, in the same Instron and tested as described above to characterize their properties and, thus, to calculate their self-healing efficiency. Since the crack length is nearly identical, the self-healing efficiency can be calculated according to the method established by Brown et al.[27] At least 10 specimens for each of the 3 different samples were tested to report the average and standard deviation values.

Results and Discussion

3.1 Morphology of MFC and SPI-PLGA-MCs

Figure 2 shows typical SEM images of MFC network containing micro- and nano-fibrils, used in this study. These images confirm the observations by earlier researchers that the MFC is a mixture of micro-fibrils and nano-fibrils with have a very broad diameter size, ranging from a few nano-meters to micro-meters.[3] The micro- and nano-fibrils also show an entangled or interconnected network-like structure. MFC have been used earlier to improve mechanical properties of the composites.[10-12, 38] MFC with its large surface area can increase the mechanical interaction with the resin in a composite.[39] Additionally, because of large number of hydroxyl (-OH) groups on the surface, MFC can also hydrogen bond with resins such as soy protein that contain polar groups. Such fiber/resin interfacial interaction can be an important

variable that can affect the mechanical and physical properties of the composites. High interfacial interaction allows efficient stress transfer between broken and intact fibers resulting in high mechanical properties in composites.[10]

Figure 2. Typical SEM images of MFC containing micro- and nano-fibrils.

Figure 3 shows the morphology of SPI-PLGA-MCs and their size distribution histogram. Figure 3(a) shows typical SEM image of SPI-PLGA-MCs (left) and an enlarged image containing a broken SPI-PLGA-MC (right). As can be seen from Figure 3(a) most of the SPI-PLGA-MCs are spherical and have smooth surface. The broken SPI-PLGA-MC seen in Figure 3(a) had a diameter of 1.2 μm and shell thickness of approximately 0.34 μm which occupied about 37vol% of the microcapsule. Figure 3(b) shows the diameter distribution histogram of SPI-PLGA-MCs measured from randomly selected areas of SEM images using ImageJ software ($N \geq 500$). While the diameters of SPI-PLGA-MCs ranged between 0.21 and 3.2 μm, the mean diameter was 0.73 μm.

Figure 3. Morphology of SPI-PLGA-MCs, (a) SEM images along with a broken SPI-PLGA-MC, (b) the diameter distribution histogram of SPI-PLGA-MCs.

3.2 Internal structure and protein loading of SPI-PLGA-MCs

Figure 4 shows the internal structure of SPI-PLGA-MCs by CLSM. Figure 4(a) shows a bright field image of microcapsules whereas Figure 4(b) shows a fluorescent image in which protein loading is shown in red color. Images of the SPI-PLGA-MCs confirm their spherical shape, free of debris, with well-formed shell walls with thickness of approximately 0.35 μm. Inside SPI-PLGA-MCs, presence of SPI stained with rhodamine B appears in red color under fluorescence microscope. As can be seen in Figures 4(a) and (b) no large blank spaces, attributed to voids or bubbles, can be observed inside the SPI-PLGA-MCs. In order to determine protein loading of SPI-PLGA-MCs, a modified Bradford test described in the earlier study was followed.[40] SPI-PLGA-MCs were found to have protein loading of 50 ($\pm$ 4)%.

Figure 4. The internal structure of SPI-PLGA-MCs by CLSM, (a) the bright field image (b) the fluorescent image (red color corresponds to SPI, stained with rhodamine B).

3.3 Characteristics of SPI composites

Figure 5 shows SEM images of fracture surfaces of SPI resin, SPI composite containing MFC and self-healing SPI composites fractured in tensile mode. Figure 5(a) shows fracture surface of pure SPI resin without any MFC. Brittle features and sharp cracks were observed on the surface. These layered surface structures are similar to the typical fracture surfaces observed for rigid/brittle fractures of thermoset SPI resins.[41] Figure 5(b) shows SPI composites containing 10wt% MFC but without any SPI-PLGA-MCs. The fracture surface of SPI composite is rougher compared to pure SPI resin and shows just a few and short protruding micro-fibrils on the surface. This is a result of hydrogen bonds between the polar groups present in both MFC and SPI resin.[10] Figure 5(c) shows the fracture surface of self-healing SPI composites containing both 10wt% MFC and 15wt% SPI-PLGA-MCs. The fracture surface of self-healing SPI composites also shows rough surface and a few protruding micro-fibrils. Both broken as well

as unbroken SPI-PLGA-MCs were observed on the fracture surface.

Figure 5. Typical SEM images of tensile fractured surfaces of (a) SPI resin, (b) SPI composite containing 10wt% MFC and (c) self-healing SPI composites containing 10wt% MFC and 15wt% SPI-PLGA-MCs.

In order to examine whether SPI-PLGA-MCs and MFC were dispersed evenly in the composites as well as to see if the SPI-PLGA-MCs remained unbroken in composites after the

curing (hot pressing) process, composite specimens were analyzed using CLSM in Z-stacking mode. Confocal microscopy was performed to locate fluorescent probes in the self-healing SPI composite cross-sectional planes at varying depths. CLSM images were taken through a total depth of 27 μm , with optical sections taken at every 3 μm depth. Figure 6(a) shows a few of the typical confocal Z-stack images of self-healing SPI composite containing 15wt% SPI-PLGA-MCs and 10wt% MFC. In Figure 6(a), the content of SPI resin and MFC are seen in green color (without rhodamine B stain) under fluorescent images. In the same image, micro-fibrils of MFC (dark green color) can be clearly observed as long strings or as rigid rod shape depending on their orientation. From the images in Figure 6, it can also be concluded that MFC is uniformly dispersed in the resin.

SPI-PLGA-MCs prepared using stained SPI slurry with rhodamine B are seen as red colored circles under fluorescent images in Figure 6(a), because the dye molecules are encapsulated within the spherical SPI-PLGA-MCs. All images of the SPI composites show a strong red signal consistent with the presence of protein within SPI-PLGA-MCs at all different depths. This confirms that both SPI-PLGA-MCs and MFC are dispersed uniformly in the composites and also that the SPI-PLGA-MCs can survive under processing and curing conditions of temperature and pressure. Hence, the SPI-PLGA-MCs could act as the healing agent in these composites when microcracks are created. Figure 6(b) shows a bright field image of SPI composite containing MFC and SPI-PLGA-MCs at 18 μm depth corresponding to the image shown in Figure 6(a). Distinct SPI-PLGA-MCs are seen as circular dots and well-distributed in the self-healing SPI composite. Figure 6(c) shows the fluorescent image at the same depth of 18 μm , matching the image in Figure 6(b). Again, these images confirm that SPI-PLGA-MCs are dispersed uniformly in the composite and that they remain unbroken after the composite fabrication process.

Figure 6. Typical confocal Z-stack images of self-healing SPI composite by CLSM, red color corresponds to strained SPI (core) inside the SPI-PLGA-MCs, (b) the bright field image taken at 18 μm depth and (c) the fluorescent image taken at 18 μm depth.

3.4 Self-healing efficiency of SPI composites

Figure 7 shows SEM images of bridging zones inside the microcracks after 24 h of healing, taken at different magnifications. Figure 7(a) shows fractured surface of SPI resin (without MFC or SPI-PLGA-MCs) after 24 h healing. No healing or bridging features can be seen between the two sides of the fracture (microcrack). Rather, sharp cracks and layered fracture surface similar to those shown in Figure 7(a) for pure SPI resin can be seen.[4] Figure 7(b) shows fracture

surface of SPI composite containing MFC. In this case the fracture surface shows some MFC micro-fibrils protruding inside the microcrack. Most protruding MFC fibrils are very short and some of them are in an aggregated form. These surface characteristics are similar to those shown in Figure 5(b) earlier and suggest that 10wt% of MFC is not sufficient to connect or bridge two fractured halves due to the limitation of MFC length in the range from 10 nm to a few μm . [1] However, adding 10wt% of MFC to SPI increases its strength from $8 (\pm 1)$ MPa to $25 (\pm 2)$ MPa because of the inherent high strength of MFC as well as due to strong intramolecular hydrogen bonding between MFC and SPI resin and is discussed later. [10] Figures 7(c) and (d) show SEM images of bridging zones in self-healing SPI composites (MFC + SPI-PLGA-MCs) taken after 24 h of healing. The healing agent (SPI) released from the SPI-PLGA-MCs can be easily seen connecting or bridging the two fracture halves. The released SPI can cross-link with the excess GA (cross-linking agent) present in the resin and, thus, self-heal the composite. [42, 43] Figure 7(d) shows low magnification (left) and high magnification (right) SEM images of healed microcrack in self-healing SPI composite (scale bars are 100 and 10 μm , respectively). A few unbroken SPI-PLGA-MCs (shown in circles) can also be seen within the microcrack along with several bridges formed by the SPI released from the broken SPI-PLGA-MCs. Since unbroken SPI-PLGA-MCs cannot release the SPI, they limit the self-healing ability. Major reasons for SPI-PLGA-MCs to remain unbroken are; a) shell wall thickness may be too large and b) bonding between the SPI-PLGA-MCs and the resin may be less than desired and needs to be optimized to obtain higher self-healing efficiency.

Figure 7. SEM images of bridging (healing) zones in the microcracks after 24 h healing, (a) pure SPI resin (SPI), (b) SPI composite (SPI + 10wt% MFC), (c) self-healing SPI composite (SPI+ 10wt% MFC + 15wt% SPI-PLGA-MCs) and (d) self-healing SPI composite at low magnification, left, and high magnification, right. Circles in all images indicate unbroken SPI-PLGA-MCs and rectangles indicate MFC fibers.

Figure 8 shows typical nominal stress vs. deformation plots of SPI composite (SPI + MFC) and self-healing SPI composite (SPI + MC + MFC) in their virgin form as well as after 24 h of healing. In this study, pure SPI resin properties were characterized using the same fracture toughness test used in the earlier study.[31] The values for fracture stress and Young's modulus (with their standard deviations) were observed to be $8 (\pm 1)$ MPa and $326 (\pm 48)$ MPa, respectively.[31] With MFC (10wt%) in SPI composites the fracture stress and Young's modulus were $25 (\pm 2)$ MPa and $1400 (\pm 214)$ MPa, respectively, significantly higher compared to pure SPI resin. This increase in tensile properties is attributed to the inherent high tensile properties of MFC and good bonding with SPI resin through hydrogen bonds.[10, 12] The fracture toughness of SPI composites (SPI + MFC), also increased significantly from 0.5 to $1.1 (\pm 0.1)$ MPa·mm as was expected. It should be noted that fracture toughness is reported simply as the area under the

curve during the self-healing tests and gives an easy way to compare the changes. MFC has been reported as both toughening and strengthening agent, through crack bridging, for SPI resin.[44] After 24 h of healing, SPI composites containing 10wt% MFC (SPI + MFC) showed almost no load, i.e. no self-healing.

For self-healing SPI composites (15wt% SPI-PLGA-MCs and 10wt% MFC), the fracture stress and Young's modulus decreased from 25 ($\pm$ 2) MPa to 15 ($\pm$ 2) MPa and 1400 ($\pm$ 214) MPa to 970 ($\pm$ 86) MPa compared to SPI composites containing the same 10wt% MFC. However, the fracture toughness increased from 1.1 ($\pm$ 0.1) to 1.3 ($\pm$ 0.1) MPa*mm, primarily because of the higher fracture strain. This might be because SPI-PLGA-MCs, particularly those that are small and/or not as well bonded to the SPI resin as MFC, and, hence, provide some molecular mobility in self-healing composites.

Figure 8. Typical nominal stress vs. deformation plots of SPI composite (10wt% MFC) and self-healing SPI composite (10wt% MFC and 15wt% SPI-PLGA-MCs) tested using mode I fracture toughness test, before (virgin) and after 24 h healing.

Self-healing SPI composites (15wt% SPI-PLGA-MCs and 10wt% MFC) showed fracture stress of $4 (\pm 0.3)$ MPa after 24 h of healing while the virgin self-healing composite had $15 (\pm 2)$ MPa at 0 h. This result indicates a self-healing efficiency of $27 (\pm 4)\%$. Kim and Netravali had earlier showed that pure SPI resin containing 15wt% SPI-PLGA-MCs and 12wt% GA resulted in close to 50% healing efficiency.[31] In this system, damage such as microcrack was shown to serve as the trigger for self-healing mechanism through the rupture of embedded SPI-PLGA-MCs which released the healing agent (SPI) inside the microcracks. Cross-linking reaction was initiated by direct contact with the excess GA (cross-linking agent) presented in the SPI resulting in microcrack bridging. In the present case, the self-healing efficiency is much lower than that resulted from self-healing SPI resin. This is because the self-healing mechanism occurs only for the SPI resin and not for the MFC fibrils. Kessler et al. have reported similar phenomenon for self-healing epoxy composites reinforced with woven glass fabric containing DCPD-loaded urea-formaldehyde microcapsules and Grubb's catalyst.[26] They showed 38% self-healing efficiency for composites while pure epoxy resin containing same DCPD-loaded urea-formaldehyde microcapsules and Grubb's catalyst resulted in about 100% healing efficiency.[26] The fracture stress of self-healing SPI composite was $4 (\pm 0.3)$ MPa after 24 h healing time, compared to self-healing pure SPI resin that showed fracture stress of $4 (\pm 0.4)$ MPa after 24 h healing.[31] The healing of microcracks in both cases is by bridging of the two resin surfaces and hence, it may be expected to result in similar fracture stress. However, in the case of the SPI composites, it is possible that the released SPI healant from the broken SPI-PLGA-MCs can form strong hydrogen bonding with the MFC in the composites.[1, 45] This bonding would result in a slightly higher fracture stress of self-healing SPI composites than the pure self-healing SPI resin.

Based on the self-healing results obtained from Figure 8, released healing agent, SPI, from SPI-PLGA-MCs and MFC could retard crack growth and, thus, increase its fracture toughness.

The fracture toughness of the virgin SPI composite was 0.5 MPa*mm whereas the fracture toughness of the self-healing composite was 1 ($\pm$ 0.1) MPa*mm. After 24 h of healing the toughness of the self-healing composites was 0.5 MPa*mm, giving 38 ($\pm$ 3)% in fracture toughness recovery. It has been reported that the effect of fibers or particles could increase fracture toughening by various phenomena such as crack pinning and bridging microcrack or deflection.[46, 47] SPI composites containing only MFC, on the other hand, did not show any healing while their toughness was higher compared to pure SPI resin.

3. Conclusions

Self-healing MFC-SPI composites were developed using PLGA microcapsules containing SPI as the healing agent. The SPI-PLGA-MCs prepared using a green solvent, ethyl acetate, had diameters ranging between 0.21 and 3.2 μ m with an average of 0.73 μ m. The protein loading of SPI-PLGA-MCs was 50 ($\pm$ 4)%. SPI composites reinforced with 10wt% MFC resulted in significantly higher tensile properties due to the inherent high strength of the MFC fibrils as well as good MFC-SPI resin bonding because of the polar groups present on both. The fracture stress and Young's modulus of self-healing SPI composites containing 15wt% SPI-PLGA-MCs were 15 ($\pm$ 2) MPa and 970 ($\pm$ 86) MPa, respectively. Both these values are significantly higher than 8 ($\pm$ 1) MPa and 326 ($\pm$ 48) MPa obtained for pure SPI resin. Average fracture toughness of self-healing SPI composites was also significantly higher than that of pure SPI resin. The healing efficiency of the self-healing SPI composites was 27 ($\pm$ 4)%. Microcracks serve as the trigger for self-healing mechanism through the rupture of SPI-PLGA-MCs present inside the microcracks. The fractured MCs release the SPI that allows cross-linking reaction between SPI and excess GA present in the SPI to occur, resulting in microcrack bridging.

This self-healing system presented here can be useful in extending the life of the green composites. The newly designed self-healing SPI composites may be used, in many applications

where conventional petroleum-derived composites are currently being used, for long and safe service life of green composites.

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