Self-Healing Starch-based ‘Green’ Thermoset Resin

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Abstract

In the present research, self-healing green thermoset resin has been developed using waxy maize starch. Self-healing was achieved using waxy maize starch-loaded poly(d,l-lactide-co-glycolide) microcapsules (WMS-PLGA-MCs). Hydroxyl groups of WMS released from WMS-PLGA-MCs can bridge the microcrack surfaces by forming ester linkages between the carboxylic acid groups of *Meso*-1,2,3,4-butanetetracarboxylic acid (BTCA) used in the resin as the crosslinker. Self-healing WMS resin containing 20% WMS-PLGA-MCs by weight showed self-healing efficiency in fracture stress of up to 51% and recovered about 66% of the original fracture toughness after 24 h of healing at room temperature. Self-healing starch-based resin developed in this study is not only green and sustainable but the fabrication processes including microencapsulation are water-based and can be easily scaled up. The nontoxic starch based green resin can be useful for fabricating green composites in many indoor applications such as automotive, aerospace and packaging, to replace currently used petroleum-derived composites.

Keywords : Self-healing green resin; waxy maize starch; microcapsules; Starch based resin; butanetetracarboxylic acid

1. Introduction

Most of the resins such as epoxies, poly(methyl methacrylate) (PMMA), polyimides, polyurethanes (PU), polyesters and polypropylene (PP) that are used in commercial products including composites are derived from petroleum [1]. All of them are associated with end-of-life disposal problems because they do not biodegrade for decades or even centuries under current waste processing treatments such as landfilling and composting [2]. Since reinforced plastics or composites, which are made by bonding two distinct constituents, cannot be recycled or reused easily, most of them are discarded in landfills at the end of their life [2, 3]. Another problem is

related to the sustainability of petroleum itself. By some estimates we are consuming petroleum at 100,000 times the rate at which the earth can produce [2, 3]. End-of-life disposal and sustainability issues have been responsible for the current push to develop biodegradable polymers using renewable resources, most commonly from the yearly renewable plants. In the past decade, such polymers have been showing up as replacements for petroleum-based polymers [4]. Among many plant-based materials investigated as potential alternatives for petroleum-based products, starch has received considerable attention [5]. This is primarily because starch is inexpensive and yearly renewable plant-based polysaccharide. In addition, it is produced worldwide in large quantities and can be used as a raw material to produce biodegradable resins and composites [4]. In spite of these advantages use of starch as resin has been limited in durable goods applications, due to its low mechanical properties and brittleness, compared to petroleum-based polymers [6].

All polymers and composites develop microcracks when they experience stress [1, 7]. Over time, these microcracks continue to grow, decreasing the properties of composites and ultimately leading to their premature failure, thus, significantly reducing their service life [8]. To tackle this issue, self-healing polymers have been developed that can repair the damage autonomously and prevent the associated property deterioration [9]. Using such self-healing polymers can significantly improve the safety, service life, energy efficiency and environmental impact of the products [9].

Up to date, development of self-healing systems have been limited to petroleum-based polymers only [10-20]. As a result, literature on self-healing polymers derived from fully green resources is almost non-existent. One of the major reasons for this is that green polymers are new and still being developed.

Many microcapsule-based self-healing systems for synthetic polymers have been developed to date. Commonly used materials such as urea-formaldehyde (UF) [10], melamine-

formaldehyde (MF) [11], melamine-urea-formaldehyde [12], polyurethane (PU) [13], acrylates [14] or poly urea-formaldehyde (PUF) [15], have been used by many researchers as microcapsule shells for encapsulating healants such as epoxy [16], polydiethoxysiloxane (PDMS) [17], isocyanate [18], dicyclopentadiene (DCPD) [19] or glycidyl methacrylate (GMA) [20]. Such microcapsules have proven to be sturdy enough to withstand the processing conditions used to cure thermoset resins and composites and achieve successful healing in use, thus, extending their service lifetime [10-20].

Some research on self-healing has also been conducted on materials that are called partially sustainable and/or green [21-28]. For example, self-healing property of blends of *cis*-1,4-polyisoprene and epoxidized natural rubber resin containing dicumyl peroxide (DCP) as the crosslinking agent was investigated by T-peel tests [21]. A higher epoxidation level was observed to enhance self-healing of rubber due to increase in crosslink density between the epoxy groups and peroxide at room temperature (RT) [21]. In another study self-healing property of sulfur vulcanized natural rubber by polysulfide crosslinking reactions was demonstrated [22]. The results showed 100% full recovery of tensile properties at RT [22]. The poly(vinyl alcohol) (PVA) hydrogel containing 4% microfibrillated cellulose from bamboo pulp and 10% borax hydrogels showed self-healing property by diol–borax reaction and hydrogen bonding between $-B(OH)_4$ of borax and $-OH$ of microfibrillated cellulose [23]. Surface scratches on epoxy films containing Tung oil and linseed oil-loaded PUF microcapsules have been shown to disappear after 72 h of healing [24]. Self-healing vulcanized rubber containing $CuCl_2$ as catalyst showed almost 100% recovery of its original tensile properties, by rearranging disulfide linkages within the microcracks, when kept at $110^\circ C$ [25]. Bio-based self-healing epoxidized soybean oil resin with citric acid as the crosslinking agent recovered its original stress and strain properties after processing at $160^\circ C$ [26]. In a very recent study, soy protein isolate (SPI) based green resin was shown to self-heal with poly(d,l-lactide-*co*-glycolide) (PLGA) microcapsules containing SPI as

the healant [27]. In this case the SPI healant released from the microcapsules was shown to crosslink with glutaraldehyde (GA) present in the resin and bridge the microcracks. This resulted in a self-healing efficiency of about 48% [28].

Green polymeric materials such as hydrogels that heal themselves at damage site under wet or moist conditions have been developed for biomedical applications [29]. For example, Ahn et al. showed copolymer of urea and polydimethylsiloxane to crosslink under wet condition via hydrogen bonding of urea units [30]. Self-healing supramolecular polymers have also been developed using amidoethyl imidazolidone, di(amido ethyl) urea and di(amido tetraethyl) triurea from fatty dimer acids derived from vegetable oils. Self-healing results showed about 80% fracture stress recovery to 2.7 MPa, after 3 h at 20°C [31]. In yet another study, self-healing hydrogel composed of *N*-carboxyethyl chitosan and adipic acid dihydrazide with disperse oxidized sodium alginate, showed 94% healing efficiency in terms of rheological recovery [32].

In the case of brittle materials derived from green resources, a key challenge is to develop a self-healing system that can not only provide mechanical properties required for industrial applications but also significantly longer service life so they can replace petroleum-based polymers.

This paper presents a microcapsule-based system, developed using fully green resources, to obtain self-healing thermoset waxy maize starch (WMS) resin. The self-healing thermoset WMS resin is formed by the crosslinking reaction between the carboxyl groups of 1,2,3,4-butane tetracarboxylic acid (BTCA) present in the resin and the hydroxyl groups from the starch released from the WMS-loaded PLGA microcapsules (WMS-PLGA-MCs) within the microcracks, catalyzed by sodium hypophosphite (SHP). The schematic of the microcrack healing mechanism in WMS resin is presented in Fig. 1(a). In the present microcapsule-based system, resin is prepared by uniformly dispersing microcapsules containing the healant, WMS in

this case. The healant remains encapsulated in the microcapsules until the microcracks are formed in the resin. As the microcracks form, microcapsules in the path of the microcracks rupture allowing the healant to come out. The catalyst and the crosslinking agents present in the resin and the newly released healant react to form crosslinks and solidify, thus, healing or bridging the microcracks. This results in restoring the mechanical properties of resin [33]. Crosslinking starch with multifunctional carboxylic acids to form thermoset starch has been shown to improve its mechanical and physical properties [34]. For example, crosslinking of starch with BTCA by forming ester bonds with the hydroxyl groups has shown significant improvement in its tensile and thermal properties as well as reduced dissolution in water [34]. Crosslinking starch films with citric acid has also been shown to increase the tensile strength by 150% to about 24 MPa [35]. Poly(vinyl alcohol) (PVA) which contains hydroxyl groups can also be crosslinked in a similar way using multifunctional carboxylic acids [36]. Possible reactions of starch and BTCA are shown in Fig. 1(b). In the present case, PVA added during the fabrication of WMS-PLGA-MCs covers the microcapsule surface and improves the interfacial bonding with the resin through hydrogen bonding and, perhaps, by covalent ester bonding similar to starch [28, 37].

Fig. 1. Microcapsule-based self-healing model for starch, (a) Schematic of the microcrack healing mechanism for WMS starch resin and crosslinking reaction between starch (WMS) and BTCA in the resin catalyzed by SHP and (b) Crosslinking reaction between PVA on the surface of WMS-PLGA-MCs and BTCA present in the WMS resin.

2. Experimental

2.1. Materials

WMS was purchased from Now Foods Co., Bloomingdale, IL. PLGA with a copolymer ratio of 50:50 lactide:glycolide (%) (the molecular weight is between 15,000 and 25,000 Da) was purchased from Birmingham Polymers (Birmingham, AL, USA). Poly(vinyl alcohol) (PVA, average MW 31-50K, 88% hydrolyzed), ethyl acetate, sodium hydroxide pellets ($\geq 97.0\%$),

BTCA, (purity $\geq 99\%$), sodium hypophosphite monohydrate (SHP, $\geq 99\%$), sodium hydrogen chloride solution, sodium dodecyl sulfate (SDS), rhodamine B and Lugol's iodine solution were purchased from Sigma Aldrich Chemical Co. (St. Louis, MO, USA).

2.2. Preparation of WMS-PLGA-MCs

Water-in-oil-in-water (w/o/w) double emulsion solvent evaporation technique was used to produce WMS-PLGA microcapsules [38]. The gelatinized solution containing 1 g of WMS in 20 mL of deionized (DI) water (the internal aqueous phase) was prepared by stirring at 90°C for 1 h. The WMS solution was emulsified (w/o emulsion) by adding 1% (w/v) PLGA dissolved in 50 mL of ethyl acetate (the oil phase) using a homogenizer (model 200, VWR international, Radnor, PA, USA) for 10 min at 10,000 rpm. The w/o emulsion was added to 6% (w/v) PVA solution prepared in 100 mL of DI water (an external aqueous phase). Emulsification was continued using a homogenizer at 10,000 rpm for 10 min. The solution was stirred at 300 rpm overnight at RT to allow ethyl acetate to evaporate and to obtain microcapsules. The microcapsules were collected after centrifugation at 5,000 rpm for 25 min. The microcapsules were then filtered, washed with DI water and freeze dried at -50°C for 6 h.

2.3. Determination of starch loading

Freeze dried microcapsules (10 mg) were added to 10 mL of 0.1 M NaOH solution containing 5% SDS. The solution was stirred for 24 h at 300 rpm until a clear solution was obtained. The solution was centrifuged for 20 min at 5000 rpm (Thermo scientific SupernovaTM, Waltham, MA, USA). Pure WMS, as a reference (2, 4, 6, 8 and 10 mg), was added to 10 mL of 0.1 M NaOH solution and stirred for 60 min. Then a few drops of Lugol's iodine

solution was added to all samples until blue-black color was attained. The starch loading from WMS-PLGA-MCs was measured by UV/Vis spectrometer (Perkin-Elmer Lambda 35, Waltham, MA, USA) as absorbance at 548 nm wavenumber. The starch loading was then calculated using the Beer-Lambert law (concentration and absorbance are proportional), compared with known concentrations of pure WMS standard solutions (2, 4, 6, 8 and 10 mg) by Equation (1) [39].

$$\text{Starch loading (\%)} = \frac{\lambda_{\max} \text{ of microcapsules}}{\lambda_{\max} \text{ of pure starch solution}} \times 100 \quad (1)$$

where $\lambda_{\max}$ is the maximum absorption at 548 nm.

2.4. Preparation of WMS resin containing WMS-PLGA-MCs

WMS (10 g) was dissolved in DI water (200 mL) and the mixture was heated at 90°C for 1 h with constant stirring at 300 rpm for gelatinization. Gelatinization of WMS is important as it ruptures the starch granules allowing the hydroxyl groups present on the starch to be accessible for crosslinking reaction. BTCA as a crosslinking agent (40wt% of WMS) was added to WMS resin. This amount was in excess of 25wt% that had shown the highest tensile properties [40]. The purpose of the excess 15wt% of BTCA was to make sure that it was readily available to react with the WMS released from microcapsules within the microcracks for effective healing. SHP (50wt% of BTCA), as a catalyst, was also added to the gelatinized WMS solution. The mixture was heated at 90°C for 1 h with constant stirring at 300 rpm after which it was allowed to cool down to RT. WMS-PLGA-MCs (0 to 20wt%) were added to WMS mixture and stirred for 30 min at RT. This solution was then poured into a Teflon[®] mold (15 x 15 cm) and pre-cured in an air circulating oven at 40°C for 12 h to form a sheet of about 1.3 mm thickness. The sheet, peeled off from Teflon[®] mold, was cured at 90°C and under a small pressure of 0.43 MPa for 10 min in a hot press. Specimens were then cut using a laser cutter to obtain final dimensions of 32

mm x 30 mm x 1.3 mm, as per ASTM E647-08, and conditioned at 65% RH and 21°C for 72 h before conducting the tests [41].

2.5. Characterization of WMS-PLGA-MCs

Scanning electron microscopy (SEM, Tescan Mira3 FESEM, Kohoutovice, Czech Republic) was used for investigating the morphology and surface topography of the microcapsules. WMS-PLGA-MCs containing WMS stained with 0.5% rhodamine B and self-healing WMS resin were also studied using a confocal laser scanning microscope (CLSM; Zeiss LSM710, Thornwood, NY) equipped with 25 mW Argon and HeNe lasers. Filter for 514 nm excitation wavelength with 40x water immersion lens and 63x oil immersion lens were used for CLSM imaging. In addition, transmission electron microscopy (FEI T12 Spirit TEM STEM, Hillsboro, OR) was used to verify internal structure of the microcapsules. Freeze dried WMS-PLGA-MCs suspension was deposited on the carbon film placed on a TEM copper grid for TEM observations.

2.6. Self-healing efficiency of WMS resin containing microcapsules

The tensile properties and fracture toughness of control (without microcapsule), virgin (with 20wt% microcapsules) and healed specimens (after 24 h) were characterized in accordance with ASTM E647-08 [42]. The specimens were strained at 0.3 mm/min displacement rate on an Instron universal tester (Model 5566, Instron Co., Canton, MA) up to a distance of 10 mm until crack initiated. Two fractured halves of the specimen were held together after realigning and allowed to heal in the conditioning room at 21°C and 65% RH for 6 h and 24 h. After 6 or 24 h of healing, control and healed specimens were placed in the same Instron and tested as described above to characterize their properties and, thus, to calculate their self-healing efficiency. Some specimens were also tested immediately (0 h of healing). Since the crack length is nearly

identical, the self-healing efficiency can be simplified to Equation (2) which was used in this study [43].

$$\eta = \frac{P_{lc \text{ healed}}}{P_{lc \text{ unhealed}}} \quad (2)$$

where η is crack self-healing efficiency, $P_{lc \text{ unhealed}}$ is the peak fracture load of the virgin and $P_{lc \text{ healed}}$ is the peak fracture load of the healed specimen.

3. Results and discussion

Fig. 2 shows the morphology and internal structure of WMS-PLGA-MCs using different techniques. It is clear that the WMS-PLGA-MCs, produced using the w/o/w solvent evaporation method, have spherical shape and pore-free surface. Average diameter of the microcapsules determined from randomly selected areas within the SEM images shown in Fig. 2(a), using ImageJ software ($N \geq 500$), was $1.26 \mu\text{m}$ ($\sigma = 0.38$). The WMS-PLGA-MCs also showed a broad size distribution between 0.26 and $3.2 \mu\text{m}$. Fig. 2(a) shows the size distribution in the form of histogram in the inset. SEM image in Fig. 2(b) shows a broken WMS-PLGA-MC with a diameter of about $2.5 \mu\text{m}$ and shell thickness of approximately $0.43 \mu\text{m}$ indicating that the core (WMS) occupied about 56% of the total microcapsule volume. In order to determine starch loading of WMS-PLGA-MCs, Lugol's method, described in the experimental section, was used and the average starch loading (on wt basis) of WMS-PLGA-MCs was found to be $50.4 \pm 2.1\%$ [39].

A brightfield image of WMS-PLGA-MCs taken by confocal laser scanning microscopy (CLSM) as shown in Fig. 2 (c) confirmed their spherical shape with well-formed shell walls. The shell wall thickness of WMS-PLGA-MCs from these images was in the range of 0.15 to $0.60 \mu\text{m}$. The microcapsules are also free of subcapsules. Fig. 2(d) presents a fluorescent image that indicates the presence of WMS slurry stained with rhodamine B appearing in red color, inside

the WMS-PLGA-MCs. The internal structure of WMS-PLGA-MCs was further verified by TEM to confirm the nonexistence of voids or subcapsules in Fig. 2(e).

Fig. 2. The morphology and internal structure of WMS-PLGA-MCs. (a) SEM image of WMS-PLGA-MCs with size distribution histogram in the inset, (b) SEM image showing the shell thickness of WMS-PLGA-MCs, (c) Confocal brightfield image of WMS-PLGA-MCs, (d) Confocal fluorescent image of WMS-PLGA-MCs (WMS slurry stained by rhodamine B during microencapsulation process shown in red) and (e) TEM image of WMS-PLGA-MCs.

To observe the dispersion of WMS-PLGA-MCs within the resin, CLSM Z-stacking mode was used. The self-healing WMS resin containing 20wt% WMS-PLGA-MCs, 40wt% BTCA (based on WMS) and 50wt% sodium hypophosphite (SHP, based on BTCA) was used. CLSM images shown in Fig. 3(a) were taken through a total depth of 27 μm, with an optical section taken at every 3 μm. The WMS resin appears in green color (without rhodamine B stain) in fluorescent images while WMS-PLGA-MCs prepared using WMS slurry stained with rhodamine B appear in red color. These images again confirm the spherical shape of the WMS-PLGA-MCs. Most importantly, based on the fact that no red color is seen in the resin (other than

microcapsules), it can be concluded that almost all microcapsules resist the rigors of processing (hot pressing) the resin. 3-D front and side images of the resin specimen are shown in Fig. 3(b) (from top) and Fig. 3(c) (side view). These images confirm that the WMS-PLGA-MCs are dispersed more or less evenly in the resin. Well dispersed WMS-PLGA-MCs should act as the healing source for the WMS resin wherever the microcracks are formed.

Typical SEM images showing tensile fracture surfaces of WMS resin containing 20wt% WMS-PLGA-MCs are shown in Fig. 3(d). The bursting of the WMS-PLGA-MCs at the microcracks and the fiber-like streams of the released healant can be observed on the fracture surface. This clearly suggests that WMS-PLGA-MCs break at the fracture surface as expected and desired for healing to occur. As the WMS-PLGA-MCs break, the healant (WMS) is squirted out instantaneously forming fibrous streams.

Fig. 3. Self-healing WMS resin containing 20wt% WMS-PLGA-MCs. (a) Confocal Z-stack micrographs of WMS resin containing 20wt% WMS-PLGA-MCs, a total depth of 27 μm , with an optical section of 3 μm , red color corresponds to strained core WMS inside WMS-PLGA-MCs, (b) The front view of 3-D fluorescence image of self-healing WMS resin, (c) The side view of 3-D fluorescence image of self-healing WMS resin and (d) SEM images of tensile fracture surfaces of self-healing WMS resin, white arrows indicate the healant released from WMS-PLGA-MCs forming fibrous streams on the fracture surfaces.

Fig. 4 shows the CLSM images of self-healing WMS resin containing 20wt% WMS-PLGA-MCs in microcracks after 24 h of healing at RT and 65% RH. Images of the WMS resin taken with optical sections at every 3 μm from the center of the specimen are presented in Fig. 4(a). WMS-PLGA-MCs containing WMS slurry stained with rhodamine B as the core are seen as red colored (or lighter) circles under fluorescence (right). The WMS released from the microcapsules crosslinks with the excess BTCA present in the resin, thus making strong, load bearing WMS bridges between the two surfaces of the microcracks. A few unbroken (circular) WMS-PLGA-MCs can also be seen in the microcracks. At a few locations within the microcracks, WMS healant released from the broken WMS-PLGA-MCs can be seen in the smeared form, in red color, and connecting or bridging the two microcrack surfaces.

To observe the healed microcracks in Fig. 4(a) closely, areas marked by white squares were magnified and images were taken in both brightfield (left) and under fluorescence (right) and are shown in Fig. 4(b). Aggregated and broken WMS-PLGA-MCs can be observed within the microcracks as well as in their close proximity. The fluorescent images clearly show that the WMS healant released from microcapsules flows into the microcracks and fills the gap, thus, bridging them (as shown by arrows). As mentioned earlier, the released WMS reacts with the excess BTCA in the resin forming ester linkages. As unbroken microcapsules cannot release the healant, they tend to reduce self-healing ability. Major reason for WMS-PLGA-MCs to stay unbroken could be that the shell walls are too thick or weak resin-microcapsule interfacial bonding.

Fig. 4. CLSM images of the healed microcracks after 24 h healing. (a) Microcrack healing in self-healing WMS resin containing 20wt% WMS-PLGA-MCs at low magnification and (b) High magnification images of areas shown in squares, red color corresponds to WMS present inside the microcapsules as well as that released from the broken microcapsules. Images on the left side are brightfield and images on the right side are taken under fluorescence.

Laser-cut WMS resin specimens were characterized for their self-healing characteristics using mode I fracture toughness test. Fig. 5(a) shows SEM images of typical healing (bridging) zones inside the microcracks of WMS resin specimens containing different loadings of WMS-PLGA-MCs from 0 to 15wt% after 24 h healing. Control WMS resin without the microcapsules shows no bridging whereas WMS resin containing WMS-PLGA-MCs shows the released WMS bridging the two fracture surfaces of the microcracks. With increased loading of WMS-PLGA-MCs more bridges can be observed in the microcracks. It is intuitive that more bridges will result in higher self-healing efficiency. Fig. 5(b) shows stress-deformation plots of control and self-healing WMS resin specimens containing 20wt% WMS-PLGA-MCs at 0 h (virgin) and after 6 h and 24 h of healing. Fig. 5(b) also shows SEM images of the bridging zone of the self-healing WMS resin specimen. The average fracture stress of the specimens without microcapsules (control) containing 40wt% BTCA was about 16.8 ($\sigma = 2.2$) MPa. The average fracture stress of the virgin specimens containing 20wt% WMS-PLGA-MCs was 12.7 ($\sigma = 1.8$) MPa, about 24% lower than the control specimens. The decreased tensile stress about 24% could be a result of weak resin-microcapsule interfacial bonding and improved bonding could help reduce this decrease. For 0 h of healing, these specimens showed almost no load, i. e., no self-healing ability. After 6 h of healing, the specimens showed marginal self-healing with fracture stress of 2.2 MPa (about 17% healing efficiency) and after 24 h of healing, the fracture stress was 6.4 ($\sigma = 1.1$) MPa, indicating about 51% self-healing efficiency. Healing time beyond 24 h showed no additional healing efficiency.

In order to make sure that self-healing was indeed a result of the WMS-PLGA-MCs embedded in the resin, solely water (solvent) induced self-healing resin tests were conducted. To conduct this test, water-filled PLGA microcapsules were separately prepared and added (20wt%) to the WMS resin. These specimens showed self-healing efficiency of less than 1%, after 24 h of

healing. In addition, no fiber-stream feature seen in the case of WMS-PLGA-MCs were observed. This confirmed that the self-healing was achieved only due to the WMS-PLGA-MCs.

Fig. 5(c) shows self-healing efficiencies of WMS resins containing 0 to 20wt% WMS-PLGA-MCs after 24 h of healing. The self-healing efficiency of the resin in terms of fracture strength increased from 12 to 51% with increase in WMS-PLGA-MCs loading of 5 to 20wt%. The self-healing WMS resin containing 20wt% WMS-PLGA-MCs also recovered 66% of the fracture toughness after 24 h of healing. Some synthetic self-healing systems such as epoxy resins containing 20wt% DCPD-loaded PUF microcapsules have been reported to show up to 45% self-healing efficiency after 24 h of healing at RT [44]. In another study researchers were able to show higher self-healing efficiencies for epoxy and poly(ethylene oxide) resins using DCPD-loaded PUF microcapsules [45]. In the case of epoxy resins the healing efficiency was 63% while for poly(ethylene oxide) it was above 100%, after 24 h of healing. However, in this case the specimens were heated to 150°C [45].

In the present system, it is clear that the damage such as microcrack serves as the trigger for self-healing mechanism through the rupture of WMS-PLGA-MCs in the path of the microcracks which release the healant (WMS) that bridges the two fracture surfaces. Crosslinking reaction initiated by direct contact between the healant (WMS) and the BTCA (a crosslinking agent) present in the WMS resin results in strong bridges.

Fig. 5. Self-healing WMS resins containing different loadings of WMS-PLGA-MCs. (a) SEM images showing bridging zones of WMS resins containing microcapsule loadings of 0, 5, 10 and 15 wt% after 24 h of healing, (b) Typical stress-displacement plots of WMS resin containing 20 wt% WMS-PLGA-MCs and control (without WMS-PLGA-MCs) at 0 h and 24 h of healing, inset images show a laser-cut specimen containing 20 wt% WMS-PLGA-MCs and bridging zones at different magnifications and (c) Fracture stress and healing efficiency of WMS resins containing 0, 5, 10, 15, or 20 wt% WMS-PLGA-MCs, virgin and after 6 h and 24 h of healing.

4. Conclusions

Fully green self-healing starch-based thermoset resin has been developed using a green water-based fabrication process. The results clearly indicate that increased loading of WMS-PLGA-MCs reduces the fracture stress of the resin. However, the self-healing efficiency increases with microcapsule loading. Lower microcapsule loading in the WMS resin showed fewer bridges across the microcracks and resulted in lower self-healing whereas loading of 20wt% resulted in the highest recovery of 51% after 24 h of healing at RT. Self-healing was also found to be dependent on the healing time. After 6 h of healing only 17% recovery in fracture stress was obtained while after 24 h of healing the recovery was 51% for specimens loaded with 20% microcapsules. The results indicate that the self-healing WMS resin has reasonable tensile properties with fracture stress of about 6.4 MPa even after healing and may be used in some indoor applications such as automotive, packaging, biomaterials, etc., to replace currently used petroleum-derived resins. Further studies are required to optimize the process to increase the self-healing efficiency of green resins closer to 100%. The self-healing of WMS resin obtained in this study can be easily extended to other starches because of their chemical similarity. The newly developed fully green self-healing WMS resin can extend the useful life of green composites made using it and make it easier for them to offer safe, durable and longer service life.

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