



Self-healing of 'green' thermoset zein resins with irregular shaped waxy maize starch-based/poly(D,L-lactic-co-glycolic acid) microcapsules

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ABSTRACT

Self-healing 'green' thermoset zein resin was developed using elongated multi-geometrical poly (D,L-lactic-co-glycolic acid) (PLGA) microcapsules (MCs) containing waxy maize starch (WMS) or oxidized WMS (OWMS) as healing agents. A novel method combining co-axial injection and emulsion-solvent evaporation technique was developed to fabricate multi-geometrical MCs with aspect ratios greater than 1. While their rougher surface enhances the resin-MC mechanical bonding, higher aspect ratio increases the probability of MC being in the path of microcracks. Also, the OWMS, containing aldehyde groups, forms covalent bonds with zein, whereas WMS only provides H-bonding. Results indicated that zein resins with 15 wt% WMS/PLGA and OWMS/PLGA MCs had self-healing efficiencies of 51% and 72% in fracture stress, respectively. This significant enhancement for OWMS healant is possibly due to covalent bonding with zein resin. This study demonstrates that self-healing thermoset zein resin can be a promising 'green' solution with longer service life, for a broad range of applications.

1. Introduction

Most commonly used resins in conventional composites such as polyurethanes (PU), epoxy, polyesters, poly (methyl methacrylate) (PMMA) and many others are synthesized using petroleum as raw material [1–7]. Many researchers have predicted that world petroleum resources will be fully depleted in the next 60 years at the present rate of consumption which is estimated at 100,000 times the rate at which earth can generate it [3,7]. Besides the sustainability issue of petroleum-based materials, they also face serious end-of-life disposal problems since they do not degrade naturally in normal aerobic environment such as compost for several decades and for centuries in anaerobic conditions such as landfills. In case of reinforced thermoset composites, strong reinforcement agent-resin bonding as well as crosslinked nature of the resin prevent them from being recycled and reused easily; thus, they are all directed towards landfills [1,6,8]. In order to address these problems, environment-friendly and sustainable green composites made using natural sources such as plant-based proteins, polysaccharides, oils, and other agricultural products have been developed in the past couple of decades [4,6,9]. These green substitutes for petroleum-based polymers are becoming popular due to their sustainability, biocompatibility and worldwide availability of raw materials [6,9,10]. Zein protein obtained from maize has great potential as a biodegradable bio-based thermoset resin for green composites. Zein

protein possesses many functional sites such as amine, carboxyl, and hydroxyl that can be used to form crosslinks to obtain thermoset resins with enhanced mechanical properties and further to fabricate green composites [1,5,8,11,12]. However, thermoset zein resins are known to be brittle and have low resistance to crack propagation [13,14]. Many researchers have tried to enhance the toughness of zein resins via addition of plasticizers and toughening agents [15–17]. Although introducing toughening agents can suppress the brittleness of zein resins, they cannot prevent failure of zein resin from damages caused during service.

All resins and composites during use are exposed to different types of stresses that results in microcracks. Continuous exposure to stresses can significantly decrease their mechanical properties and result in early failure of the composites [1,18]. In order to alleviate this problem, many types of self-healing polymers have been employed that can repair such micro-damages autonomously and, thus, provide longer lasting and safer products [18,19]. It should be pointed out that most of the self-healing materials are limited to petroleum-based synthetic polymers and research on self-healing systems for green resins has been very rare [19–22]. Many self-healing systems such as microcapsule (MC)-based, microvascular, and intrinsic systems have been developed to provide self-healing properties for synthetic polymers [4,23]. Among all these methods, MC-based self-healing materials are perhaps the most favorable materials that have been used in various self-healing

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composites [24]. MC-based systems consist of a healing agent/s (healants) that are encapsulated in polymer microcapsules (shell) which are then dispersed uniformly in the resin. When microcracks are created in the resin under stress, microcapsules present in the path of the microcrack break and release the encapsulated healing agents. The healants fill the crack and bridge the two surfaces created by the microcrack, effectively healing the resin. Many studies have reported encapsulation of various synthetic healing agents such as epoxy [25–27], dicyclopentadiene (DCPD) [28–30], polydiethoxysiloxane (PDMS) [31,32], glycidyl methacrylate (GMA) [33,34], isocyanate [19,35], etc., in different polymer shell materials [20,22,32,36,37]. Few other studies have also reported the development of self-healing green thermoplastic composites [1,4,30,38,39].

Self-healing microcapsules are commonly fabricated through an emulsification-solvent evaporation technique. Kim and Netravali [1,4], Liu et al. [40], and Jeffery et al. [41] reported that a simple water in oil (w/o) emulsification method is inefficient for encapsulation of water-soluble proteins. Kim and Netravali successfully employed a water-in-oil-in-water (w/o/w) emulsification-solvent evaporation method to encapsulate waxy maize starch (WMS) inside poly (lactic-co-glycolic acid) (PLGA) shell [1,5,42]. In their process, the primary w/o emulsion was created by adding the water-based gelatinized WMS into an oil phase containing PLGA in ethyl acetate and homogenized at 10,000 rpm to form fine microdroplets. The prepared emulsion was then added to a large volume of PVA emulsifier and homogenized to create w/o/w emulsion. The final emulsion was then stirred to allow ethyl acetate to evaporate. Spherical microcapsules obtained by this process were then separated by centrifuging and washing/filtration and finally freeze drying. These and other studies showed that PLGA is an appropriate green shell polymer due to its low brittleness and good fracture toughness, low heat distortion, biodegradability and hydrolytic instability [43]. The studies also showed that w/o/w emulsion-evaporation technique results in high encapsulation efficiency of the healing agent. However, due to the nature of this technique only spherical microcapsules could be obtained. Spherical microcapsule geometry possesses the lowest aspect ratio ($L/D = 1$) which makes it somewhat harder to disperse them into the resin. An irregular geometry with aspect ratios greater than 1 was thought to be more effective in enhancing the MC-resin bonding as well as cover larger volume within the resin and, as a result, increase the self-healing efficiency by increasing the probability of being in the path of the microcracks.

In this study, self-healing thermoset zein resin was developed using both WMS and oxidized WMS (OWMS) loaded PLGA microcapsules having elongated multi-geometrical shapes and their healing efficiencies have been compared. Zein resins were crosslinked using glutaraldehyde (GA). Also, the WMS or OWMS released from the broken capsules have the possibility to get crosslinked with GA to heal the thermoset zein resin. Since WMS only has hydroxyl groups in its chemical structure, interactions between zein and WMS can only be weak through hydrogen bonds. In order to enhance the bonding between the resin and the healant, WMS was oxidized using sodium periodate (NaIO_4) to create aldehyde functional groups on the structure of starch. A novel co-axial injection of WMS-based healant (core) and PLGA (shell) in PVA solution was developed to make elongated multi-geometrical microcapsules with aspect ratios greater than 1, ($L/D > 1$). This combination method results in significant improvement in resin-MC bonding via both hydrogen bonding between PVA and zein as well as mechanical bonding between MCs and resin.

2. Materials and methods

2.1. Materials

Zein protein from maize (powder), poly (vinyl alcohol) (PVA, average $M_w = 30\text{--}50\text{K}$ and 88% hydrolyzed), analytical glutaraldehyde (GA, 25 wt% in water) as crosslinking agent, and rhodamine B were

purchased from Sigma Aldrich Chemical Co., St. Louis, MO. Waxy Maize Starch (WMS) was obtained from Now Foods, Co., Bloomington, IL. Poly (lactic-co-glycolic acid) (PLGA) was purchased from Durect Corp., Cupertino, CA. Sodium periodate (NaIO_4) and barium chloride (BaCl_2), ethanol (EtOH, 99% purity), and ethyl acetate were obtained from Fisher Scientific, Pittsburgh, PA. All chemicals were utilized as received without further purification.

2.2. Oxidation of WMS (OWMS)

Oxidized waxy maize starch (OWMS) was obtained via NaIO_4 cleavage following the work reported by Xu et al. [44] and Barry and Mitchell [45]. WMS powder was gelatinized in DI water by stirring at 90 °C and 400 rpm for 1 h to obtain a 5 w/v% solution. Gelatinized WMS solution was then cooled to room temperature (RT). NaIO_4 was then added to the gelatinized WMS solution (WMS: NaIO_4 ratio = 1:2) and stirred overnight at RT in a lightproof (dark) condition. BaCl_2 was then added to the mixture with the 1:1.8 ratio with respect to NaIO_4 and stirred for 1 h and stored in a refrigerator at 5 °C for 12 h to allow complete precipitation of $\text{Ba}(\text{IO}_4)_2$. The supernatant was then centrifuged and filtered to obtain a 5 w/v% liquid oxidized waxy maize starch (OWMS) with polyaldehyde functional groups [46]. The formation of aldehyde groups was confirmed via attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (see Fig. S1 in the supporting information).

2.3. Preparation of WMS/PLGA and OWMS/PLGA MCs

A novel technique of using co-axial injection technique followed by water-in-oil-in-water (w/o/w) emulsion-solvent evaporation method was developed to produce elongated and multi-geometrical shaped WMS/PLGA microcapsules. WMS (5 w/v%) was gelatinized in DI water by stirring at 90 °C for 1 h. PLGA and PVA were dissolved in ethyl acetate and DI water, respectively, to obtain 1 and 6 w/v% solutions. 100 mL WMS (core) and PLGA (shell) solutions (WMS:PLGA = 5:1) were then co-injected into 200 mL of PVA at an injection rate of 200 $\mu\text{L}/\text{min}$ and stirred at 70 °C and 500 rpm using a 30 mm PTFE coated cylindrical magnetic stirrer. The final WMS/PLGA/PVA w/o/w emulsion was then stirred at 350 rpm overnight at RT to fully evaporate ethyl acetate. The microcapsules were then obtained after centrifuging at 12,000 rpm for 20 min. The same procedure was used to prepare elongated and multi-geometrical shaped OWMS/PLGA MCs simply by substituting WMS with OWMS.

2.4. Preparation of elongated multi-geometrical MCs

Fig. 1 shows the scheme of co-axial injection technique followed by a water-in-oil-in-water (w/o/w) emulsion-solvent evaporation method to produce elongated multi-geometrical WMS/PLGA or OWMS/PLGA microcapsules. Aqueous healant material and PLGA were loaded in separated 30 mL syringes. The solutions were pumped slowly (200 $\mu\text{L}/\text{min}$) through the co-axial nozzle into a hot PVA solution (about 70 °C), while stirring at 500 rpm. The nozzle was kept just above (about 5 mm) the PVA solution surface. It was found that this positioning is helpful in creating microcapsules with different geometries besides spheres. As the droplets came in contact with the rotating solution and the shear stresses generated by it, they got elongated. Since the PVA solution temperature was close to the boiling point of ethyl acetate ($T_b = 77^\circ\text{C}$), the ethyl acetate evaporated fast allowing the PLGA shells to solidify, leading to the formation of elongated microcapsules. Rapid stirring along with fast solvent evaporation resulted in a mixture of microcapsules with various shapes such as dog-bones, ellipses, irregular cylinders, spheres, etc., depending on the local stress conditions. The PVA molecules attached to the PLGA shell material act as surfactant to help the dispersion in the resin since PLGA is a hydrophobic polymer [4]. As mentioned before, spheres possess the lowest aspect ratio of 1 amongst

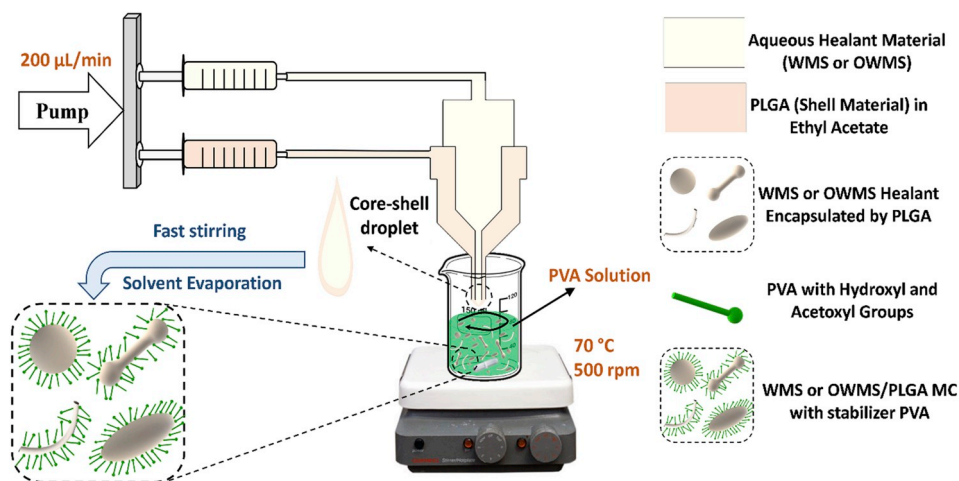


Fig. 1. The scheme of co-axial injection technique followed by a water-in-oil-in-water (w/o/w) emulsion-solvent evaporation method to produce elongated multi-geometrical WMS/PLGA or OWMS/PLGA microcapsules.

all the geometries created in the present study. Given the geometry and smoothness of the surface of the spheres, the interaction between the spherical microcapsules and the resin is weak. As a result, when a microcrack is created, there is strong possibility of the crack going around the spherical surface of MCs which can keep them from rupturing. Since the healing agent is not released, low self-healing efficiency is obtained. As a result, obtaining elongated multi-geometrical MCs in geometries with aspect ratios greater than 1 and different surface textures was expected to be critical for enhancing resin-MC interactions as well as increasing the possibility of MC being in the path of the microcrack and, hence, rupturing. This could certainly improve the self-healing efficiency of the resin. Self-healing results discussed later in this article confirm this hypothesis.

2.5. Preparation of MC-loaded zein resins

Zein protein (20 w/v%) was dissolved in aqueous ethanol (85 vol%) and the solution was stirred for 1 h at 500 rpm at 50 °C. Glutaraldehyde (GA) was then added to the mixture as crosslinking agent with concentration of 18 wt%, based on the weight of zein, and stirred for another hour. Our previous study had shown that thermoset zein resin containing 8 wt% GA had the highest mechanical properties [12]. The extra 10 wt% of GA was added in order to ensure that it is available to immediately react with the healing agents, WMS or OWMS, released from the microcapsules during the self-healing. Predetermined amount of microcapsules were added to the zein resin and stirred for 1 h. The loading of MCs was varied between 0 and 15%, in steps of 5%, based on the weight of zein. Zein resins containing different MC contents were cast in Teflon®-coated glass molds (10 cm × 10 cm) and dried and precured at 60 °C in an air circulating oven for 72 h to form zein sheets having a thickness of 2.3–2.5 mm. The sheets were then fully cured in a hot press at 95 °C with 2.0 mm spacers and under a small pressure of 0.5 MPa for 20 min to complete the zein-GA crosslinking reaction. All self-healing zein resin sheets having about 2 mm thickness were conditioned at 21 °C and 65% relative humidity (RH) for 24 h prior to any testing. The resin sheets were then laser cut into test specimens (32 × 30 × 2 mm) following slightly modified ASTM E647-08 standard.

2.6. Self-healing efficiency of zein resins containing MCs

Mechanical properties such as tensile strength and fracture toughness of pure zein resin (control), virgin zein resins (with different loadings of MCs), and healed specimens (conditioned for 24 h after testing) were studied following the ASTM E647-08 standard [30]. The

resin specimen tests were conducted at 0.3 mm/min displacement rate using an Instron universal testing machine Model 5566 (Instron) until the crack initiated and propagated to a length of about 1 cm. The specimen was then taken out and the fracture surfaces of the specimen were aligned and pressed together and kept in the conditioning room (at 21 °C and 65% RH) for 24 h to allow healing. The tensile properties of the conditioned (healed) specimens were characterized on Instron under same testing standards after the 24 h healing period to calculate their self-healing efficiency. Since the crack length was fixed to 1 cm for all the specimens, self-healing efficiency of the resin, E_{SH} , can be calculated using equation (1) below [47]:

$$E_{SH} = \frac{\sigma_{healed}}{\sigma_{virgin}} \quad (1)$$

where σ_{healed} is the maximum fracture load of the healed specimen (conditioned for 24 h after testing), and σ_{virgin} is the maximum fracture load of the virgin specimen. Five specimens were tested for each condition to ensure the reproducibility of the results.

2.7. Characterization

A scanning electron microscope (SEM), Leica model 440X, was used to characterize the microstructures and topographies of microcapsules and tested resins. Microcapsules containing stained healant with 0.1% rhodamine B was studied under a confocal laser scanning microscope (CLSM, Zeiss LSM710 equipped with 25 mW Argon and HeNe lasers). For CLSM imaging, a filter suitable for 514 nm excitation wavelength with 60x oil immersion lens was utilized. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR spectrometer, Frontier, PerkinElmer, Waltham, MA) was used to investigate the chemical composition of oxidized waxy maize starch after the oxidation reaction. All tests were conducted from 4000 to 800 cm^{-1} wavenumbers with total of 32 scans and resolution of 4 cm^{-1} .

3. Results and discussion

3.1. Morphologies and topographies of WMS/PLGA and OWMS/PLGA MCs

Fig. 2 shows the morphology of elongated multi-geometrical MCs. Fig. 2a–d shows the typical SEM images of WMS/PLGA MCs. It can be seen from Fig. 2a–d that the WMS/PLGA MCs were formed in a mixture of geometries including elongated cylinder, ellipses, spheres, dog-bones, etc. While most of the MCs have somewhat smooth surface, a few do not. The elongated MCs possess a length in the range from 10 to

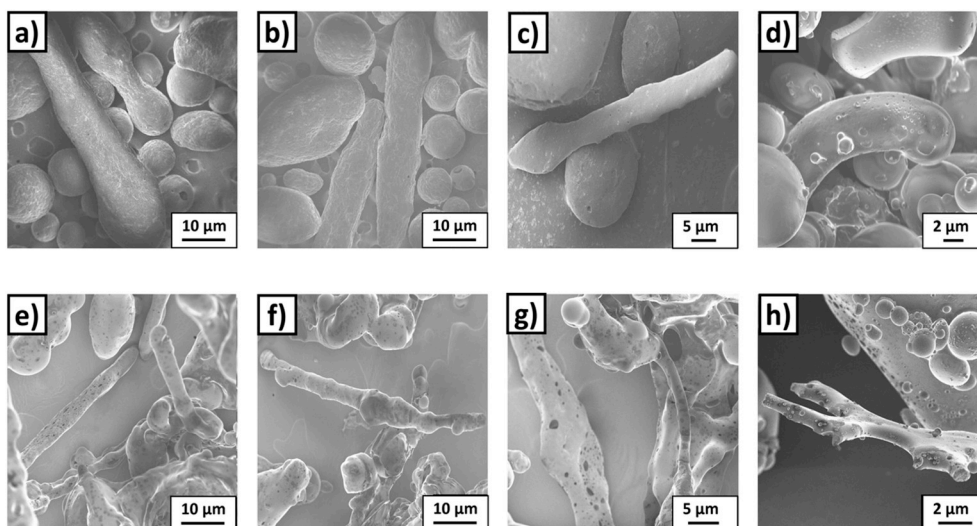


Fig. 2. SEM images of (a–d) WMS/PLGA MCs and (e–h) OWMS/PLGA MCs.

50 μm and width of about 5–10 μm , which results in an aspect ratio of about 4, whereas spherical MCs have diameters between sub-micrometers and around 20 μm . Fig. 2e–h shows the morphology of OWMS/PLGA MCs. It can be observed that most of the OWMS/PLGA MCs possessed rougher surface and also that they formed more irregular shapes compared to WMS/PLGA MCs. In addition, although the length of the elongated OWMS/PLGA MCs were similar to that of WMS/PLGA MCs, the widths or diameters were much smaller and fell in the range of 1–7 μm , resulting in higher aspect ratios of about 7. It should be noted that the oxidation reaction caused a noticeable decrease in the viscosity of the WMS solution. It is believed that the reduction in viscosity is the main reason behind the difference in the geometry of OWMS/PLGA MCs. As mentioned earlier, co-axial technique along with the high speed stirring and fast evaporation of ethyl acetate solvent leads to the formation of multi-geometrical and elongated MCs depending on local stresses. Since the viscosity of OWMS is lower than WMS, it eases the movement of the wet microdroplets under stirring and depending on the local stresses helps to create elongated thin MCs as well as other shapes and the evaporation of ethyl acetate helps maintaining the shape. The rougher surface of OWMS/PLGA MCs can immensely enhance the resin-MC mechanical bonding and the elongated shape ensures higher probability of MC coming in the path of the microcrack and fracturing. Both these events increase the self-healing efficiency. The encapsulation of healing agents was confirmed by investigating the internal structure of MCs via atomic force scanning microscopy (CLSM) (see Fig. S2, Supporting Information). The healing agent was stained with Rhodamine B which appears in color (usually red) under fluorescence microscope.

3.2. Microstructure of healed zein resins

Fig. 3 shows SEM images of cross section of microcracks appeared in self-healing zein resins under tensile tests. Fig. 3a–d shows microcracks formed in the self-healing zein resin samples containing 15 wt% WMS/PLGA MCs, based on the weight of zein. Looking into the crack, it can be seen that the healing occurs mostly in the form of microcrack bridging. It can be seen from Fig. 3b that a microcrack went around some of the MCs leaving them intact, whereas from Fig. 3c and d it is clear that starch released from WMS/PLGA MCs forms bridges inside microcracks and heals the resin. On the other hand, it can be seen from Fig. 3e–h that for the zein resin containing 15 wt% OWMS/PLGA MC loading the healing occurs in two ways: 1) microcrack filling and 2) microcrack bridging. Fig. 3e shows a microcrack passing through a cluster of MCs which ruptured some of them and the OWMS slurry filled

the microcrack in the middle. It is also clear that the spherical microcapsules did not fracture. In addition, from Fig. 3f–h it can be observed that the OWMS released from the microcapsules formed many bridges between the microcracks and held the two sides together. As mentioned earlier, OWMS has aldehyde groups. This allows it to react with the amine groups present in zein molecules much more efficiently and even covalently bond with them. This is expected to significantly increase the self-healing efficiency. The self-healing efficiency and tensile recovery results of the self-healing zein resins discussed later further confirm this hypothesis.

3.3. Self-healing efficiency of zein resins

Fig. 4 shows the schematic illustration of self-healing testing method, typical load-extension plots for pure zein resin, zein resins containing 15 wt% of WMS/PLGA MCs or 15 wt% OWMS/PLGA MCs both in their virgin form and after 24 h healing. Fig. 4 also includes self-healing efficiencies for zein resins containing different loadings of MCs. All specimens were tested at 0.3 mm/min displacement rate until a crack propagated from the notch to the smiley indent placed at 1 cm from the notch. Then the cracked specimens were aligned, kept under minimal pressure, and conditioned for 24 h to allow healing process to take place. The healed specimens were tested again until complete failure occurred (see Fig. 4a). It can be seen from Fig. 4b and Table 1 that pure zein resin required a maximum force of 90.4 N to create/propagate a 1 cm crack. After the cracked control specimen was conditioned for 24 h, it was found that the complete failure required a maximum force of 10.5 N. It is noted that test specimens possess a thickness of 2 mm. To simplify the fracture stress calculations, the width of the specimen was taken to be 0.5 mm; thus, the fracture stress value is in fact equal to the force only in MPa unit. It can be seen from Fig. 2b that zein resin containing 15 wt% WMS/PLGA MCs in its virgin form showed a strength (force) of about 86.7 N while after 24 h of healing, the specimen showed a force of about 54.2 N. This recovery is due to the crosslinking reaction between released WMS and excess GA existing in the resin and formation of bridges inside the microcracks, as mentioned earlier for Fig. 3 a–c. In the case of zein resin containing OWMS/PLGA MCs with the same loading, the virgin and healed forms showed maximum force of around 79.1 and 63.7 N, respectively. Due to the presence of aldehyde groups in the structure of OWMS, the interaction and bonding between zein resin and released OWMS from MCs is much enhanced and results in higher strength recovery. Since the control specimens do not contain any MCs, no healing can be expected, and that the force needed is primarily to break the remaining part

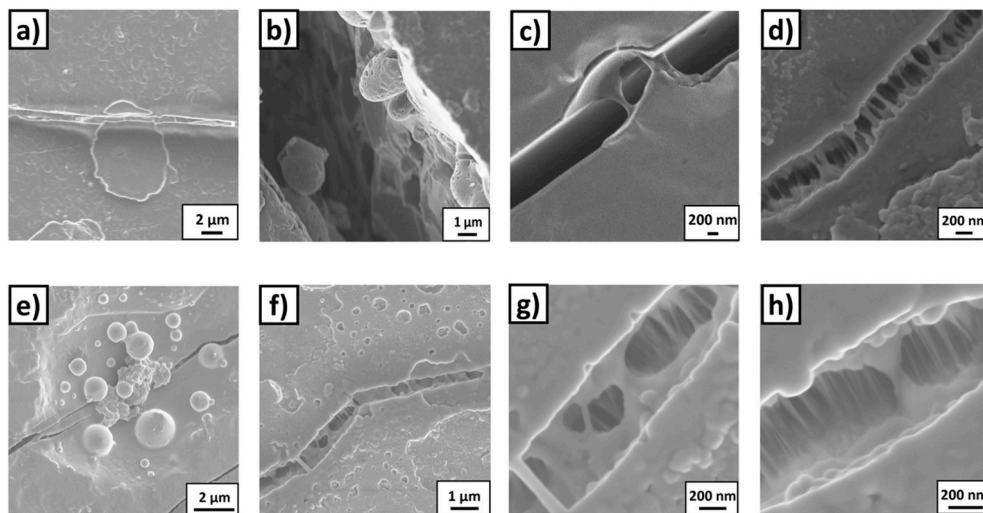


Fig. 3. SEM images of the microcracks formed in the zein resin samples with 15 wt% of (a–d) WMS/PLGA MCs and (e–h) OWMS/PLGA MCs. All microcracks show the healing agent forming bridges.

(about 0.5 cm) of the specimen beyond the smiley indent. Since all self-healing specimens possess same thickness and subjected to the exact same testing procedure, it would be appropriate and correct to assume that the force required to break the remaining part after the smiley indent for all specimens is proportional to force needed to create/propagate the 1 cm crack in the virgin form. Therefore, for all self-healing resin specimens, the proportional force value needed to break the remaining part after the smiley indent was subtracted from the maximum force value obtained for the healed specimens and the self-healing efficiencies of the resins were calculated based on the modified values.

It can be seen from Fig. 4c and Table 1 that $\sigma_{\text{Max-virgin}}$ was slightly decreased after MC loading in both WMS/PLGA and OWMS/PLGA cases. This is normal because added micro-additives can act as

mechanical defects and stress concentration points which can result in lower strength. As expected, the recovery force or $\sigma_{\text{Max-healed}}$ and, as a result, self-healing efficiency ($E_{\text{SH}}\%$) increased with MC loading. For WMS/PLGA MC-loaded zein resins, self-healing efficiency enhanced from 8.4 to 50.8% as the MC loading increased from 5 to 15 wt%, respectively. It was found that by substituting WMS/PLGA MCs with OWMS/PLGA MCs, E_{SH} was significantly improved. As can be seen from Table 1 as well as Fig. 4c the specimen with 5 wt% loading of OWMS/PLGA MC showed E_{SH} value of 22.1% compared with E_{SH} of 8.4% obtained for the same loading with WMS/PLGA MC. Similar to the WMS/PLGA case, self-healing efficiency of zein resins containing OWMS/PLGA MCs increased from 22.1 to 72.2% as MC loading increased from 5 to 15 wt%. In an earlier study Kim and Netravali showed about 51%

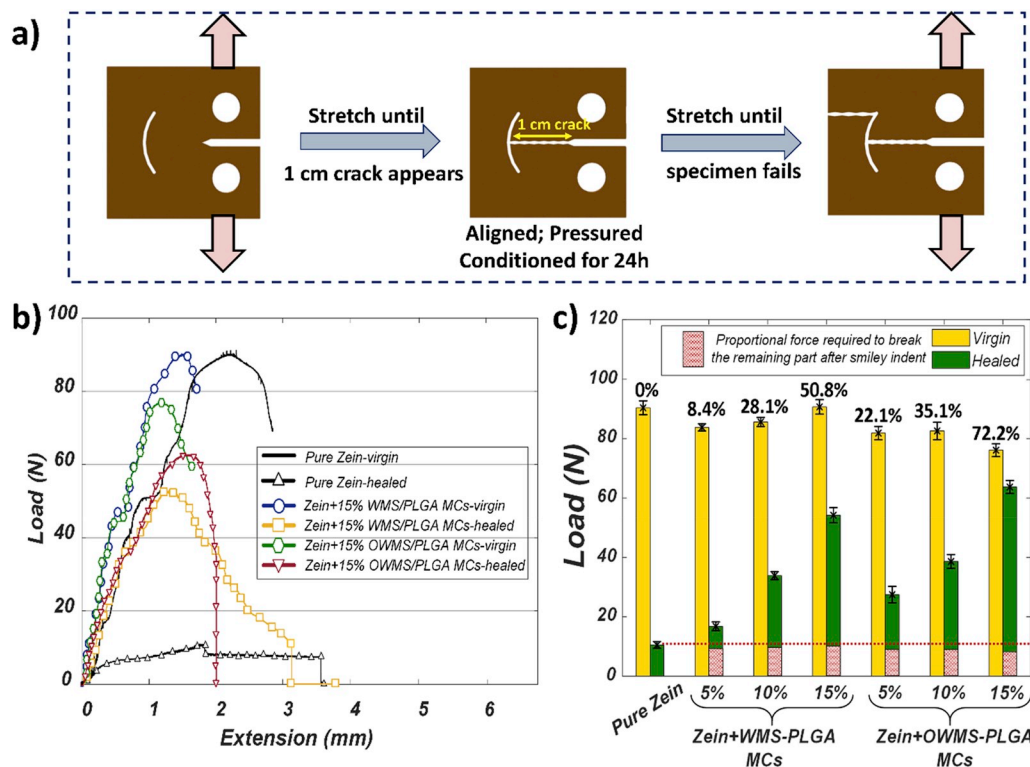


Fig. 4. a) Schematic of self-healing testing; b) Typical Load-Extension plots of virgin and healed pure zein resin, zein resin containing 15 wt% WMS/PLGA and 15 wt% OWMS/PLGA MC; c) Self-healing efficiency of zein resins containing different loadings of WMS/PLGA or OWMS/PLGA MCs.

Table 1
Self-healing efficiency of zein resins containing different loadings of MCs.

Resin Specimens	MC Loading (wt%)	$\sigma_{\text{Max-virgin}}$ (N)	$\sigma_{\text{Max-healed}}$ (N)	E_{SH} (%)
Pure Zein	0	90.4	10.5	0
WMS/PLGA loaded Zein	5	83.8	16.8	8.4 $\pm$ (0.9)*
	10	85.6	33.9	28.1 $\pm$ (1.2)
	15	86.7	54.2	50.8 $\pm$ (1.5)
OWMS/PLGA loaded Zein	5	81.8	27.5	22.1 $\pm$ (1.1)
	10	82.6	38.6	35.1 $\pm$ (1.5)
	15	76.1	63.7	72.2 $\pm$ (1.3)

*The values in parentheses represent standard deviations.

self-healing efficiency for WMS/PLGA MC (spherical shaped)-loaded WMS resin with 20 wt% MC loading [1]. It is noted that the virgin strength of OWMS/PLGA-loaded resins were slightly lower than that of the WMS/PLGA-loaded resins. It is believed that this phenomenon may have been due to slight difference in distribution/dispersion of MCs in the resin. One possibility is that the difference is caused by the irregular shape of the MCs, but more studies have to be conducted to fully understand the reason behind this phenomenon.

It was found in this study that the elongated multi-geometrical WMS/PLGA MC-loaded zein resin possessed the same self-healing efficiency with only 15 wt% MC loading compared to the earlier study which required 20% MC loading [1]. This result confirms the hypothesis that elongated MCs with higher aspect ratio and multi-geometrical shapes do increase the mechanical bonding with the resin and facilitate the bridging process and improve the self-healing efficiency. In addition, as discussed earlier, the interaction between zein molecules and reactive aldehyde groups of OWMS is another major reason behind the significant enhancement in self-healing efficiency compared with that of WMS/PLGA MC-loaded zein resins. The reaction of the oxidized starches or sugars with protein has been confirmed in a recently published study [48] (Patil, N. V. and Netravali, A. N., *Enhancing Strength of Wool Fiber using Soy Flour Sugar-based 'Green' Crosslinker*, *ACS Omega*, **4**, 5392–5401, 2019. DOI: [10.1021/acsomega.9b00055](https://doi.org/10.1021/acsomega.9b00055)).

4. Conclusions

Fully eco-friendly and 'green' self-healing thermoset zein composite has been developed using multi-geometrical waxy maize starch (WMS) and oxidized WMS (OWMS) based microcapsules. A novel method consisting of co-axial injection combined with emulsion-solvent evaporation technique was developed to fabricate elongated multi-geometrical MCs. It was found that higher aspect ratio ($L/D > 1$) of MCs enhanced mechanical bonding between MC and resin. This, also increased the possibility of the MC rupture because of the higher likelihood of them being in the path of the microcracks. It is noted that WMS and zein do not have strong interactions with each other besides hydrogen bonding. To improve the interaction and zein-WMS bonding, WMS was oxidized using sodium periodate to create aldehyde groups on starch. Fracture strength and self-healing efficiency of both WMS/PLGA and OWMS/PLGA MC-loaded zein composites were investigated. The results indicate that although the fracture strength of the resin decreased slightly with MC loading in both cases, the self-healing efficiency increased significantly after MC loading. It was found that multi-geometric WMS/PLGA MCs resulted in higher self-healing efficiency with lower loadings compared with similar studies reported earlier. Specimens with 15 wt% WMS/PLGA MCs showed about 51% self-healing efficiency after 24 h at RT. OWMS/PLGA MC-loaded zein resin with 5 wt% MC loading resulted in about 22% efficiency which is almost 3 times higher than that of WMS/PLGA MC-loaded resin (about 8%). The resin specimens with 15 wt% OWMS/PLGA MCs demonstrated the highest self-healing efficiency of about 72%. This significant

improvement is due to strong interaction and, possibly, covalent bonding between amine groups in zein resin and aldehyde groups in OWMS healing agent. This study shows promising self-healing 'green' thermoset resins based on natural proteins that offer safer and more reliable resins with longer service life which can be utilized in a broad range of applications, replacing some of the current petroleum-based resins.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.compscitech.2019.107831>.

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