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Polylactic Acid with Improved Heat Deflection Temperatures and Self-Healing Properties for Durable Goods Applications

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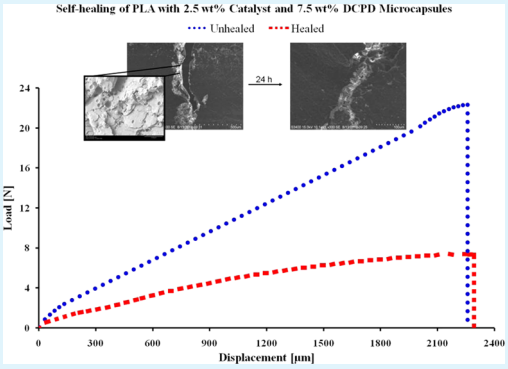
ABSTRACT: A method to recover fracture toughness after failure and increase thermal properties of polylactic acid (PLA) for use within durable goods applications is presented. Microcapsules were incorporated into PLA to form a composite material in which the microcapsules served the dual purpose of (1) releasing self-healing additives to fracture regions and (2) serving as nucleating agents to improve the PLA composite's thermal tolerance. Self-healing was achieved though embedment of dicyclopentadiene-filled microcapsules and Grubbs' first generation ruthenium metathesis catalyst, the former being autonomically released into damage volumes and undergoing polymerization in the presence of the catalyst. This approach led to up to 84% recovery of the polymer composite's initial fracture toughness. Additionally, PLA's degree of crystallinity and heat deflection temperature were improved by ∼11% and ∼21 °C, respectively, relative to nonfilled virgin PLA, owing to microcapsule-induced nucleation. The self-healing system developed here overcomes many property limitations of PLA that can potentially lead to its incorporation into various durable goods.



KEYWORDS: *polylactic acid, renewable, microcapsules, self-healing, sustainable, in situ polymerization*

INTRODUCTION

The sources that are used to prepare conventional polymers are coming under scrutiny due to the increased cost of petroleum, sustainability concerns, and their potentially hazardous byproducts.[1−3] With these concerns, there is a growing shift toward polymeric materials prepared from renewable feedstocks such as plant oils, polysaccharides, and proteins.[4−6]

One of the most widely investigated renewable materials for replacement of polymers derived from petroleum is polylactic acid (PLA).[7] PLA is a renewable and biocompatible polymer produced from starch in corn feedstocks.[8] PLA has been explored in a number of applications such as diapers, plastic bags, and disposable cups and plates.[9] However, PLA has found limited use in durable goods due to its inherent brittleness,[10] low fracture toughness,[11] hydrolytic instability,[12] and low heat distortion temperature (HDT),[13] thus leading to only single-use and disposable applications. Although PLA has found widespread use in packaging and fibers, the use of PLA in the preparation of durable goods is primarily plagued by the brittleness and nonrecoverable fracture toughness after failure of the PLA homopolymer.[14] We have explored the use of PLA in polymer blend applications to replace polycarbonate resins,[15] but for polymers such as PLA, the toughness of the material is greatly dependent on its resistance to crack propagation, particularly microcracks that form deep within a material and can coalesce to catastrophic damage.[16] There are many methods that can be employed in order to toughen PLA including improving stereochemistry, crystallinity, processing techniques, additives such as plasticizers and fillers, and blends with other renewable and nonrenewable polymers.[17]

Another approach, to render these types of polymers crack resistant, is to incorporate a self-healing property into the material. There are several methods to incorporate a self-healing function into polymers such as inclusion of microcapsules, vascular networks, etc.[18] In self-healing materials, when a crack propagates in the material, microcapsules, vascular networks, etc., rupture thus allowing the encapsulated core monomer to flow into the crack and react with the exposed catalyst to form new polymer. This new polymer within the damage zone of the material impedes further crack propagation through the fracture plane.

In this paper, we have developed a microcapsule-based self-healing system as a means of arresting crack propagation in PLA. This microcapsule system was not only selected to impart a self-healing function to PLA but also to serve as a crystallinity-enhancing nucleating agent, because the microcapsules can be prepared in a range of sizes (10−1000 μm)[19] which overlaps with that of common PLA nucleating agents (0.01−20 μm).[20] Hence, induction of an increased degree of crystallinity also serves to improve the thermal properties of PLA.

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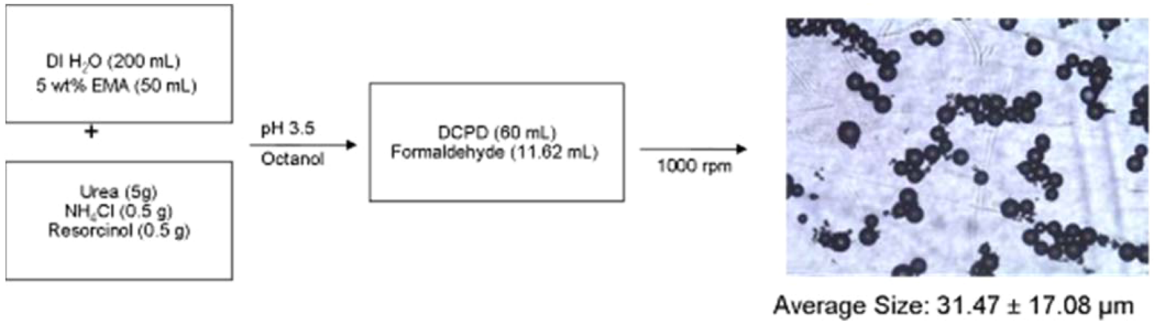

Figure 1. Microencapsulation of DCPD using in situ polymerization of urea and formaldehyde.

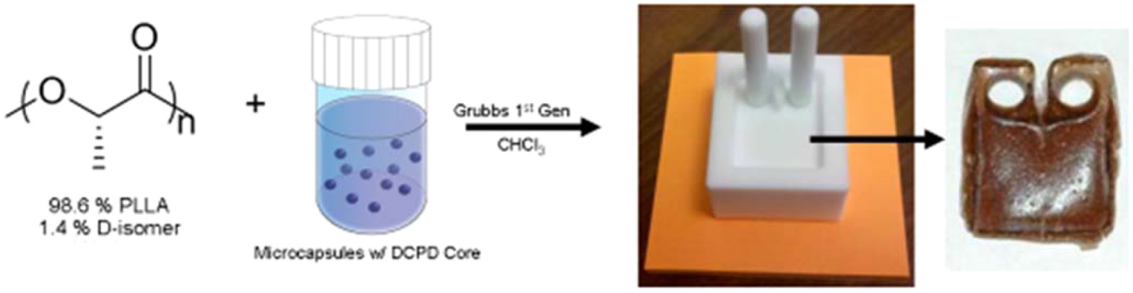

Figure 2. Preparation of PLA films containing DCPD filled microcapsules and Grubbs' catalyst.

MATERIALS AND METHODS

Materials. Urea (>98%), resorcinol (99%), ammonium chloride, 1-octanol, 37 wt % formaldehyde solution, and Grubbs' first generation ruthenium metathesis catalyst were all purchased from Sigma-Aldrich Chemical Co. and used without further purification. Dicyclopentadiene (>95%) was purchased from Acros Organics and passed through a column of alumina to remove the inhibitor. ZeMac E400 was provided by Vertellus Specialties Inc. Polylactic Acid (PLA-4032, Ingeo Biopolymer, 940399510, lot# XL0728B111) was kindly provided by NatureWorks, LLC.

Preparation of Dicyclopentadiene (DCPD) filled Urea Formaldehyde Microcapsules. Microcapsules were prepared similar to that described by Brown et al.[19] with minor modifications (Figure 1). To a 1000 mL beaker, deionized water (200.0 mL) and 2.5 or 5.0 wt % EMA copolymer solution (50 mL) were added and mixed at room temperature with a mechanical stirrer at 1000 rpm. The beaker was then suspended in an oil bath at room temperature. To this solution, urea (5 g, 8.32×10^{-2} mol), ammonium chloride (0.5 g, 9.34×10^{-3} mol), and resorcinol (0.5 g, 4.54×10^{-3} mol) were added and dissolved. The pH was adjusted from 2.60 to 3.50 by addition of 10 wt % sodium hydroxide and concentrated hydrochloric acid. To eliminate surface bubbles, 1-octanol (1−2 drops) was added. A slow stream of dicyclopentadiene (58.8 g, 4.44×10^{-1} mol) was then added and stirred for 10 min to form a stable emulsion. After stabilization, a 37 wt % formaldehyde solution (12.67 g, 4.22×10^{-1} mol) was added to obtain a 1:1.9 molar ratio of formaldehyde to urea. The emulsion was then covered with aluminum foil and heated to 55 °C at a rate of 1 °C/min. After 4 h of continuous agitation at 1000 rpm, the mixer and hot plate were turned off and the emulsion was allowed to cool to ambient temperature. After cooling, the microcapsules were isolated with a coarse-fritted filter. Microcapsules were then rinsed with deionized water (3×, 200 mL) and air-dried for 24−48 h. Capsules were then sieved through a 250 μm sieve, dispersed in tetrahydrofuran, and refiltered and dried at 50 °C.

Preparation of Microcapsule-Catalyst-PLA Composites. Samples were prepared as follows and outlined in Figure 2: PLA (0.45 g) was dissolved in chloroform (4 mL) that had previously been degassed by bubbling with argon for 30 min. Once dissolved, Grubbs' first generation ruthenium metathesis catalyst (0−5.0 wt %) was added along with sieved, DCPD-filled microcapsules (0−15.0 wt %). The PLA solution was then stirred for 5 min under argon and cast into Teflon molds under a glass lid. Also under the glass lid was a crystallization dish filled with chloroform to allow for chloroform vapor saturation and therefore slow evaporation of the PLA solutions to allow for good film formation. After 24 h, the cast films were removed from Teflon molds and dried at 50 °C for 24 h.

Instrumentation. Microcapsules were prepared using a mechanical stirrer (Chemglass) with a 30 mm low profile/low shear 3 blade propeller. Polylactic acid was cast into Compact Tension (CT) molds that were machined from Teflon. The mold dimensions were determined based on ASTM E647-08 to produce films with final dimensions of 31.25 × 30.00 × 1.25 mm. Optical microscopy was performed on a Nikon Measurement MM-11. Scanning electron microscopy of the uncoated samples was performed on a Hitachi S-3400N at 15 keV. Mechanical testing (detailed information below) was performed on an Instron universal tester model 5965. Thermal gravimetric analysis was performed on a TA Instruments TGA Q100 with a nitrogen atmosphere (60 mL/min) and a heating rate of 10 °C/min. Microcapsule particle size was determined using a Malvern Zetasizer Nano-S. 3D microscopy was captured on a Keyence VK-X100 Series 3D laser scanning microscope. Degree of crystallinity was evaluated using a TA Instruments DSC Q-100 from 30 to 250 °C at a rate of 5 °C/min. Heat deflection temperature (HDT) was evaluated using a Rheometric Scientific DMTA IV according to a modified ASTM D648. To accommodate the DMTA used, HDT samples with dimensions of 50.8 × 6.35 × 1.25 mm were utilized.

Mechanical Testing of As Prepared PLA Films with Self-Healing Properties. Self-healing efficiency of the PLA composites was determined through fracture testing (ASTM E647-08) of virgin and healed samples.[21] The samples were pulled at a rate of 10 mm/min. The Instron was programmed so that cracks would propagate to a distance of ∼10 mm. Sample thickness and crack distance were measured for each sample. Once the samples were fractured, they were returned to the zeropoint and removed from the instrument. Samples were then left for 24 h at room temperature with no additional clamping force to realign the fracture halves. Healed samples were then placed in the Instron for subsequent testing.

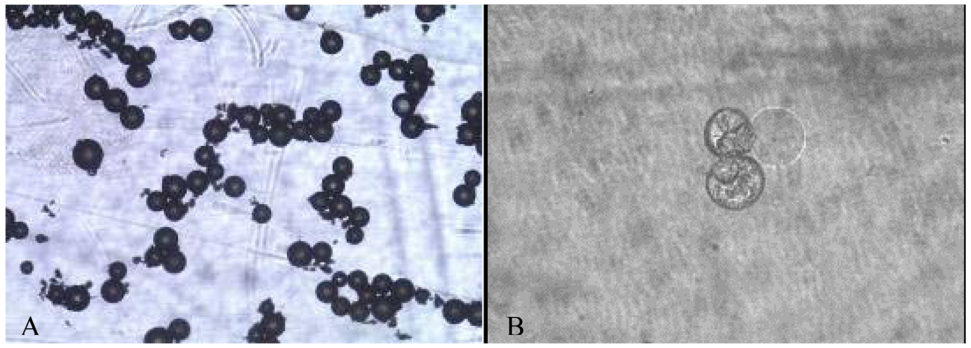

Figure 3. (A) Optical microscopy image showing the spherical microcapsules prior to filtering. (B) Microcapsules ruptured under coverslip showing release of liquid DCPD (to the right of the upper capsule).

RESULTS AND DISCUSSION

Microencapsulation and Characterization. Microcapsules were produced using an in situ polymerization with slight modifications from the previously reported synthesis[19] (Figure 1). The microencapsulation process entails an oil-in-water emulsion procedure in which the use of a surfactant is critical in processing the spherical capsules. It was previously reported that the use of ZeMac E400 (ethylene maleic anhydride copolymer, M_w = 400 000) as a surfactant, was ideal for this type of encapsulation.

Inspection of ruptured microcapsules under an optical microscope shows the release of DCPD from within the capsule (Figure 3), indicating that the encapsulation was successful. The as-synthesized microcapsules were spherical and contained ~76 wt % DCPD, determined by TGA as the weight-loss difference from the point where DCPD begins to boil off (120 °C) until a constant weight is maintained.

The surface roughness was determined by 3D microscopy and showed some nodules and texture along the capsules surface, which most likely is due to excess urea-formaldehyde debris bonding to the surface (Figure 4). This textured surface

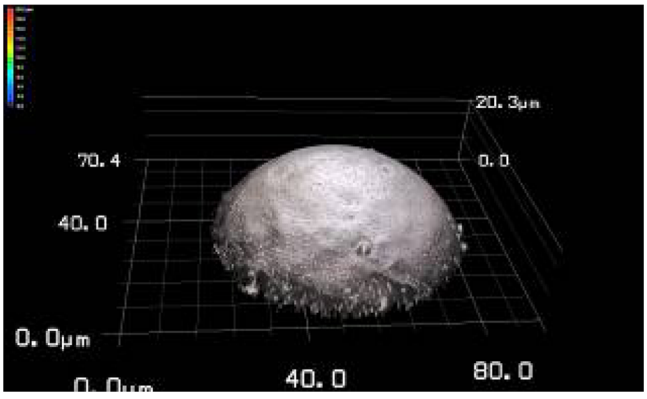

Figure 4. 3D microscopy showing surface roughness of the microcapsule's shell wall.

is believed to aid in increasing the mechanical adhesion of the microcapsules to the PLA polymer matrix, but this was not investigated in detail in this study. Particle size was determined using dynamic light scattering to have an average particle size being 31.47 ± 17.08 μm. This capsule size was targeted by adjusting the agitation speed of the mechanical stirrer during synthesis to ~1000 rpm, which yielded particle sizes in the approximate range of common nucleating agents (<20 μm), thereby allowing for tailoring of additional properties, such as the HDT.

Autonomous Self-Healing. Self-healing of PLA composite films was evaluated by measuring the recovery of the virgin material's fracture toughness after healing. CT specimens were formed by casting films into Teflon molds as outlined in Figure 2. Microcapsules and Grubbs' first generation ruthenium metathesis catalyst were added to the PLA casting solutions at 0−15 wt % and 0−5 wt %, respectively. Grubbs' catalyst was soluble in the casting solvent, leading to a very high dispersion of the catalyst in the resulting PLA films. Films were initially cast under argon in order to protect the Grubbs' catalyst from decomposition, which resulted in purple-colored films similar to the color of the catalyst. Films cast in air yielded brown-colored films, which was thought to be related to deactivated catalyst, but it was found that samples cast in air yielded similar mechanical and healing results as those processed under argon. This coloration is likely due to the small amount of oxidation of Grubbs' catalyst in air. Films were removed from molds and dried at 50 °C prior to testing.

Here, we tested self-healing using an Instron test fixture to investigate crack propagation through fracture testing. The test sample was placed into the test fixture and tested as outlined in the methods section. Once the load dropped to zero due to crack formation, thus causing microcapsule rupture and the release of the healing monomer, the test sample was removed and allowed to heal for 24 h. Healed samples were subsequently tested following the same protocol.

SEM images of fracture surfaces (Figure 5) show the presence of voids, indicating that the microcapsules were present along the fracture path. Following a 24 h room temperature healing process to allow DCPD to react with Grubbs' catalyst, a newly formed polymer bridges the crack planes (Figure 5b) to arrest further crack propagation and heal the PLA composite. The self-healing agent released from the microcapsules upon rupture acts as a fluid and flows into the cracked interface. The filling of the gap between the two surfaces provides micromechanical adhesion between the two edges allowing for bonding to occur between the PLA and the DCPD.

Fracture toughness was evaluated both on the virgin composite film and after a subsequent 24 h healing period, after which point poly(dicyclopentadiene) had formed in the damage region. Recovery of fracture toughness, otherwise known as healing efficiency (η), is defined as the ratio of the healed material's fracture toughness ($K_{IC\ (healed)}$) to that of the virgin material ($K_{IC\ (unhealed)}$) (eq 1).[22,23] Crack lengths in fractured virgin and healed samples are near-identical, so eq 1

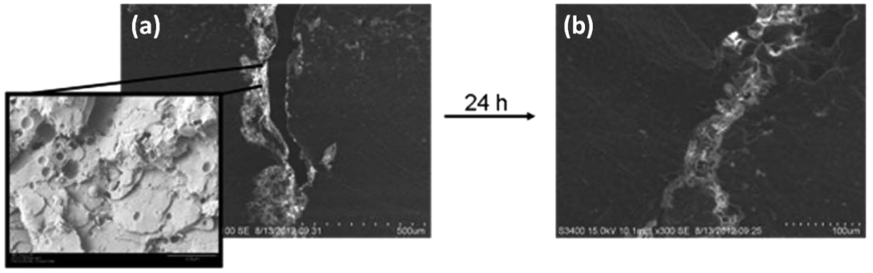

Figure 5. SEM images showing an initial crack that has formed (a) followed by the healing of the crack within a 24 h period (b). Microcapsules were present at the crack surface (inset).

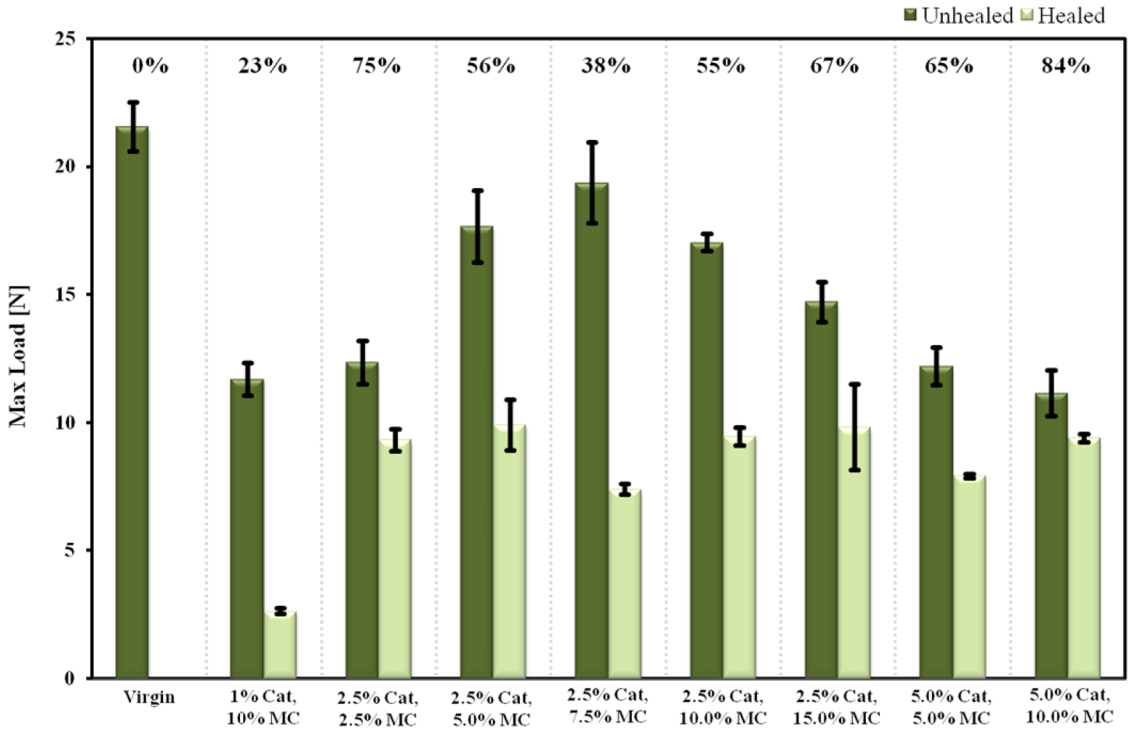

Figure 6. Peak load values of both as-casted composites (dark green) and healed (light green) PLA composites. Nonfilled virgin PLA results in 0% healing efficiency.

can be simplified to a ratio of the peak fracture load of the healed ($P_{C(healed)}$) to the virgin ($P_{C(unhealed)}$) samples in their load−displacement curves (eq 2).

$$\eta = \frac{K_{IC(healed)}}{K_{IC(unhealed)}} \quad (1)$$

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

Addition of microcapsules imparts an inherent toughening effect to the virgin PLA samples. This is indicated by a marked increase in the maximum load of unhealed samples when microcapsule loading increases from 2.5 wt % to 7.5 wt % (at a constant 2.5 wt % loading of catalyst), which is a phenomenon often attributed to microcapsule-induced crack branching serving as localized wells for absorbing mechanical energy.[24] Further increasing microcapsule loading above 7.5 wt % leads to a reduction in maximum load. Hence, the optimal concentration of microcapsules is 7.5 wt % when the microcapsule size is ∼31.5 μm. Furthermore, catalyst loading appears to negligibly affect healed samples fracture toughness at concentrations ≥2.5 wt %.

Healing efficiencies ranged from 23 to 84% (Figure 6) with the optimal formulation of 2.5 wt % catalyst and 7.5 wt % microcapsules yielding a 38 ± 3% recovery of the PLA composites original properties (Figure 7). This optimal concentration yields both a high average virgin peak load (19.37 ± 3.15 N) and is comparable to nonfilled, virgin PLA (indicates microcapsules and catalyst do not reduce mechanical properties within the composite) and has a good recovery percentage (38 ± 3%) using only a minimal amount of catalyst and microcapsules (7.5 wt %). Interestingly, the healed maximum load measured for nearly all composites tested were similar, and thus, the healed composite's mechanical properties are likely dependent on adhesion of the poly(dicyclopentadiene) to the PLA matrix or cohesive failure of the poly(dicyclopentadiene), which is expected to be mostly invariable in the different compositions. Due to the similar healed maximum loads, the optimal concentration was selected on the basis of the highest average virgin peak load, as this concentration of catalyst and microcapsules resulted in optimal virgin properties. That is, the higher healing efficiency

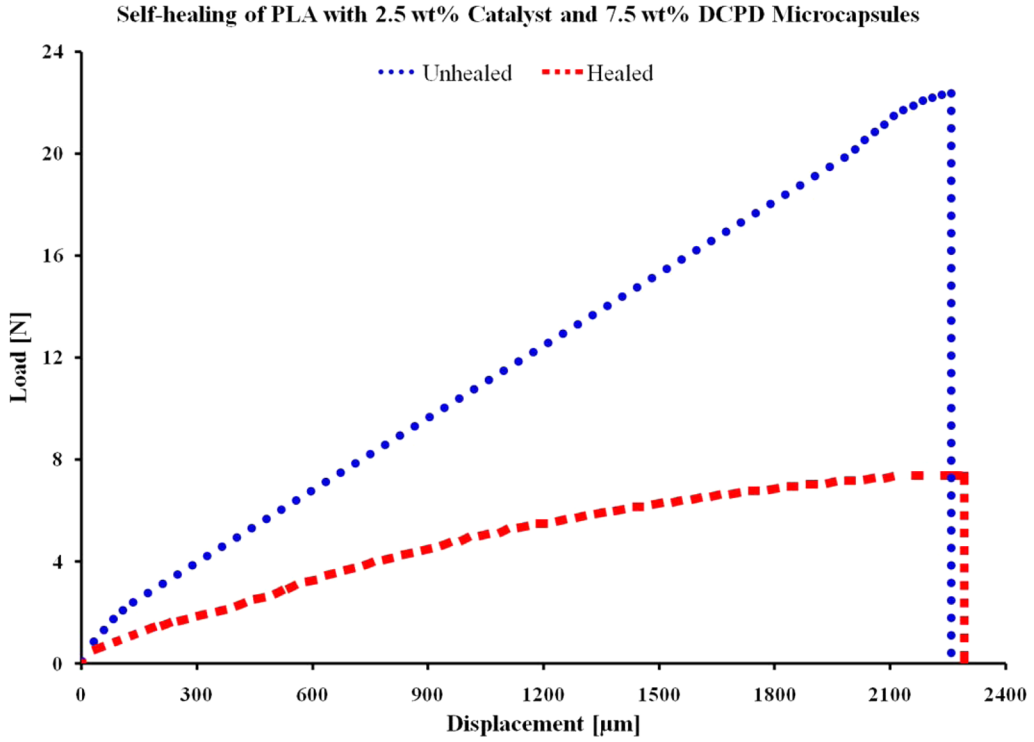

Figure 7. Load−displacement curve for 2.5 wt % catalyst and 7.5 wt % microcapsule composite film's initial (blue circles) and healed (red squares) properties.

percentages of several other compositions in Figure 6 are misleading in that their initial as-cast material properties are significantly diminished compared to as-cast nonfilled virgin PLA.

Polymer Composite Properties. Self-healing additives in polymer composites often have varying effects (typically negative) on the composite's properties that limit their use as durable goods. These effects are generally ignored or underemphasized throughout literature, likely due to their unattractive implications. For example, modulus and strength are often depressed in self-healing polymer composites containing microcapsules as the microcapsules can be considered to be mechanically equivalent to hollow voids within the polymer.[25,26] Additionally, embedded catalyst is comparable to a small-molecule plasticizer that can lower Tg, HDT, and strength.[27] Overcoming these limitations to create a truly multifunctional composite that has both improved material properties and self-heals is desirable.

Typically, as molded PLLA has a degree of crystallinity of approximately ∼30%[28] and a HDT of approximately ∼57 °C.[29] This low crystallinity and HDT excludes PLA's use in durable goods applications due to deformation of the polymer at moderately high temperatures (>60 °C). In addition to triggering self-healing, it was hypothesized that the incorporation of microcapsules approximately within the size range of traditional PLA nucleating agents (0.01−20 μm) could replace these traditional nucleating agents in PLA formulations to extend the polymer's temperature use range.

Rectangular PLA composites containing 0−15% DCPD-filled microcapsules were prepared by the solvent casting and drying method described above. Baseline films without microcapsules degree of crystallinity and HDT were measured using DSC and DMTA, as outlined in the methods section, and found to be approximately ∼30.55% and ∼57 °C (Table 1), respectively,

Table 1. Degree of Crystallinity (χ_c) and Heat Distortion Temperature (HDT) at Different Microcapsule Loadings in PLA

film type	χ_c	HDT [°C]
virgin PLA	30.55 ± 0.37	57.02 ± 1.81
5 wt % capsules	35.41 ± 0.71	78.05 ± 2.05
10 wt % capsules	41.78 ± 0.63	73.73 ± 2.18
15 wt % capsules	38.53 ± 0.85	74.93 ± 1.96

which is similar to previously reported values.[28,29] The addition of 10 wt % microcapsules increased the degree of crystallinity by greater than 36%. With a 5 wt % loading of microcapsules, we found that the heat deflection temperature through DMTA increased to 78.05 °, 21 °C improvement, indicating enhanced crystallinity due to successful microcapsule-induced nucleation. These results are consistent with previous reports of increases in PLA HDT concomitant with increased crystallinity when various nucleating agents such as talc,[30] nanoclay,[31] carbon nanotubes,[32] layer metal phosphate,[33] amide derivatives,[34] hydrazide compounds,[35] and cyclodextrin[36] were used.

CONCLUSIONS

In this work, we have developed the first known self-healing PLA composite that overcomes the typical low fracture toughness of the polymer, which is one of the most significant drawbacks for use of PLA in durable goods. Through optimization of the microcapsules and catalyst, a 38 ± 3% recovery of fracture toughness was obtained while maintaining the virgin material's fracture toughness. Additionally, the microcapsules served as nucleating agents capable of increasing the degree of crystallinity and heat deflection temperature to 41.78 ± 0.63% and 78.05 ± 2.05 °C, respectively. Simultaneous improvement in the thermal tolerance of PLA could lead to its

use in new applications that require extended product lifetimes and broader temperature ranges.

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Notes

The authors declare no competing financial interest.

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