Self-healing and self-cleaning nanocomposite coatings

Kenan Song

Department of Manufacturing Engineering, Arizona State University, 7001 E Williams Field Rd, Mesa, AZ 85212. Email: kenan.song@asu.edu

ABSTRACT

This work reports on the introduction of self-cleaning and self-healing properties in polymer/nanoparticle composites. A series of epoxy/halloysite nanotubes (HNTs)/cellulose acetate butyrate (CAB) composites with various CAB concentrations were developed and subjected to different levels of mechanical loading. The optimized concentration of nanoparticle is 1.0 vol% and for CAB concentration of 3.0 vol% based on the mechanical reinforcements and wear-resistance. The addition of CAB can significantly modify the surface chemistry and reduce roll-off angles of water droplets from 90º to 20º, and benefit the self-healing properties. Nanoscale scratching and macro-level Taber Abrasion tests were used to damage the surfaces. The initiated damages of roughness and surface scratch up to hundreds of nanometers were healed upon heating. The water sliding angles and mechanical integrity for epoxy-based composites were reserved after healing, suggesting broad applications in optical systems, energy components, and mechanical parts requiring structural behaviors and multi-functionalities.

Keywords: self-cleaning, self-healing, HNT, composite, mechanics, indentation

1 INTRODUCTION

Polymer-based composites are susceptible to many different types of mechanical damages that reduce their structural reliability, thermal conductivity, optical transparency, and surface merits, thereby potentially decrease the overall lifetime of these products.[1-9] Take airplane fuselage and wings for example; the repair strategies have mainly been external patches, complex intrusive tapered scarf or stepped-in fixation, which are difficult to execute, not truly healing cracks and costly to apply.[10] By implementation of self-healing technologies, the overall lifetime of these polymer composites can be prolonged.[11]

Within self-healing material systems, especially multiphase composites, most attention has been so far attracted to extrinsic healing strategies.[12] In those composites, an external (liquid or gel) healing agent capable of restoring either the matrix or the filler-matrix interface is encapsulated and embedded in the matrix.[13-14] The mechanism indeed works, but there are many issues to be resolved. First, the healing only works locally in regions closer to healing agents[11]. Second, the healing works once and, when the healing agents are consumed by the polymer matrix, the polymerization reaction terminate[15]. Third, the introduction of soft healing agents and ductile agent carriers deteriorate the mechanical robustness in composites[16]. Last but not the least, effective capsules carrying self-healing agents are usually micro to hundreds micro size and negatively influence dispersion quality, fiber architecture in bulk composites, the surface smoothness, and, optical homogeneity in almost all thin films and packaging-purpose polymers.[17] The biggest obstacle to using extrinsic self-healing products in the industry is the high cost of most healing catalysts,[18-19] not to mention their moisture and oxygen sensitivity and short lifetime in the nature environment.[20] Therefore, the usage of intrinsically healing polymer materials in such composites is considered to be more optimal because of the ease of processing, the flexibility of choosing miscible polymer blends, the potential of the infinite amount of healing cycles, and the synergy of mechanics as well as optical property control.[21-22] Additionally, the intrinsic healing leaves the optimized nanoparticle dispersion quality or macroscopic reinforcement-fiber architectures for high-level mechanical properties unaffected.

In most studies about the self-healing polymer composites, the research has focused on the healing of damage after cutting, static overloading or debonding between toughening interlayers in laminates.[23-24] Intrinsic self-healing materials have been demonstrated using three main schemes. (1) Reversible bonding schemes make use of the reversible nature of specific chemical reactions that have been adapted to self-healing applications, an example of which is the Diels-Alder healing system.[25] (2) Chain entanglement approaches utilize mobility at crack faces to entangle chains that span the crack surfaces, an example of which is the self-healing epoxy containing phase-separated polycaprolactone.[26-27] (3) Non-covalent self-healing systems rely on reversible hydrogen bonding or ionic clustering that manifests as reversible cross-links in polymers, an example of which is the polyethylene-co-methacrylic acid (EMAA) self-healing ionomer.[28-29] Introduction of healable behaviors in multi-functional composites (e.g., coatings, fibers, adhesives, packaging, microelectronics) with structural durability, optical transparency, and, even surface hydrophobicity/hydrophilicity is attractive.[30-31] However, despite continuing advances in intrinsically self-healable polymers, few examples fully leverage the potential of composite manufacturing or use structural matrices, such as epoxy resins, in preparing multi-functional materials with mechanical durability, optical transmittance, and self-healing capabilities.[25, 32-34]

Our group has recently reported on the fabrication of epoxy-based transparent composite coatings.[35-36] Due to the refractive index matching between the HNTs and polymer matrix (n ~ 1.5 for both), the resultant composites display high transparency of 90% even at a high halloysite concentration of 20 wt%.[35-36] These transparent coatings with well-controlled thickness are attractive for fabricating multi-functional composites. However, it is challenging to find polymer additives incorporated in epoxy with remaining merits of epoxy miscibility, high transparency, and unaffected mechanical robustness.[37] Currently, several additive thermoplastics have frequently been studied in epoxy matrix regarding their intrinsic self-healing efficiencies and mechanisms. Nonetheless, all of these polymers were incorporated into epoxy as particulate states due to the epoxy immiscibility and the solvent dissolubility; what made it worse was the mismatching of refractive indices that prohibited the transmittance of light thus made the composites translucent.

An esterification derivative of cellulose, cellulose acetate butyrate (CAB), induces solubility in a wide range of solvents, melts process-ability, and manageable transition temperatures and viscosities.[38] CAB in our material system is considered a good candidate to compound with epoxy because of the natural resourced materials of cellulose, excellent miscibility with epoxy and high mechanical rigidness. This study is the first investigation on the reversible self-repair of intrinsically self-healing polymer blends/nanoparticle composites after mesoscale damage loading conditions. In this work, epoxy/HNTs/CAB composites were developed and subjected to different levels of mechanical damages, including nanoscratching and Taber-Abrasion tests. The damages were then healed upon heating after which water roll-off angles and mechanical parameters were recovered. This study enlarges the self-healing candidate pool to include CAB materials and suggests a useful strategy for producing multifunctional material systems with enhanced mechanical durability, transparent optical properties, self-healable behaviors, as well as self-cleaning performances.

2 EXPERIMENTATION

Dragonite HNT clay was obtained from Applied Minerals. Epoxy (purchased from Epoxy Technology, Inc., density 1.18 g·cm^{-3}) and acetone (purchased from VWR, density 0.79 g·cm^{-3}) were used as obtained. All the composite films were coated on glass slides with different viscosity levels. Compositions of these materials can be found in our previous report[35]. Water contact angle and roll-off angle measurements were performed using a Ramé-Hart model 590 Goniometer after vertically dispensing sessile droplets (volume of 30 μL) of deionized water (γ = 72.8 mN/m) on various surfaces. Advancing water contact angles were measured as deionized water was supplied via syringe, whereas receding contact angles were measured as deionized water was removed via syringe. Measurements were taken over three or more different locations on each surface, and the reported uncertainties are standard deviations associated with the measurement of these independent contact angle values. Water roll-off angle was conducted from 0 to 90° within 1000 steps till both sides of the water droplet move on tilted sample surfaces.

Static tensile test was conducted using a dynamic mechanical analyzer (RSA-G2 series, manufactured by TA Instruments) with a gauge gap of 20 cm and extension rate of 0.05 mm min^{-1}, where 15 coating stripes were tested for each sample batch (i.e., original, abraded, healed samples). **AFM measurements** were used to check some of the residual post-scratch depths after healing at specific temperature for specific time.[39] To quantify the morphology and topography of the scratched traces, AFM imaging in tapping mode (Dimension^{TM} 3100, Digital Instruments Vecco Metrology Group) were used.

3 RESULTS AND DISCUSSIONS

The water roll-off angles were measured by dropping 30 μL water on tilted coatings. Addition of CAB$_{HM}$ decreased the roll-off angle of epoxy, 87°, to values as low as 17°. The healed samples showed similar values; and this low water roll-off angle can also benefit the self-cleaning properties of these coatings.

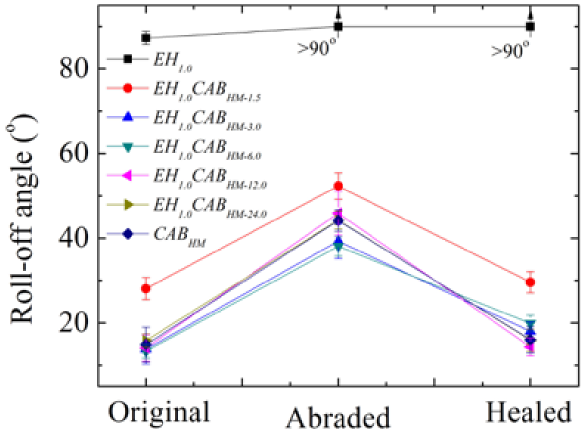

Figure 1 Goniometer measurement of water roll-off angle on all sample surfaces of $EH_{1.0}CAB_{HM\text{-}y}$, where volume concentration percentage y=0, 1.5, 3.0, 6.0, 12.0, 24.0 while

HNTs concentration remains 1.0 vol% and CAB_{HM}. The surfaces were damaged using Taber Abrasion tests with 1 kg weight on both wheels and abrasion of 40 cycles and the healing was conducted at 110 ºC in oven overnight. For water roll-off angle measurements, distilled water droplet is of 30 µL volume. Water roll-off angle was conducted from 0 to 90º within 1000 steps till both sides of the water droplet moves on tilted sample surfaces. During water roll-off angle measurements, epoxy surfaces after mechanical damages and healing were so rough and hydrophilic that water droplet won't fall at highest tilted angle of 90º. During water cleaning demonstrations, the tilted angle of both samples were 20 º, with average sand particle size of 1 µm and sand weight of 200 mg on sample surfaces being cleaned by water droplets of 2.5 ml.

The efficiency of the crack healing is assessed by the ability to recover the mechanical integrity; in this study the elastic stiffness (*E*). Figure 2 showed the average modulus values. Taber Abrasion created cracks on the coatings surface and led to drop of the modulus. Healing of these cracks was found to be effective when the concentration went beyond 3.0 vol%, reaching healing efficiency as high as 100%; however, higher loadings decreased the mechanical properties in original samples.

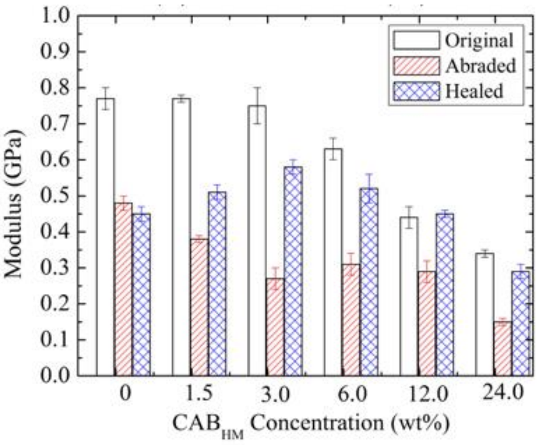

Figure 2 Average mechanical parameters of modulus from static mechanical tests of $EH_{1.0}CAB_{HM\text{-}y}$ where CAB_{HM} volume concentration percentage y=0, 1.5, 3.0, 6.0, 12.0, 24.0 in original, abraded and healed samples, demonstrating efficient healing degree of mechanical parameters with CAB_{HM} concentration of more than 3.0 vol%

All samples were scratched with controlled depth of 300 nm using Hysitron NanoIndenter. The mechanically created depth was also confirmed by AFM imaging before healing. The healing procedures were captured as a function of healing temperature and healing time. The scratches were heated between 90 and 120 ºC for optimal healing temperatures. The heating at 120 ºC obvious went beyond the thermal transitions of all samples and was most efficient in recovering surface smoothness. $EH_{1.0}CAB_{HM\text{-}3.0}$ composites recovered fully at 120 ºC, with higher temperatures healing for shorter time. As a comparison, the pure epoxy did not show any changes for the scratches created initially on the surfaces.

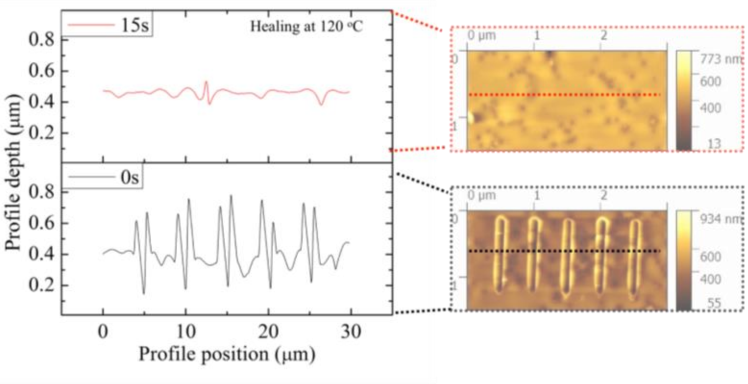

Figure 3 The healing of $EH_{1.0}CAB_{HM\text{-}3.0}$ samples at 120 ºC for 15s displayed the recovered smoothness on coating surfaces

4 CONCLUSION

This research focuses on the reversible recovery of optical and mechanical damages. $EH_{1.0}CAB_{HM\text{-}3.0}$ was optimized with the best compositions for mechanical durability, self-healing, and self-cleaning properties. The coating system in this research will be applicable in optical protections, packaging systems, and epoxy-based composites required for structural performances.

REFERENCES

1. Trask, R.; Williams, H.; Bond, I., Self-healing polymer composites: mimicking nature to enhance performance. *Bioinspiration Biomimetics* **2007,** *2* (1), 1-9.
2. Tuteja, A.; Choi, W.; McKinley, G. H.; Cohen, R. E.; Rubner, M. F., Design parameters for superhydrophobicity and superoleophobicity. *MRS Bull.* **2008,** *33* (08), 752-758.
3. Youngblood, J. P.; Sottos, N. R., Bioinspired materials for self-cleaning and self-healing. *MRS Bull.* **2008,** *33* (08), 732-741.
4. Yuan, Y.; Yin, T.; Rong, M.; Zhang, M., Self healing in polymers and polymer composites. Concepts, realization and outlook: a review. *Polym. Lett* **2008,** *2* (4), 238-250.
5. Kessler, M., Self-healing: a new paradigm in materials design. *Proc. Inst. Mech. Eng., Part G* **2007,** *221* (4), 479-495.
6. Song, K.; Zhang, Y.; Meng, J.; Minus, M. L., Lubrication of poly (vinyl alcohol) chain orientation by carbon nano-chips in composite tapes. *J. Appl. Polym. Sci.* **2013,** *127* (4), 2977-2982.
7. Song, K.; Zhang, Y.; Meng, J.; Minus, M. L., Spectral Analysis of Lamellae Evolution and Constraining

Effects Aided by Nano-carbons: A Coupled Experimental and Simulation Study. *Polym.* **2015,** *75*, 187-198.

8. Song, K.; Zhang, Y.; Minus, M. L., Polymer Interphase Self-Reinforcement and Strengthening Mechanisms in Low-Loaded Nanocomposite Fibers. *Macromol. Chem. Phys.* **2015,** *216* (12), 1313-1320.

9. Tajaddod, N.; Song, K.; Green, E. C.; Zhang, Y.; Minus, M. L., Exfoliation of Boron Nitride Platelets by Enhanced Interfacial Interaction with Polyethylene. *Macromol. Mater. Eng.* **2016,** *30* (3), 315-327.

10. Bond, I. P.; Trask, R. S.; Williams, H. R., Self-healing fiber-reinforced polymer composites. *MRS Bull.* **2008,** *33* (08), 770-774.

11. Blaiszik, B.; Kramer, S.; Olugebefola, S.; Moore, J. S.; Sottos, N. R.; White, S. R., Self-healing polymers and composites. *Annu. Rev. Mater. Res.* **2010,** *40*, 179-211.

12. Bergman, S. D.; Wudl, F., Mendable polymers. *J. Mater. Chem.* **2008,** *18* (1), 41-62.

13. White, S. R.; Sottos, N.; Geubelle, P.; Moore, J.; Kessler, M. R.; Sriram, S.; Brown, E.; Viswanathan, S., Autonomic healing of polymer composites. *Nat.* **2001,** *409* (6822), 794-797.

14. White, S. R.; Caruso, M. M.; Moore, J. S., Autonomic healing of polymers. *MRS Bull.* **2008,** *33* (08), 766-769.

15. Mauldin, T. C.; Kessler, M., Self-healing polymers and composites. *Int. Mater. Rev.* **2010,** *55* (6), 317-346.

16. Yang, Y.; Urban, M. W., Self-healing polymeric materials. *Chem. Soc. Rev.* **2013,** *42* (17), 7446-7467.

17. Wool, R. P., Self-healing materials: a review. *Soft Matter* **2008,** *4* (3), 400-418.

18. Billiet, S.; Hillewaere, X. K.; Teixeira, R. F.; Du Prez, F. E., Chemistry of Crosslinking Processes for Self-Healing Polymers. *Macromol. Rapid Commun.* **2013,** *34* (4), 290-309.

19. Teixeira, R. F.; Hillewaere, X. K.; Billiet, S.; Du Prez, F. E., Chemistry of Crosslinking Processes for Self-Healing Polymers. In *Self-Healing Polymers: From Principles to Applications*, 1 ed.; Binder, W. H., Ed. Wiley-VCH Verlag GmbH & Co. : Weinheim, Germany, 2013; pp 215-246.

20. Williams, K. A.; Dreyer, D. R.; Bielawski, C. W., The underlying chemistry of self-healing materials. *MRS Bull.* **2008,** *33* (08), 759-765.

21. Habault, D.; Zhang, H.; Zhao, Y., Light-triggered self-healing and shape-memory polymers. *Chem. Soc. Rev.* **2013,** *42* (17), 7244-7256.

22. Wu, M.; Johannesson, B.; Geiker, M., A review: Self-healing in cementitious materials and engineered cementitious composite as a self-healing material. *Construction and Building Materials* **2012,** *28* (1), 571-583.

23. Thakur, V. K.; Kessler, M. R., Self-healing polymer nanocomposite materials: A review. *Polym.* **2015,** *69*, 369-383.

24. Gibson, R. F., A review of recent research on mechanics of multifunctional composite materials and structures. *Compos. Struct.* **2010,** *92* (12), 2793-2810.

25. Burattini, S.; Greenland, B. W.; Chappell, D.; Colquhoun, H. M.; Hayes, W., Healable polymeric materials: a tutorial review. *Chem. Soc. Rev.* **2010,** *39* (6), 1973-1985.

26. Rodriguez, E. D.; Luo, X.; Mather, P. T., Linear/network poly (ε-caprolactone) blends exhibiting shape memory assisted self-healing (SMASH). *ACS Appl. Mater. Interfaces* **2011,** *3* (2), 152-161.

27. Luo, X.; Mather, P. T., Shape memory assisted self-healing coating. *ACS Macro Letters* **2013,** *2* (2), 152-156.

28. Kalista, S. J.; Ward, T. C., Thermal characteristics of the self-healing response in poly (ethylene-co-methacrylic acid) copolymers. *J. R. Soc., Interface* **2007,** *4* (13), 405-411.

29. Pingkarawat, K.; Wang, C.; Varley, R.; Mouritz, A., Self-healing of delamination cracks in mendable epoxy matrix laminates using poly [ethylene-co-(methacrylic acid)] thermoplastic. *Composites Part A: Applied Science and Manufacturing* **2012,** *43* (8), 1301-1307.

30. Ionov, L.; Synytska, A., Self-healing superhydrophobic materials. *Phys. Chem. Chem. Phys.* **2012,** *14* (30), 10497-10502.

31. Roy, D.; Cambre, J. N.; Sumerlin, B. S., Future perspectives and recent advances in stimuli-responsive materials. *Prog. Polym. Sci.* **2010,** *35* (1), 278-301.

32. Samadzadeh, M.; Boura, S. H.; Peikari, M.; Kasiriha, S.; Ashrafi, A., A review on self-healing coatings based on micro/nanocapsules. *Prog. Org. Coat.* **2010,** *68* (3), 159-164.

33. Syrett, J. A.; Becer, C. R.; Haddleton, D. M., Self-healing and self-mendable polymers. *Polymer Chemistry* **2010,** *1* (7), 978-987.

34. Wu, D. Y.; Meure, S.; Solomon, D., Self-healing polymeric materials: a review of recent developments. *Prog. Polym. Sci.* **2008,** *33* (5), 479-522.

35. Song, K.; Polak, R.; Chen, D.; Rubner, M. F.; Cohen, R. E.; Askar, K. A., Spray-Coated Halloysite-Epoxy Composites: a Means to Create Mechanically Robust, Vertically Aligned Nanotube Composites. *ACS Appl. Mater. Interfaces* **2016,** *8* (31), 20396–20406.

36. Song, K.; Chen, D.; Polak, R.; Rubner, M. F.; Cohen, R. E.; Askar, K. A., Enhanced Wear Resistance of Transparent Epoxy Composite Coatings with Vertically Aligned Halloysite Nanotubes. *ACS Appl. Mater. Interfaces* **2016,** *8* (51), 35552-35564.

37. Murphy, E. B.; Wudl, F., The world of smart healable materials. *Prog. Polym. Sci.* **2010,** *35* (1), 223-251.

38. Gooch, J. W., Cellulose Acetate Butyrate. In *Encyclopedic Dictionary of Polymers*, 2 ed.; Springer: New York, 2011; Vol. 1, pp 128-128.

39. Friedrich, K.; Sue, H. J.; Liu, P.; Almajid, A. A., Scratch resistance of high performance polymers. *Tribol. Int.* **2011,** *44* (9), 1032-1046.