Water-Triggered Self-Healing Coatings of Hydrogen-Bonded Complexes for High Binding Affinity and Anti-oxidative Property

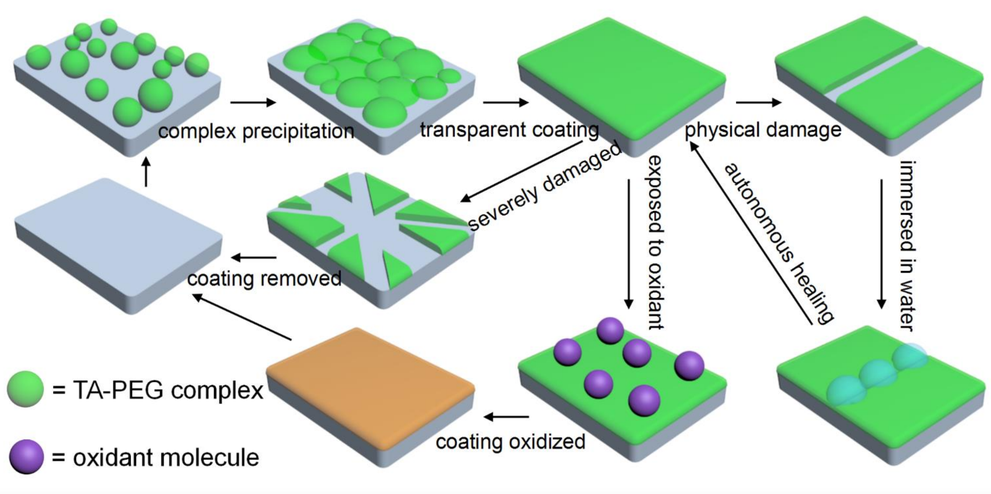
杜勇，邱文泽，吴子良*，任鹏飞，郑强，徐志康*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization,
Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Introduction

Recent years have witnessed the rapid developments of self-healing coatings because they can protect materials from diverse risks and are able to autonomously heal after being physically damaged. Here, we report a universal yet facile method with high time and cost efficiency to fabricate transparent water-enabled self-healing coatings on various substrates by precipitating hydrogen-bonded tannic acid (TA)-polyethylene glycol (PEG) complexes in aqueous solution. The precipitated complexes coalesce to form uniform and transparent coatings on the substrates; after drying, mechanically robust coatings are obtained. TA endows such coatings with strong adhesion to a wide range of substrates and admirable antioxidant properties. Repeatable self-healing of the coatings is realized by simply exposing them to water or humid environment. Furthermore, these coatings can be readily erased by soaking them in basic solution, if needed.

Results and Discussions



Scheme 1. Fabrication and multifunctions of TA-PEG water-enabled self-healing coatings on various substrates.

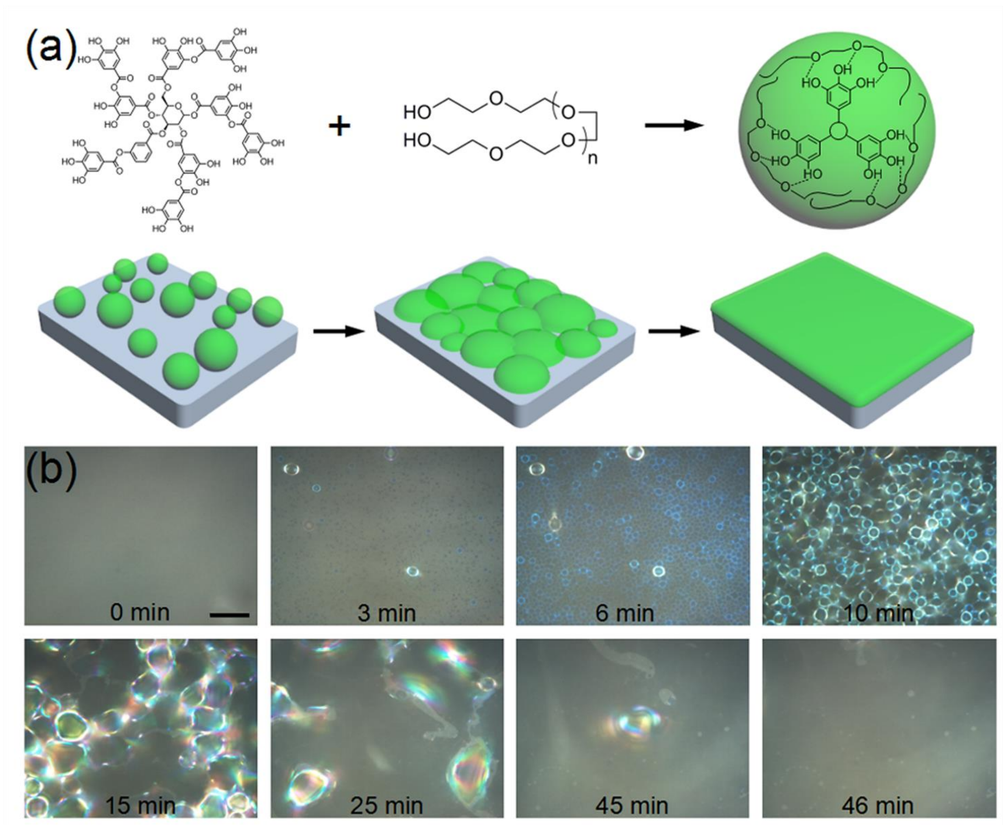


Fig. 1 (a) Scheme for the formation of TA-PEG hydrogen-bonded complexes and the fabrication of the coatings. (b) Microscopic images to show the precipitating and coalescing process of TA-PEG complexes to form uniform coatings. Scale bar, 50 μm.

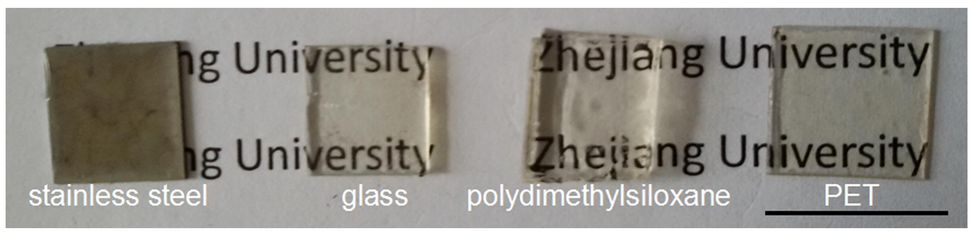


Fig. 2 Digital images of TA-PEG coatings on various substrate materials. Scale bar represents 1.5 cm.

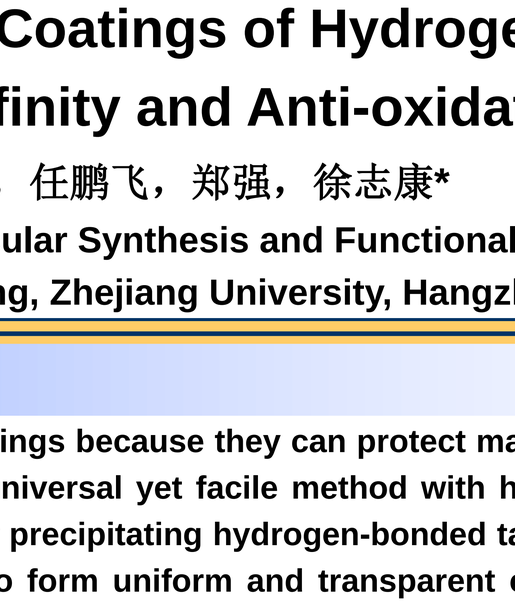


Fig. 3 (a, b) SEM images of TA-PEG coatings on PS substrates before (a) and after (b) peeled with an adhesive Scotch tape for ten times. Scale bar, 50 μm. (d) Load−displacement curves for the adhesion of TA-PEG coatings to various substrates, measured by lap shear tests. The area of coatings is 5 × 5 mm².

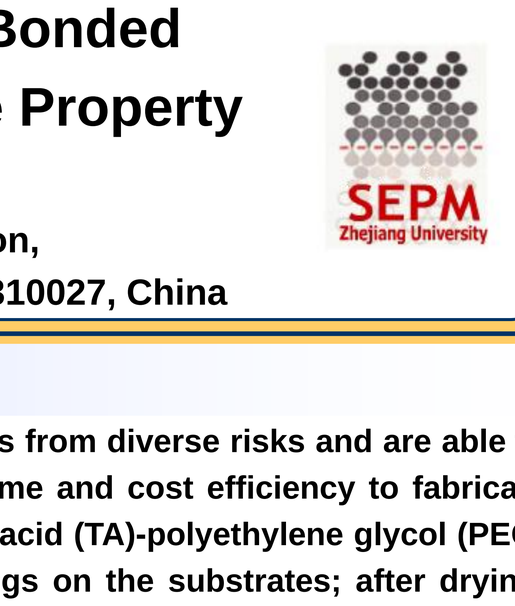


Fig. 4 (a) Digital images to show the erasure process of the TA-PEG coatings on PET substrates by soaking it in 0.01 M NaOH aqueous solution for 10 min. Scale bars, 1.5 cm. (b) FT-IR/ATR spectra of the TA-PEG coatings before and after removed from the PET substrates. FT-IR/ATR spectrum of blank PET substrates is also shown for comparison.

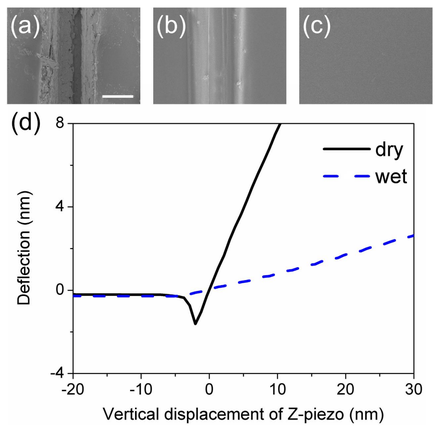


Fig. 5 (a-c) SEM images of a dry TA-PEG coating damaged with a knife (a), partially or completely healed after being immersed in water for 20 s (b) or 5 min (c), respectively. Scale bar, 50 μm. (d) Deflection-displacement loading curves of dry and wet TA-PEG coatings.

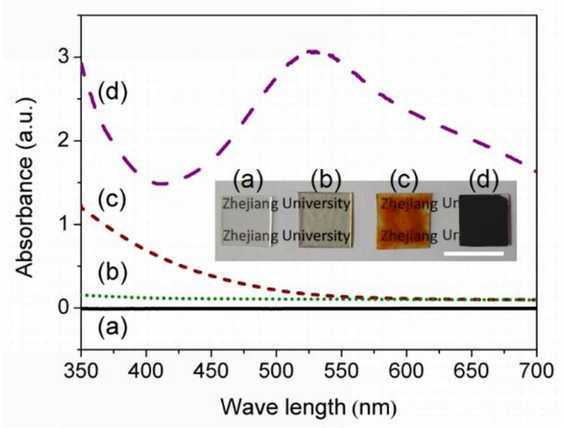


Fig. 6 UV-vis spectra of bare and TA-PEG coated PET substrates at different states. (a) Bare PET substrates; (b) TA-PEG coated PET substrates; (c) TA-PEG coated PET substrates dripped with DPPH solution; (d) PET substrates dripped with DPPH solution. Insets are digital images of corresponding samples; scale bar, 1.5 cm.

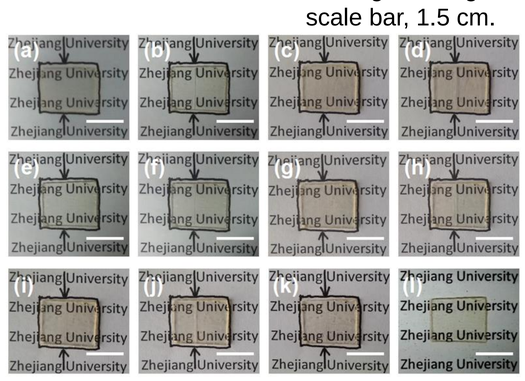


Fig. 7 Digital images of a TA-PEG coating on a PS substrate for repeated damaged-healing process in water. (a) Freshly-prepared TA-PEG coating. And the TA-PEG coating for the (b, c) first, (d, e) second, (f, g) third, (h, i) fourth and (j, k) fifth cycles of damaging and healing. (l) The same sample placed in air at room temperature for over 5 months. Scale bars, 1.5 cm.

Conclusion

- This is the first self-healing coating having versatile properties, including repeatedly healing capacity, good transparency, high mechanical toughness, high binding affinity to various substrates, easy erasure on demand, and admirable antioxidant properties.
- The fabrication method provides superior efficiency in time and cost.
- Such coatings can be used to protect biomaterials, precision instruments, etc.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (Grant No. 21534009).

Reference

[1] X. Wang, F. Liu, X. Zheng, J. Sun, *Angew. Chem. Int. Ed.* **2011**, 50, 11378-11381.

[2] A. B. South, L. A. Lyon, *Angew. Chem. Int. Ed.* **2010**, 49, 767-771.

[3] Y. Wang, T. Li, S. Li, R. Guo, J. Sun, *ACS Appl. Mater. Interfaces* **2015**, 7, 13597-13603.