

Rapid Communication

**BARK-MIMETIC LAYER-BY-LAYER ASSEMBLED
MONTMORILLONITE/POLY(*p*-AMINOSTYRENE) FLEXIBLE
NANOCOMPOSITES SHIELDING ATOMIC OXYGEN EROSION***

Min Gao^a, Bing-jun Liu^a, Long-cheng Gao^{a**}, Peng-gang Yin^a, and Lei Jiang^{a, b}

^a Key Laboratory of Bio-inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, BeiHang University, Beijing 100191, China

^b Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Abstract Inspired by the birch bark, which has multilayered structures, we fabricated layer-by-layer (LbL) assembled montmorillonite (MMT) and poly(*p*-aminostyrene) (PPAS) nanocomposites on cotton fiber curved surfaces to provide protection from atomic oxygen (AO) erosion. The multilayer coated fibers had high flexibility, uniformity, defect free, ease of preparation and low cost. The AO erosion durability has been dramatically enhanced which was evidenced by testing in the ground-based AO effects simulation facility. And the dimension and surface morphologies of the fibers observed by SEM had few changes, indicating excellent AO erosion resistant ability of the coatings. These results provide us a new method to design fibrous materials exposed directly in low earth orbit environment.

Keywords: Layer-by-layer assembly; Atomic oxygen; Biomimetics; Adhesion; Aerospace materials.

INTRODUCTION

Atomic oxygen (AO) erosion is one of the severe degrading factors to the space polymeric materials exposed in the low earth orbit (LEO), due to its high chemical reactivity and high impinging energy (approximately 5 eV)^[1]. There are mainly two methods to improve space materials' tolerance against AO. One method is to design new kinds of polymers, incorporating functional groups, such as silicon-, phenylphosphine oxide (PPO)-containing (co)polymers^[2–11], which are converted to stable surface layer by AO interaction and inhibit further oxidation. This is so called “self-healing” ability. The other option, which is more frequently applied, is to introduce directly inert thin coatings (*ca.* 50–200 nm) of inorganic oxides on top of the polymeric materials, for instance, aluminum oxide-, silicon oxide-, phosphorous nickel-containing polymers, and so on^[12–15]. To provide maximum protection, the coatings need to be relatively uniform and defect free. However, the inorganic coatings are somehow very brittle, and possess a crack tendency.

Our inspiration for AO erosion protection comes from the outermost bark layer of a tree stem, which protects the interior tissues from external physical threats such as rain, hail and snow, and biological threats such as animals, insects, fungi and bacteria. Taken birch bark as an example, it is composed of densely interconnected, elongated cells, thus with large aspect ratio, forming multilayered structure^[16, 17]. The

* This work was supported by the Specialized Research Fund for the Doctoral Program of High Education (Nos. 20111102120050 and 20101102110035) and National Basic Research Program of China (No. 2010CB934700).

** Corresponding author: Long-cheng Gao (高龙成), E-mail: lcgao@buaa.edu.cn

Received September 5, 2012; Revised September 26, 2012; Accepted September 28, 2012

doi: 10.1007/s10118-013-1213-z

multilayered structure has high values of Young's modulus (0.94 GPa), ductility (100%), and toughness (4×10^4 J/kg), suiting for the maximum intensities of bending and twisting stresses at the curved surface. Furthermore, the bark is renewable with increasing circumference of the twig's axis. We learn from nature, utilizing a simple and common method to fabricate multilayers of flat montmorillonite (MMT) nanoparticles, which has excellent mechanical strength and toughness, large surface-area-to-mass ratios, imitating the stretched cells in the bark, and of poly(*p*-aminostyrene) (PPAS) as the stick of the building bricks. The technique is called layer-by-layer (LbL) assembly^[18]. Alternating monolayers are attracted to each other by electrostatic and van der Waals interactions^[10, 19, 20]. It could increase concentration of inorganic filler, while reduce the phase segregation and make composites highly homogeneous, with nanoparticles and polymers well dispersed and interpenetrated, resulting in high stiffness and tensile strength^[21-23]. It is worth noting that the multilayers are flexible due to noncovalent bonding^[24, 25], enabling the fibers woven avoiding crack. Silicate MMT is highly AO inert, and the compact assembly inhibits AO attack. As far as we know, this is the first time to use LbL technique to fabricate flexible multilayer coatings on fibers for testing the AO erosion durability.

EXPERIMENTAL

Polystyrene (PS) with molecular weight of $MW \approx 1.7 \times 10^5$ (Sigma-Aldrich) was used as received. Na⁺-montmorillonite (MMT) powder (Nanocor Corp.) was prepared and dispersed in deionized water under vigorous stirring for 1 week, then centrifugated under 4000 r/min before use. PPAS was synthesized by sequential nitration and reduction of PS. Degreasing cotton (Beijing Chemical Corp.) was treated as described in literature^[29].

In the deposition process, the positively charged cotton fibers were immersed into the following solutions alternately for 5 min periods: (a) the anionic MMT solution, (b) the deionized water, (c) the cationic PPAS solution and (d) the deionized water. This deposition cycle was repeated until 25-layer MMT/PPAS films were deposited on cotton fibers. Multilayer film coated cotton fibers were dried at 80°C in vacuum for 1 night.

The prepared multilayer coated cotton fibers as well as uncoated fibers were tested in the ground-based AO effects simulation facility at Beihang University. The configuration and characteristics of the facility were illustrated in references^[26]. In the experiment, fibers were placed on a circular holder at the facility with diameter of 160 mm, and one end was covered with a small metal screw cap in order not to be blown away during air charge. All samples were held at a vacuum level of 1.5×10^{-1} Pa with oxygen as the medium. The AO tests were conducted with a flux at the target of 3.6×10^{20} atoms/cm², which was calculated from the mass loss of the standard Kapton sample. The test periods were within 16 h. The mass change of all the samples was measured every 4 h using a DT-100 optical balance with a sensitivity of 0.5×10^{-4} g.

RESULTS AND DISCUSSION

We applied cotton fiber as the substrate of the multilayer coatings, for the consideration of its weak AO durability. In this case, we can easily estimate the AO shielding effect. In order to bind the multilayers successfully, pre-treatment of the hydroxyl group on the surface of cotton fibers with 2,3-epoxypropyltrimethylammonium chloride was carried on to create cationic charges. Then LbL assembly of oppositely charged MMT and PPAS surrounds the cotton fiber entirely (see Fig. 1a). Figure 1(c) shows SEM photograph of fiber coated with MMT/PPAS multilayers from side view. Dense and defect-free multilayers were successfully fabricated. MMT contour interlocking in the adjacent layers can be seen, due to the different MMT sizes, location and the curvature of the surface. The cross-sectional view of SEM photograph in Fig. 1(b) gives us clearly curved multilayer shell around the cotton fiber core, indicating the successful formation of birch bark-like protective multilayers. The coatings are flexible and stable at wide range of temperature. They can be bent arbitrarily even frozen in liquid nitrogen without break, crack or flaking off. Compared to the multilayer film fabricated on the flat substrate, the curved multilayers surrounding the fibers can be stuck tight once the entire film is completed.

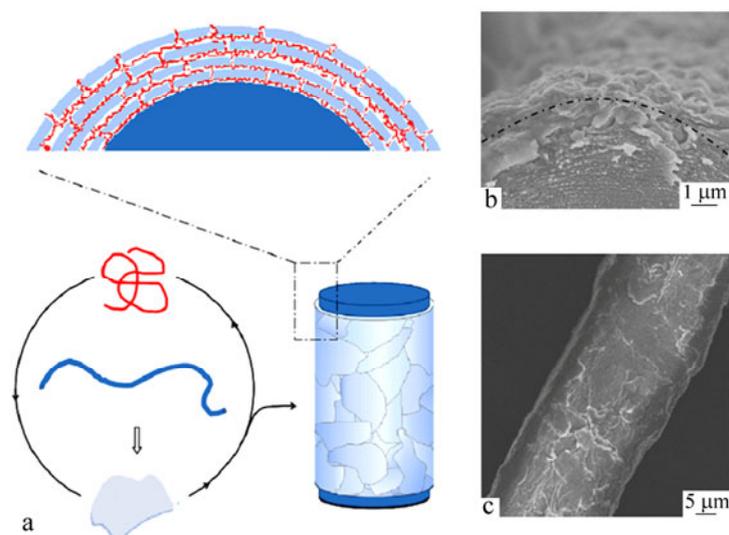


Fig. 1 Schematic procedure of multilayer-coated cotton fibers (a) prepared by cyclic deposition of anionic MMT and cationic PPAS onto the curved surface of cotton fibers; SEM photographs of the cross-sectional (b) and side-view (c) of the treated fiber indicating the successful formation of birch bark-like multilayers. The dashed line in (b) is the approximate interface between the cotton fiber and the multilayer coating.

The multilayer-coated cotton fibers and naked fibers without coatings were tested in the ground-based AO effects simulation facility^[26]. The normalized mass changes are shown in Fig. 2(a). For the naked cotton fiber exposed to the AO, the weight decreases dramatically with the erosion time increase. The organic matter is favorite reagent for AO. After 16 h of irradiation, the residual cotton is closed to zero (curve I in Fig. 2a). The SEM micrograph of cotton fiber surface after AO erosion is shown in Fig. 2(b). It is worth noting that the cotton fibers were so reactive that few fibers left after 16 h of erosion. We collected carefully small pieces of relics under the metal screw cap for SEM examination. The dramatic change in fiber diameter and numerous surface fragments indicated that the fiber was severely eroded by AO.

Compared to the mass loss of cotton fibers, the fibers coated with 25-layer MMT are much more stable in the same AO fluence (curve II in Fig. 2a). Most of the weight loss happened at the beginning, probably as a result of the outest PPAS layer, isolated fragments, contamination deposit in the composite. After this, the final weight remains approximately constant (*ca.* 92%), indicating that the left MMT multilayers provided excellent shielding from AO attack. SEM photographs show the details of the surface morphologies. One end of the fibers was not protected if cut by scissors before AO erosion. The inner cotton disappeared and the outer multilayers remained, forming a hollow pipe (Fig. 2c). From the image, we can calculate the thickness of the multilayer, which is around 350 nm. The physical dimension of the multilayer-coated fibers remained mostly intact. No apparent surface cracking or structural deterioration was observed. The wrinkle became more obvious from Figs. 2(d), and 2(e), because the PPAS interlayer was reactive to AO resulting in the mass loss, while the MMT part was chemically inert. The outside MMT nanosheet could prevent AO attack the PPAS inside, and PPAS provide the bond to the outside MMT nanosheet. Therefore, the AO is hard to reach deeply to oxidize the polymer. If MMT nano-sheets deposited on the surface isolated instead of inter-stack, they could be flaked off the surface. AO could attack the polymers below, resulting small shallow holes. However, this erosion could be stopped by the lower continuous inorganic layers, preventing the weak cotton from AO exposure. That's to say, the protecting layers can be self healed. MMT/polymer composites system with lower MMT content have been considered as AO shielding materials^[27, 28]. However, the high content of polymer provided more opportunities to react with AO resulting more mass lost.

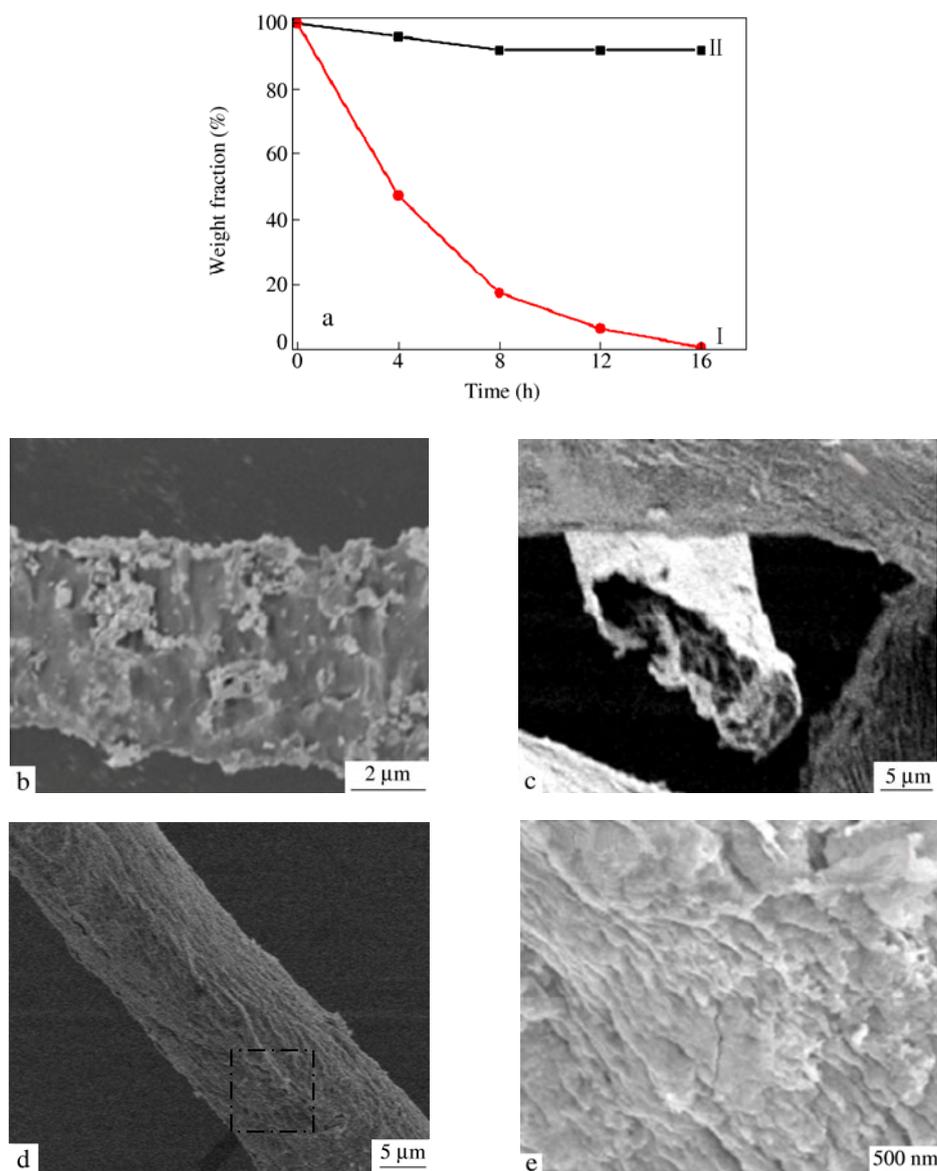


Fig. 2 (a) The weight fractions as function of AO erosion time of naked (I) and multilayers coated (II) cotton fibers, indicating excellent protection provided by the coatings; SEM photographs of the naked fiber (b) and multilayers coated cotton fiber (d) and (e) after AO erosion showing the surface morphologies eroded by AO attack; (c) SEM photograph of a hollow pipe obtained from a coated fiber with one of its ends exposed to AO

CONCLUSIONS

We successfully developed the *LbL* assembly of inorganic MMT nanosheet and PPAS on cotton fibers to form uniform, flexible and defect-free multilayers coatings, which was inspired by the multilayer structure of birch bark. The multilayer coatings have excellent stability at a wide temperature range and AO environment, so as to provide the inner cotton fiber core effective protection from AO attack. These results lead us to design new fibrous materials exposed directly in LEO environment, which can be tolerant of AO erosion.

REFERENCES

- 1 Masahito, T. and Kumiko, Y., *Acta Astronaut.*, 2008, 62(2-3): 203
- 2 Devapal, D., Packirisamy, S., Korulla, R.M. and Ninan, K.N., *J. Appl. Polym. Sci.*, 2004, 94(6): 2368
- 3 Packirisamy, S., Schwam, D. and Litt, M.H., *J. Mater. Sci.*, 1995, 30(2): 308
- 4 Smith, J.G. Jr, Connell, J.W. and Hergenrother, P.M., *Polymer*, 1994, 35(13): 2834
- 5 Smith, J.G. Jr, Thompson, C.M., Watson, K.A. and Connell, J.W., *High Perform. Polym.*, 2002, 14(2): 225
- 6 Gilman, J.W., Schlitzer, D.S. and Lichtenhan, J.D., *J. Appl. Polym. Sci.*, 1996, 60(4): 591
- 7 Devapal, D., Packirisamy, S., Nair, C.P.R. and Ninan, K.N., *J. Mater. Sci.*, 2006, 41(17): 5764
- 8 Yan, L., Gao, X., Bungay, C. and Woollam, J.A., *J. Vac. Sci. Technol.*, 2001, 19(2): 447
- 9 Jin, J., Smith, D.W. Jr., Topping, C.M., Suresh, S., Chen, S., Foulger, S.H., Rice, N. and Mojazza, B., *Macromolecules*, 2003, 36(24): 9000
- 10 Fischer, H.R., Tempelaars, K., Kerpershoek, A., Dingemans, T., Iqbal, M., Lonkhuyzen, H., van Iwanowsky, B. and Semprimoschnig, C., *ACS Appl. Mat. Interfaces*, 2010, 2(8): 2218
- 11 Connell, J.W., Smith, Jr J.G., Kalil, C.G. and Siochi, E.J., *Polym. Adv. Technol.*, 1998, 9(1): 11
- 12 Minton, T.K., Wu, B., Zhang, J., Lindholm, N.F., Abdulagatov, A.I., O'Patchen, J., George, S.M. and Groner, M.D., *ACS Appl. Mat. Interfaces*, 2010, 2(9): 2515
- 13 Gouzman, I., Girshevitz, O., Grossman, E., Eliaz, N. and Sukenik, C.N., *ACS Appl. Mat. Interfaces*, 2010, 2(7): 1835
- 14 Hu, L.F., Li, M.S., Xu, C.H., Luo, Y.M. and Zhou, Y.C., *Surf. Coat. Technol.*, 2009, 203(22): 3338
- 15 Lee, J.W., Ohlemacher, C.J., Krech, R.H., Watkins, A.N. and Yang, R.L., "Multifunctional fiber for space applications", 41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Tucson, Arizona, 2005
- 16 Xu, X., Schneider, E., Chien, A.T. and Wudl, F., *Chem. Mater.*, 1997, 9(9): 1906
- 17 Xu, X., Schneider, E., Zaremba, C., Stucky, G.D. and Wudl, F., *Chem. Mater.*, 1998, 10(11): 3523
- 18 Decher, G., *Science*, 1997, 277(5530): 1232
- 19 Picart, C., Mutterer, J., Richert, L., Luo, Y., Prestwich, G.D., Schaaf, P., Voegel, J.C. and Lavalle, P., *Proc. Natl. Acad. Sci. USA.*, 2002, 99(20): 12531
- 20 Liang, H.W., Liu, S. and Yu, S.H., *Adv. Mater.*, 2010, 22(35): 3925
- 21 Podsiadlo, P., Kaushik, A.K., Arruda, E.M., Waas, A.M., Shim, B.S., Xu, J., Nandivada, H., Pumphlin, B.G., Lahann, J., Ramamoorthy, A. and Kotov, N.A., *Science*, 2007, 318(5847): 80
- 22 Chen, S.F., Zhu, J.H., Jiang, J., Cai, G.B. and Yu, S.H., *Adv. Mater.*, 2010, 22(4): 540
- 23 Yu, S.H. and Yoshimura, M., *Adv. Mater.*, 2002, 14(4): 296
- 24 Kharlampieva, E., Kozlovskaya, V., Gunawidjaja, R., Shevchenko, V.V., Vaia, R., Naik, R.R., Kaplan, D.L. and Tsukruk, V.V., *Adv. Funct. Mater.*, 2010, 20(5): 840
- 25 Priolo, M.A., Gamboa, D., Holder, K.M. and Grunlan, J.C., *Nano Lett.*, 2010, 10(12): 4970
- 26 Zhao, X.H., Shen, Z.G., Yu, S.X. and Ma, S.L., *J. Phys. D: Appl. Phys.*, 2001, 34(15): 2308
- 27 Fong, H., Vaia, R.A., Sanders, J.H., Lincoln, D., Vreugdenhil, A.J., Liu, W., Bultman, J. and Chen, C.G., *Chem. Mater.*, 2001, 13(11): 4123
- 28 Awaja, F., Moon, J.B., Gilbert, M., Zhang, S., Kim, C.G. and Pigram, P.J., *Polym. Degrad. Stab.*, 2011, 96(7): 1301
- 29 Hauser, P.J. and Tappa, A.H., *Coloration Technol.*, 2001, 117(5): 282