Shielding Kevlar fibers from atomic oxygen erosion via layer-by-layer assembly of nanocomposites

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ABSTRACT

Highly uniform and defect-free multilayer coatings of montmorillonite (MMT) and poly (p-amino-styrene) (PPAS) on Kevlar fibers were generated to provide protection from atomic oxygen (AO) erosion, one of the greatest causes of degradation of polymeric materials used in the low earth orbit. The quantified protective MMT/PPAS layer was successfully deposited through a layer-by-layer assembly technique, as confirmed by Fourier-transform infrared spectroscopy and scanning electron microscopy. The accelerated AO durability was tested in a ground-based AO-effects simulation facility. The results show that the multilayers provide the Kevlar fibers an excellent protection from AO erosion.

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1. Introduction

Spacecrafts in a low earth orbit (LEO) encounter a number of different environmental factors, such as atomic oxygen (AO), vacuum ultraviolet radiation (VUV), thermal cycle, space debris, and the plasma environment (ions and electrons). Of these factors, AO is the one which causes the most severely damage to space materials [1,2]. AO is formed by the photodissociation of diatomic oxygen exposed to solar photons with a wavelength of less than 243 nm, and has a high chemical reactivity and high impinging energy (approximately 5 eV) [3,4]. Materials consisting of organic polymers are particularly susceptible to AO attack. When AO reacts with polymeric materials, volatile fragments, such as short-chain oxidation products, may leave the surface. The surface may also become populated with excited-state fragments, radicals, or polymeric molecules with oxygen-containing functionalities.

There are two principal methods to improve the tolerance of space materials against AO [2]. The first option is to design new kinds of polymers which either do not react with AO, or form an *in situ* self-protecting oxide coating so that the underlying materials are free of AO, such as silicon − [5–8] or phenylphosphine oxide

(PPO)-containing (co)polymers [9–11]. However, during the formation of such a self-coating layer, density differences may cause the coating to shrink. Local shrinkage generates a microporous structure which slows but does not stop oxidation. Furthermore, macroscopic shrinkage stresses the coating, causing crack formation. Fluorinate-containing polymers have also been considered [10,12], and have been shown to have low, but non-negligible, erosion yields because oxidation of the C−F bond is endothermic.

The second, and most common, option to improve AO tolerance is to introduce inorganic coatings onto the surface of the polymeric materials. Aluminum oxide or converted aluminum oxide [13–15], silicon oxide or converted silicon oxide [16,17], and phosphorous nickel [18], etc. have been used as protective coatings. To provide maximum protection, the coatings should be relatively uniform and defect free. However, inorganic coatings have a tendency to crack due to their poor flexibility. Special care must therefore be taken during the procedure.

The Kevlar fiber has a distinct chemical composition consisting exclusively of aromatic polyamides, and possesses a unique combination of high tensile strength and modulus, toughness, and thermal stability. Kevlar fiber is extensively used for light weight composite structures for space applications. However, without treatment, Kevlar fibers can be severely eroded by AO (up to approximately $2 \sim 4 \times 10^{-24}$ cm^3/atom) [19], including changes of optical properties and surface morphology, loss of mass and

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mechanical strength, according to the post-flight research [20]. To improve Kevlar fiber compatibility with the AO environment in LEO, protective coatings are required.

In this work, a simple and common method was used to create thin films of montmorillonite (MMT) and poly(*p*-aminostyrene) (PPAS) on Kevlar fibers. The technique is known as layer-by-layer (LbL) assembly [21–23]. In our previous work, we fabricated LbL assembled MMT/PPAS multilayers on the cotton fiber surface to evaluate the effect of shielding AO erosion [24]. Alternating layers of clay nanosheets and polyelectrolytes are attracted to each other through electrostatic and van der Waals interactions [25–28]. The resulting multilayer film has relative flexibility and high strength [29–32]. Although the nanoparticle content are very high, the phase segregation is suppressed and the composites show highly homogeneous nature. Furthermore, MMT has a high oxygen-to-silicon ratio, which has shown greater resistance to AO attack [33]. When the MMT nanosheets assemble together, they form a tight structure, with only a small space between adjacent nanosheets. Therefore, multilayers could provide Kevlar fibers with high durability against AO. A simple and common method (LbL assembly) was used to create thin films of MMT and PPAS on Kevlar fibers to shield against AO erosion.

2. Experimental parts

2.1. Materials

Polystyrene (PS) with molecular weight of MW $\approx$ 170,000 was purchased from Sigma–Aldrich and used as received. Na^+-Montmorillonite powder (Nanocor Corp.) was dispersed in deionic water under vigorous stirring for 1 week, then centrifugated under 4000 rpm before use. PPAS was synthesized by sequential nitration and reduction of PS [34]. Kevlar fiber was purchased from XuanYue Science & Technology New Materials Co. Ltd. and the pre-treatment was used a chemical modification procedure described in literature. Kevlar fibers were positively charged with amino groups by nitration and subsequent reduction of nitro groups [35]. Briefly, Kevlar fibers were put into solution (30/70 by volume) of concentrated H_2SO_4 (98%) and HNO_3 (65%) at 45 °C for 12 h, then washed by water. After this, the reduction procedure was taken by $SnCl_2/HCl$ solution at 60 °C over night.

2.2. Buildup of multilayered films on Kevlar fibers

In the deposition process, the positively charged Kevlar 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; (d) the deionized water. This deposition cycle was repeated until 25-layer MMT/PPAS films were deposited on Kevlar fibers. Multilayer film coated Kevlar fibers were dried at 80 °C in vacuum for 1 night.

SEM images of samples were taken on Hitachi S-4800, with an accelerating voltage of 5 kV. FTIR spectra were measured with a Magna-IR 750 in ATR model with wave number of 4000 ~ 650 cm^{-1}. Thermogravimetric analysis (TGA) of Kevlar fibers (unmodified) and multilayer-coated fibers were performed with a Q600 SDT instrument at heating rates of 20 °C/min under an air atmosphere. The AO durability of the fibers was tested in the ground-based AO effects simulation facility at Beihang University. The configuration and characteristic of the facility were illustrated in Ref. [36] 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 blew 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/cm^2, 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 0.00005 g.

3. Results and discussion

As described above, Kevlar fibers, like other polymeric materials, can be eroded in an AO environment. In order to bind the multilayers successfully, amino groups were introduced onto the surface of the Kevlar fibers by nitration and subsequent reduction of the nitro groups. The LbL assembly of oppositely charged MMT and PPAS was carried out surrounding the Kevlar fiber entirely. Fourier-transform infrared (FTIR) spectroscopy was used to verify protected multilayers. From the FTIR spectrum of pure Kevlar fibers (Fig. 1), a characteristic peak at approximately 825 cm^{-1} can be seen, corresponding to the out-of-plane C–H vibration, as well as peaks at 1018 cm^{-1} reflecting the in-plane aryl C–H vibration, 1651 cm^{-1} representing the C=O stretching frequency, and 3319 cm^{-1} corresponding to N–H stretching frequency. These peaks are also visible in the spectra of the multilayer-coated Kevlar fibers. For pure MMT, the band near 3350 cm^{-1} has been assigned to the stretching vibrations of structural OH groups attached to either Al^{3+} or Mg^{2+}. Furthermore, the peak at 888 cm^{-1} has been specifically assigned to OH groups attached to Fe^{3+} ions [37]. These peaks remain visible in the multilayer-coated Kevlar fibers after AO erosion, indicating the successful introduction of the MMT onto the fiber surface. Although the characteristic peaks from the vibration frequencies of PPAS/MMT are not evident, the presence of a loose covering across the fiber surface is not possible, because such a loose structure would be removed in the sequent water washing procedure.

Fig. 2A shows a scanning electron microscope (SEM) image of a fiber coated with MMT/PPAS multilayers from the side view. Dense and defect-free multilayers were successfully generated. MMT nanosheets deposited randomly on the surface of the Kevlar fiber, due to the MMT nanosheets shared diverse sizes, locations, and positions. A curved surface is also seen, indicating that the MMT nanosheets incurvated to adapt to the topographical fiber surface. Fig. 2B shows the cross-sectional view of SEM photograph. The cross-section was obtained by cutting the liquid nitrogen-frozen samples with scissors. It gives us clearly that the bent multilayers cover the Kevlar fiber, indicating the successful formation of multilayers. Furthermore, the multilayer coatings are flexible and stable, even in the severe condition of liquid nitrogen.
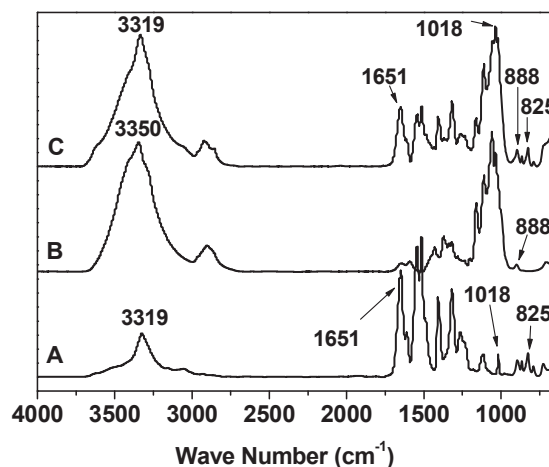

Fig. 1. FTIR spectra of Kevlar fibers (A), pure MMT (B), and MMT/PPAS multilayer-coated Kevlar fibers after AO erosion (C).
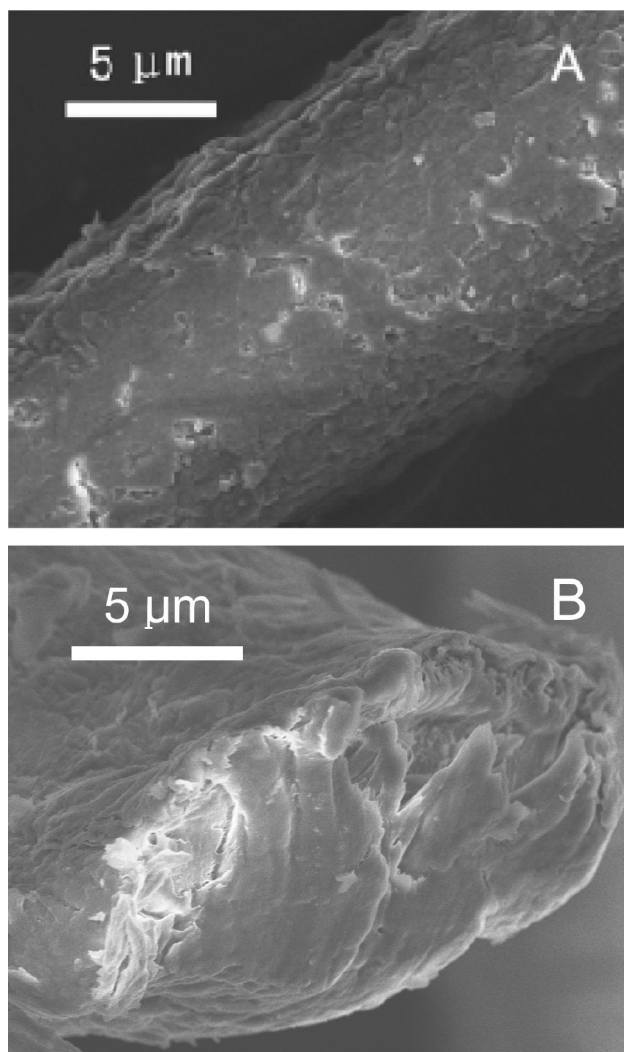
Fig. 2. (A) SEM image of side-view of multilayer MMT/PPAS-coated Kevlar fiber, indicating the successful creation of a protective coating on the fiber surface. (B) SEM image of cross-sectional multilayer MMT/PPAS-coated Kevlar fiber, indicating the flexibility of the multilayer.

Thermogravimetric analysis (TGA) curves of Kevlar fibers (unmodified) and multilayer-coated fibers obtained at heating rates of 20 °C/min under an air atmosphere are shown in Fig. 3. For Kevlar fibers, a single-stag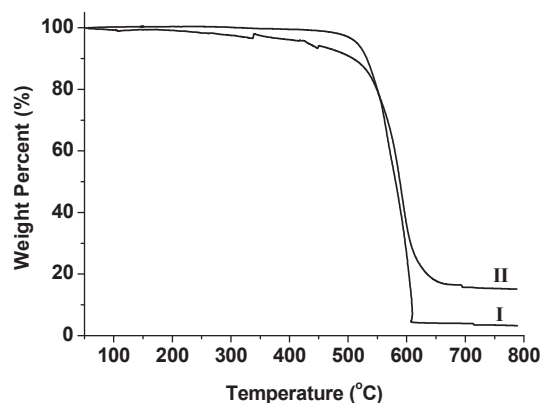e degradation process is indicated. The residual mass at an ultimate temperature of 800 °C is close to zero. The multilayer-coated fibers have similar a degradation process, although the 5% weight loss temperature is lower. However, the residual mass of the multilayer-coated fibers after degradation is much higher than that of the Kevlar fibers (15%) due to the inorganic component. From this point of view, the total content of inorganic component in the multilayer-coated fibers is about 15%.

The Kevlar fibers and multilayer-coated fibers were tested in a ground-based AO-effects simulation facility. The normalized mass changes are shown in Fig. 4. For the Kevlar fiber exposed to AO, the weight decreases approximately linearly with increasing erosion time. After 16 h of irradiation, with an AO flux of approximately 3.6×10^{20} atoms/cm^2, as calculated from the mass loss of the standard Kapton sample, the residual percentage is approximately 27%. SEM micrographs of unmodified Kevlar fiber surface after AO erosion are shown in Fig. 5A. The dramatic change in fiber diameter and the roughness of the surface indicate that the fibers were severely eroded by AO.

However, multilayer-coated fibers were much more stable than the uncoated fibers in the same AO fluence (see Fig. 4-II). Most of the weight loss occurred at the beginning, as a result of the priority reaction with the surface organic matter, or release of isolated fragments. After this, the total weight remained almost constant (at approximately 88% compared with the original weight), indicating that the residual MMT multilayers provided excellent shielding from AO attack. Fig. 5B shows SEM photograph of a multilayer-coated Kevlar fiber after AO erosion. The physical dimensions of the protected fibers are mostly intact. No apparent surface cracking or structural deterioration is observed, consistent with the results from the ground-based AO-effects simulation facility. However, there are isolated fragments which seem to be detached from the Kevlar fiber. The fragments may be resulted from the loose aggradation of excess MMT, leading to weight loss upon AO attack. Nevertheless, the multilayers below remain intact. Therefore, we concluded that the MMT/PPAS multilayer provided excellent protection from AO erosion. AO-inert MMT nanosheets overlapped each other with a single layer PPAS spacer, and the AO could not enter inside. Instead, AO mostly rebound from the MMT layer. Thus, the underlying Kevlar fiber was free of AO attack.

As mentioned above, Kevlar fibers are not resistant to AO erosion. The organic component reacts with AO and is released from the surface, resulting in dramatic loss of weight and mechanical strength. By applying the LbL technique to generate MMT/PPAS multilayers onto the Kevlar fiber surface, a robust protection is formed. AO is blocked by the coating, and dissipated.
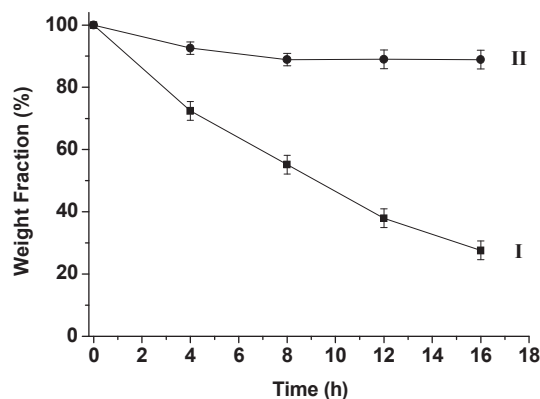

Fig. 3. Thermogravimetric analysis curves of Kevlar fibers (I) and multilayer-coated fibers (II) under an air atmosphere (20 °C/min).

Fig. 4. Weight fractions of Kevlar fibers (I) and multilayer-coated fiber (II) versus AO erosion time, indicating that the multilayer coatings provide excellent protection from AO erosion.
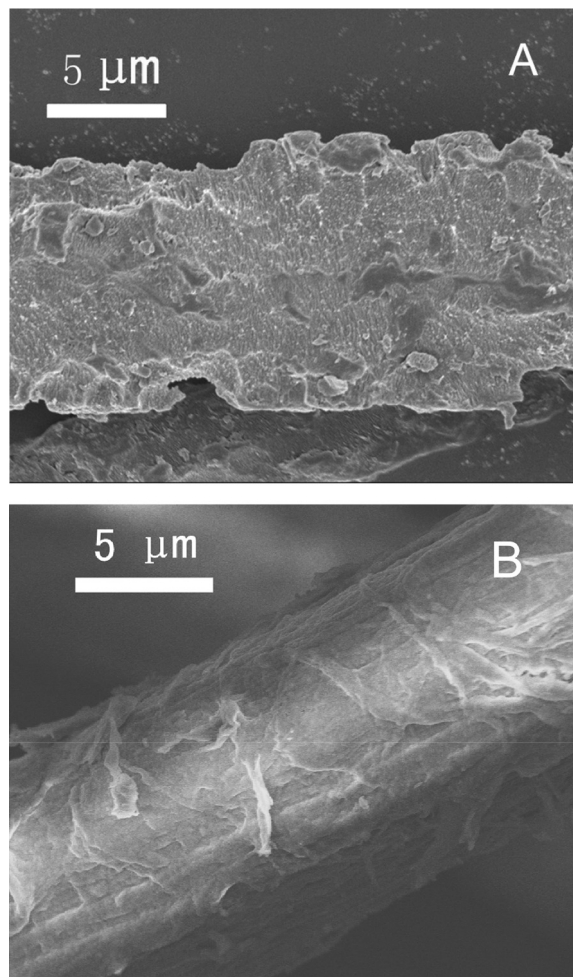
Fig. 5. (A) SEM image of a Kevlar fiber (unmodified) after AO exposure, showing severe erosion by AO attack. (B) SEM image of a multilayer MMT/PPAS-coated Kevlar fiber after AO attack, demonstrating the excellent protection provided by MMT/PPAS multilayers.

4. Conclusions

In conclusion, an LbL-assembly technique has been applied to coat MMT/PPAS multilayers onto the surface of Kevlar fibers. The multilayers provide an excellent AO-shielding effect. Fibers with no such multilayer protection were severely eroded by AO, causing dramatic weight loss and formation of a rough surface. When the fibers were coated with flexible MMT/PPAS multilayers, AO was not able to penetrate and react with the fibers, and was reflected away.

These results provide a potential route to the direct application of Kevlar fibers in the LEO environment. Furthermore, other polymeric fibers bearing high strength and low weight, such as polybenzoxazole (PBO), polyimide (PI), and polybenzimidazole (PBI), may be protected using the LbL method.

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