

Improved Atomic Oxygen Resistance in Polyimide/Graphene Oxide Composite Films via Mechanical Mixing

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Abstract

PI composite films with different GO loading(0, 0.1wt%, 0.2wt% and 0.5wt%) were prepared via mechanical mixing and hot compression. With a tiny addition (0.5wt%) of GO, AO resistance property of PI films was obviously improved by approximately 20%. At the same time, thermal stability and mechanical properties of composite films were increased: the temperature of mass residue at 95%(T_{d95}) of PI/GO(0.5wt%) films was 519°C, 14°C higher than that of pure PI; tensile strength and Young's modulus were improved by 3.3MPa and 0.1GPa, respectively. By means of a simple blending and compression method, PI/GO films demonstrated excellent comprehensive properties. Compared with in situ polymerization, our method is much easier to operate and control, which make it possible for manufacturing PI/GO films on a large scale.

Key words: Graphene oxide; Polyimide; Atomic oxygen; Mechanical mixing.

Introduction

In low earth orbit (LEO) environment, atomic oxygen (AO) is a threat to the mechanical and chemical properties of polymers used on aircrafts. Polymers exposed directly to a LEO environment collide with AO at spacecraft velocities of about 8 km/s. The translational energy of this kind of collision is approximately 5eV, which substantially erodes polymer surfaces. Eventually, the polymers lose their mass and exhibit a rough texture,^[1] leading to the failure of space missions.

Polyimides (PIs) have characteristics of high thermal stability (>300°C), high glass transition temperature (T_g >200°C), high tensile strength, etc., which make them attractive materials for aeronautics and space structural components.^[2] However, pure PIs, are easily eroded by AO, which greatly limits their long-term applications in LEO environment. Researchers have done amounts of work to improve AO resistances of PIs. Addition of thin films as overlay protective coatings have been considered to be the simplest method. Many types of protective coatings such as SnO₂, Al₂O₃ or SiO₂ have been proposed.^[3] However, this method is not so reliable since pinholes and cracks in the protective coatings are easily introduced, leading to the undercutting or damages.^[4] To find out a more effective solution, a new concept by developing PI films with "self-healing" ability in AO environments was proposed. Based on this concept, a series of inherently AO-resistant PIs has been reported. Typically the ones contain some organic molecules like polyhedral oligomeric silsesquioxane (POSS) and phenylphosphine oxide (PPO)^[5, 6] or some metal oxide like Al₂O₃, SiO₂ and ZrO₂^[7, 8]. They are often prepared via in situ polymerization, which ensures the strong interaction between PI and additives, and desirable endurance in the AO environment. However, the process of synthesis is always complicated and hard to control, and AO resistance needs to be further improved, too. Therefore, simple methods and new additives with better properties are still under investigation.

As the precursor of chemically converted graphene, graphene oxide (GO) is generally prepared by oxidation of graphite and given an abundance of oxygen-containing groups, which enables

modification of GO sheets with desirable molecules or polymers covalently^[9]. There have been many reports about the brilliant performance of PI/GO composites, such as massively increased thermal, mechanical and dielectric properties.^[10-12] Moreover, certain types of PI/GO composites even have marvelous shape memory properties^[2] or act as electromagnetic interference shielding^[13]. Owing to their extraordinary properties, PI/GO composites have been placed high hopes in space areas. Certainly, AO resistance have to be considered firstly. To the best of our knowledge, there have been barely any reports about the influence of GO on the AO resistance of PI. Zhang et al.^[14] added GO into epoxy resins and found out that the AO resistance of composites was improved obviously. The result naturally inspires that GO perhaps may have the same effect on PI.

In this work, PI films with different GO loading were prepared simply by mechanical mixing and hot compression. AO resistance of PI/GO composite films was tested in ground simulation AO environment. Thermal stability and mechanical properties were also investigated.

Experimental

Polyimide (YGPI-M-200) was purchased from Changchun Gaoqi Polyimide Material Co., Ltd. (Changchun, China) and used as received. Graphite was purchased from Qingdao Haida Graphite Co., Ltd. (Qingdao, China) and used as received.

Graphene oxide was synthesized from graphite powder via modified Hummers method.^[15] Neat PI and PI/GO films were prepared by mechanical mixing and hot compression. Specifically, 60g PI/GO compounds with different GO loading (0, 0.1wt%, 0.2wt%, 0.5wt%) were mixed in mill at the speed of 5500 r/min for 30 minutes, to ensure the GO uniformly dispersed in PI. PI/GO composites were mechanically pressed at the pressure of 10 MPa and the temperature of 300 °C for 5 minutes; subsequently, pressed at the pressure of 10 MPa and at room temperature for another 5 minutes before PI/GO films were finally prepared.

The thermal properties of PI/GO films were tested by Thermo gravimetric Analyzer (TGA) (Q50, TA, US) in nitrogen from room temperature to 800 °C at a heat ramp of 20 °C·min⁻¹. The mechanical properties of PI/GO composite films were measured by computer-controlled electronic tensile testing machine (CMT3502, Sansi, China) according to GB/T 1040-92. Ground-based AO exposure measurements of PI/GO films were performed on a combined space effects testing facility equipped with neutral AO beam and vacuum ultraviolet ray (VUV) sources. All samples were handled in vacuum chamber and irradiated to various AO fluences at 4.40 atomscm⁻² (Exposure time were 5h). Surface morphologies of PI/GO films before and after AO exposure were observed by a Scanning Electron Microscope (SEM) (MERLIN, Carl Zeiss AG, Germany).

Results and Discussion

1. Atomic Oxygen Resistance

Mass loss (normalized to the surface area) of PI/GO films in simulated AO environment are presented in Table 1. As indicated, at a given AO fluence (4.4×10^{19} atomscm⁻²), PI/GO films exhibits less mass loss than pure PI films. And, the more the GO loading, the less the mass loss. After being exposed in AO environment for 5h, the weight of PI films with 0.5wt% GO lose only 5.79mg, about 20% less than that of pure PI. This AO resistance property of PI/GO films is comparable to that of the POSS hybrid PI films prepared by in situ polymerization at the same concentration of additives.^[16] In situ polymerization, although ensuring better dispersion of additives, is complicated to operate and difficult to repeat or yield on a large scale. Instead, our method, i.e., mechanical mixing and hot

compression, is much simpler and can still achieve a desirable result.

Table 1. Mass loss of PI/GO composite films after exposure under AO environment for 5 h

GO content /wt%	Mass loss/mg	Normalized mass loss/%
0	7.05	100.00
0.1	6.51	92.33
0.2	6.27	88.89
0.5	5.78	82.05

To further confirm the mass loss of PI/GO films, surface morphologies of PI membranes before and after AO exposure are observed by SEM, as shown in Figure 1. The surface morphologies of all the samples have changed significantly, from flat appearance before exposure in AO environment to “carpet-like” appearance afterwards, because of AO erosion. Moreover, PI/GO films demonstrate less and smaller erosion areas than pure PI film, suggesting that the addition of GO has a positive effect on maintaining the surface topography. And, with the increasing GO content, AO survivability of composite films is further improved. GO is an impermeable sheet with large surface and high aspect ratio. When dispersed in polymer matrix, it may form a large number of curved paths, delaying AO from diffusing in the matrix, on one hand. On the other hand, GO can easily react with AO to form some epoxy bonds with high covalent bond energy, which may defend the attack of AO. As a result, PI/GO films exhibit better AO resistance and less mass loss after exposure in AO environment.

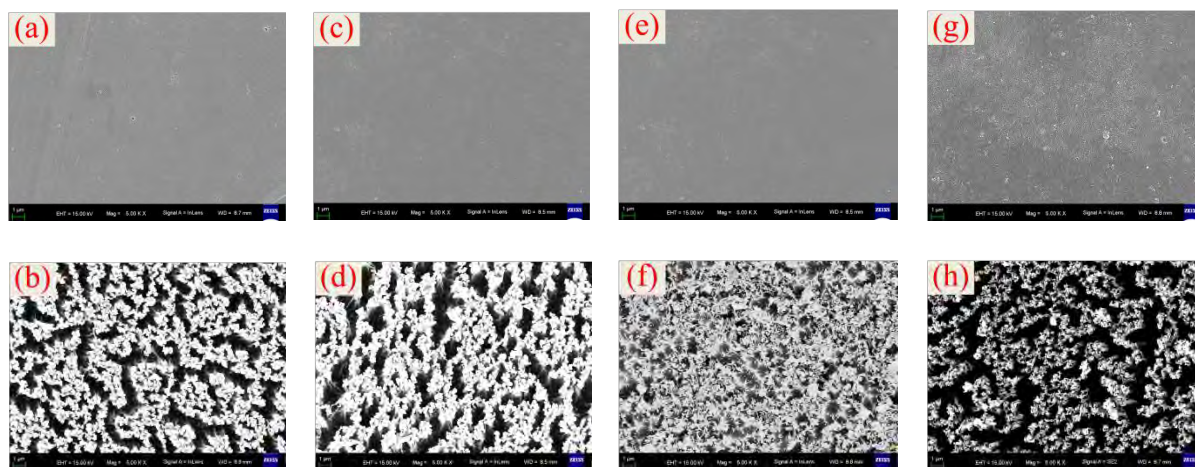


Figure 1. SEM images of PI/GO films before (a: pure; c: 0.1wt% GO; e: 0.2wt% GO; g: 0.5wt% GO) and after (b: pure; d: 0.1wt% GO; f: 0.2wt% GO; h: 0.5wt% GO) AO exposure for 5h.

2. Thermal Stability

Excellent thermal stability of PIs ensures the long-term usage in space environment. T_{d95} and mass residue at 800 °C of all the samples are listed in Table 2. As shown, T_{d95} of PI/GO films increase with the increase of GO content. Specifically, T_{d95} of PI films with 0.5wt% GO loading is 519°C, 14°C higher, compared to that of pure PI films (505°C). The mass residue of PI/GO films also increase with the GO content. Figure 2 shows the normalized mass evolution of PI/GO films with the increasing temperature. It can be seen that the decomposition of PI/GO films have been postponed with the addition of GO. In the PI matrix, GO network can act as a free radical scavenger to adsorb free radicals, thereby delaying the occurrence of thermal degradation; furthermore, GO has a high thermal

conductivity, which would help cool down the matrix and slow down the rise of temperature.^[17, 18]

Table 2. T_{d95} and mass residue at 800 °C of PI/GO films.

GO content/wt%	$T_{d95}/^{\circ}\text{C}$	Mass residue at 800°C/%
0	505	52.59
0.1	513	52.74
0.2	517	53.17
0.5	519	54.12

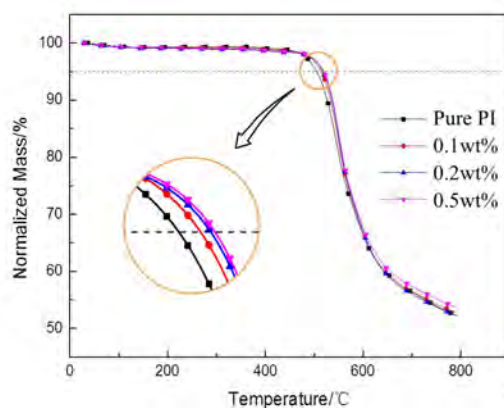


Figure 2. Normalized mass changes of PI/GO films with the increasing temperature.

3. Mechanical Properties

The tensile strength, Young's modulus and elongation at break of all the samples are summarized in Figure 3. GO is an inorganic rigid material with excellent mechanical property. When added into PI matrix, it can obviously improve the tensile strength and mechanical modulus.^[11] Analogical results are also found in our case. All the PI/GO films demonstrate the improved mechanical properties, compared to pure PI film, although the mechanical properties slightly drop when the GO content increases from 0.1wt% to 0.5wt%. This may be due to the inherent rigid structure of GO or the weak interface between GO and PI.

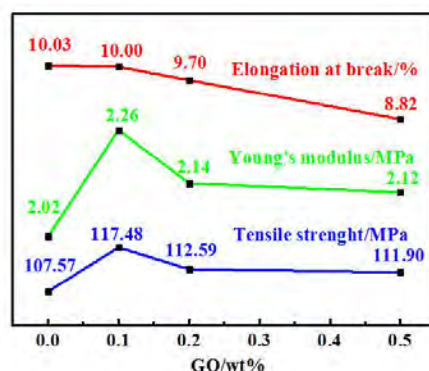


Figure 3. Tensile strength, Young's modulus and elongation at break of PI/GO composite films.

Conclusions

PI composite films filled with different GO loading (0, 0.1wt%, 0.2wt% and 0.5wt%) were prepared via mechanical mixing and hot compression. The PI/GO films demonstrated excellent AO

resistance property, thermal stability and mechanical properties. When the GO content is 0.5 wt%, AO resistance property was improved by approximately 20%; T_{d95} had an 14 °C improvement; tensile strength and Young's modulus were increased by 3.3MPa and 0.1GPa, compared to pure PI film. In our future work, we consider to add more GO to PI matrix to further promote the comprehensive properties of PI/GO composite films.

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