European Polymer Journal 105 (2018) 115–125

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Enhanced resistance to the atomic oxygen exposure of POSS/polyimide composite fibers with surface enrichment through wet spinning

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ARTICLE INFO

Keywords:
Polyimide fibers
Polyhedral oligomeric silsesquioxane
Atomic oxygen
Surface enrichment

ABSTRACT

We report a series of PI composite fibers containing polyhedral oligomeric silsesquioxane (POSS). These fibers were fabricated by a three-step process consisting of the in situ polycondensation of POSS and polyamic acid, wet spinning, and thermal imidization. X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy proved that POSS enriched the surface of POSS/PI composite fibers during wet spinning. This surface enrichment enhanced the resistance to atomic oxygen (AO) erosion. After exposing the POSS/PI composite fibers to AO fluence up to 2.93×10^{20} atoms cm^{-2}, the fibers still displayed excellent AO resistance. With increased POSS content from 0 wt% to 20 wt%, the retention of fracture strength and initial modulus considerably improved from 54% to 93% and from 64% to 91%, respectively. Moreover, the decay rates of fracture strength of the composite fibers obviously decreased at the same AO fluence with increased POSS content from 0 wt% to 20 wt%. AO erosion at a larger fluence further resulted in more effective AO resistance for composite fibers with higher POSS content. XPS results suggested as well that silicate passivated layers formed on the fiber surfaces after AO exposure, and these layers prevented the fibers from further AO erosion.

1. Introduction

Polymeric fibers and fabrics have been applied extensively to the flexible construction elements of spacecraft mounted on their external surfaces. Such elements include different fastener assemblies, tensional cables, flexible sheetings and screens, railings, and safety lines used by astronauts [1,2]. These polymeric fibers are subjected to high-energy atomic oxygen (AO) attack (~4.5 eV) in low Earth orbit (LEO), which is the dominant composition of the upper atmosphere of Earth in the altitude between 200 and 700 km [3]. Such attack causes the rapid degradation of polymer materials and leads to hazards on the mechanical properties [4–9]. The resistance of polymeric fibers to AO attack can be improved by utilizing AO-durable coatings, such as SiO_2, Al_2O_3, or SnO_2 [10–13]. However, these inorganic coating materials are prone to crack and even peel off from the fiber surface during thermal cycling, folding, or bending because of the insufficient adhesive strength and the difference in thermal expansion coefficients between the inorganic coatings and polymeric fibers [14]. The cracks in the coating allow AO to attack the underlying polymeric fibers and can result in undercutting phenomena, and ultimately, mechanical failure of the polymeric fibers.

A promising approach for producing LEO survivable polymeric fibers is incorporating oxidation-resistant nanoscale components in the form of additives into the polymer matrix. Polyhedral oligomeric silsesquioxane (POSS, empirical formula $RSiO_{1.5}$) are ideal candidates for this approach [15–19]. POSS-containing polymer nanocomposites have shown significantly lower AO erosion yields versus pure polymer. In Minton's study [16], POSS was incorporated into the main chain and side chain of polyimide (PI) backbone to produce two types of POSS/PI. After AO erosion, these two types showed similar resistance performances. Depending on the weight percentage of the POSS cage, the erosion yield of the POSS/PI may be as low as ~0.01 that of the pure PI (or Kapton H). With a hyperthermal AO fluence of 2.70×10^{20} atoms cm^{-2}, the erosion yields of 7.0 wt% Si_8O_{12} side chain POSS/PI and 7.0 wt% Si_8O_{11} main chain POSS/PI were 0.15 and 0.13×10^{-24} cm^3 $atom^{-1}$, respectively. According to Lei's report [20], POSS modified by two amine was copolymerized with 4,4′-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) to prepare POSS/PI. The composites containing 29.7 wt% POSS showed the lowest erosion yield of 0.9×10^{-25} cm^3 $atom^{-1}$. The as-prepared POSS/PI copolymers not only manifested excellent AO resistance but also displayed good thermal and mechanical properties. Nevertheless, the preparation process was complicated, difficult to operate, and relatively costly. In this regard, Qian et al. [17] prepared several trisilanolphenyl (TSP) POSS/PI blends with different contents of POSS, and the AO resistance of the

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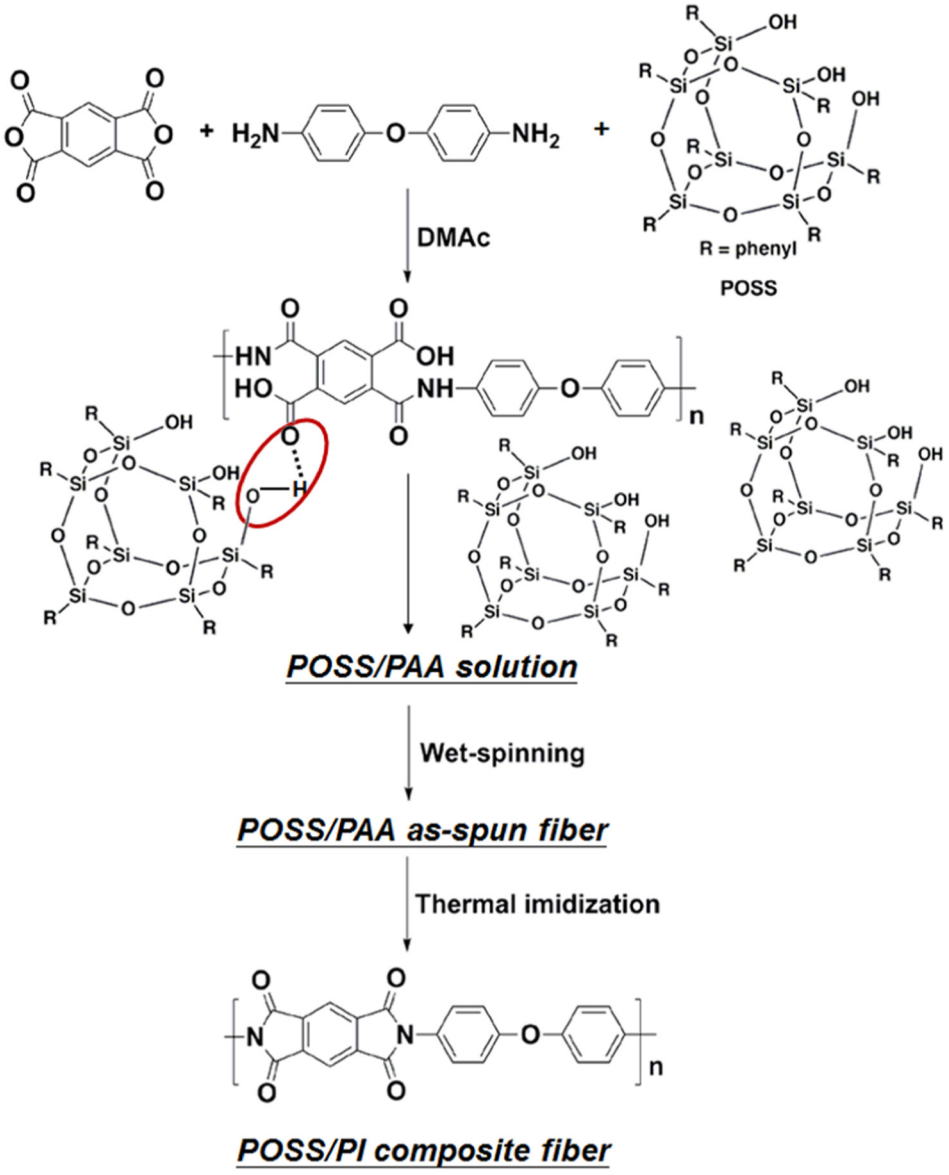
https://doi.org/10.1016/j.eurpolymj.2018.05.022
Received 23 March 2018; Received in revised form 17 May 2018; Accepted 20 May 2018
Available online 21 May 2018



Scheme 1. Synthetic route of POSS/PI composite fibers.

blends and POSS/PI copolymers was further investigated. For all POSS/PI materials, the AO resistance increased with increased POSS cage loading, which became more effective at higher AO fluence. Under similar POSS cage loadings and exposure conditions, the TSP POSS/PI blends showed comparable erosion yields to the POSS/PI copolymers, with specific samples of blends and copolymers achieving erosion yields as low as $0.066 \times 10^{-24}\,cm^3\,atom^{-1}$ with an AO fluence of $5.93 \times 10^{20}\,atoms\,cm^{-2}$.

A major challenge in the development of polymer nanocomposites is the control of nanoparticle dispersion in polymer matrix [21,22]. However, these studies essentially focused on the efficient and homogenous dispersion of nanoparticles within a whole matrix and the suppression of aggregation of a nanoparticulate phase; scarce literature reported on utilizing enrichment in polymer/nanoparticle nanocomposites to create surfaces with specific morphologies [23,24]. Certain applications can benefit from the targeted arrangement of nanoparticles on polymer surfaces [25]. The ideal situation for the resistance to AO erosion involves the nanoparticles being confined to the polymer surface.

Surface enrichment in melt-blended POSS/polymer nanocomposites has been reported [26]. Researchers demonstrated that the surface enrichment of POSS nanoparticles helps improve the surface hydrophobicity and tribological properties of POSS/polymer nanocomposites by annealing the melt and heating the solid blend [27]. POSS nanoparticles show preferential enrichment to air–polymer interfaces, which are driven by low surface energy, and the formation of larger aggregates at the surface than in the bulk [28,29]. However, the majority of these studies to date have focused on polymer bulk and film materials [30]. Only few works centered on nanoparticle dispersion and morphological evolution in polymer fibers during wet spinning, which is commonly utilized in high-performance fiber manufacturing for materials such as aramid, poly(p-phenylenebenzobisoxazole), carbon, and PI fibers. In wet spinning, the dual diffusion of the solvent and nonsolvent between the fresh fluid filament and the coagulation bath cause the polymer solidification, which is the fundamental process governing the fiber structure [31,32]. The migration of POSS in nanocomposites may be driven by the counter diffusion of solvent and nonsolvent, which are totally different from the surface enrichment of the POSS in melt-blended POSS/polymer nanocomposites.

Aromatic PI fibers are desirable spacecraft materials because of their excellent thermal stability, chemical resistance, and outstanding mechanical properties [33–38]. However, PI fibers are eroded significantly