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Preparation and atomic oxygen erosion resistance of silica films formed on polymethyl methacrylate by solvothermal method

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ABSTRACT

Silica films were prepared on the surface of polymethyl methacrylate (PMMA) via sol solution and solvothermal treatment, after modifying the surface of PMMA by solvothermal method. The samples were irradiated by atomic oxygen in a ground-based simulation system. The surface morphology and structure of silica films were investigated by atomic force microscopy, scanning electronic microscopy and attenuated total reflectance-Fourier transformed infrared spectroscopy. In addition, dry and wet thermal cycling tests were performed to investigate the adhesion behavior of silica films on PMMA. The results indicated that a uniform film was easily formed on the surface of PMMA. After atomic oxygen exposure, the silica film becomes more compact, without peeling off, and has good optical transparency.

1. Introduction

Polymethyl methacrylate (PMMA) as an excellent optical polymer has widespread applications in both everyday life and high technologies because of its unique properties, including lightweight, optical transparency, mechanical properties and ease in mass production [1,2]. However, its relatively low abrasion resistance and environment degradation have hindered many important applications. In low earth orbit (LEO) environment, especially, the polymer may suffer accelerated erosion by atomic oxygen (AO). AO attack can cause severe surface degradation of polymers due to its high-chemical reactivity and high-impinging energy, which may significantly affect the performance of spacecraft. Researches have shown that AO is the most prevalent of the atmospheric species in LEO atmosphere and polymers may fail to function due to the AO erosion [3–5]. The excellent optical property of PMMA has long been a focus of aerospace researchers, but the presence of AO in LEO environment has limited its application. The most common method used to overcome this limitation is to apply inorganic coatings on the surface of PMMA [6]. The oxide film such as SiO_2 or Al_2O_3 is typically used as AO protective coatings due to its high stability under oxidation environment.

A number of film deposition techniques have been employed to form inorganic coatings on the polymers. Vapor phase techniques, such as evaporation, sputtering and chemical vapor deposition, produce high quality films, but they are expensive, requiring sophisticated vacuum equipment, and often require substrates to be maintained at high temperatures. In addition, uniform coatings of complex-shaped substrates are difficult with line-of-sight vacuum techniques [7,8]. To solve this problem, various solution deposition techniques have been extensively studied for the deposition of oxide or oxide-based coatings on complex shaped substrates. Comparatively, sol–gel method is a simple and inexpensive technique for preparing coatings, and is especially suitable for application on complex shapes [9,10]. However, post deposition heat treatment at elevated temperatures is required to convert the porous structure to a dense coating in the sol–gel preparation of silica coatings on PMMA substrates [11]. Because PMMA substrates have poor high temperature resistance, the heat treatment of the coatings must be kept at about 80 °C, which is lower than the glass transition temperature of PMMA. Heat treatment at 120 °C for longer than 5 min could not be carried out because the PMMA substrate exhibited viscous flow [12]. This means that the formation of dense silica coatings on PMMA substrates is very difficult by direct heat treatment of the silica gel coatings. Therefore, development of a process with a relatively low temperature for densification may be more favorable. On the other hand, the instability of adhesive bonding at the interface between the coating and the polymer surface is also a problem to be solved. Polymer surfaces have been proved to be technically difficult to deposit oxide or oxide-based coatings directly on them, leading to necessary surface treatment or modification for improved wetting behavior. As a result, a variety of surface treatment techniques such as mechanical scratching, plasma etching, and surfactant or silane coupling agent assemblies have been studied to achieve wetting and adhesion for deposition of oxide coatings by changing the polymer's surface chemistry [13,14]. In general, using silica alkoxide precursors through hydrolysis under certain conditions, a $C-O-Si$ bond may be formed between sol–gel-derived silica coatings and the treated polymer surface. But there is a potential problem in the hydrolysis formed

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C–O–Si bond. When exposed to moisture or water, sol–gel-derived silicon dioxide coatings may delaminate and lose adhesion from the polymer surface [15]. Therefore, it is desired to develop a strategy to form stable, unhydrolyzable bonds at the interface between coating and polymer.

In general, the solvothermal process, which is conducted at low temperature, has been proven to be a powerful route for preparing nanophase materials of different sizes and shapes. Solvothermal process can be defined as chemical reactions or transformations in a solvent under supercritical conditions or near such a pressure–temperature domain. The specific physico-chemical properties of solvents in these conditions can, in particular, markedly improve the diffusion of chemical species. These processes have been mainly developed for preparing functional materials [16,17]. So for the surface treatment methods of polymer, the solvothermal process may be a good choice.

Normally, the solvothermal method is mainly used in the preparation of micro/nano powders. In this paper, we are trying to use this method for the surface treatment of PMMA. Tetraethoxysilane (TEOS) or γ-methacryloxypropyltrimethoxysilane (MPS) was used to modify the surface of PMMA substrate. The solvothermal process was carried out in a Teflon-lined stainless autoclave. The inner pressure caused by the closed autoclave tended to introduce an interlocking network within the polymer matrix. And then a silica film was prepared on the PMMA substrate by silica sol solution and solvothermal method at a relatively low temperature. The adhesion behavior of silica films on the PMMA substrate was analyzed by dry and wet thermal cycling tests. The samples are irradiated by AO in a ground-based simulation system.

2. Experimental details

2.1. Materials

PMMA substrate used in this work was purchased from Tianjin Special glass Ltd. Co. Other materials γ-methacryloxypropyltrimethoxysilane, Tetraethoxysilane, ethanol (EtOH), hydrochloric acid (HCl), acetic acid (CH_3COOH) and ammonia (NH_3 H_2O) were purchased from qualified chemical suppliers, and were used as received without further purification.

2.2. Sol preparation

The silica-based sol used to coat the PMMA substrates was obtained through the following three methods including acid catalyzed, base catalyzed and acid/base catalyzed sol solution. First, the acid sol was prepared using sol–gel method as following: TEOS (5 ml) was added to 25 ml of ethanol, and the resulting solution was stirred at room temperature. 2 ml of water and 0.1 ml HCl were added to another 25 ml portion of ethanol. The ethanol/water/HCl solution was slowly added to the TEOS/ethanol solution under stirring at 300 rpm, 30 °C for 1 h. The resulting mixture was kept at 70 °C for 6 h and then stored at room temperature for a week. The alkaline sol was prepared using the same method, only replaced water and HCl with 4 ml NH_3 H_2O. Finally, the two solutions were mixed and stirred for at least 2 h to obtain the acid/base sol solution.

2.3. Fabrication of coating films

In order to degrease the surface and remove impurities that may affect the solvothermal coating process, PMMA substrates (50 mm×20 mm×2 mm) used in this study were initially cleaned and rinsed with ethanol and deionized water. The solvothermal coating process was carried out in a Teflon-lined stainless autoclave. The solvothermal process is briefly shown in Fig. 1. The procedures of coating process were as follows: (1) Placed 1 ml TEOS and 49 ml EtOH, in Teflon-lined stainless autoclave and stirred well. The pristine PMMA sheet was dipped into the autoclave vertically. The autoclave was sealed and heated, and then kept at 65 °C for 60 min. (2) Cooled to room temperature, opened the autoclave, and then added 0.5 ml H_2O and one drop acetic acid, stirred for 30 min. (3) Took out the PMMA sample, rinsed it with ethanol for at least 3 times and put it in another autoclave with the ready-prepared silica sol solution. (4) Kept at 65 °C for 20 min, let cool to room temperature, and then lifted up the PMMA sheet vertically. The lifting velocity was varied in the range of 1.0–5.0 cm min^{-1}. The thickness of the coatings was controlled by changing the lifting speed of the substrates. (5) Finally, the coated PMMA substrates were

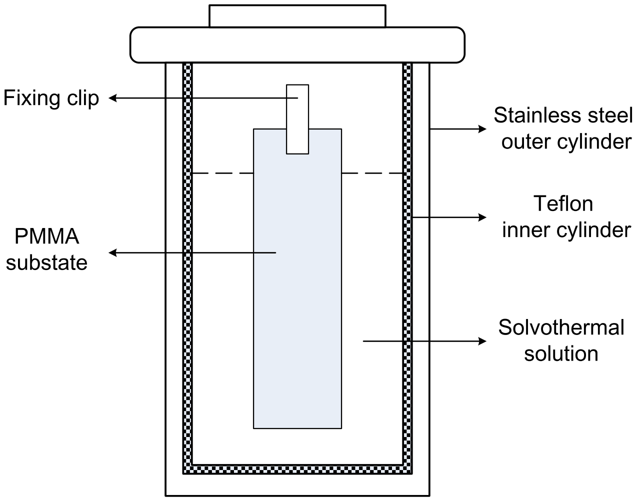

Fig. 1. Schematic illustration of the solvothermal process.

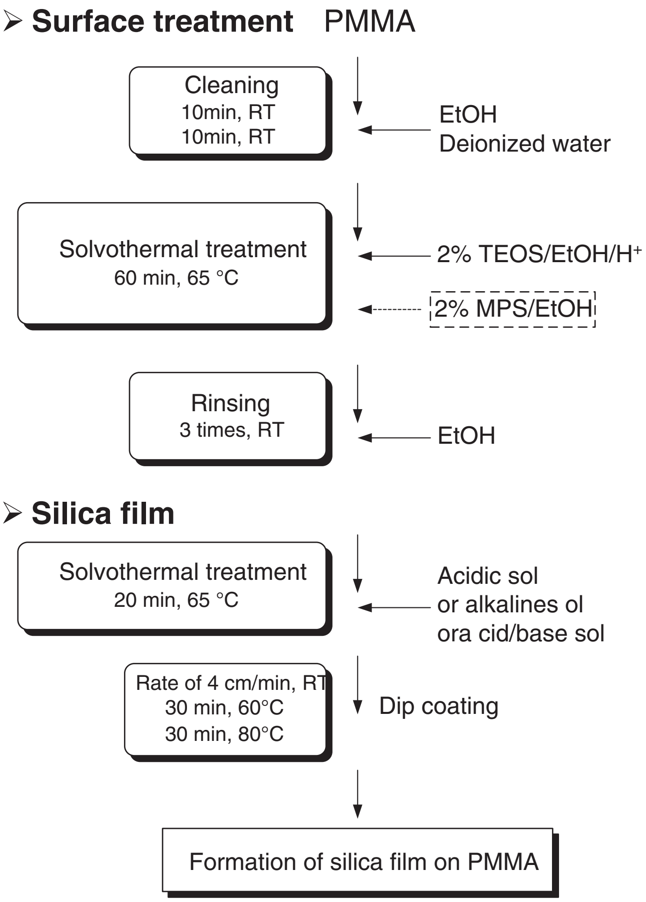

Fig. 2. Preparation process of silica films on PMMA substrate.