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Unified model for low-Earth-orbital atomic-oxygen and atomic-oxygen/ultraviolet induced erosion of polymeric materials

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A B S T R A C T

An attempt is made by applying the chain reaction theory on the study of the interactions of atomic-oxygen and atomic-oxygen/ultraviolet radiation (referred to as atomic-oxygen and synergistic effects, respectively) with polymeric materials. A unified kinetic model describing the non-branching chain reacting processes induced by atomic-oxygen and synergistic effects on hydrogen-containing polymers is first constructed. A unified form of equations in terms of mass change of polymeric materials is then deduced by incorporating the kinetic model into the mass loss model due to Colin et al. The resulting equations can be simplified under certain conditions, and analytic solutions describing the nonlinear mass variation can be obtained via the bulk reactive rate in the fractal reaction dynamics. For demonstration, the mass change associated with four types of polyethylene and Kapton were simulated, and the results are in good agreement with the experimental data. The dependencies of the mass loss on crystallinity, the fractal dimensions of erosion surface, and environmental factors for all four types of polyethylene are explained briefly. The theoretical framework is generalized to yield a mass evolution prediction formula for heterogeneous media induced by the diffusion–reaction process of incoming particles impinging into the media. Hereby, mass losses of polymers such as Teflon FEP, etc., as well as polymer-layered silicate nanocomposites caused, respectively, by the vacuum ultraviolet irradiation and oxygen plasma are simulated. The fitted curves agree well with the experimental data. The validation through the chosen materials reveals that the present unified model is capable of providing a tool for evaluating the nonlinear mass loss of both polymers and nanocomposites.

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1. Introduction

The mass loss of polymer used on the spacecraft exterior surface is mainly induced by the erosion of the atomic oxygen (AO), ultraviolet (UV) radiation, and/or their combined effects [1,2]. AO is the major constituent, roughly 80%, of the Earth atmosphere in low Earth orbit (LEO). AO has both high translational kinetic energy of ∼5 eV and the sufficiently high flux of approximately 10^{14}–10^{15} atoms/cm^2 s, owing to the spacecraft orbital velocity of approximately 8 km/s. In addition, materials of spacecraft surfaces are not only oxidized via AO, a highly chemically oxidant, but the erosion is also accelerated through hyperthermal AO collisions with those materials energetically. Polymeric films of space vehicle surfaces are disintegrated and corroded mainly by chain reactions. Flight experiments have confirmed that one of the main factors

responsible to the degradation of polymeric films of the spacecraft exterior surface is AO [3].

Polymeric materials are also vulnerable to the ultraviolet radiation. Since the wavelength of UV radiation in LEO ranges approximately from 100 to 400 nm, equivalent to the total radiation energy of about 8% of the solar constant 136.7 mW/cm^2, it may easily cause a photo-degradation to the materials. As a molecule in a polymer with chromophores or impurities lying in a singlet ground state, the absorption of a photon raises the molecule to an excited singlet or triplet state. If the molecule has a sufficient energy in the excited state, the bond dissociation may take place and thus break the organic structural bonds (such as C=C, C=O) and functional groups. Free radicals as reactive intermediates can be generated within organic molecules to cause photochemical reactions which induce negative effects, e.g., the material discoloration due to the increment in solar absorptance, or loss of mechanical properties by chemical changes in the material. In addition, in the de-excitation processes of excited molecules returning to the ground state without producing a chemical change, either heat or energy ($h\gamma$) may emit in the form of fluorescence

or phosphorescence. The electronic energy in excited group may transfer to a ground state group in the vicinity of the excited group, causing the degradation to take place [4–7].

The degradation induced by synergistic effects of mechanisms in LEO environment on materials is often worse than that induced by the individual mechanisms [8]. The combined effects of AO and UV radiation on polymer materials of spacecraft exterior surface may increase the erosion yield. As for the chain reactions participating in synergistic effects, the free radicals present in the initial reaction consist of the ones originated by the chain initiation reaction of AO with polymer, and those formed by polymer absorbing UV. In addition, the presence of AO raises the quantum yield of polymer materials. Thus, the increment in the concentration of free radicals which plays the key role in material degradation leads to speeding up the diffusion–reaction of free radicals and lifting the erosion yield of the material. Ground-based experimental results have shown that when Kapton or polyethylene simultaneously expose to UV radiation and AO, the resulting erosion yields increase 30% [9] or 30 ~ 100% [10], respectively.

There are three approaches for performing the investigation on the interactions between spacecraft surface materials and LEO environment, namely, the short- and long-duration flight experiments, ground-based experiments and theoretical analyses. Theoretical studies on LEO environmental effects against spacecraft surface materials became active in the early nineties of the last century. One of the quantities for assessing the degradation of polymer materials would be the material mass loss due to AO and the synergistic effects of AO and UV radiation.

Banks et al. [11] proposed a cutting model for estimating the mass loss of the spacecraft materials in 1992. Based on the fact that AO reacted more readily with the polymer having weaker bonds, Whitaker and Jang [12] developed an oxidation model, together with an equation of mass loss rate following the Arrhenius law with a constant activation energy in 1993. However, their deduction of the mass-loss-rate equation simply reflects a linear correlation between the mass loss and the exposure time, which is unable to interpret the nonlinear reality of the process. Koontz et al. (1995) constructed a reactive scattering model describing the reaction dynamics of AO with polymers [13]. By assuming preferential reactions of the decarbonylation with intra-molecules, Iskanderova et al. [14] constructed a model on mass density of the effective carbon in the polymer. Baird (1998) developed a one-dimensional bond orientation model to explain the shag-carpet appearance of the eroded surface of polymers [15]. Lee and Chen [16,17] proposed a classical scattering model for predicting the reaction probability of AO colliding with polymers. Kinoshita et al. [18] presented a model for the carbon abstraction and deduced an equation for the nonlinear mass change phenomenon of polyimide films under the hyperthermal AO beam exposure. By assuming the "stripping" of oxygenated macromolecules along the main polymer chain to be the major process of the formation of gaseous products, Dorofeev [19] constructed a model for the rupture of main polymer chains, and derived a set of equations based on free radical chemistry for predicting the reaction efficiency of the etching of polyethylene by AO. Under the assumption that a bulk material can be subdivided into an array of finite volumes, the associated volumetric reaction probability depends on both the total amount of kinetic energy stored in the volume by an AO flux and the cohesive energy of the volume itself. Based on the assumption, Allegri et al. (2003) proposed a Monte Carlo approach to correlate the mean erosion thickness with the AO fluence for Kapton exposed to the LEO environment [20]. Troya and Schatz developed in 2004 a coupled model in the framework of quantum mechanics in conjunction with the molecular dynamics for analyzing hyperthermal $O(^3P)$ collisions with hydrocarbon self-assembled monolayers [21].

There have been three theoretical models readily established for synergistic effects. By making use of the fact that atomic groups are excited by UV together with associated concentration boosts, and assuming that the excited atomic groups behave as a diffusing substance to which the AO may react with, Gao et al. (2002) derived a diffusion–reaction equation to govern the process [22]. Their calculated results qualitatively explained the pattern of the cutting curve for Kapton due to synergistic effects. Yotota et al. (2004) proposed a two-stage reaction model consisting of a gasification reaction following an oxidation reaction [10,23]. In order to explain the cause on more mass loss of Kapton found in the synergistic process than the one produced by AO erosion alone, they asserted that UV favors the gasification reaction, and took as a rate-limiting step in the mass loss reaction. Vasiliew (2004) established the mathematical model of material damage which was applied to evaluate the variation of α_s, an integral absorption coefficient for solar radiation, for spacecraft coatings with long period of exposure [24].

As for the above-stated physical models related to either AO or synergistic effects, only the works by Whitaker and Jang [12], Kinoshita et al. [18], and Allegri et al. [20] attempted to correlate the mass loss of the surface materials caused by the environmental corrosion with exposure time. Mass variations with respect to time are not expressed explicitly in all of the remaining models.

The ground-based experimental results have shown that the evolution of material mass loss is characterized by nonlinearity which depends upon the nature of the material [18,25]. The chemical structure and the environment factors of the material make the prediction of its mass loss rather difficult. As aforementioned, no suitable theoretical model has yet been available for simulating the nonlinear evolvement of the material mass loss. The present work attempts to construct a unified model for material mass variation by making use of chain-, diffusion-, and fractal-reaction dynamics for predicting the mass loss of the hydrogen-containing solid polymers exposed to the AO or/and UV radiation. The constructed framework is generalized subsequently to simulate the mass change on heterogeneous media caused by the diffusion–reaction processes due to the impingement of incoming particles into the media. Finally, for demonstration purpose, numerical simulations are performed to fit the mass evolvement on four different types of polyethylene, Kapton, as well as Teflon FEP, LDPE, BOPP, PMMA, PS, and polymer-layered silicate nanocomposites.

2. Theoretical model

2.1. Unified model for non-branching chain reactions

Due to the fact that the aging process in most of the polymeric materials is characterized by reactions involving either the homolytic dissociation of the main chain in polymers, or the homolytic abstraction of atoms or radicals from side groups, the free radical plays a primary role in the degradation of polymeric materials. As for the AO and synergistic effects on hydrogen-containing polymers of solid phases, the necessary conditions for sustaining the chain reaction are provided by a continued generation of free radicals. The process is driven by the hydrogen abstraction due to AO collisions together with the breaking of chemical bonds due to UV radiation. The mass loss of the material, in turn, takes place due to the diffusion–reaction of AO and the reaction between AO and free radicals in the material. Accordingly, in order to develop a unified theoretical formalism for predicting the mass losses, a model for unified non-branching chain reactions is proposed in conjunction with the diffusion–reaction equation of AO.

The theory of chain reactions claims that a complex process can be decomposed into a series of elementary reactions. The analysis