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# Influence of Content and Structure of Hydrocarbon Polymers on Erosion by Atomic Oxygen

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**From a comprehensive analysis of erosion data for materials exposed to low-Earth-orbit space environment, to fast atomic-oxygen beams, and in plasma facilities it is shown that different correlations can be found between the thermal and hyperthermal atomic-oxygen erosion yield of hydrocarbon polymers and their chemical structure and content. Correlations have been found of the hyperthermal atomic-oxygen erosion yield of many polymeric materials in flight experiments with their inverse mass density of effective (not bonded with oxygen) carbon atoms, and with their degree of aromaticity. These correlations were used to identify the rate-limiting factors of erosion processes and to predict the erosion rate for polymer-based materials in low Earth orbit. The first correlation was not found in the interaction of thermal atomic oxygen with a number of polymers, and the second is strongly pronounced. The results are explained on the basis of physical and chemical processes affecting differently the erosion rates of polymers by thermal and by fast atomic oxygen. Subthreshold bombardment-induced and -enhanced degradation and surface chemical etching are proposed to be the major mechanisms of erosion by fast atomic oxygen.**

## Nomenclature

$E$ = energy of the incident particle or beam, eV
$E_a$ = activation energy, eV
$E_b$ = bond energy, eV
$E_{th}$ = threshold energy for physical sputtering, eV
$E_{tr}$ = kinetic translational energy, eV
$M$ = molecular weight of polymer repeat unit (PRU), a.u.
$\bar{M}$ = average atomic weight in PRU, a.u.
$N_C$ = number of carbon atoms in a PRU
$N_C^O$ = number of carbon atoms bonded with intramolecular oxygen atoms in PRU
$N_O$ = number of oxygen atoms in a PRU
$N_S$ = number of sulfur atoms in a PRU
$N_T$ = total number of atoms in PRU
$n_{C=C}^{ar}$ = number of aromatic double bonds
$n_{Cb}$ = total number of carbon bonds in PRU
$R_e$ = erosion yield of materials, cm$^3$/atom
$R_e^{LEO}$ = $R_e$ in low-Earth-orbit environment, cm$^3$/atom
$R_e^{FAO}$ = $R_e$ in fast atomic-oxygen facilities, cm$^3$/atom
$R_e^{TAO}$ = reaction rate of materials in thermal atomic-oxygen facilities, cm$^3$/atom
$\alpha$ = degree of aromaticity
$\gamma, \gamma'$ = efficient carbon chemical content factor
$\varphi$ = angle of incidence of bombarding species
$\rho$ = density of the polymer material, g/cm$^3$

## Introduction

THE reaction of atomic oxygen (AO) with polymers has been known for some time (and mostly studied in glow discharges); the erosion of organic polymers in the low Earth orbit (LEO) space environment due to interaction with AO is a special recent example. The apparent rate at which all hydrocarbon polymeric materials reacted in LEO was over two orders of magnitude greater than one would have predicted on the basis of past studies of the effects of AO on polymers.[1–10] The accelerated erosion in LEO was also evident for carbon films and graphite.[4–10] A distinguished surface morphology, which includes oriented, conelike surface features closely resembling surface reliefs characteristic of physical sputtering processes,[11] was observed in space-flight samples.[2,4–10,12,13] Very similar patterns, dependent on beam directionality, have been developed in samples subjected to accelerated testing in ground-based AO beam facilities.[14–19] Such "carpetlike" surface structures do not develop after testing of polymers in plasma ashers ("in glow")[1,3,15] or in a flowing afterglow environment ("out of glow").[3,20] The very high erosion rate and the similarity of surface morphologies in physical sputtering processes and in-flight and ground-based experiments was quite unusual and unexpected. The kinetic energy translated by AO impact with materials in the ram direction ($E_{tr} \leq 5$ eV) is much lower than the common threshold energies required for kinetic physical sputtering processes[21] to take place, i.e., the erosion of polymers in LEO can be attributed to "subthreshold" effects.[22] Unfortunately, there are no particular data for threshold energies $E_{th}$ for physical (total or selective) sputtering of polymers to illustrate this statement quantitatively. It is interesting to note that for graphite sputtering by C$^+$, which has a mass quite close to O, we have[21] $E_{th} = 44$ eV, which is an order of magnitude higher than the AO translational energy in space. The most obvious difference in the exposure conditions of shuttle flights,[2,4–10,12] the fast-atomic-beam experiments,[14–19,23] and the thermal-AO (TAO) experiments (based on plasma ashers[1,3,20,24–27]) is the translational energy with which the oxygen atom strikes the polymer surface. Energy ranges correspond approximately to 4.5–5 eV, 1–5 eV (in special cases the range of fast AO (FAO) beam facilities was extended to[23] 15 eV and even[23] 50 eV), and 0.04 eV for the shuttle, the FAO beams, and TAO, respectively. Another important difference is the directionality of the atomic fluxes in flight and beam testing as compared to TAO conditions. The goal of this paper is to understand better the influence of both these factors, to establish the relationship of the content and structure of carbon-based polymers with their resistance to FAO, and to compare with the results for TAO.

## Overview of Past Experimental Work and the Proposed Mechanisms

The majority of erosion yield data for various materials ($R_e^{LEO}$) exposed to AO in LEO has been compiled and discussed in Refs. 3–10. The various AO reactions with polymeric materials based on

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fundamental studies for organics[29,30] and possible mechanisms of erosion in LEO and in FAO beams were discussed in Refs. 6 and 27. These basic reactions, as well as potential pathways of $O(^3P)$ oxidation of polymers, can be assumed for the interaction of polymers with TAO. The contribution of the translation energy or, more generally, of low-energy surface atomic collisions still remains unclear. The possibility of activated absorption, i.e., increased sticking coefficient, has been assumed for FAO,[18,31] but the idea was presented in a very general form.

Hydrogen abstraction was postulated[15,20,27] to be the key reaction controlling the erosion rate of saturated hydrocarbon polymers by TAO, as well as FAO. However, the extrapolation of hydrogen-atom abstraction as the rate-limiting step at FAO was not finally confirmed in the experiments with fully deuterated polyethylene.[27] The relatively low reaction efficiency in TAO of polymers having aromatic or olefinic content is probably related to the reactions of addition and insertion of oxygen atoms.[27] The similar role of these reactions under FAO seems unlikely. Moreover, the attempt to find the activation energy $E_a$ of the hydrogen abstraction by FAO as a rate-limiting process[15,27] was not rigorous in a statistical sense,[4] and was based on the existing data containing a sharp increase of reaction probability around $E_{tr} = 1$ eV, followed by a smooth dependence of erosion yield on energy, i.e., an almost constant value[15,27] of $R_e$ for $E_{tr} =$ 1–5 eV.

These results, however, like many others in testing facilities, were obtained with beams having very wide kinetic energy distribution functions. The high-energy tail in the beam distribution could contribute differently to the etching than the low-energy part. The averaging could be masking important effects. It can be suggested that the more energetic part of the beam initiates the reactions mostly through creation of surface active sites, followed by attack by lower-energy oxygen species, similarly to the interaction of both ions and neutrals in plasma etching.[32] Such a mechanism is possible, since $E_{tr} \approx 2$–5 eV is comparable with the bond energy $E_b$ of all single chemical bonds in hydrocarbons (but not the double bonds, as in $>\mathrm{C{=}O}$ and $>\mathrm{S}\substack{=\mathrm{O}\\ =\mathrm{O}}$ groups).

Enhanced etching of Si has been observed during exposure to a neutral fast chlorine beam ($E = 0.4$–2 eV) with a variable kinetic energy distribution.[33] The sustained etching rate, even for a less energetic $Cl_2$ beam, was over 10 times faster than for thermal $Cl_2$. An additional increase by a factor of 3.6 was observed in the etching rate when the beam contained $Cl_2$ at energies $>3$ eV, which is comparable with the silicon–silicon bond energy of $E_b = 2.3$ eV. This faster reaction also produces[33] products with kinetic energies above 0.5 eV.

Recent data from a narrow-beam energy testing facility[23] operated at $E = 2$–15 eV are totally different from the previous results, viz., $R_e^{\mathrm{FAO}}$ for graphite, Kapton®, polyethylene, and FEP Teflon® increases proportionally to $E^2$. These results, if valid, do not agree with the powerlike[3,14] or steplike[15,27] energy dependence for Kapton. Hence the real energy dependence is still unclear. It is also interesting to note that for graphite, where no hydrogen at all is involved in the accelerated oxidation and erosion by FAO, the erosion yield is also increased comparably to that for TAO, and is close to the value for some hydrocarbons, following the trends mentioned above.

A number of results indicate the importance of bond strength, size of pendant groups, and degree of fluorination for the resistance of certain polymers to attack by AO in oxygen-based plasmas.[1,24–27] However, only qualitative attempts, without any quantitative correlations to identify the rate-determining factors of plasma etching, were made in these studies. Based on experiments in a plasma asher (in glow), it was suggested[26] that AO reaction in polymers is a thermally activated two-step process, with AO diffusion being the rate-limiting step. It should be noted, however, that the activation energies $E_a$ for erosion of many polymers, mostly in the temperature range 0 to 200°C, measured in FAO beams and in space flights,[4–10,18,27,31,34] are very low, varying from a few tenths to a few kilojoules per mole. These values, on average, are one order of magnitude smaller than for etching of hydrocarbons in a plasma asher.[26] For a set of polymeric materials (Kapton, Mylar®, polymethylmethacrilate, and polyethylene) a weak temperature dependence of $R_e^{\mathrm{FAO}}$ has also been found[35] for a range of temperatures $-125°\mathrm{C} \leq T \leq 125°\mathrm{C}$, i.e., including, for the first time, ground-based FAO testing at $T < 0°\mathrm{C}$. At the same time, the development of the specific conelike microrelief has been shown to be temperature-dependent,[35] in agreement with the suggested model of migration-induced surface morphology evolution. Low $E_a$ values were obtained for organic polymers under reactive ion etching (RIE) conditions[36] and were attributed to the ion-induced etching mechanisms.

Summarizing this brief review, it is evident that despite all this intensive work, there is still no clear understanding of the mechanisms of enhanced oxidative chemical erosion of organic polymers in LEO and by FAO. All the proposed mechanisms are based mainly on the scheme of radical reactions and on the oxidative degradation of polymers. The role of low-energy surface atomic collisions, causing energy and momentum transfer in these processes, remains unclear. No quantitative correlations for $R_e^{\mathrm{LEO}}$ with the content and/or structure of polymeric materials are established.

The relative rates of reactions of hydrocarbon polymers with TAO in plasmas are, in general, related to their ease of oxidation during simple thermal oxidation.[1,37] This relationship means that there is a certain correlation between thermal oxidation of these polymers and plasma oxidation, although the stepwise degradation may be different. The reaction rates of some hydrocarbon polymers in TAO (out of glow, i.e., in a flowing afterglow environment) vary over two orders of magnitude, and differ strongly for aromatic and aliphatic polymers.[3,20] By contrast, for carbon, graphite, and many hydrocarbon polymers and composites interacting with AO in LEO conditions, the erosion behavior is similar, and the values of $R_e^{\mathrm{LEO}}$ were found to be[4–10,17,27] mostly in a narrow range of $(1$–$4) \times 10^{-24}$ $\mathrm{cm}^3$/atom. Only a few results of higher erosion yields $R_e^{\mathrm{LEO}}$ for homopolymers have been published,[31,34,38] and we will discuss these data later. For polymers with very different thermal stability and resistance to regular oxidative degradation (for instance, Kapton and polyethylene), the erosion yields in LEO and in HAO beam facilities are very close to each other.[5,6,15]

In studies of the energy distribution of the erosion products for Kapton with HAO beams, CO and $CO_2$ volatile reaction products with thermal and hyperthermal ($E = 0.5$–0.7 eV) energies have been found.[39] The energetic final products are indicative of reactions with not only thermalized surface oxygen atoms (possibly through collisionally induced active surface sites), but also with hot[40] atoms or bombardment-enhanced desorption processes, which are important in chemical-assisted etching of many semiconductors.[41,42]

In the mechanism involving thermalized atoms' surface reactions, the molecular products will have a modified Maxwellian energy distribution at the local surface temperature. The mechanisms of hot-atom reactions and bombardment-enhanced desorption should be connected with the hyperthermal peak in the energy distribution, i.e., with some energy and momentum transfer. The most important distinction between these two groups of mechanisms is that energy is a scalar quantity, whereas momentum is a vector quantity. It means that $R_e^{\mathrm{LEO}}$ (and $R_e^{\mathrm{FAO}}$) may be angle-dependent for a momentum transfer mechanism, but must be nearly independent of angle for erosion by thermalized species.

It has been shown[41–44] that physical sputtering yields are strongly angle-dependent, with maximum yield occurring for an angle of incidence of 40–80 deg. The chemically enhanced bombardment-induced etching yields are practically independent of the angle of incidence, with the maximum etching rate obtained at an angle of incidence of 0 deg in the systems investigated.[42,44–47] The only observed[36] exception occurred for $E = 300$–500 eV, when the angular dependence of the normalized etch rate of three organic polymers for RIE in an oxygen plasma was similar to the results for physical sputtering in an argon plasma.

If the dependences of surface erosion on angle of incidence found in space[4,5] and the normalized mass loss rate in testing facilities,[17] both being $\propto (\cos\varphi)$,[1,5] are valid, then, for this special case, $R_e \propto \sqrt{\cos\varphi}$, i.e., not only the energy, but also the momentum transfer, is actually involved in LEO and FAO beam erosion. More detailed information can be obtained from investigations of the angular distribution of the final erosion products.

Fluorine-containing, and especially perfluorinated, polymers are more resistant to AO than hydrocarbons.[1–10,17,23,26,27] For perfluorinated polymers, such as Teflon, in TAO (out of glow[3,20]), in some FAO beam testing facilities and in short space missions in LEO, the values of $R_e$ are 2–4 orders of magnitude smaller than for hydrocarbon polymers. However, in some cases it was found that the $R_e$ values for Teflon are increased and even are close to those of hydrocarbons.[1,17,23,48] This may be attributed to the synergistic effects of AO and VUV (Refs. 17, 48) and to the presence of a certain amount of $O^+$ in the atomic flux.[23]

## Results and Discussion

An extensive analysis of the existing data on erosion of polymers in the LEO environment and in FAO beam facilities led us to analyze quantitatively the relationship between the polymers' chemical structure and content and their resistance to erosion by thermal and hyperthermal AO, with special attention paid to flight experiments.

During the interaction of polymer surfaces with AO in LEO and FAO beam facilities, the low-energy atomic collisions with the surface layer atoms occur randomly, but the response, caused by inelastic energy transfer, should be quite sensitive to the energies and structure of the chemical bonds. For instance, graphite shows increased erosion under FAO beams and in space. For diamondlike carbon, with a significant amount of stable $sp^3$ bonds, the erosion is much lower, being insignificant for diamond.[6,10,49] For hydrocarbon polymers, the energetically preferred processes such as hydrogen abstraction, excitation, and rupture of weak bonds (mainly the single bonds with heteroatoms) will take place first. Such qualitative correlations, or trends, have been discussed in plasma etching,[50] where high-heteroatom-content aliphatic polymers were etched at the highest rates and low-heteroatom-content aromatic polymers were etched at the lowest rates. The C–C bond excitation or rupture seems also to be energetically possible (especially by the species in the high-energy tail), a fact that is important for the explanation of accelerated erosion of carbon films, graphite, and carbon-fiber-reinforced polymers.

In addition, by analogy with combustion[51] or plasma stripping,[52] one can assume, if a polymer has oxygen atoms in its repeat unit, that oxygen is available to aid in the degradation process. In general, it is difficult to predict which collisionally induced and enhanced oxidative degradation pathways will be realized in LEO and FAO conditions. The strongly bonded functional groups, such as carbonyls $>C{=}O$ have double-bond energies[53] $E_b = 7.7$–$7.8$ eV that are much higher than those of regular carbon bonds [C–C, $E_b = 3.5$ eV (Ref. 53)] and other single bonds, and can play an important role in the formation of a stable molecule of carbon monoxide (CO).

The existence of other oxygen-containing functional groups in the polymer can lead to formation of different final products, including $CO_2$ and $CO + CO_2$ mixtures. Following Ref. 54 and as a working hypothesis, we assumed[55,56] that the preferential processes with intramolecular oxygen were decarbonylation, or CO formation, i.e., bonding of one intramolecular oxygen atom with one C atom. (Some additional considerations justifying this approach will be given later.) Therefore, one can conclude that for hydrocarbon polymers, the etching yields in the LEO space environment and by FAO beams in ground facilities should be limited primarily by the effective number of resistant carbon atoms that will be oxidized in the reactions with the incoming oxygen flux and carried away as the final volatile products. Hence, the erosion yield should be inversely proportional to the mass density of the effective carbon in the polymer (i.e., density times mass fraction of effective carbon).

The number of carbon atoms in a unit volume of a polymer is given by[54]

$$\text{number of C atoms per unit volume} = \frac{\rho}{M} N_C = \frac{\rho}{\bar{M} N_T} N_C \qquad (1)$$

Assuming preferential reactions of decarbonylation with the intramolecular oxygen, i.e., using, instead of $N_C$, $N_C^* = N_C - N_O$, and $\bar{M}/\rho \approx$ const for hydrocarbon polymers,[57] a content parameter $\gamma = N_T/(N_C - N_O)$ was introduced, which allows one to express the erosion yield in LEO ($R_e^{\text{LEO}}$) as follows[55,56]:

$$R_e^{\text{LEO}} \approx \frac{\bar{M}}{\rho} \cdot \frac{N_T}{N_C - N_O} \approx \frac{\bar{M}}{\rho} \gamma \approx \text{const} \cdot \gamma \qquad (2)$$

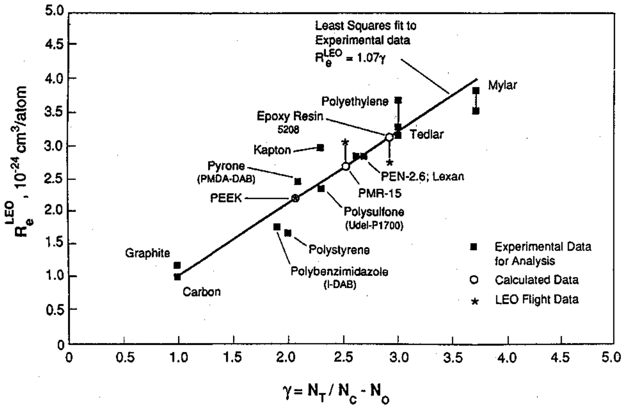

**Fig. 1 Variation in erosion yield of carbon, graphite, and polymeric materials with effective carbon content factor for LEO exposure.**

In an extensive analysis of flight data, a reasonable linear correlation (Fig. 1) was found over the range of $\gamma = 1$–$4$. Figure 1 presents data for 15 materials, including carbon films, graphite, and many hydrocarbon polymers tested in LEO. Among the possible sources of scatter in the data one can include the supramolecular structure of the materials, molecular weight, and, for some of the materials, the degree of crystallinity and possible variations in content of industrially produced materials.[37,51,58] It should be noted that a large pool of data became available to the authors after all correlations were established and the major part of this paper was prepared. The new data from ISAC[49] and EOIM[34,59] LEO flight experiments are in reasonable agreement with the established correlations. That is true not only for a number of materials tested before, such as Kapton, Mylar, CR-39, high-density polyethylene (HDPE), polysulfone, Lexan, etc., but also for some polymers, tested for the first time in LEO,[34,49] such as nylon 6 ($\gamma = 3.8$, $R_e^{\text{LEO}} = 4.2 \times 10^{-24}$ cm³/atom), liquid-crystal polymers,[59] Xydar ($\gamma \approx 2.35$, $R_e^{\text{LEO}} = 2.9 \times 10^{-24}$ cm³/atom), and LCP 4100 ($\gamma \approx 3.2$, $R_e^{\text{LEO}} = 3.2 \times 10^{-24}$ cm³/atom), etc. The $\gamma$ value for PEEK in Ref. 59 is significantly lower than in Ref. 34, but is still considerably higher than in Refs. 7 and 60, or from our estimates. The cause for this discrepancy is not clear to date. The reason for the higher $R_e^{\text{LEO}}$ values than in earlier flights[4–9] and from our estimates that are shown by linear straight-chain hydrocarbons in EOIM[10,59] may be due in part to the higher VUV radiation dose received by the EOIM-3 payload, as mentioned in Ref. 59. The actual chemical composition of these polymers [e.g., $\approx$(3–4)% of O in polyethylene[59]], can also influence their erosion. In general, the estimates and predictions, based on the proposed $\gamma$-correlation, can be viewed as lower limits, based on hypothetical pure materials, and without any synergistic effects.

A very important feature of the $R_e^{\text{LEO}}(\gamma)$ relationship in Fig. 1 is that this correlation can be used for estimating the erosion yields for various hydrocarbon polymeric materials in LEO, including new and untested materials.

Only a few results on $R_e^{\text{LEO}}$ are available for higher $\gamma$ values ($\gamma = 4$–$7$), i.e., for the two hydrocarbon homopolymers polymethylmethacrylate (PMMA)[31,38] and for an allyl diglicol carbonate (CR-39).[31,34,59] In general, they follow the trends of the $R_e^{\text{LEO}}(\gamma)$ relationship. For PMMA, the spread of the available data, however, is unusually wide [$R_e^{\text{LEO}} = 3.1 \times 10^{-24}$ (Ref. 38), $4.8 \times 10^{-24}$ and (Refs. 31, 38), $6 \times 10^{-24}$ (Refs. 8, 38) cm³/atom]. The reasons for such a spread in the data are not very clear. Consequently, these data were not included in the least-squares analysis presented in Fig. 1.

The results for the correlation of $R_e^{\text{LEO}}$ with $\gamma' = (\bar{M}/\rho)\gamma$, i.e., taking into account the values[58,60,61] of $\rho$, including PMMA and CR-39, are presented in Fig. 2. For some of the materials, such as Kapton, the agreement with the experimental values is much better than in Fig. 1. The results for PMMA and CR-39 were added to illustrate the trends for higher $\gamma'$ values, which are still not fully understood because of the limited pool of data available to date.

The assumption of preferential formation of CO with intramolecular oxygen that was used to obtain Eq. (2) may not be valid for

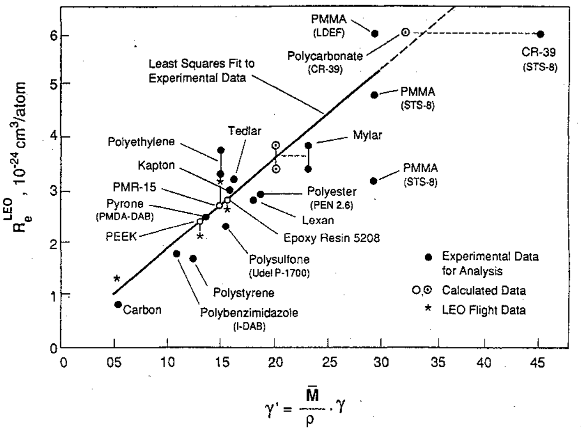

**Fig. 2 Variation in erosion yield of carbon, graphite, and polymeric materials with $\gamma' = (\bar{M}/\rho)\gamma$ for LEO exposure.**

some of the oxygen-rich polymers. It is well known that decomposition of polymers with different oxygen-containing groups can go through either decarbonylation or decarboxylation, i.e., CO or $CO_2$ elimination. Simultaneous elimination of CO and $CO_2$ due to complex intramolecular rearrangement or intramolecular oxygen transfer cannot be excluded either.[37,51]

For some of the polymers containing complex ester or carboxyl groups in their structure, it is reasonable to assume partial formation of $CO_2$, i.e. decarboxylation, due to oxidative degradation in LEO and by FAO. Formation of mixed products with participation of oxygen atoms from the incoming flux is also possible. Thus, Eq. (2) can be rewritten in a more general form:

$$R_e^{\mathrm{LEO}} \approx \frac{\bar{M}}{\rho} \cdot \frac{N_T}{N_C - N_C^O} \tag{3}$$

where $N_C^O$ is the number of C atoms that can be removed from the polymer repeat unit by bonding to one or two intramolecular oxygen atoms, depending on the molecular structure and preferential pathways of oxidative degradation by FAO.

The shift of the Mylar and CR-39 data, based on the assumption of decarboxylation of the ester groups, to better agreement with the correlation parameters illustrates the advantages of using Eq. (3) for polymers with oxygen-rich functional groups. This approach can be also specified for materials containing oxygen strongly bonded with sulfur and other elements that can form additional volatile products.

Thus, for the case of polysulfones, the $>\mathrm{S}\lessgtr^{\mathrm{O}}_{\mathrm{O}}$ group [with the strong S=O bonds ($E_b = 5.6$ eV), but weakly bonded to the chain ($E_b = 2.4$ eV for C–S)[53]] can be viewed as a precursor for volatile $SO_2$ formation. In this case, Eq. (3) can be modified to the form

$$R_e^{\mathrm{LEO}} \approx \frac{\bar{M}}{\rho} \cdot \frac{N_T}{N_C - (N_O - 2N_S)} \tag{4}$$

Experiments with labeled $^{18}O$ can be very useful in verifying these models. For some of the oxygen-rich ether polymers the predicted erosion yield, based on the simplest approach for $\gamma$ estimation, i.e., in Eq. (2), seems to be unusually high. For instance, for polyoxiethylene $\gamma \approx 7$, and it goes to infinity for polyoximethylene $(CH_2\text{–}O)_n$, or polyacetal. Even assuming the possibility of the formation of mixed CO + $CO_2$ final volatile products, including intramolecular oxygen, the estimates still predict high erosion yields. But from the general physical–chemical considerations it is reasonable to assume that, for very high $\gamma$ values, the erosion yield can gradually come to saturation. This is a question for further investigation.

The etching rates for polyoxiethylene[62] and formaldehyde polymers[1] in oxygen-based plasmas were found to be indeed quite high. Industrially produced polyformaldehydes, i.e., polyacetal resins (Delrin, Acetal, etc.), have not been tested in LEO or FAO beams, but note that they are stabilized through end-group capping or copolymerization.[63] A program is now in progress at the University of Toronto Institute for Aerospace Studies (UTIAS) and the Integrity Testing Laboratory, where a number of specially selected pure and industrially produced polymers will be tested in the LEO space simulator and in space-flights. The preliminary results of ground-based testing conducted at UTIAS agree reasonably well with the published flight data and confirm the $\gamma$ correlation.[64] It should be noted that Eqs. (2) and (3) are not valid for estimating erosion rates of fluoropolymers and organosilicons, where the rate-limiting steps are different (defluorination and formation of protective silicon oxides, respectively).

Many advanced materials and composites have a complex multicomponent content.[65–69] The flight results for a number of matrix materials based on cured epoxy resins [934, 5208, MY-720 (Refs. 57–61)] are in the range $R_e^{\mathrm{LEO}} \approx (2\text{–}3)\times 10^{-24}$ cm$^3$/atom,[4,5,60,67] as for most hydrocarbon homopolymers. Experimental data with $R_e^{\mathrm{LEO}}$ in the range $(5\text{–}6)\times 10^{-24}$ cm$^3$/atom were obtained in recent space-flight experiments, mostly for complex materials, including some blends[65] that are used as matrix materials for composites. Thus, $R_e^{\mathrm{LEO}}$ estimates based on $\gamma$ or $\gamma'$ correlation can be made for epoxy resins, including cured materials, since they belong to the same family of hydrocarbons.[66] Since the epoxy materials usually are used in cured form,[66,69] the curing agent and the ratio of resin monomer units to the curing monomer units (i.e., the structure of the cured polymer repeat unit) should be known for $R_e$ prediction. For materials used in aerospace applications, the above-mentioned ratio is[68,69] close to 0.85:1 or 1:1. As can be seen from Figs. 1 and 2, good agreement was found between the calculated values for 5208 epoxy resin and the STS-8 flight data for 5208/T300 composite,[5] where the epoxy top surface layer was eroded. The calculated values of $R_e$ for PEEK (polyetheretherketone) and PMR-15 polyimide, used as the matrix for composites, are also in reasonable agreement with Refs. 7 and 60 and with recent flight data.[65]

An analysis of the erosion data for hydrocarbon polymers in the TAO (out-of-glow) environment where[27,70–72] the low-energy atomic collisions and ion-induced interaction with $O_2$ are absent, and only the chemical interaction with $O(^3P)$ is significant, was also conducted. No such correlation as in Figs. 1 and 2 was found for the available data.

The majority of polymers tested in LEO conditions and plasma ashers are aromatic. The higher erosion resistance of aromatic polymers was noticed[25,50,73,74] during experiments on organic-film removal or resist etching in plasmas. The nature of this effect was especially highlighted in Refs. 73 and 74. It was suggested[73–75] that the observed stability can be linked to the known ability of ground-state oxygen atoms to react with aromatic rings to form phenols.

For these reasons, another variable $\alpha$, which represents the degree of aromaticity of these materials, was chosen to analyze the relationship between the etching of polymers in AO and their chemical structure. The variable $\alpha$ is defined as the ratio of the number of carbon double bonds in the phenolic rings to the total number of carbon bonds in a polymer repeat unit:

$$\alpha = \frac{n_{\mathrm{C=C}}^{\mathrm{ar}}}{n_{\mathrm{Cb}}} \times 100\% \tag{5}$$

Figures 3 and 4 present the correlations between $R_e$ and $\alpha$ for TAO conditions based on the data[3,20] and for a range of aromatic polymers in LEO, respectively. These results show a very strong inverse dependence of $R_e^{\mathrm{TAO}}$ on $\alpha$, i.e., a sharp decrease of $R_e^{\mathrm{TAO}}$ with an increase in the degree of aromaticity. Because of the limited amount of data, the relationship $R_e^{\mathrm{TAO}}(\alpha)$ represents a trend and not a firm quantitative dependence.

The $R_e^{\mathrm{LEO}}(\alpha)$ correlation is much weaker for erosion data from LEO flights, as one can see from Fig. 4. A more rigorous analysis is required for the trends within aliphatic polymers as new experimental data become available. Note that, for aromatic materials used mostly as matrix for composites (PEEK, 5208 epoxy resin, and PMR-15), the predictions of erosion behavior are in reasonable agreement with the experimental results for both $R_e^{\mathrm{LEO}}(\gamma)$ and $R_e^{\mathrm{LEO}}(\alpha)$ (see Fig. 4). The mentioned recent data for Xydar and LCP-4100 are also in good agreement with $R_e^{\mathrm{LEO}}(\alpha)$.

For perfluorinated polymeric materials, such as PTFE and FEP Teflons, the situation is quite different. The two types of valence binding forces present in the PTFE and FEP Teflon structures are

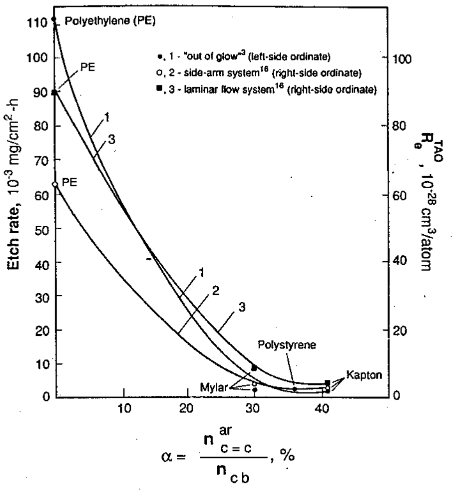

**Fig. 3 Variation in etch rate and reaction rate with degree of aromaticity of polymers exposed to thermal AO in different experimental systems.**

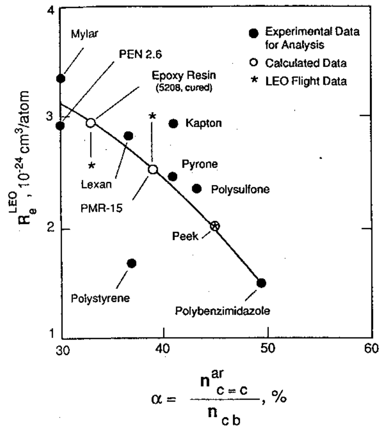

**Fig. 4 Variation in erosion yield of polymeric materials with degree of aromaticity for LEO exposure.**

the carbon–carbon bonds, which form the backbone of the polymer chain, and the carbon–fluorine bonds. The stability of fluorocarbon polymers has been attributed to the high carbon–fluorine bond strength[53] ($E_b = 5.5$ eV) and to the shielding effect that the highly electronegative fluorine atoms may have on the carbon chain. This sheath shields the carbon chain from attack and confers chemical inertness and stability on Teflon. It is strong enough to prevent the collisionally induced reaction initiation and enhancement in LEO conditions (or FAO facilities at $E_{\mathrm{tr}} \leq 5$ eV).

## Possible Mechanisms

The initiating role of low-energy atomic collisions of reactive O($^3P$) atoms with polymer surfaces was used in the hypothesis that led to the development of $R_e^{\mathrm{LEO}}(\gamma)$ relationships. That initiation created active sites susceptible to attack by thermalized surface oxygen atoms or, to some extent, by hot atoms from FAO flux. Thermal and, possibly, bombardment-induced desorption of final volatile products of oxidative degradation seem to be the last stages of erosion. The energy and directionality of AO flux in LEO and FAO beams can play an important role in energy transfer for bond breaking, in hot-atom reactions, and in bombardment-enhanced desorption. All of these factors, important for collisionally induced and enhanced processes, can actually increase the erosion yields.

These assumptions agree well with the more common idea of subthreshold effects in insulators and semiconductors,[22,76–78] which manifest themselves mainly as low-energy sputtering and radiation-enhanced atomic processes such as diffusion, defect formation, and reactions in solids, activated through excitation, rupture, and rearrangement of the chemical bonds. The recent results on unusually high total sputtering yields of some insulators (LiF crystals) bombarded by hyperthermal ($E = 5$–$500$ eV) rare-gas ions[78] can be used as an example. Even at energies around 20 eV, the sputtering yield was about 0.6 molecule/ion. These data suggest an erosion mechanism where effects different from kinetic sputtering are involved. The enhanced erosion of polymers by FAO, being also subthreshold, has mostly a chemical nature.

Here, the processes are enhanced via the very strong chemical reactivity of AO, which probably leads to new, original subthreshold effects in bombardment-induced chemical etching. For carbon films and graphite, where the carbon fraction is equal (or close) to one, all carbon atoms should be oxidized by the incoming AO flux. The mechanism of accelerated erosion by FAO and low-energy $O^+$ (Refs. 70 and 79) should be similar and can be viewed as chemical sputtering, that is, a process where ion (or atom) bombardment induces a chemical reaction that produces a weakly bound molecule, which desorbs from the surface.[41,79] Chemical sputtering usually has a pronounced temperature dependence, as for graphite under hydrogen bombardment.[79] The weak temperature dependence of LEO and FAO erosion of polymers and graphite,[23,31,34,35] even at temperatures[35] below 0°C, seems to be caused by unusually high chemical reactivity of AO, which probably leads to a new original subthreshold effect in bombardment-induced chemical etching. The low value of the barrier to reaction obtained from a comparison of the experimental $R_e^{\mathrm{FAO}}(E)$ data for Kapton and the collisional-reaction dynamic model, in a sputtering near-threshold law,[59] may be proof of chemical etching. Erosion of carbon and polymer-based materials by FAO can be related to a physical–chemical phenomenon that can be named bombardment-induced and -enhanced surface chemical etching (BESCE).

The evaporation or bombardment-induced desorption of polymer chain segments (chunks) following FAO-induced "chopping" from the polymer matrix can also play a role in special cases in linear nonpolar polymers at low-flux conditions.[80] This additional mechanism can also explain the fact that the $R_e^{\mathrm{LEO}}$ values for polyethylene[58,81] and polypropylene[58] in EOIM-III are higher than the predictions made on the basis of our $\gamma$ and $\gamma'$ correlation.

The synergistic effect between (V)UV and AO for degradation and erosion of PTFE and FEP Teflon was studied in LEO and in space simulators.[17,48,82] VUV radiation has been shown to create free radicals in polymers, as observed by ESR.[82] The radicals, once formed, can create damage that remains trapped within the polymer after the C–F bond has been broken and the fluorine atom has drifted away, i.e. the photogeneration of radical species in the polymer matrices can be the initial steps in the degradation process.

A similar mechanism is likely to cause the high erosion rate of Teflons by HAO, when the $O^+$ ionic component of the AO flux is high enough.[23] Because of the highly electronegative nature of fluorine atoms, it is possible that they can be preferentially attacked by $O^+$ ions, with the breaking of the C–F bond. The results of computer calculations of electron density distributions in PTFE Teflon, using the Molecular Orbitals Package (MOPAC[83]), seem to support this assumption, showing that F atoms have an effective negative charge of (0.115–0.121) $e$, i.e., they can be viewed as an effective center for $O^+$ attack.

Such a route can be responsible for the collisional ion-induced initial stage of degradation of Teflons with the following O($^3P$) attack on the carbon backbone atoms, and can explain many experimental observations of increased erosion as AO–$O^+$ effects.[4–10,17,23,48,84]

## Conclusions

From the analysis of the erosion of carbon, graphite, and organic polymers in LEO, fast AO beams, and different plasma environments, it is postulated that atomic collisions, with energy and momentum transfer, and chemical oxidative degradation processes are involved in the etching mechanisms.

It was found that in TAO interactions with polymers, the surface chemical reaction rate falls off sharply for polymers with higher degrees of aromaticity. In the interaction of hydrocarbon polymers with AO in LEO, the dependence of the erosion yield $R_e^{\mathrm{LEO}}$ on degree of aromaticity is much weaker, but still exists. It would appear that collisionally induced and enhanced processes are smoothing the aromaticity dependence of the structure resistance of hydrocarbon polymers to AO attack.

Erosion of polymer-based materials in LEO and by FAO beams can be viewed as a special subthreshold case of a general physical–chemical phenomenon, which we termed bombardment-induced and -enhanced surface chemical etching (BESCE). It is conjectured that for carbon films and graphite, the erosion by FAO can be described as a subthreshold, low-temperature mechanism of chemical sputtering.

Bombardment-induced and -enhanced oxidative degradation constitutes the main destructive process for hydrocarbon polymers in LEO conditions and FAO beams. The content of hydrogen and volatile weakly bonded heteroatoms contribute to the bombardment-induced erosion due to hydrogen abstraction, and weak-bond excitation and rupture with the effective mass density of carbon being the rate-limiting factor. A procedure to calculate the number of effective carbon atoms in a material was established, assuming the intramolecular oxygen can fully participate in the degradation and destruction processes together with the incoming FAO flux. A useful linear relationship was found between $R_e^{\mathrm{LEO}}$ and an effective-carbon chemical content factor ($\gamma$ or $\gamma'$), based on LEO data. No such correlation was found for TAO in flowing afterglow conditions. This relationship can take into account the atomic densities of the material and possible pathways of partial decomposition (decarbonylation and decarboxylation) for some oxygen-containing polymers due to bombardment-enhanced oxidative degradation. The $R_e^{\mathrm{LEO}}(\gamma)$, $R_e^{\mathrm{LEO}}(\gamma')$, and $R_e^{\mathrm{LEO}}(\alpha)$ correlations have important implications for predicting erosion yields of many hydrocarbon polymeric materials and composites.

For perfluorinated polymers, photo- or ion-induced radical generation is likely the initiating step for the degradation and erosion sequences. There is growing evidence that both physical and chemical processes produce collisionally induced distortion and rupture of chemical bonds and drive the bombardment-enhanced chemical etching kinetics.

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