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Linear Pyrolysis of Thermoplastics in Chemically Reactive Environments

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The surface pyrolysis rate of two common thermoplastics, polystyrene (PS) and polymethylmethacrylate (PMM), has been measured in inert and chemically reactive environments, using the exhaust gas of a small rocket motor as a source of intense surface heating. Small plastic beads were employed to fabricate porous plastic specimens through which metered quantities of ten selected gases individually were passed; this novel porous plug technique permitted close experimental control of test gas concentration at the site of degradation. At a constant surface heating exposure (approximately 20 cal/sec-cm^2) the pyrolysis rate of PMM was unaffected by all ten, whereas that of PS was accelerated equally by both Cl_2 and NO_2. It is hypothesized that the acceleration is a result of Cl and NO_2 substitutions in the PS chains, primarily at the tertiary hydrogen locations, thereby creating "weak links" that enhance thermal degradation. In direct conflict with previous bulk degradation results of others, the presence of ClO_3F, O_2, and other less chemically reactive gases did not accelerate the surface degradation of PMM or PS; a rational basis for resolving this paradox is presented. Of considerable interest for propulsion applications is the implied invalidity of extrapolation of bulk degradation data obtained at very mild heating rates in chemically reactive environments to high surface heat flux conditions.

Background and Introduction

RECENTLY there has developed considerable interest in the linear pyrolysis (*surface* degradation due to intense surface heating) of thermoplastics, as the process has been incorporated in a pivotal way in current theories of solid propellant ignition[1, 2] and flame spreading,[3] as well as deflagration,[4–6] protective ablation of atmospheric re-entry vehicles,[7, 8] and hybrid (solid fuel) rocket motor combustion.[9, 10] Much speculation has centered on the possibility of chemically reactive gases in the surrounding atmosphere accelerating the pyrolysis rate either by attacking directly the decomposing polymer surface, or by exothermally reacting with polymer decomposition products in the gas phase to produce an increase in surface heating, or both. Evidence in support of this possibility is drawn from the results of widely used *bulk* degradation kinetics experiments as well as from laboratory experiences with each of the aforementioned phenomena, but all of these experiments suffer from inherent limitations that preclude elucidation of the role of the chemically reactive environment. These limitations are summarized in the following paragraph.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA), both bulk heating techniques, indicate that O_2 (apparently the only chemically reactive gas ever studied extensively) in the surrounding atmosphere usually produces an acceleration of the thermoplastic bulk degradation rate.[11–14] These techniques, as a result of relatively mild heating exposures, produce degradation rates less than one-thousandth of those of interest in propulsion applications, although the reactive gas concentration at the sample surface can be controlled quite accurately. On the other hand, much higher regression rates are obtained when, for example, a high energy arcjet[8] is employed as a source of intense surface heating in chemically reactive (O_2) and inert (N_2) environments. However, this technique, as well as attempts to examine the role of O_2 by experimenting with laboratory hybrid motors, cannot discriminate between degradation acceleration produced by direct attack on the polymer surface and that produced by heat feedback from nearby, gas phase, exothemic, chemical reactions with polymer vaporization products. Also, in this class of experiments, the reactive gas concentration at the polymer surface cannot be accurately controlled.

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Bulk Degradation Studies

Thermoplastic degradation by thermal means (pyrolysis) is understood to be a chemical reaction in which macromolecules or polymer chains are decomposed to fragments approximately the same size as the monomer.[12] Also, the presence of chemically reactive gases may result in thermochemical degradation. For example, it has been well established that the presence of O_2 considerably accelerates the rate of bulk degradation of many thermoplastics during mild heating exposures by attacking the polymer chains to form hydroperoxides, etc., in accordance with the generally accepted "weak link" theory of thermochemical degradation.[11, 12] It has been well established also that the thermochemical decomposition rate at any local reaction site in the polymer bulk is a function of the local concentration of reactive species and depends exponentially on the local absolute temperature level. Therefore, uniform temperature and species distributions are both necessary for uniform degradation rates throughout a sample. Both TGA and DTA techniques are based upon an assumed uniform bulk degradation rate; consequently, to meet this condition during an experiment, the rate of surface heating must be low enough, and the rate of reactive gas diffusion through the sample must be high enough, to prevent the reaction rate in the interior from becoming diffusion limited. Although these techniques have been employed quite widely and, indeed, classically for determining polymer degradation reaction kinetics in inert environments, serious questions have arisen concerning their accuracy when chemically reactive environments are involved; weight loss data can be obscured by product gas absorption throughout the sample,[15] and there are definite indications that the size of the specimens tested may influence the degradation rate data.[12] This latter observation is indicative of the existence of temperature and/or species concentration profiles, in violation of the fundamental assumptions of temperature and concentration uniformity, and apparently is the major cause of poor data correlation among different investigators.[12, 16]

Attempted Extrapolations of Bulk Degradation Data

Numerous attempts have been made, particularly by researchers in propulsion and re-entry phenomena, to extrapolate TGA and DTA bulk degradation data, obtained in O_2 environments, to surface degradation conditions generated by intense surface heating in O_2 or other chemically reactive environments. (These intense heating exposures produce extremely steep temperature gradients in the plastic, typically 25,000°C/cm.) But because of the vast differences in heating exposure, this is a dubious procedure and has never resulted in a successful correlation. (Chaiken[17, 18] has pointed out that even in inert environments the chemical kinetics of thermoplastic bulk and surface degradation are, apparently, fundamentally different.) A typical impasse in this regard was encountered by Houser and co-workers,[10, 14] following their observation that polystyrene (PS) and polymethylmethacrylate (PMM) exhibited widely different behavior when burned with O_2 in a tubular hybrid rocket motor; ensuing TGA of PMM revealed an order of magnitude increase in degradation rate could be produced by substituting environmental O_2 for N_2; but extrapolation of these data to hybrid combustion conditions resulted in completely unrealistic predictions of motor regression rate. (Recently, it has been proposed that the difference in the regression rates of these thermoplastics when burned with O_2 in a hybrid rocket motor stems from their different combustion flame zone structures.[6])

Attempted Direct Examination of Thermochemical Attack

Houser and his co-workers[10, 14] conducted a separate series of experiments designed to measure O_2 concentration at the fuel surface in the motor by withdrawing gas samples, with the hope of correlating the surface O_2 concentration with the fuel regression rate. Over and above unavoidable inaccuracies generally encountered with gas withdrawal techniques, leading to uncertainties in the measured composition at the fuel surface, the basic nature of the classical hybrid motor combustion process, unfortunately, precludes independent experimental variation of surface heating exposure and O_2 concentration at the regressing surface. Similarly, the inseparability of surface heating exposure and O_2 concentration also has obstructed screening studies of thermoplastic ablators' resistance to thermochemical attack of atmospheric O_2 during re-entry.[7, 8]

Previous Linear Pyrolysis Experiments (Inert Environment Only)

Barsh, Anderson, et al.[19] have developed a technique in which a strand of thermoplastic is linearly pyrolyzed by pressing it against a heated plate; because of the intense surface heating so produced, pyrolysis kinetics data in the range encountered in propulsion applications were generated. For example, these data were subsequently employed by Chaiken and Anderson[5] in a study of the role of the thermoplastic binder in composite solid propellant combustion. However, recently the accuracy of data obtained by this technique has been challenged.[20, 21] In addition, they were obtained in an inert environment; consequently, they may be of limited value in the chemically reactive environments typical of those encountered in propulsion applications.

In summary, there was no accurate means of obtaining surface degradation data produced by intense surface heating in chemically reactive environments (in fact, only the effects of O_2 in bulk degradation were studied extensively in the past) prior to the inception of the present program.

Experimental Approach

Two fundamentally different types of experiments were performed. One was rather ordinary, similar to many which others had executed previously, and yielded essentially the same type of results. The other was quite novel, and for the first time, a technique was utilized which provided controlled variation of chemically reactive species in the environment of a pyrolyzing surface, independently of the surface heating exposure. The ordinary experiment is described first.

Solid plastic specimens were subjected to intense surface heating produced by immersion in the exhaust jet of a small laboratory rocket motor burning C_3H_8-O_2-N_2 mixtures, and the surface regression rate was measured. The O_2 content of the exhaust was varied by substituting additional O_2 for N_2 in the already oxygen-rich propellant mixture, allowing the exhaust gas stagnation enthalpy and velocity to be held nearly constant. Thus, for a constant specimen geometry, the convective heating exposure was held constant, while the O_2 concentration in the surrounding atmosphere was varied from 12 to 83 mole percent. Flat-faced, cylindrical 1-cm-diam samples of PS, PMM, and Delrin (acetal polymer of E. I. duPont de Nemours Co.) exhibited regression rates that were insensitive to O_2 concentration. However, for identical motor operating conditions, conically-tipped (15° included angle, 1-cm o.d.), cylindrical specimens of Delrin exhibited a strong dependence of regression rate on O_2 concentration (e.g., 30% increase between the foregoing experimental limits); a visible flame cap appeared over the conical region in the higher range of O_2 concentrations. With this ordinary experiment it was impossible to discern the cause of this increase, i.e., by thermochemical O_2 attack on the surface, or by increased surface heating due to polymer gaseous decomposition products burning with environmental O_2, or both. However, the experiments with the flat-faced specimen configuration yielded an important result: this geometry precluded significant gas-phase reactions (combus-

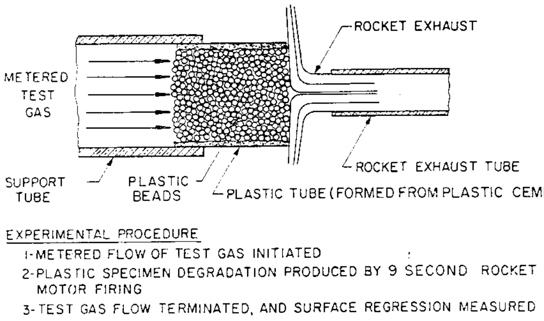

Fig. 1 Schematic of porous plug technique for linear pyrolysis measurements.

tion), even with large quantities of O_2 present in the environment. This finding was exploited in the design of further experiments.

Eventually, a novel testing technique was developed which permitted closely controlled experimental variation of any selected test gas concentration at the regressing surface, independently of the composition of the motor exhaust and/or the surface heating rate. The vital element of the technique is a porous test specimen similar to that recently developed in this laboratory and successfully employed in closely related investigations.[6] It is fabricated in the form of a cylinder (1-cm diam × 6 cm long) by point-of-contact bonding together spherical PS or PMM beads. The specimen is then coated with plastic cement to produce a solid, encasing, tubular surface to contain the metered throughput of test gas, which flows axially to the flat, heated surface during a run (Fig. 1). PS (Dylene 8X, Koppers Co., Plastics Division, Monaca, Pa.) test specimens were fabricated in four different bead size ranges: 210–250 μ, 350–420 μ, 420–500 μ, and 500–590 μ. PMM (ground from type VS-100 Plexiglas, Rohm and Hass Co., Philadelphia, Pa.) test specimens were fabricated in a single bead size range of 420–500 μ.

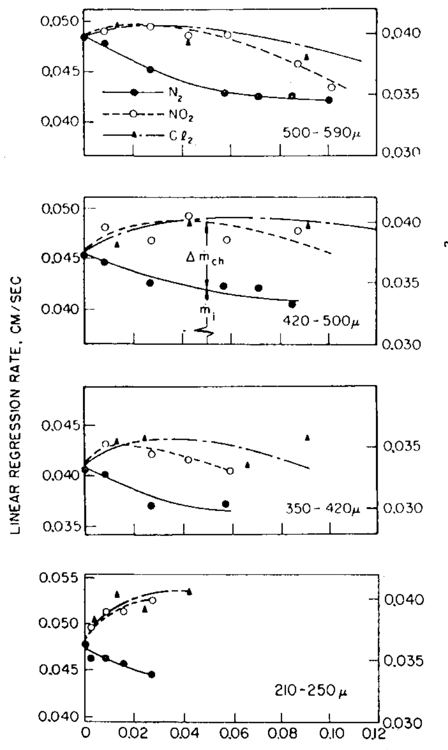

Fig. 2 PS degradation rate vs test gas throughput rate for four bead sizes, at constant heating rate.

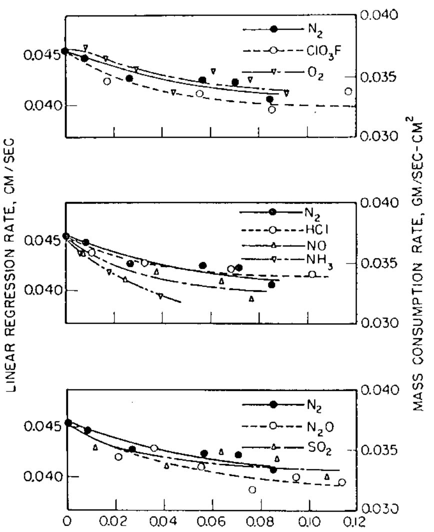

Fig. 3 PS (420–500 μ beads) degradation rate vs test gas throughput rate, at constant heating rate.

The rocket motor was operated at a constant condition throughout all runs; the exhaust gas stagnation temperature was approximately 1100°C and the Mach number 0.4. A surface-temperature-corrected heating rate of approximately 20 cal/sec-cm² was measured with a flat-faced, water-cooled, copper calorimeter having the same geometry as the test specimens. The composition of the exhaust was determined by Orsat analysis to be 77% N_2, 9% O_2, 8% H_2O, 6% CO_2. Ten test gases, N_2, O_2, ClO_3F, NO, N_2O, NO_2, Cl_2, HCl, NH_3, and SO_2, were employed with the 420–500 μ PS and PMM specimens, and after determining that only Cl_2 and NO_2 appreciably altered the PS degradation rate, and none affected that of the PMM, only these two reactive gases, in addition to N_2, were employed with the remaining three PS bead size ranges. The regression rate was obtained by measuring the distance that the heated surface regressed during the rocket motor firing interval of 9 sec (held constant for all runs), and sufficiently long to render negligible the approximately 0.5-sec heating transient following commencement of exposure.

Results

Degradation rates for both PS and PMM specimens were obtained for various throughput rates of different test gases; these data are shown in Figs. 2, 3, and 5; they exhibited an average fractional deviation of approximately 0.025. Significantly, none of the gases tested produced a noticeable change in the PMM degradation rate due to thermochemical reactions, and in this context none appear to be nonreactive. Only Cl_2 and NO_2 changed (by accelerating) the PS degradation rate, as indicated in Fig. 2, by a positive deviation (approaching 20%) from that produced by an equivalent N_2 throughput.

Contrary to the bulk degradation results of others obtained by TGA or DTA, the O_2 and ClO_3F data closely follow those of N_2 for both plastics, indicating that, at the conditions tested, no significant thermochemical attack took place.

The continuous decrease of the PS and PMM regression rates with increasing nonreactive test gas throughput rates (Figs. 3 and 5) can be predicted on the basis of a simplified theory of transpiration cooling,[22] demonstrating that the surface heating rate decreases with decreasing average molecular weight of the gases leaving the surface (both monomer vapor and test gas) and with increasing test gas throughput rate. Close correlation with the theory is precluded by insufficiently accurate data, the partial dissociation of certain test gases‡

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‡ Particularly NH_3.

at the high temperatures present (which can significantly lower their average molecular weight), and the possibility of slight thermochemical reactions between the plastics and test gases (other than Cl_2 and NO_2) that were considered essentially nonreactive.

The extent of thermochemical attack by both the Cl_2 and NO_2 on the PS was approximately equal throughout the range of parameters tested. It increased with decreasing specimen bead size, as shown in Fig. 2. Before analyzing the influence of bead size, it is convenient to make the following definitions:

$\dot{m}_i$ ≡ PS degradation rate produced by surface heating in inert atmospheres (linear pyrolysis rate), g/sec-cm²
$\Delta\dot{m}_{ch}$ ≡ increase in PS degradation rate, over and above $\dot{m}_i$, due to thermochemical attack (produced either by Cl_2 or NO_2), /gsec-cm²
$\dot{m}_i + \Delta\dot{m}_{ch}$ ≡ total degradation rate due to all effects
$\dot{m}_{tg}$ ≡ test gas throughput rate, g/sec-cm²

The data in Fig. 2 were treated in the following manner. First, $\Delta\dot{m}_{ch}/\dot{m}_i$ was computed and then plotted as a function of $\dot{m}_{tg}$ with bead size as a parameter; it was noticed that a linear relationship existed in the region of low $\dot{m}_{tg}$. These linear slopes were measured, normalized by multiplying by $\dot{m}_i$ (evaluated at $\dot{m}_{tg} = 0$), yielding $\Delta\dot{m}_{ch}/\dot{m}_{tg}$, and finally this quantity was plotted as a function of bead size in Fig. 4. A hyperbola through the arbitrarily selected point (385, 0.238), represents the inverse dependence of surface-to-volume ratio on bead size. The close conformity of the thermochemical attack data to this hyperbola suggests quite strongly that the bead surface is the site of thermochemical attack; for example, calculation of $\Delta\dot{m}_{ch}/\dot{m}_{tg}$ divided by the surface-to-volume ratio (for spherical beads six times the reciprocal diameter) yields a constant, 1.46×10^{-3} cm ($\pm 11\%$ average deviation), for the four bead sizes tested.

Qualitatively, this behavior may be explained by the following thesis. The regression rates (with $\dot{m}_{tg} = 0$) of the four bead size PS samples are approximately constant.§ Therefore, the thickness of the preheat region¶ (or thermal layer) behind the heated surface may be considered constant for specimens fabricated from each of the four bead sizes. Since the mass per unit length of the samples is constant, the outside surface area of the beads (in the preheat region) available for a high temperature reaction with either Cl_2 or NO_2 varies directly with the surface-to-volume ratio of the beads utilized. Also, if in the time available for a reaction (the bead passes through the preheat region in approximately one second) the Cl_2 or NO_2 reacts with each bead surface to a specific depth, then the number of "weak links" formed, and presumably the increase in the regression rate, should vary directly with the surface-to-volume ratio of the beads utilized. This conclusion is consistent with the results displayed in Fig. 4.

The $\dot{m}_{tg}$ values plotted on the abscissa in Figs. 2 and 5 represent the measured total throughput rates of Cl_2 or NO_2. However, it is likely that only a small fraction of this total reacts with the surface of the PS beads; the major fraction simply passes out through the degrading surface of the specimen and, as in the case of inert N_2, reduces the heating exposure actually experienced by the specimen surface. Further, it is reasonable to expect that the exhaust gas penetrates and/or diffuses into the void spaces between the beads in the preheat region, thus diluting the concentration of Cl_2 and NO_2 at the surface of the beads. Therefore, initially increasing the throughput rate of Cl_2 or NO_2 increases the concentration of these gases at the surface of the beads by displacing the inert exhaust gas and thus increases the regression rate, as shown in Fig. 2. The decreasing regression rates produced by increasing the Cl_2 and NO_2 throughputs beyond approximately 0.03 g/sec-cm² are thought to spring from a saturation of reactive species at bead surface reaction sites coupled with reduced surface heating exposure. As a result of this dilution effect, the concentrations of Cl_2 and NO_2 at the surface of the beads are, unfortunately, not accurately known, although they can be closely controlled.

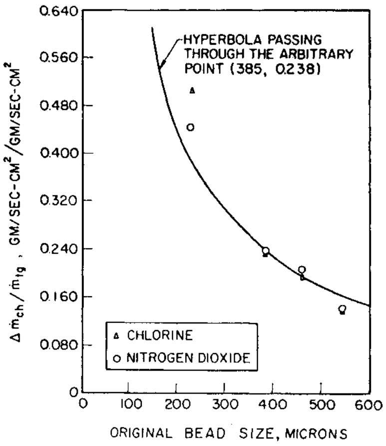

Fig. 4 Influence of PS bead size on thermochemical increase of degradation rate, at constant heating rate.

In addition to the foregoing, certain auxiliary experiments were performed:

1) PS degradation rate data obtained with the rocket motor operating at the stoichiometrically correct fuel-air ratio were comparable to those heretofore obtained with 9% O_2 in the exhaust; thus indicating that, in the configuration employed, neither the exhaust gas O_2 nor its possible interaction with the test gases affect the degradation process in a significant way.

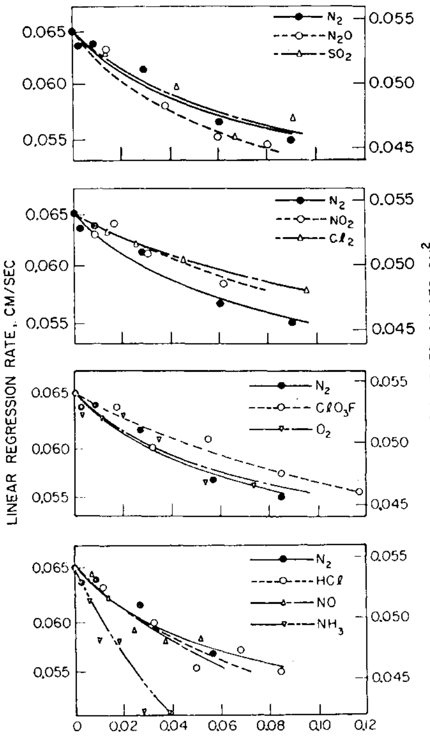

Fig. 5 PMM (420–500 μ beads) degradation rate vs test gas throughput rate, at constant heating rate.

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§ Actually, as can be seen from Fig. 2, the basic regression rate increases slightly with bead size. This is probably caused by increased surface heating as a result of increased surface roughness.

¶ For discussion purposes, the preheat region thickness may be considered to be that depth below the surface in which 95% of the temperature difference occurs (bulk temperature to surface temperature).

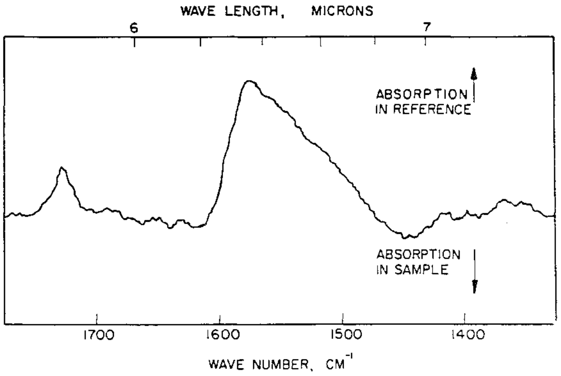

Fig. 6 Partial infrared spectrum: heated PS exposed to chlorine referenced to heated PS exposed to nitrogen.

2) For the same heating rate, the regression rate of PMM was approximately 50% greater than that of PS. Several runs with PMM were conducted with the motor heating rate considerably reduced, resulting in a lower regression rate, a more favorable situation for detection of a thermochemical attack. Even under this condition, the PMM degradation rate was not affected by any of the test gases.

3) Evidence of the nature of the thermochemical attack on PS was obtained by comparing the infrared spectra of heated PS specimens exposed to Cl_2 or NO_2 to that of N_2 exposed specimens (Fig. 6). An infrared spectrophotometer (Model IR-7, Beckman Instruments Inc., Fullerton, Calif.) was employed for analysis of samples obtained by shaving the ends of the porous specimens after typical runs with the three test gases. (All analyses were quantitative, employing constant strength solutions of the shavings dissolved in CS_2.) These spectra indicate that, for both the Cl_2 and NO_2 exposed specimens, the nature of the benzene ring, double-bond motion (characteristic of the 1500–1600 wave number region) has been altered, perhaps by substitution of Cl or NO_2 for an H atom in the benzene ring group of PS. However, these substitutions are not believed to accelerate thermal degradation; rather, it is likely that Cl and NO_2 are also substituted at the tertiary H locations in the main chain of PS (not easily detected in IR spectra[23]). Previously,[24, 25] Cl_2 and NO_2 were found to react with PS at room temperature and to weaken the material, presumably by lowering the average molecular weight. It is proposed here that the substitutions at the tertiary H locations form "weak links" similar to those generally believed to occur during the bulk degradation of PS in O_2 environments.[12] The notable lack of O_2 reactions with PS in the present surface heating experiments is believed to be caused by a competitive situation in which the thermal degradation rate is sufficiently faster than the reaction rate with O_2 (but not Cl_2 or NO_2), so that the latter takes place only to a negligible extent. On the other hand, in bulk degradation experiments the rate of thermal degradation is much lower, permitting the O_2 reaction to play a significant role.

4) As mentioned in the foregoing, Cl_2 and NO_2 were previously observed to react with PS at room temperature. These reactions also were observed in the subject program; for example, passage of either of these gases through a porous specimen for $\frac{1}{2}$ min produced no noticeable effect, but a 3-min exposure produced appreciable softening (degradation). (Specimens subjected to the $\frac{1}{2}$-min exposure exhibited the same degradation rate as unexposed specimens when tested with an N_2 throughput in a typical run.) At the surface temperature level (experimentally determined to be approximately 550°C) produced by exposure to the motor exhaust, the degradation rate data indicate that the attack of these gases takes place at a rate that is very much greater than at room temperature. This sensitive temperature dependence suggests a process controlled by chemical kinetics.

5) Preliminary tests employing a radiative heat source in place of the rocket motor have yielded results consistent with those just obtained, thus indicating that they are independent of the mode of heating.

Conclusions

A new experimental technique, utilizing porous plastic specimens, has been developed which is capable of revealing, for the first time, the influence of chemically reactive environments on the surface degradation rate of thermoplastics exposed to intense surface heating. It makes possible accurate control, over a wide range, of the concentration of virtually any test gas at the pyrolyzing surface, independently of the surface heating exposure.

Employing this technique, it has been determined that, for surface exposures typical of propulsion applications, O_2, and even ClO_3F, does not have a sufficiently fast rate of surface reaction with either PS or PMM to accelerate noticeably their degradation rates; neither Cl_2 nor NO_2 thermochemically alter the degradation rate of PMM; however, PS suffers thermochemical attack by Cl_2 and NO_2, and at a rate sufficiently large to produce a noticeable increase in its degradation rate. Cl_2 and NO_2 undergo a substitution reaction with PS, apparently at some benzene ring and tertiary H locations; it is proposed that the latter reaction creates "weak links" similar to those generally believed to occur in PS degradation under somewhat different conditions. These "weak links" are broken relatively easily and thus accelerate normal thermal degradation. The substitution reaction is strongly temperature dependent, and is reaction rate and/or diffusion rate limited so that it occurs in the outer surface layer of the beads as they pass through the preheat region below the pyrolyzing surface. Evidently the molecular structure of PMM precludes a similar reaction with Cl_2 or NO_2.

The presence of O_2 in the surrounding atmosphere did result in an accelerated regression rate in situations that permitted it to support combustion with emerging plastic vapors sufficiently close to the regressing surface to augment the heating exposure. However, it was possible to select a test specimen geometry that precludes any regression rate acceleration as a result of gas-phase combustion reactions, thus permitting an unobscured study of the nature of thermoplastic degradation rate acceleration resulting from direct surface attack by chemically reactive species.

In light of the results of the present work, it is suggested that the fundamental assumption upon which the hypergolic ignition theory of solid propellants[2] is based, a rapid, exothermic, heterogeneous reaction between external gaseous oxidizers and the propellant fuel component, be carefully re-examined, particularly in the case of O_2 and ClO_3F. Also, it appears that, in order to be complete, theories of ammonium perchlorate composite propellant deflagration should incorporate in some way the effect of the oxidizer decomposition products (which include substantial quantities of Cl_2 and NO_2) at the pyrolyzing binder surface. Further, it is not likely that O_2 reacts significantly with intensely heated thermoplastic surfaces under the conditions present in conventional hybrid rocket motors and on re-entry vehicle ablative surfaces (at least in the range of regression rates investigated herein).

It appears as if current DTA and TGA bulk degradation techniques are of dubious value because of the existence of temperature and/or species concentration gradients throughout the polymer bulk, especially in chemically reactive environments. And certainly extrapolation of data produced in this way to intense surface heating conditions is futile. However, even if accurate bulk data were available it has been suggested by Chaiken[17] that such extrapolation would be invalid as surface degradation and bulk degradation are fundamentally different processes; however, his technique obtained surface degraduation data has been severely criticized.[20, 21] Therefore, the subject porous specimen thchnique appears to offer the best hope at present of yielding surface degradation kinetics produced by intense surface heating exposures in a wide range of chemically reactive environments, and it is currently being exploited for this purpose.[26]

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