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A STUDY OF OXYGEN EFFECTS ON NONFLAMING TRANSIENT GASIFICATION OF PMMA AND PE DURING THERMAL IRRADIATION*

TAKASHI KASHIWAGI AND THOMAS J. OHLEMILLER
Center for Fire Research
Bldg. 224, Room B260
National Bureau of Standards
Washington, D.C. 20234

The effects of gas phase oxygen on the rate of gasification and surface temperature of PMMA and low density PE samples (4 × 4 cm) were investigated under transient, nonflaming heating by thermal radiation. Five different ambient gas mixtures, 100% nitrogen, 5% O_2/95% N_2, 10% O_2/90% N_2, 20% O_2/80% N_2, and 40% O_2/60% N_2, were used. The vertically oriented samples were subjected to two different radiant fluxes, 1.7 and 4.0 W/cm^2. For PMMA, large bubbles are formed in the hottest, near-surface layer in a nitrogen environment; these bubbles are smaller and more frequent in oxygen-containing environments. It appears that the molten surface layer of PMMA becomes less viscous in an oxygen-containing environment and this enhances bubbling mass transfer of in-depth-decomposition products to the surface; the bubbles in turn affect the depth to which oxygen alters the decomposition process. The surface of PE turns brown in oxygen-containing environments, increasing the local absorption coefficient and hence increasing the rate of heating. An increase in gas phase oxygen concentration increases the gasification rate of PMMA and PE substantially. With PMMA, when the rate of gasification becomes substantial, the effect of oxygen on the gasification process is reduced; the counterflow of gases from the surface apparently serves to reduce the oxygen supply rate to the condensed phase. An increase in oxygen concentration significantly decreases the surface temperature of PMMA and even more significantly increases that of PE. Neither polymer gasifies like a liquid in the sense of having constant surface temperature and mass flux proportional to energy input.

1. Introduction

Polymeric materials are increasingly common as components of furnishings; they constitute a substantial fraction of the fuel load in typical modern residential dwellings and other buildings. It is important to understand why these materials behave as they do in a fire environoment. Of particular interest are the factors which control the rate of polymer gasification under transient heating such as occurs in the initial stages of fire growth (both in ignition and flame spread over solids). A proper understanding of the rate of polymer gasification in a fire environment is essential to the mathematical prediction of fire growth on such materials. In this paper we confine our attention to clarifying the behavior of non-charring thermoplastic polymers.

In previous studies, the rate of transient gasification of thermoplastic polymeric materials in ignition and flame spread situations has been expressed by an Arrhenius type dependence based only on surface temperature (1,2). The values used for kinetic constants in the Arrhenius type expression have frequently been derived from thermogravimetric analysis (TGA) in an inert atmosphere with much slower heating rates than those encountered in a fire environment. Alternatively the concept of vaporization of a liquid at a constant surface temperature has been used with the rate of gasification proportional to the rate of energy input (3,4). A limited amount of work has been done in which a more realistic account is taken of the polymer decomposition/gasification behavior in the condensed phase mainly in steady gasification (5, 6,7) and to a lesser extent for transient conditions (8,9,10). The details of the transient gasification of thermoplastics with internal temperature gradients have not been carefully examined.

There is limited information available about the effect of oxygen on gasification processes under the transient conditions common in a fire environment. Even in steady-state burning of certain polymers, contradictory results have been obtained regarding the role of gas phase oxygen in the gasification pro-

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cess; some studies have indicated a significant role of oxygen in the gasification process (7,11) while others have indicated no such role of oxygen (12,13). A recent study of counter-diffusion-type *steady-state* burning of polyethylene yielded an estimate that the *maximum* contribution of surface oxidation is twenty percent of the energy required for fuel pyrolysis (14).

This paper reports experimental observations of the effects of ambient oxygen on the rate of polymer gasification and surface temperature history during transient, nonflaming heating. An external thermal radiation source is used to simulate the primary mode of energy transfer in a developing room fire, i.e., radiation (15). Polymethylmethacrylate (PMMA) and low density polyethylene (PE) are the thermoplastics examined. The normal modes of non-oxidative thermal degradation of these two polymers present two extremes of behavior: unzipping to monomer for PMMA and random scission to a wide (and variable) spectrum of molecular fragments for polyethylene (16). Furthermore, at least at low temperatures, these two polymers differ in their susceptibility to oxidation. PMMA is rather resistant (17); polyethylene is less resistant (18).

2. Experimental Procedure

A schematic illustration of the experimental apparatus is shown in Figure 1. A large graphite plate of 10 × 13 cm rectangular shape is heated electrically by a well-regulated power supply. Gray body emission from the graphite simulates the thermal radiation from the flames of a developing room fire. The plate was held at about 1260° C for the work reported here; this corresponds to a blackbody radiation peak at about 2 μm (near infrared). A 9 × 9 cm square water-cooled light pipe is located in front of the graphite plate and transmits the radiation out toward the sample while assuring its spatial uniformity; its inside walls are coated with gold for high infrared reflectance. The exit of the light pipe is sealed by a sodium chloride window.

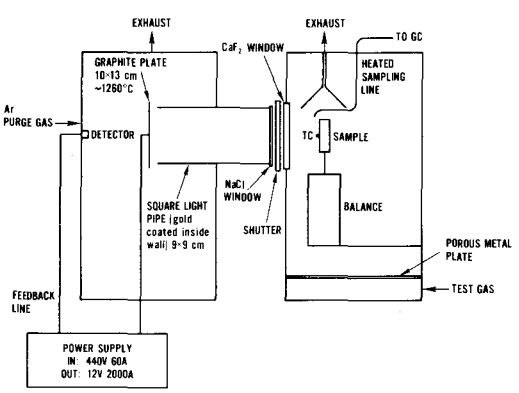

FIG. 1. Schematic illustration of the experimental apparatus.

The test chamber is shown on the right side of Fig. 1. The desired ambient gas is fed from the bottom of the chamber through a porous metal plate at a uniform upward flow of less than 1 cm/sec. The sample is mounted vertically on an electromechanical balance which can sense a 1 mg change in a total mass of up to 50 g; the balance has a response time of 80 msec. A 25 μm wire diameter chromel-alumel thermocouple is spread across the front surface of the sample with the junction near the center. To assure good contact between the thermocouple and the sample surface, the thermocouple was heated electrically and pressed into the surface prior to a test. Close examination shows that the thermocouple stays in good contact with the sample surface during the entire experiment. Any increase in temperature of the thermocouple by direct adsorption of the external radiation is at most 7° C for the radiant fluxes used in this study (19). This magnitude of temperature increase is comparable to the reproducibility of the measured surface temperature.

A calcium fluoride window on the front of the test chamber transmits the radiation from the graphite plate to the sample; this window is opaque beyond 10 μm. The level of the radiant flux at the sample surface is controlled by simply changing the distance between the exit of the light pipe and the test chamber. The uniformity of the radiant flux distribution over the sample surface is ±2% at 1.7 W/cm^2 and ±3% at 4 W/cm^2, the two radiant fluxes used in this study.

Commercially available PMMA (Rohm and Haas Plexiglas G)* and low density PE (Rohm and Haas) were used as the polymer samples. The former samples were 4 × 4 cm square with a 1.5 cm thickness and the latter were 4 × 4 cm square with a 1.25 cm thickness. Five different ambient gases were used: nitrogen, 5% O_2/95% N_2, 10% O_2/90% N_2, 20% O_2/80% N_2 and 40% O_2/60% N_2 (V/V). The weight of the sample, surface temperature and radiant flux seen by a reference flux meter next to the sample are recorded simultaneously by a digital data system during the experiment. Generally, three experiments were repeated

*In order to adequately describe materials it is occasionally necessary to identify commercial products by manufacturer's name. In no instance does such identification imply endorsement by the National Bureau of Standards nor does it imply that the particular product is necessarily the best available for that purpose.

at the same conditions. The reproducibility of the data is within 5% for mass flux and within 3% for temperature except in a nitrogen environment in which occasional bursting of large bubbles caused somewhat irregular surface temperature fluctuations. This scatter does not affect the qualitative conclusions obtained in this study. The experiment is typically terminated at 3~4% sample weight loss for PMMA and at about 1% for PE.

It should be noted that neither type of polymer sample contains any opacifiers. The PMMA samples at the thickness used in this study are transparent to visible radiation but they are opaque above a wavelength of 2 μm due to their thickness. At room temperature the PE samples scatter visible radiation, but where the local temperature exceeds 100–150° C, the PE is visually transparent. The PE samples at the thickness used in this study are also opaque beyond 2 μm. Infrared spectra (2.5–10 μm) on thin sheets of the two polymers imply that most radiation beyond a wavelength of 2.5 μm is absorbed in less than a 1 mm depth for PMMA and a 1–2 mm depth for the PE (the absorption depth varies strongly with wavelength, of course, being least near vibrational bands of specific functional groups). For the exposure conditions and sample thicknesses used here the samples are initially thermally thick but, by the later part of the radiation exposure, the thermal wave reaches the rear side of the sample.

3. Results and Discussion

3.1 *PMMA*

3.1.1 *Visual Observations*

The effects of gas phase oxygen on the transient surface mass flux and surface temperature of PMMA were studied at radiant fluxes of 1.7 and 4.0 W/cm^2; flaming ignition never occurred. Visual observations reveal that the surface behavior changes markedly in the presence of oxygen in the gas phase. In a nitrogen environment, rough-surfaced, snowball-like bubbles develop and grow with time at 1.7 W/cm^2 as shown in Fig. 2(a). By the end of the exposure, these bubbles (up to ~1 mm dia.) have formed up to 2–3 mm below the sample sur-

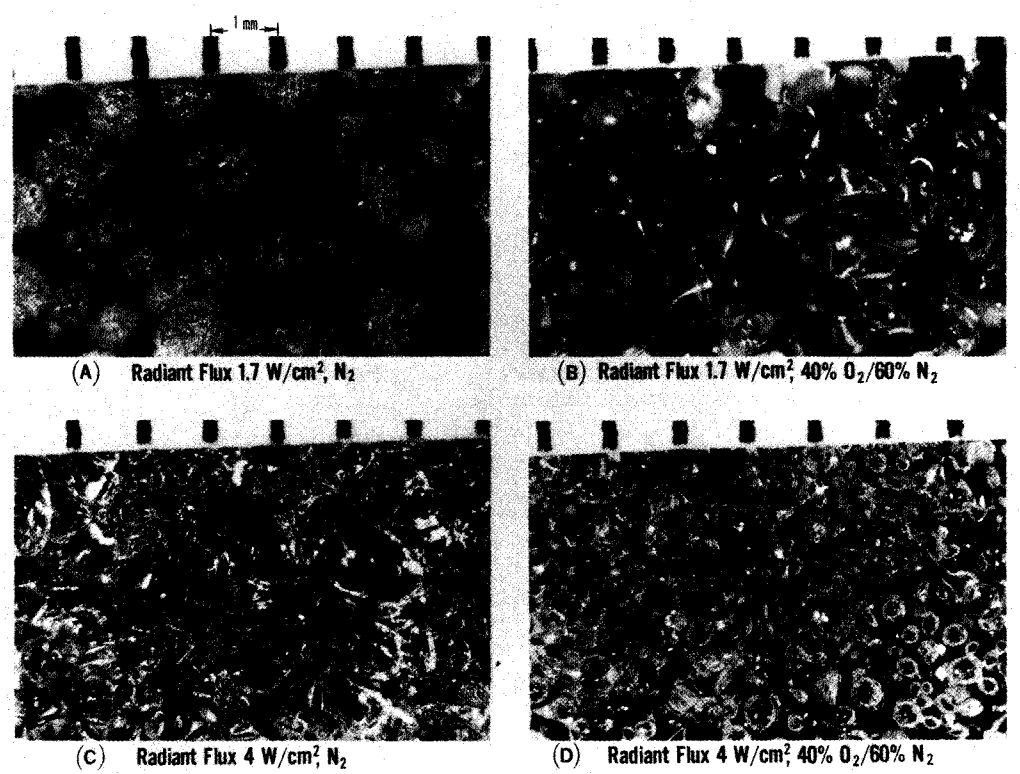

FIG. 2. Microscope pictures of PMMA surface layers exposed to different radiant fluxes and environmental gases. The distance between two dark bars in the top part of each picture is 1 mm.

face consistent with the thick thermal wave penetration resulting from extended heating (15 min.) at this low flux. When sub-surface bubbles form, they attempt to grow toward the direction offering least resistance, i.e., the front surface of the sample. However, the viscosity of the molten polymer layer near the surface appears to be extremely high. Only bubbles within 1 mm or so of the surface are able to burst directly through the front surface and they do so through very small holes. However, some bubbles further below the surface burst through small neck-like holes into the near-surface bubbles, thus venting their contents to the gas phase. The burst process is violent and can cause vapor jets that extend a few centimeters out from the surface; it also throws some molten material into the gas phase. The bubbling frequency is relatively low (compared to cases with ambient oxygen) but it appears that in the last 1/3 or so of the irradiation period this in-depth generation of decomposition gases could easily match the mass flux coming directly from the exposed front surface of the sample. The latter must be formed within some monomer diffusion distance of the front surface, probably less than 1 μm (20,21).

When oxygen is present in the ambient gas, the viscosity of the near-surface layer of degrading PMMA appears to be substantially less (increasingly less with high O_2 levels). The bubbles start earlier, the bubble frequency is higher, and the bursting process is less violent. The burst bubbles leave large open holes (up to ~1 mm dia) in the front surface of the sample which admit oxygen to their interior volume (Fig. 2b). This permits oxygen to have an effect over a thicker layer of near-surface material than it could otherwise reach by diffusion alone through the molten layer (~1 mm versus a few μm), i.e., a greater surface area of heated polymer is exposed to oxygen. Below this level the snowball-like bubbles still form as in the pure nitrogen case and some probably burst through to the surface as indicated above for a nitrogen environment.

At higher fluxes the differences in the near-surface behavior due to inert and oxidizing atmospheres are less pronounced but still present; Fig. 2(c) and (d) compare pure N_2 and 40% O_2 cases at 4 W/cm^2. In both atmospheres, the snowball-like bubbles are smaller because of the thinner thermal layer and shorter exposure time. The higher flux raises the surface temperature, as described later, and apparently lessens the degrading polymer viscosity even in the pure N_2 case. However, the mean bubble size in the 40% O_2 case is clearly less (1/3 to 1/4 that in N_2) and some persisting holes through the surface into sub-surface bubbles are still seen. The same phenomena are thus still present but to a less marked degree.

We note that bubbles add another complication by altering the optical properties of the sample. The bubbles are scattering centers that change the effective reflectivity of the sample and the in-depth radiation extinction coefficient.

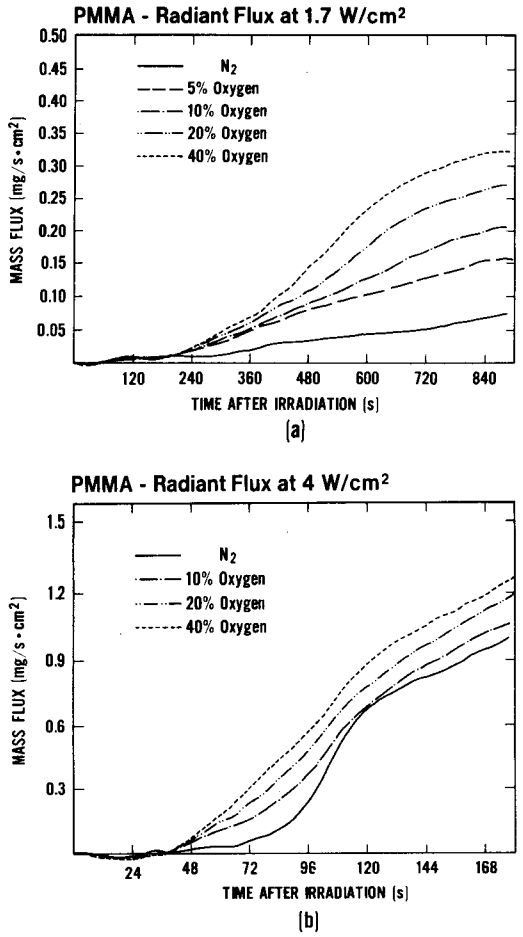

FIG. 3. History of mass flux from PMMA after the start of irradiation with various oxygen mole fractions in the gas phase, (a) 1.7 W/cm^2, (b) 4 W/cm^2.

3.1.2 *Mass Flux from the Polymer Surface*

The change in mass flux with time is shown in Fig. 3(a) for a flux of 1.7 W/cm^2 and in Fig. 3(b) for 4.0 W/cm^2. These results are calculated by dividing the time derivative of the measured weight transient by the front surface area of the sample. The results in Fig. 3(a) indicate that at 1.7 W/cm^2 mass flux increases strongly with increasing oxygen content in the gas phase. The results at 4 W/cm^2 shown in Fig. 3(b) indicate a weaker oxygen effect compared to that at 1.7 W/cm^2 except shortly after the start of the weight loss. From approximately 40 to 90 seconds after the start of irradiation, the

effect of gas phase oxygen on mass flux is as large as that at 1.7 W/cm^2 and the mass flux level is comparable to the largest levels at 1.7 W/cm^2. After approximately 120 seconds, the rate of the increase in mass flux is about the same for all environments. This overall behavior is consistent with the idea that, when the mass flux is low (e.g. for all of Fig. 3(a)), appreciable gas phase oxygen can diffuse to the PMMA surface against a weak flow of decomposition gases leaving the surface. However, as the mass flux increases, the oxygen flux is lessened by the counterflow of gasification products. The competition between the diffusion of oxygen to the surface and the convective flow of decomposed gases leaving the surface influences the magnitude of the effect of gas phase oxygen on the mass flux. Clearly the effect will also be configuration dependent since this can influence the oxygen diffusion length in the gas phase.

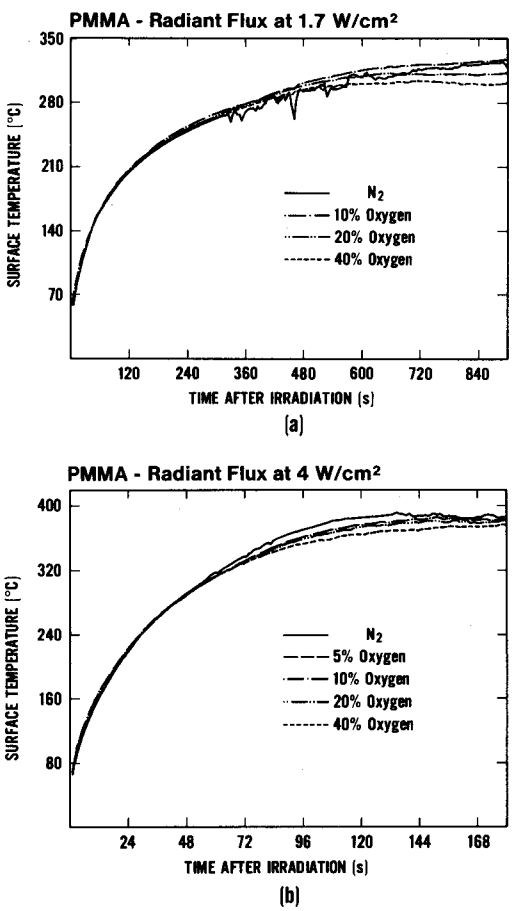

FIG. 4. Surface temperature change with time for PMMA in various gas phase oxygen mole fractions, (a) 1.7 W/cm^2, (b) 4 W/cm^2.

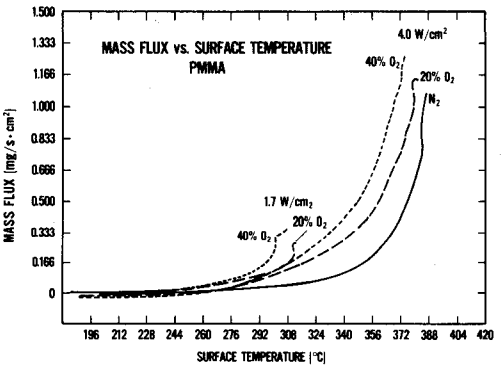

FIG. 5. The relationship, for PMMA, between surface temperature and mass flux for various oxygen mole fractions and radiant fluxes.

3.1.3 *Surface Temperature and Its Relation to Mass Flux*

The effects of gas phase oxygen on surface temperature are shown in Fig. 4(a) at 1.7 W/cm^2 and in Fig. 4(b) at 4 W/cm^2. The surface temperature for the various oxygen-containing environments is not strongly changed at either radiant flux; however, the surface temperature definitely does tend toward lower values as the ambient oxygen level increases. A similar trend was also observed for polystyrene in steady-state gasification [22]. By the end of the test, the surface temperature asymptotically approaches plateau values for each radiant flux, about 365–380° C for 4 W/cm^2 and 300–330° C for 1.7 W/cm^2; the spread in surface temperature at each flux is due to the effect of oxygen level.

Since mass flux under transient gasification conditions has often been computed from a simple Arrhenius type expression based only on surface temperature, the relationship between mass flux and surface temperature is plotted in Fig. 5 using the results from Figs. 3 and 4 to examine the validity of the use of such an expression. The data for a nitrogen environment at 1.7 W/cm^2 are not included because of the irregular temperature fluctuations caused by occasional bubble bursts near the junction as shown in Fig. 4(a). All of the temperature-mass flux curves are different; mass flux cannot be expressed as a unique function of surface temperature. Another important result shown in Fig. 5 is the effect of radiant flux on the relationship between mass flux and surface temperature. The figure shows that the mass flux at 1.7 W/cm^2 is always larger than that at 4 W/cm^2 for the same surface temperature and atmosphere. The temperature distribution in the solid at 1.7 W/cm^2 is thicker than that at 4 W/cm^2 at the same surface temperature (achieved at a later time for the lower flux). The larger mass flux at 1.7 W/cm^2 compared

to 4 W/cm^2 at the same conditions implies that indepth decomposition contributes to the gasification flux through diffusion and the previously discussed bubbling. Since the difference in mass fluxes at the two different radiant fluxes shown in Fig. 5 is not negligible, the rate of gasification is not a unique function of surface temperature. The figure clearly shows that PMMA does not have any unique, so-called surface vaporization temperature; also the rate of gasification cannot be described simply as being proportional to the rate of energy input. Therefore, PMMA does not gasify like a boiling liquid.

3.2 *Low Density Polyethylene*

3.2.1 *Visual Observations*

As the local temperature reaches about 120° C, the PE becomes visually transparent (starting from the surface and moving inward) due to melting of crystallites. With continued irradiation in a nitrogen environment, a small amount of gasification and weight loss is observed without any further physical changes. The molten surface layer that subsequently develops is much less viscous than that of PMMA and the test must be terminated earlier due to dripping and sagging of the sample. No significant bubbling is observed. With oxygen in the gas phase, the sample behaves similarly to that in a nitrogen environment until the first appearance of vapor in the gas phase. Shortly thereafter, the color of the surface starts to turn brown and some bubbles are also observed. The surface color is darker with increasing oxygen content in the gas phase. Shortly after the appearance of bubbles, the experiment must be terminated due to downward flow of the molten surface layer.

The tendency for the PE to bubble during transient gasification is markedly less than that of PMMA. Infrared spectra of the two samples show that the PE has a somewhat higher transmissivity, at least beyond a wavelength of 3.5 μm. Thus the thermal wave in PE tends to be deeper than that in PMMA for equal surface temperatures; this would imply more in-depth bubbling for PE than for PMMA. The lower viscosity of the near surface material also would imply less resistance to bubble growth for PE compared to PMMA. However, two factors counter this expectation that PE would bubble more than PMMA. The effective activation energy for the degradation/gasification process is more than twice as large for PE as for PMMA (272 KJ/mol (65 Kcal/mol) vs. 130 KJ/mol (31 Kcal/mol)) (23,24). For comparable total rates of gasification the depth of degradation/gasification is thus sharply curtailed in PE despite the somewhat thicker thermal wave. Furthermore, it has been estimated that less than half of the products of PE degradation

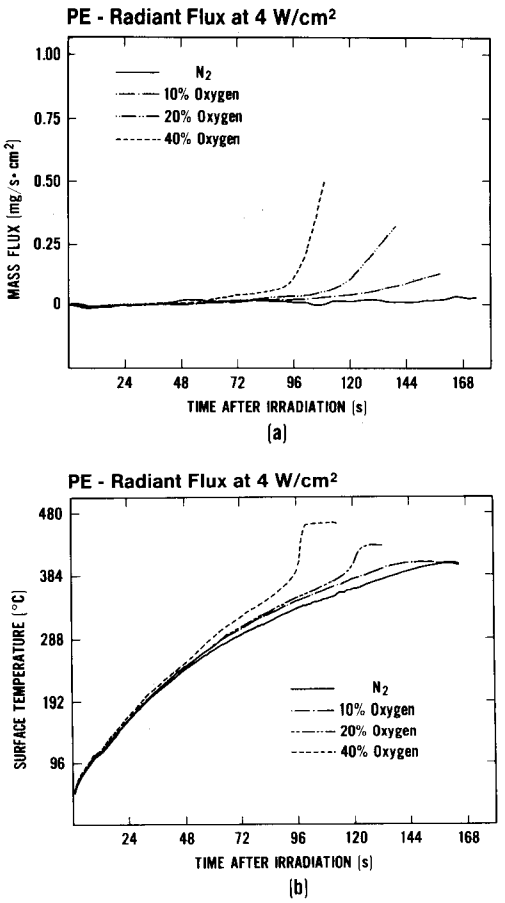

FIG. 6. Effects of oxygen mole fraction on mass flux and surface temperature history for PE at 4 W/cm^2, (a) mass flux, (b) surface temperature.

(mixed alkanes and alkenes up to C_{100}) at 1 atmosphere pressure are capable of boiling out of the condensed phase even at 460° C (23); in contrast, methyl methacrylate, the main product formed in PMMA degradation, has a normal boiling point of 100° C. This will give a high vapor pressure at the near-surface temperatures and thus it will be possible to nucleate bubbles.

3.2.2 *Mass Flux and Surface Temperature*

The mass flux histories for various environments in Fig. 6(a) (at 4 W/cm^2) show a much stronger effect of gas phase oxygen than those with PMMA. The reduction (at long times) in the oxygen effect on mass flux observed for PMMA is not observed here due to termination of the irradiation when the sample starts to melt excessively. The sudden sharp increases in mass flux for 20% O_2/80% N_2 and 40% O_2/60% N_2 shown in Fig. 6(a) coincide with the observed start of the color change in the surface

layer and with sudden sharp increases in surface temperature as shown in Fig. 6(b). In contrast to PMMA, the surface temperature of PE becomes higher with an increase in gas phase oxygen content. The exact nature of the interaction between the ambient oxygen and the PE surface that results in the behavior in Figs. 6 is not completely clear at present. The formation of a colored residue on the surface appears to be the initial stages of char formation implying oxygen participation in a cross-linking process. At the same time, the increased gasification rate implies oxygen assistance in the polymer degradation to vaporizable fragments. There is a large literature concerning the effects of oxygen on polyolefins, primarily in milder conditions of heat and oxygen exposure (25); the applicability of that work to the present situation requires exploration.

There is a physical effect of the surface reaction that may be more important than its probable exothermicity. The darkening of the near-surface layer to a brown color as discussed above implies a change in the absorption characteristics of the PE in oxygen-containing environments. To assess this effect, infrared transmission spectra were taken from 2.5 μm (4000 cm^{-1}) to 16 μm (~600 cm^{-1}) for an unexposed sample, one irradiated in a nitrogen environment and one irradiated in a 40% O_2/60% N_2 environment. The results indicate little difference in the spectra between the unexposed sample and the sample exposed to a nitrogen environment. The sample exposed in the 40% O_2/60% N_2 environment shows two types of change. First, there is considerable strengthening of absorption bands attributable to carbonyl groups (between 1800 cm^{-1} and 1700 cm^{-1}) [26]. This indicates significant incorporation of oxygen in the PE surface during the irradiation. Second, there is a roughly 50% increase in the average absorption coefficient from 2.5 to 15 μm. This increase in average absorption coefficient significantly increases the speed of heating the near surface region and thus contributes to the sharp increase in surface temperature and mass flux shown in Figs. 6.

4. Summary and Conclusions

The conclusions obtained from these experiments are as follows:

(1) The presence of oxygen in the gas phase increases the mass flux from PMMA and PE significantly. This effect is greater with PE than with PMMA. When the gasification rate from PMMA becomes significant, the effect of oxygen on mass flux is reduced apparently due to the decrease in oxygen supply rate to the surface as the counterflow of decomposition gases grows.

(2) Bubbles comprise a substantial mechanism of mass transport from the degrading surface region of PMMA. Their role interacts strongly with the viscosity of the near surface melt, being enhanced as viscosity decreases. This viscosity appears to decrease with increased surface temperature and especially with increased gas phase oxygen. Open bubbles on the gasifying surface enhance the depth of the layer affected by oxygen.

(3) An increase in oxygen concentration slightly reduces the surface temperature of PMMA but it significantly increases the surface temperature of PE (relative to the pure nitrogen cases).

(4) The surface of degrading PE turns brown in the presence of oxygen probably as a result of char-forming reactions. This increases the in-depth absorption coefficient and enhances the rate of surface heating and thus its rate of gasification.

(5) The rate of transient gasification cannot be described simply as a function of surface temperature or proportional to energy input. A model for predicting the rate of transient gasification should include condensed phase oxidative chemical reactions, in-depth thermal decomposition, mass transfer in the sample (diffusive and bubble-induced), changes in molecular weight and thus in viscosity of the molten layer, and changes in the in-depth absorption characteristics of the sample layer.

5. *Acknowledgments*

The authors would like to thank Mr. William Wooden for his assistance in conducting the experiments and Messrs. David Tate and Emil Braun for their help in programming and analyzing the data collection process.

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COMMENTS

M. M. Hirschler, The City University, London, England. I wonder if you could help me to clarify the object of the research in your interesting paper. On the surface of it, it seems to me that you have found a series of results which were very predictable. In other words, it was to be expected that an added external stimulus such as the presence of oxygen in the atmosphere, must effect much more strongly a polymer such as polyethylene (where thermal decomposition occurs by random chain-scission to give very small gaseous aliphatic products) than polymethylmethecrylate (which unzips to produce relatively unreaction monomer molecules). Furthermore, since a larger heat flux clearly causes more drastic effects on the polymer, the added effect of the other external stimulus, viz. the oxygen, will be less evident.

It is not clear to me whether, even though your heating rates are quite high, you regard the process occurring as thermal decomposition or as combustion.

Just in passing I would like to add that in our laboratories we have found, at low heating rates (5–100 Min^{-1}), that both the reaction order in polymerand the activation energy for the poly (vinylidene fluoride) are effected by the presence of oxygen in the atmosphere (1). I mention this because poly (vinylidene fluoride) is a polymer which decomposes by a different mechanism to those for either polyethylene or poly (methyl methacrylate), namely chain-stripping.

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Author's Reply. It is, of course, well known that in slow heating experiments, oxygen attacks PMMA and PE. What this paper addresses is whether such attack is significant to fire research. In fire environments, the decomposition of polymers proceeds by two competing mechanisms; one is thermal decomposition and the other is oxidative decomposition controlled by the rate of oxygen supply from the gas phase. If the heating rate is high as in fire environments (~10° C/sec) compared to the slow heating rate of conventional TGA (1 ~ 10° C/min.), it is not clear what the outcome will be and whether

the effect of oxygen on the rate of gasification is still significant. Previously, no oxygen effect on the gasification rate has been included in flame spread, ignition and flash-over models commonly used in the fire research field. There have been no previous studies to demonstrate the effect of oxygen on the gasification rate in these contexts. For this reason, we were motivated to conduct experiments to clarify this point.

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T. Niioka, National Aerospace Lab., Japan. When the surface temperature attains a constant value, we usually consider that the steady state of gasification is established. It must be true even in the presence of oxygen, although the amount of the mass flux in the steady state may increase. Why do your mass fluxes continue to increase in spite of a constant surface temperature?

Author's Reply. In our experiment, a steady state condition is not reached despite the apparent constant surface temperature after several minutes heating. The sample thickness is finite and the temperature distribution inside the sample is always changing for the exposure times used here; it is becoming flatter. As noted in the paper, there is a definite contribution to the rate of gasification (mass flux) from the sub-surface region of the sample. The in-depth contribution is affected by the temperature distribution inside the sample. Therefore, the mass flux continues to increase with a deeper penetration of the thermal wave into the sample despite the apparent constant surface temperature. As noted in the Conclusions, the mass flux cannot be expressed by an Arrhenius-type expression based only on surface temperature.

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T. Hirano, University of Tokyo, Tokyo, Japan. You mentioned that the behavior of bubbles formed inside of a PMM piece depends on the exposed gas. What is the mechanism by which the exposed gas influences the bubble formation?

Author's Reply. Preliminary gel permeation chromatography experiments indicate a significant reduction in average molecular weight (~2 X) for the layer of PMMA near the surface when the sample is exposed to a 40% O_2 atmosphere as compared to a nitrogen atmosphere. This implies a reduction in melt viscosity of the molten PMMA layer of about a factor of ten. Bubbles (presumably monomer) nucleate in this molten layer as it passes about 250° C. In a less viscous layer, the cycle of bubble growth and collapse is accelerated and one sees higher frequency bubbles of smaller average size compared to the pure nitrogen case. In addition to this physical effect, which facilitates faster transient gasification, we have preliminary evidence, from TGA and IR spectroscopy studies, that oxygen accelerates the early decomposition process in PMMA.