

Oxidative Pyrolysis of Polymers before Flaming Ignition

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ABSTRACT

Thin films of polyethylene, polystyrene and poly(methyl methacrylate) were exposed to the wake of a lean hydrogen-oxygen flat flame. Exposure was terminated at times ranging up to the point when flaming combustion began. The films were then analyzed by infrared spectroscopy.

Oxidation of polyethylene and polystyrene occurred after a latency period but before ignition. The oxidation rate remained constant despite changes in flame-polymer separation and flame gas equivalence ratio. The latency period before oxidation observed for polyethylene depended on equivalence ratio and separation. No oxidation was observed with poly(methyl methacrylate).

A comparison of infrared spectra obtained by transmission through films with spectra obtained by internal reflection spectroscopy, demonstrated that oxidation of polyethylene and polystyrene before ignition is confined to within approximately 5 μm of the exposed surface.

KEYWORDS

Polyethylene, polystyrene, poly(methyl methacrylate), hydrogen-oxygen, flame, infrared spectroscopy, oxidative pyrolysis, ignition.

INTRODUCTION

Study of chemical changes that occur during polymer combustion has been primarily confined to indirect methods such as thermal analysis and to analysis of gases evolved during pyrolysis or formed in the gas phase during burning (1). Studies of the chemical changes in the condensed phase of polymer combustion systems have usually been made during steady-state candle-like combustion of polyolefins (2,3), by neutron activation analysis for oxygen. This work has resulted in a controversial theory that oxidative pyrolysis can be an important contributor to the energy balance at the surface of a burning polymer (4).

Transient phenomena that occur on burning polymer surfaces have not been extensively studied. Jakes and Drews (5) reported oxidation of polypropylene in samples removed from a slab along which a flame had been allowed to burn;

samples were analyzed by iodometry for peroxide and hydroperoxide and by hydrazine-hydrazone derivatization for carbonyl functions.

Nothing appears in the literature on condensed phase chemical changes during the ignition delay of polymers exposed to flames. In previous publications (6-8) Clark reported differences between the gas phase events surrounding such ignition of polystyrene, polyethylene and poly(methyl methacrylate). Spectrometric measurements of oxidation on the surface of those polymers, made during the ignition sequence using the same apparatus and exposure conditions, are reported in this paper.

EXPERIMENTAL DESCRIPTION

Materials

Low molecular weight poly(methyl methacrylate) powder (Aldrich 18, 223-0) was hot pressed onto aluminum foil (221°C, 8.6 MPa) to form films of 40-100 μm thickness. High density polyethylene pellets (Aldrich 181, 190-0) were hot pressed onto aluminum foil (154°C, 17 MPa) to form films of 60-70 μm thickness. Polystyrene pellets (Aldrich 18242-7) were hot pressed onto aluminum foil (204°C, 17 MPa) to form films of 50-80 μm thickness.

Exposure

The burner used (Fig. 1) was after a design of Botha and Spalding (9), using principles described by Hunter and Hoshall (10). A lean hydrogen-oxygen flat flame was supported above the polymer film sample, which was sandwiched

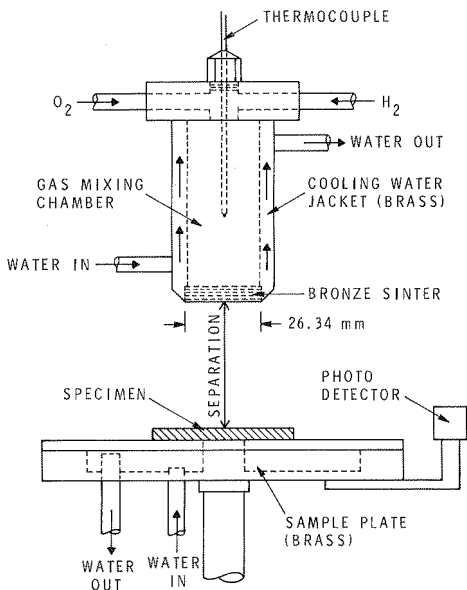


Figure 1. The burner

between a metal plate with a central circular orifice of 4.0 cm diameter and an asbestos mat 2 mm thick on the watercooled base.

The flame was in the form of an invisible flat circular disk 25 mm across and its wake extended to the polymer surface. Ignition of a polymer film was signalled by the first appearance of a very bright disk of light just above the polymer surface. Heat transfer was primarily by convection; at an equivalence ratio of 0.1 the total flux at the polymer surface had a maximum measured value of $19.7 \text{ kw}\cdot\text{m}^{-2}$, of which no more than $3 \text{ kw}\cdot\text{m}^{-2}$ was by radiation. (Equivalence ratio is defined as the volume of oxygen required for complete conversion of the hydrogen to water divided by the actual values of oxygen supplied.) The burner gases moved with a velocity that ensured laminar flow; the Reynolds number was about 558.

Infrared Spectroscopy

A Nicolet Model 6000 Fourier transform infrared spectrometer was employed, fitted with a broad bandwidth mercury-cadmium telluride (MCT) detector. Each spectrum was the average of 200 scans collected at 4.0 cm^{-1} resolution with Happ-Genzel apodization and single order zero filling.

Spectral examination of the films was conducted in two ways. The object of the first, termed the reflection-transmission technique, was to direct the collimated beam of the spectrometer through the entire area of exposed film, to reflect off the aluminum foil, and through the film a second time. This was achieved by replacing an existing plane mirror near the detector with the film-foil laminate, complete with the metal plate with the 4 cm orifice used in the burner exposure. The collimated beam of the spectrometer is approximately 5 cm in diameter, and thus absorptions over the entire flame-exposed film were observed. Commercial accessories for the spectrometric examination of large areas provided coverage of less than 1/7 of the area covered by this technique.

The second method of spectroscopic inspection involved the use of a conventional internal reflection apparatus (a Wilks Model 9) fitted into the normal sample port of the Nicolet spectrometer. A nominal 30 reflection KRS-5 (45° bevel) element was employed throughout.

Spectral deconvolution

In an attempt to determine the mode of oxidation of polymer films, Fourier self-deconvolution techniques (11) were applied to bands observed in the carbonyl region of infrared spectra of sample films of each polymer after flame exposure. The intrinsic bandwidths of infrared absorptions of this class are often greater than the separation between bands. The deconvolution technique computes the bandshapes at reduced bandwidths, allowing resolution of otherwise hopelessly overlapping bands. The technique was found most valuable in this study in demonstrating that oxidation had not occurred; in this case deconvolution of spectra of films before and after flame exposure showed that no new bands had been formed. The technique also allowed the complexity of the oxidation process for polyethylene and polystyrene to be observed (Figs. 2, 3).

Data handling

Spectra obtained of exposed polymer films by the reflection transmission technique were stored for later processing. The transmission spectra were converted to absorbance spectra. Spurious bands due to adventitious water in

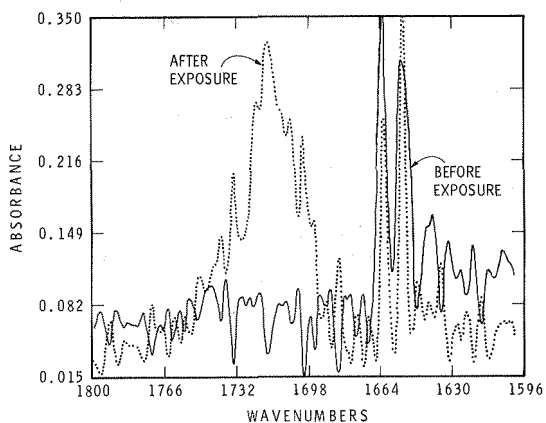


Figure 2. Deconvolved spectra of polyethylene before and after exposure

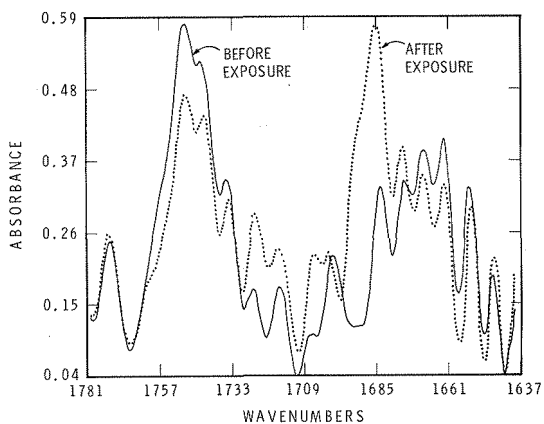


Figure 3. Deconvolved spectra of polystyrene before and after exposure

the system were removed by automated subtraction. Next a small positive y axis shift was added by coadding a straight line to each spectrum. A spectrum of unexposed polymer was then subtracted from that of the exposed polymer. At this stage the effects of oxidation were clearly apparent, especially in the carbonyl region of the spectrum. With suitable baseline correction, the area under the carbonyl peak was then calculated ($1770-1635\text{ cm}^{-1}$ for polystyrene, $1770-1683\text{ cm}^{-1}$ for polyethylene). At very low levels of oxidation, noise in

the spectrum occasionally led to negative areas being reported; this problem was avoided by the y axis displacement mentioned above.

RESULTS

Ignition delays

Previous work with this equipment (6-8) was conducted with thermally-thick slabs. It was of interest therefore to check that ignition delay times with polymer films were as reproducible as those recorded with polymer slabs. Table 1 shows the range of values obtained in runs of 10 exposures to ignition in various conditions; the reproducibility recorded gave confidence that different films exposed for varying times before spectroscopic analysis could be meaningfully compared.

TABLE 1. Ignition delay times at equivalence ratio 0.1; figures are averages of 5 determinations

	Polyethylene	Polystyrene	Poly(methyl methacrylate)
Separation (mm) 20	6.1 ± 0.2	13.0 ± 2.0	8.5 ± 0.5
15	5.3 ± 0.1	8.5 ± 0.5	
10	4.4 ± 0.2	4.7 ± 0.2	

Consistent with the increase in gas temperature (6) at the polymer surface as burner-polymer separation decreased, the ignition delays increased with separation.

Homogeneity

Oxidation before ignition was observed for polyethylene and polystyrene, but not for poly(methyl methacrylate) (Figs. 2, 3). For those films that oxidized, substantial variation in carbonyl concentration was observed across the exposed surface, ranging from no oxidation to a maximum, even at the end of the ignition delay. The reason for this is not clear but it could have been due to irregularities in the flat flame. However, spectroscopic examination by the reflection-transmission technique allowed measurement of the average degree of oxidation of the whole exposed film for a given exposure time.

Location of Oxidation

Films of polystyrene and polyethylene were exposed to the flame until oxidation was apparent in the reflection-transmission spectrum. The exposed and unexposed faces of each film were then examined by internal reflection spectroscopy. In this technique, the depth of penetration of the analyzing infrared beam is about 1 μm . The exposed faces of films of both polymers showed substantial oxidation products in both carbonyl (approximately 1700 cm^{-1}) and hydroxyl (approximately 3200 cm^{-1}) regions. By contrast, the unexposed faces of both polymers showed no sign of oxidation. These experiments demonstrate that oxidation upon exposure to flame did not penetrate right through the polymer films.

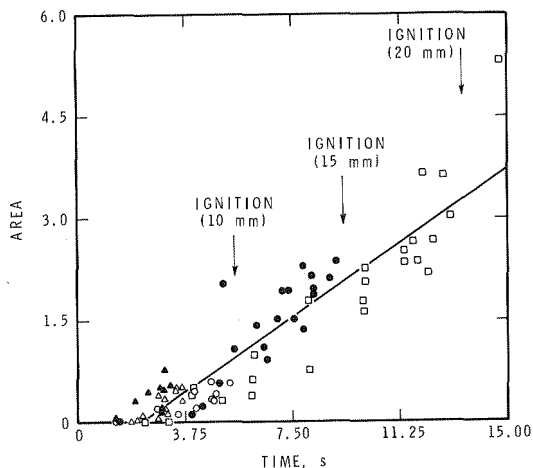


Figure 4. Oxidation of polystyrene before ignition, relative area of carbonyl band; 0.1 equivalence ratio: \circ 10 mm separation, \bullet 15 mm separation, \square 20 mm separation; \triangle 20 mm separation, 0.13 equivalence ratio, \blacktriangle 20 mm separation, 0.15 equivalence ratio

The relative sizes of the O-H stretch and the adjacent C-H stretches were approximately the same in the surface and by reflection-transmission, indicating that the bulk of the oxidation was very close to the exposed surface.

Variation of Flame-Polymer Separation and Flame Gas Equivalence Ratio

Figures 4 to 6 show the changes in carbonyl concentration in polystyrene and polyethylene films for various exposure times at three different burner-polymer separations and three different flame gas equivalence ratios. Each point represents analysis of the carbonyl region of the spectrum of a different, but very similar, film exposed to the flame and analyzed by the reflection transmission technique.

Despite changes in flame-polymer separation and flame gas equivalence ratio, the locus of all points on the oxidation-time plot for polystyrene was constant to the limits of error (Figure 4). Oxidation began after a very similar period of exposure and oxidation to produce carbonyl functions occurred at the same rate until ignition. Time to ignition, as noted above, was related to the flame-polymer separation.

The onset of oxidation of polyethylene was more sensitive to flame-polymer separation, but once oxidation had begun, the rate of oxidation was similar at the two separations at which the data scatter was small enough to allow meaningful comparison (Figure 5). Changing the equivalence ratio of the flame also influenced the time of onset of oxidation; the richer the flame, the shorter the initiation period. After initiation the rate of oxidation was high and similar for each fuel ratio (Figure 6).

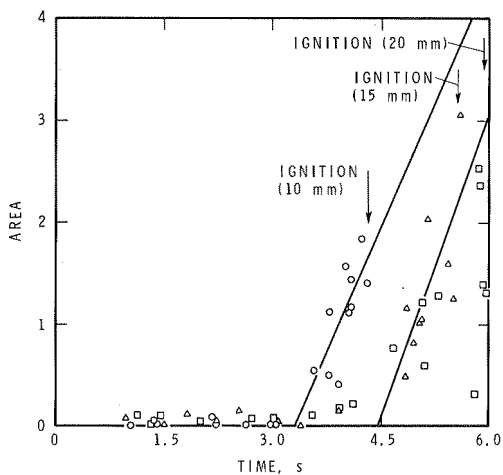


Figure 5. Oxidation of polyethylene before ignition at 0.1 equivalence ratio, relative area of carbonyl band: \circ 10 mm separation, Δ 15 mm separation, \square 20 mm separation

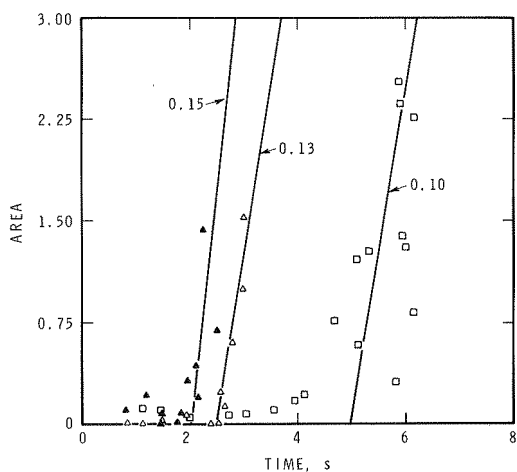


Figure 6. Oxidation of polyethylene before ignition at 20 mm separation, relative area of carbonyl band: \square 0.1 equivalence ratio, Δ 0.13 equivalence ratio, \blacktriangle 0.15 equivalence ratio

Poly(methyl methacrylate)

The analysis of this polymer was complicated by the presence of strong carbonyl absorptions in the infrared spectrum of the unexposed polymer. The

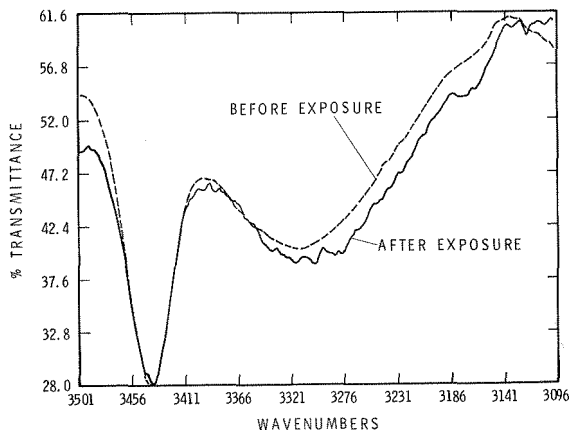


Figure 7. Poly(methyl methacrylate) just before ignition (9 s exposure) and before exposure

appearance of spectra of films before and after flame exposure was identical and this similarity persisted after implementation of the spectral deconvolution technique described above.

The spectrum of poly(methyl methacrylate) above 3000 cm^{-1} is less cluttered. However, hydroxyl absorption is generally broader and less easily distinguishable from the baseline than are carbonyl absorptions. Nonetheless, unlike polyethylene and polystyrene, flame exposed poly(methyl methacrylate) showed no evidence of hydroxyl bands (Figure 7). Poly(methyl methacrylate) is not oxidized in the condensed phase under these conditions.

DISCUSSION

Hirschler recently queried the value of the study of chemical changes in polymers in fire conditions, arguing that much had already been determined about polymer pyrolysis (12). In reply, Kashiwagi and Ohlemiller pointed out that slow pyrolysis is not necessarily a good process to study in order to ascertain performance in fire conditions, since pyrolysis rates in fire conditions are at least two orders of magnitude faster.

The present study provides support to the latter view; the phenomena observed would have been difficult to predict from published reports on the (slow) pyrolysis of the polymers burned. Varying the conditions of fire exposure changed the mode of pyrolysis observed. Thus, in the radiant exposure conditions used by Kashiwagi and Ohlemiller (12), poly(methyl methacrylate) was responsive to oxygen concentration, while under the convective heat transfer conditions used in the present work, condensed phase oxidation was not observed.

Polystyrene and polyethylene show similarities and differences in their pre-ignition behaviour. Both exhibit rather constant rates of oxidation, over the range of conditions used. However, for polyethylene the oxidation process

is initiated after a time which depends on equivalence ratio and flame proximity; these factors are less noticeable for polystyrene.

The two polymers undergo fundamentally different pyrolysis reactions; polystyrene decomposes by random- and end-chain scission into a mixture of monomer and oligomeric fragments, while polyethylene, in a random scission process (1), produces little monomer. The behaviour observed in this study can be accounted for by assuming that the surface of polyethylene is more sensitive to oxygen than that of polystyrene, because of a greater concentration of unsaturated sites.

One finding of possible industrial importance is that oxidation in these conditions was confined to very near the exposed surface. To the extent that pre-ignition oxidation should be restricted, the provision of fire retardant chemicals throughout a polymer may be an unnecessary and ineffective mode of protection. The results suggest surface treatment with fire retardants may be all that is required. If reactive fire retardants are required, surface grafting may be the method of choice.

However, the finding that oxidation occurs before ignition does not necessarily mean that control of this oxidation will result in increased resistance to ignition. Such an extrapolation must await the results of further study.

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