

Effect of Gas Phase Oxygen on Chain Scission and Monomer Content in Bulk Poly(methyl methacrylate) Degraded by External Thermal Radiation

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BACKGROUND

The effect of the atmosphere on the thermal degradation and gasification of bulk polymeric materials is not fully understood with respect to ignition and flame spread [1]. It is of interest to know whether molecular oxygen influences these aspects of polymer flammability through direct attack on the condensed phase.

Poly(methyl methacrylate), PMMA, is often used as a model to study thermoplastics decomposition in fire-like environments. PMMA has been well characterized with respect to its gasification behavior in inert atmospheres. The gasification can be initiated from weak links in the polymer chains at lower temperatures and from random scissions along the polymer chains at higher temperatures [see for example ref. 2]. In the presence of oxygen the initiation and gasification proceed at an intermediate temperature. These characterizations were made on very small samples without a significant temperature gradient in the polymer or composition gradient for the atmosphere in contact with the polymer [3]. In some fire environments a polymeric material undergoing gasification may be subjected to broad temperature gradients and atmospheres of widely different compositions.

OBJECTIVE

To investigate, at the molecular level, the effect of the concentration of atmospheric oxygen on the decomposition of bulk PMMA at different incident heat flux levels simulating radiative heating of the surface by fires.

APPROACH

The approach used to ascertain the effect of oxygen on PMMA degradation was to determine the number of chain scissions experienced by the residual polymer after a period of exposure to thermal radiation. Degradation was achieved by exposing 1 cm thick PMMA plates in atmospheres containing 0, 10, 21, and 43 % oxygen in nitrogen to black body radiation simulating the radiant energy flux of fire environments. Molecular weight measurements, from which the scission numbers are calculated, and residual monomer content were determined on successive thin layers about 0.1 mm thick cut from the exposed surface and at various deeper levels throughout the sample showing indications of decomposition by bubble formation. These determinations were made on solutions of PMMA in tetrahydrofuran. The analyses were made by gas chromatography and size exclusion chromatography for monomer content and molecular weights, respectively.

RESULTS

Figure 1 shows that at an irradiance of 17 kW/m^2 oxygen enhances the scission number of the degraded surface layer to a depth of about 1 mm or less, apparently, as a result oxygen entrapment in openings formed by bursting bubbles of escaping monomer vapor. Figure 2 illustrates a similar oxygen effect when the polymer was degraded at a higher irradiance, 30 kW/m^2 , except that the effect is somewhat less pronounced when the scission number in nitrogen is compared to those in the presence of oxygen. The higher irradiance is expected to be sufficiently energetic to induce random scissions in the polymer chains but these scissions are evidently enhanced by the presence of oxygen.

The scission numbers calculated from the M_n values of the surface layers for each exposed sample are plotted against the mole fraction of oxygen in the surrounding atmosphere and shown in figure 3. The chain scissions appear to follow a linear relationship with oxygen concentration at both irradiance levels.

The monomer content of the near surface was found to be greater in the PMMA degraded at the lower flux, 17 kW/m², than at the higher flux, 30 kW/m², when oxygen is present. This is attributed to a lower temperature and a larger melt viscosity due to fewer chain scissions at the lower flux, both of which impede volatilization of the monomer. At the higher flux the sample temperature is also sufficiently elevated so as to increase evaporation of the monomer and to contribute to the lower melt viscosity by a greater number of random chain scissions. This is illustrated in figure 4 where the monomer content of the upper most surface layer (about 0.1 mm thick) is plotted against the oxygen mole fraction of the atmospheres in which the surfaces were irradiated.

REFERENCES

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2. MacCallum, J. R. Makromol. chem. 83, 137 (1965).
3. Kashiwagi T, Inaba, A., Brown, J. E., Hatada, K., Kitayama, T, and Matasuda, E., Macromolecules 19, 2160 (1986).

Figure 1. Chain Scission Number of the Surface of PMMA Radiatively Heated at 17 kW/sq. m for 420 s

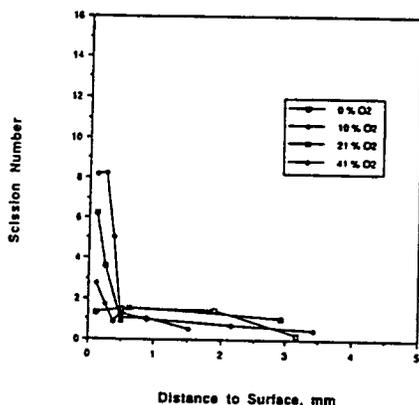


Figure 2. Chain Scissions near the Surface of PMMA Radiatively Heated at 30 kW/sq. m for 420 s

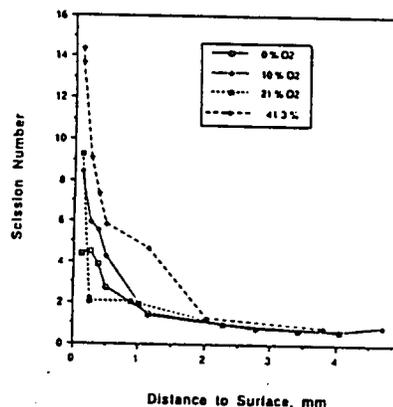


Figure 3. Comparison of the the Scission Number Dependence on Oxygen Concentration at Two Flux Levels

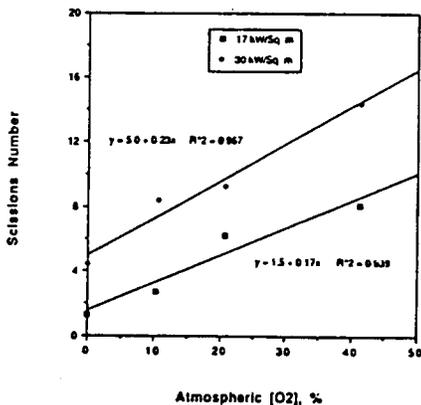


Figure 4. Comparison of the Monomer Content at the Surface layer of PMMA with Respect to Oxygen Concentration and External Flux

