Differences in PMMA Degradation Characteristics and Their Effects on Its Fire Properties

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ABSTRACT

Thermal degradation and thermal oxidative degradation characteristics of Plexiglas G and Lucite were determined using thermogravimetry. The results show that degradation rate of Plexiglas G is sensitive to gas phase oxygen but that of Lucite is much less so. Comparison of derivative thermogravimetry curves between the two samples indicates that at low temperatures Plexiglas G is more stable with respect to degradation in nitrogen. Lucite is initially more stable with respect to degradation in air than is Plexiglas G. A similar trend was observed in a nonflaming gasification study using external radiative heating. It appears that the chemical nature of the degradation processes of the two samples is the same for slow heating thermogravimetry and for more rapid heating (gasification study) simulating a fire environment. In piloted radiative ignition at 1.8 W/cm^2, the ignition delay time of Plexiglas G is about 15% less than that of Lucite. Increasing the radiant flux reduces the difference in ignition delay time between the two samples. The downward flame spread velocity of Lucite is about 20% faster than that of Plexiglas G, but the difference in burning rate between the two samples is very small.

INTRODUCTION

Materials involved in fire are generally categorized only by their general chemical structure, for example, polystyrene, polyurethane, polyethylene, etc. However, within any one such general category there are significant property differences. These include molecular weight, impurities, plasticizer, additives, copolymer and so on. At present, it is not clear whether these differences affect such fire properties as ignition, flame spread and burning rates. This study examines whether such differences can have significant effects on fire properties for one type of material, poly(methylmethacrylate) (PMMA).

PMMA is studied because of its high purity polymer composition (it contains no plasticizers, it is not a copolymer and it generally contains few additives) and also because it has a relatively simple and well understood degradation mechanism (1-3). Therefore, this examination of the behavior of PMMA from two different manufacturers is only a first look at the impact of differing material source; more complex commercial polymers have greater potential to behave differently. Another advantage of using this material is that the principal degradation product is the monomer even when PMMA is manufactured by different companies. Therefore, it seems reasonable to assume that the gas phase behavior should be the same for different PMMA samples and that any observed differences are probably due to their condensed phase degradation characteristics.

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This study consists of three parts. First, thermogravimetry (TG) is used to study a small PMMA sample at low heating rates: differences in global degradation chemistry between selected samples are examined. Second, nonflaming gasification of the samples under well-controlled thermal radiation conditions simulating material behavior in fire environments is examined. In this part of the study, the gasification process includes not only the degradation chemistry but also effects due to heat and mass transport processes. Third, some fire properties of selected samples are measured to determine whether they differ among samples. The measured fire properties are piloted radiative ignition delay time, downward flame spread velocity, and mass burning rate.

EXPERIMENTAL SECTION

Materials. The PMMA materials used in this study were commercial Plexiglas G (Rohm and Haas, Inc.)* and Lucite (E.I. Dupont de Nemours & Co.) in sheet form. The specimens for the TG study were disk-shaped, about 5.5 mm in diameter and about 200 μm thick; they were milled from commercially available sheet stock. The specimens for nonflaming gasification and also for piloted ignition under external radiative heating were 4 cm x 4 cm x 1.2 cm thick; they were 10 cm x 10 cm x 1.2 cm thick for the study of burning rates and 10 cm width x 30 cm length x 1.2 cm thick for the study of flame spread. All samples with 1.2 cm thickness had the original unmachined surface.

Thermogravimetry. Weight loss from the sample was measured using a Mettler Thermoanalyzer TA 2000. Heating rates of 0.5, 0.7, 1, 2, 3 and 5°C/min were used to obtain the overall kinetic constants for weight loss. Sample weight, temperature and time were simultaneously recorded with a computer. The reproducibility of TG and DTG was generally excellent and temperature at a peak weight loss rate could be reproduced within 2°C.

Apparatus for Nonflaming Gasification Under Radiative Heating. A detailed description of the experimental apparatus and procedure for the radiative heating pyrolysis study has previously been reported (4). Briefly, uniform thermal radiation from an electrically heated graphite plate was used to irradiate a vertically mounted sample at radiant flux of 2.2 W/cm^2 in a specified gas environment. No flaming occurred during the irradiation period. The sample was mounted on an electromechanical balance which could sense a 1 mg change in a total weight of up to 50 g. A 25 μm wire diameter chromel-alumel thermocouple was laid across the front surface of the sample with the junction near the center of the sample. To assure good contact between the thermocouple and the sample surface, the thermocouple was heated electrically and simultaneously pressed into the surface prior to a test. Any increase in temperature of the thermocouple by direct absorption of the external radiation was at most 5°C for the radiant fluxes used in this study (5). This magnitude of temperature increase is comparable to the reproducibility of the measured surface temperature. The reproducibility of the data is within 5% for mass flux and within 3% for temperature.

Apparatus for Piloted Radiative Ignition. The same apparatus as described above was used. Again the sample was mounted vertically. The only addition was a pilot electrically heated platinum wire (0.375 mm wire diameter) over and across the top edge of the sample. The distance between the bottom of the spiral wire (about a 6 mm diameter spiral) and the top edge of the sample was about 1.5 cm. The reproducibility of ignition delay time is within 5%.

Downward Flame Spread Study. A vertically mounted sample was supported between two marinite plates along its vertical edges. Flame spread was

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*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.

initiated by igniting an adhesive cement on the top edge of the sample with a match. Flame spread down over both sides of the sample. A 25 μm wire diameter chromel-alumel thermocouple spread across the surface of the sample parallel to the flame front, with the junction near the center of the sample, was used to measure the local surface temperature history. The reproducibility of flame spread rate is within 5%.

Mass Burning Rate Study. A sample was mounted horizontally on noncombustible fiber insulation. Flame spread along side edges of the sample was inhibited by cementing 1 mm thick pieces of cardboard on them so as to promote one-dimensional burning as much as possible. A 25 μm wire diameter chromel-alumel thermocouple with the junction near the center of the sample was used to measure surface temperature, and an electromechanical balance was used to measure the change in weight of the sample. The reproducibility of mass buring rate is about 5%.

RESULTS AND DISCUSSION

1. Thermogravimetry

Weight loss. Derivative thermogravimetry (DTG), i.e., weight loss rate vs temperature, of Lucite and Plexiglas G was measured at various heating rates. The DTG results were obtained by taking the time derivative, (d(W/Wo)/dt), of the ratio of the sample weight, W, to the initial sample weight, Wo. Typical DTG results for Lucite and Plexiglas G in nitrogen and in air are shown in Fig. 1. The results for Lucite show that rapid weight loss starts slightly below 260°C in nitrogen and also in air at a heating rate of 5°C/m indicating small dependency on oxygen.

The results for Plexiglas G degrading in nitrogen show that a small weight loss appears around 160°C and rapid weight loss starts at about 300°C at a heating rate of 5°C/m. The early small weight loss may be caused by volatilization of unreacted monomer in the sample. Weight loss of Plexiglas G degrading in air starts rapidly at about 230°C and this is followed by a complex pattern of weight loss rate changes with increases in temperature, instead of by one major peak, as observed in nitrogen. Four DTG peaks are observed at all different heating rates. The difference in the temperatures at which rapid weight loss begins between nitrogen and air is about 70°C at a heating rate of 5°C/m. The thermal degradation of Plexiglas G is very sensitive to gas phase oxygen.

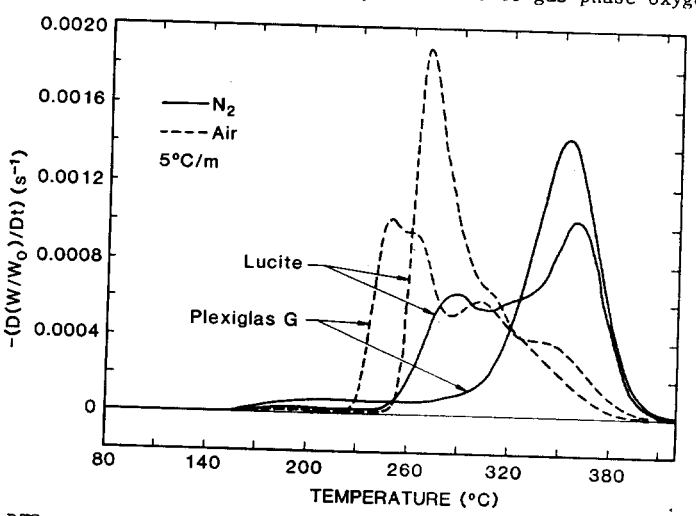

FIGURE 1. DTG curves in nitrogen and in air.

Neglecting the small early weight loss which starts at about 160°C for both samples, one sees that Lucite starts to lose weight in nitrogen about 50°C lower than does Plexiglas G (i.e., 250°C vs 300°C) at a heating rate of 5°C/m. The second peak of weight loss rate for Lucite nearly overlaps the major peak for Plexiglas G. This behavior indicates that Lucite degrades easier in nitrogen than does Plexiglas G at low temperatures. The comparison of results in air indicates that Plexiglas G starts to lose weight rapidly at about 230°C compared to about 260°C for Lucite. The rate of weight loss for Lucite is very large from 260°C to 300°C at a heating rate of 5°C/m. The pattern of weight loss rate above about 320°C is roughly the same for both samples. This behavior indicates that Plexiglas G degrades in air at a lower temperature than does Lucite, but the difference between them is relatively small. These qualitative trends are also observed with TG and DTG at the low heating rates.

Global kinetic rate constants. Global kinetic rate constants based on the rate of sample weight loss were determined from the DTG results at the various heating rates for Plexiglas G and Lucite. The relatively simple Kissinger's method (6) was used to determine the kinetic constants. The relation derived by Kissinger is as follows:

$$\ln\left(\phi/T_m^{\,2}\right) = \ln\left(nRAW_m^{n-1}/E\right) - E/RT_m$$

ϕ is the heating rate in the TG experiment, T_m is the temperature at the maximum rate of weight loss, R is the universal gas constant, E is the activation energy, A is the pre-exponential factor, W_m is the fraction of the sample weight at the maximum rate of weight loss, and n is the apparent order of the reaction with respect to the sample weight. Activation energies were determined from the slopes of the straight lines. The results for both samples are listed in Table 1 and they confirm the above indication that the degradation of Plexiglas G is more sensitive to gas phase oxygen than is Lucite.

Molecular weight of the two samples. The molecular weight distributions of both samples were measured using gel permeation chromatography. The molecular weight distribution of Lucite is broad with a shoulder in a low molecular side. The number average molecular weight is 179,000 and the polydispersity (ratio of weight average molecular weight against number average molecular weight, a measure of the width of the molecular weight distribution) is 4.2. The molecular weight distribution of Plexiglas G is unimodal. The number average molecular weight is 402,000 and the polydispersity is 2.2. This indicates that there are differences in the length of polymer chains between the two samples and some complex molecular weight distribution for Lucite.

Sample purification effects. Another important factor, which strongly affects the degradation of polymers, is impurities in the sample. It is expected that the commercial samples used in this study contain some impurities: unreacted initiator, monomer, ultraviolet absorber, etc. The effects of impurities on the degradation of Plexiglas G and Lucite were examined by TG of purified samples; the results were compared with the original samples. The purification procedure is described in the previous study (8).

TABLE 1. Activation energy of TG weight loss (first peak)

	Nitrogen		Air
Lucite	84 kJ/mol		95 kJ/mol
Plexiglas G*	210 kJ/mol	First Peak	174 kJ/mol
		Second Peak	156 kJ/mol
		Third Peak	114 kJ/mol

* Values were determined in the authors' previous study (7).

The weight loss and DTG of the purified Plexiglas G and Lucite degraded in nitrogen and in air were compared with those of the original samples degraded in nitrogen and in air, respectively. The effects of sample purification on the DTG of both samples degrading in nitrogen is very small, except for an increase in stability at low temperatures probably due to removal of unreacted monomer from the sample. However, the effect of the purification of Plexiglas G on weight loss in air is significant. As shown in Fig. 2, there is only one peak in the DTG for purified Plexiglas G compared with the four peaks observed for the original sample. Furthermore, the stability of the sample increases significantly with an increase in the threshold of weight loss from about 210°C to 260°C at a heating rate of 2°C/m. There is little effect of the purification of Lucite on weight loss in air.

2. Nonflaming Gasification Due to Radiative Heating

The above TG study was based on small samples heated at rates much slower than those applicable to fire. The objective was to determine chemical behavior of the sample under conditions in which effects of mass and heat transport processes on weight loss are minimized. Further study is needed to demonstrate the impact of differing chemical behavior under conditions similar to those in fire, i.e., higher heating rates and substantial transport processes. For this reason, both samples were heated by a well-defined thermal radiation flux.

Surface temperature. Sample surface temperatures were measured when both samples were heated at a thermal radiant flux of 2.2 W/cm^2 in air and in nitrogen. The results are shown in Fig. 3. The range of measured surface temperatures is about the same as that used in the above TG study, although the heating rates were much higher. The results indicate that the surface temperatures of both samples heated in nitrogen are slightly higher than those heated in air. This trend is consistent with a previous study (4), indicating that the overall gasification process of Plexiglas G and of Lucite is endothermic even in air. Surface temperature curves of both samples heated in nitrogen show more roughness compared with those heated in air. This was caused by the more violent rupture of larger bubbles in nitrogen than in air due to the more viscous (higher molecular weight) molten polymer layer near the surface in

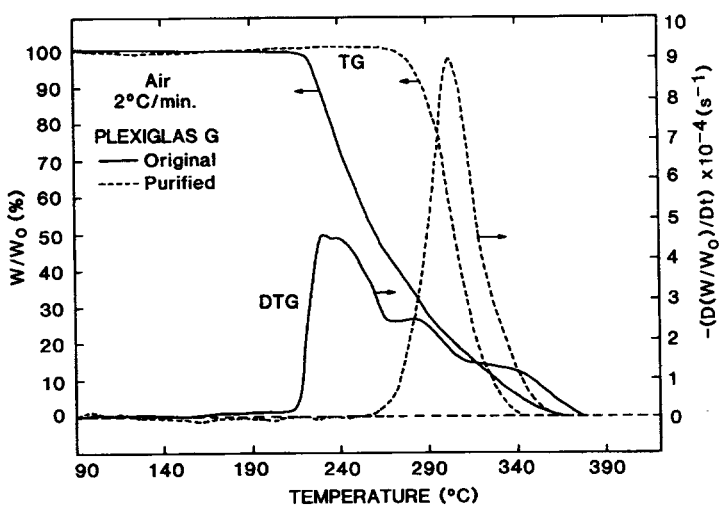

FIGURE 2. Comparison of TG and DTG curves or original Plexiglas G against purified Plexiglas G degrading in air.

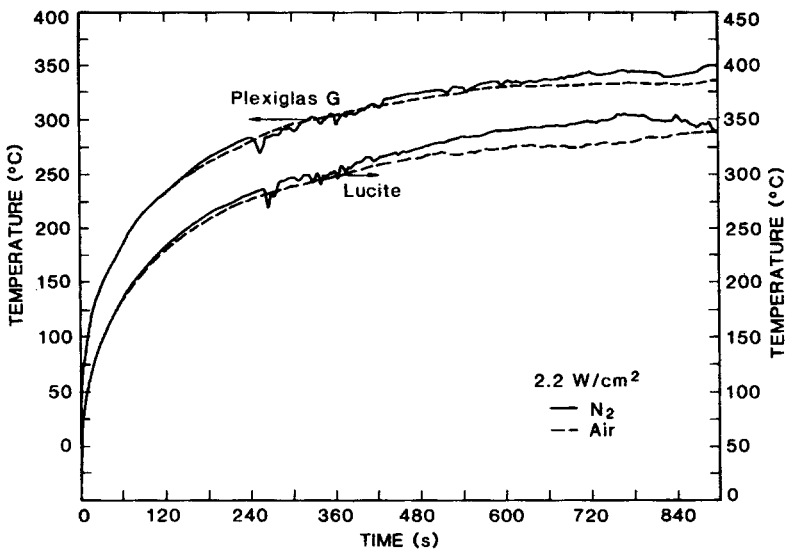

FIGURE 3. Comparison of surface temperature history with time heated at radiant flux of 2.2 W/cm^2 in nitrogen and in air.

nitrogen than in air (9). Overall, Fig. 3 shows that there is little difference in surface temperature history between Plexiglas G and Lucite heated in air or in nitrogen at the same radiant flux. This indicates that thermal properties of the two samples should be the same. This is confirmed: the specific gravity is 1.19*, the specific heat is 1.5 J/g°C* and the thermal conductivity is 0.13 J/ms°C** for both samples.

Gasification rates. The dependence of mass flux on time is shown in Fig. 4(a) at a radiant flux of 2.2 W/cm^2 in nitrogen and in air. These results are calculated by dividing the time derivative of the measured transient weight by the front surface area of the sample. The results indicate that the mass flux of Lucite increases slightly when it is degrading in air compared to degradation in nitrogen. The mass flux increases significantly before 500 seconds when Plexiglas G is degrading in air compared to degradation in nitrogen. These trends, weak effect of gas phase oxygen on weight loss for Lucite and a strong effect for Plexiglas G, are consistent with those obtained from the above TG study.

In Fig. 4(b), the mass flux of Lucite degrading in nitrogen from 240 to 720 s, is significantly larger than that of Plexiglas G and beyond 720 s the mass flux is about the same for both samples. In this time range, the surface temperature is in the range between 275 and 350°C as shown in Fig. 3. The TG study shown in Fig. 1, also shows that at low temperatures (250 ~ 300°C), at a heating rate of 5°C/m, Lucite loses weight more rapidly than does Plexiglas G. Above 320°C the weight loss rates for both samples are about the same. This observation is qualitatively consistent with nearly equal mass fluxes measured beyond 720 s.

Comparison of the change in mass flux with time between Lucite and Plexiglas G degrading in air is complex. Although the difference in mass flux between the two samples is small, there are three regimes similar to those

*Manufactor's values.
**Our measured values.

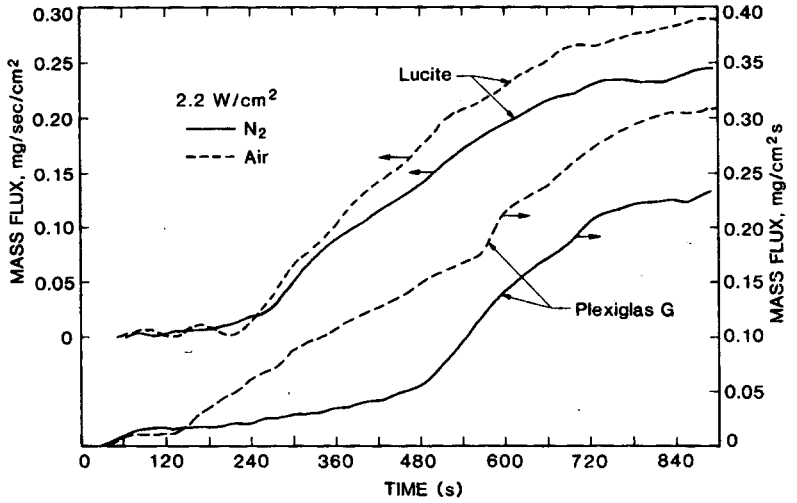

FIGURE 4(a). Comparison of history of mass flux at radiant flux of 2.2 W/cm² between nitrogen and in air.

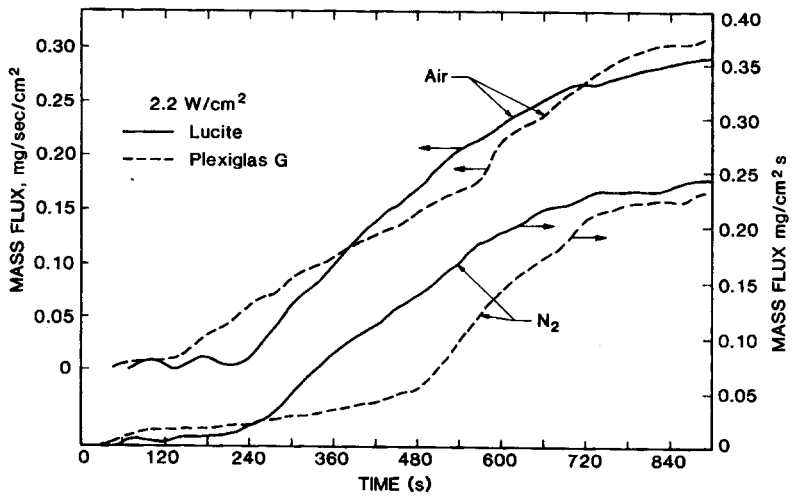

FIGURE 4(b). Comparison of history of mass flux at radiant flux of 2.2 W/cm² between Lucite and Plexiglas G.

observed in the TG comparison shown in Fig. 1. The first regime is between 120 and about 380 s corresponding to 225°C to 300°C determined from Fig. 3. In this regime the mass flux of Plexiglas G is larger than Lucite. This regime appears to correspond to the temperature range from 230°C to 260°C in Fig. 1. In making such comparisons, the heating rate is generally higher in the radiative heating experiment; this shifts the reaction to higher temperatures. In addition, the mass flux from the radiative heating experiment is integrated over the same in-depth temperature distribution. The second regime is between 380 and 720 s in Fig. 4(b), corresponding to 300°C to 350°C in Fig. 3. In this regime the mass

flux from Lucite is slightly larger than that of Plexiglas G. This regime appears to correspond to the temperature range from 260°C to 320°C in Fig. 1. The third regime is beyond 720 s in Fig. 4(b), corresponding to about 350°C in Fig. 3. In this regime the mass flux from Plexiglas G is slightly larger than that of Lucite. This regime appears to correspond to the temperature range above 320°C in Fig. 1.

Overall, the characteristics of the degradation of Plexiglas G and Lucite determined by the TG study agree well qualitatively with those determined by radiative heating, simulating conditions in a fire. It appears that the chemical degradation behavior of both samples determined from the slow heating TG study is qualitatively the same as that which controls their degradation under more rapid heating conditions. The above study shows clearly that there are distinct differences in degradation characteristics between Plexiglas G and Lucite.

3. Fire Properties

Piloted radiative ignition delay time. Surface temperature and weight loss for Plexiglas G and Lucite were measured during the ignition period; the results are shown in Fig. 5. Piloted ignition occurred at a surface temperature of about 275°C for both samples. The ignition delay time for Plexiglas G is about 45 s less than that for Lucite. Since the controlling step in piloted radiative ignition is the supply of combustible fuel gases from the sample, the larger mass flux from Plexiglas G compared to that for Lucite causes Plexiglas G to ignite earlier than Lucite. At 1.8 W/cm^2, both samples were exposed mainly to the first regime of the degradation discussed above, where Plexiglas G degrades faster than Lucite. At higher radiant fluxes, surface temperature at ignition tends to increase and the sample would be degraded in the second or the third regime described above. In this case, it would be expected that the difference in ignition delay time between the two samples should then become less. To demonstrate this predicted trend, ignition experiments were conducted at 4 W/cm^2 for both samples. The measured surface temperature at ignition was close to 300°C, and ignition delay time was reduced to about 60 s, yielding less time for the sample to be exposed to air above 200°C. The difference in ignition delay time between the two samples at 4 W/cm^2 was about 6% compared to about 15% at 1.8 W/cm^2. At lower radiant fluxes, the ignition delay time becomes longer, and the sample is exposed to air for a longer time above 200°C.

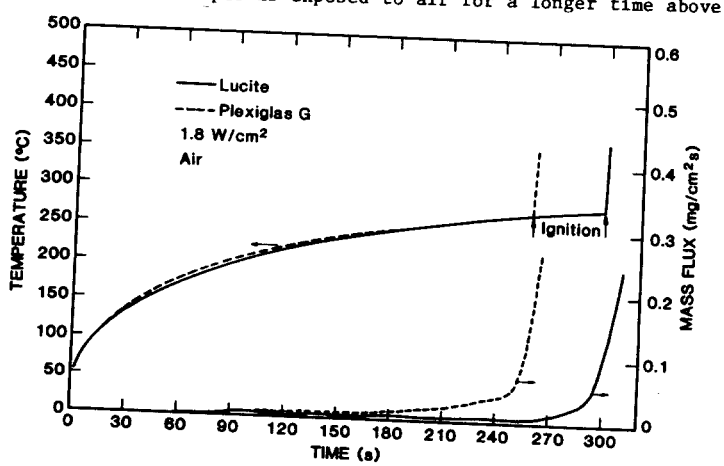

FIGURE 5. Comparison of surface temperature and mass flux histories between Lucite and Plexiglas G under piloted radiative ignition.

In this case, the differences in oxidative degradation characteristics between the two samples noticeably affect ignition delay times for the samples. For this reason, it is expected that the minimum radiant flux to cause pilot ignition would be less for Plexiglas G than Lucite. However, at higher radiant fluxes, the differences in oxidative degradation characteristics between the two samples become unimportant.

Downward flame spread velocity. Some phenomenological differences in flame front behavior between the two polymer samples were noticed. The flame front shape over the Lucite surface was uniform and the flame spread uniformly over the surface. However, the flame front shape over the Plexiglas G surface was sometimes disturbed by an accumulation of a black tar-like material. The black tar-like material was apparently formed on the violently bubbling surface behind the flame front possibly in conjunction with the deposition of soot-like particles from the flame. Since the surface temperature of the burning Plexiglas G is high, as shown in Fig. 6, the melt viscosity of the molten layer is quite low and the molten layer ends up slowly flowing down toward the flame front. This slow flow of the molten layer accumulates black tar-like material near the flame front. The black tar-like material appeared not to gasify or burn under this condition; occasionally it glowed. Near the flame-front, the black tar-like material formed several small spheres (diameter up to 3-4 mm). Sometimes these small black tar-like spheres obstructed the spread of the flame front; at other times they enhanced the spread of the flame front as they slid down and pulled the molten polymer locally ahead of the rest of the flame front. These effects caused a ragged flame front. It is not clear at present what net effect these black tar-like spheres have on flame spread velocity. Since a plot of flame front location with time shows a reasonably straight line, overall flame spread occurs with a constant speed. The black tar-like spheres were never observed in flame spread over Lucite.

The measured flame spread velocity over the Plexiglas G surface was 4.2×10^{-3} cm/s; it was 5.0×10^{-3} cm/s over the Lucite surface. Therefore, downward flame spread over the Lucite surface is about 20% faster than over Plexiglas G. Assuming that the black tar-like material does not affect the average flame spread velocity, one must look elsewhere to see what causes this difference in flame spread velocity. Since there are no differences in values

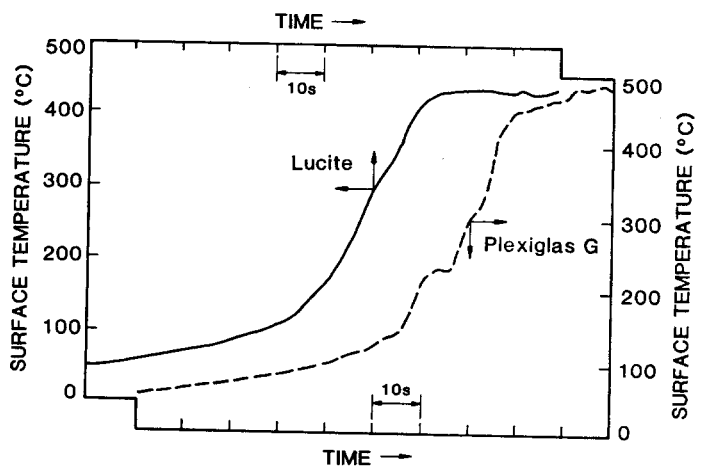

FIGURE 6. Surface temperature history across approaching downward traveling flame front.

of thermal properties between the two samples, the amounts of heat transferred through the sample from the flame front to the surface ahead of the flame should be the same for both samples. The surface temperature rise across the approaching flame front as shown in Fig. 6 indicates that the heating rate is about 10°C/s. With this heating rate, it takes about 20 s for the sample surface to heat from 100°C to 300°C. It appears that the difference described in the above first stage degradation in air is not detected during this rapid heating process. Although the surface temperature at the flame front was not precisely determined, it appears to be above 300°C from visual observation of the flame front location relative to the thermocouple bead. This puts the degradation in the second regime in air in which Lucite degrades faster than Plexiglas G or in nitrogen without any oxidative degradation where Lucite also degrades faster than Plexiglas G (such as shown in Figs. 1(a) and 4(b)).

Burning rate. Material burning was initiated by piloted radiative ignition using an electrically powered cone shape heater (10). This caused sample burning over almost the entire top surface shortly after ignition. This ignition period corresponds to the period up to about 220 s in Fig. 7. Once ignition occurred, electric power to the heater was turned off and the heater was moved away so as not to interfere with the experiment. This period corresponds to about 220 s to 300 s in Fig. 7. Burning conditions without the heater are defined as those after about 300 s. The difference in measured mass flux during the burning period between Plexiglas G and Lucite is very small, although repeated experiments always indicate that the mass flux from Lucite is slightly larger than that from Plexiglas G. This is because the surface temperatures of both samples were in the range of 350°C to 400°C. These temperatures are so high that the difference in degradation behavior between the two samples at low temperatures (as shown in Figs. 1 and 4) is washed out.

All results and discussion described in this paper apply only to the comparison between Plexiglas G and Lucite. Although the differences in measured fire properties between these two samples are small, it does not necessarily mean that there are small differences in fire properties among other polymers even including PMMA from another manufacturer. The intention of this work is to raise awareness of differences among the same generically classified polymeric materials and the fact that these differences may cause significant differences in fire properties under certain conditions.

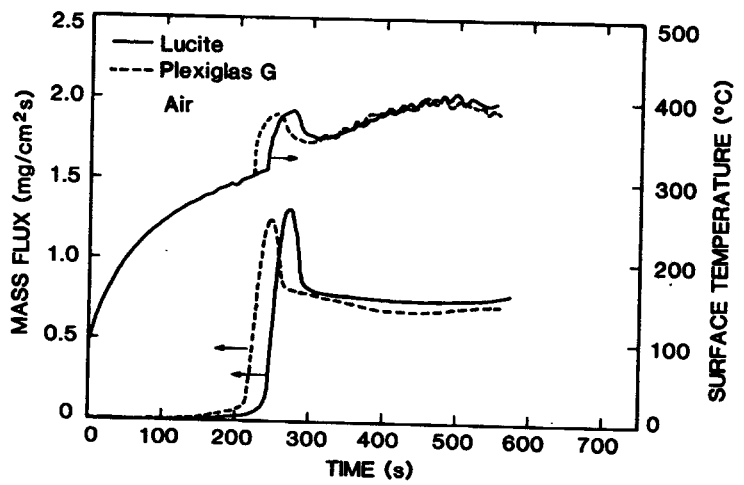

FIGURE 7. Comparison of surface temperature and mass flux histories between burning Lucite and Plexiglas G including initial piloted ignition.

CONCLUSIONS

(1) The TG study shows that the degradation rate of Plexiglas G is sensitive to gas phase oxygen, but that of Lucite is less so. Comparison of DTG curves between Plexiglas G and Lucite indicates that Plexiglas G is more stable with respect to degradation in nitrogen at low temperatures than lucite, but Lucite is more stable initially with respect to degradation in air than is Plexiglas G.

(2) The nonflaming gasification study under external radiative heating indicates that the comparative mass flux behavior for the two polymers agrees qualitatively with that of the TG study although the heating rates together with the heat and mass transport processes are different from the TG study. Therefore, the chemical nature of the degradation process of each of the two samples is the same for slow heating TG and the more rapid heating gasification study simulating a fire environment.

(3) In piloted radiative ignition at 1.8 W/cm^2, the ignition delay time of Plexiglas G is about 15% less than that of Lucite. Increased radiant flux reduces the difference in ignition delay time between the two samples because shorter ignition delay times reduce the time for the sample to be exposed to air above 200°C.

(4) Downward flame spread velocity over Plexiglas G is about 20% slower than over Lucite. However, the difference in burning rate between the two samples is negligible. This indicates that, if these two samples are heated rapidly to high degradation temperatures, differences in the chemical nature of their degradation would not be detected. The difference may become important when the two samples are heated at low temperatures for a sufficiently long period.

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