Effects of Polymer Characteristics on Flammability Properties

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ABSTRACT

The effects of material characteristics on piloted ignition, horizontal flame spreading, and heat release rate were studied by using two different polystyrene, PS, samples and two different poly(methyl methacrylate), PMMA, samples. The difference between the two PS samples was melt viscosity due to two different initial molecular weights and that between the two PMMA samples was thermal stability and melt viscosity also due to two different initial molecular weights. The results indicate that thermal stability of the material has significant effects on piloted ignition delay time, flame spread rate and heat release rate. The effects of melt viscosity, the transport of indepth degradation products through the molten polymer layer inside the sample, are negligible on piloted ignition. However, they are significant on horizontal flame spreading behavior and reduce its rate by forming opposed slow fluid motion of molten polymer along the inclined vaporizing surface against the traveling flame front.

Introduction

There have been numerous studies to determine the effects of polymer characteristics on flammability properties. Most of these studies were based on the comparison of flammability properties of many different polymer samples. Since there were always many differences in thermal properties, degradation characteristics, and gas phase oxidation chemistry due to differences in degradation products among polymer samples, these studies could not clearly explain why the flammability properties of polymer A were different from those of polymer B. In order to avoid this uncertainty, the effect of one or two differences in material characteristics on flammability properties were studied.

Initial molecular weight, MW, and thermal stability of the sample were selected as the two material characteristics. Since melt viscosity of molten polymer depends strongly on its molecular weight, varying initial molecular weight shows which flammability properties are affected by the melting characteristics of the sample without significantly modifying other material characteristics. Two types of polymers, poly(methyl methacrylate) (PMMA) and polystyrene (PS), were selected because the thermal degradation of PMMA is controlled mainly via the depropagation reaction[**1**,**2**], and the thermal degradation of PS is controlled mainly via the intermolecular- and intramolecular-transfer reaction[**3**,**4**]. Thus, it is expected that the thermal stability of PMMA is sensitive to initial molecular weight due to a change in the number of weak linkages in the polymer chains[**1**,**2**], but the thermal

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stability of PS is not sensitive to initial molecular weight. The difference in flammability properties between two PS samples with two different initial molecular weights should indicate only the effects of initial molecular weight (and thus melt viscosity) of the sample. The difference in flammability properties between two PMMA samples with two different initial molecular weights should indicate the combined effects of initial molecular weight and thermal stability of the sample.

A detailed discussion of each flammability measurement and the results were published elsewhere, for example, piloted ignition is presented in Ref. 6, flame spreading in Ref. 7, and non-flaming gasification in Ref.9. The objective of this paper is to combine these results to understand the effects of material characteristics on flammability properties.

EXPERIMENTAL

The two PMMA samples were ELVACITE 2009 (MW 47,000, low MW PMMA) and 2041 (MW 200,000, high MW PMMA) (E.I. Dupont de Nemours & Co.) and the two PS samples were STYRON 6065 (MW 64,000, low MW PS) and 6069 (MW 120,000, high MW PS) (Dow Chemical Co.). Since thermal properties of linear polymers do not change significantly with a change in molecular weight, as long as the number of monomer units in the polymer chain exceeds approximately one hundred, differences in thermal properties such as thermal conductivity and specific heat between the two PMMA samples and between the two PS samples are negligible. Furthermore, the initial molecular structures are almost the same between the two PMMA samples and the two PS samples. The difference is about 1 unit per 1000 units. During degradation this might become 1 unit per 100 units, but still effects on thermal properties and infrared absorption characteristics are negligible. However, this is not true for polymers which cross-link during degradation.

The sample specimens were cast to make a plate about 10 cm wide x 36 cm long x 1.3 cm thick for the flame spreading study, about 7.5 cm x 7.5 cm x 1.3 cm thick for the piloted ignition study, and about 10 cm x 10 cm x 1.3 cm thick for the burning experiment. The sample was mounted horizontally in this study; a more detailed description can be found in Ref.5 for flame spreading and in Ref.6 for piloted ignition. Heat release rate was measured by the Cone Calorimeter[**7**], which measures the consumption rate of oxygen during burning of the sample[**8**]. Although some of the non-flaming radiative gasification rate data[**9**] will be used for comparison of surface temperature, detailed results are not discussed in this paper.

RESULTS AND DISCUSSION

Thermal Stability: Derivative thermogravimetry(DTG), i.e., normalized weight loss rate of the four samples was measured at a heating rate of 5 °C/min. Results for the PS samples are shown in Fig.1 and those for the PMMA samples are shown in Fig.2. Since thermal oxidative degradation and thermal degradation might occur near the sample surface[**10**], degradation characteristics were determined both in nitrogen and in air. The important result obtained from these figures is that there are no significant differences in thermal stability between the two PS samples, as we expected.

For the two PMMA samples, there are three peaks for the high MW sample degrading in nitrogen. Since this sample was polymerized by a free radical method, it is expected that the first peak at around 170 °C is caused by scission at the weak linkage of the head-to-head structure[**2**,**11**], the second peak at around 280 °C is due to radical initiation at the unsaturated chain ends[**1**,**2**,**11**], and the third peak at around 370 °C is due to random scission at the main chain linkages. Higher stability for low MW PMMA sample (only one high temperature peak) indicates that the low MW sample was polymerized with a chain transfer agent to avoid the formation of the weak linkages in the polymer chains during its polymerization process[**2**]. Results of the samples degrading in air show an increase in thermal stability at the low temperature range (the disappearance of the first peak for the high MW sample) and significant reduction in thermal stability at the high temperature range. This is consistent with our previous study of oxygen effects on PMMA degradation[**2**].

Piloted Ignition: The relationship between ignition time and incident external radiant flux is a straight line in the logarithmic plot shown in Fig.3 for the four samples. The results show that ignition delay times of low MW PMMA samples are much longer than those of high MW PMMA samples. However, there are no significant differences between the two PS samples. Ignoring heat losses and assuming the sample to be inert and thermally thick (inert model), the slope of the above relationship is approximated to be -2.0[**6**]. However, the slopes shown in Fig. 3 are -2.8 for the high MW PMMA, -3.2 for the low MW PMMA, and -2.9 for the PS samples. There are many reasons in which the simple inert model cannot be applied to this study such as that the sample used in this study is not thermally thick, and there are additional complexities of indepth absorption of the incident radiation by the sample, of re-radiation loss from the sample, small sample weight loss by endothermic degradation prior to ignition, and changes in surface reflectance and absorption characteristics with radiant flux due to a change in source temperature. Measured surface temperatures at ignition for low MW PMMA samples gradually increase with external radiant flux from about 320°C to 340°C and those for high MW PMMA samples were nearly constant at about 260-270°C[**6**] as shown in Fig.4. They were nearly constant at about 350-370°C for both low and high MW PS samples in the range of external radiant flux used in this study. By referring to Figs. 1 and 2, these ignition surface temperatures indicate that thermal oxidative degradation might significantly contribute to the generation of combustible gases during the ignition process of these samples. These results indicate clearly that the thermal stability of the material strongly controls the piloted ignition process and thus surface temperature at ignition of the low MW PMMA samples are much higher than those of the high MW PMMA samples.

Flame Spreading: The relationship between the location of the flame front and time for the two PMMA samples in Fig.5 and for the two PS sample in Fig.6 shows significant differences in flame spread rate. The average flame spread rate was 2.3×10^{-3} cm/s for the low MW PMMA and 8.5×10^{-3} cm/s for the high MW sample. Similarly, it was 6.7×10^{-3} cm/s for the low MW PS sample and 8.5×10^{-3} cm/s for the high MW PS sample.

Flame spread behavior over the surface of the low MW samples was quite transient and different from the high MW samples. The sample with high MW did not form molten polymer near the flame front so the flame spread steadily. However, flame spread over the low MW PMMA sample was quite complex, similar to flame spread over the low MW PS sample. A schematic illustration of flame spread behavior over the two PMMA samples is described in Fig.7. Flame spread very slowly after reaching about 8 cm location. The energy feedback from the flame to the surface ahead of the vaporization front appeared to be insufficient to degrade the thermally stable low MW sample ahead of the vaporization front. Therefore, the regression rate normal to the surface was larger than the flame spread rate, and the wall described in Fig.7b was formed. Once the wall was formed, the blue flame front was absent and the flame almost stopped spreading. When a small particle was put on the top of the wall, a slow downward movement of the particle toward the bottom of the wall was observed, which indicates the existence of a slow fluid motion of the molten polymer against flame spread direction. When the flame front reached approximately the 10 cm location, burnout of the downstream part of the sample occurred and the center of the flame moved forward due to narrowing of the width of the flame by the burnout. Under this condition, air was entrained mainly from the downstream side of the flame instead of from both sides (upstream and downstream) of the flame. It appeared that the wall acted as an obstacle to air entrainment from the upstream side of the small flame. This caused the flame to lean forward and to move back and forth as described in Fig.7c. Although there was no visible blue flame front, energy feedback from the flame to the wall was temporally enhanced when the flame leaned forward. The wall was rapidly smoothed by the enhanced degradation due to temporally enhanced energy feedback and the flame climbed partially over the step. The flame continued to spread in this mode. The flame spread rate appeared to be sensitive to the aerodynamics of the air entrainment, which was also sensitive to the shape of the burning surface contour. Therefore, there was some scatter in the flame spread rate over the low MW PMMA sample. This effect of fluid motion of the molten polymer (low MW sample) on vertical downward and upward flame spreading is more severe than for horizontal flame spreading. The large difference in flame spread rate between the two PMMA samples indicates also that thermal stability of the material significantly affects flame spreading rate.

Heat Release Rate: The changes in heat release rate and also in heat of combustion per unit sample weight loss with time are shown in Fig. 8 for the two PMMA samples and in Fig. 9 for the two PS samples at an external radiant flux of 40 kW/m^2. The results show that the heat release rate of the high MW PMMA sample is as much as 30% larger than that of the low MW PMMA sample. However, the heat of combustion per unit sample weight loss is almost the same for the two PMMA samples. This indicates that gas phase flame processes are almost the same for the two PMMA samples but the gasification rate(burning rate) for the high MW PMMA sample is higher (as high as 30%) than that for the low MW PMMA sample. However, heat release rates and heats of combustion per unit sample weight loss of the two PS samples are practically the same at various external radiant fluxes regardless of the molecular weight differences.

It appears that the mass transfer process for indepth degradation products through the molten polymer layer to the sample surface might not be important for determining burning rate of the PS samples. Further studies are needed to make it more general because the degradation of the PS samples occurs within a relatively narrow temperature range as shown in Fig. 1. The indepth degradation tends to be quite close to the sample surface where sample temperature is high. On the other hand, the high MW PMMA sample degrades over a wide temperature range compared to the low MW PMMA sample, as shown in Fig.2. Therefore, the indepth degradation tends to occur more deeply for the high MW PMMA sample than for the low MW PMMA sample. However, since melt viscosity of the high MW sample is much higher than that for the low MW sample, the transfer rate of the degradation products through the highly viscous layer of the high MW sample would be much lower than that for the low MW sample. These opposing two factors for the high MW PMMA sample, thermally unstable and highly viscous molten polymer, might reduce the difference in heat release rate between the two PMMA samples. At present, it is not clear how much each of these two factors affected the difference in heat release rate of the two PMMA samples as shown in Fig.8.

Surface Temperature: Since the same four types of sample were used for the measurements of various flammability properties, the surface temperatures for piloted ignition, flame spread and non-flaming radiative gasification are compared to determine whether a unique vaporization surface temperature exists for each sample. The surface temperature of the two PS samples during non-flaming radiative gasification is in the range 380-420°C[**9**]. The surface temperature at piloted ignition is in the range 350-370°C[**6**] and the vaporization temperature during horizontal flame spreading is about 470-500°C. Since the exact location of the vaporization front for the flame spreading study could not be precisely determined, the surface temperature is approximately 400°C if the flame front is about 0.1 cm ahead of the vaporization front, as defined in Ref.5 (This possibility is reinforced by the fact that there were sharp breaks in temperature rise around this temperature in Fig.5 of Ref.5.). For the low MW PMMA sample, the piloted ignition surface temperature is about 320-340°C and the vaporization temperature during horizontal flame spreading is roughly 400°C. The vaporization surface temperature during non-flaming radiative gasification is in the range 370-420°C. For the high MW PMMA sample the piloted ignition temperature is about 260-270°C and vaporization during horizontal flame spreading occurs at about 420°C. The vaporization temperature during non-flaming radiative gasification is in the range 360-410°C.

These results indicate that the piloted ignition surface temperature is much lower than the vaporization temperatures occurring in horizontal flame spreading and in non-flaming radiative gasification. With samples having as many different chemical degradation paths as the high MW PMMA sample shown in Fig.2, the piloted ignition temperature tends to be much lower than the vaporization temperatures. It is curious that there is a large difference in surface temperature between piloted ignition and horizontal flame spreading. If flame spreading is considered to be a successive piloted ignition process, the surface temperature for both cases should be the same. The difference could be caused by the difference in heat flux to a sample; the maximum flux is about 7 W/cm^2 for horizontal flame spreading[**12**] and the radiant flux range

was 1.0-2.7 W/cm^2 for piloted ignition. The difference in surface temperature between piloted ignition and non-flaming radiative gasification could be due to a large difference in mass flux between the two cases. The mass flux during non-flaming radiative gasification is about 20 times larger than for piloted ignition, which tends to be more influenced by degradation path particulary for a low external radiant flux. There are no significant differences in surface temperature for horizontal flame spreading and non-flaming radiative gasification among the four samples.

Conclusion

1. Thermal stability of polymeric materials has significant effects on piloted ignition delay time, flame spread rate and heat release rate. Surface temperature at piloted ignition is controlled by detailed chemical degradation path of the material and is not necessarily the same as the vaporization temperature at the flame front.
2. The transport process of indepth degradation products of PS and PMMA through the molten polymer layer inside the sample has a negligible effect on piloted ignition. However, the sample with low initial molecular weight forms a molten polymer and the opposed slow fluid motion of molten polymer along the inclined vaporizing surface against the traveling flame significantly affects flame spreading behavior and reduces its rate.

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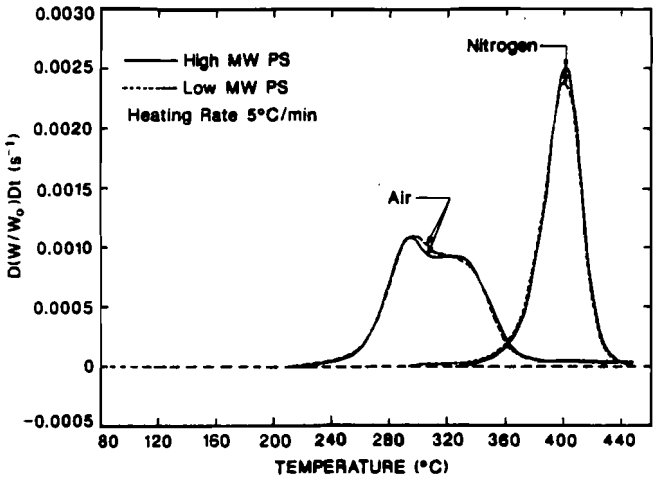


Fig. 1. Comparison of DTG curves of the two types of the PS samples degrading in nitrogen and in air.

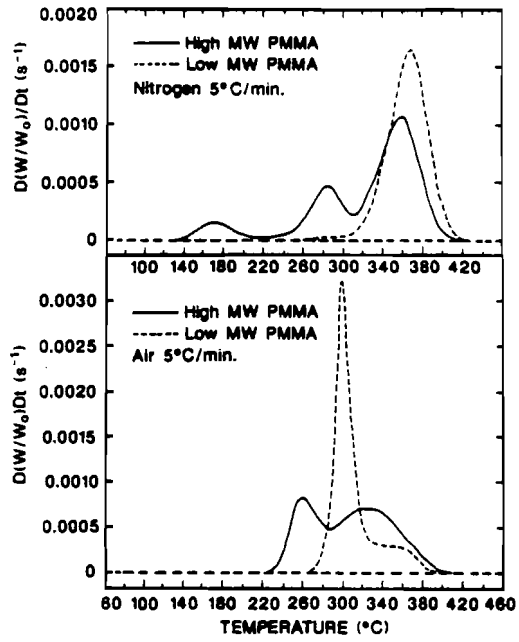


Fig. 2. Comparison of DTG curves of the two types of the PMMA samples degrading in nitrogen and in air.

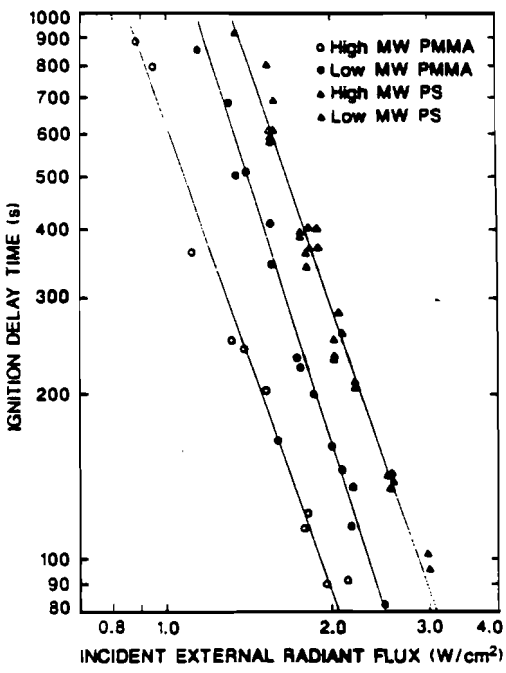


Fig. 3. The relationship between ignition delay time and incident external radiant flux for the four samples.

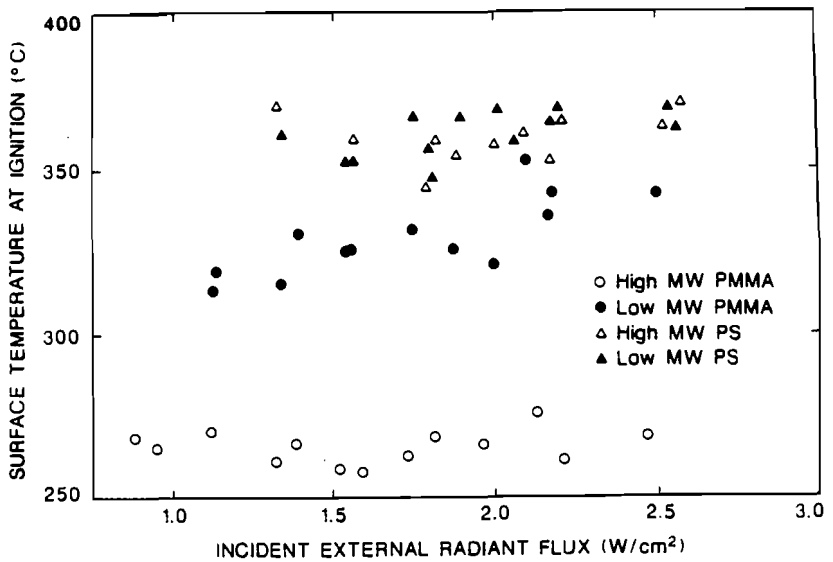


Fig. 4. The relationship between surface temperature at ignition and incident external radiant flux.

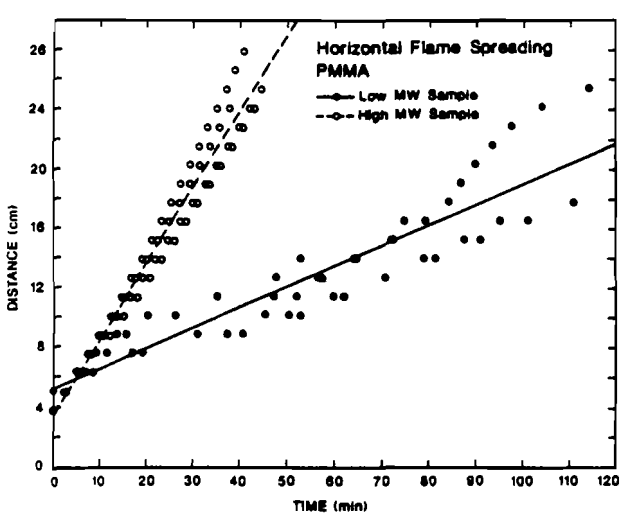


Fig. 5. Plot of flame front position with time for the PMMA samples.

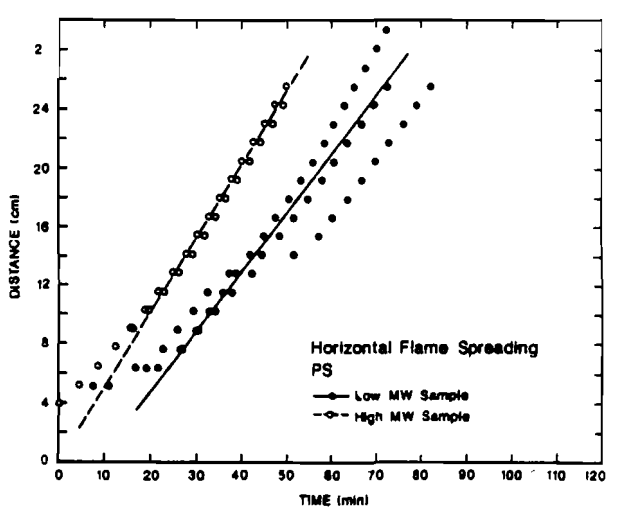
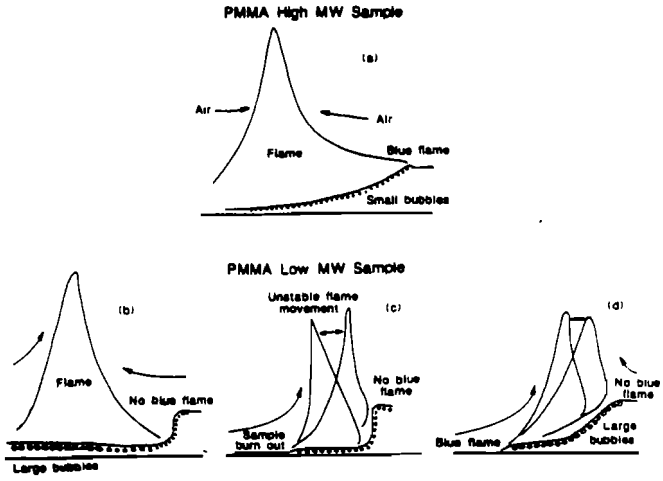


Fig. 6. Plot of flame front position with time for the PS samples.

Fig. 7. A schematic illustration of flame spread behavior over the PMMA samples. (a) over the high MW sample, (b) over the low MW sample with the wall, (c) over the low MW sample with unstable flame movement, and (d) over the low MW sample with air entrained mainly from the downstream side of the flame.



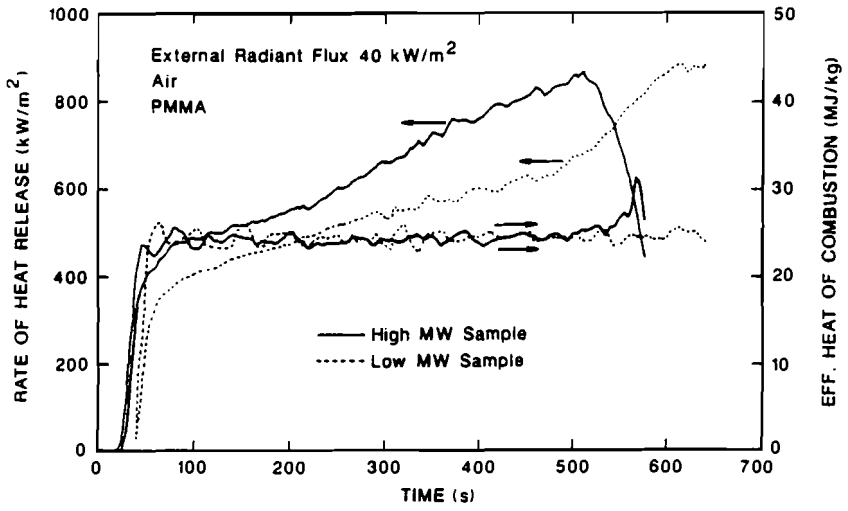


Fig. 8. Comparison of heat release rate and effective heat of combustion between the two PMMA samples at 40 kW/m^2.

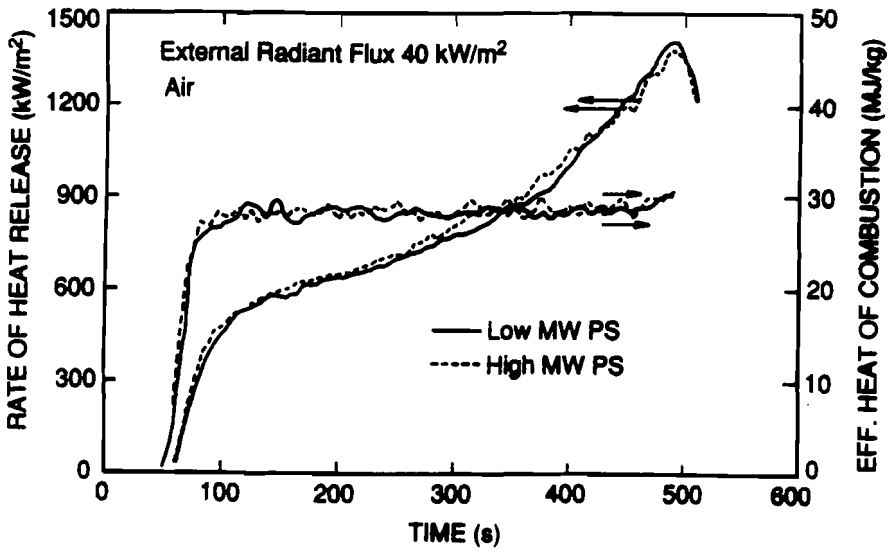


Fig. 9. Comparison of heat release rate and effective heat of combustion between the two PS samples at 40 kW/m^2.