

A NEW GENERATION OF FIRE RESISTANT POLYMERS: Part II SILICONE-CONTAINING POLYCARBONATE

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ABSTRACT

Various flammability properties of a silicone-containing polycarbonate sample were measured and compared with those of a pure polycarbonate sample. The results show that peak heat release rate for the silicone-containing polycarbonate sample is significantly reduced (less than half) compared to that for the pure polycarbonate sample with two different sizes of sample, 10cmx10cm and 40cmx40cm. However, the ignition delay time for the silicone-containing sample is shorter than that for the pure polycarbonate sample. Also, the flame spread rate with external radiant fluxes for the silicone-containing sample becomes faster than that for the pure polycarbonate sample. The observed char behavior, such as char depth, physical nature and apparent combustibility, and its impact on flammability properties are discussed.

1. INTRODUCTION

As discussed in the progress report which is presented in this Section, non-halogenated flame retardant treatments might become more important in the future. Therefore, the U.S. plastics industry is interested in developing such new retardants. As an example, the Corporate Research and Development Center of General Electric Co. and NIST are collaborating to do so. One of their basic polymers is polycarbonate. Although roughly 25% of the initial sample weight is left as a residual char when a polycarbonate sample is burned at an external radiant flux of 40 kW/m², the peak heat release rate measured in the Cone Calorimeter is as high as 800 kW/m² and GE is quite interested in how to reduce the peak heat release rate without using any halogenated compounds.

2. Results Measured by Cone Calorimeter (Small Samples)

Various amounts of silicone-containing compounds were added to polycarbonate as a copolymer or as additives. The sample size was about 10 cm x 10 cm x 3 cm thick. The tests were conducted in the "NF" sample configuration which means no grid or metal frame around the sample[1]. This configuration allows a char to intumesce and not lose any heat to a metal frame. Typical heat release rate curves measured by the Cone Calorimeter at an external radiant flux of 40 kW/m² are shown in Fig.1. The thin solid line represents the heat release curve for the pure polycarbonate sample. The results show that an increase in the amount of silicone-containing compounds decreases ignition delay time and also peak heat release rate. Thermogravimetric analysis of these samples shows a reduction in thermal stability from the original polycarbonate sample with an increase in the amount of the silicone-containing compounds. This indicates that the thermal stability of the silicone-containing compounds is less than that for the pure

polycarbonate sample. Therefore, ignition delay time becomes less with an increase in the amount of the silicone-containing compounds. A sharp reduction in peak heat release rate occurs with a small increase in the amount of the silicone-containing compounds as shown in Fig.2. However, peak heat release rate does not decrease any further beyond the addition of a certain amount of the silicone-containing compounds.

Although peak heat release rate is significantly reduced by the addition of the silicone-containing compounds, the total heat release is not affected by the addition as shown in Fig.3. Since the total heat release is the integral of the heat release rate curve, the trend of nearly constant total heat release can be explained from the results shown in Fig.1. The samples with the silicone-containing compounds generate lower peak heat release rates but tend to burn much longer than the pure polycarbonate sample. Therefore, the area under the heat release rate curve is about the same for all samples shown in Fig.3. Corresponding to this, the total sample mass loss is about the same for the all samples as shown in Fig.4. This indicates that the addition of the silicone-containing compounds does not substantially increase the amount of residual char from polycarbonate. However, it appears that there are some differences between the residual char formed from the samples with and without the silicone-containing compounds. The polycarbonate sample generates a brittle, thin shell type char layer. The samples with the silicone-containing compounds generate foamy, spongy char. At present, it is not clear whether there are any differences in chemical structure of the two different types of char. However, heat insulation by the foamy, spongy char appears to be better than by the brittle, thin shell type char. It is planned to analyze the structure of the two chars and their heat insulation characteristics in the future. Soot yields were obtained by measurement of the weight of the collected particulates on a filter divided by the total sample weight loss. The effects of the addition of the silicone-containing compounds on soot yields are shown in Fig.5. Soot yield appears to decrease gradually with an increase in the amount of the compounds except at the high loading end. One high soot yield, about 14%, in the middle range of the compounds addition appears to be an experimental error.

The above results are encouraging for a reduction in peak heat release rate without using any halogenated-compounds and also with slight reduction in soot yield. Furthermore, a significant reduction in peak heat release rate can be achieved with a relatively small quantity of the addition of the silicone-containing compounds, typically less than 5%. The addition of the small quantity of the compounds to polycarbonate does not significantly affect the physical properties of polycarbonate compared to that with the addition of generally large quantity of metal hydrates needed for effective flame retardancy. However, one must be careful not to jump to conclusion regarding the flame retardant performance of the silicone-containing polycarbonate sample. Two further studies were conducted: one to determine the effects of the addition of the silicone-containing compounds on flame spread characteristics and the other to determine the effects of the sample size on flame retardant performance. As discussed above, the piloted ignition delay time for the silicone-containing polycarbonate sample becomes less than that for the original polycarbonate sample at the same external radiant flux due to the former sample becoming thermally less stable. Since the process of flame spread can be considered as successive piloted ignition, it is important to examine the effects on flame spread characteristics of the addition of the silicone-containing compounds to polycarbonate on flame spread characteristics.

4. Flame Spread

The HIFT (horizontal ignition and flame spread test) device was used to measure flame spread characteristics.* The sample was preheated for 180 s and then a small pilot flame was rapidly inserted about 7 cm above the one end of the sample surface where the external flux was highest, at 40 kW/m^2 . The history of the flame front position for the two samples is shown in Fig.6 (Two tests were repeated for each sample.). Time zero in the figure corresponds to the initiation of the preheating. The external flux decreases rapidly from 40 kW/m^2 with an increase in the flame front position initially and it decreases more slowly beyond 300 mm. The results show more rapid flame spread shortly after ignition for the silicone-containing polycarbonate sample than for the pure polycarbonate sample. Beyond 400 mm, there is no significant difference between the two samples, which might be caused by a reduction in external flux for the silicone-containing sample due to a partial blockage of external radiation from the panel surface to the unburned sample surface by a large intumesced char mound, shaped like a loaf of a bread. It is important to point out that the intumesced char mound was formed behind the flame front and its top nearly reached the panel surface. However, there was no loaf-shaped char mound for the pure polycarbonate sample. Its char was localized, small ragged/curled shape, scattered over the insulation board surface and its height was less than 5 cm. Also, the char was formed behind the flame front. Therefore, the char does not interfere to prevent or even slow down flame spread and does not have any significant effects on the flame spread process for both polycarbonate samples. Furthermore, the chars formed from the two samples continued to burn during the test.

When flame spread over a polyetherimide sample was measured, char was formed before ignition and also before the arrival of the flame front. Furthermore, the char appeared to be very resistive to burning and only small localized scattered flames were observed over the surface exposed to high external fluxes. Heat release rate (peak heat release rate was between $150 - 200 \text{ kW/m}^2$) and mass loss (about 40%) for the polyetherimide sample were much less than those of the polycarbonate sample. Since the principal difference in the chemical structure between the two polymers is a carbonate link vs an imide link, the nature of the imide link appears to control the structure and thermal stability of the char formed. A more detailed analysis of the residual char is needed to understand how char is formed for the two different polymers. Such information would be quite important for use as a guideline to improve fire performance of polymeric materials to form more and better fire resistant char.

5. Results measured by Furniture Calorimeter (Large Samples)

* Since polycarbonate is a thermoplastic, it flows when it reaches its melting temperature. If the conventional LIFT (lateral ignition and flame spread test) configuration is used, the polycarbonate sample melts down during the pre-heating period and meaningful data cannot be obtained. However, the HIFT configuration has one disadvantage compared to the LIFT configuration: it is the interaction of a flame and the gas panel so that the external flux from the panel changes during a test [1].

When heat release rate is measured by the Cone Calorimeter, the size of a sample is about 10 cm x 10 cm. The above polycarbonate samples were burned without suppressing intumescence of the char (without using any grid and metal frame). The height of the intumesced char mound was about 2 - 3 cm for the silicone-containing polycarbonate sample. It appears that this height might be determined by the sample size. Since the intumesced char height might be related to heat insulation performance of the char, it is important to determine whether the above observed flame retardancy of the silicone-containing polycarbonate sample depends on the sample size or not. For this reason, large burn tests were conducted using the NIST Furniture Calorimeter with a new electrically heated radiant source which consists of two large panels as shown in Fig.7. Two different sample sizes were used; one was about 40 cm x 40 cm and the other was 61 cm x 61 cm. Since the estimated peak heat release rate for the polycarbonate sample was close to the maximum capability for the Furniture Calorimeter, only the smaller size was used for the polycarbonate sample. A relatively high content of the silicon-containing polycarbonate sample was used (in the region of plateau peak heat release rates shown in Fig.2).

The comparison of heat release rate curves between the two polycarbonate samples is shown in Fig.8. Two tests were repeated for each sample. Although ignition delay time for the polycarbonate samples was different between the two tests, the trend is very clear. Heat release rate of the silicone-containing polycarbonate sample is much lower (about one third) than that for the pure polycarbonate sample; also the ignition delay time for the former sample is much less than that for the latter sample. These results are consistent with those measured in the Cone Calorimeter. Therefore, the size of the sample does not significantly affect the flame retardant performance of the silicone-containing polycarbonate sample. The only significant difference between the small sample and the large sample is in the total mass loss from the sample. Both samples lost about 90% of the initial weight for the large size experiment compared to about 70% for the small size experiment (Cone Calorimeter). Correspondingly, total heat release per unit surface area for the larger sample is about 90 MJ/m² compared to about 60 MJ/m² for the small sample. The height of the intumesced char mound for the large silicone-containing polycarbonate sample reached to about 15 cm but it continued to burn. The residual char after the test is quite porous and fragile and looks like coral. There was no char mound formed for the polycarbonate sample and its residual char was ragged/curled and scattered around.

7.SUMMARY

The above results show that the peak heat release rate of the silicone-containing polycarbonate sample is significantly reduced (less than half) from that for the pure polycarbonate sample. However, total heat release per unit surface area is about the same for both samples. However, piloted ignition delay time for the silicone-containing polycarbonate sample is much shorter than that for the pure polycarbonate sample and the flame spread rate with external radiant fluxes for the silicone-containing sample is higher than that for the pure polycarbonate sample. This is caused by the reduction in thermal stability for the silicone-containing sample.

Overall, the silicone-containing sample appears to generate char at an early stage and also to create a thicker intumesced char layer. However, the formation rate of char is still not fast

enough to interfere in the flame spread process. Although a thick intumesced char layer is formed for the silicone-containing sample, the char appears to be relatively easily combustible and does not have strong flame resistance like the char from polyetherimide.

Reference

1. Kashiwagi, T. and Cleary, T.G., "Effects of Sample Mounting on Flammability Properties of Intumescent Polymers" to appear in *Fire Safety J.*

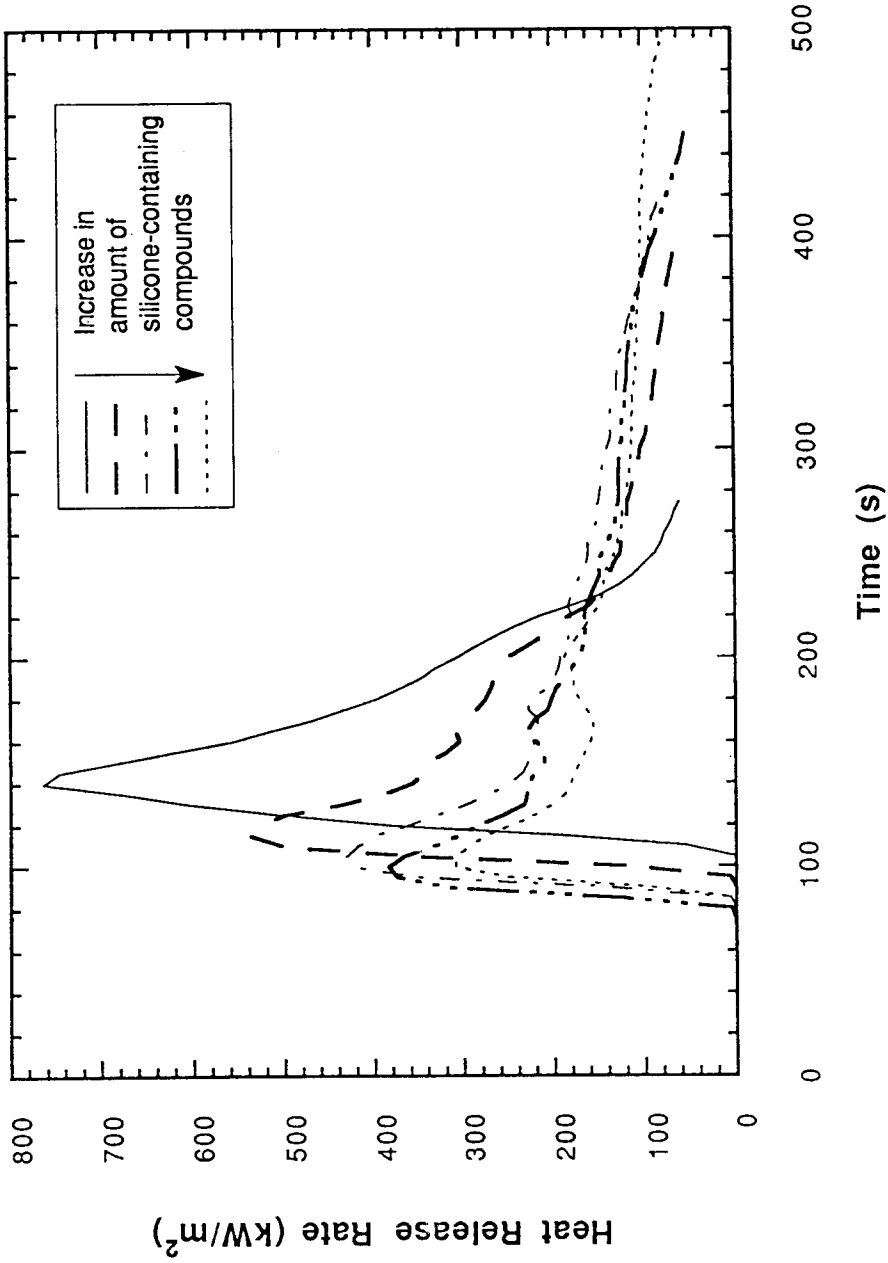


Fig.1 The effects of amount of silicone-containing compounds on heat release rate curve at external radiant flux of 40 kW/m².

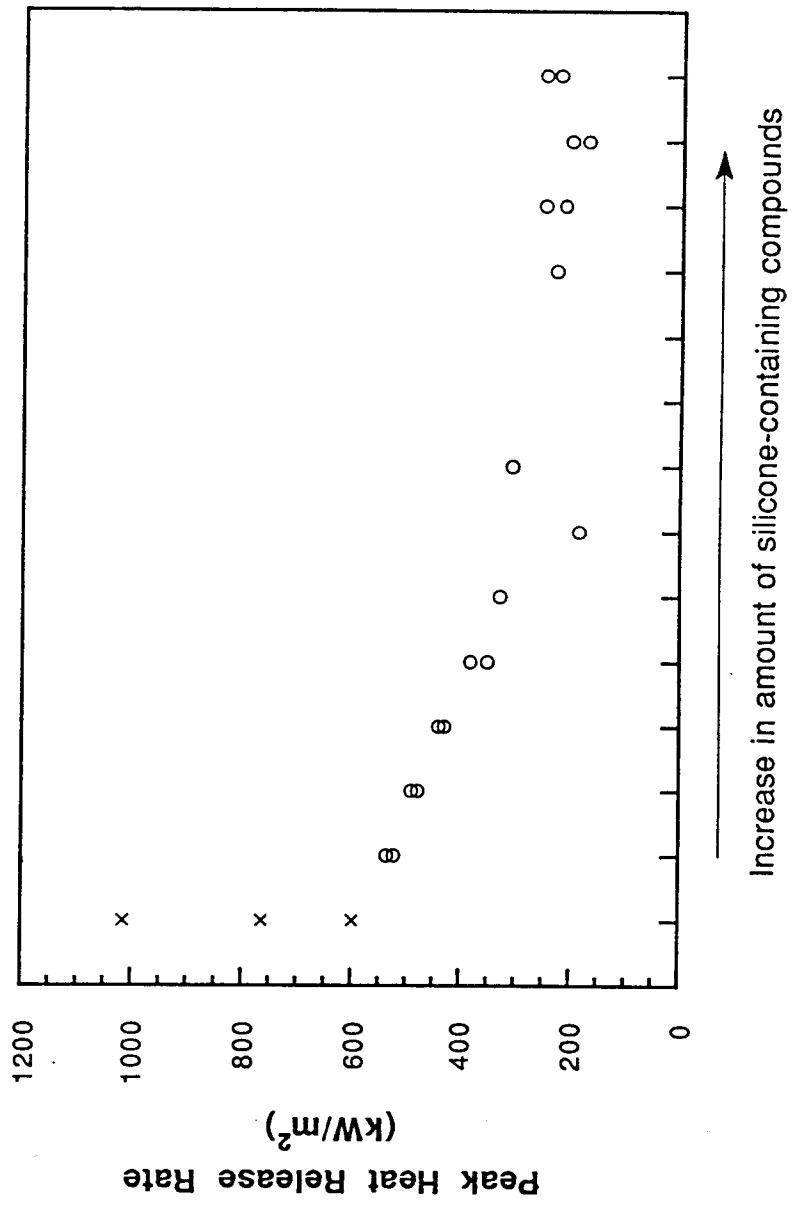


Fig. 2 The effects of amount of silicone-containing compounds on peak heat release rate at external radiant flux of 40 kW/m².

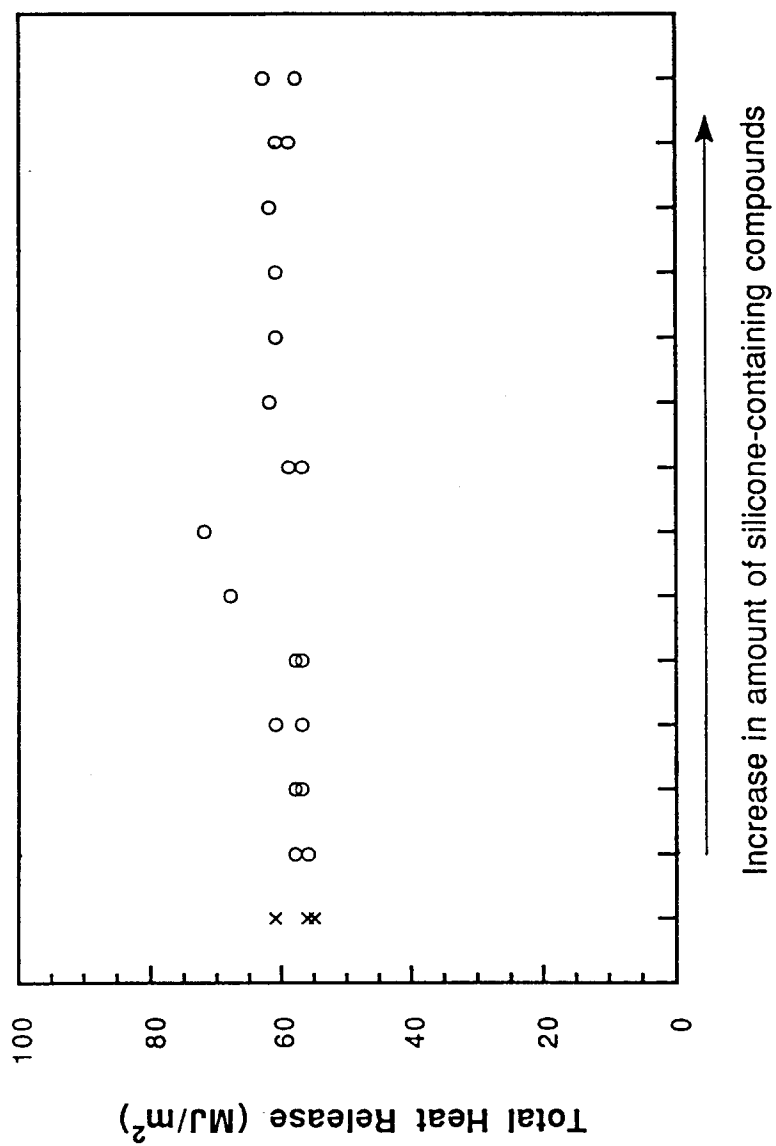


Fig. 3 The effects of amount of silicone-containing compounds on total heat release at external radiant flux of 40 kW/m².

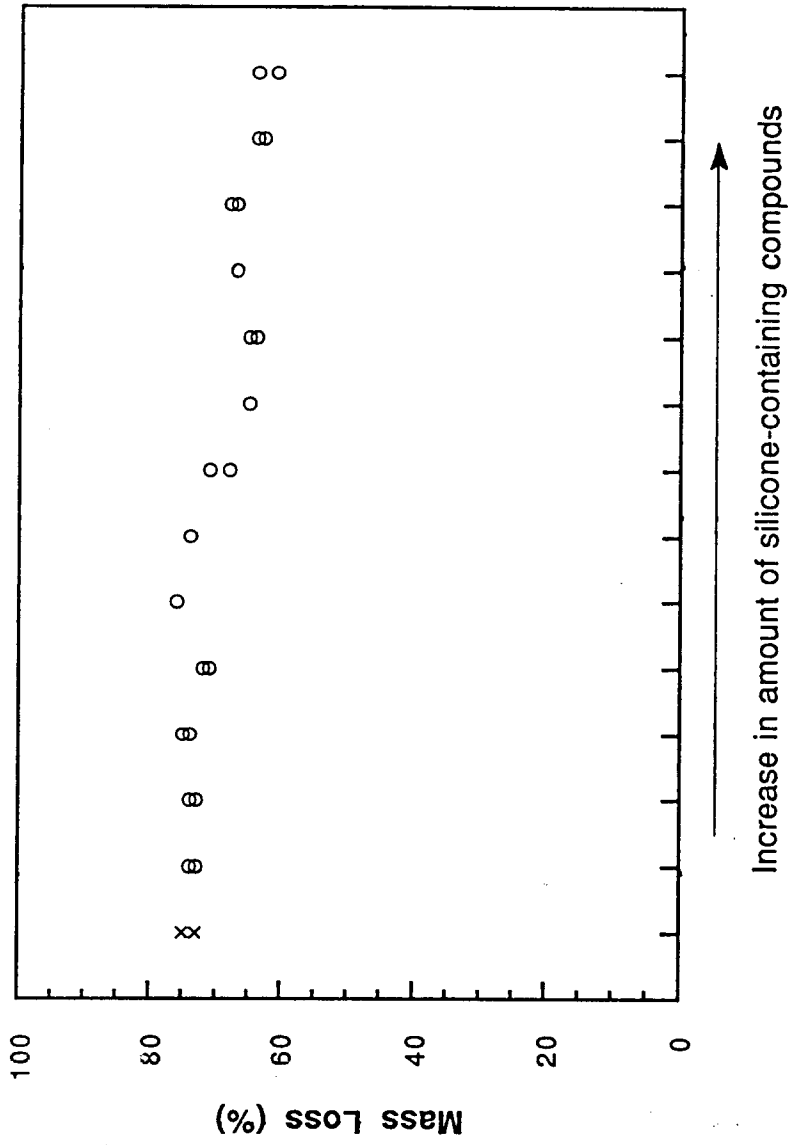


Fig. 4 The effects of amount of silicone-containing compounds on total mass loss of the sample at external radiant flux of 40 kW/m².

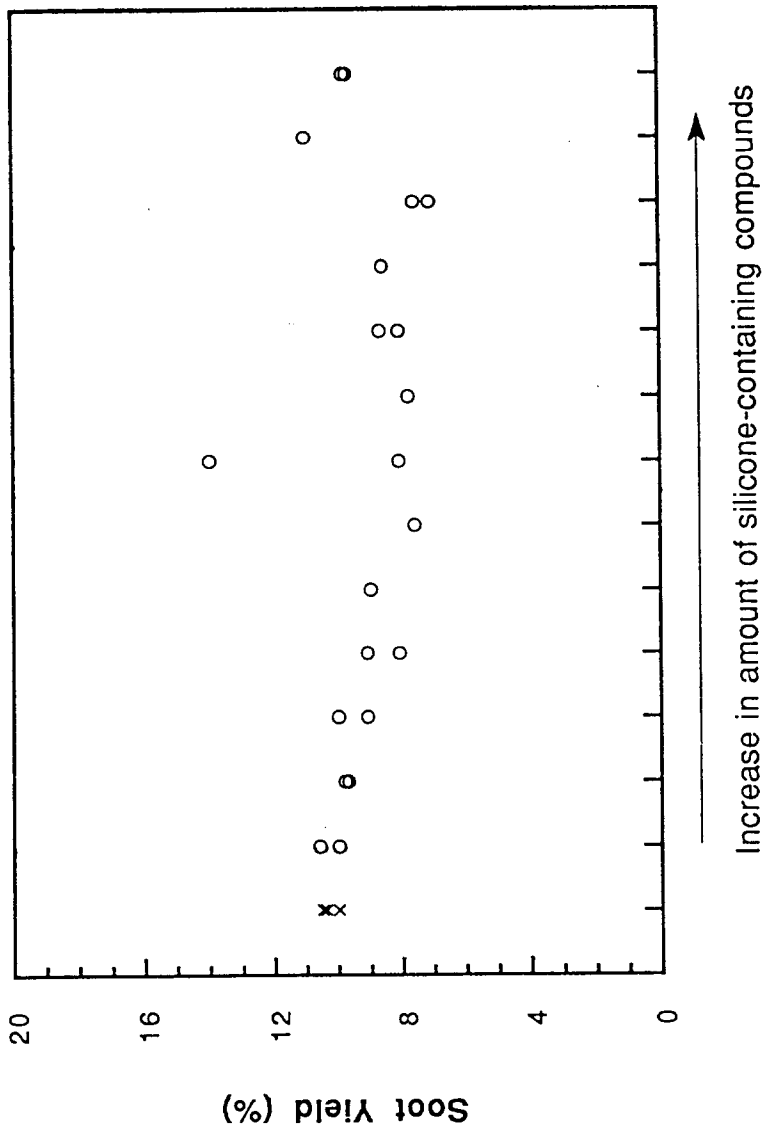


Fig. 5 The effects of amount of silicone-containing compounds on soot yield at external radiant flux of 40 kW/m².

HIFT Flame Spread

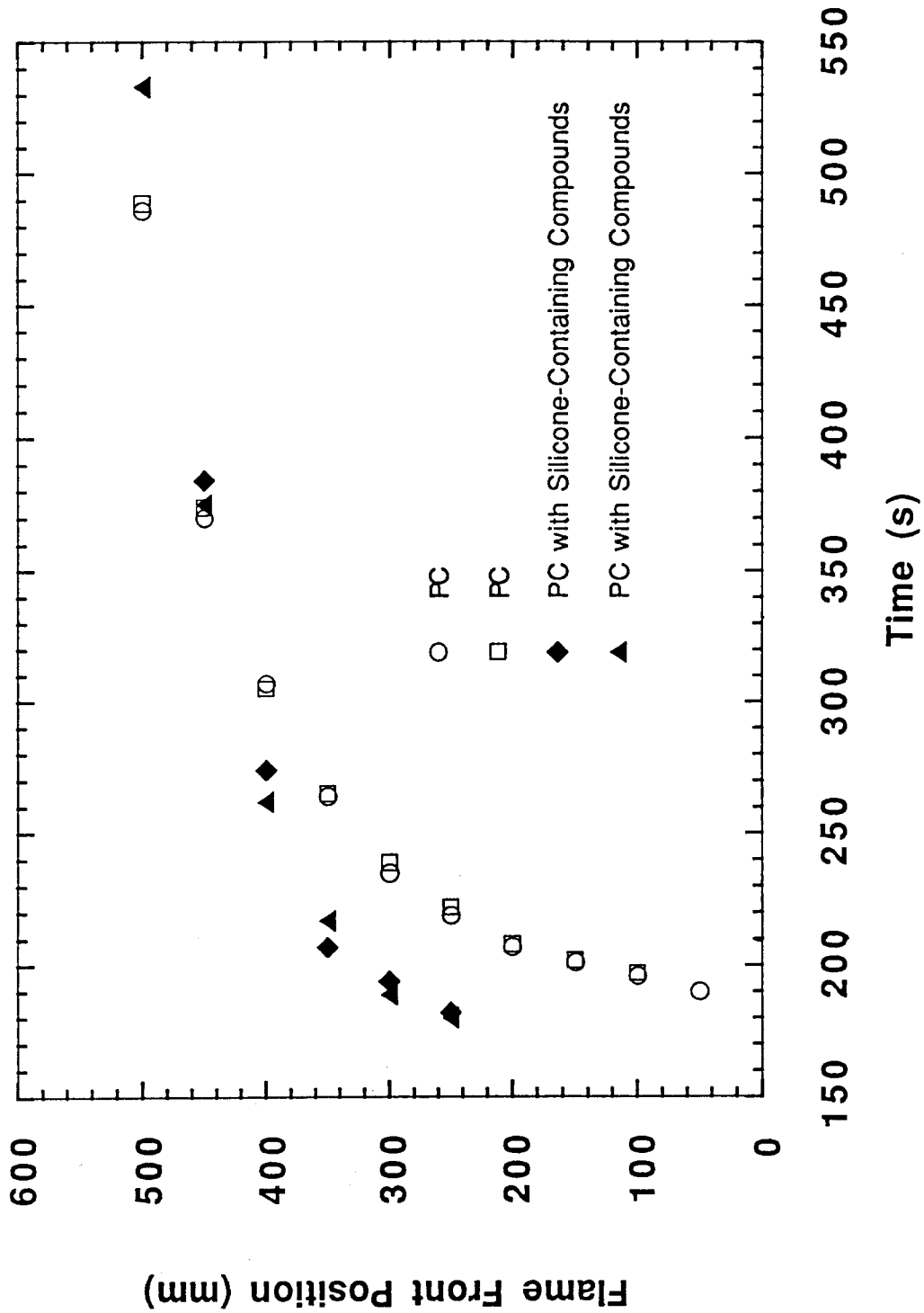


Fig. 6 Comparison of history of flame front position between the two samples (two repeated tests for each sample).

Radiant Panel Test Apparatus

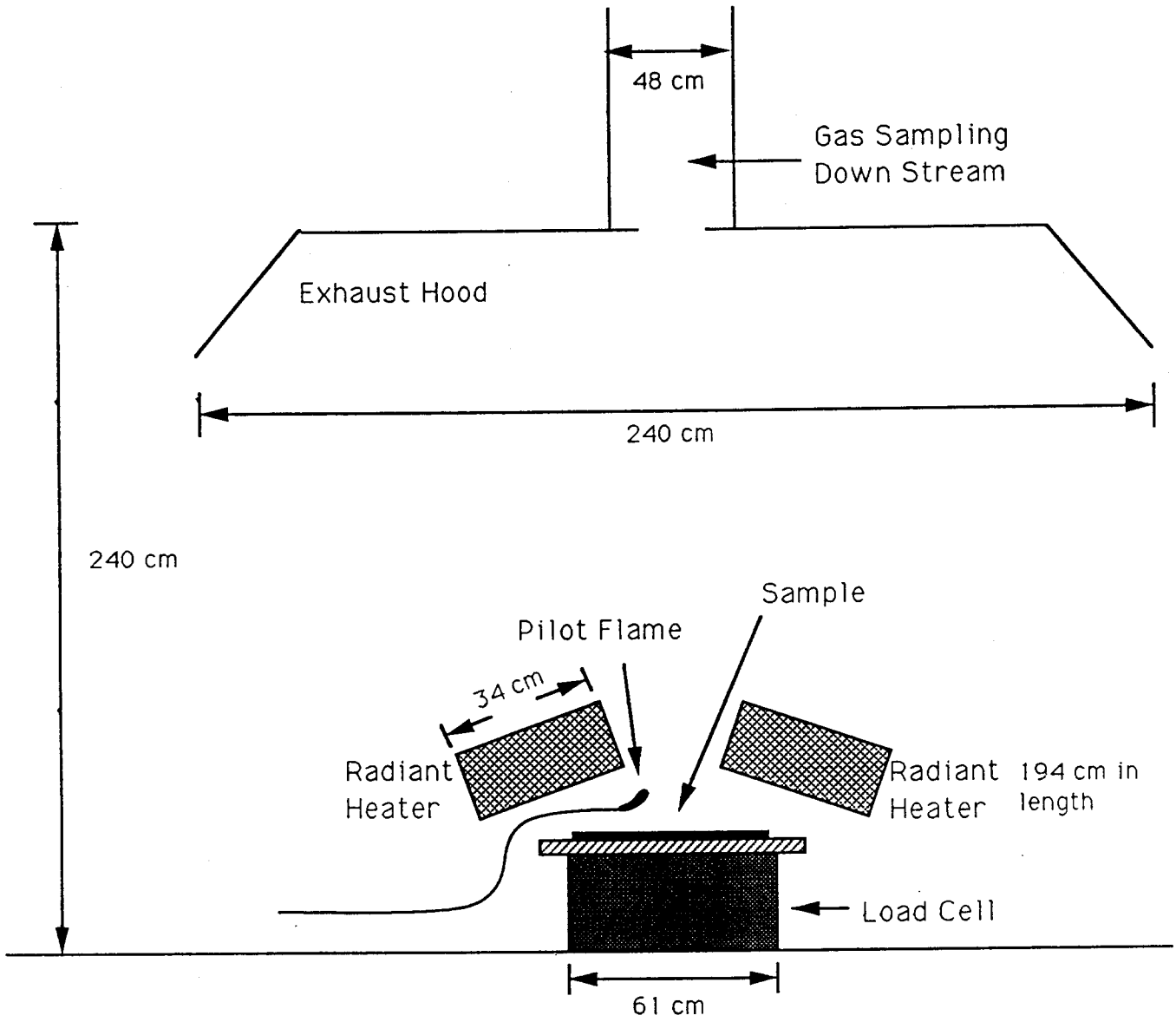


Fig.7 Schematic illustration of the large radiant panel test apparatus.

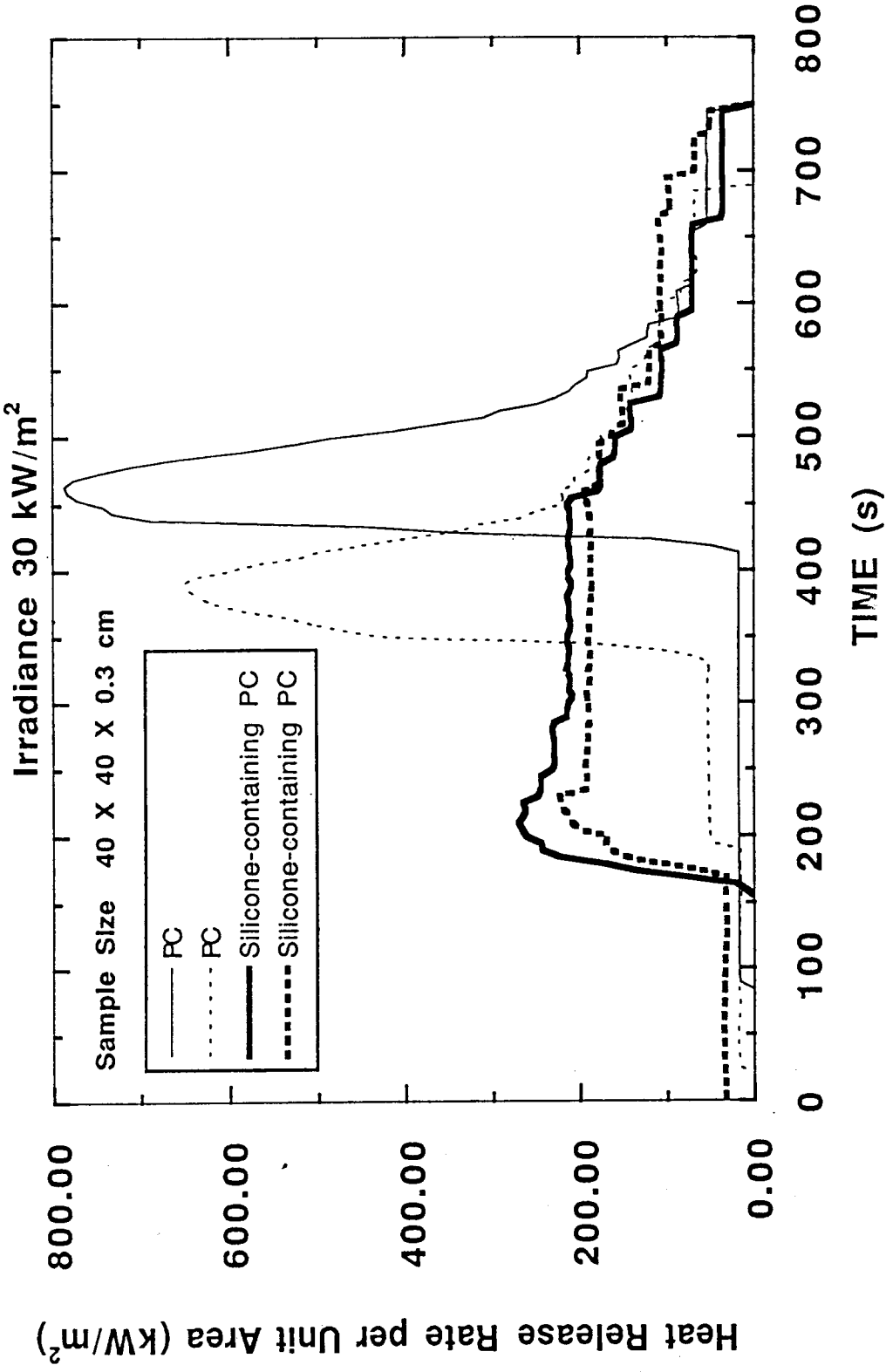


Fig.8 Comparison of heat release rate curve between the two large size samples at external radiant flux of 30 kW/m² (two repeated tests for each sample).