

# A NON-HALOGENATED, FLAME RETARDED POLYCARBONATE

Takashi Kashiwagi and Thomas G. Cleary

Building and Fire Research Laboratory  
National Institute of Standards and Technology  
Gaithersburg, MD 20899

and

Gary C. Davis and John H. Lupinski

Chemical Research Center  
Corporate Research and Development  
General Electric Co.  
Schenectady, NY 12345

## ABSTRACT

Various flammability properties of a siloxane-containing bisphenol-A polycarbonate sample, with the siloxane as an additive or as a copolymer, were measured and compared with those of a pure polycarbonate sample. The results show that the peak heat release rate for the siloxane-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 siloxane-containing sample is shorter than that for the pure polycarbonate sample. Also, the flame spread rate under an external radiant flux becomes faster for the siloxane-containing sample 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.

## INTRODUCTION

After the implementation of the stringent new FAA low heat release rate regulation (two minute heat release of  $65 \text{ kW-min/m}^2$  and peak heat release rate of  $65 \text{ kW/m}^2$ )[1], enhanced fire resistance of aircraft interior materials has become a challenge to the aircraft industry. Furthermore, two important recent trends which have started to affect the fire aspects of materials are non-halogenated flame retardant treatments and polymer recycling. Due to negative publicity about dioxin and furan as possible degradation products, some brominated flame retardants have received a negative public perception in Europe[2]. Regulations on the use of certain types of these flame retardants have been proposed in Germany. Although the use of halogenated flame retardants is still showing an upward trend, some concerns have been raised, and there is a definite trend to seek alternatives. Also, the huge waste volume of plastics is becoming a problem to modern societies. A popular solution is the recycling of waste plastics. In Germany, even now, plastic products for packaging have to be taken back by the producer or retailer for recycling or disposal. This will be extended to include electronic scrap, such as old computers, with an obligation to recycle as far as possible. Corresponding to these requirements, the labeling of all plastic components of computers to identify their material and manufacturers has already been implemented by IBM [3]. The emphasis on recycling might affect the selection of the base polymer and flame retardant treatment on the basis of ease of recycling and also on durability. It could be possible that material selections will be more limited than in the past.

Therefore, some U.S. plastics companies are interested in developing new non-halogenated 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 bisphenol-A 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  $40 \text{ kW/m}^2$  in the Cone Calorimeter, the peak heat release rate measured in the Cone Calorimeter is as high as  $800 \text{ kW/m}^2$ ; and GE is quite interested in hearing how to reduce the peak heat release rate without using any halogenated compounds.

## RESULTS MEASURED BY CONE CALORIMETER (SMALL SAMPLES)

Various amounts of a siloxane-containing compound were added to bisphenol-A polycarbonate as an additive. The sample size was about  $10 \text{ cm} \times 10 \text{ cm} \times 0.3 \text{ cm}$  thick. Since it is not clear what sample mounting configuration is the most appropriate to measure flammability properties of intumescent polymers in the Cone Calorimeter, the tests were conducted in two different mounting configurations[4]. One configuration is designated as "WG" in which a standard metal frame container and a grid were used. Initially, the sample was mounted such that the sample surface was  $0.5 \text{ cm}$  below the grid. In this configuration, intumesced char was prevented from swelling fully by the grid. The other configuration is designated as "NF" which means no grid or metal frame container around the sample. This configuration allows the char to intumesce and not lose any heat to a metal frame. Typical heat release rate curves for polycarbonate samples with the siloxane-containing additive measured by the Cone Calorimeter at an external radiant flux of  $40 \text{ kW/m}^2$  are shown in Fig.1 for the "WG" configuration and in Fig.2 for the "NF" configuration, respectively. In Fig.1, the addition of small amounts of siloxane, even  $0.25 \text{ wt}\%$ , significantly reduces the heat release rate. However, it increases the burnout time and also tends to yield two peaks in the curve instead of one large peak as for the sample without any siloxane. The incremental effectiveness of additional siloxane in reducing the heat release rate decreases with an increase in siloxane percentage. In Fig.2, the heat release rate initially increases sharply with time, compared to the results shown in Fig.1. The freely rising, intumesced char reduces the distance between the char surface and the Cone heater. This had two effects on heat release rate measured in the "NF" configuration: one was an increase in the sample surface area (heat release rate was calculated with the initial sample surface area) and the other was an apparent increase in the incident radiant flux to the sample. These two effects tend to an increase heat release rate. However, after the char is well intumesced, it protects the original polymer layer more than the suppressed intumesced char in the "WG" configuration. This reduces the gasification rate of the sample. Poor heat insulation by the suppressed, dense intumesced char does not reduce the gasification rate nearly as much. Therefore, the heat release rate remained nearly constant with time in the "WG" configuration as shown in Fig.1.

The results shown in the two figures indicate that an increase in the amount of the siloxane-containing additive decreases an ignition delay time. Thermogravimetric analysis of these samples shows a reduction in thermal stability from the original polycarbonate sample with an increase in the amount of the siloxane-containing additive. This indicates that the thermal stability of the siloxane-containing additive is less than that for the pure polycarbonate sample. Since piloted ignition is controlled by the supply of fuel gases[5], less thermally stable samples tend to ignite at an earlier time. Therefore, ignition delay time becomes less with an increase in the amount of the siloxane-containing additive. The effects of the amount of siloxane on piloted ignition delay time are shown in Fig.3. The results show that ignition delay time decreases rapidly with the addition of a small amount of siloxane and this decrease becomes more gradual above  $1\%$  of siloxane. Ignition delay time measured in the "WG" configuration tends to be slightly longer than that measured in the "NF" configuration presumably due to an apparent increase in the incident radiant flux on the rising polymer surface.

The effects of the amount of siloxane on peak heat release rate are shown in Fig.4. An addition of a small amount of siloxane, up to 1%, significantly decreases the peak heat release rate and a gradual decrease is observed above 1% of siloxane. The peak heat release rate measured in the "NF" configuration is significantly higher than that measured in the "WG" configuration due to the above-described reasons. Although peak heat release rate is significantly reduced by the addition of the siloxane-containing additive, the total heat release is not significantly affected by the addition, as shown in Fig.5. Since the total heat release is the integral of the heat release rate curve shown in Figs. 1 and 2, the trend of nearly constant total heat release can be explained from the results shown in these figures. The samples with the siloxane-containing additive 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.5 except the sample with 5% of siloxane measured in the "WG" configuration. At present it is not clear whether a large percentage of siloxane might generate more heat release due to a significant decrease in thermal stability of the sample. On the other hand, there are clearer trends for the effects of the addition of siloxane on the sample mass loss, as shown in Fig.6, than those on the total heat release. The mass loss gradually decreases with the addition of siloxane when the sample was measured in the "NF" configuration. However, in the "WG" configuration, mass loss decreases up to 1% of siloxane and it remains nearly the same up to 4%. The sudden increase in mass loss at 5% of siloxane is similar to that for the total heat release.

It appears that there are some differences between the residual char formed from the samples with and without the siloxane-containing additive. The polycarbonate sample generates a brittle, thin shell-like char layer. The samples with the siloxane-containing additive tend to generate foamy, less brittle char. In the latter part of this paper, the results of an elemental analysis of these char layers will be presented to indicate whether there are significant differences in chemical structure between the samples with and without siloxane. It is also planned to analyze their heat insulation characteristics in the future.

Soot yields were obtained by measurement of the weight of collected particulates on a filter divided by the total sample weight loss. The effects of the addition of the siloxane-containing additive on soot yields are shown in Fig.7. Although there is significant scatter in the results, it appears that the addition of the siloxane-containing additive does not increase soot yield. Since soot yield is normalized by weight loss rate, soot generation rate could be significantly reduced for the polycarbonate samples with the siloxane-containing additive due to much lower weight loss rate (nearly proportional to heat release rate curve as shown in Figs.1 and 2). This trend will be seen for the large size sample discussed later.

The above results are encouraging with regard to the goal of a reduction in peak heat release rate without using any halogenated-compounds. Furthermore, a significant reduction in peak heat release rate can be achieved with a relatively small quantity of siloxane, typically much less than 5%. The addition of such a small quantity of the compounds to the polycarbonate assures that the addition does not significantly affect the physical properties of the polycarbonate compared to that with the addition of a generally large quantity of metal hydrates needed for effective flame retardancy. However, one must be careful not to jump to conclusions regarding the flame retardant performance of the siloxane-containing polycarbonate sample. Two further studies were conducted: one to determine the effects of the addition of the siloxane 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 siloxane-containing polycarbonate sample becomes less than that for the original polycarbonate sample at the same external radiant flux due to the former sample becoming less thermally stable. Since the process of flame spread can be considered as successive piloted ignitions, it is important to examine the effects on flame spread characteristics of the addition of siloxane to polycarbonate. In order to conduct the above two studies, a relatively large size sample was needed. Since such a large sample with the siloxane-containing compounds was available only as a copolymer,

a relatively high content of the siloxane-polycarbonate copolymer sample (about 4.2 wt%) was used for the next two studies.

## FLAME SPREAD

The HIFT (horizontal ignition and flame spread test) device was used to measure flame spread characteristics.\* The sample size was about 15 cm width x 80 cm length x 0.3 cm thickness for this experiment. 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  $40 \text{ kW/m}^2$ . The history of the flame front position for the two samples is shown in Fig.8 (Two tests were repeated for each sample.). Time zero in the figure corresponds to the initiation of the preheating. The external flux initially decreases rapidly from  $40 \text{ kW/m}^2$  with the movement of the flame front position and it decreases more slowly beyond 300 mm. The results show more rapid flame spread shortly after ignition for the polycarbonate-siloxane copolymer 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 the external flux for the polycarbonate-siloxane copolymer sample due to a partial blockage of external radiation from the panel surface to the unburned sample surface by the 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 prevent or even slow down flame spread and does not have any significant effects on the flame spread process for both polycarbonate samples (apart from the possible shadowing of the panel, just mentioned), with and without siloxane. 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  $120 \text{ kW/m}^2$  measured in the "WG" configuration) and mass loss (about 30%) 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.

## RESULTS MEASURED IN A FURNITURE CALORIMETER (LARGE SAMPLES)

When heat release rate is measured in the Cone Calorimeter, the sample size is about 10 cm x 10 cm. The height of the intumesced char mound was about 2 - 3 cm for the siloxane- polycarbonate sample. It appeared that this height might be determined by the sample size. Since the intumesced char height might be related to the heat insulation performance of the char, it is important to determine whether the above-observed flame retardancy of the siloxane-containing polycarbonate sample depends on the sample size or

---

\* Since polycarbonate is a thermoplastic, it flows when it reaches its melt temperature range. 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: there is an interaction of the sample flame and the gas panel so that the external flux from the panel changes during a test [4].

not. For this reason, larger 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.9. Two different sample sizes were used; 40 cm x 40 cm and 61 cm x 61 cm. Since the estimated peak heat release rate for the pure polycarbonate sample was close to the maximum capability for the Furniture Calorimeter, only the smaller size was used. The polycarbonate-siloxane copolymer sample was used, due to the reason described above, instead of the siloxane-containing additive sample.

The comparison of heat release rate curves between the two samples is shown in Fig.10. Two tests were repeated for each sample. Although the ignition delay time for the pure polycarbonate samples was different between the two tests, the trend is very clear. Heat release rate of the polycarbonate-siloxane copolymer 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 trends 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 siloxane-containing polycarbonate sample. The only significant differences between the small sample and the large sample are in the total mass loss from the sample and also in the total heat release. Both samples lost about 90% of the initial weight for the large size experiment compared to about 70% for the small size experiment in the "NF" configuration. (The difference becomes much larger if the results measured in the "WG" configuration are used.) Correspondingly, total heat release per unit surface area for the larger sample is about 90 MJ/m<sup>2</sup> compared to about 60 MJ/m<sup>2</sup> for the smaller sample. The height of the intumesced char mound for the large siloxane-containing copolymer polycarbonate sample reached about 15 cm, but it continued to burn. The residual char after the test is quite porous and fragile. There was no char mound formed for the pure polycarbonate sample and its residual char was ragged/curled and scattered around.

Extinction area was calculated from the measured He-Ne laser beam transmission through the exhaust duct of the Furniture Calorimeter divided by the exhaust duct diameter multiplied by the exhaust volume flow rate. Thus, extinction area is related to the amount of particulates; higher extinction area means more mass of particulates. The comparison of the measured extinction area curve between the polycarbonate-siloxane copolymer sample and the pure polycarbonate sample is shown in Fig.11. The results show clearly that the peak extinction area for the polycarbonate-siloxane copolymer sample is roughly one sixth of that for the pure polycarbonate sample. This is mainly due to more vigorous burning of the pure polycarbonate sample and is not due to a reduction in soot yield because soot yield measured by the Cone Calorimeter is about the same for the two samples and also for the polycarbonate sample with the siloxane-containing additive sample, as shown in Fig.7.

As discussed above, two different siloxane-containing treatments were used for polycarbonate; one was as an additive and the other as a copolymer. Although the former sample was tested at 40 kW/m<sup>2</sup> and the latter sample at 30 kW/m<sup>2</sup> in the Cone Calorimeter and the Furniture Calorimeter, the results show very similar trends such as much lower peak heat release rate, nearly same heat release and sample loss compared to the pure polycarbonate sample. The difference in flammability properties between the two treatments is not significant.

## DISCUSSION

Although the addition of siloxane significantly reduced peak heat release rate for polycarbonate, it is not clear how it is that siloxane affects heat release rate. It is particularly important to notice that the addition of siloxane not only slightly increases char yield and but also produces some physical differences in the char, as discussed above. Therefore, there might be chemical or physical differences or both in the char structure with and without siloxane in polycarbonate. In order to help discern such differences, elemental analysis of the char was conducted, as a first step. The char samples were generated at an external flux of

50 kW/m<sup>2</sup>, simulating flaming conditions under an external flux. The sample was heated in a nearly inert atmosphere of nitrogen (with 1 - 2% oxygen due to leaks in the system) using the second Cone Calorimeter at NIST. Samples were heated for 2, 4, and 6 minutes without any gas phase combustion and char was collected from different parts of the intumesced char mound. In this paper, B denotes the char collected from the bottom part of the mound just above the virgin polymer, T is from the top part and BT is from the middle part. The collected char was well ground using a ceramic mortar and pestle and fine-powdered char samples were sent to a commercial analytical laboratory for the elemental analysis. The preliminary results are shown in Fig.12 for pure polycarbonate and Fig.13 for the polycarbonate-siloxane copolymer samples. In these figures, normalized C/H is calculated from the carbon weight percentage divided by hydrogen weight percentage and normalized by the C/H value of the original sample; normalized C/O is calculated from carbon weight percentage divided by oxygen weight percentage and normalized by the C/O value of the original sample. The calculated ratios of the number of carbon atoms to the number of hydrogen atoms and of the number of carbon atoms to the number of oxygen atoms for the original polycarbonate are 1.21 and 5.38 obtained by accounting for the degree of polymerization and for the two end groups at the polymer chain ends. These values are reasonably close to the measured results of 1.1 and 5.5.

The results in Figs.12 and 13 show that oxygen is lost from the sample faster than carbon and hydrogen. This indicates that carbonate in the polycarbonate structure is lost at the fastest rate and is probably followed by the two methyls in the bisphenol. The relatively high amount of hydrogen after 6 minutes exposure time at the top part of char mound implies that hydrogens in the rings are not lost. This is confirmed by the ratio of the number of carbon atoms to the number of hydrogen atoms in the char is roughly two to one which implies the structure of C<sub>8</sub>H<sub>4</sub> which is a ring at backbone locations of polymer chains. The high number for normalized C/O indicates that there is only one oxygen for every 23 carbons in the char after 6 minutes exposure. Since there are not enough data for comparison between the results for polycarbonate and the copolymer sample, at present it is not clear whether the addition of siloxane causes significant difference in the chemical structure of the char. However, the preliminary results indicate that the rate of loss of silicon from the sample tends to be slower than total mass loss rate for the sample (normalized silicon weight percentage is larger than that in Fig.13). More silicon tends to stay in the sample but it is not clear as to what form is. Further continuation of the elemental analysis and more detailed analysis of the char are planned to find how siloxane reduces heat release rate.

## SUMMARY

The above results show that the peak heat release rate of the siloxane-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. In addition, piloted ignition delay time for the siloxane-containing polycarbonate sample is much shorter than that for the pure polycarbonate sample and the flame spread rate under an external radiant flux for the siloxane-containing sample is higher than that for the pure polycarbonate sample. This is caused by the reduction in thermal stability for the siloxane-containing sample.

Overall, the siloxane-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 siloxane-containing sample, the char appears to be relatively easily combustible and does not have strong flame resistance like the char from polyetherimide.

## ACKNOWLEDGEMENT

This work is supported by the Chemical Research Center of General Electric Co. Corporate Research and Development at Schenectady, NY.

## REFERENCES

1. "Aircraft Material Fire Test Handbook" DOT/FAA/CT-89/15, FAA Technical Center, September 1990.
2. Grimmelt, F.G.F., "The European Scene on PBBE's and Recycle" presented at the Third Annual BCC Conference on Flame Retardancy, Stamford CT, May 1992.
3. Petrella, R., Wadehra, I. and Zimmerman, R., "Fire Safety Testing for Information Processing Machines - Present and Future", presented at the Third Annual BCC Conference on Flame Retardancy, Stamford CT, May 1992.
4. Kashiwagi, T. and Cleary, T.G., "Effects of Sample Mounting on Flammability Properties of Intumescent Polymers" to appear in *Fire Safety J.*

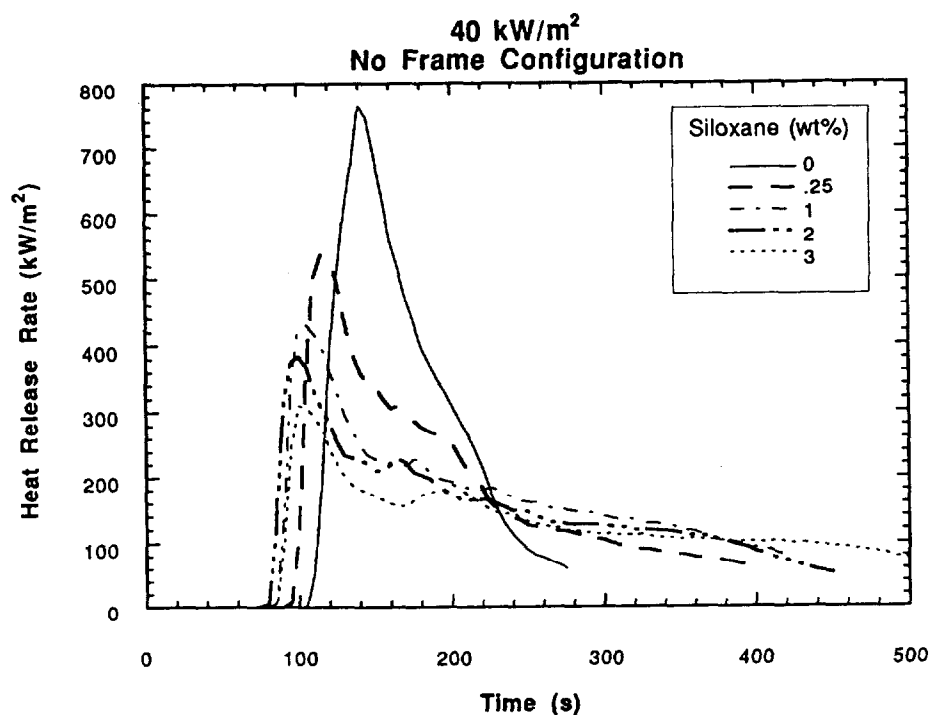


Figure 1. The effects of amount of siloxane on heat release rate curve of polycarbonate measured in the no frame configuration at external radiant flux of 40 kW/m<sup>2</sup>.

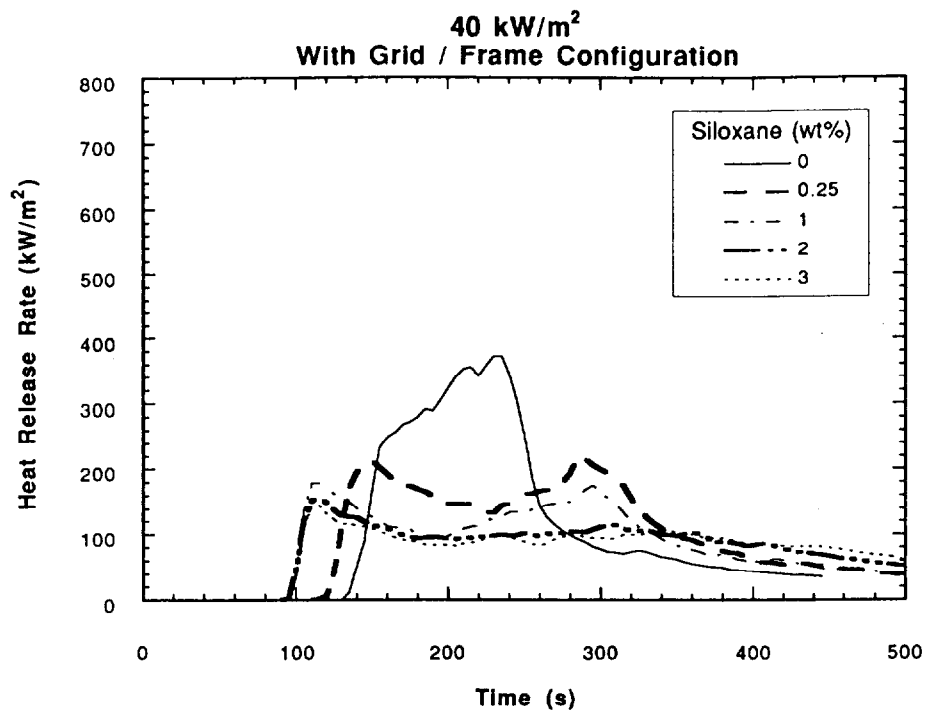


Figure 2. The effects of amount of siloxane on heat release rate of polycarbonate in the frame/grid configuration at external radiant flux of 40 kW/m<sup>2</sup>.

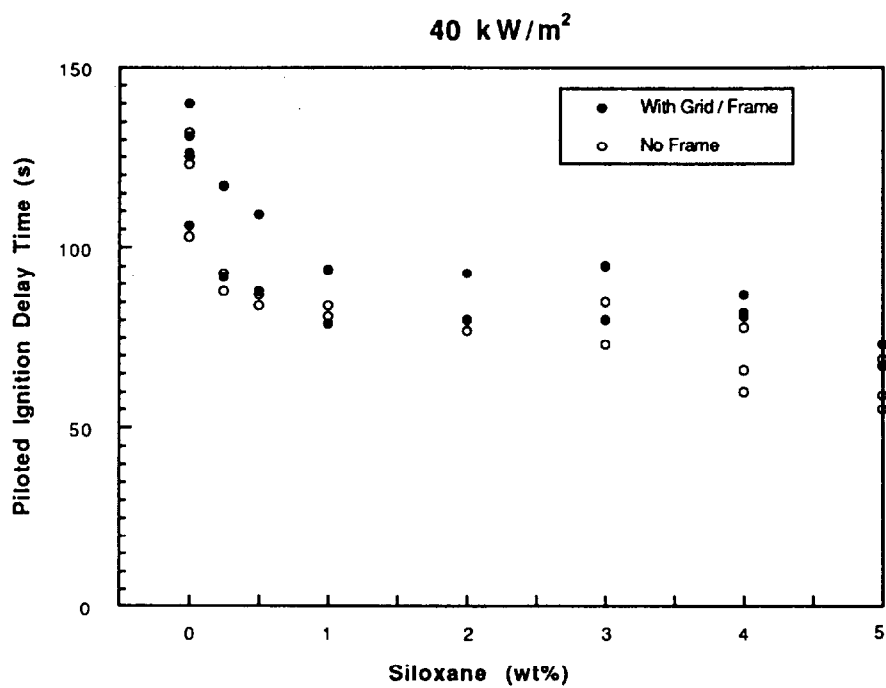


Figure 3. The effects of amount of siloxane on piloted ignition delay time of polycarbonate at external radiant flux 40 kW/m<sup>2</sup>.



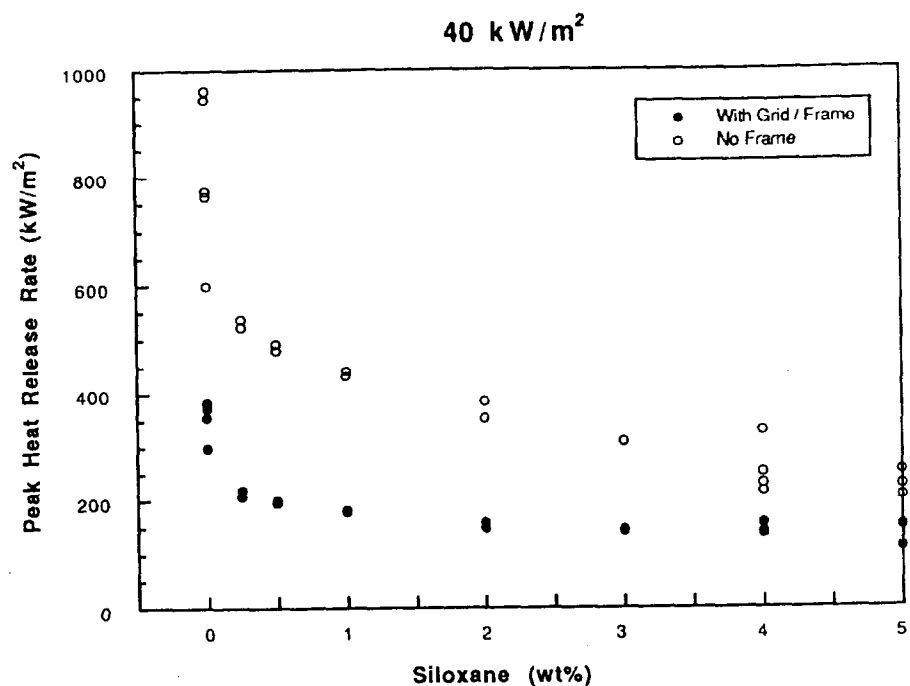


Figure 4. The effects of amount of siloxane on peak heat release rate of polycarbonate at external radiant flux of 40 kW/m<sup>2</sup>.

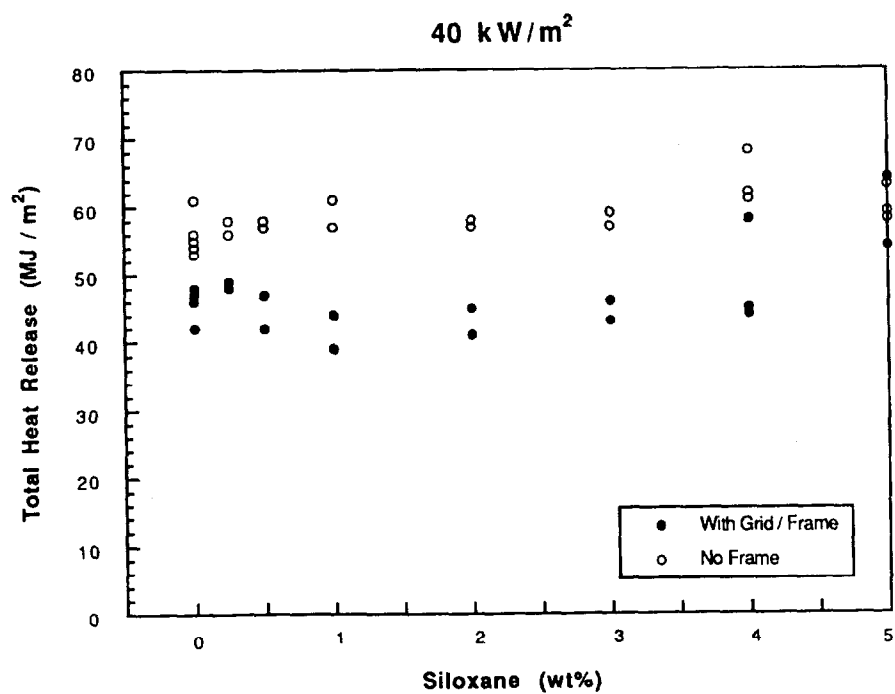


Figure 5. The effects of amount of siloxane on total heat release of polycarbonate at external radiant flux 40 kW/m<sup>2</sup>.

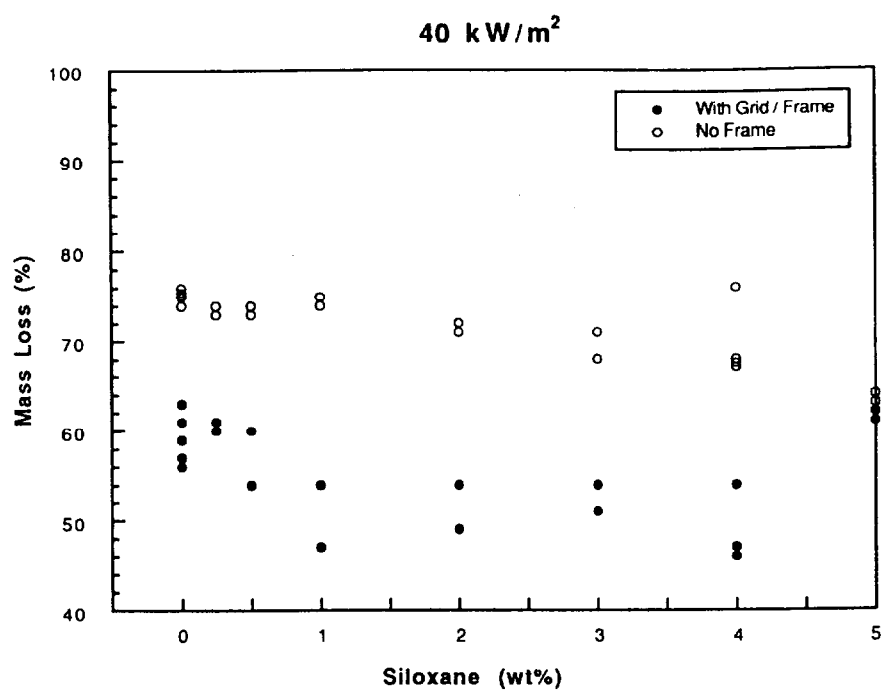


Figure 6. The effects of amount of siloxane on total mass loss of polycarbonate at external radiant flux of 40 kW/m<sup>2</sup>.

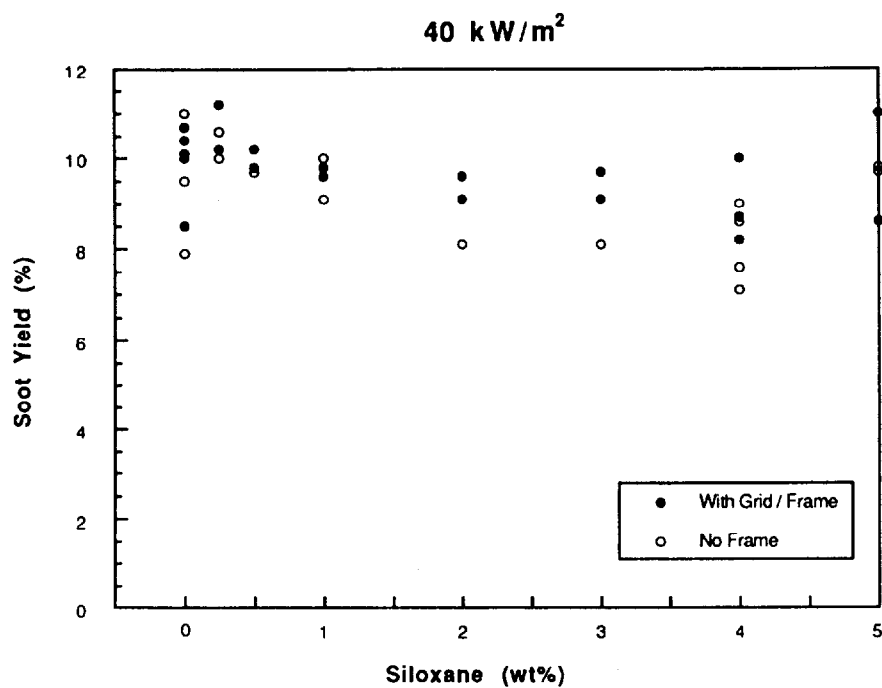


Figure 7. The effects of amount of siloxane on soot yield of polycarbonate at external radiant flux 40 kW/m<sup>2</sup>.

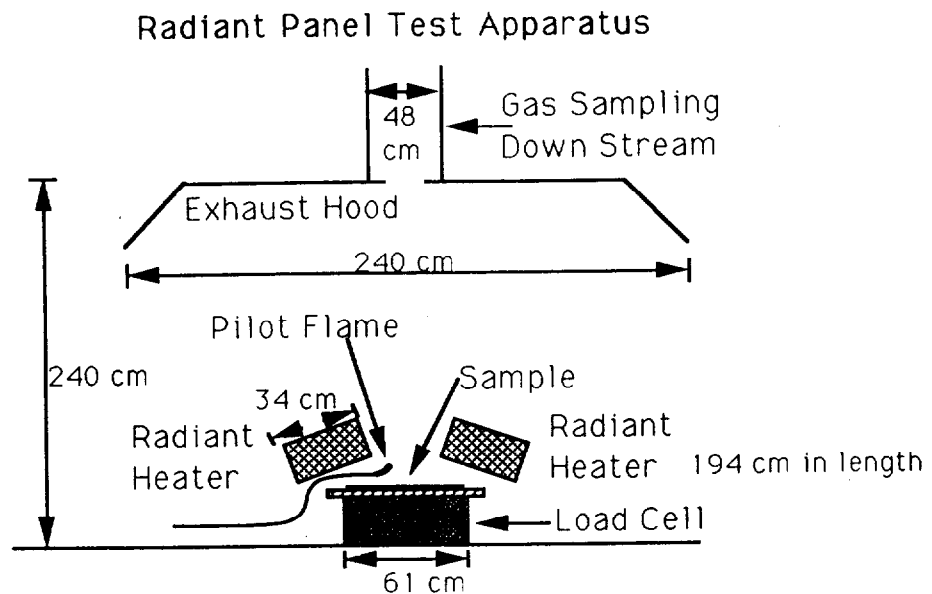


Figure 8. Schematic illustration of the large radiant panel test apparatus.

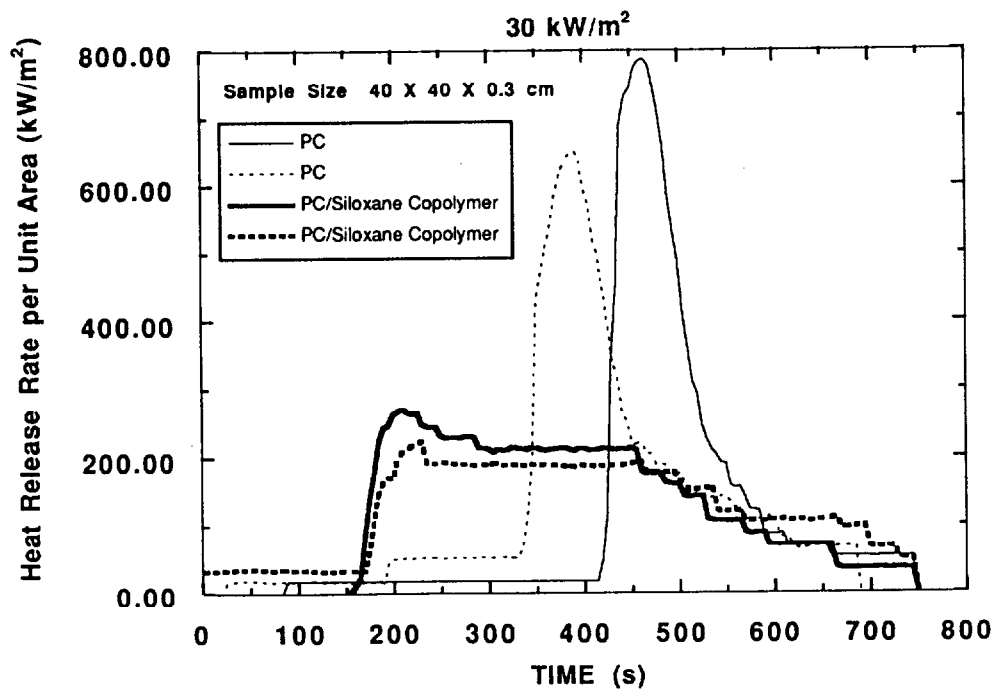


Figure 9. Comparison of heat release rate curve between the two large sample sizes at external radiant flux of 30 kW/m<sup>2</sup> (two repeated tests for each sample).

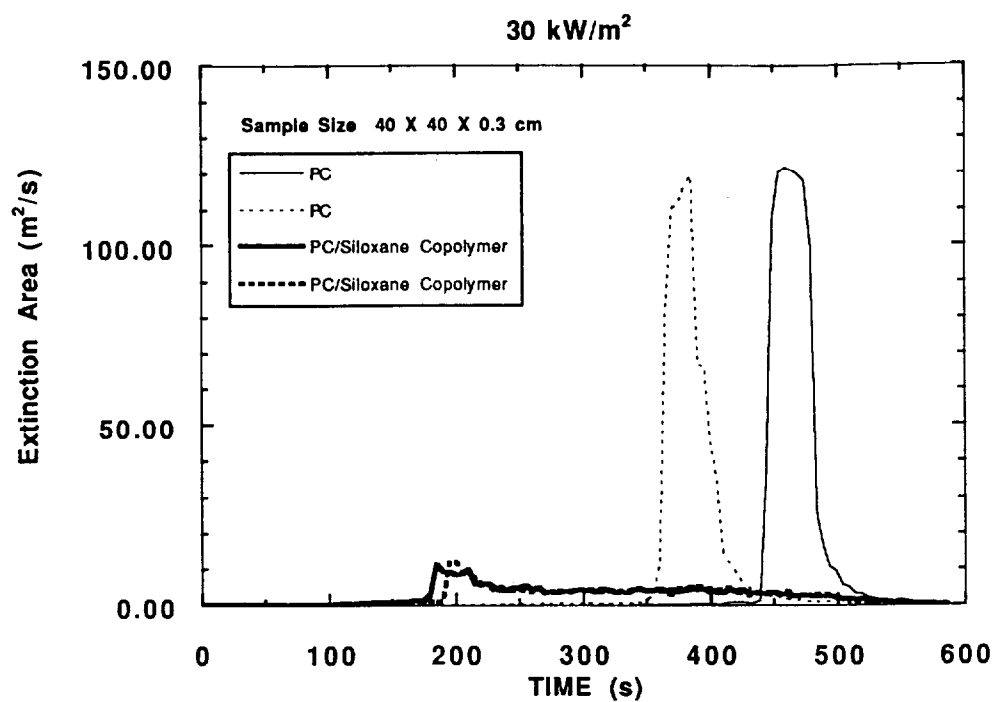


Figure 10. Comparison of extinction area between the two large size samples at external radiant flux of 30 kW/m<sup>2</sup> (two repeated tests for each sample).

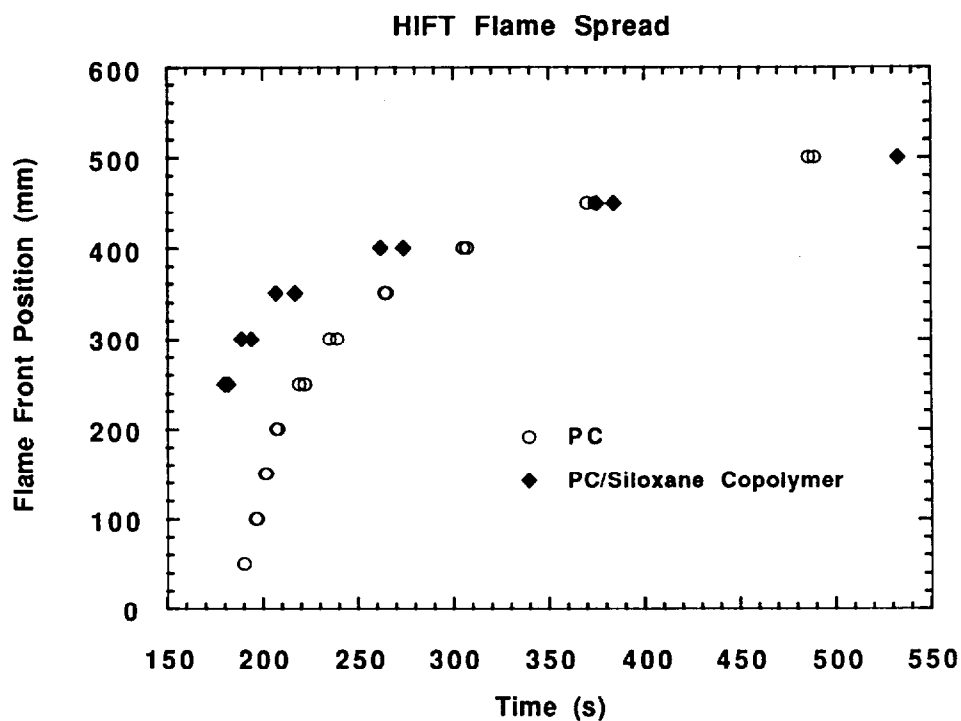


Figure 11. Comparison of history of flame front position between the pure polycarbonate sample and the polycarbonate-siloxane copolymer (two repeated tests for each sample).

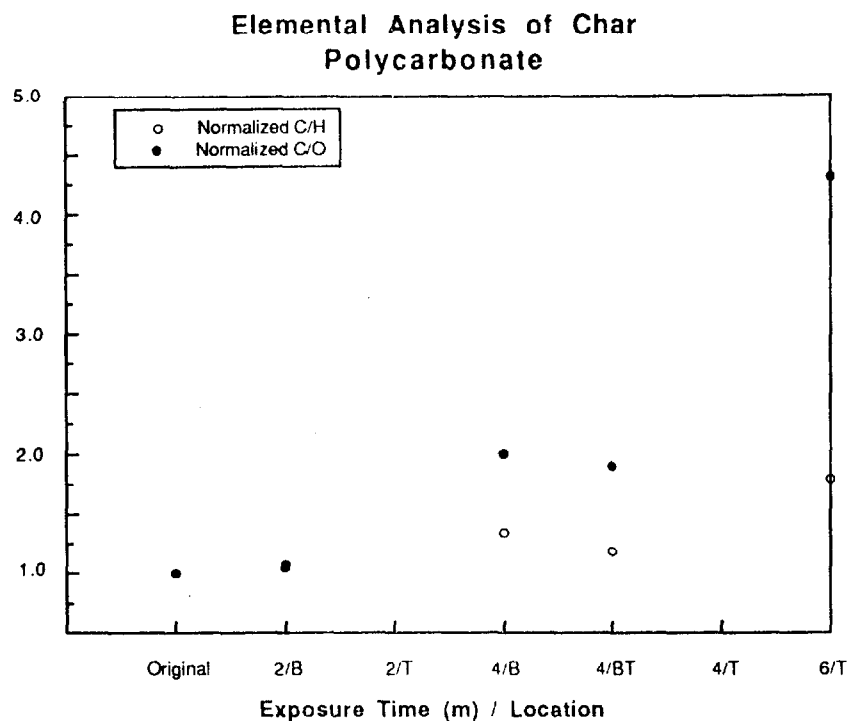


Figure 12. The effect of exposure time/location on normalized C/H ratio and normalized C/O ratio in char from pure polycarbonate.

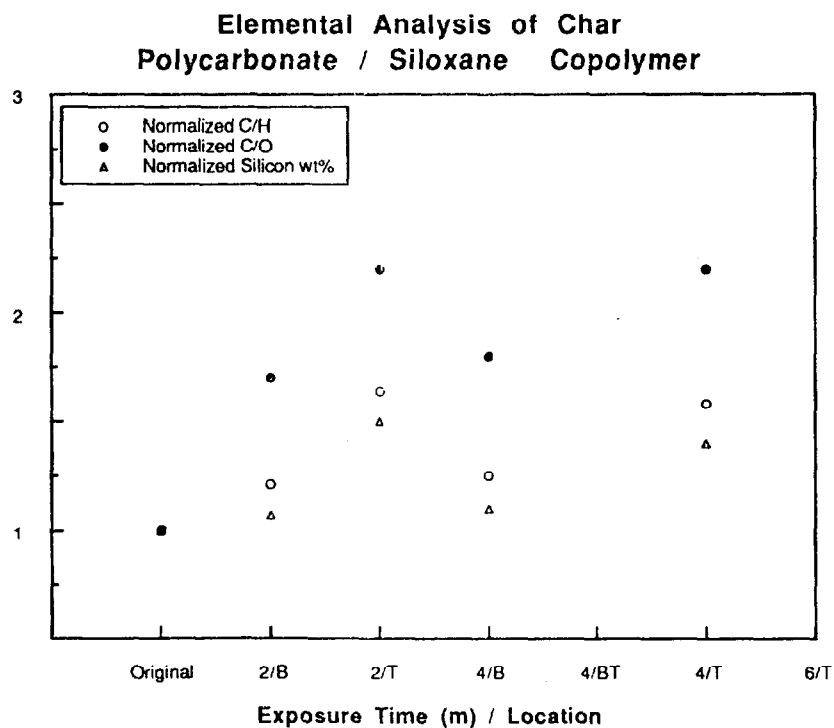


Figure 13. The effect of exposure time/location on normalized C/H , and C/O ratio and normalized silicon weight percentage in char from the polycarbonate-siloxane copolymer.