Flammability Resistance Synergism in BPA Polycarbonate–Silicone Block Polymers

R. P. KAMBOUR, *General Electric Research and Development Center, Schenectady, New York*

Synopsis

The synergism in limiting oxygen index found in BPA carbonate–dimethylsiloxane block polymers (BPAC/DMS) is correlated with a rise in yield of pyrolytic char and an improvement in char oxidation resistance. These changes in turn are related to a peaking of fractional silicon retention in the char at a resin composition of 50 mole % DMS. This behavior, the fine dispersion of silicon in the char, and analyses of the pyrolysates suggest that an important feature of char formation in the block polymers is a polycondensation reaction between pyrolysis products from the two blocks. In addition to the role of chars in withholding fuel from the flame, they are thought to function effectively as thermal insulators.

INTRODUCTION

In a preceding article,[1] a survey was reported of the behavior of several families of dimethylsiloxane (DMS) copolymers (mostly block polymers) in the Fenimore–Martin limiting oxygen index (LOI) test. A synergistic enhancement of LOI was found in some of these families, notably those based on bisphenol A polycarbonate (BPA PC) and bisphenol fluorenone polycarbonate (BPF PC).

A previous study of LOI chars from BPFC/DMS resins of low silicone content showed that the silicon content of the chars increased in proportion to the DMS content of the resin approximately.[2] Furthermore, an electron microscopy investigation of one of these chars revealed a hard, brittle, amorphous, electron-dense substance that appeared to line the pores of the char. On this basis principally, it was suggested that LOI enhancement by silicone occurred because this layer (thought then to be silica) tended to protect underlying carbonaceous char from oxidative attack. This protection was thought to allow the char to remain thicker and to be a more effective thermal insulator than it would otherwise have been. No quantitative data on char yields, densities, morphologies, etc., were available to support this contention, however.

Moreover, this mechanism has been afflicted from its conception by a major weakness when viewed in the framework of the generally accepted scheme for burning of organic solids.[3] In this scheme the oxidation processes that produce the heat occur largely in the outer portions of the flame. The inner portion of the flame is considered to be deficient in oxygen. Essentially no external oxygen penetrates the solid: Here, only pyrolysis occurs, the pyrolysates simply diffusing and effusing out through the degrading solid to be burned in the flame. Thus, the contradiction: How could dimethylsiloxane be oxidized to silicon dioxide in the reducing atmosphere of the solid interior?

A somewhat different view of the LOI synergism in silicone polycarbonate resins has emerged from the studies described here. These studies were pri-

marily focused on the chars produced from BPAC/DMS resins. What were thought to be silica layers are now realized to be carbon and silicon-containing char membranes. The new view of the synergism still focuses on these brittle, electron-dense, oxidation-resistant membranes. However, the understanding of their production mechanism, composition, and function in raising LOI has changed.

In summary, in the view provided by the following account, these friable membranes are currently thought (1) to arise under pyrolytic conditions, by rather specific chemical processes involving bisphenols from the hard block and DMS or its products, and (2) to produce the synergism by altering the yield and oxidation resistance of the pyrolytic portion of the char.

The experimental work underlying this new view deals with two subjects: (1) LOI chars—their yield, composition, and resistance to further oxidation; the morphologies of these chars and the silicaceous residues left by their complete oxidation; and (2) pyrolysis products, i.e., the chars and pyrolysates produced by vigorous pyrolysis under inert atmospheres—their compositions, structures, and morphologies.

EXPERIMENTAL

LOI Chars

A modified LOI test was devised that allowed measurement of the yield of char per unit weight of resin. A piece of LOI test specimen $\frac{3}{8}$–$\frac{1}{2}$ in. long was cut off and a small hole drilled into the piece from one end. The piece and a 2-in. diam. aluminum weighing cup were each weighed. The cup was impaled on a steel needle mounted in the LOI specimen clamp (Fig. 1). The mantle of the apparatus was put in place and the oxygen index set at the LOI previously determined. The top of the specimen was lighted with the torch in the standard way. The flame progressed as usual down the sides of the specimen and soon engulfed it completely. At the end of the flaming process, the normal char would be left sitting whole on the end of the needle. The cup could then be pulled off the needle taking the char along, often completely intact. The cup and char were weighed once again and the char yield calculated. Yields of BPAC/DMS chars from this test were found to increase linearly with resin DMS content (Fig. 2). These chars were also analyzed for carbon, hydrogen, and silicon (Fig. 3).

A further modification of this test resulted from the discovery that if the OI had been set sufficiently high, the char would continue to glow for some time after the flame had gone out and the resultant residue was completely white throughout. Thus, for one set of BPAC/DMS resin specimens, combustion was carried out at OI = 41 (41 ⩾ LOI of all the resins so tested) and the time of this period of flameless combustion (the afterglow period) determined with a stopwatch for each specimen. In contrast to char yield and composition (Figs. 2 and 3), the plot of afterglow period versus BPAC/DMS resin DMS content (Fig. 4) shows a strong resemblance to the dependence of LOI on DMS content (Fig. 2 of ref. 1).

Other specimens were burned at OI = 41 until the end of the flaming portion of combustion and quenched by switching to 100% nitrogen; the resultant char yields were the same as those produced at each LOI (Fig. 2). Thus, char yield
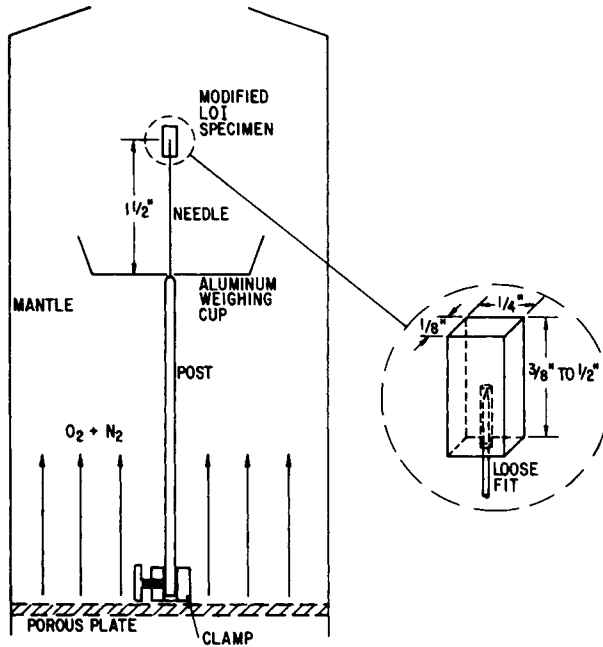
Fig. 1. Schematic of modified LOI test for studying char yield and combustion.

during the pyrolysis stage is insensitive to OI setting (as long as it is greater than LOI, of course).

The kinetics of combustion of these chars at OI = 41 were assessed for BPA PC and two block polymers by quenching and weighing chars after varying periods of combustion. Weight loss rates for the three are similar in the early stages
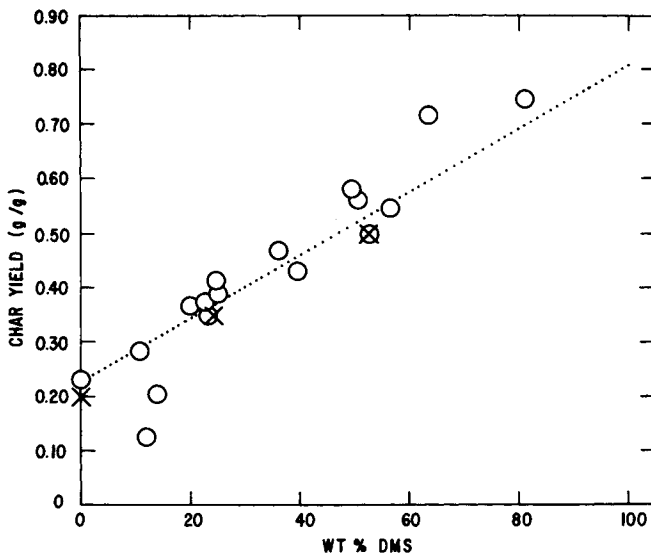

Fig. 2. BPAC/DMS char yield from modified LOI test (O) vs. resin silicone content. Char yield from test at OI = 41 followed by quenching in pure nitrogen at end of flame period of burning (×). Dotted line theoretical: yield from BPAC fraction = 0.23 g/g, 100% DMS converted to SiO_2.
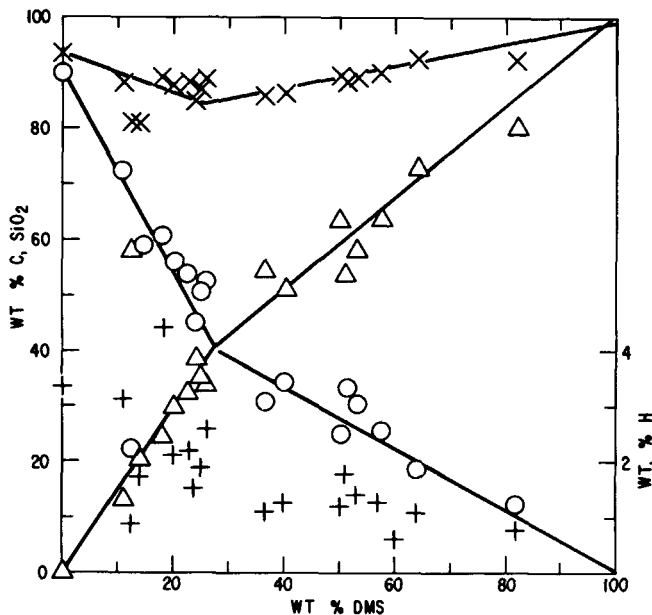
Fig. 3. Compositions of BPAC/DMS chars from modified LOI tests. Left-hand scale: carbon (O), SiO_2 yield on complete oxidation (△), total carbon, hydrogen + SiO_2 (×). Right-hand scale: hydrogen (+).

of combustion but become much smaller for the block polymer chars in the latter part of the afterglow period (Fig. 5). (This behavior differs from air oxidation results at 580°C, carried out in a conventional thermogravimetric analysis apparatus; at this temperature, weight loss rates normalized for the amount of combustible material present are identical for pyrolytic chars of BPA polycarbonate and a 25% DMS copolymer. Presumably this difference arises from sample size and/or temperature differences.)

During the afterglow period, the appearances of the polycarbonate char and the block polymer chars differ increasingly. The polycarbonate char becomes steadily smaller in overall size but otherwise changes little in appearance, the whole char continuing to glow. With a block polymer char, there develops a white, dead residue surrounding a shrinking glowing core. The deceleration in weight loss with such chars corresponds to the combustion of this inner core.
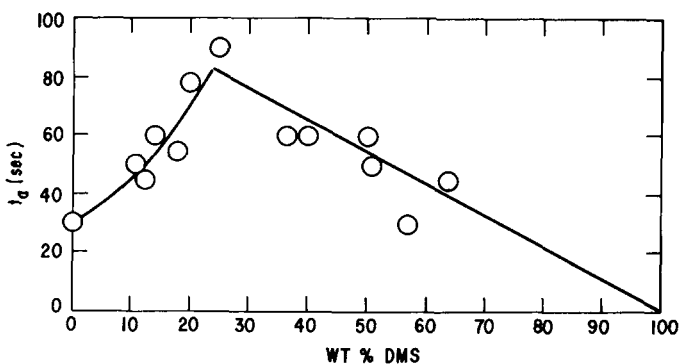

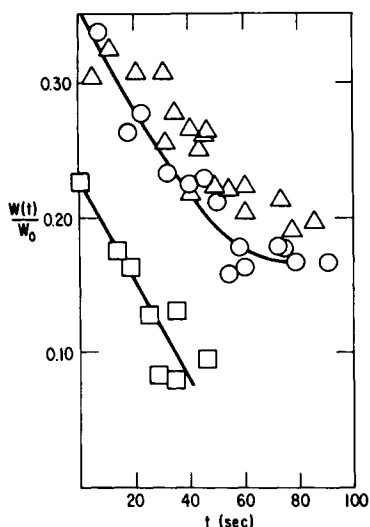Fig. 4. Afterglow period in OI = 41 test of BPAC/DMS resins vs. resin DMS content.

Fig. 5. Specimen weight $W(t)$ during afterglow period for BPA polycarbonate (□) and BPAC/DMS resins of 25 (O) and 53 (△) % DMS. W_0 = resin specimen weight.

LOI chars were examined by scanning electron microscopy (SEM) and transmission electron microscopy. The white residues left upon complete oxidation of the block polymer chars were also examined. Finally, some chars were inspected following digestion in warm hydrofluoric acid (which converts most of any silicaceous material to SiF_4 which volatilizes).

Two regions are distinguishable in each of these chars—an inner region composed of a continuous membrane or interconnected webbing and an outer region made up of a weak agglomerate of discontinuous particles. The relative amounts of the two regions and the morphology of the inner region change with resin composition (Figs. 6 and 7). The inner region is true *in situ* pyrolysis char as judged by its resemblance to chars produced in special pyrolysis experiments (see section on pyrolysis char below). The outer agglomerate is a "soot" formed apparently from vapors produced by pyrolysis inside and transported outward toward the flame where they undergo further pyrolysis and/or oxidation. The soot contains both white and black particles in amounts that vary with resin composition.

The morphology of the pyrolysis char changes markedly beginning at a resin composition of 20–25% DMS. With polycarbonate and all resins up to this level, the char looks like a closed cell foam, the walls of which are studded with what appear to have been bubbles, or are punctured by holes apparently formed by the breaking of such bubbles (Figs. 8 and 9). Above 25% DMS, the chars become more and more like open cell foams in appearance (Fig. 10).

The bubble residue is of such shape that an extension ratio λ can be calculated for it often (surface area of bubble divided by surface area of base). This ratio is commonly 2 or more. In one case (Fig. 11), $\lambda \cong 12$.

The SEM appearances of the white residues produced by complete oxidation and the black residues left upon hydrofluoric acid digestion are identical to those of the parent chars.
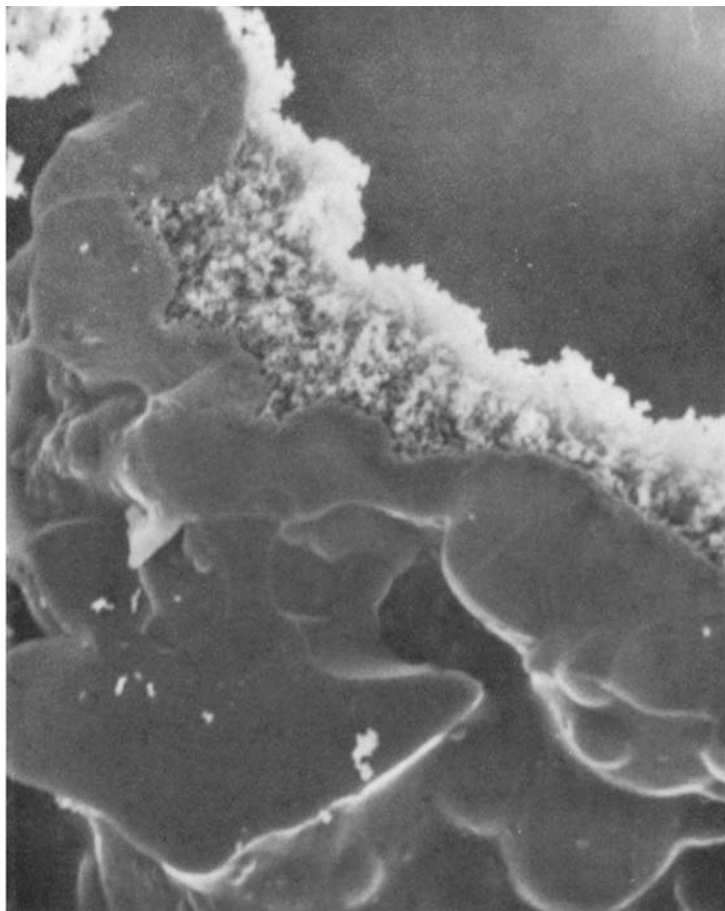
Fig. 6. Cross section of BPA polycarbonate LOI char showing surface deposit of fine black particles (soot) (SEM). 22500×.

Pyrolysis Chars

BPA polycarbonate, SE-30 silicone gum, and several of the block polymers were subjected to vigorous pyrolysis (VP) in nitrogen atmospheres under strong heating conditions until no more vapors were evolved. This work utilized small pieces of $\frac{1}{8}$-in.-thick moldings placed in the bottom of Pyrex tubes heated with a Meeker burner. While red hot, each tube was plunged in water, which cracked the tube and freed the solid residue, usually in one piece, that rose to the surface of the water. The chars were dried and weighed.

The dependence of VP char yield on resin DMS content displays a pronounced maximum at the position of the LOI maximum (Fig. 12). This behavior contrasts markedly with the results from TGA pyrolyses run at a heating rate of 10°C/min. For the homopolymers char yields by the two methods are the same (20% for BPAC, zero for PDMS), while block polymer char yields are much greater on the whole from the vigorous heating method.

The VP chars were oxidized completely in a 650°C muffle furnace. White residues (presumably SiO_2) were left from the block polymer chars. Their yields computed as a fraction of resin silicon retained in the char are very sharply

Fig. 7. Laminar deposits of silica particles in surface of char of BPAC/DMS resin of 18% DMS burned out at OI = 41 (SEM). 1100×.

peaked at about 20% DMS (Fig. 13). Fractional retention of the nonsilicone portions of most of these resins as VP char is also much greater than under TGA pyrolysis conditions, though not sharply peaked like silicon retention. In Figure 14, these yields are replotted versus mole fraction of DMS in the resin. The marked symmetry in the SiO retention curve is discussed later.

The VP chars exhibited morphologies resembling those of the inner portions of the LOI chars. None of the soot constituting the outer portions of the latter chars was found. Moreover, the morphologies of the residues from high temperature oxidation and from hydrofluoric acid digestion were identical to those of the parent VP char body.

Transmission Electron Microscopy of LOI and VP Chars

Finally, LOI char cores, VP chars, and their oxidative and HF residues were examined by transmission electron microscopy. Specimens were vacuum impregnated with epoxy, which was hardened prior to ultramicrotomy. The thin sections were backed with carbon for stability.
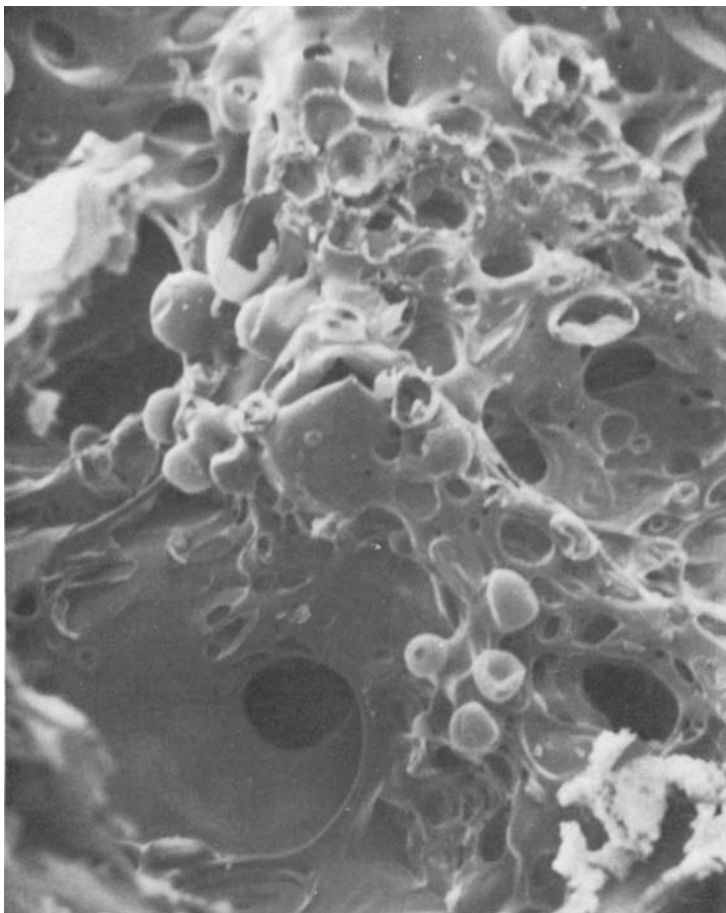
Fig. 8. Interior of modified LOI test char from BPA polycarbonate (scanning electron micrograph). 1100×.

Friable, electron-dense, heat-stable layers, similar in appearance to those found in bisphenol fluorenone carbonate/silicone block polymer LOI chars, were found in the BPAC/DMS LOI and VP chars (Figs. 15 and 16). Indeed, the VP chars seemed to consist of little else but these layers. Regions showing collections of heat-stable fine particles (e.g., upper part of Fig. 15) have been seen in both BPFC/DMS and BPAC/DMS LOI chars; in contrast to prior belief, these regions are now thought to consist of epoxy impregnant in which soot particles deposited from the gas phase have become suspended. The electron-dense layers on top of underlying char are now realized to be the only continuous structures present in chars prior to epoxy impregnation. In short, these layers and the membranes seen by SEM are the same.

As before, electron diffraction attempts produced no evidence of silica crystallinity in the friable layers. Also, some of the ultrasections were subject to hydrofluoric acid treatment for 17 hr at room temperature: No discrete holes could be seen in the layers so treated, even at 300,000 magnification. Thus, the silicon present must have been dispersed on a scale between 1 and 50 Å.
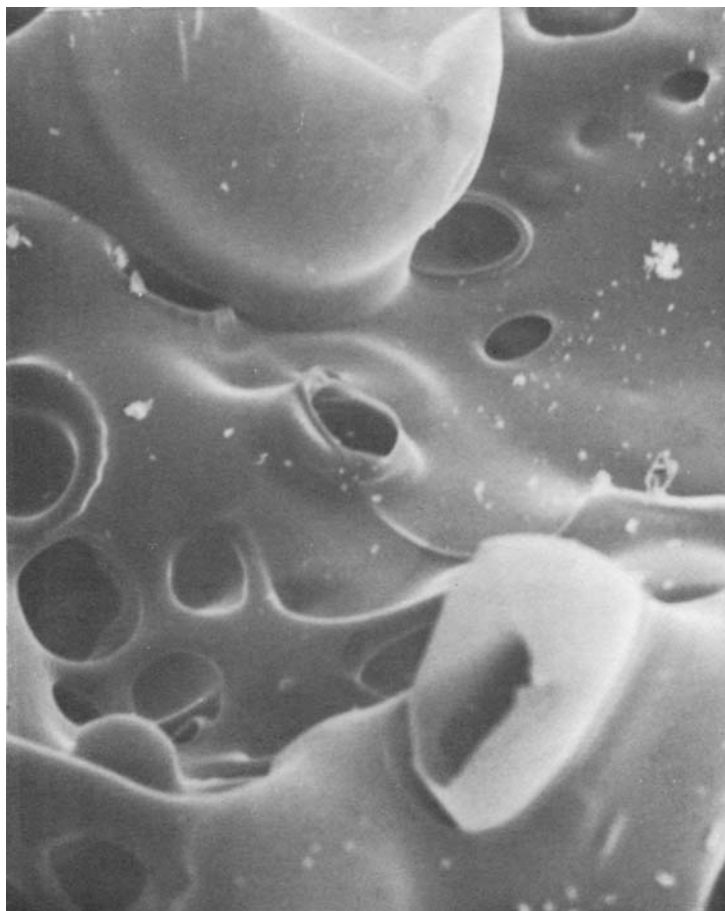
Fig. 9. Interior of LOI test char of BPAC/DMS resin of 18% DMS (SEM). 4450×.

Pyrolysates

Pyrolysis of silicones at temperatures of 600°C and lower results in almost complete volatilization in the form of silicone cyclics.[4] Very little residue is left. The same has been found for the silicone portion of BPFC/DMS block polymers.[1,5] Pyrolysis of silicones at temperatures of 600–800°C produces SiO and compounds containing silmethylene, silicon trioxy, and silyl hydride groups.[4] The SiO is known to be an OH radical scavenger.

The pyrolysis of BPA polycarbonate produces a host of volatile products including water, methane, carbon dioxide, BPA, phenol, various alkyl phenols, and isopropenyl phenol.[6,7] One of the BPAC/DMS block polymers of 25% DMS was pyrolyzed in quantity and the condensable volatiles collected. Silicon-29 Fourier transform nuclear magnetic resonance revealed a methyl trioxysilane compound and a large quantity of a broad distribution of organosilicates; further structural details were not worked out.

Gas chromatography up to 300°C has separated one component of mass 272 from the block polymer pyrolysate, a component not present in the pyrolysate from BPA polycarbonate. Tandem mass spectroscopy indicated that this component is a trioxy silicon compound containing other moieties similar to those
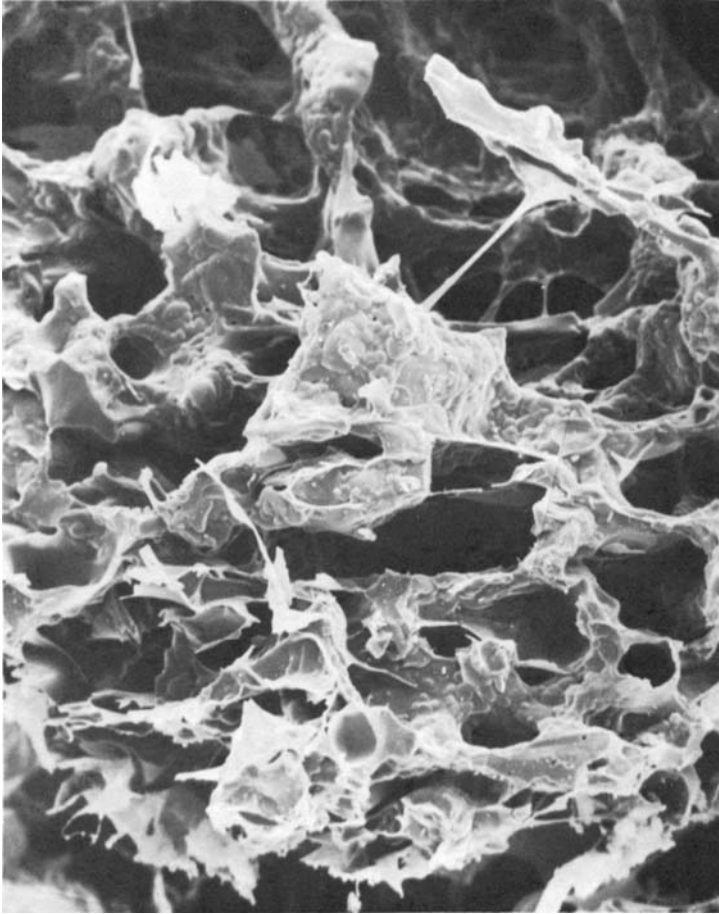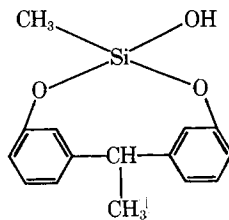
Fig. 10. Interior of LOI test char of BPAC/DMS resin of 36.5% DMS (SEM).   1100×.

produced by BPA polycarbonate pyrolysis.   The structure is believed to be close to that shown below:

DISCUSSION

The experiments described above make it clear that LOI char has a twofold nature: an *in situ* pyrolytic char and what might be termed soot or condensed smoke.   The mature *in situ* pyrolytic char consists of homogeneous continuous membranes or strings of friable material.   The soot consists of weak collections
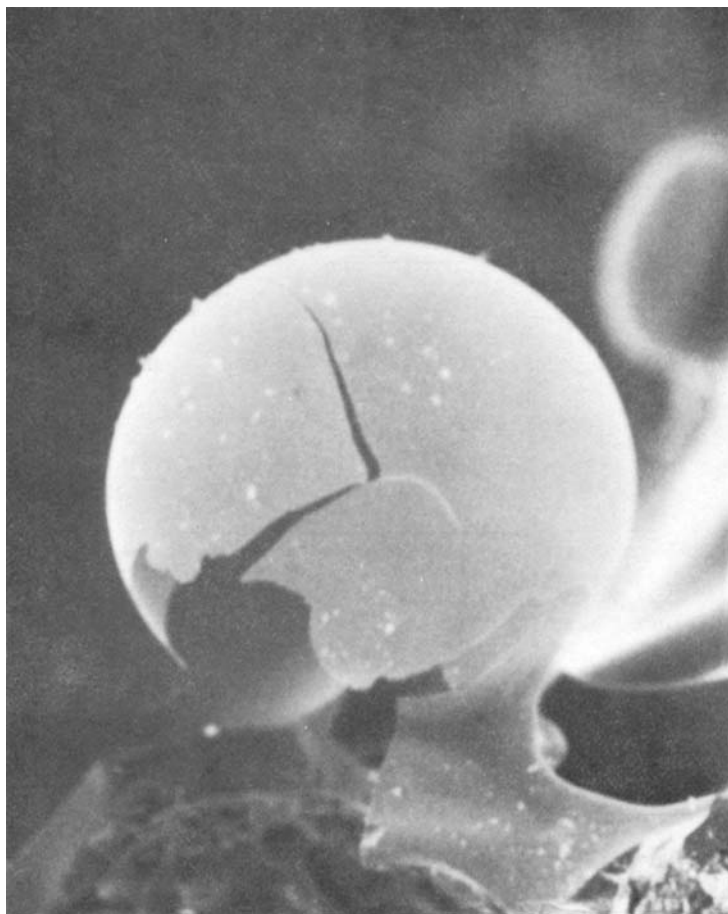
Fig. 11. Interior of same LOI test char as in Fig. 9 (18% DMS) (SEM). 4450×.

of carbonaceous and silicaceous particles. Soot is found, of course, on the exterior (particularly the uppermost regions) of the burnt specimen, being deposited largely from the inner regions of the flame. Soot is also found in pockets of the *in situ* char, although in smaller amounts.

These experiments also suggest that the coupling between the characteristics of whole LOI chars and the LOI synergism is weak at best. Of all these characteristics only the afterglow period mimics LOI in its dependence on resin DMS content (Fig. 4). And this appears to be the case only because variations in the time for complete oxidation of the *in situ* portion of the LOI char. The LOI enhancement mechanism for the BPAC/DMS resins appears to revolve about the production and combustion of the pyrolytic portion of the LOI char and the role of this material as a thermal insulator and perhaps as a barrier to pyrolysate vapor transport.

The keys to understanding the maximizing of char yield appear to lie in the char morphologies seen by SEM and in the symmetrical peaking of the silicon retention curve at about a 1:1 molar ratio of DMS to BPA. The char morphologies, especially those for low DMS content resin, indicate that resin undergoing conversion to char never loses its high molecular weight character.
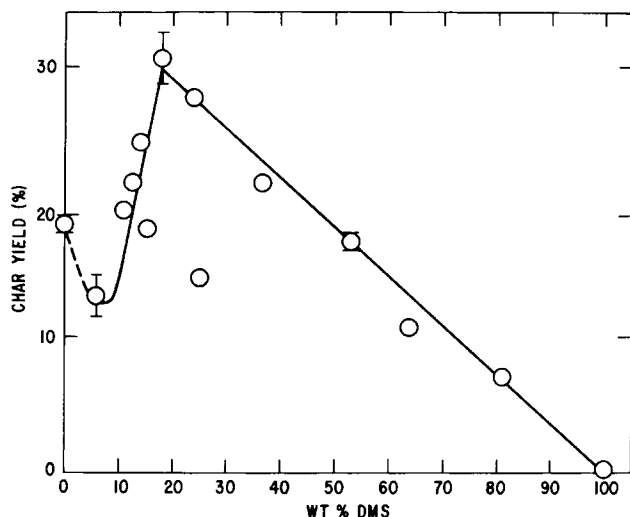
Fig. 12. Yields of pyrolysis chars from BPAC/DMS resin vs. resin DMS content.

That is, rather than degrading first to low molecular weight species before agglomerating into a highly crosslinked network, the resin undergoes crosslinking even as the original linear chains are being cleaved. If this were not so, the bubbles would break before becoming immobilized.

The symmetrical, sharp peaking of silicon retention at a 1:1 molar ratio of DMS to BPA suggests that the crosslinking process is a polycondensation involving these species or some of their degradation products. The principal reason for invoking polycondensation here is that in such a reaction between dissimilar monomers (e.g., $COCl_2$ and BPA), the production of high molecular weight
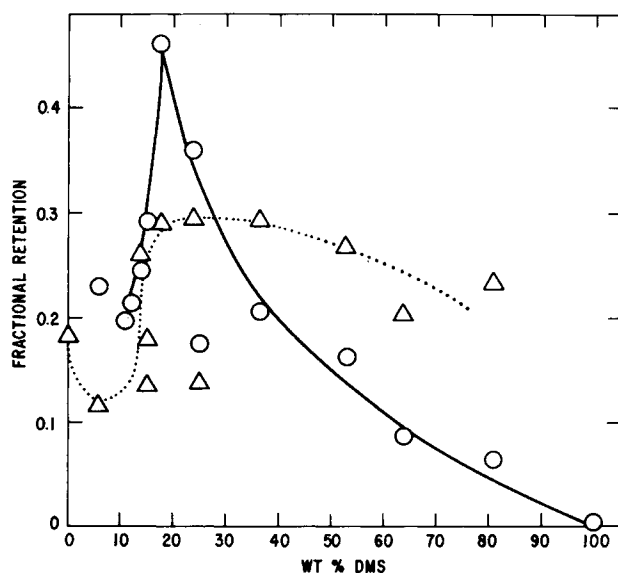

Fig. 13. Fractional retentions in pyrolysis chars from BPAC/DMS resins: (O) silicon yield/DMS weight fraction; (△) (char yield minus SiO yield)/BPAC wt. fraction.
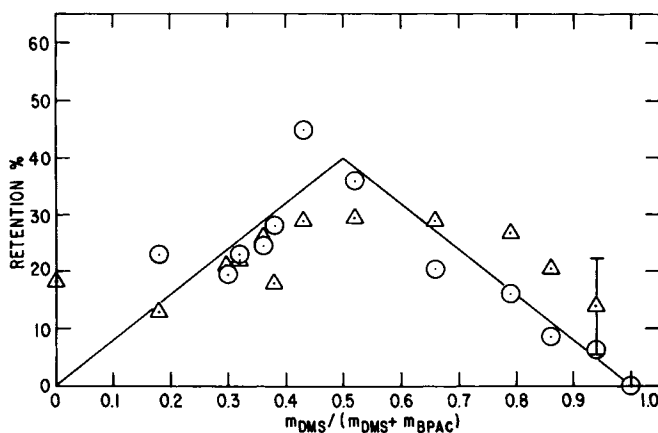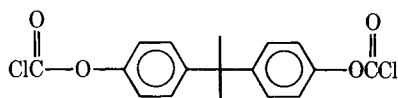
Fig. 14. Replot of yields from Fig. 13 vs. mole fraction M of DMS in resin.

polymers requires reactant concentrations close to stoichiometry. At reactant ratios far from ideal, the monomer in excess simply caps the other, for example,

and the products are low molecular weight substances.

The chars are leaky reactors at best and at combustion temperatures low and medium weight substances will tend to volatilize and diffuse out quickly. Thus, on one side of stoichiometry, excess BPA and species like BPA'–DMS'–BPA' are presumably lost, while on the other side excess DMS and species like DMS'–BPA'–DMS' are lost. (The primed symbols are meant to stand for chemical species derived from BPA and DMS.)

Knowledge of the chemistry of crosslinking process is clearly rudimentary. Two possibilities seem most attractive at present. The first involves condensation of pyrolytic SiO with bisphenols:
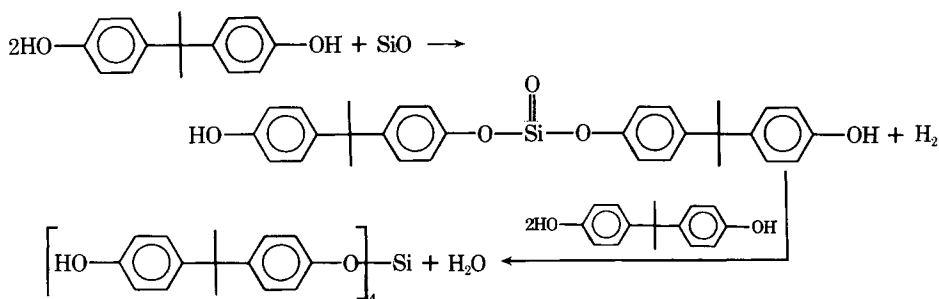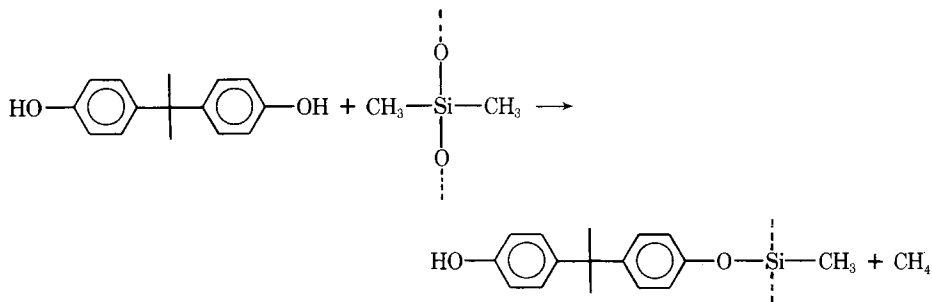

The second, based on the known attack of OH^- on the carbon silicon bond in

Fig. 15. Transmission electron micrograph of ultrasection of epoxy-impregnated LOI char from BPAC/DMS resin of 12% DMS showing friable electron-dense layers. 7500×.

silicones at high temperature is as follows[8]:

$$HO-\langle\bigcirc\rangle-|-\langle\bigcirc\rangle-OH \ + \ CH_3-\underset{O}{\overset{O}{\underset{|}{Si}}}-CH_3 \ \longrightarrow$$

$$HO-\langle\bigcirc\rangle-|-\langle\bigcirc\rangle-O-\underset{|}{Si}-CH_3 \ + \ CH_4$$

The finding of trioxysilicon and tetraoxysilicon groups in the pyrolysates supports both mechanisms. The existence of the cyclic siloxane–bisphenol compound supports the second reaction sequence. Both sequences are still only speculative, of course.

It is currently difficult to assign a level of significance vis-à-vis char yield to

Fig. 16. Ultrasection of pyrolysis char from BPAC/DMS resin of 18% DMS showing char wall of same character as friable layers in Figure 15. 7500×.

the change in pyrolytic char morphology that begins at about 20% DMS. It has been tempting to speculate that the closed cell morphology seen at low DMS content retards the loss of volatiles better than does the open cell morphology that gradually develops above 20% DMS. Such retardation should result in higher efficiencies in silicon retention. Since the silicon retention peak is symmetrical about the stoichiometric composition, it seems more likely that the change in char morphology is largely an incidental effect of the change in resin composition. The melt rheological behavior of this family of resins is known to vary with DMS content; it seems likely that the melt elasticity needed for the formation of stable bubbles deteriorates above 25% silicone. This aspect of the chars is clearly far from being resolved.

The presence of silicon in the pyrolytic char membrane appears to raise its oxidation resistance under combustion conditions. The most plausible reason for this is that as a given char membrane begins to be oxidized, a surface agglomerate of fine silica particles is produced that retards the oxidation rate of the substrate membrane. The result would be longer life for the membrane as a relatively gas-tight structure. In this respect, the currently favored mechanism

bears some resemblance to that proposed before in connection with BPFC/DMS resins.

Although the mechanism of the LOI synergism is not well understood, it clearly differs from that for organic homopolymers proposed by Van Krevelen.[3]   In Figure 17, LOI is plotted versus pyrolytic char yield for several homopolymers and for the BPAC/DMS block polymers.   Though the pyrolysis conditions employed here differ from Van Krevelen's, homopolymer data obtained here fall on his universal correlation line.   By contrast, data for all the BPAC/DMS block polymers fall on a different line that extrapolates to the point for silicone gum.   Subtraction of the SiO content from the chars makes the contrast even greater.

Van Krevelen suggested that charring effects a decrease in the yield of combustible vapors, thus raising the LOI.   The contrast evident in Figure 17 makes it clear that the withholding of fuel (at least as a characteristic measured in pyrolysis experiments) is not sufficient to explain fully the char effects on the LOI, even LOIs of organic homopolymers.   The existence of correlation lines based on the amount of char indicates that the additional functions of char are also dependent on char mass and/or volume.   Again, this is suggestive of functions relating to heat or vapor transport.

Of course, char is not immune to combustion and results here suggest that a LOI for any given char could be determined.   Van Krevelen's correlation line extrapolates to LOI = 58 at 100% char; he points out that graphite, which may be considered as a 100% yield char, has a LOI of 58.   Results here from the modified LOI test run at various high OIs indicate that the char from BPA polycarbonate has a LOI of about 40.   These meager results suggest that a LOI specimen under test should be looked upon as a two-layer solid, the outer layer
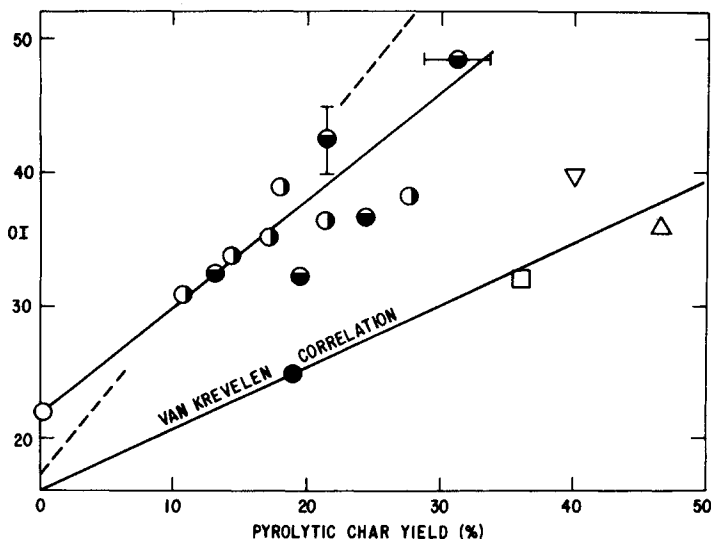

Fig. 17. LOI vs. pyrolytic char yield for BPA polycarbonate (●) polydimethylsiloxane (O) and several of their block polymers of DMS contents equal to or less than 18% (◐) and greater than 18% (◖).   Pyrolytic char yield (this work) for polysulfone (□), BPF polycarbonate (▽), and poly(2,6-diphenyl-1,4-phenylene oxide) (△).   Dotted line: best line for LOI vs. char yield minus SiO yield.

of which (the pyrolytic char) has its own peculiar oxidation properties. The more the char is resistant to oxidation, the less rapidly it will be oxidized, the better its thickness and density will be preserved and thus the better a transport barrier it will remain.

Thus, the study of the combustion resistance of char-forming organic polymers should henceforth encompass the investigation of chemical and physical characteristics of chars, not simply measurements of char yields.

SUMMARY

This study has suggested that the LOI synergism in BPAC/DMS block polymers results from (1) an increase in the yield of the pyrolytic portion of the LOI char and (2) an improvement in the pyrolytic char as a transport barrier. The improvement may stem principally from enhanced oxidation resistance arising from the silicon retained in the char and converted to a continuous protective silica layer during oxidation. Silicon retention may arise via a chain-building reaction between DMS pyrolysis products and bisphenols. The work suggests that char formation in all polymers raises LOI for reasons beyond the fact that char is fuel withheld from the flame.

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