

Metals as Synergistic Fire Retardants in Polyethylene-Silicone Blends

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Synopsis

The role of lead compounds in blends of polyethylene and silicone has been studied as a flame retardant. It has been established that these compounds work in the solid phase and that a gas-forming reaction is important to produce a foamed char which retards further combustion.

INTRODUCTION

It has recently been shown¹ that small amounts of lead compounds together with a silicone gum improve the fire resistance of crosslinked low density polyethylene. The importance of this observation can be understood when it is realized that heretofore large amounts of halogenated compounds were needed to attain similar fire resistance in polyethylene. A significant increase in our understanding of fire-resistant technology would result if we were able to determine the mechanism of this lead-silicone synergism and use this understanding to replace or supplement the current halogenated fire retardants.

We report herein our results on the synergistic use of certain lead compounds and silicone gum on the flammability characteristics of low density polyethylene.

EXPERIMENTAL

The low density polyethylene samples were prepared by mixing on a roll mill at 225–250°F (ca. 110°C), pressing into a mold at 250°F and raising the temperature to 375°F (ca. 180°C) for about 3 min. The samples that contained peroxide and were to be cured were held at 375°F for 30 min. The uncured samples were heated at 375°F for only 2 min.

Gel and swell measurements were made on all samples. A weighed sample (ca. 0.5 g) was enclosed in a tared nickel wire screen (200 mesh) and extracted with refluxing toluene under a nitrogen atmosphere in a soxhlet extractor for 16 h. The hot swollen sample was weighed to determine the weight of toluene absorbed. This was a fairly reproducible measurement, but a potential error could arise because, as the polyethylene cools below its melting point, toluene was extruded from the surface. Therefore, the hot sample must be weighed quickly. The extracted sample was dried at 110°C under vacuum for 24 h. The gel content was then determined. Gel % = extracted

weight \times 100/original weight. Swell % = (swollen weight—extracted weight) \times 100/extracted weight.

The oxygen index of all samples was determined using the ASTM-D2863-70 method. The measurements were obtained on a General Electric Flammability Gauge Model CR280FM11B. A modified UL-94 horizontal flame spread test was developed as an additional flammability measurement. Strips of sample were cut ($0.5 \times 4 \times 0.125$ in. or 0.0625) and marked at 0.5 and 2.5 in. intervals. The sample was held horizontally with the width (0.5 in.) vertical and ignited with a small natural gas air flame adjusted to 0.5 in. height. The first 0.5 in. of sample was heated and ignited. The time it took to burn between the two marks (2 in. total) was determined. The least flammable samples self-extinguished before burning to the 2.5 in. mark and are reported as self-extinguishing.

The silicone gum used, except where noted, was a polydimethyl siloxane with about 0.2 mol % vinyl methyl siloxane units from General Electric's Silicone Products Department, Waterford, N.Y. The lead compound used, except where noted, was 70% lead phthalate dispersed in polybutene. Fumed silica, MS-7 from Cabot Corp., was used as filler. Dicumyl peroxide was the only peroxide used in these studies. Triallylcyanurate was used as a crosslinking aid in many of the formulations. The polyethylene used in all experiments was Allied Chemical A-C 617.

RESULTS AND DISCUSSION

Extent of Cure versus Flammability

Based on previously reported² results on the effect of crosslink density on the flammability of silicone rubber, it was of interest to determine if a similar relationship occurred for polyethylene. Samples were prepared (Table I) and cured either with various levels of dicumyl peroxide or by exposure to x-rays.³

The peroxide levels were varied between 0.1 and 3.5 parts and as expected, the gel increased from 70.6 to 96.8% (Table II). A commercial crosslinked LDPE will be more than 90% gelled. The radiation cured samples (Table II) have a wider range of gel values because it was easy to control the times of exposure and thus the level of cure. Exposure times ranged from 0.5 to 16 min, which correspond to 1.6–50.6 Mrads of radiation for the equipment used. It should be noted that the addition of 1 part fumed silica has little or no effect on the gel/swell of these radiation-cured samples.

TABLE I
Basic Lead/Silicone Polyethylene Formulations

Material ^a	Parts
LDPE	100
Silicone	4
Lead	3
Triallylcyanurate	1.5
SiO ₂	1 or 0

^a See Experimental for detailed description.

TABLE II
Gel and Swell Values^a for Crosslinked LDPE With Lead/Silicone Additives

<i>Peroxide cure (parts)</i>	0	0.1	0.3	0.6	1.2	3.5	
% Gel	0	70.6	84.5	88.5	91.7	96.8	
% Swell	b	1100	730	560	450	290	
<i>Radiation cure (Mrad) with SiO₂</i>	0	1.6	3.2	6.3	12.6	25.3	50.6
% Gel	0	0	27.7	51.6	61.7	74.8	83.7
% Swell	b	b	3070	1880	1130	670	410
<i>Radiation cure (Mrad), no SiO₂</i>	0	1.6	3.2	6.3	12.6	25.3	50.6
% Gel	0	0.5	27.6	50.5	62.2	75.2	84.7
% Swell	b	4070	3340	1940	1140	660	430

^a Extracted with toluene.

^b Sample was completely soluble.

The results of both oxygen index measurements and the horizontal flame spread test (Table III) indicate that crosslinking is very important in building char and giving a self-extinguishing or slow-burning material. It does not seem to matter whether the sample is chemically crosslinked with peroxide or radiation cured. It should be noted that even at the lowest level of crosslinking (e.g., 1.6 Mrad), where the sample is still completely soluble, the results of the horizontal burn test are identical to a completely cured sample. This result suggests that very low levels of branching or silicone grafting are very important in the formation of char. The burned samples shown in Figure 1 dramatically show that the lowest levels of peroxide cure and radiation cure stop the sagging and dripping seen in the uncured sample and that various cure levels exhibit similar char formation. The OI for styrenated unsaturated polyester resins as a function of styrene loading was reported^{4a} to be a maximum at about 25 wt % styrene. This is the level of maximum expected crosslinking (1:1 mole ratio). At higher levels of styrene the OI decreased toward the OI of polystyrene. Below the 1:1 mole ratio the OI was significantly lower than the samples with 0% styrene. This is in contrast to our results where very low levels of crosslinking dramatically increase the OI and the horizontal burn times. A similar effect of cure on flame spread rate but not on OI has also been observed in a polyester system.^{4b}

The oxygen index values of these samples is puzzling yet typical of all our results; that is, burning times and OI values often do not correlate. Also, the OI values are very sensitive to the method of sample preparation.

TABLE III
Oxygen Index and Horizontal Burn Times for Radiation and Peroxide Cured DLPE

<i>Peroxide cure (parts)</i>	0	0.1	0.3	0.6	1.2	3.5	
OI	20.8	23.2	24.2	23.6	24.3	24.3	
Horizontal burn time (min) ^a	1.1	SE	SE	SE	SE	SE	
<i>Radiation cure (Mrad) with SiO₂</i>	0	1.6	3.2	6.3	12.6	25.3	50.6
OI	29.2	25.8	29.2	29.2	29.2	22.0	24.0
Horizontal burn time (min) ^a	1.2	SE	SE	SE	2.3	1.9	2.7
<i>Radiation cure (Mrad)</i>	0	1.6	3.2	6.3	12.6	25.3	50.6
OI	27.5	29.9	28.9	29.9	27.9	24.0	24.0
Horizontal burn time (min) ^a	1.2	SE	SE	SE	2.6	2.0	SE

^a Time to burn 2 in.; SE = self-extinguished.

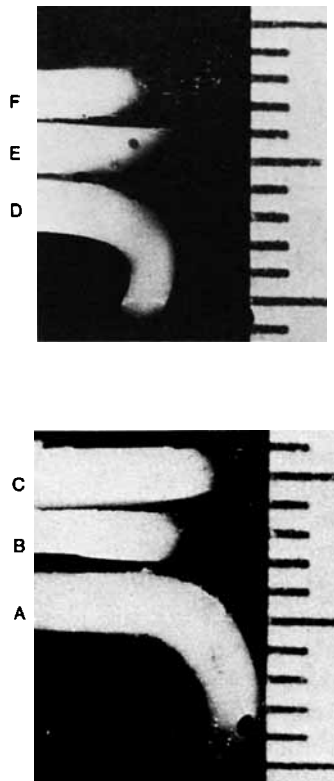


Fig. 1. Effect of cure on flame-retarded low density polyethylene (scale in mm). (A-F) Peroxide-cured LDPE with lead/silicone. (A) No peroxide; (B) 0.1 part; (C) 3.5 parts; radiation-cured (D) no radiation; (E) 1.6 Mrad; (F) 50.6 Mrad.

For example, the uncured sample in the peroxide series has an OI of 20.8 while the uncured sample in the radiation series had an OI of 27.5. These samples were prepared about 6 months apart but had identical formulations. The horizontal burn times for this pair are in good agreement (1.1 vs. 1.2 min), indicating that this test is less sensitive to variations in sample preparation than the oxygen index test; however, crosslinked samples with the same degree of crosslinking as measured by toluene swell and gel results have almost the same OI, that is, 0.1 part peroxide is about equivalent to 25.3 Mrads. Thus, the optimum level of crosslinking from a flammability standpoint was found to be much less than would normally be found in a useful, crosslinked product.

Effects of Metals on the Thermal Degradation of Silicone/LDPE Blends

Silicone and polyethylene are inherently incompatible, but it has been reported⁵ that under normal processing conditions, a uniform dispersion is formed. This dispersion consists of microgelled and grafted particles of silicone gum evenly distributed throughout the sample. Examination of uncured samples of polyethylene and silicone by scanning electron microscopy showed regions of silicone having diameters of 600–800 nm uniformly dis-

persed throughout the sample. Neither the addition of lead compounds nor curing of the samples had any effect on the size or distribution of these regions. However, since irradiated polyethylene crosslinks mainly within its amorphous phase,⁶ one would expect that the introduction of a silicone polyethylene graft may change the distribution of crosslinks between the amorphous and crystalline phases. The results reported above support the idea that subtle changes in crosslinking and/or grafting are significant factors in determining the flammability behavior of these polyethylene systems.

The thermal oxidative stability of silicones has been studied extensively since the late 1940s.⁷ It was reported by Murphy et al.⁷ that copper, lead, selenium, and tellurium greatly accelerated the volatilization of both polydimethylsiloxane and polyphenyl methylsiloxane at temperatures between 200 and 250°C. On the other hand, viscosity measurements over the same temperature range indicated that tellurium and antimony accelerate that rate of gelation due to oxidation of the methyl group and subsequent crosslinking due to siloxane formation. The other metals studied (e.g., cadmium, nickel, platinum, silver, tin, and zinc) did not significantly affect the stability of these fluids. The volatile compounds were found to be formic acid, formaldehyde (oxidation products of silicon methyl bond cleavage), and low molecular weight silicones.

More recent work by Willis and Shaw⁸ suggested that a metal oxide surface was the active catalyst in the thermal oxidative decomposition. Oxygen uptake experiments⁹ showed that partially degraded silicones were *more* resistant to oxidation than the original material. It was also reported⁹ that the type and rate of thermal degradation depended on the partial pressure of oxygen. This last observation suggests that the chemistry at a flame front, with varying oxygen concentrations, will be difficult to quantitatively measure or predict.

Careful analysis of thermogravimetric data reveals that the two degradation pathways for silicones have activation energies of 30 and 42 kcal/mol.¹⁰ The lower energy thermal oxidative pathway predominates at 380°C while the thermal depolymerization starts around 400°C.

It was of interest to determine the effect of metals other than lead on the flammability behavior of the silicone-polyethylene system. As noted by Murphy,⁷ lead and tellurium were the *most* active metals in the low temperature volatilization of silicone fluids. If formation of gaseous compounds is important in the fire-retardant mechanism, then evidence of a bubble or foam structure should be evident. The three partially burned samples shown in Figure 2 are all peroxide crosslinked polyethylene. The top sample contains three parts lead phthalate, the middle sample contains four parts silicone gum, and the bottom material contains both the lead and silicone. The synergism between lead phthalate and silicone gum is evident. Not only is a foam structure evident, but enhanced carbonization seems to have taken place. Foam formation is clearly important but not the only factor. As noted above, the enhanced char/foam is only formed in cured polyethylene.

Since it has been shown that both metals and metal oxides are catalysts for the thermal decomposition of silicone, experiments were done to deter-

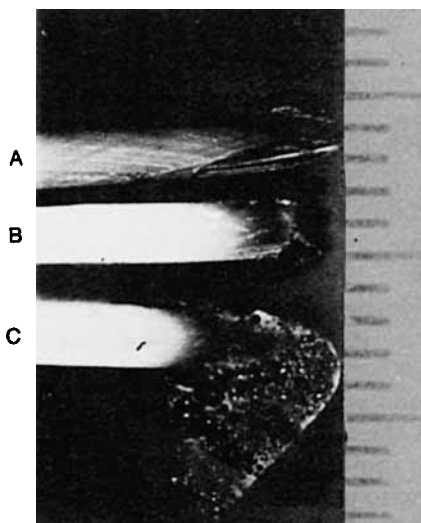


Fig. 2. Synergistic effect of lead phthalate and silicone gum in partially burned crosslinked low density polyethylene. (A) Three parts lead phthalate in LDPE; (B) four parts silicone gum in LDPE; (C) lead phthalate and silicone gum in LDPE.

mine whether a distinction could be made among various metals and their oxides. It is known that metal carboxylates will thermally decompose to form either a pyrophoric metal¹¹ or the metal oxide.¹² Several of these metal salts were compounded into a silicone-polyethylene blend, and the polymer was crosslinked using our standard process. Toluene extraction and swell measurements indicate that all these formulations are highly crosslinked. The oxygen index and horizontal burn times (Table IV) are consistent with the hypothesis that lead oxide is the active species required for high OI and long horizontal burn time. Lead citrate thermally decomposes to pyrophoric metallic lead,¹¹ and exhibits poorer fire resistance than the other lead compounds that decompose to lead oxide. None of the samples, except those that formed lead oxide, showed the foamed structure shown in Figure 2. Tellurium compounds were not compounded into a silicone-polyethylene

TABLE IV
Effect of Metal and Metal Oxides on Oxygen Index and Horizontal Burn Times in Crosslinked Silicone-Polyethylene^a

Metal additive	Decomposition product	LOI	Burn time (min)
Lead phthalate	PbO	24.3	SE
Lead acetate	PbO	21.2	3.3
Lead citrate	Pb	19.2	1.5
Manganese acetate	MnO ₂	17.8	2.4
Titanium stearate	TiO ₂	18.3	1.9
Vanadium oxide bis	V ₂ O ₅	20.4	2.0
Tin oxalate	Sn	19.2	1.6
Copper citrate	Cu	17.4	1.6
None	—	17.4	1.8

^a Composition parts: LDPE (100), silicone (4), triallycyanurate (1.5), SiO₂ (1), peroxide (3.5), metal additive (3.0). All compositions are greater than 87% gel as determined by toluene extraction.

blend, but, based on the previously reported similarity between lead and tellurium, one could anticipate that tellurium and silicone would afford a foam similar to the lead-silicone foam.

Silicone Effect

Phenyl silicones are more thermally stable than methyl silicones. However, when a phenyl silicone gum¹³ was substituted for the methyl vinyl silicone used in all other samples, no marked difference in fire resistance was noted. The oxygen index was good (28.2) and the horizontal burn time was long (2.4 minutes). Crosslinking was just as important in this phenyl system as in the vinyl methyl system. The oxygen index and horizontal burn time for an uncured formulation were 24.7 and 1.5 min.

Possible Gas Phase Activity

Tetraalkyl lead compounds, iron pentacarbonyl and manganese methyl cyclopentadienyl tricarbonyl are known flame poisons. Tetraethyl lead and manganese carbonyl complexes have been used as gasoline additives for their antiknock or combustion modification properties. These metal compounds may be as much as 2 orders of magnitude more effective in inhibiting methane flames than halogen. Thus, if even a small amount of lead were to be volatilized, it might have a large effect on the flame.

Careful analysis of condensed volatiles showed no detectable lead, and analysis of the remaining char could account for all of the lead originally added. ESCA and microprobe analysis also confirmed the presence of both lead oxide and metallic lead.

Another criterion for gas phase flame inhibition is to compare the oxygen index and nitrous oxide index for a series of polyethylene mixtures that exhibit increasing fire resistance. The data shown in Table V support the results given above which suggest that the lead-silicone system is a solid phase fire retardant. One would anticipate that if a gas reaction were important, there would be a large difference between OI and NOI, but the difference is constant (about 20 units) regardless of the composition of the polyethylene mixture. It can also be noted that addition of tetraphenyl lead to crosslinked polyethylene had no effect on oxygen index or horizontal

TABLE V
Nitrous Oxide and Oxygen Index Values as Support for Solid Phase Reactivity

Composition ^a	NOI	OI	Difference	Horizontal burn time (min)
LDPE + silicone	36.6	17.4	19.2	1.3
LDPE + Pb phthalate	40.8	17.8	23.0	1.7
LDPE + Silicone + Pb phthalate	42.3	22.4	19.9	1.3
LDPE/silicone/Pb phthalate ^b	45.0	24.3	20.7	SE
LDPE + tetraphenyl lead	—	16.5	—	1.9

^a Composition (parts): LDPE (100), silicone (4), lead phthalate (3), triallylcyanurate (1.5), SiO₂ (1), peroxide (3.5).

^b Formulation included SiO₂.

burn times. Tetraphenyl lead is volatile and if a flame poison were important, then the addition of a known, preformed volatile lead compound should have been effective.

Effect of Silica Gel and Triallylcyanurate

In a filled silicone rubber system, the oxygen index and UL-94 results are sensitive to the nature of the surface of the silica used for filler.² To determine if these silica surface effects are important in this system, three types of fumed silica were compounded into the lead-silicone-polyethylene system under two conditions of cure. In one set of formulations the curing aid, triallylcyanurate, was included; in the other, the curing aid was left out. Thus, these three pairs of samples were identical except for degree of crosslinking and filler surface treatment. The first silica was untreated, the second treated with cyclic dimethylsiloxane tetramer, and the third treated with both cyclic tetramer and hexamethyldisilazane. Infrared analysis of these fillers show that the silanol levels are much reduced when treated with cyclic tetramer and further reduced when subsequently treated with hexamethyldisilazane. The data are shown in Table VI. Three important observations can be made. First, the samples that contain the crosslinking aid, triallylcyanurate, had a lower oxygen index than those which do not contain cyanurate. Second, the three samples with lower oxygen indices all self-extinguish whereas the three less well-cured samples burn. And third, there is little or no distinction among various filler pretreatments.

As measured by gel percent, no distinction could be made between any of these samples. The gel percent ranged between 96.6 and 97.1. However, the swell values clearly showed the expected trend; that is, those samples containing triallylcyanurate swell less (are more crosslinked) than samples which do not contain the crosslinking aid. For these samples, the two flammability tests made a clear distinction. Oxygen index and horizontal burning rates were both sensitive to the extent of cure. The more highly crosslinked samples had lower oxygen indices but slower horizontal burning rates. What

TABLE VI
Effect of Silica Pretreatment and Crosslink Density on the Fire Resistance of Crosslinked Silicone-Lead-LDPE

Composition ^a	Oxygen index	Burn time (min)	% Gel	% Swell
SiO ₂ ^b	28.6	2.1	96.6	250
SiO ₂ ^b + triallylcyanurate	23.6	SE	96.8	230
SiO ₂ ^c	26.2	1.7	97.0	240
SiO ₂ ^c + triallylcyanurate	20.8	SE	97.1	210
SiO ₂ ^d	27.9	2.3	96.9	260
SiO ₂ ^d + triallylcyanurate	22.0	SE	97.1	220

^a Composition (parts): LDPE (100), silicone (4), lead phthalate (3), peroxide (3.5), SiO₂ (1), optional, triallylcyanurate (1.5).

^b Cab-o-sil MS-7.

^c MS-7 treated with cyclic dimethylsiloxane tetramer.

^d MS-7 treated with cyclic tetramer and hexamethyldisilazane.

is not obvious is which test is relevant to a particular application. The answer is critical to any further chemical and structural understanding or development of improved fire resistant materials.

Glass and Char Formation

The combustion of carbon is one of the most studied reactions. Not only is carbon oxidation an important source of heat but the gasification to form useful organic molecules is becoming increasingly significant. It has been known for a long time that the gasification of carbonaceous materials can be accelerated by various inorganic elements.¹⁴ One of the most active metal oxides studied by McKee¹⁵ and others is lead oxide. For example, the self-ignition temperature for pure graphite is 740°C in oxygen, but if just 0.15% lead oxide is added to the graphite, the ignition temperature is reduced to 382°C. It has now been found by McKee¹⁶ that the addition of silicone gum to a lead phthalate-graphite mixture inhibits the catalytic activity of lead so that no ignition temperature is observed. There is a slow uniform loss of weight even at 1000°C. Examination of the resultant graphite shows that a glassy solid coats the graphite. It can be supposed that the lead oxide was deactivated by the formation of a lead silicate glass.

These results suggest that if a carbonaceous char is formed, the lead oxide will catalyze its oxidation. However, if a lead silicate is formed, the char should be more difficult to oxidize. It is not unreasonable to suppose that one of the modes of action of the lead-silicone synergism is to form a glass that retards oxygen diffusion. However, examination of chars from many of the least flammable formulation showed no evidence for glass formation. The TGA char was in all cases less than 4% in both air and nitrogen, and the char yield from combustion in air under a radiant heat source was also less than 4%. One can observe in the residue both a yellow powder, lead oxide, and a white powder, silica. Analysis by both energy dispersive X-ray using a scanning electron microscope and ESCA indicated that lead was present as the metal and the oxide. It was not possible by SEM to identify any structures that could reasonably be considered glassy.

The char samples shown in Figures 1 and 2 were obtained by quenching a burning sample in an atmosphere of nitrogen. Although there appeared to be lots of char formed, it was in fact caducous char, that is, the char formed at one temperature is rapidly consumed by the higher flame temperature. The rate of reaction of this char is an important factor in the burning behavior of the sample.

Deliberate addition of soft glasses, ceramic glazes, and low melting glass precursors (Table VII) to the silicone polyethylene blend afforded composites with mixed fire retardance. Those samples that contained significant amounts of lead tended to be less flammable as measured by the horizontal burn test. Even in these cases where preformed glass had been added, there was no evidence for a glassy structure coating the underlying polymer, but rather the foamed char seen in Figures 1 or 2 was observed. This suggests that glass formation is unimportant, that lead oxide is the important reactant, and that lead is effective even in the presence of glass and glass forming materials.

TABLE VII
Effect of Low Melting Glass on the Fire Resistance of Blends of Silicone and Polyethylene^a

Additive ^b	Oxygen index	Horizontal burn (min)
CV101 ^c (softening point 372°F)	23.2	SE
CV102 ^c (softening point 346°F)	22.8	SE
Glaze ^d 850 yellow	20.8	SE
Glaze ^d 850 turquoise	19.6	3.1
Glaze ^d 900 clear	18.7	2.6
Glaze ^d 850 white	19.2	SE
Glass ^e 00158 (softening point 441°F)	19.2	3.3
Al ₂ O ₃	17.4	2.5
Na ₂ O, Pb phthalate ^f	17.4	2.6
Na ₂ O, Sn oxalate, Pb phthalate ^f	17.8	2.4
Na ₂ O, B ₂ O ₃ , TiO ₂ , Na ₂ SiF ₆ ^f	17.4	2.1
Pb phthalate, B ₂ O ₃ ^g	16.5	1.9

^a Composition (parts): LDPE (100), silicone (2), peroxide (3.5).

^b Six parts added to polyethylene bend.

^c Owens-Illinois Glass.

^d Ceramic glaze, American Art Co., Indianapolis, Indiana.

^e Microelectronics.

^f Two parts each.

^g Four parts each.

Lead in Other Polymers

It is clear that the lead-silicone synergism is critical in the polyethylene system. What about other silicone containing polymers? The addition of 2% lead oxide into a filled silicone rubber raised the oxygen index from 20.8 to 22.0, but in a UL-94 vertical burn test the sample consumed itself in flame. By comparison, the addition of only 50 ppm platinum to the same silicone rubber raised the OI to 29.5 and the sample self-extinguished.²

The addition of 2.6% lead phthalate to a silicone BPA polycarbonate block copolymer afforded a seriously degraded sample. The molecular weight was decreased by ½, and upon molding, the sample foamed and became highly colored. The oxygen index decreased from 33.8 to 26.2. The addition of lead oxide to these two materials was not a successful transfer of this fire-retardant technology.

Oxygen Index Relationships

It has already been noted that oxygen index and horizontal burn times are influenced in opposite ways by changes in crosslink density. It has also been observed that the oxygen index does not predict burning rate behavior for uncured samples. Figure 3 graphically illustrates for both cured and uncured flame retarded polyethylene that OI can range from 17 to 29.2 while burn times vary between 1 and 3 min. For burn times greater than 3 min the samples tended to self-extinguish. The paired samples, connected by a line, differ only in the addition of triallylcyanurate (a crosslinking aid). It is obvious that those samples that are more highly crosslinked are self-extinguishing in a horizontal burn but have lower OIs than the less well-cured samples.

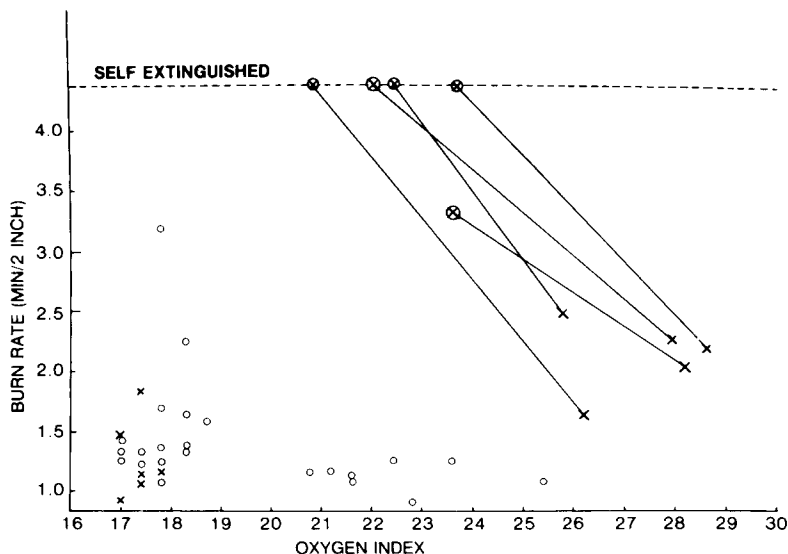


Fig. 3. Horizontal burn rate vs. oxygen index for flame-retarded polyethylene: (x) cured; (o) uncured; (⊗) cured with crosslink aid.

CONCLUSIONS

It has been established that the lead-silicone interaction is critically dependent on the solid state reactions of the polymer matrix. There is no evidence for either gas phase reactivity or for the formation of glass in these polyethylene formulations. The extent and kind of crosslinking is crucial in allowing the reaction between lead and silicone to form the slow burning foamed caducous char that is necessary to afford a fire-resistant material.

The relationship between flammability tests (candle oxygen index and horizontal burn times) has been shown to be sensitive to the physical-chemical properties of these samples. These tests do not measure just one property, and our understanding of just what these tests do measure is poor. There does not seem to be *one* flammability test of choice, but rather one must use several tests to evaluate potential fire retardants.

We thank M. Knapp and M. Mosley of the General Electric Co. Wire and Cable Department for their help in sample preparation, and L. A. Gruenke for his assistance with X-ray irradiation of our samples. A. Factor, J. C. Carnahan, and R. E. Hanneman provided stimulating and useful discussion.

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on a water-cooled metal block, and the sides were reversed after half the desired exposure time. The samples were post cured at 85°C in nitrogen for 16 h.

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Received February 28, 1984

Accepted June 1, 1984