Use of Polymer-Bound Metals as Fire Retardants in Polyethylene–Silicone Blends

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Synopsis

Lead compounds and silicone gum when blended into polyethylene act as a synergistic fire retardant. The incorporation of lead into the polymer network via lead carboxylate formation through polyethylene grafted with maleic anhydride has been studied as a means of improving the metal dispersion and flammability behavior. Lead was also incorporated directly into a polymer backbone via the formation of lead polyesters. The use of other metal compounds as fire retardant additives has also been studied. No special behavior was seen for polymer-bound lead relative to non-polymer-bound lead, and other metals were not found to be effective replacements for lead in polyethylene graft maleic anhydride.
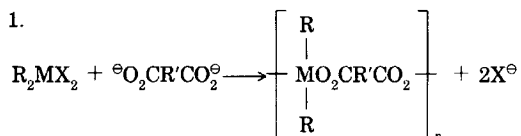
INTRODUCTION

It has been known for several years that small amounts of lead compounds and silicone gum act as synergistic fire retardants in crosslinked low-density polyethylene.[1] Crosslinking has been shown to be necessary for this synergistic effect.[2] Since in previous work the lead compound and silicone gum were merely blended with polyethylene, it was of interest to determine if the flame retardance could be improved by chemically bonding the lead directly to a polymer backbone. It was expected that dispersion would be greatly enhanced and that there might be some exceptional properties of these organometallic polymers.

Carraher[3] and co-workers have synthesized and characterized a variety of organometallic polymers that do exhibit good thermal stability. Their syntheses have been primarily of two types: (1) inclusion of metals into polymer backbones via direct polymerization and (2) modification of polymers via reactions of functional groups with added metallic compounds. These synthetic routes are outlined in Scheme I, showing general reactions for the inclusion of organometallic halides in carboxy polymers.
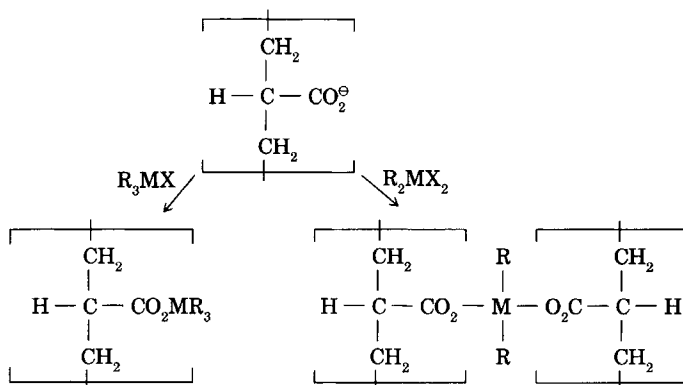
Many of these organometallic polymers show moderate to very good thermal stability as measured by thermogravimetric analysis (Table I). If a correlation exists between thermal stability and flammability, these thermally stable polymers would be interesting to study from the flammability standpoint.

A study was therefore undertaken to incorporate various metals into carboxy-modified polyethylene. Direct inclusion of metals into the polymer network might afford better dispersion and decrease the amount of metal required to exhibit the same fire retardant effect in combination with the silicone gum. It was also thought that metals other than the previously

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Route 1.

$$R_2MX_2 + {}^{\ominus}O_2CR'CO_2^{\ominus} \longrightarrow \left[\begin{array}{c} R \\ | \\ MO_2CR'CO_2 \\ | \\ R \end{array} \right]_n + 2X^{\ominus}$$

Route 2.

$$H - \overset{\overset{\displaystyle CH_2}{|}}{\underset{\underset{\displaystyle CH_2}{|}}{C}} - CO_2^{\ominus}$$

R_3MX ⟋   ⟍ R_2MX_2

$$H - \overset{\overset{\displaystyle CH_2}{|}}{\underset{\underset{\displaystyle CH_2}{|}}{C}} - CO_2MR_3 \qquad H - \overset{\overset{\displaystyle CH_2}{|}}{\underset{\underset{\displaystyle CH_2}{|}}{C}} - CO_2 - \overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{M}} - O_2C - \overset{\overset{\displaystyle CH_2}{|}}{\underset{\underset{\displaystyle CH_2}{|}}{C}} - H$$

Scheme I.

reported[1] lead system might afford a thermally stable and flame-resistant polyethylene.

EXPERIMENTAL

All polymer formulations, except where noted otherwise, were processed in a Brabender heated mixing bowl for 30 min at ca. 120°C. All samples were then compression molded into 4 × 0.125 in. square plaques for 30 min at ca. 180°C, to insure complete cure. Gel and swell measurements were made on most samples in order to determine the degree of crosslinking. A weighed sample (0.1–0.3 g) was enclosed in a tared nickel screen (200 mesh) and extracted in refluxing toluene in a Soxhlet extractor for at least 24 h. The hot swollen sample was weighed quickly to determine the weight of toluene absorbed. This weight must be measured as rapidly as possible because as the polyethylene cools below its melting point, toluene is extruded from the polymer surface. The extracted sample was dried at ca. 100°C under vacuum for 24 h. The weight of material after extraction was determined and swell and gel calculations done, i.e., % gel = extracted weight × 100/original weight, % swell = (swollen weight − extracted weight) × 100/extracted weight.

The oxygen index of all samples was determined in the standard manner. A horizontal burn test was developed as another means of evaluating flammability. Strips of sample were cut 4 × 0.5 × 0.125 in. (0.0625 in. only where noted), and marked 1 in. from each end. The sample was held horizontally and ignited with a small gas flame. The time (or rate) of burning between the marks was determined. The least flammable samples would self-extinguish prior to the flame reaching the second mark.

TABLE I
Thermal Stability of a Few Organometallic Polymers

	20% wt loss (°C)	50% wt loss (°C)	% Metal oxide[a]	Ref.
$\begin{bmatrix} Cp \\ \mid \\ Ti-O-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-O \\ \mid \\ Cp \end{bmatrix}_n$	Air:N$_2$ 250:350	Air:N$_2$ 250:500	TiO$_2$—23	3
$\begin{bmatrix} Et \\ \mid \\ Pb-O-\overset{O}{\overset{\|}{C}}-C_6(CH_3)_4-\overset{O}{\overset{\|}{C}}-O \\ \mid \\ Et \end{bmatrix}_n$	360:440	>600 both	PbO—46	b
$\begin{bmatrix} Et \\ \mid \\ Pb-O-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-O \\ \mid \\ Et \end{bmatrix}_n$	440:490	>600 both	PbO—52	b
$\begin{bmatrix} Ph \\ \mid \\ Sn-N \diagdown N \\ \mid \\ Ph \end{bmatrix}_n$	220:200	250:250	SnO$_2$—42	3
$\begin{bmatrix} Cp \\ \mid \\ Zr-O-C_6H_4-O \\ \mid \\ Cp \end{bmatrix}_n$	600:600	>800 both	ZrO$_2$—37	3
$\begin{bmatrix} Cp \\ \mid \\ Ti-O-\overset{O}{\overset{\|}{C}}-CH-\overset{CH_2}{\underset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O \\ \mid \\ Cp \end{bmatrix}_n$	300:300	900:900	TiO$_2$—26	3
$\begin{bmatrix} Cp \\ \mid \\ Hf-O-\overset{O}{\overset{\|}{C}}-CH-\overset{CH_2}{\underset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O \\ \mid \\ Cp \end{bmatrix}_n$	500:500	>1200 both	HfO$_2$—48	3

[a] The % metal oxide is wt. percent of polymer that can be attributed to the metal oxide.
[b] Polymers made by A.L. Schroll and described in this report.

The silicone gum used in all formulations was a 0.2% vinyl methyl gum, from the General Electric Co., Silicone Products Business Department. Metal compounds used are indicated in the tables. The peroxide used in all formulations was dicumyl peroxide.

Preparation of Lead Polyesters[4]

The disodium salts of the acids (terephthalic and tetramethylterephthalic) were prepared by addition of sodium hydroxide, 0.712 g (0.0178 mol), to a solution of the acid, 0.0089 mol, in 30 mL of a 50% DMSO/H$_2$O solution.
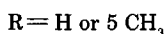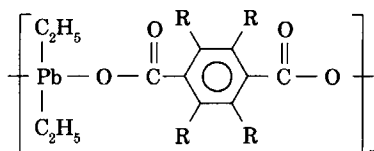
To this rapidly stirred solution was added dropwise a solution of diethyllead dichloride, 3.00 g (0.0089 mol) in 250 mL DMSO. The polymer precipitated from solution and was collected by filtration.

ANAL. Calcd for terephthalic acid/lead polymer: C, 33.6%; H, 3.3%; Cl, 0%; Pb, 48.1%. Found: C, 24.6%; H, 1.3%; Cl, 0.1%; Pb, 52.2%. Calcd for tetramethylterephthalic acid/lead polymer: C, 39.6%; H, 4.6%; Cl, 0%: Pb, 42.7%. Found: C, 29.7%; H, 2.6%; Cl, 0.7%; Pb, 46.4%.

IR(KBr) 1530 cm^{-1} (C=O) compare with acid (C=O) 1685 cm^{-1}.

DISCUSSION

Two lead-containing polymers were made following the synthetic procedure outlined by Carraher,[4] and their stability and flammability characteristics after blending with polyethylene and silicone gum were studied. Diethyllead dichloride and the 1,6-benzenedicarboxylic acid afforded a polymer of the following structure:

$$\left[\begin{array}{c} C_2H_5 \\ | \\ Pb - O - C \\ | \\ C_2H_5 \end{array} \overset{O}{\underset{}{\overset{||}{C}}} \overset{R \quad\quad R}{\underset{R \quad\quad R}{\bigcirc}} \overset{O}{\underset{}{\overset{||}{C}}} - O \right]_n$$

R = H or 5 CH$_3$

Each polymer was blended with the silicone gum into low-density polyethylene, and the resultant mixture was cured with dicumyl peroxide. The flammability of these materials was evaluated by OI and the horizontal burn test (Table II). The polymer containing the terephthalic acid showed good fire resistance as measured by these tests while the tetramethylterephthalic acid polymer was a slightly less effective fire retardant. It is reasonable to expect this trend since the tetramethylterephthalic lead polymer was shown by TGA to be oxidatively less stable than the terephthalate lead polymer [Figs. 1(a) and (b)]. These flammability results correspond closely to the results seen for the previously reported lead silicone synergistic fire retardancy.[2] By TGA (Fig. 1), each material had an initial weight loss of less than 5% at 100°C, in both air and nitrogen, corresponding to loss of water. In air a further weight loss occurred at 440°C for the terephthalic acid polymer and 350°C for the tetramethylterephthalic acid poly-

TABLE II
Burn Data for Polyethylene Containing Lead Polymers and Silicone Gum

Lead polymer[a]	OI[b]	Horizontal burn time (min)
Terephthalic acid polymer (3.3 parts)	22.8	SE
Tetramethylterephthalic acid polymer (3.8 parts)	20.4	> 3.5 min[c]

[a] Sample compositions: low density polyethylene, 100 parts; lead polymer, 7.8 mmol Pb; silicone gum, 4.4 parts; dicumyl peroxide, 4.0 parts.

[b] Oxygen index for polyethylene is 17.0.
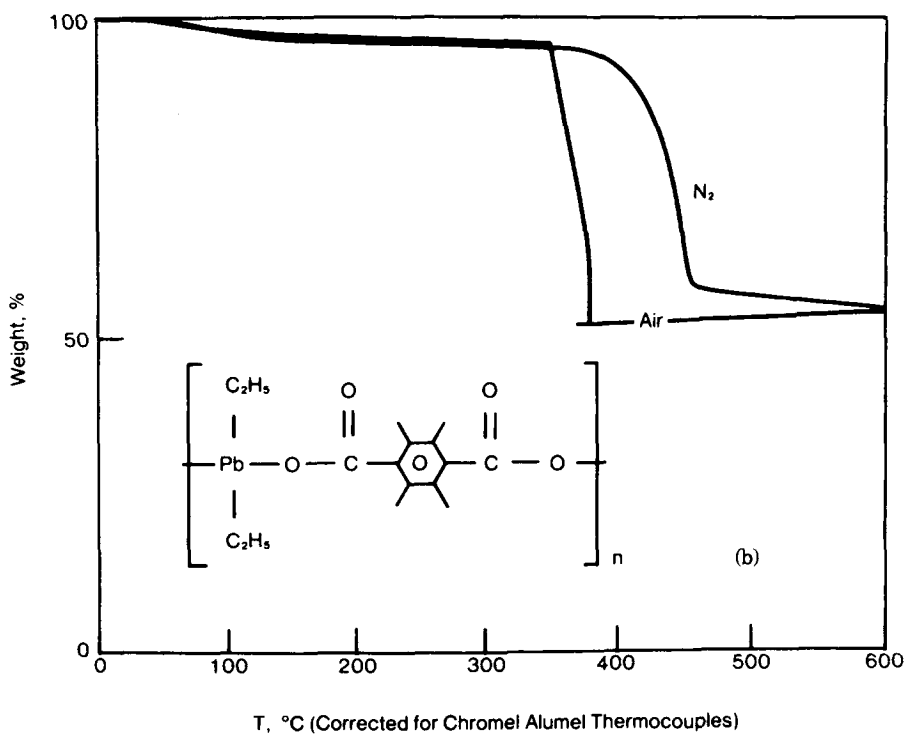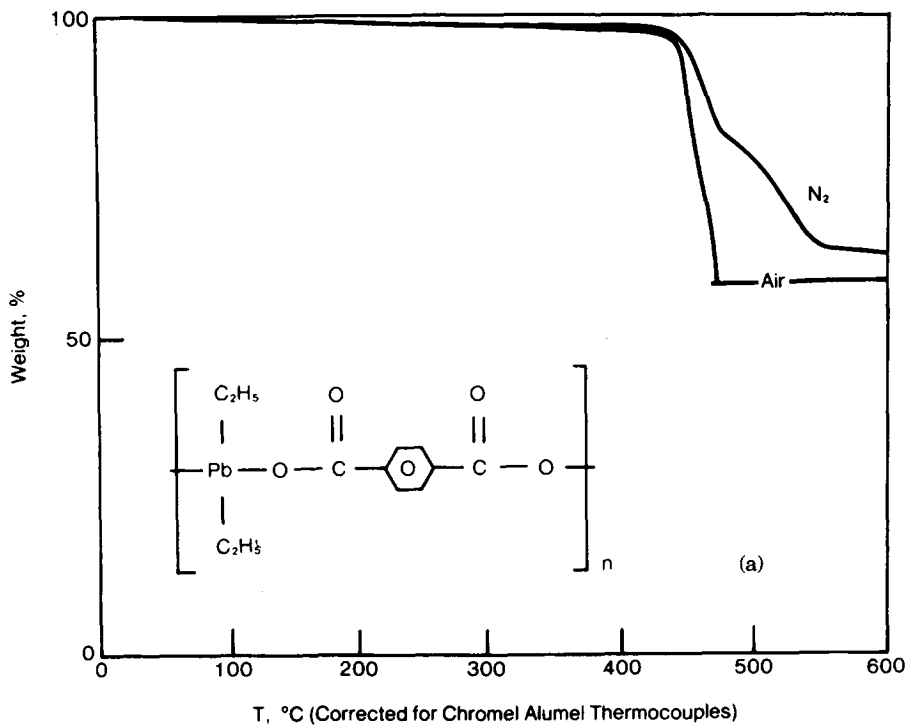
[c] Borderline SE character.

Fig. 1.   Thermogravimetric analysis of lead polymer.

mer. The weight loss in nitrogen occurred at higher temperatures for each material. Final weight retention (at 600°C) corresponded primarily to PbO; however, there was as much as 6% extra residue. The terephthalic acid polymer exhibited a final weight retention of greater than 58% (when corrected for H_2O loss), which was greater than the expected retention of 52% for PbO present in the polymer. The tetramethylterephthalic acid polymer also showed weight retention greater than expected if only PbO remained (> 52% relative to an expected 46%). These results suggest that carbonization has occurred indicating incomplete oxidation of the polymers.

As an extension of these results, it was thought that direct modification of polyethylene with lead polyesters would be appropriate for study. This approach correspnds to route 2 shown in Scheme I.

Polyethylene which had been treated with maleic anhydride and peroxide to afford a maleic anhydride grafted polyethylene, (PE-g-MA) was available for our use in this study.[5*] An IR spectrum of a pressed film of the PE-g-MA revealed that well over 50% of the anhydride was present in the acid form (see Fig. 2). A general reaction of PE-g-MA with a metal dihalide (dialkylmetal dihalide) is shown in Scheme II. Note that Route 1 affords crosslinked material whereas Route 2 does not. In either case, the metal is incorporated into the polymer network.

Scheme II.

The possibility that crosslinking could occur via other mechanisms has been considered. For example, metal-catalyzed decarboxylation reactions are known (such as the Hundsdiecker reaction)[6] and are thought to occur via free radical mechanisms. The presence of free radicals in the PE-g-MA system would indeed crosslink the polymer. Our results indicate, however, that any crosslinking due to radical formation from decarboxylation is not of primary importance. The infrared results indicate little if any change

* PE-g-MA used in this study was grafted as 1.25% by weight maleic anhydride. We received the material from R. R. Gallucci.

in carbonyl absorbance for starting PE-*g*-MA and PE-*g*-MA after reaction with diethyllead dichloride.

Table III outlines flammability data for LDPE and PE-*g*-MA with and without lead/silicone addition. These results are reference data for later comparisons. As Table III indicates, both LDPE and PE-*g*-MA have low OIs, 17.0 and 16.5, respectively. PE-*g*-MA burned more slowly than LDPE perhaps because the maleic anhydride groups afford stability through some interchain crosslinks. In the lead/silicone system, both LDPE and PE-*g*-MA samples self-extinguished on the horizontal burn test. OI data was difficult to interpret since duplicate OIs revealed an OI difference of over two units. Generally, OI differences of three or more units are considered significant. It is fair to conclude that the lead/silicone synergism functions in PE-*g*-MA as well as, but probably no better than, in LDPE. The presence of maleic anhydride groups probably had no effect on the fire-retardant behavior since bonding interaction was not expected between the maleic acid groups and the lead compound.

Table IV lists examples of lead incorporation into the PE-*g*-MA polymer structure. The first example consists of PE-*g*-MA and diethyllead dichloride. While swell and gel data indicate that crosslinking and, therefore, some reaction has occurred, the sample did not exhibit improved fire-retardant properties. A % gel of over 50 indicates that more than half of material was toluene-insoluble. LDPE is completely toluene-soluble under our extraction conditions and leaves 0% gel. (The PE-*g*-MA itself has 0–14% gel due to the use of peroxide in the initial grafting reaction.) Swell numbers also indicate degree of crosslinking since an uncrosslinked sample of PE-*g*-MA yields an infinite swell number.

IR spectra for these systems are shown in Figure 2. The sample PE-*g*-MA/$(C_2H_5)_2PbCl_2$ (d) revealed a less intense carboxylic acid stretch (1721 cm^{-1}) relative to heat-treated PE-*g*-MA (c) and also showed the appearance of a new band in the 1510–1540 cm^{-1} region, which was attributed to metal carboxylate formation.* Furthermore, a small torque increase was observed upon sample mixing that was not seen in the absence of diethyllead dichloride. These results indicated that some crosslinking has occurred. The sample PE-*g*-MA/$(C_2H_5)_2PbCl_2$ had undergone reaction as shown in Scheme II with at least some of the acid groups reacting to form interchain lead carboxylates.

Samples 2A and B (Table IV) revealed real differences in burn character according to horizontal burn data, although oxygen indices were identical. Initially one might attribute this discrepancy to crosslink density difference. It is known from previous results that certain flammability measurements are sensitive to crosslink density.[2] The two samples exhibited nearly identical % gels, but the % swells were significantly different with high swell numbers corresponding to faster burning samples. (Swell numbers are more sensitive to crosslinks than gel numbers.) Note that the first sample on Table IV also revealed a large difference in swell number, and this difference may be attributed to variations in the PE-*g*-MA. The maleic anhydride was grafted on LDPE via a peroxide-induced free radical mechanism, and, in turn, the presence of free radicals could initiate crosslinking of the poly-

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* New band does not correspond to any bands in Et_2PbCl_2 spectrum.
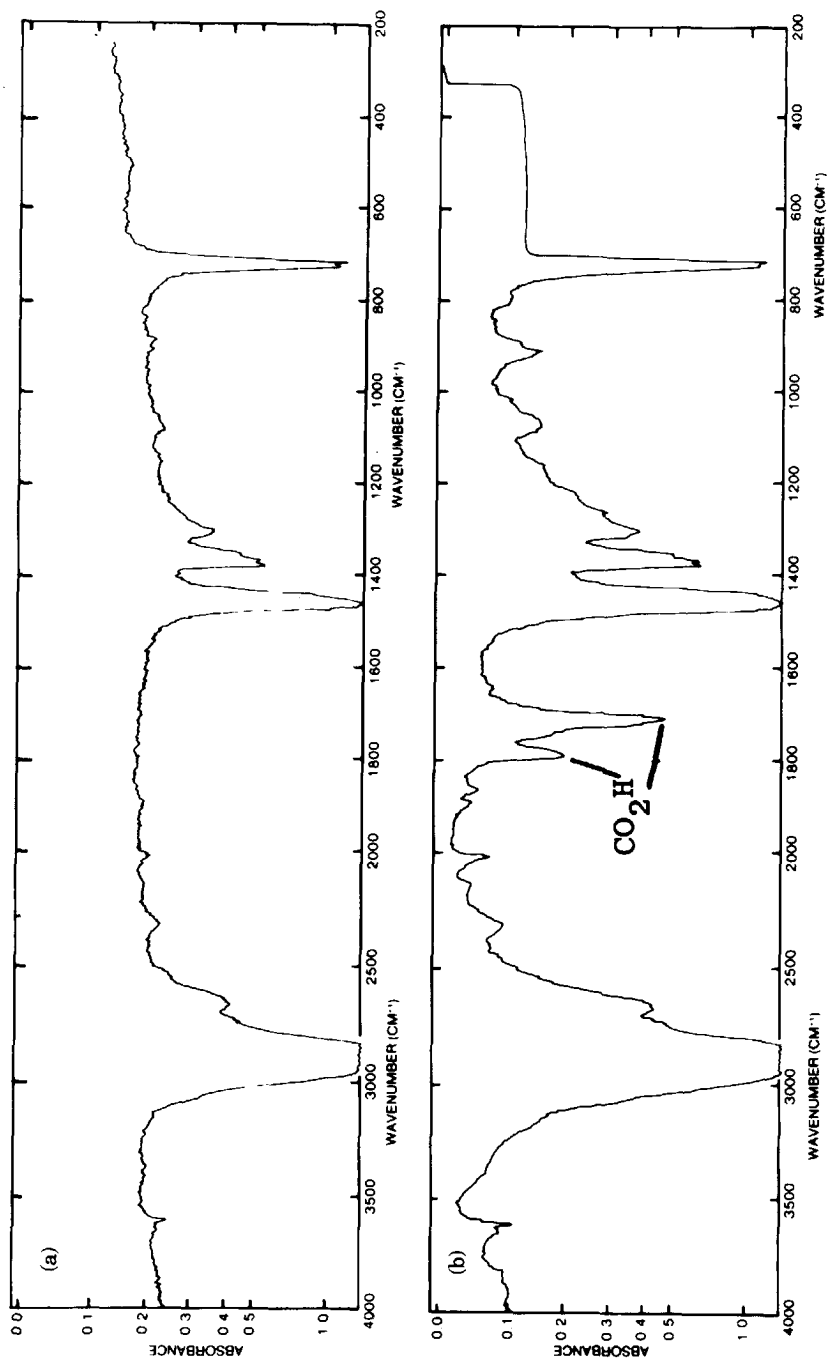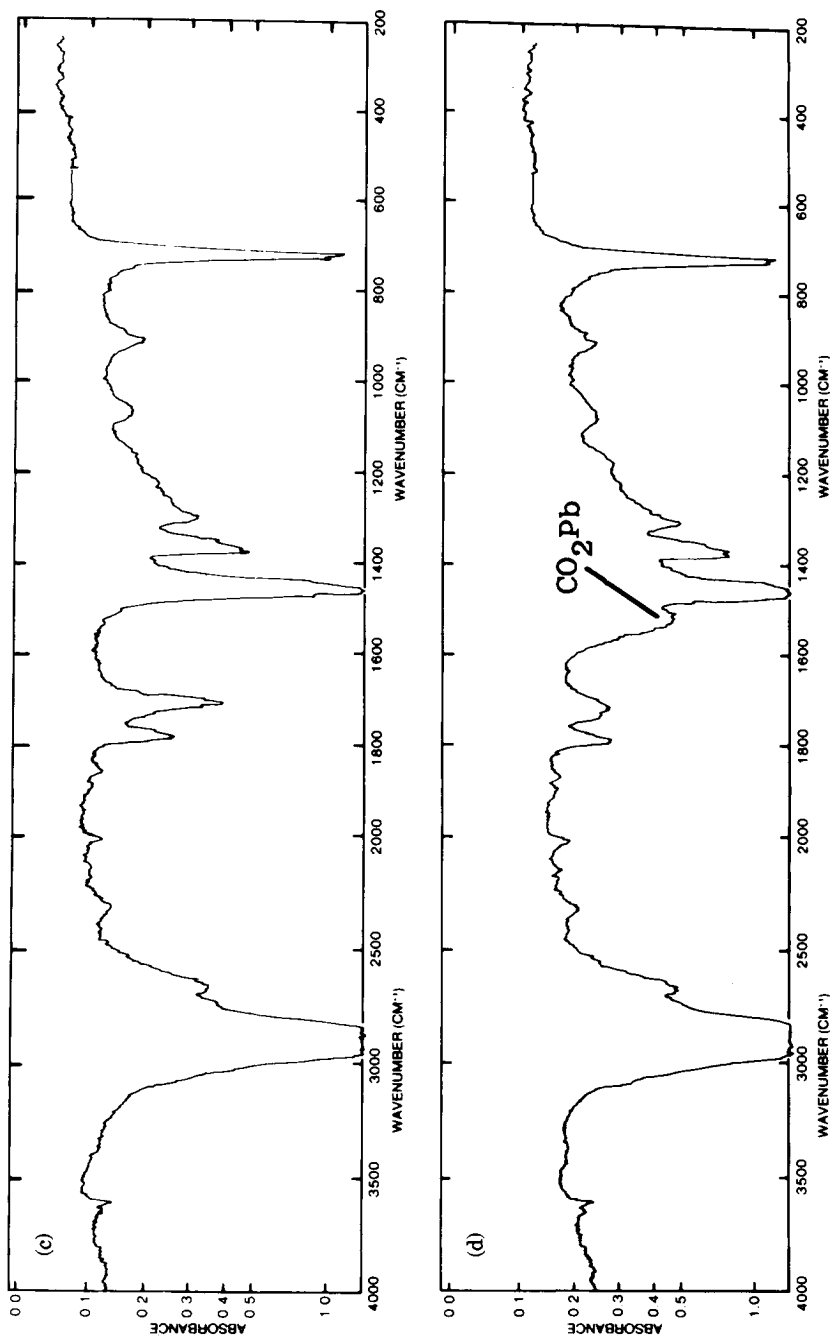
Fig. 2. IR spectra (pressed films 0.1–0.2 mm thick): (a) LDPE; (b) PE-g-MA prior to processing; (c) PE-g-MA after processing for 5 min at 115°C; (d) PE-g-MA/$(C_2H_5)_2PbCl_2$ after processing at 120°C for several min.

TABLE III
Comparative Flammability Performance

	OI	Horizontal burn time (min)
LDPE	17.0	2.0
PE-*g*-MA	16.5	2.5–2.8
LDPE, Pb,[a] silicone, peroxide[b]	20.8, 23.6	SE[c]
PE-*g*MA, Pb,[a] silicone, peroxide[b]	24.7	SE

[a] Proprietary lead organocarboxylate dispersed in polybutene.

[b] Sample compositions: polymer, 100 parts; Pb, 4.2 parts; silicone, 4.4 parts; dicumyl peroxide, 4.0 parts.

[c] Self-extinguishing.

ethylene backbone. The degree of backbone crosslinking has apparently varied throughout the particular samples of PE-*g*-MA used in these experiments as evidenced by the variability in swell and gel numbers for identical formulations.

Infrared spectra for samples containing $(C_2H_5)_2PbCl_2$ and silicone are shown in Figure 3. Sample 3 (Table IV) exhibited poor OI and was fast burning. This indicates that even a fully crosslinked system (96.4% gel; 390 swell) does not exhibit outstanding fire retardance. It appears that the one self-extinguishing sample (2A) may have been an anomaly since increased crosslinking did not bring about self-extinguishing character as would be expected if high crosslink were critical to fire retardant behavior.

These results indicate that lead carboxylates were formed, but the burn properties were not analogous to the previously reported lead/silicone fire retardant system in LDPE.[2]

PE-*g*-MA was also processed with diphenyllead dichloride (at the same molar concentration) to form the diphenyllead carboxylate polymer and the results are summarized in Table V. IR spectra are shown in Figure 4. None of the samples exhibit good OIs or burn times. As before, variability was seen in swell and gel results. The IR data did not exhibit the appearance

TABLE IV
Flammability Behavior of PE-*g*-MA Containing Diethyllead Dichloride[a]

	Additive[b]	OI[c]		Horiz. burn time (min)		% Swell		% Gel[d]	
		A	B	A	B	A	B	A	B
1.	$(C_2H_5)_2PbCl_2$	17.4	17.9	2.00	2.02	480	1900	58.4	50.9
2.	$(C_2H_5)_2PbCl_2$, silicone gum	19.2	19.2	SE	2.38	1050	1990 ($\pm$40)	50.4	50.2
3.	$(C_2H_5)_2PbCl_2$, silicone gum, Vulcup-R	—	18.7	—	2.47	—	390 ($\pm$30)	—	96.4

[a] See Figures 2 and 3 for IR spectra. All five samples exhibit new band in region 1510–1540 cm^{-1}.

[b] Sample compositions: PE-*g*-MA, 100 parts; $(C_2H_5)_2PbCl_2$, 4.2 parts; silicone gum, 4.4 parts; Vulcup-R, 4.0 parts.

[c] Samples A and B are two separately prepared formulations.
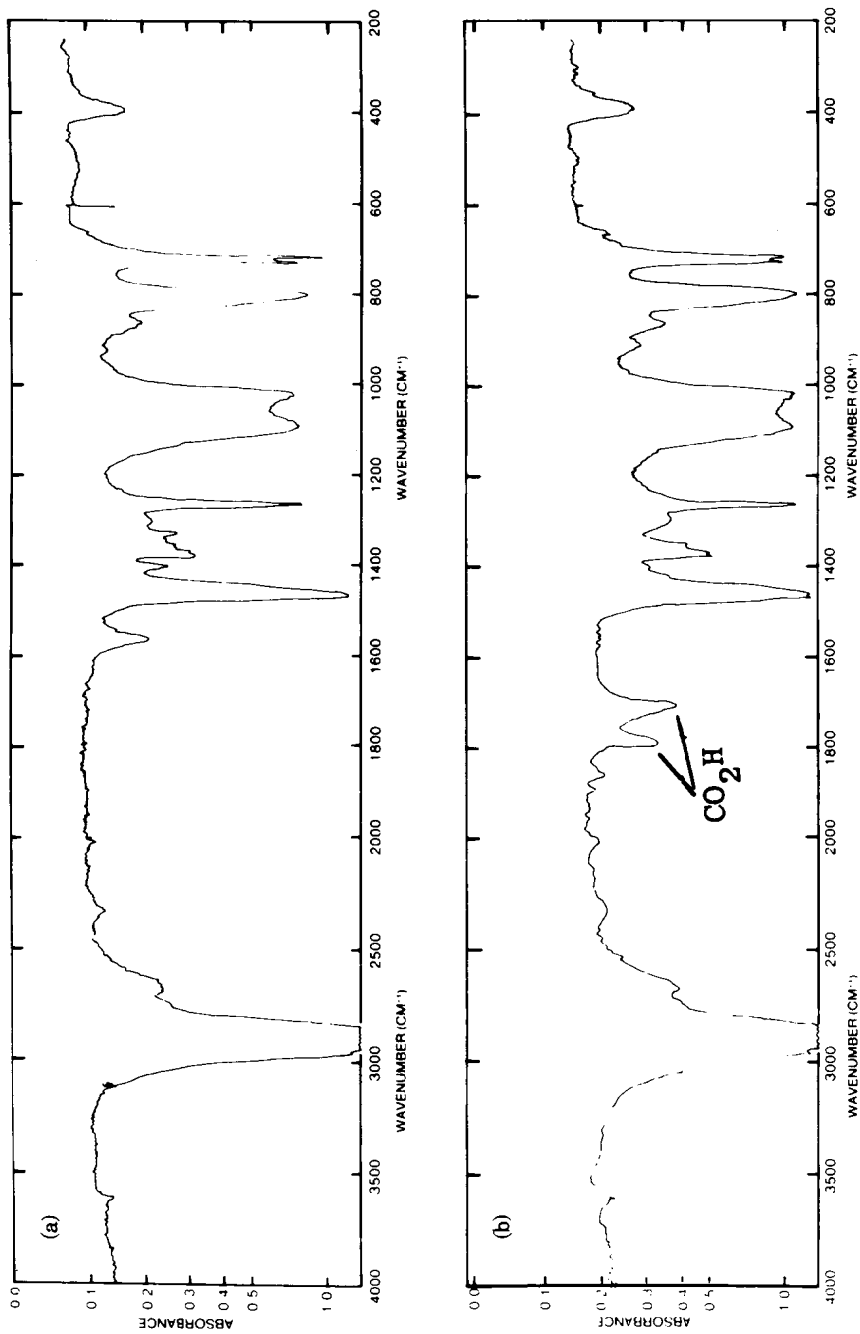
[d] Average values with error less than $\pm$ 0.1.

Fig. 3. IR spectra (pressed films 0.1–0.2 mm thick): (a) LDPE/silicone gum; (b) PE-*g*-MA/silicone gum; (c) PE-*g*-MA/(C_2H_5)$_2$PbCl$_2$/silicone gum (the spectrum for the peroxide-cured sample (c) is identical to this spectrum).
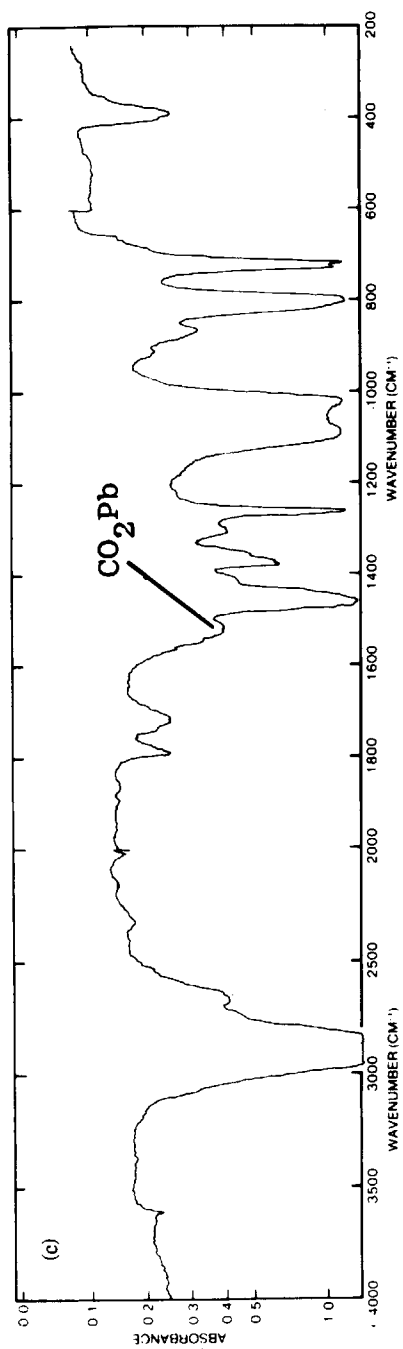
Fig. 3. *(Continued from the previous page.)*

TABLE V
Flammability Behavior of PE-*g*-MA Containing Diphenyllead Dichloride

	Additive[a]	OI	Horiz. burn (min)	% Swell[b]	% gel
1.	$(C_6H_5)_2PbCl_2$	17.2	1.5	1845 ($\pm$1150)	38.1 ($\pm$4.8)
2.	$(C_6H_5)_2PbCl_2$ silicone gum	17.0	1.77	1885 ($\pm$1250)	43.7 ($\pm$8.7)
3.	$(C_6H_5)_2PbCl_2$, silicone gum, Vulcup-R	18.7, 17.0[c]	2.9, 2.6	290, 260–350	95.1, 94.8

[a] Sample compositions: PE-*g*-MA, 100 parts; $(C_6H_5)_2PbCl_2$, 5.5 parts; silicone gum, 4.4 parts; Vulcup-R, 4.0 parts.
[b] % swell and gel data from several toluene extractions.
[c] Duplicate formulations.

of a new band in the 1510–1540 cm^{-1} region as had been seen when diethyllead dichloride was used to form the carboxylate. In addition, the swell and gel data for these samples indicated only minimal crosslinking. Note that the IR spectrum for diphenyllead dichloride sample showed a more intense carbonyl band at 1720 cm^{-1}. It is known that the anhydride groups will hydrolyze the carboxylic acid within several hours of exposure to atmospheric moisture. The IR spectrum of this sample was recorded after the pressed film had been exposed to air for a long period of time. It is apparent that the diphenyllead dichloride did not react to form significant amounts of lead carboxylate.

OTHER METAL FORMULATIONS

Several other metal-containing compounds were blended with PE-*g*-MA and silicone for the purpose of testing their fire retardant behavior. Some of these formulations are summarized in Table VI.

To determine if Pb(II) would form a carboxylate, $PbCl_2$ was blended with PE-*g*-MA. An IR spectrum of the sample, however, revealed no band at 1510–1540 cm^{-1}, and, therefore, it appears that no carboxylates were formed. The long horizontal burn times were merely a result of known lead/silicone synergistic fire retardancy.[2]

Copper citrate and tin oxalate samples (2–5) were examined primarily in an effort to find other metal compounds to replace lead. Bonding interaction with the maleic anhydride would not be expected in these samples. The burn data did not, however, indicate a significant fire-retardant effect.

The known synergistic effects of lead and vanadium in inhibiting the oxidation of sugars[7] lead us to determine whether a lead/vanadium synergism would also inhibit oxidation of a predominantly hydrocarbon polymer. The samples containing vanadium (IV) oxide bis (2,4-pentane dionate) exhibited slightly improved burn properties, but self-extinguishing character and high OI are ultimate goals. Sample 8 contained vanadium and lead compounds and exhibited fair fire-retardant behavior, whereas Sample 9, which was crosslinked, self-extinguished on the horizontal burn test and exhibited the highest OI on this table.
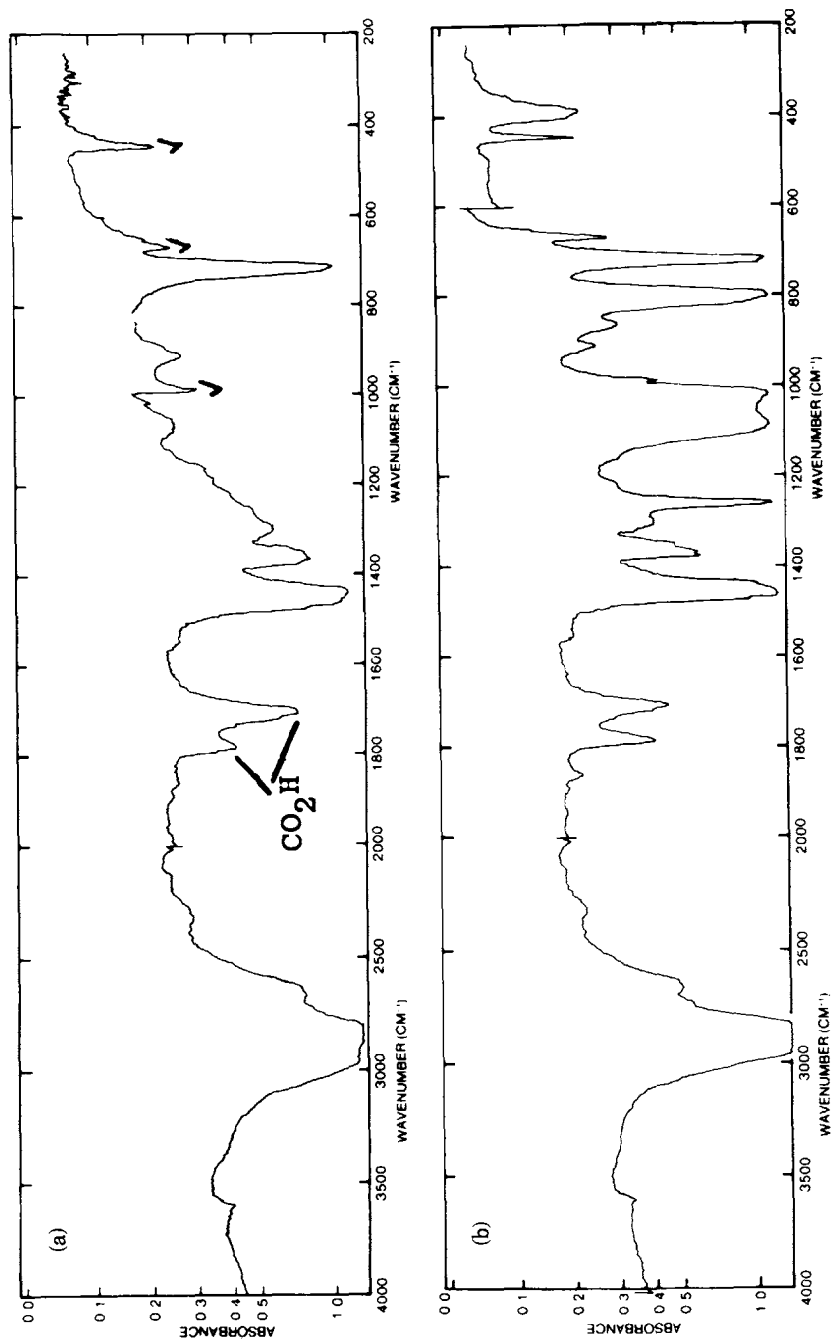
Fig. 4. IR spectra (pressed films 0.1–0.2 mm thick): (a) PE-g-MA/$(C_6H_5)_2PbCl_2$ after processing at 120°C for several min; checked peaks can be attributed to $(C_6H_5)_2PbCl_2$; (b) PE-g-MA/$(C_6H_5)_2PbCl_2$/silicone gum.

TABLE VI
Formulations and Flammability Behavior of PE-g-MA Containing Other Metal Compounds

	Sample								
	1	2	3	4	5	6	7	8	9
PE-g-MA	50 g	45 g →							
Metal compounds	PbCl$_2$, 1.05 g	Cu citrate 1.9 g	Cu citrate 1.9 g	Tin oxalate 1.9 g	Tin oxalate 1.9 g	Vanadium oxide bis Ac–Ac, 1.9 g	Vanadium oxide bis Ac–Ac, 1.9 g	Vanadium oxide bis Ac–Ac, 1.0 g Pb phthalate, 1.0 g	Vanadium oxide bis Ac–Ac, 1.0 g Pb phthalate, 1.0 g
Silicone gum 81690	X	X	X	X	X	X	X	X	X
Dicumyl peroxide, 1.8 g	X		X		X		X		X
OI	18.7	18.7	18.3	21.6	20.8	21.2	20.4	21.6	22.4
Horiz. burn time (min)	3.24 2.99	2.72	2.60	2.54	3.13	3.40	2.56	3.05	SE

In order to test this possible lead/vanadium synergism in low density polyethylene, four samples were prepared (Table VII). Sample 1 contained only the vanadium compound in crosslinked LDPE, and it is clear from the burn data that this formulation was not fire retardant. Sample 2 contained vanadium and silicone gum in crosslinked LDPE and the resulting formulation exhibited burn data less impressive than the lead/silicone system. The combination of lead and vanadium (sample 3) exhibited burn data comparable to LDPE. Finally, the complete system (crosslinked LDPE/silicone/lead/vanadium) exhibited the highest OI and self-extinguished in the horizontal burn test. The fire-retardant character, however, offers no improvement over the previously reported lead/silicone system.[2] If a synergistic effect were operative, one would anticipate that the fire-retardant character (particularly OI) would be greater than that seen in the lead silicone system. With this in mind, as well as the fact that the vanadium/silicone formulation did not act to retard burning of LDPE, it is evident that the vanadium/lead combination did not function synergistically to inhibit oxidation of LDPE. The fire retardant character seen in comparable formulations (sample 4, Table VII and sample 9, Table VI) was merely the known lead/silicone synergism.

CONCLUSIONS

Two lead polyesters were made following the procedure of Carraher, and these materials were found to have good thermal stability and act as fire retardants when in combination with silicone gum in crosslinked LDPE. In general, the chemical form of added lead was shown not to be an important factor in the flammability characteristics of polyethylene–silicone blends, and these results support our previously reported results.[2] A study was then undertaken to determine the effect on flammability of bonding lead to the polymer backbone through the formation of lead carboxylates in polyethylene grafted with maleic anhydride (PE-g-MA).

Lead carboxylates were formed when PE-g-MA was treated with die-

TABLE VII
Lead and Vanadium Polymer Formulations[a]

	1	2	3	4
LDPE, 100 g	X	X	X	X
Silicone gum 81690, 4 g	—	X	—	X
Pb,[b] 1.5 g	—	—	X	X
Vanadium oxide bis Ac–Ac	3.0 g	3.0 g	1.5 g	1.5 g
TAC[c] 1.5 g	X	X	X	X
SiO$_2$,[d] 1.0 g	X	X	X	X
Dicumyl peroxide, 3.5 g	X	X	X	X
OI	17.0	20.4	17.8	22.0
Horiz burn[e] time (min)	1.07	1.98	1.45	SE

[a] Samples were milled at 238–240°F and cured for 30 min at 360–375°F.

[b] See Table III, footnote a.

[c] Triallylcyanurate (TAC) was used as a crosslinking aid in these formulations.

[d] Fumed silica, MS-7, from Cabot Corporation was used as a filler.

[e] Samples were pressed as 0.0625 in. plaques rather than 0.125 in., and, therefore, horizontal burn times were shorter for these samples relative to all previous formulations.

thyllead dichloride, but carboxylate formation was not detected when diphenyllead dichloride was used. It has been proposed by Carraher[8] that (d–p) π-bonding occurs between the phenyl π-electrons and empty d orbital on the lead. Such (d–p) π-bonding could reduce the electronegativity of the lead atom and/or reduce the availability of the d orbitals to participate in accepting the carboxylate ion via an associative reaction pathway. Either of these reasons could account for the absence of lead carboxylate formation when Ph_2PbCl_2 was allowed to react with PE-*g*-MA.

The use of lead carboxylates in combination with silicone gum in PE-*g*-MA did not improve the flammability characteristics. In fact, the samples with lead carboxylates and silicone gum were less fire-retardant than the previously reported[2] lead/silicone combination in low density polyethylene.

Vanadium copper and tin compounds did not offer any fire-retardant effect when in combination with the silicone gum in either low density polyethylene or PE-*g*-MA.

References

1. (a) J. E. Betts and F. F. Holub, *Chem. Abstr.*, **90**, 138660e (1979); Ger. Offen. 2821807 (1979); U.S. Appl. 816854 (1977); (b) J. E. Betts and F. F. Holub, U.S. Pat. 4,123,586 (1979).

2. M. R. MacLaury and A. L. Schroll, to appear.

3. C. E. Carraher, Jr., *Am. Chem. Soc., Div. Org. Coat. Plast. Chem.*, **35**(2), 380 (1975).

4. C. E. Carraher, Jr., and C. D. Reese, *J. Polym. Sci., Polym. Chem. Ed.* **16**, 491 (1978).

5. P. C. Juliano and R. T. Swiger, U.S. Pat. 4147740 (1979).

6. R. K. Ingham and R. G. Johnson, *Chem. Rev.*, 219 (1956).

7. T. Buch, J. A. Caneiro, and J. A. Guala, *Carbon*, **16**(5), 377 (1978).

8. C. E. Carraher Jr., and C. D. Reese, in *Organometallic Polymers*, Academic, New York, 1978, pp. 101–106.