# Polymer Flame Retardancy: A New Approach

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ABSTRACT: New types of ecologically friendly polymer flame-retardant systems were proposed for Nylon 6,6 and polypropylene [high temperature polymer-organic char former, poly(vinyl alcohol), and silicon-inorganic system]. These systems can act in condensed and gaseous phases. The cone calorimeter and LOI tests indicated the improvement of fire-retardant properties for compositions of flame retardants with Nylon 6,6 and polypropylene in comparison with pure polymers. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 715-725, 1998

**Key words:** carbonization; char former; combustion; ecology; flame-retardant; nylon 6,6; polypropylene; polyvinyl alcohol; silicon

## INTRODUCTION

In the modern polymer industry, different types of flame retardants that are used in polymers are based on halogens (Cl and Br), heavy and transition metals (Zn. V. Pb. and Sb), or phosphorusorganic compounds that may reduce hazards during polymer pyrolysis and combustion, yet may present ecological issues. The use of halogenated flame retardants is still showing an upward trend, but these concerns have started a statistic search for environmentally friendly polymer additives.<sup>1</sup> The European Community proposed restrictions in the use of brominated diphenyl oxide flame retardants because of the potential formation of highly toxic and potentially carcinogenic brominated furans and dioxins during combustion. The International Program for Chemical Safety of the World Health Organization has made several recommendations. Polybrominated diphenyls production and use should be limited because of the concern over high persistency, bioaccumulation, and potential adverse effects at low levels, especially for pentabromodiphenyl oxide. In 1994, the U.S. Environmental Protection Agency released a final draft of exposure and risk assessment of

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dioxins and similar compounds.<sup>2</sup> This reassessment finds the risk greater than previously thought. The tetrachlorodiphenyl dioxins and related compounds are potent toxicants in animals with the potential to produce a wide spectrum of effects. Some of these effects may be occurring in humans at very low levels, and some may result in adverse impacts on human health. It was concluded that dioxin should remain classified as a probable human carcinogen. As a result of these trends, it is quite possible that the available selections of polymer flame retardants will be more limited than in the past.

In our research, we have focused on ecologically safe, flame-retardant systems [high temperature polymer–organic char former, poly(vinyl alcohol) (PVA), and [silicon (Si)–inorganic system] that can act: 1) by the formation of a barrier (char)<sup>3</sup> that hinders the supply of oxygen and reducing the thermal conductivity of the material to limit heat transfer; and 2) by trapping the active radicals in the vapor phase (and possibly in the condensed phase).

#### High-Temperature Polymer-Organic Char Former

There is a strong correlation between char yield and fire resistance.<sup>4</sup> This follows because char is formed at the expense of combustible gases and because the presence of a char inhibits further

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flame spreading by acting as a thermal barrier around the unburned material. The tendency of a polymer to char can be increased with chemical additives and by altering its molecular structure. We have studied polymeric additives (PVA systems) that promote the formation of char. This polymeric additive usually produces a highly conjugated system: aromatic structures that char during thermal degradation and/or transform into crosslinking agents at high temperatures. Decomposition of PVA goes in two stages. The first stage, which begins at 200°C, mainly involves dehydration accompanied by formation of volatile products. The residues are predominantly poly-

$$-CH - CH_2 \leftarrow CH = CH_2 )_n - CH - CH_2 - - - CH - CH_2 \leftarrow CH = CH_2 )_n - CH - CH_2 - - CH - CH_2 \leftarrow CH = CH_2 )_n - CH - CH_2 - CH = CH_2 )_n - CH - CH_2 - CH_2 )_n - CH - CH_2 )_n - CH$$

In the second-stage pyrolysis of PVA, volatile products consist mainly of hydrocarbons (i.e., n-alkanes, n-alkenes, and aromatic hydrocarbons<sup>5</sup>).

Thermal degradation of PVA in the presence of oxygen can be adequately described by a twostage decomposition scheme, with one modification. Oxidation of the unsaturated polymeric residue from dehydration reaction introduces ketone groups into the polymer chain. These groups then promote the dehydration of neighboring vinyl alcohol units producing a conjugated unsaturated ketone structure.<sup>6</sup> The first-stage degradation products of PVA pyrolyzed in air are fairly similar to those obtained in vacuum pyrolysis. In the range of 260°-280°C, the second-order reaction expression satisfactorily accounts for the degradation of 80% hydrolyzed PVA up to a total weight loss of 40%. Changes in the infrared (IR) spectra of PVA subjected to heat treatment have been reported.<sup>6</sup> On heating at 180°C, air bands appeared at 1,630  $\text{cm}^{-1}$  (C=C stretching in isolated double bonds), 1,650 cm<sup>-1</sup> (C=C stretching in conjugated diens and triens), and 1,590  $\overline{cm}^{-1}$  (C=C stretching in polyenes). The intensity of carbonyl stretching frequency at 1750 to 1720 cm<sup>-1</sup> increased, although the rate of increase of intensity was less than that of the polyene band at low temperatures. Above 180°C, although dehydration was the predominant reaction at first, the rate of oxidation increased after an initial induction period.

Identification of a low concentration of benzene among the volatile products of PVA has been taken to indicate the onset of crosslinking taking mers with conjugated unsaturated structures. In the second stage, polyene residues are further degraded at 450°C to yield carbon and hydrocarbons. The mechanism involved in the thermal decomposition of PVA has been clarified by Tsuchiya and Sumi.<sup>5</sup> At 245°C, water is split off the polymer chain, and a residue with a conjugated polyene structure results:

$$\begin{array}{c} (-CH=CH_2)_n - (H-CH_2 - \cdots \rightarrow (-CH=CH_2)_n - (H-CH_2 - + H_2 O)_{H-CH_2} - H_2 O)_{H-CH_2} \\ (-CH=CH_2)_n - (H-CH_2 - + H_2 O)_{H-CH_2} - H_2 O)_{H-CH_2} \\ (-CH=CH_2)_n - (H-CH_2 - + H_2 O)_{H-CH_2} - H_2 O)_{H-CH_2} \\ (-CH=CH_2)_n - (H-CH_2 - + H_2 O)_{H-CH_2} - H_2 O)_{H-CH_2} \\ (-CH=CH_2)_n - (H-CH_2 - + H_2 O)_{H-CH_2} - H_2 O)_{H-CH_2} \\ (-CH=CH_2)_n - (H-CH_2 - + H_2 O)_{H-CH_2} - H_2 O)_{H-CH_2} \\ (-CH=CH_2)_n - (H-CH_2 - + H_2 O)_{H-CH_2} - H_2 O)_{H-CH_2} \\ (-CH=CH_2 - H_2 O)_{H-CH_2} - H_2 O)_{H-CH_2} - H_2 O)_{H-CH_2} \\ (-CH=CH_2 - H_2 O)_{H-CH_2} - H_2 O)_{H-CH_2}$$

Scission of several carbon—carbon bonds leads to the formation of carbonyl groups. For example, aldehyde groups arise from the reaction:

$$\begin{array}{c} -CH - CH_2 \leftarrow CH = CH_2 \right)_n - CH + H_3C - CH - H_3C - H_$$

place by a Diels-Alder addition mechanism.<sup>6</sup> Clearly benzenoid structures are ultimately formed in the solid residue, and the IR spectrum of the residue also indicated the development of aromatic structures.



Acid-catalyzed dehydration promotes the formation of conjugated sequences of double bonds [see (a) in the next structure] and Diels-Alder addition of conjugated, and isolated double bonds in different chains may result in intermolecular crosslinking producing structures that form graphite or carbonization [see (b) in the following structure]



In contrast to PVA, it was found <sup>7,8</sup> that, when Nylon 6,6 was subjected to temperatures above 300°C in an inert atmosphere, it completely decomposed. The wide range of degradation products, which included several simple hydrocarbons, cyclopentanone, water, CO,  $CO_2$ , and  $NH_3$  suggested that the degradation mechanism must have been highly complex. Further research has led to a generally accepted degradation mechanism for aliphatic polyamides<sup>9</sup>:



- 1. Hydrolysis of the amide bond usually occurred below the decomposition temperature.
- 2. Homolytic cleavage of C—C, C—N, and C—H bonds generally began at the decomposition temperature and occurred simultaneously with hydrolysis.
- 3. Cyclization and homolytic cleavage of products from both of the above reactions occurred.
- 4. Secondary reactions produced CO, NH<sub>3</sub>, nitriles, hydrocarbons, and carbon chars.

The idea of introducing PVA into a Nylon 6,6 composition is based on the possibility of hightemperature, acid-catalyzed dehydration. This reaction can be provided by the acid products of Nylon 6,6 degradation hydrolysis that would promote the formation of intermolecular crosslinking and char. Such a system we have called "synergetic carbonization" because the char yield and flame suppression parameters of the polymer blend of PVA and Nylon 6,6 are significantly better than pure PVA and Nylon 6,6 polymers.

It is well-known that nylons have poor compatibility with other polymers because of their strong hydrogen bonding characteristics. The compatibility of Nylon 6 with poly(vinyl acetate) and PVA has been studied.<sup>10</sup> Compatibility was judged from the melting temperature depression. Results indicate that Nylon 6,6–PVA blends are partially compatible. "Compatibility" in this work does not mean thermodynamic miscibility, but rather easiness of mixing blends to achieve small size domains. The next step in our plan to improve the flammability of PVA–Nylon 6,6 system was the substitution of pure PVA by PVA oxidized by potassium permanganate (PVA-ox). This approach was based on the fire behavior of (PVA-ox) itself. The dramatic decrease of the rate of heat release and significant increase in ignition time for the oxidized PVA in comparison with the original PVA was shown experimentally (cone calorimeter).

Literature on the oxidation of macromolecules by alkaline permanganate presents little information about these redox systems. One set of workers investigated<sup>11,12</sup> the oxidation of PVA as a polymer containing secondary alcoholic groups by KMnO<sub>4</sub> in alkaline solution. It was reported that the oxidation of PVA in alkaline solutions occurs through formation of two intermediate complexes (1) and/or (2)<sup>12</sup>:



Reactions (a) and (b), in the above structure, lead to the formation of poly(vinyl ketone) [note (3) from the above structure] as a final product of oxidation of the substrate. Poly(vinyl ketone) was isolated and identified by microanalysis and spectral data.<sup>13</sup>

### Si-Inorganic Systems

According to recent patents, silicone (additives) may be considered as an universal additive to improve the flammability properties of polymers and to decrease the harmful impact on environmental safety.

Our informal preliminary studies have found that the addition of relatively small amounts of Si-inorganic additives (SI) to various polymers significantly reduce their flammability. We have proposed a Si-inorganic system (SI) that, in the first place, inhibits gaseous phase combustion and also affects char formation in the solid phase. This system was incorporated into two different types of polymers: polypropylene and Nylon 6,6.

The proposed mechanism of SI flame suppression is based on gaseous phase inhibition by  $SiCl_4$  and HCl, which can be produced at temperatures above  $300^{\circ}-500^{\circ}C$ ,<sup>14</sup> exactly the temperatures realized on the surface of burning polymers:

1.	$\begin{array}{l} 350{-}500^\circ\mathrm{C}\text{:}\\ 2\mathrm{SnCl}_2+n\mathrm{Si}=2\mathrm{Sn}+(n-1)\mathrm{Si}+\mathrm{SiCl}_4\\ \mathrm{SiCl}_4+2\mathrm{H}_2\mathrm{O}=4\mathrm{HCl}+\mathrm{SiO}_2 \end{array}$
	410°C:
2	$2 \operatorname{PbCl}_{2} + n \operatorname{Si} = 2 \operatorname{Pb} + (n - 1) \operatorname{Si} + \operatorname{SiCl}_{2}$

2. 
$$2 \operatorname{PDC1}_2 + n \operatorname{SI} = 2 \operatorname{PD} + (n - 1) \operatorname{SI} + \operatorname{SIC1}_4$$
  
 $280^\circ - 350^\circ \operatorname{C}:$ 

3. 
$$4 \operatorname{CuCl} + n\operatorname{Si} = 4 \operatorname{Cu} + (n-1)\operatorname{Si} + \operatorname{SiCl}_4$$
  
300°C

4.  $2 \operatorname{CaCl}_2 + n \operatorname{Si} = 2 \operatorname{Ca} + (n-1)\operatorname{Si} + \operatorname{SiCl}_4$ 400°C

5. 4  $\operatorname{FeCl}_3 + n\operatorname{Si} = 4\operatorname{Sn} + (n-1)\operatorname{Si} + 3\operatorname{SiCl}_4$ 

The Si analogous of the halogenated carbons, in particular, would be expected to be effective flame inhibitors. This hypothesis was confirmed early on, at least with respect to SiCl<sub>4</sub>. There are, however, significant differences in the behavior of these compounds in the atmosphere. Unlike the halons, the halosilanes readily hydrolyze in moist air.<sup>15</sup> An important consequence is that these compounds will undergo rapid decomposition in the troposphere and would therefore be expected to have correspondingly low potentials for ozone depletion and global warming than halons. Unfortunately, this beneficial property is offset by the fact that hydrogen halides are produced in the hydrolysis of halosilanes. This effect is so pronounced that the presence of a single Si—halogen bond in a molecule is sufficient to make its vapors corrosive and dangerous to breathe.<sup>16</sup> But, for the SI flame-retardant, Nylon 6,6, this harmful influence is not so important because HCl forms in the zone of combustion only at the temperatures above  $500^{\circ}$ - $600^{\circ}$ C and also takes part in the flame inhibition and reactions with tin (apparently SnCl<sub>4</sub> formation).

A list of results was published in Lyon's<sup>17</sup> book on fire retardants and in a review article.<sup>18</sup> The tabulated values are the volume percent of inhibitor corresponding to the peak in the flammability curve for a premixed *n*-heptane flame. The value reported for SiCl<sub>4</sub> was 9.9%. On the basis of this criteria, the flame suppression efficiency of SiCl<sub>4</sub> is between CF<sub>3</sub>Br and CCl<sub>4</sub>, which were found to have peak values of 6.1 and 11.5%, respectively.

In an independent study, flame velocity measurements were conducted for a series of additives, including some halosilanes and related compounds.<sup>19</sup> The figure of merit was the volume percent of inhibitor required to reduce the burning velocity of a premixed (stoichiometric) *n*-hexane flame by 30%. On this basis, it was determined that the flame inhibition activity of SiCl<sub>4</sub> (0.56%) was comparable with Br<sub>2</sub>(0.7%), but considerably more effective than CCl<sub>4</sub> (1.38%). The hierarchy for inhibition: SnCl<sub>4</sub> > GeCl<sub>4</sub> > SiCl<sub>4</sub> > CCl<sub>4</sub> was also found to apply to increases in the ignition temperatures of hydrocarbon/(O<sub>2</sub> + N<sub>2</sub>) mixtures.<sup>20</sup>

The mechanism by which the halosilanes effect flame inhibition is similar, if not identical, to the well-known halogenated carbons.<sup>18-20</sup>

# **EXPERIMENTAL**

## Materials

The polymers used in this work were PVA, 99% hydrolyzed, molecular weight 86,000, Nylon 6,6 and polypropylene, isotactic, were supplied by Scientific Polymer Products, Inc. The inorganic additives are potassium permanganate (BA Chemicals Ltd.), Si, metal, 325 mesh, 99% (Aldrich Co.), stannous chloride A.C.S.,  $SnCl_2 \cdot 2H_2O$  (REACHIM),  $ZnCl_2-R$  (REACHIM),  $MnCl_2 \cdot 4H_2O$  A.C.S. (REACHIM),  $CoCl_2 \cdot 6H_2O - R$  (REACHIM),  $CuCl_2 \cdot 2H_2O$  A.C.S. (REACHIM),  $BaCl_2 \cdot 4H_2O$  A.C.S. (REACHIM), and  $CaCl_2 \cdot 6H_2O$  A.C.S. (REACHIM).



Figure 1 Rate of Heat Release vs. time for: Nylon 6,6; Nylon 6,6–PVA (80 : 20 wt %); and Nylon 6,6–PVA oxidized by  $KMnO_4$  (80 : 20 wt %); at a heat flux of 50 kW m<sup>-2</sup>.

#### **Preparation of Samples: Incorporation of Additives**

Blends of Nylon 6,6, PVA, and PVA-ox were prepared in a laboratory blender at room temperature (10 min). The mixed samples were compressionmolded at temperatures of  $220^{\circ}-240^{\circ}$ C for 10 min. PVA (10 wt % aqueous solution) was oxidized by KMnO<sub>4</sub> in ratio: 5 wt % KMnO<sub>4</sub> : 95 wt % PVA.

PVA was oxidized by  $KMnO_4$  in an aqueous solution. A 10 wt % aqueous solution of PVA was

prepared at 90°C in a laboratory vessel.<sup>21</sup> KMnO<sub>4</sub> (5 wt % of original PVA) was added into the hot aqueous solution of PVA. After a fast reaction (1.5-2 min), the solution became dark brown in color. It was allowed to cool to room temperature. Then, water was removed *in vacuo* at 50°C to yield soft elastic material. This material was heated in an oven for 24 h at 120°C to give a hard plastic material. The resulting material was milled in a laboratory ball mill to produce a dark brown powder.



**Figure 2** Rate of Heat Release for polypropylene composition at a heat flux of  $35 \text{ kW m}^{-2}$ .

Material (Heat Flux, kW m <sup>-2</sup> )	Char Yield (wt %)	Ignition (Time, s)	$\begin{array}{c} Peak \ Rate \ of \\ Heat \ Release \\ (kW \ m^{-2}) \end{array}$	$\begin{array}{c} Total \ Heat \\ Release \\ (MJ \ m^{-2}) \end{array}$
PVA, 20 kW $m^{-2}$	8.8	39	255.5	159.6
PVA, 35 kW $m^{-2}$	3.9	52	540.3	111.3
$PVA, 50 \text{ kW m}^{-2}$	2.4	41	777.9	115.7
PVA-ox KMnO <sub>4</sub> , 20 kW m <sup><math>-2</math></sup>	30.8	1,127	127.6	36.9
$PVA$ -ox $KMnO_4$ , 35 kW m <sup>-2</sup>	12.7	774	194.0	103.4
$PVA$ -ox $KMnO_4$ , 50 kW m <sup>-2</sup>	9.1	18	305.3	119.8
Nylon 6,6, 50 kW $m^{-2}$	1.4	97	1,124.6	216.5
Nylon 6,6 + PVA (8 : 2), 50 kW $m^{-2}$	8.7	94	476.7	138.4
Nylon 6,6 + PVA-ox KMnO <sub>4</sub> (8 : 2), 50 kW m <sup>-2</sup>	8.9	89	399.5	197.5

Table I Cone Calorimeter Data of Nylon 6,6-PVA System

Inorganic additives were mixed with polypropylene powder in a laboratory blender (in ratio of 95% polypropylene: 3% Si : 2% SnCl<sub>2</sub>). Samples were prepared by press-molding at temperatures of  $120^{\circ}-140^{\circ}C$ .

Samples for combustion measurements (Nylon 6,6 + SI) were compression-molded at temperatures of  $240^{\circ}-280^{\circ}C$  in ratio Nylon  $6,6:Si:MeCl_2$  (95: 3:2%, w/w/w).

LOI tests of the samples, as bars (d = 4 mm), were conducted according to ASTM-D2863. Selfignition tests were performed using the ICP Furnace (5–10 mg). Thermal analyses (thermal gravimetric analysis) were performed in air using the DERIVATOGRAPH Q thermoanalyzer (at a heating rate of 10°C min<sup>-1</sup>). Cone calorimeter tests on the polymer samples, as disks (radius 35 mm), were conducted according to ASTM 1356-90 under a heat flux of 20, 30, 35, and 50 kW m<sup>-2</sup>. Each specimen was wrapped in aluminum foil, and only the upper face was exposed to the radiant heater.

Table II Cone Calorimeter Data of the Heat of Combustion and the Flame-Out Time for Nylon 6,6 Compositions at a Heat Flux of 50 kW m<sup>-2</sup>

Composition	Flame-Out Time (s)	$\begin{array}{c} Average \\ Heat \ of \\ Combustion \\ (MJ \ kg^{-1}) \end{array}$
Nylon 6,6	512	31.50
Nylon 6,6–PVA (80 : 20) Nylon 6,6–PVA oxidized	429	25.15
by KMnO <sub>4</sub> (80 : 20)	747	29.52

# **RESULTS AND DISCUSSION**

#### PVA-Nylon 6,6 System

Preliminary cone tests for PVA and PVA oxidized by KMnO<sub>4</sub> were conducted at heat fluxes of 20, 35, and 50 kW m<sup>-2</sup> (see Table II). It is clearly seen that carbon residue (wt %) and the peak of heat release rate (Peak Rate of Heat Release, kW m<sup>-2</sup>) suggest substantial improvement of fire resistance characteristics for PVA oxidized by KMnO<sub>4</sub>, in comparison with PVA. PVA oxidized by KMnO<sub>4</sub> gives about half the peak of heat release rate (Peak Rate of Heat Release, kW m<sup>-2</sup>) when compared with pure PVA. Even at 50 kW  $m^{-2}$ , the yield of char residue for PVA oxidized by  $KMnO_4$  was 9.1%. One reason for this phenomenon may be explained by the ability of PVA oxidized by KMnO<sub>4</sub> [poly(vinyl ketone) structures] to act as a neutral (see "1" in structure below) and/or monobasic (see "2" in structure below) bidentate ligand.<sup>9</sup>

Table III	Cone Calorimeter Data of the	е
Si-Polypr	opylene System at a Heat Flu	x
of 35 kW 1	$n^{-2}$	

Cone Data	Polypropylene	$\begin{array}{c} PP + Si \\ + SnCl_2 \\ (95:3:2) \end{array}$
Char yield (wt %)	0.0	10.1
Ignition time (s)	62	91
Peak RHR (kW m <sup>-2</sup> ) Total Heat Release	1,378.0	860.1
$(MJ m^{-2})$	332.0	193.7

PP, polypropylene; RHR, Rate of Heat Release.



Figure 3 Ignition time delay for polypropylene composition at a heat flux of 35 kW  $m^{-2}.$ 



The experimental results of others (IR and electronic spectra)<sup>9</sup> provide strong evidence of coordination of the ligand (some metal ions  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$ ) through the monobasic bidentate mode (see "2" in the structure above). Based on the above, the following structure can be proposed for polymeric complexes:



#### M - metal

The result of elemental analysis of PVA oxidized by  $\rm KMnO_4$  indicates the presence of 1.5% of Mn remaining in this polymeric structure. Thus, we can tentatively suggest that this catalytical amount of chelated Mn structure incorporated in the polymer may provide the rapid high-temperature process of carbonization and formation of char.

The fire tests at 50 kW  $m^{-2}$  for Nylon 6,6 and PVA (80 : 20%) compositions (typical rate of heat release curves for each sample are shown in Fig. 1) confirmed the assumption of the synergistic effect of carbonization. Each of the individual polymers is

less fire-resistant than their composition. The scheme of "synergistic" carbonization of Nylon 6,6 and PVA is shown herein. Similar trends are observed for Average Heat Release, which was calculated over the total flame-out period (Fig. 2). The sample with PVA oxidized by KMnO<sub>4</sub> displayed even better flame-retardant properties due to the catalytical effect of Mn chelate fragments on the formation of char (Table I). The superior Rate of Heat Release properties of PVA oxidized by KMnO<sub>4</sub> are clearly shown by comparison of the values of Maximum Rate and Average Rate of Heat Release given in Figure 2. However, a less satisfactory correlation is given in the determination of Total Heat Release date (Table I). Although, the cone calorimeter measurements indicate a decrease of Total Heat Release for Nylon 6,6-PVA and Nylon 6,6-PVA oxidized by KMnO<sub>4</sub> in comparison with pure PVA, the sample of Nylon 6,6 with PVA oxidized by KMnO<sub>4</sub> gives a higher value of Total Heat Release than Nylon 6,6 with PVA (Table I). We have qualitatively explained this fact by the influence of a catalytical amount of chelated Mn structure incorporated in the polymer on the smoldering of polymer samples.<sup>9</sup> The flame-out time for Nylon 6,6 with PVA oxidized by KMnO<sub>4</sub> is larger than the flameout times of Nylon 6,6-PVA and Nylon 6,6 (see Table III). The values of Average Heat of Combustion indicate the exothermal process of smoldering provided by chelated Mn structures (Table II). That is why we have found the approximately equal amount of char yield for Nylon 6,6-PVA and Nylon 6,6-PVA oxidized by KMnO<sub>4</sub> (Table I).

The structure below depicts synergistic carbonization of the Nylon 6,6–PVA blend of volatile products and char.

$$\begin{bmatrix} 0 \\ -C - (CH_2)_x - C - NC - (CH_2)_y - NH - \end{bmatrix}_n \xrightarrow{H_2O} \begin{bmatrix} -C - (CH_2)_x - C - OH + H_2N - (CH_2)_y - NH - \end{bmatrix}_n$$

$$+$$

$$(-CH - CH_2)_n - CH - CH_2 - \longrightarrow (-CH = CH_2)_n - CH - CH_2 - + H_2O$$

$$0H$$

$$0H$$

$$T$$

$$-C - (CH_2)_x - C - O - CH - CH_2 - + H_2O$$

$$(-C = CH_2)_n - CH - CH_2 - + H_2O$$

$$(-C = CH_2)_n - CH - CH_2 - + H_2O$$

$$(-C = CH_2)_n - CH - CH_2 - + H_2O$$

$$(-C = CH_2)_n - CH - CH_2 - + H_2O$$

$$(-C = CH_2)_n - CH - CH_2 - + H_2O$$

# Si-Inorganic-Polypropylene-Nylon 6,6 Systems

A set of cone calorimeter tests were conducted for polypropylene composition at a heat flux of 35 kW  $m^{-2}$  (Table III). The flame-retardant composition

included 3 wt % of Si and 2 wt % of SnCl<sub>2</sub>. All cone results indicate an improvement of fire resistance of Si-polypropylene composition in comparison with pure polypropylene (Table III) (Figs. 3 and 4).

	Table IV	LOI and Thermal Ana	lysis Data of Nylon	6,6–SI Compositions
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		•		•	-
Nylon–SI Compositions (Metal)	LOI (%)	$T_{ m fus.}\ ({ m C})$	T <sub>max.</sub> (C)	T <sub>max.</sub> (C)	Char Yield (wt %, 750°C, air)
Nylon 6,6	29	252	430		0
Nylon-SnCl <sub>2</sub>	37.5	248	370	448	5.2
Nylon-BaCl <sub>2</sub>	25.5	244	418		1.2
Nylon-CaCl <sub>2</sub>	25	245	403	477	3.1
Nylon-MnCl <sub>2</sub>	26.5	255	391	459	1.3
Nylon-ZnCl <sub>2</sub>	26.7	255	388	461	2.1
Nylon-CoCl <sub>2</sub>	26.5	268	419	463	2.7
Nylon-CuCl <sub>2</sub>	27.0	248	438	—	1.1



Figure 4 Total Heat Release of polypropylene composition at a heat flux of 35 kW  $m^{-2}.$ 

Experimental results of thermal analysis and combustion tests (LOI, self-ignition) of Nylon 6,6–SI compositions are presented in Table V. LOI results clearly showed that incorporation of  $SnCl_2 + Si (2:3 \text{ wt }\%)$  SI composition in Nylon 6,6 has a substantial flame-retardant effect in comparison with other metal systems (Table IV, Figs. 5 and 6).

Thermal analysis of Nylon 6,6 and Nylon 6,6– SI compositions suggests that it may be possible to provide thermal stabilization of Nylon 6,6 with incorporation of  $SnCl_2$ ,  $CaCl_2$ ,  $ZnCl_2$ ,  $CoCl_2$ , and  $MnCl_2$ . Unlike pure Nylon 6,6 and SI compositions with  $BaCl_2$  and  $CuCl_2$  compositions with



Figure 5 LOI data for Nylon 6,6 compositions with:  $SnCl_2-Si (2:3 \text{ wt }\%)$ ,  $BaCl_2-Si (2:3 \text{ wt }\%)$ ,  $CaCl_2-Si (2:3 \text{ wt }\%)$ ,  $CaCl_2-Si (2:3 \text{ wt }\%)$ ,  $MnCl_2-Si (2:3 \text{ wt }\%)$ ,  $ZnCl_2-Si (2:3 \text{ wt }\%)$ ,  $CoCl_2-Si (2:3 \text{ wt }\%)$ , and  $CuCl_2-Si (2:3 \text{ wt }\%)$ .

 $SnCl_2$ ,  $CaCl_2$ ,  $ZnCl_2$ ,  $CoCl_2$ , and  $MnCl_2$  have the separate "second" pronounced peak in derivative termograms. This fact can also be confirmed by the difference in the char yield at 750°C (Table V). These observations indicate the process of solid-state crosslinking and char formation provided by  $SnCl_2$ ,  $CaCl_2$ ,  $ZnCl_2$ ,  $CoCl_2$ , and  $MnCl_2$ .

However, the significant flame retardancy effect (LOI = 37.5 and flame ignition time) has only SI compositions with SnCl<sub>2</sub>.

The result of elemental analysis of char from Nylon 6,6–SI composition with  $SnCl_2$  (95 : 3 : 2) indicates the presence of 5% of Sn remaining in this structure. Thus, we suggest that essential



Figure 6 Char yield (wt %) for Nylon 6,6 compositions with:  $SnCl_2-Si (3 : 2 wt \%)$ ,  $BaCl_2-Si (3 : 2 wt \%)$ ,  $CaCl_2-Si (3 : 2 wt \%)$ ,  $MnCl_2-Si (3 : 2 wt \%)$ ,  $ZnCl_2-Si (3 : 2 wt \%)$ ,  $CoCl_2-Si (3 : 2 wt \%)$ , and  $CuCl_2-Si (3 : 2 wt \%)$  (thermal gravimetric analysis, 750°C, air).

Nylon 6,6	Nylon–	Nylon–	Nylon–	Nylon–	Nylon–	Nylon–
	SnCl <sub>2</sub> –SI	MnCl <sub>2</sub> –SI	CoCl <sub>2</sub> –SI	CuCl <sub>2</sub> –SI	BaCl <sub>2</sub> –SI	ZnCl <sub>2</sub> –SI
0.5	8.8	8.0	7.6	7.0	6.6	6.2

Table V Ignition Time Delays (s) in Nylon 6,6–SI Compositions at 750°C

amount of Sn turns into a gas phase product (apparently  $SnCl_4$ ).

As described previously, the hierarchy for inhibition (SnCl<sub>4</sub> > GeCl<sub>4</sub> > SiCl<sub>4</sub> > CCl<sub>4</sub>) was found to apply to increases in the ignition temperatures of hydrocarbon/(O<sub>2</sub> + N<sub>2</sub>) mixtures.<sup>17</sup> It means that SnCl<sub>4</sub> has the highest flame-retardant effectiveness in group IVA elements. We suggest that unique flame retardancy of Nylon 6,6–SI composition (with SnCl<sub>2</sub>), as well as polypropylene composition, can be achieved by allowing SiCl<sub>4</sub>, HCl, and SnCl<sub>4</sub> to act as inhibitors of the gaseous phase combustion. These conclusions are confirmed by self-ignition tests (Table IV).

Data in Table IV show that all MeCl<sub>2</sub>–SI compositions have ignition delay in consecutive order: SnCl<sub>2</sub>–SI > MnCl<sub>2</sub>–SI > CoCl<sub>2</sub>–SI > CuCl<sub>2</sub>–SI > BaCl<sub>2</sub>–SI > ZnCl<sub>2</sub>–SI > Nylon 6,6 (0.5). But only SnCl<sub>2</sub>–SI–Nylon 6,6 composition has an essential flame-retardancy effect (LOI = 37.5), as well as a drastic change (increase) of ignition time delay *versus* T°C.

## CONCLUSIONS

A polymer–organic char former (PVA system) incorporated in Nylon 6,6 reduced the peak rate of heat release from 1124.6 kW m<sup>-2</sup> (for Nylon 6,6) and 777.9 kW m<sup>-2</sup> (for PVA) to 476.7 kW m<sup>-2</sup> and increased the char yield from 1.4% (for Nylon 6,6) to 8.7% due to a "synergistic" carbonization effect. (Cone calorimeter was operated at 50 kW m<sup>-2</sup> incident flux.)

Cone calorimeter data of Nylon 6,6 composition with PVA oxidized by  $KMnO_4$  (Mn-chelate complexes)<sup>13</sup> showed the improvement of Peak Rate of Heat Release from 476.7 kW m<sup>-2</sup> (composition of Nylon 6,6 with PVA) to 399.5 kW m<sup>-2</sup> (composition of Nylon 6,6 with PVA oxidized by KMnO<sub>4</sub>). On the other hand, the cone data indicated the exothermal process of smoldering for composition of nylon 6,6 with PVA oxidized by KMnO<sub>4</sub>. This reaction evidently was provided by chelated Mn structures that increase the Total Heat Release of Nylon 6,6 with PVA oxidized by  $KMnO_4$  in comparison with Nylon 6,6 with PVA.

A polymeric char former such as PVA and (for example) cellulose systems may present a new type of ecologically safe flame-retardant system.

The flame-retardant binary system of Si (3 wt %) and SnCl<sub>2</sub> (2 wt %) incorporated in polypropylene and Nylon 6,6 acts as an effective inhibitor of gaseous phase flame reactions and may be considered a new type of polymer flame protector based on ecologically friendly SI composition.

## REFERENCES

- 1. NBS Special Publication 749, Fire Hazard Comparison of Fire Retarded and Non-Fire-Retarded Products, July, 1988.
- U.S. Environmental Protection Agency, *EPA* / 600, Vols. I, II, and III, U.S. Government Printing Office, Washington, DC, June-August, 1994.
- 3. R. M. Aseeva and G. E. Zaikov, *Combustion of Polymer Materials*, Hanser Publishers, Munich, 1985.
- S. M. Lomakin, J. E. Brown, R. S. Breese, and M. R. Nyden, *Polymer Degradation and Stability*, Vol. 41, N2, 1993, p. 229.
- 5. Y. Tsuchiya and K. Sumi, J. Polym. Sci., 7, 3151 (1969).
- C. A. Finch, Ed., Polyvinyl Alcohol Properties and Application, John Wiley & Sons, New York, 1973.
- S. Bodrero, Macromol. Chem., Macromol. Symp., 74, 137 (1993).
- R. T. Conley, Ed., *Thermal Stability of Polymers*, Vol. 1, New York, Marcel Dekker, 1970, p. 350.
- 9. S. V. Levchik, L. Costa, and G. Camino, Macromol. Chem., Macromol. Symp., 74, 95 (1993).
- C.-S. Ha, W.-K. Lee, T.-W. Roe, and W.-J. Cho, *Polym. Bull.*, **31**, 359 (1993).
- 11. R. M. Hassan, Polym. Int., 30, 5 (1993).
- 12. R. M. Hassan, S. A. El-Gaiar, and A. M. El-Summan, *Polym. Int.*, **32**, 39 (1993).
- R. M. Hassan, M. A. Abd-Alla, and M. A. El-Gahmi, J. Mater. Chem., 2, 613 (1992).

- 14. R. J. H. Voorhoeve, Organohalosilane Precursors to Silicones, Elsevier, New York, 1967, p. 122.
- N. I. Sax and R. J. Lewis, *Dangerous Properties of Industrial Materials*, 7th ed., Van Nostrand Reinhold, New York, 1989.
- 16. E. G. Rochow, in *Comprehensive Inorganic Chemistry*, Vol. 11, Pergamon Press, New York, 1973.
- 17. J. W. Lyons, *The Chemistry and Uses of Fire Retardants*, Wiley-Interscience, New York, 1970, p. 15.
- E. T. McHale, Survey of vapor phase chemical agents for combustion suppression, *Fire Res. Abstr. Rev.*, **11**, 90 (1969).
- M. E. Morrison and K. Scheller, The Effect of Burning Velocity Inhibitors on the Ignition of Hydrocarbon-Oxygen-Nitrogen Mixtures, Combustion and Flame, Vol. 18, 1972, p. 3.
- 20. E. A. V. Ebsworth, *Volatile Silicon Compounds*, Academic Press, New York, 1975, p. 336.