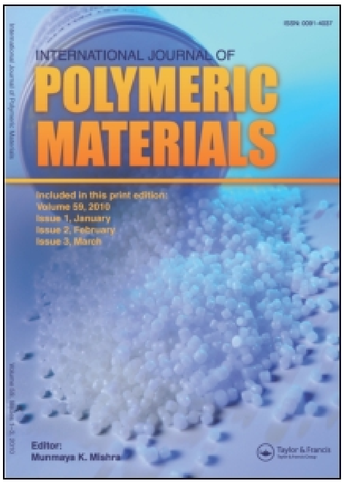

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Advances in Nylon 6,6 Flame Retardancy

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Advances in Nylon 6,6 Flame Retardancy

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The development of an ecologically safe flame retardant system for nylon 6,6 remains to be a major problem of polymer industry. This study reviews three approaches: the increase of char by addition of polyvinylalcohol (Part I), the suppression of combustion in gaseous phase by addition of melamine cyanurate (Part II), and the combination of char increase and flame suppression by addition of various Si-inorganic systems (Part III).

KEY WORDS Nylon 6,6, flame retardancy, polyvinylalcohol, melamine cyanurate, silicone-inorganic additives, ecology.

PART 1

Addition of Polyvinyl-Alcohol

INTRODUCTION

The subject of ecological safeness of polymer flame retardants has become a major problem in the modern polymer industry. The different types of polymer flame retardants based on halogens (Cl, Br), heavy and transition metals (Zn, V, Pb, Sb) or phosphorus-organic compounds may reduce risk during polymer combustion and pyrolysis, yet may present ecological issues.

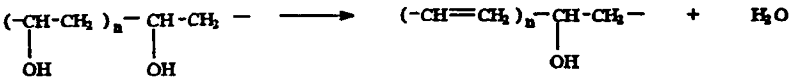
The fire retardancy of polymers can be achieved by different ways: 1) by modifying the pyrolysis scheme to produce non-volatile, or non-combustible products that dilute the flame oxygen supply; 2) by smothering the combustion through dilution of the combustible gases, or the formation of a barrier (char) which hinders the supply of oxygen; 3) by trapping the active radicals in the vapor phase (and eventually in the condensed phase); 4) by reducing the thermal conductivity of the material to limit heat transfer (char).

In our research we have focused on 2, 3 and 4. An ecologically-safe flame retardant system (high temperature polymer-organic char former) based on polyvinyl(alcohol) (PVA) in NYLON 6,6 is proposed.

High Temperature Polymer-Organic Char Former

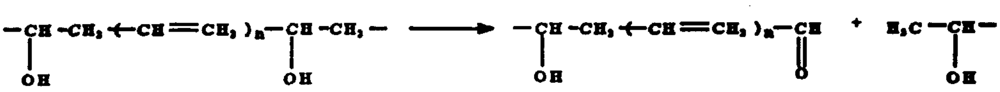
Our study has been directed at finding ways to increase the tendency of plastics to char when they are burned. There is a strong correlation between char yield and fire resistance. This follows because char is formed at the expense of combustible gases and because the presence of a char inhibits further flame spread 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 (polyvinyl alcohol systems) which promote the formation of char. These polymeric additives usually produce a highly conjugated system-aromatic structures which char during thermal degradation and/or transform into cross-linking 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 polymers 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 thermal decomposition PVA has been deduced by Tsuchya and Sumi.[1] At 245°C water is split off the polymer chain, and a residue with conjugated polyene structure results:



$$(-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2})_n-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}- \longrightarrow (-\mathrm{CH}{=}\mathrm{CH_2})_n-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}- \quad + \quad \mathrm{H_2O}$$

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



$$-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}-(-\mathrm{CH}{=}\mathrm{CH_2})_n-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}- \longrightarrow -\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH_2}-(-\mathrm{CH}{=}\mathrm{CH_2})_n-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{CH}} \quad + \quad \mathrm{H_2C}-\underset{\mathrm{OH}}{\mathrm{CH}}-$$

In the second-stage pyrolysis of PVA, the volatile products consist mainly of hydrocarbons, i.e. *n*-alkanes, *n*-alkenes and aromatic hydrocarbons (Table I).[1]

Thermal degradation of PVA in the presence of oxygen can be adequately described by a two-stage 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.[2] The first-stage degradation products of PVA pyrolysed in air are fairly similar to those obtained in vacuum pyrolysis. In the range 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%. The activation energy of decomposition appears to be consistent with the value of 53.6 kcal/mol which is obtained from the thermal degradation of PVA.[2]

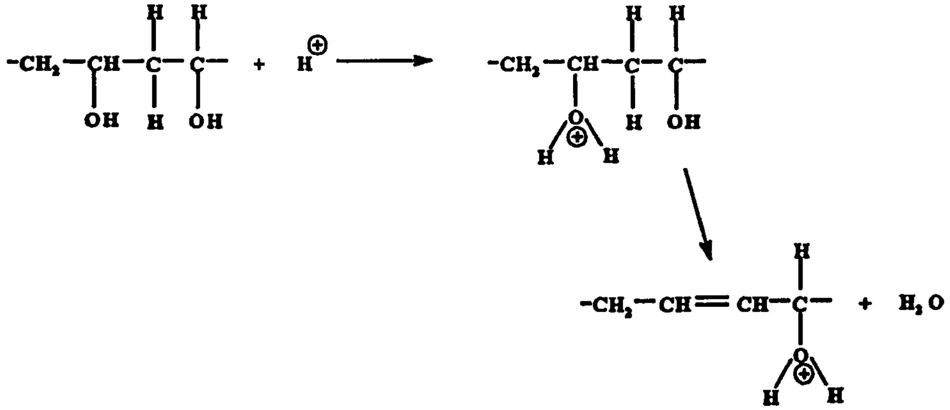
The changes in the IR spectra of PVA subjected to heat treatment have been reported.[2] After heating at 180°C in air bands appeared at 1630 $\mathrm{cm^{-1}}$ (C=C stretching in isolated double bonds), 1650 $\mathrm{cm^{-1}}$ (C=C stretching in conjugated diens and

TABLE I

Thermal decomposition products (240°C, four hours)[1]

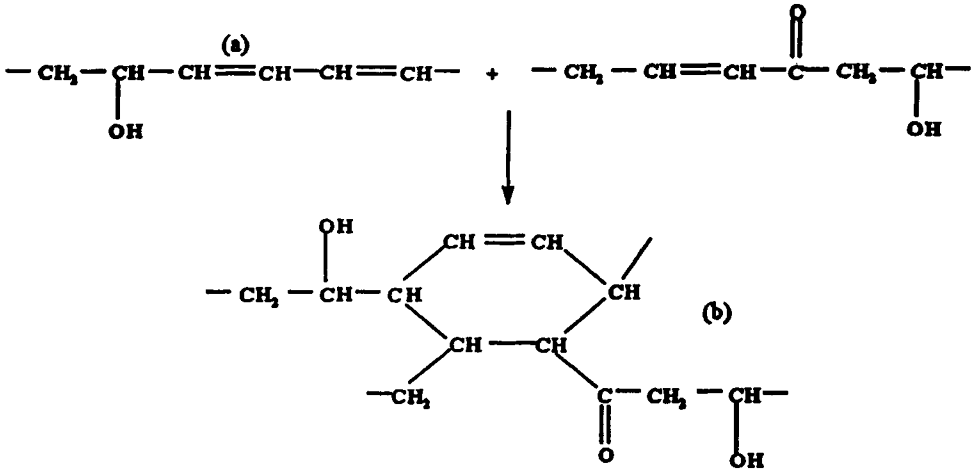
Products	% by weight of original polymer
Water	33.400
CO	0.120
CO_2	0.180
Hydrocarbons (C_1 - C_2)	0.010
Acetaldehyde	1.170
Acetone	0.380
Ethanol	0.290
Benzene	0.060
Crotonaldehyde	0.760
3-pentene-2-one	0.190
3,5-heptadiene-2-one	0.099
2,4-hexadiene-1-al	0.550
Benzaldehyde	0.022
Acetophenone	0.021
2,4,6-octatriene-1-al	0.110
3,5,7-nonatriene-2-one	0.020
Unidentified	0.082

triens), and 1590 cm^{-1} (C=C stretching in polyenes). The intensity of carbonyl stretching frequency at 1750–1720 cm^{-1} 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.

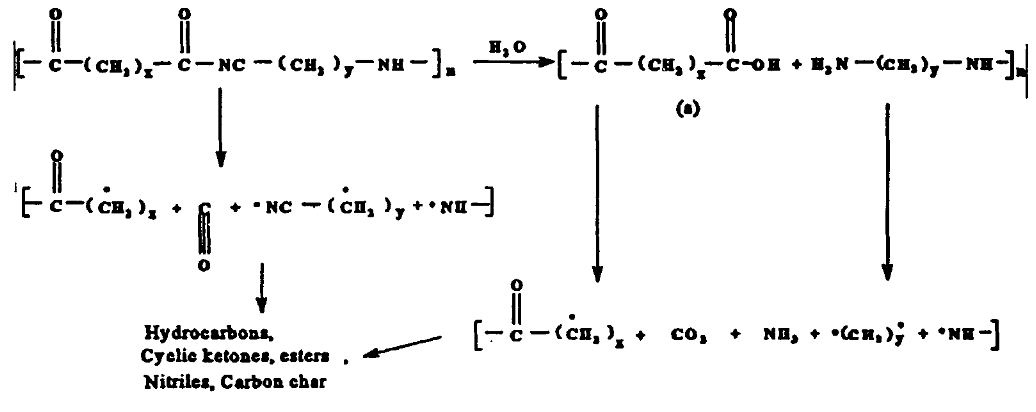


The identification of a low concentration of benzene among the volatile products of PVA[2] has been taken to indicate the onset of a crosslinking reaction proceeding by a Diels-Alder addition mechanism.[2] Clearly benzenoid structures are ultimately formed in the solid residue, and the IR spectrum of the residue also indicated the development of aromatic structures.[2]

Acid-catalyzed dehydration promotes the formation of conjugated sequences of double bonds (a) and Diels-Alder addition of conjugated and isolated double bonds in different chains may result in intermolecular crosslinking producing structures which form graphite or carbonization (b).



In contrast to PVA, it was found[3,4] 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[5]:



1. Hydrolysis of the amide bond usually occurred below the decomposition temperature.

2. Homolytic cleavage of C—C, C—N, 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_3, nitriles, hydrocarbons, and carbon chars.

The idea of introducing poly(vinyl alcohol) into nylon 6,6 composition is based on the possibility of high-temperature acid-catalyzed dehydration. This reaction can be provided by the acid products of nylon 6,6 degradation hydrolysis which would promote the formation of intermolecular crosslinking and char. Such a system we have called "synergetic carbonization" because the char yield and flame suppression

TABLE II

Cone Calorimeter Data of nylon 6,6/PVA

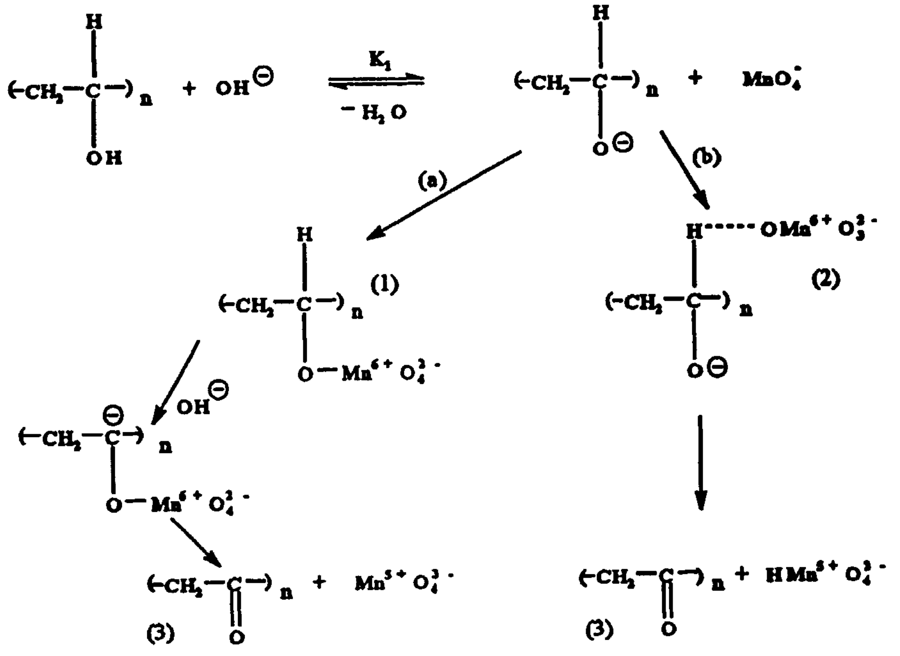
Material, Heat flux, kW/m^2	**Initial wt., g**	**Char yield, % wt.**	**Ignition time, sec.**	**Peak R.H.R., kW/m^2**	**Total Heat Release, MJ/m^2**
PVA, 20	47.6	8.8	39	255.5	159.6
PVA, 35	28.3	3.9	52	540.3	111.3
PVA, 50	29.2	2.4	41	777.9	115.7
PVA-ox $KMnO_4$, 20	27.9	30.8	1127	127.6	36.9
PVA-ox $KMnO_4$, 35	30.5	12.7	774	194.0	103.4
PVA-ox $KMnO_4$, 50	29.6	9.1	18	305.3	119.8
PVA (100°C) $KMnO_4$, 20	31.1	16.3	303	211.9	124.5
PVA (200°C) $KMnO_4$, 20	35.9	25.7	357	189.0	91.1
nylon 6,6, 50	29.1	1.4	97	1124.6	216.5
nylon 6,6 + PVA(8:2),50	26.4	8.7	94	476.7	138.4
nylon 6,6 + PVA-ox(8:2) $KMnO_4$, 50	39.1	8.9	89	399.5	197.5

parameters of the polymer blend of poly(vinyl alcohol) and nylon 6,6 are significantly better than pure poly(vinyl alcohol) 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) (PVAc) and poly(vinyl alcohol) (PVA) has been studied.[6] Compatibility was judged from the melting temperature depression. The results indicate that nylon 6/polyvinyl alcohol 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 flame resistant properties of poly(vinyl alcohol)-nylon 6,6 system was the substitution of pure poly(vinyl alcohol) by poly(vinyl alcohol) oxidized by potassium permanganate (PVA-ox). This approach was based on the fire behavior of the (PVA-ox) itself. It was shown experimentally (Cone Calorimeter) the dramatic decrease of the rate of the heat release and significant increase in ignition time for the oxidized PVA in comparison with the original PVA.

The literature on the oxidation of macromolecules by alkaline permanganate presents little information about these redox-systems. One set of workers investigated[7,8] the oxidation of PVA as a polymer containing secondary alcoholic groups by $KMnO_4$ in alkaline solution. It was reported that the oxidation of PVA by in alkaline solutions occurs through formation of two intermediate complexes (1) and/or (2)[8]:



The reactions (a) and (b) lead to the formation of poly(vinyl ketone) (3) as a final product of oxidation of the substrate. Poly(vinyl ketone) was isolated and identified by microanalysis and spectral data.[9]

EXPERIMENTAL

Materials

The polymers used in this work were poly(vinyl alcohol), 99% hydrolyzed, M. W. 86,000, nylon 6,6 and polypropylene, isotactic, were supplied by Scientific Polymer Products, Inc., USA. The inorganic additive was potassium permanganate, R. (BA Chemical Ltd.).

Preparation of Samples, Incorporation of Additive

The samples for combustion measurements (blends of nylon 6,6 and PVA, PVA-ox) were prepared in a laboratory blender at room temperature (10 min), the mixed samples were compression molded at temperature 220–240°C for 10 min.

Poly(vinyl alcohol) was oxidized by $KMnO_4$ in aqueous solution. A 10% wt. aqueous solution of poly(vinyl alcohol) was prepared at 90°C in a laboratory vessel (2 l). $KMnO_4$ (5% by 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 vacua* at 50°C to yield of soft elastic material. This material was heated in an oven for 24 hours 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.

Cone Calorimeter Tests

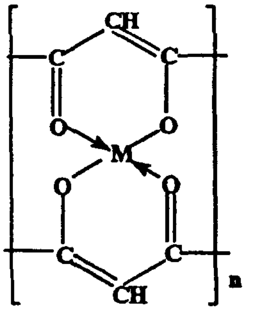
On the polymer samples, as discs (radius 35 mm), were carried out at 20, 30, 35 and 50 kW/m^2. Each specimen was wrapped in aluminum foil and only the upper face was exposed to the radiant heater.

RESULTS AND DISCUSSION

Preliminary cone tests for PVA and PVA oxidized by $KMnO_4$ were carried out at heat fluxes of 20, 35 and 50 kW/m^2 (Table II). It is clearly seen carbon residue (wt. %) and peak of heat release rate (Peak R.H.R. kW/m^2) suggest substantial improvement of fire resistance characteristics for PVA oxidized by $KMnO_4$ in comparison with PVA. PVA oxidized by $KMnO_4$ gives about half the peak of heat release rate (Peak R.H.R. kW/m^2), 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 for PVA oxidized by $KMnO_4$—(polyvinyl ketone structures) to act as a neutral (structure 1) and/or monobasic (structure 2) bidentate ligand.[9]

1 2

The experimental results of others (IR and electronic spectra)[6] provide strong evidence of coordination of the ligand (some metal ions Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+}) through the monobasic bidentate mode (structure 2). Based on the above the following structure can be proposed for the polymeric complexes:



M - metal

The result of elemental analysis of PVA oxidized by $KMnO_4$ indicates the presence of 1.5% of Mn remaining in this polymeric structure. Thus, we 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 cone calorimeter results of two PVA samples mixed with $KMnO_4$ at 100°C and 200°C clearly showed the advantage of chemical reaction of PVA with $KMnO_4$ in the liquid phase in comparison with the solid phase mixtures (Table II).

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 is shown in Figure 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 below. Similar trends are observed for Average Heat Release which was calculated over the total flame out period (Figure 2). The sample with PVA oxidized by $KMnO_4$ displayed even a better flame retardant properties due to the catalytical effect of Mn-chelate fragments on the formation of char (Table II). The superior Rate of Heat Release properties of PVA oxidized by $KMnO_4$ 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 II). Although, the Cone measurements indicate a decrease of Total Heat Release for nylon 6,6-PVA and nylon 6,6-PVA oxidized by $KMnO_4$ in comparison with pure PVA, the sample of nylon 6,6 with PVA oxidized by $KMnO_4$ gives a higher value of Total Heat Release than nylon

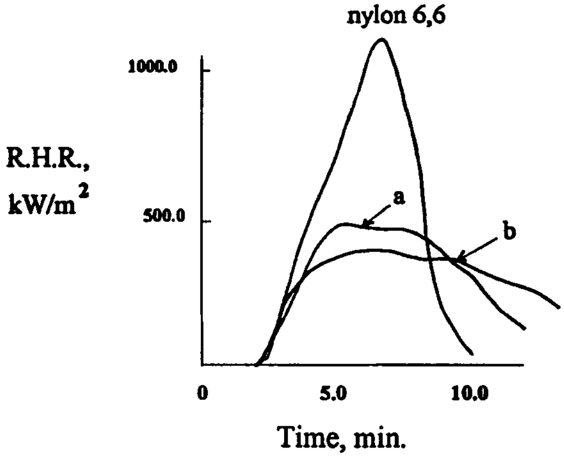


FIGURE 1 Rate of Heat Release vs. time for: nylon 6,6; nylon 6,6/PVA (80%:20% wt)—(a); nylon 6,6/PVA oxidized by $KMnO_4$ (80%:20% wt)—(b) at a heat flux of 50 kW/m².

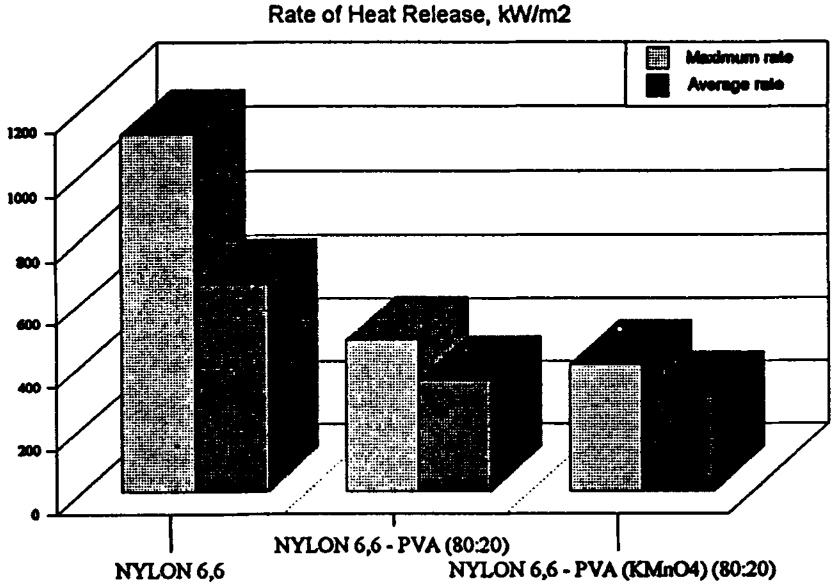


FIGURE 2 Cone Calorimeter Heat Release data for nylon 6,6-PVA compositions at 50 kW/m² of heat flux.

6,6 with PVA (Table II). We have qualitatively explained this fact by the influence of a catalytical amount of chelated Mn-structure incorporated in polymer on the smoldering of the polymer samples.[9] The flame out time for nylon 6,6 with PVA oxidized by $KMnO_4$ is larger than the flame out times of nylon 6,6-PVA and nylon 6,6 (Table III). The values of Average Heat of Combustion indicate the exothermal process of smoldering provided by chelated Mn-structures (Table III). That is why,

TABLE III

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^2

COMPOSITION	Flame out time, sec.	Aver. Heat of Comb.,MJ/kg
nylon 6,6	512	31.50
nylon 6,6-PVA (80:20)	429	25.15
nylon 6,6 - PVA -oxidized by $KMnO_4$ (80:20)	747	29.52

TABLE IV

Cone Data of Nylon 6,6-Melamine Cyanurate (90:10) composition at heat flux of 35 kW/m^2

Cone Data	Ignition time, s.	Peak RHR, kW/m^2	Total Heat Release, MJ/m^2
Nylon 6,6	139	1303	99.0
Nylon 6,6+MC	243	1487	89.0

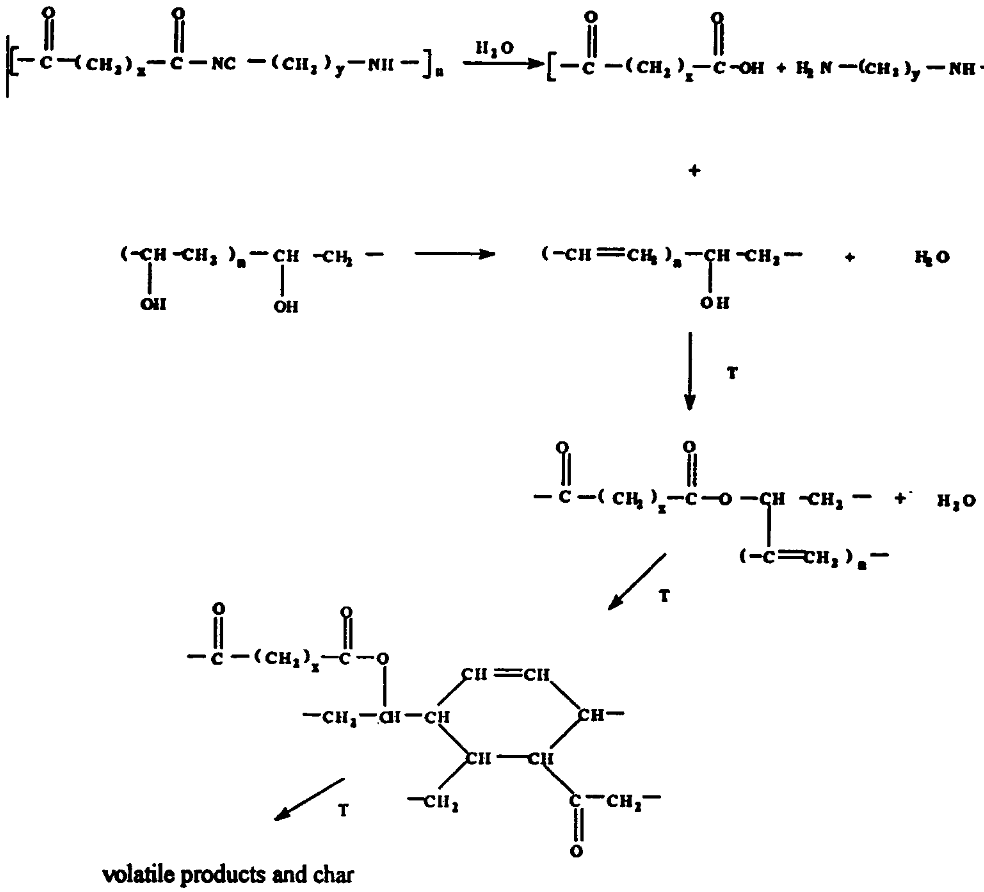
we have found the approximately equal amount of char yield for nylon 6,6-PVA and nylon 6,6-PVA oxidized by $KMnO_4$ (Table II).

CONCLUSIONS

(1) Polymer-organic char former (PVA system) incorporated in Nylon 6,6 reduced the peak rate of heat release from 1124.6 kW/m^2 (for Nylon 6,6) and 777.9 kW/m^2 (for PVA) to 476.7 kW/m^2 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^2 incident flux.)

(2) Cone Calorimeter data of Nylon 6,6 composition with PVA oxidized by $KMnO_4$ (Mn-chelate complexes[9] showed the improvement of peak rate of heat release from 476.7 kW/m^2 (composition of Nylon 6,6 with PVA) to 399.5 kW/m^2 (composition of Nylon 6,6 with PVA-oxidized by $KMnO_4$). On the other hand, the Cone Data indicated the exothermal process of smoldering for composition of nylon 6,6 with PVA-oxidized by $KMnO_4$. This reaction evidently provided by chelated Mn-structures which increases the Total Heat Release of NYLON 6,6 with PVA-oxidized by $KMnO_4$ in comparison with NYLON 6,6 with PVA.

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



SCHEME 1. "Synergistic" Carbonization of NYLON 6,6 and PVA blend.

PART 2

Addition of Melamine Cyanurate

INTRODUCTION

This part of study has been directed on finding ways to suppress the combustion of Nylon 6,6 in gaseous phase. We have studied melamine cyanurate (MC) additive which promote the formation of NH_3—well known inhibitor of gas-phase combustion.

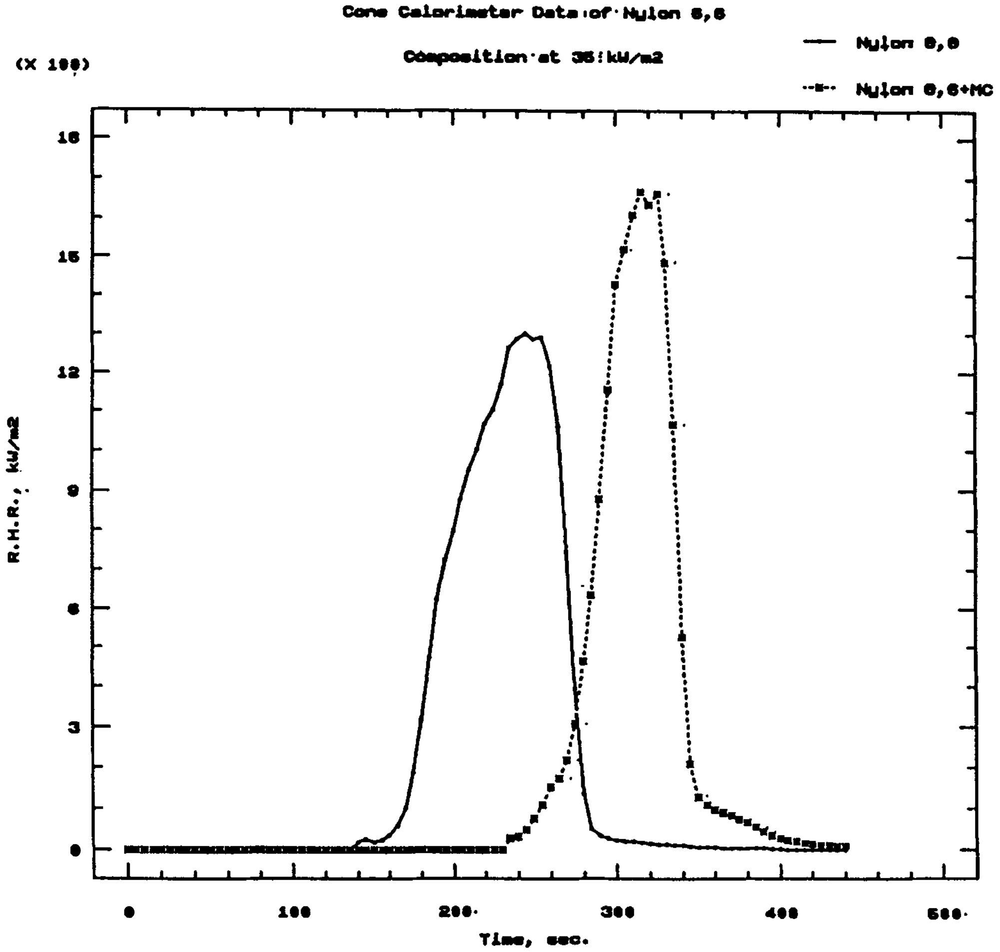


FIGURE 3 Rate of Heat Release vs. time for Nylon 6,6 compositions at heat flux of 35 kW/m^2.

EXPERIMENTAL

Preparation of Samples, Incorporation of Additive

The samples (4—two of each composition) for combustion measurements (Nylon + 10% wt of MC) were compression molded at temperature 220–240°C. Cone Calorimeter tests on the polymer samples, as discs (radius 35 mm), were carried out at 35 kW/m^2. Each specimen was wrapped in aluminum foil and only the upper face was exposed to the radiant heater.

RESULTS AND DISCUSSION

It is clearly seen that incorporation of 10% of MC increase ignition time delay about two times (Table IV, Figure 3) due to NH_3-gas phase inhibition. However, it does

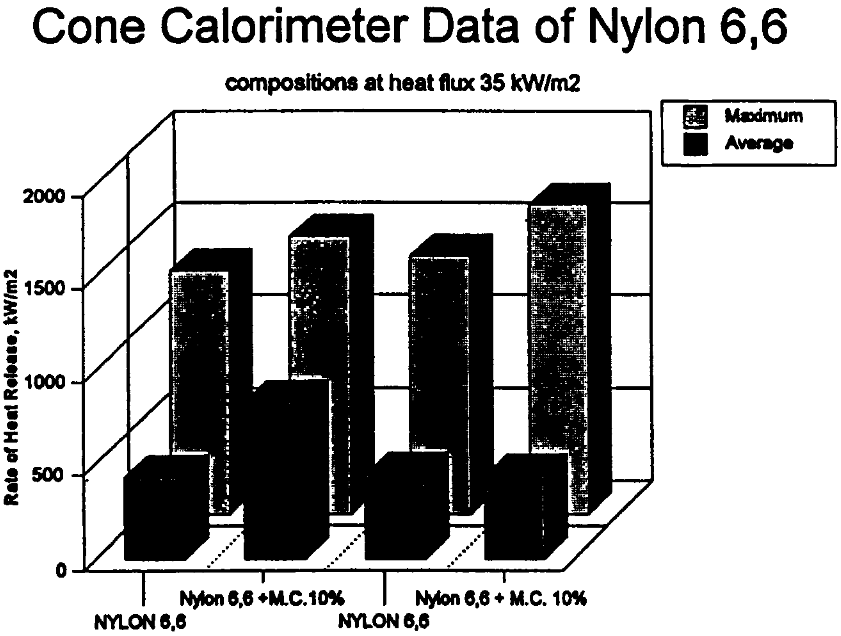


FIGURE 4 Cone Calorimeter Heat Release Rate data for NYLON compositions at 35 kW/m^2 of heat flux.

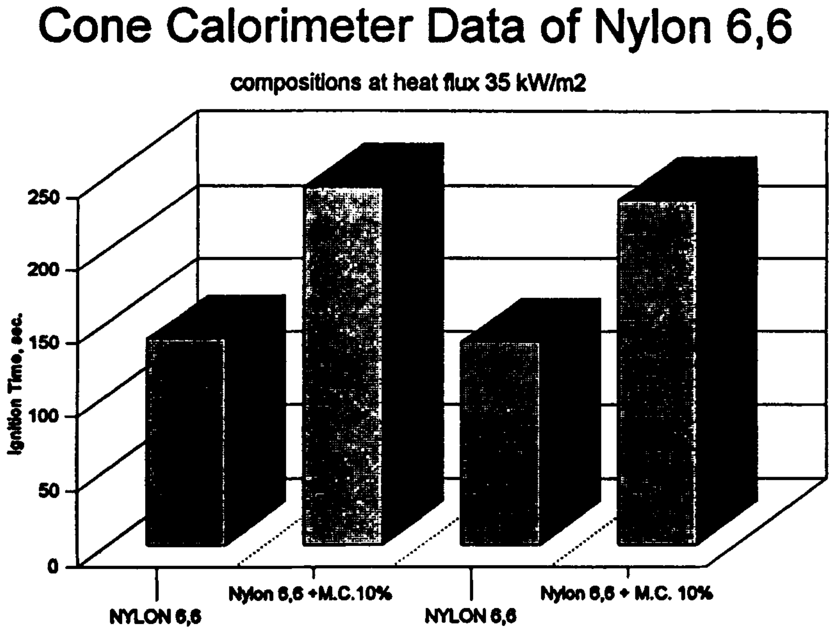


FIGURE 5 Cone Calorimeter Ignition time for NYLON compositions at 35 kW/m^2 of heat flux.

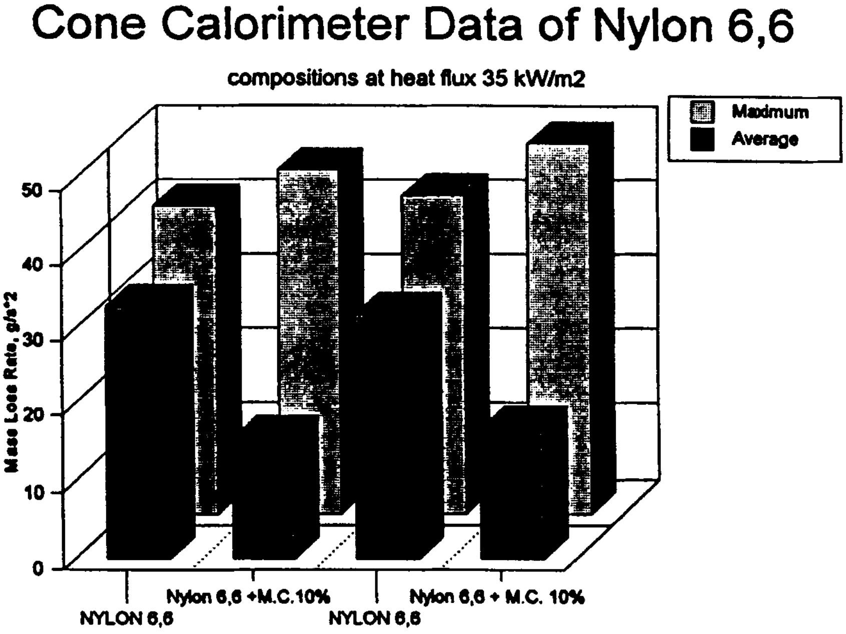


FIGURE 6 Cone Calorimeter Mass Loss Rate data for NYLON compositions at 35 kW/m^2 of heat flux.

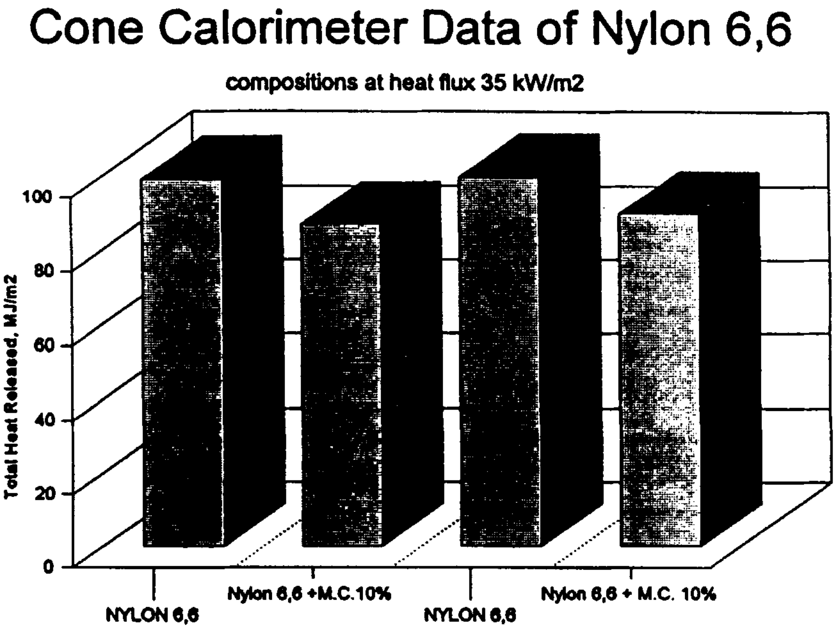


FIGURE 7 Cone Calorimeter total Heat Release data for NYLON compositions at 35 kW/m^2 of heat flux.

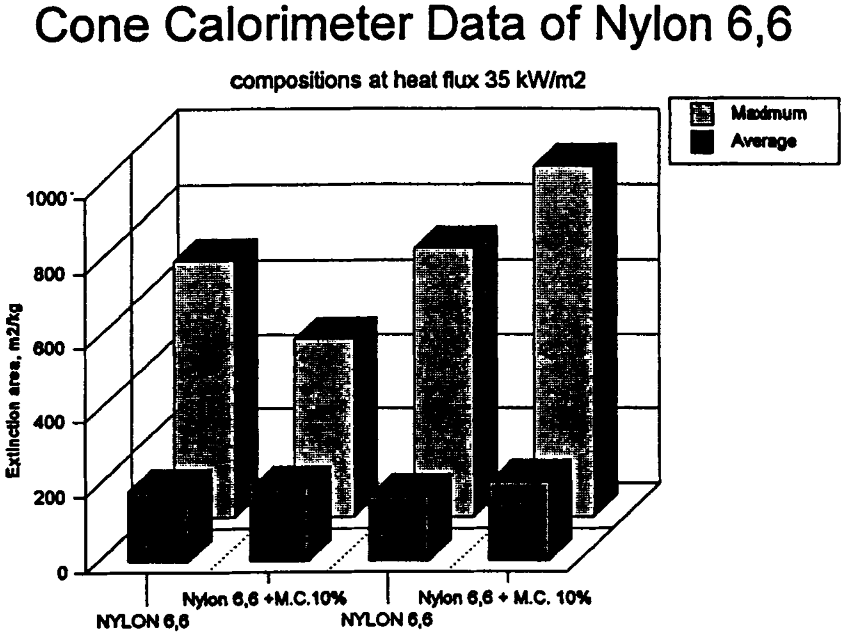


FIGURE 8 Cone Calorimeter Smoke Area data for NYLON compositions at 35 kW/m^2 of heat flux.

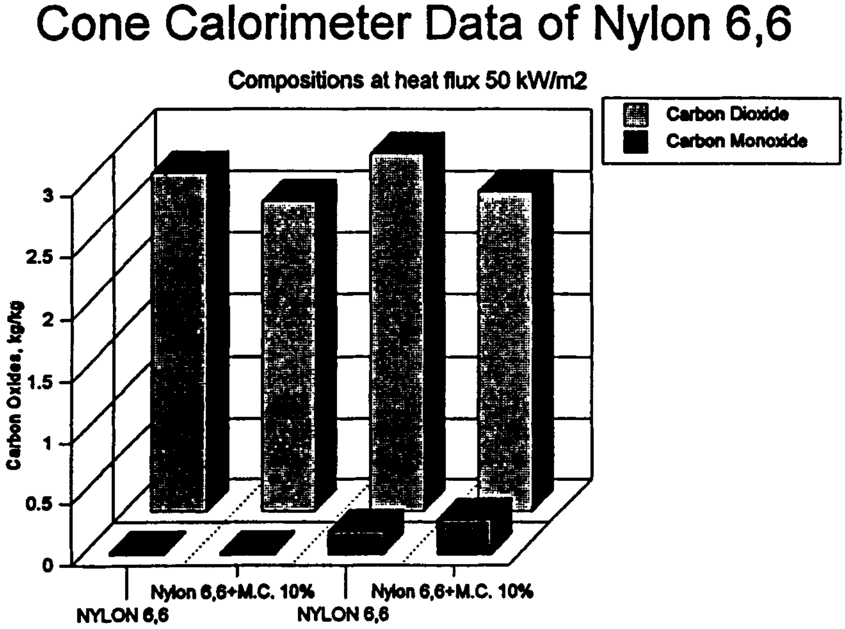


FIGURE 9 Cone Calorimeter Carbon Oxides data for NYLON compositions at 35 kW/m^2 of heat flux.

not effect the other Cone Data (Table IV, Figures 4–9). In both cases the char yield was 0.1 wt %.

CONCLUSIONS

(1) Polymer-organic flame retardant system (Nylon 6,6-MC) significantly increase the ignition period of gas combustion for Nylon 6,6.

(2) We can propose a complex flame retardant system for Nylon (PVA-10%, MC-10%, Nylon 6,6-80%) which can "effect" on the combustion process in gas phase as well as in the solid phase.

PART 3

Si-Flame Retardants Systems

INTRODUCTION

In modern polymer industry the overall use of halogenated flame retardants is still showing an upward trend, the preceding concerns have started a definite search for environmentally friendly polymer additives. As a result of these trends, it is quite possible that the available selections both of polymer materials and of flame retardants will be more limited than in the past.

According to recent patent publications silicone (additives) may be considered as a universal additive to improve the flammability properties of polymers and to decrease the harmful impact on an environment safety.

Our informal preliminary studies have found that the addition of relatively small amounts of different types of silicone (additives) to various polymers significantly reduce their flammability. Although the results suggest that the effects of the addition of silicone are most likely in the condensed phase ("preceramic-transition state" (SiPS), at present it is not clear what chemical or physical processes cause the above improvement in flammability characteristics of various polymers. At this time our study of NYLON 6,6-SiPS system is in progress. We hope finally come to the principle conclusions on SiPS-NYLON 6,6 flame behavior within a couple of months.

On the other hand we have found a very interesting Si-inorganic system (SI) which in the first place inhibits *gaseous phase* combustion, and also affects on the char formation in *solid* one. Previously we have studied some flame retardant properties of SI incorporated into different types of polymers (polypropylene, PMMA).

The mechanism of SI flame suppression based (postulated) on reaction of gaseous-phase inhibition by $SiCl_4$ and HCl which can be produced only at temperatures above 300°–500°C[10] exactly the temperatures realized on the surface of burning polymers:

350°-500°C

$$1.\ 2\ SnCl_2 + nSi = 2\ Sn + (n - 1)Si + SiCl_4$$

$$SiCl_4 + 2\ H_2O = 4\ HCl + SiO_2$$

410°C

$$2.\ 2\ PbCl_2 + nSi = 2\ Pb + (n - 1)Si + SiCl_4$$

280°-350°C

$$3.\ 4\ CuCl + nSi = 4\ Cu + (n - 1)Si + SiCl_4$$

300°C

$$4.\ 2\ CaCl_2 + nSi = 2\ Ca + (n - 1)Si + SiCl_4$$

400°C

$$5.\ 4\ FeCl_3 + nSi = 4\ Sn + (n - 1)Si + 3SiCl_4$$

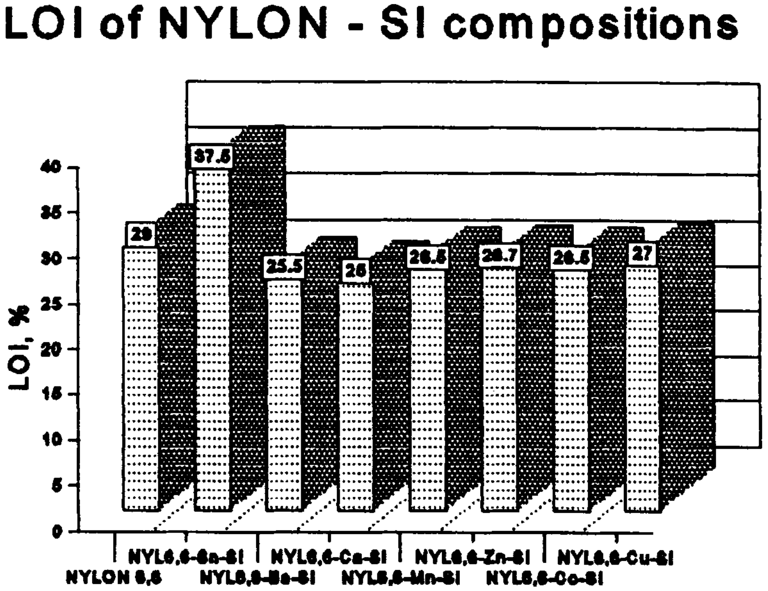
The position of silicon directly below carbon in the periodic table suggests that the chemistry of these elements will be similar. Like carbon, silicon has a valency of four. Silicon (II) is not stable, however, the tendency to form divalent compounds increases with atomic weight so that compounds of the form SnL_2 and PbL_2 (where L is used to denote an arbitrary ligand) are relatively common. The Group IVA elements, other than carbon, do not form strong bonds with like atoms. The Si—Si bond, for example, is notably weaker (222 kJ/mole) than the Si—C bond (328 kJ/mole) (Table V).[11]

The silicon analog of the halons, in particular, would be expected to be effective flame inhibitors. This hypothesis was confirmed early on, at least with respect to silicon tetrachloride ($SiCl_4$).

TABLE V

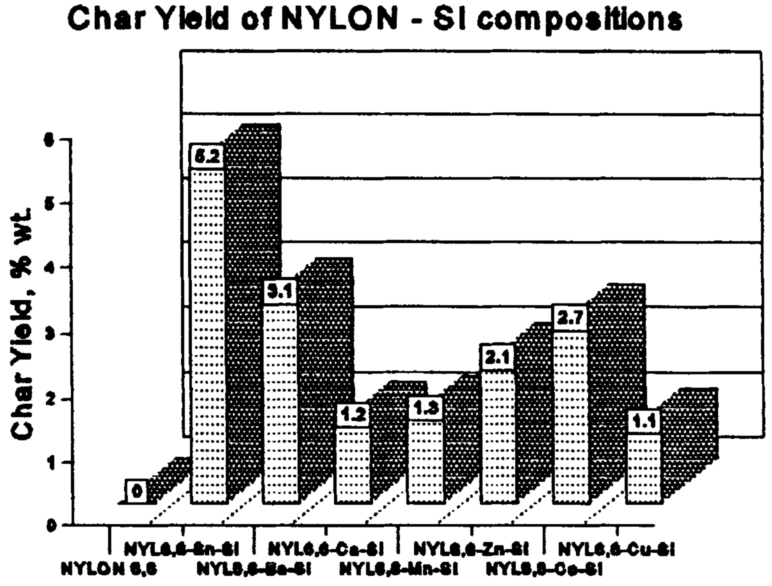
Energy of Si-El bonds

Si-El bonds	kJ/mol
Si-O	445
Si-Cl	382
Si-H	319
Si-Si	222
Si-C	328
C-O	359
C-Cl	340
C-C	348



LOI of NYLON - SI compositions

FIGURE 10 LOI data for NYLON 6,6 compositions with: $SnCl_2$-Si (2:3% wt), $BaCl_2$-Si (2:3% wt), $CaCl_2$-Si (2:3% wt), $MnCl_2$-Si (2:3% wt), $ZnCl_2$-Si (2:3% wt), $CoCl_2$-Si (2:3% wt), $CuCl_2$-Si (2:3% wt).



Char Yield of NYLON - SI compositions

FIGURE 11 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), $CuCl_2$-Si (3:2% wt) (TGA analysis, 750°C, air).

Silicon Tetrachloride

Normal boiling point (C): 58
Vapor pressure at 298 K (atm): 0.31
Heat capacity at 298 K (J K-1 mole-1): 145
Heat of vaporization at nbp (kJ mole-1): 32
Toxicity: Medium[12]

Obviously, if both families of chemicals behaved similarly with respect to all properties, including ozone depletion and global warming potentials, there would be no reason to continue this investigation. There are, however, significant differences in the behavior of these compounds in the atmosphere. Unlike the halons, all of the halosilanes readily hydrolyze in moist air.[13] 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 silicon-halogen bond in a molecule is sufficient to make its vapors corrosive and dangerous to breathe.[13]

But for (SI-flame retardant-NYLON 6,6) this harmful influence is not so important for us because HCl forms in the zone of combustion only at the temperatures above 500–600°C and also takes part (is consumed) in the flame inhibition and reactions with tin (apparently $SnCl_4$ formation).

A list of results was published in Lyon's book on fire retardants[14] and in a review article.[15] 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 $SiCl_4$ was 9.9%. On the basis of this criteria, the flame suppression efficiency of $SiCl_4$ is between halon 1301 (CF_3Br) and carbon tetrachloride (CCl_4) which were found to have peak values of 6.1% and 11.5%, respectively.

In an independent study it was conducted flame velocity measurements for a series

TABLE VI

LOI and Thermal Analysis Data of NYLON 6,6-SI compositions

Nylon - SI compositions (metal)	LOI, %	$T_{fus.}$, C	$T_{max.}^{1}$, C	$T_{max.}^{II}$, C	Char yield, % 750°C, air
NYLON 6,6	29	252	430	-	0
-"- $SnCl_2$	37.5	248	370	448	5.2
-"- $BaCl_3$	25.5	244	418	-	1.2
-"- $CaCl_2$	25	245	403	477	3.1
-"- $MnCl_3$	26.5	255	391	459	1.3
-"- $ZnCl_2$	26.7	255	388	461	2.1
-"- $CeCl_2$	26.5	268	419	463	2.7
-"- $CuCl_2$	27.0	248	438	-	1.1

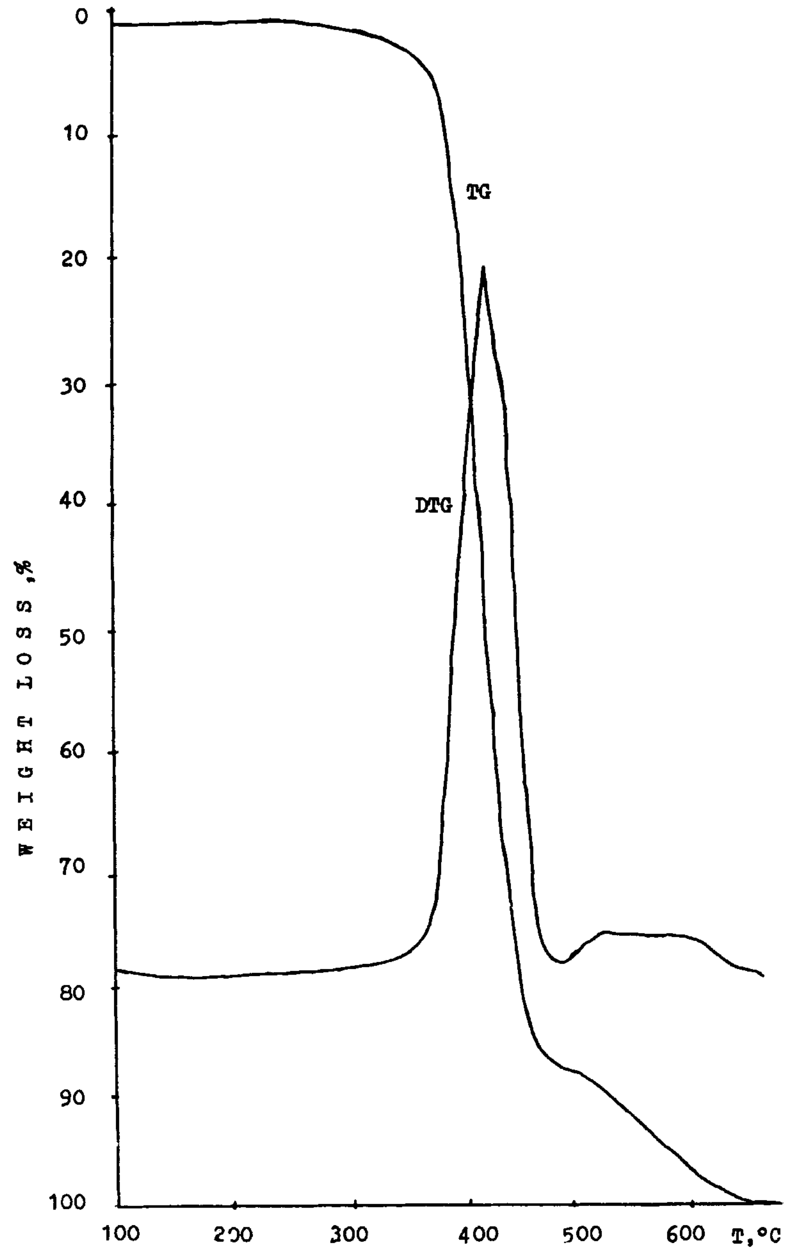


FIGURE 12 The curve of weight loss for thermal decomposition in air of nylon 6,6.

of additives including some halosilanes and related compounds.[16] 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 $SiCl_4$ (0.56%) was comparable to Br_2 (0.7%) but considerably more effective than CCl_4 (1.38%).

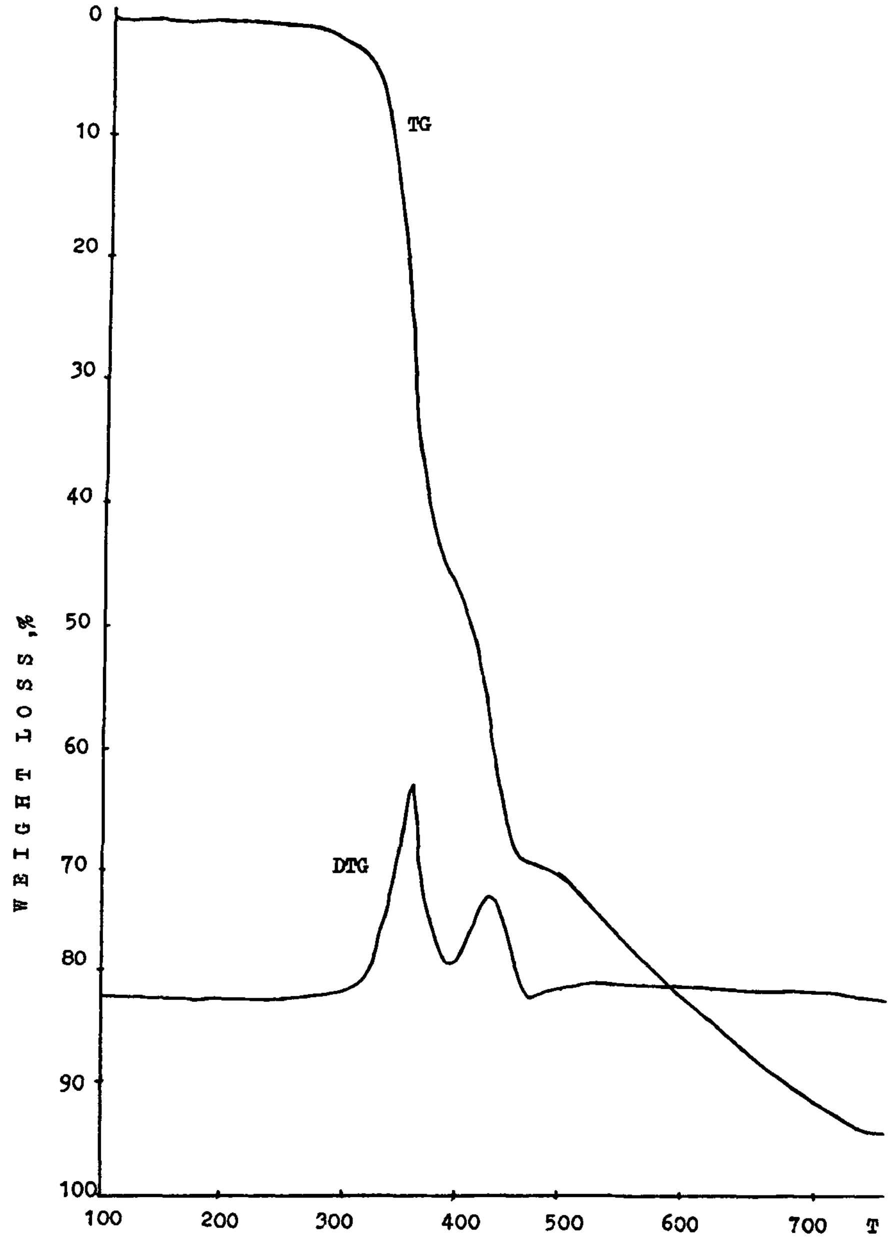


FIGURE 13 The curve of weight loss (TG) and DTG for thermal decomposition in air of the blend nylon 6,6 with Si and $SnCl_2$ (95:3:2).

Flame velocity measurements were also reported by Lask and Wagner on two additional tetrachlorides of the Group IVA elements. The values of 0.50% and 0.19% were reported for $GeCl_4$ and $SnCl_4$, respectively. The hierarchy for inhibition: $SnCl_4$ > $GeCl_4$ > $SiCl_4$ > CCl_4 was also found to apply to increases in the ignition temperatures of hydrocarbon/(O_2 + N_2) mixtures.[16] No explanation for this trend has

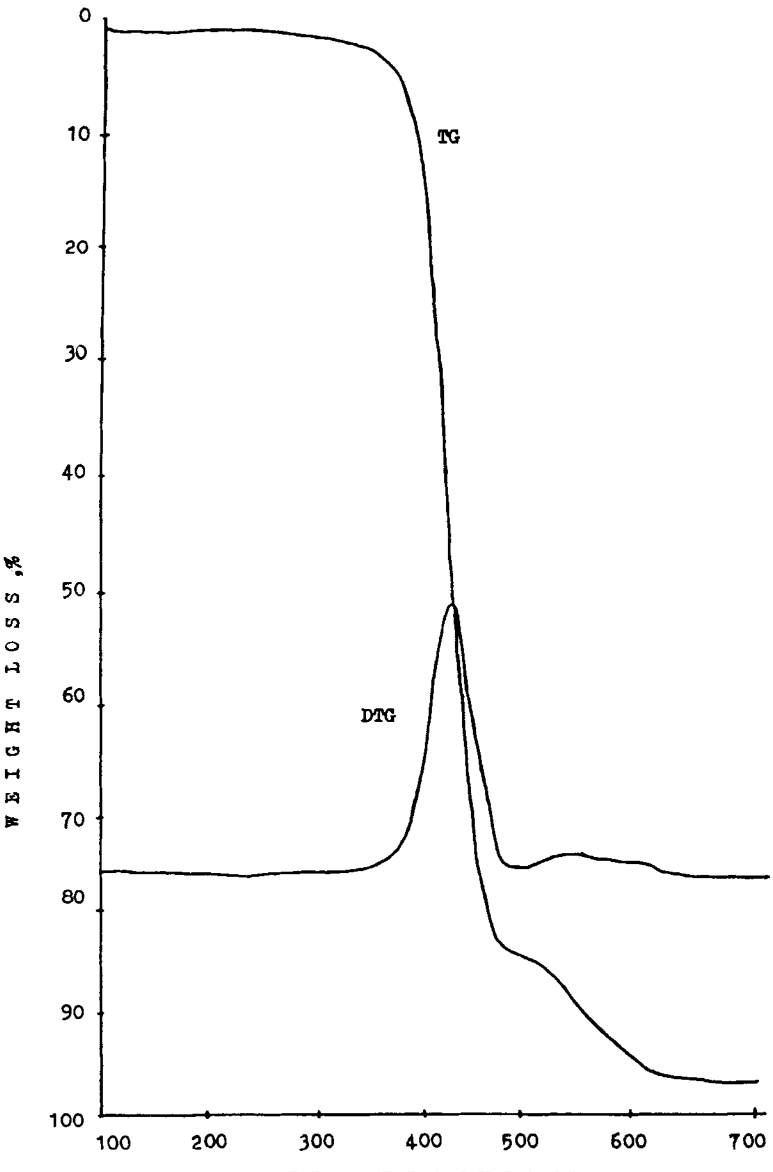


FIGURE 14 The curve of weight loss (TG) and DTG for thermal decomposition in air of the blend nylon 6,6 with Si and $BaCl_2$ (95:3:2).

been found, however, it may have some relevance to the problem of interest. It is known that the susceptibility to hydrolysis of compounds involving Group IVA elements decreases with increasing atomic weight.[17] Thus, the most potent inhibitors may, in fact, be the least corrosive. Unfortunately, the drop-off may not be fast enough to yield practical benefits. Thus, $SnCl_4$ readily hydrolyses and, as a consequence, it is highly corrosive[12]:

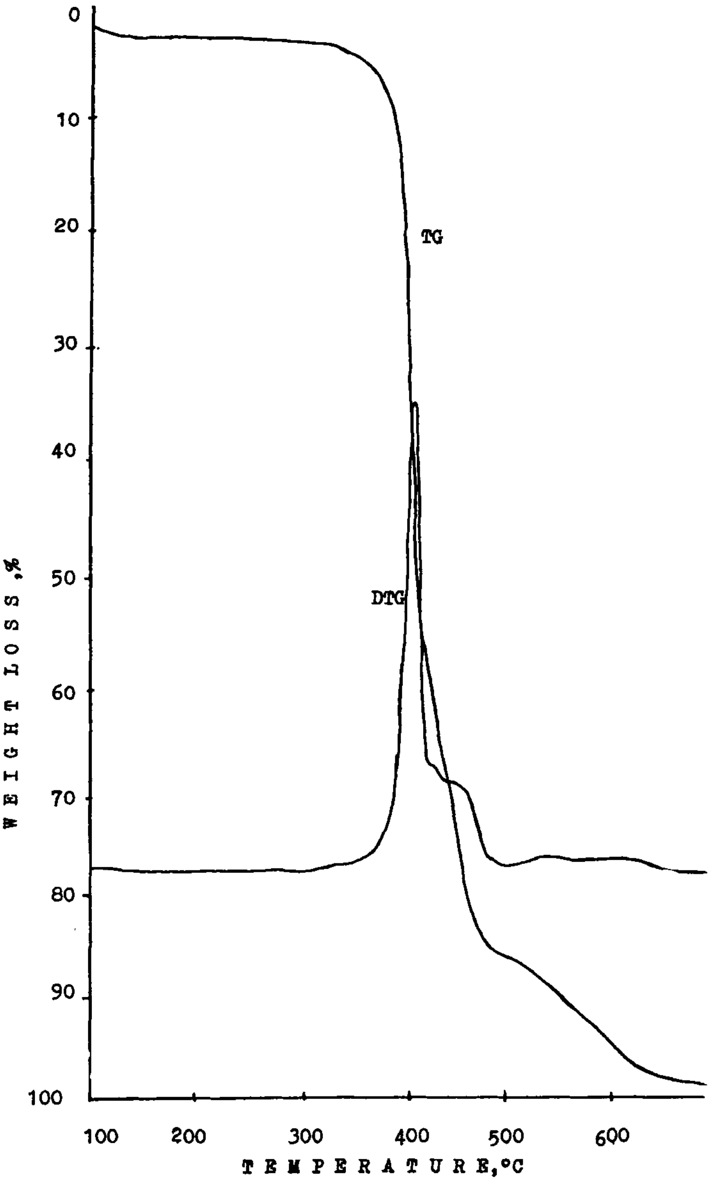


FIGURE 15 The curve of weight loss (TG) and DTG for thermal decomposition in air of the blend nylon 6,6 with Si and $CaCl_2$ (95:3:2).

Tin (IV) Chloride

Normal boiling point (C): 114
Vapor pressure at 298 K (atm): 0.030
Heat capacity at 298 K (J K-1 mole-1): 165
Heat of vaporization at nbp (kJ mole-1): 37
Toxicity: High[12]

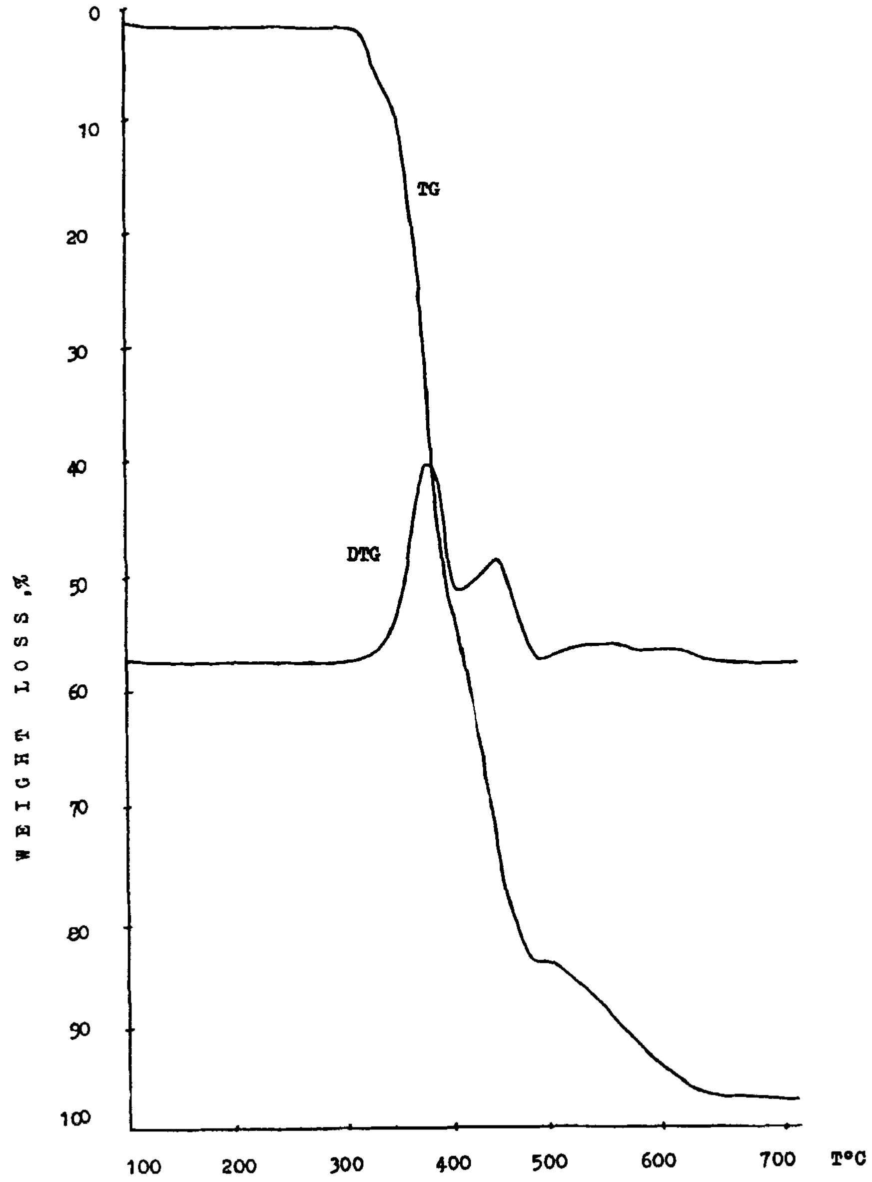


FIGURE 16 The curve of weight loss (TG) and DTG for thermal decomposition in air of the blend nylon 6,6 with Si and $MnCl_2$ (95:3:2).

On the other hand, lead chloride ($PbCl_2$), which does not hydrolyze, is a solid. The toxicity of this compound is probably due more to the presence of a heavy metal than to HCl.

The mechanism by which the halosilanes effect flame inhibition is probably similar, if not identical, to the well known halons.[14–16]

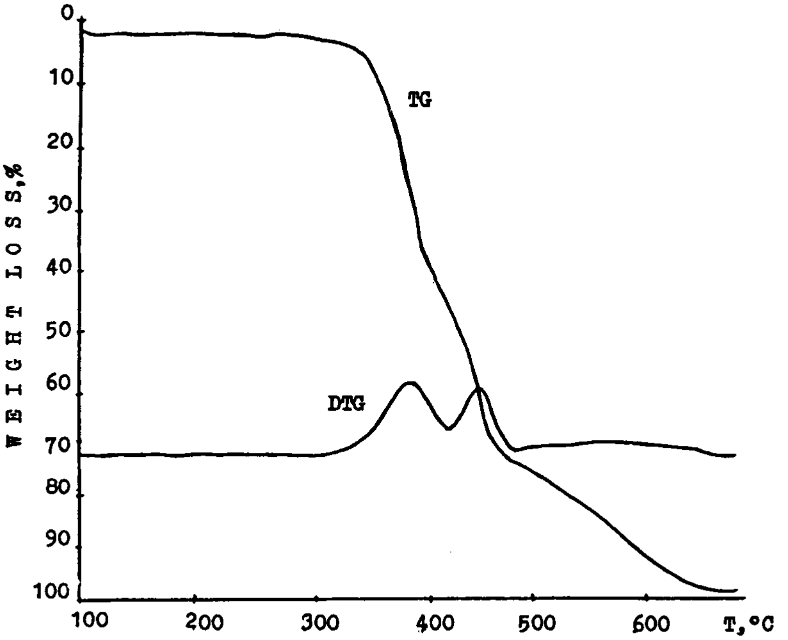


FIGURE 17 The curve of weight loss (TG) and DTG for thermal decomposition in air of the blend nylon 6,6 with Si and $ZnCl_2$ (95:3:2).

EXPERIMENTAL

Materials

The inorganic additives used in this work were, 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), $CaCl_2 \cdot 6H_2O$ A.C.S. (REACHIM).

Preparation of Samples, Incorporation of Additive

The samples for combustion measurements (Nylon 6,6 + SI) were compression molded at temperature 240–280°C in ratio NYLON 6,6:Si:$MeCl_2$-(95:3:2 % wt).

LOI tests on the polymer samples, as bars ($d = 4$ mm), were carried out at according to ASTM-D2863 (Russian Standard 12.1.044-89). Self-ignition tests were carried out using ICP Furnace (5–10 mg). Thermal analyses (TA, TGA) were performed in air using DERIVATOGRAPH Q thermoanalyzer (at heating rate of 10°C/min).

RESULTS AND DISCUSSION

Experimental results of Thermal analysis and Combustion tests (LOI, Self-ignition) of NYLON 6,6-SI compositions are presented in Table II and Figures 1–12. LOI-

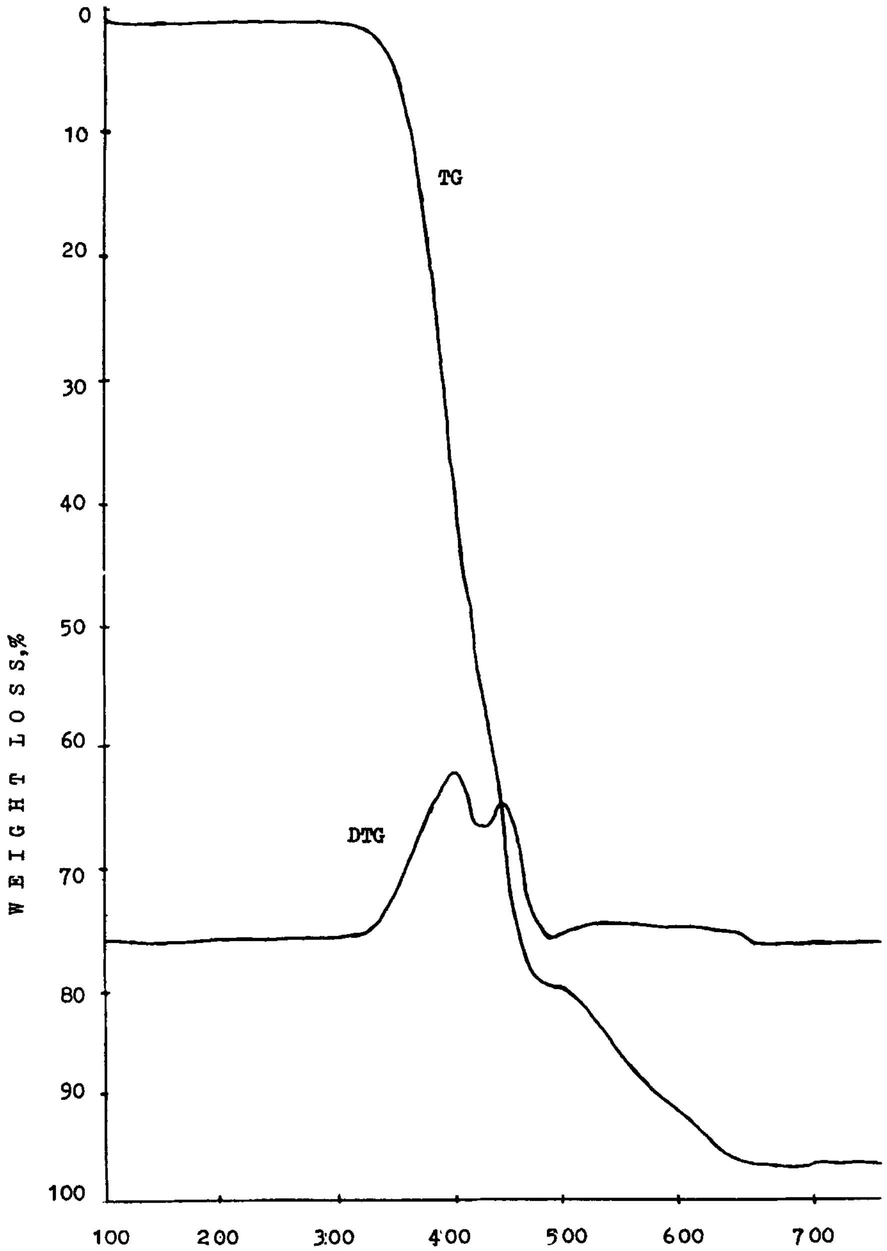


FIGURE 18 The curve of weight loss (TG) and DTG for thermal decomposition in air of the blend nylon 6,6 with Si and $CoCl_2$ (95:3:2).

results clearly showed that incorporation of only $SnCl_2$ + Si (2:3 % wt) SI-composition in NYLON 6,6 has substantial flame retardant effect in comparison with the other SI-systems (Figures 10, 11, Table VI).

The 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 incor-

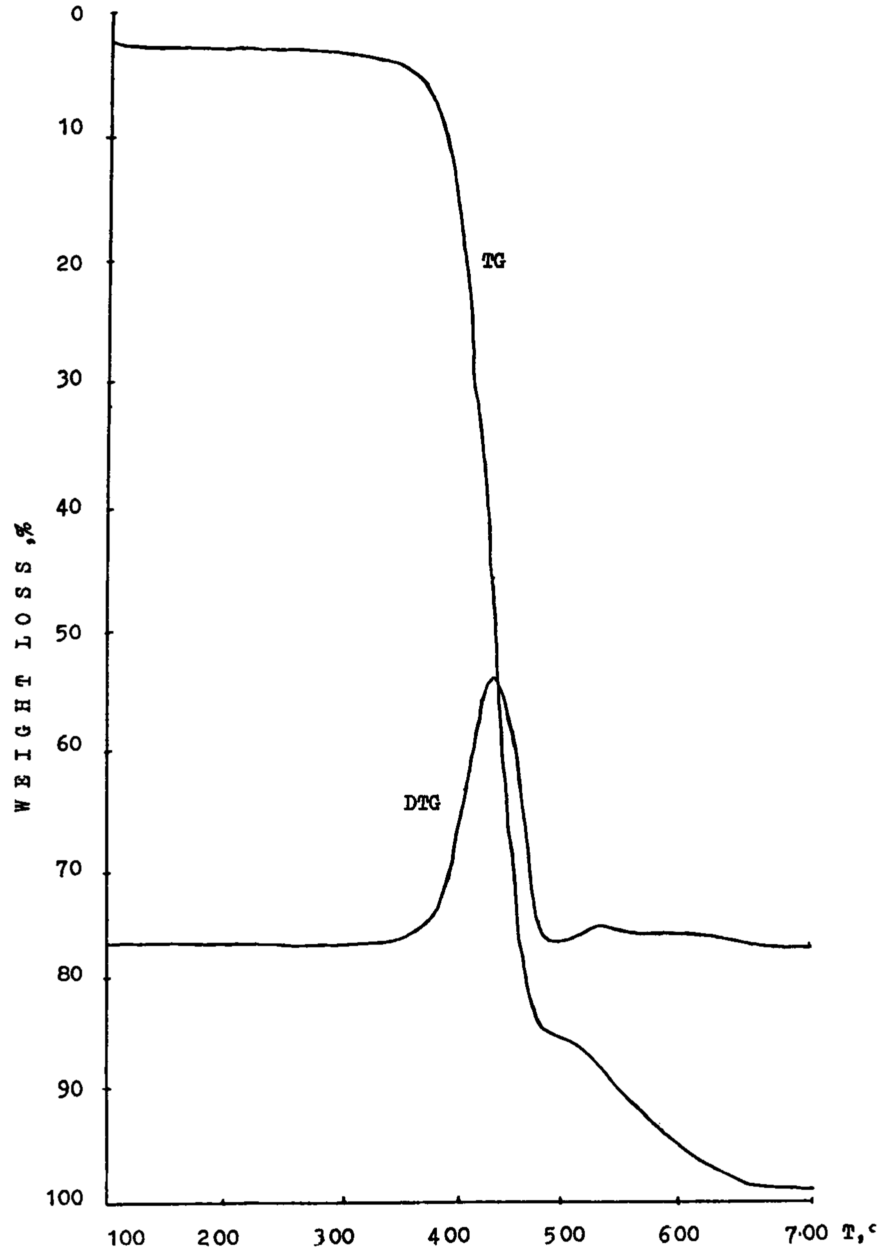


FIGURE 19 The curve of weight loss (TG) and DTG for thermal decomposition in air of the blend nylon 6,6 with Si and $CuCl_2$ (95:3:2).

poration of $SnCl_2$, $CaCl_2$, $ZnCl_2$, $CoCl_2$, $MnCl_2$ (Figures 12–14). Unlike to pure NYLON 6,6 and SI-compositions with $BaCl_2$, $CuCl_2$ compositions with $SnCl_2$, $CaCl_2$, $ZnCl_2$, $CoCl_2$, $MnCl_2$ have the separate "second" pronounced peak in derivative thermograms (Figures 3–10). This fact can be also confirmed by the difference in

TABLE VII

Ignition time delays (sec) of NYLON 6,6-SI compositions at temperature of 835°C

NYLON 6,6	NYLON - $SnCl_2$-SI	NYLON - $MnCl_2$-SI	NYLON - $CoCl_2$-SI	NYLON - $CaCl_2$-SI	NYLON - $BaCl_2$-SI	NYLON - $ZnCl_2$-SI
0	8.8	8.0	7.6	7.0	6.6	6.2

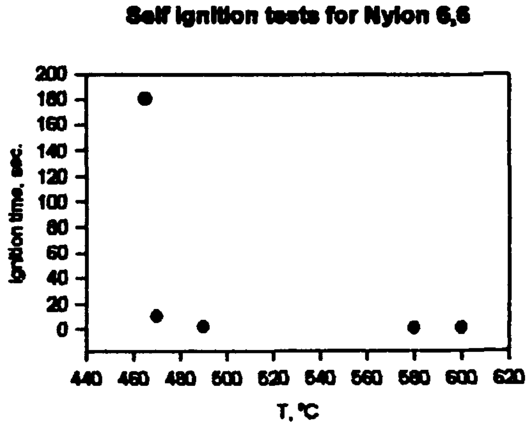


FIGURE 20 Ignition time delays vs. T°C for pure NYLON 6,6.

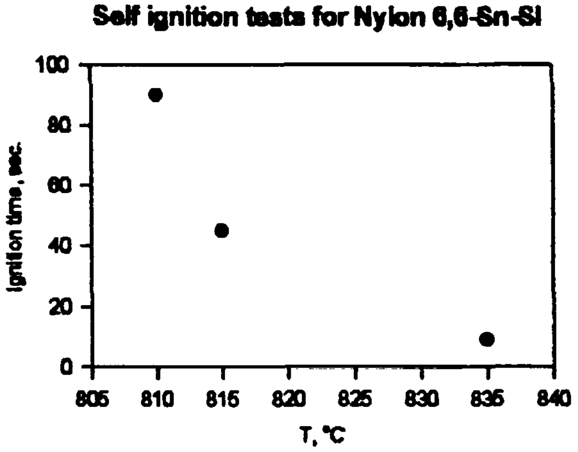


FIGURE 21 Ignition time delay vs. T°C for NYLON 6,6-Sn-SI-composition.

the char yield at 750°C (Table II). These observations can indicate the process of solid state crosslinking and char formation provided by $SnCl_2$, $CaCl_2$, $ZnCl_2$, $CoCl_2$, $MnCl_2$.

However, significant flame retardancy effect (LOI = 37.5 and flame ignition time) has only SI compositions with $SnCl_2$.

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 amount of Sn get into gas phase (*apparently $SnCl_4$ formation*).

As it was mentioned above, the hierarchy for inhibition: $SnCl_4 > GeCl_4 > SiCl_4 > CCl_4$ was found to apply to increases in the ignition temperatures of hydrocarbon/($O_2 + N_2$) mixtures.[7] It means that $SnCl_4$ has the highest flame retardant effectiveness in Group IVA elements. We may suggest that unique flame retardancy of NYLON 6,6-SI composition (with $SnCl_2$) can be achieved by acting $SiCl_4$, HCl and $SnCl_4$ as inhibitors of gaseous phase combustion. These conclusions are confirmed by the Self-ignition tests (Table VII, Figures 20, 21).

Data in Table III show that all $MeCl_2$-SI compositions have ignition delay in consecutive order: $SnCl_2$-SI > $MnCl_2$-SI > $CoCl_2$-SI > $CuCl_2$-SI > $BaCl_2$-SI > $ZnCl_2$-SI >> NYLON 6,6 (0).

But only $SnCl_2$-SI-NYLON 6,6 composition has essential flame retardancy effect (LOI = 37.5), as well as drastic change (increase) of Ignition time delay vs. T°C (Figures 20, 21).

CONCLUSIONS

The flame retardant system based on Si (3% wt) and $SnCl_2$ (2% wt) incorporated in NYLON 6,6 acts as effective inhibitor of gaseous phase flame reactions and may be considered as new type of NYLON 6,6 flame protector.

Our future goal is to study and propose a new type of Si-additive which acts in the condensed phase via "preceramic-transition state" (SiPS) and also can inhibit combustion in the gaseous one.

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