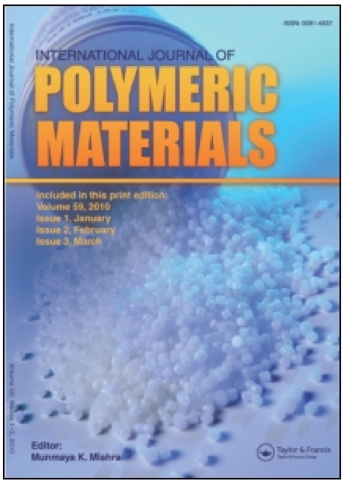

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New Types of Ecologically Safe Flame Retardant Polymer Systems

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New types of ecologically safe flame retardant composition based on poly(vinyl)alcohol and poly(vinyl)alcohol oxidized by $KMnO_4$ (polymer-organic char formers) were proposed for nylon 6,6. These systems can promote the formation of char by intermolecular crosslinking ("synergetic carbonization"). The Cone Calorimeter tests indicated the improvement of fire retardant properties for the compositions of nylon 6,6 with poly(vinyl)alcohol and poly(vinyl)alcohol oxidized by $KMnO_4$ in comparison with pure nylon 6,6.

KEY WORDS Flame retardants, nylon 6,6, poly(vinyl)alcohol, ecology.

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 poly(vinyl(alcohol) (PVA) in NYLON 6,6 is proposed.

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TABLE I

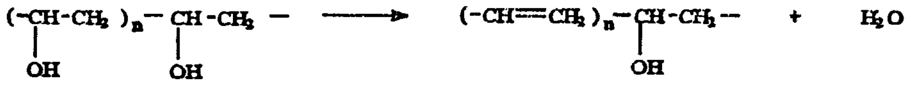
Thermal decomposition products (240°C, four hours)[1]

Products	**% by weight of original polymer**
Water	33.400
CO	0.120
CO_2	0.180
Hydrocarbons (C_1 - C_3)	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

HIGH TEMPERATURE POLYMER-ORGANIC CHAR FORMER

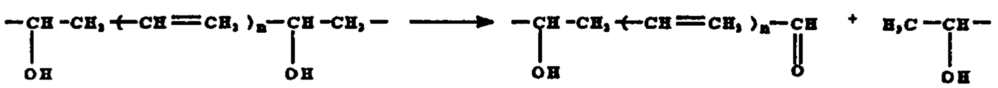
Our study has been directed at finding ways to increase the tendency of plastics to char when they are burned. There is a strong correlation between char yield and fire resistance. This follows because char is formed at the expense of combustible gases and because the presence of a char inhibits further 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:



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

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



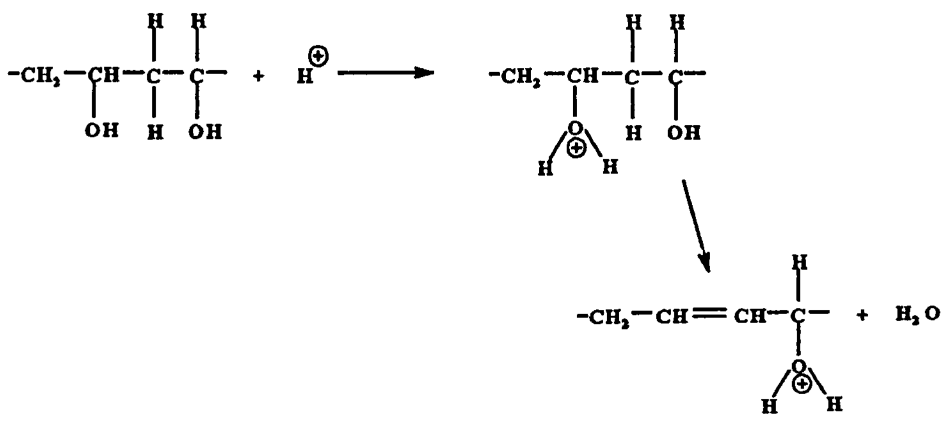
$$-\underset{OH}{CH}-CH_2-(CH{=}CH)_n-\underset{OH}{CH}-CH_2- \longrightarrow -\underset{OH}{CH}-CH_2-(CH{=}CH)_n-\underset{O}{\overset{\|}{CH}} + H_3C-\underset{OH}{CH}-$$

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]

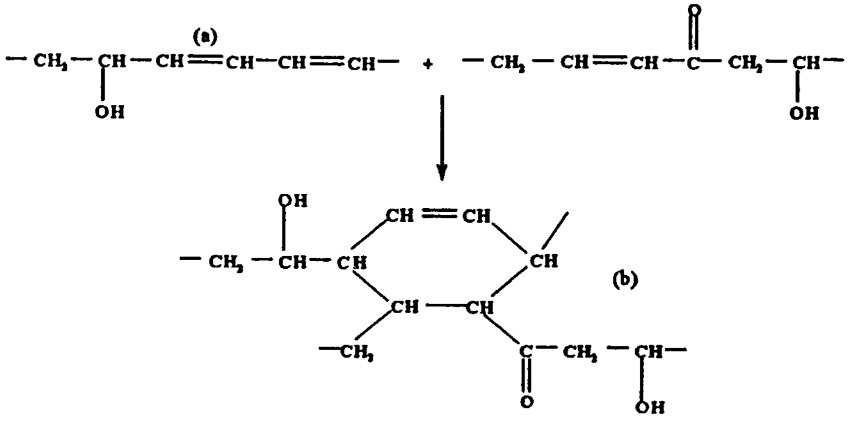
Thermal degradation of PVA in the presence of oxygen can be adequately described by a two-stage decomposition scheme, with one modification. Oxidation of the unsaturated polymeric residue from dehydration reaction introduces ketone groups into the polymer chain. These groups then promote the dehydration 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 cm^{-1} (C=C stretching in isolated double bonds), 1650 cm^{-1} (C=C stretching in conjugated diens and 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.

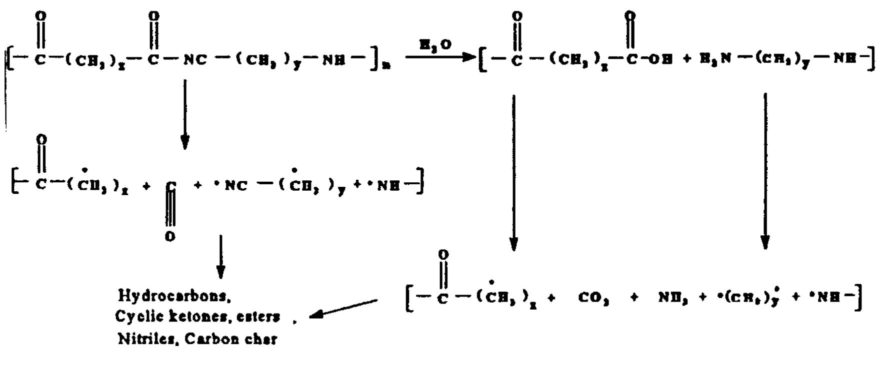
The identification of a low concentration of benzene among the volatile products of PVA[2] has been taken to indicate the onset of a crosslinking reaction proceeding by a Diels-Alder addition mechanism.[2] Clearly benzenoid structures are ultimately formed in the solid residue, and the IR spectrum of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

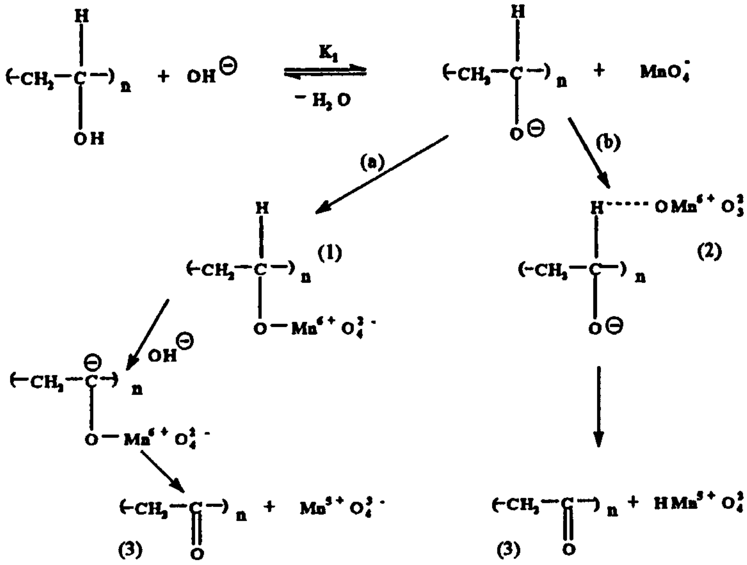


TABLE II

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

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 Chemicals Ltd.).

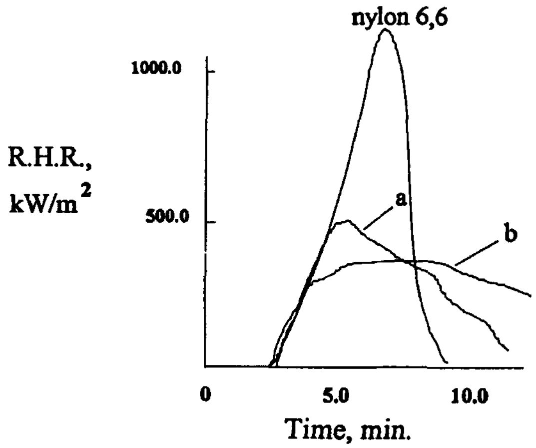


FIGURE 1 Rate of heat release vs. time for: nylon 6,6; nylon 6,6/PVA (80%:20% wt.)—(a); nylon 6,6/PVA oxidized by $KMnO_4$ (80%:20% wt.)—(b) at a heat flux of 50 kW/m^2.

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.

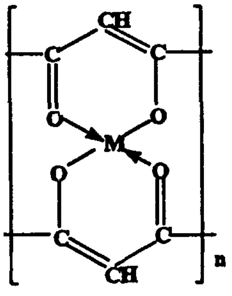
Cone calorimeter tests on the polymer samples, as discs (radius 35 mm), were carried out at 20, 30, 35 and 50 kW/m^2. Each specimen was wrapped in aluminum foil and only the upper face was exposed to the radiant heater.

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 $KMn0_4$ 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 $KMn0_4$ at 100°C and 200°C clearly showed the advantage of chemical reaction of PVA with $KMn0_4$ 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 $KMn0_4$ 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 $KMn0_4$ 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 data (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 $KMn0_4$ in comparison with pure PVA, the sample of nylon 6,6 with PVA oxidized by $KMn0_4$ gives a higher value of Total Heat Release than nylon 6,6 with PVA (Table II). We have qualitatively explained this fact by the influence of a catalytical amount of chelated

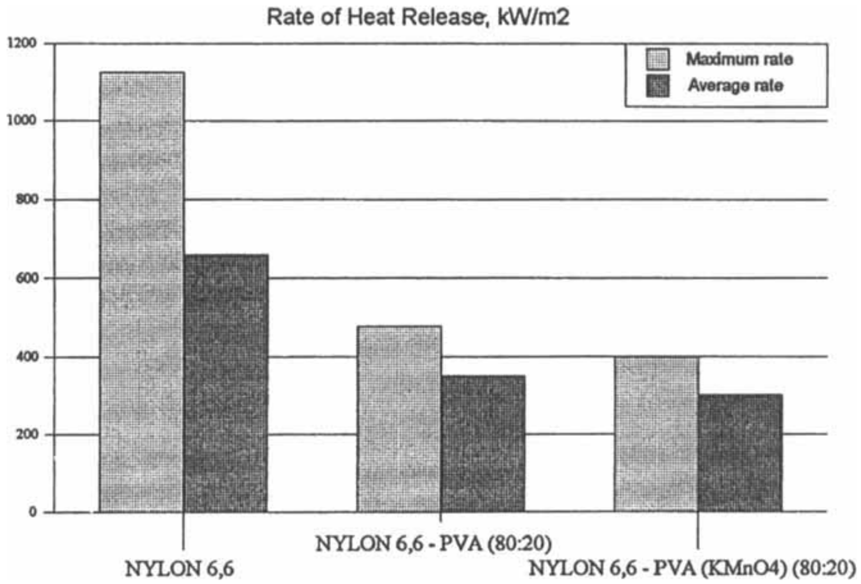


FIGURE 2 Cone Calorimeter heat release data for nylon 6,6-PVA compositions at 50 kW/m^2 of heat flux.

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

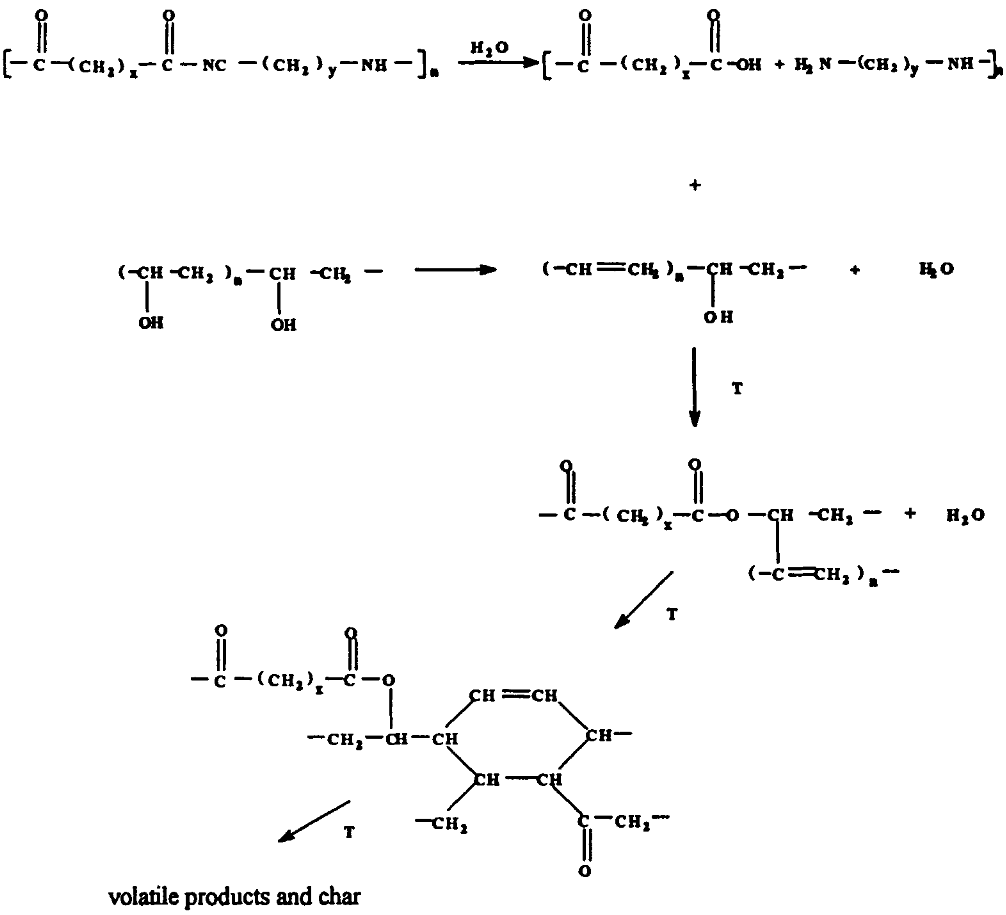
COMPOSITION	**Flame out time, sec.**	**Aver. Heat of Comb.,MJ/kg**
nylon 6,6	**512**	**31.50**
nylon 6,6-PVA (80:20)	**429**	**25.15**
nylon 6,6 - PVA -oxidized by $KMnO_4$ (80:20)	**747**	**29.52**

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, 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

Scheme of "Synergistic" Carbonization of NYLON 6,6 and PVA blend



(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 KMn0$_4$ (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 KMn0$_4$). On the other hand, the Cone Data indicated the exothermal process of smoldering for composition of nylon 6,6 with PVA-oxidized by KMn0$_4$. This reaction evidently provided by chelated Mn-structures which increases the Total Heat Release of NYLON 6,6 with PVA-oxidized by KMn0$_4$ 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.

Literature Cited

1. Y. Tsuchiya and K. Sumi, *J. Polym. Sci., A-1*, **7**, 3151 (1969).
2. "Polyvinyl Alcohol. Properties and Applications," ed. by C. A. Finch, John Wiley & Sons, London-New York-Sydney-Toronto, 1973, 622 pp.
3. B. G. Achhammer, F. W. Reinhard and G. M. Kline, *J. Appl. Chem.*, **1**, 301 (1951).
4. I. Goodman, *J. Polymer Sci.*, **13**, 175 (1954).
5. "Thermal Stability of Polymers," ed. by R. T. Conley, Marcel Dekker Inc., New York, 1970, Vol. **1**, p. 350.
6. Chang-Sik Ha, Won-Ki Lee, Tae-Woo Roe and Won-Jei Cho, *Polymer Bulletin*, **31**, 359–365 (1993).
7. R. M. Hassan, *Polymer International*, **30**, 5–9 (1993).
8. R. M. Hassan, S. A. El-Gaiar and A. M. El-Summan, *Polymer International*, **32**, 39–42 (1993).
9. R. M. Hassan, M. A. Abd-Alla and M. A. El-Gahmi, *J. Mater. Chem.*, **2**, 613 (1992).