Some Mechanistic Aspects of the Fire Retardant Action of Red Phosphorus in Aliphatic Nylons

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ABSTRACT: The fire retardant action of red phosphorus in nylon 6 was improved by co-addition of ferric/ferrous oxides. It was found that the activity of Fe oxides depends on the product grade. Polymer formulations, non-ignitable in air were obtained by co-addition of Fe_3O_4/Fe_2O_3 = 3:2 with red phosphorus. Scanning electron microscopy showed that ferric oxide contributes beneficially to the fire retardancy, probably because it modifies the morphology of the char. Red phosphorus coated by Fe_3O_4 and encapsulated with phenol formaldehyde resin provided further improvements of fire retardancy and significantly decreased the rate of evolution of phosphine. Mechanistic studies did not support the hypothesis reported in the literature, that the fire retardant action of red phosphorus is due to its oxidation by oxygen of air.

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INTRODUCTION

DESPITE ITS OWN flammability, red phosphorus has been found to be a powerful flame retardant additive that is now used in Europe for nylon [1,2]. We have not been able to confirm any significant commercial use of red phosphorus in the U.S. The balance of concern about phosphine evolution (which even with stabilized red phosphorus is still detectable) outweighs any motivation to avoid halogens in the U.S., unlike in some parts of Europe. Stabilization and coating of the phosphorus greatly reduces the tendency to emit phosphine, but apparently it does not totally eliminate it. The levels of phosphine produced are almost certainly below a toxic level, but it may still be detectable by its characteristic odor under humid exposure of the plastic.

In the previous study [3] of the fire retardant action of red phosphorus in aliphatic nylons, we found that red phosphorus exhibits condensed phase activity. As was seen from thermal analysis, red phosphorus reacts with nylon 6 at thermal decomposition in air and in inert atmosphere. Phosphoric esters are formed by interaction of red phosphorus with the polymer as shown by infrared and by solid state NMR. The chemical mechanism of interaction of red phosphorus with nylon 6 is not clear; however, it was shown that red phosphorus increases the free radical concentration in the char formed at thermal decomposition of nylon 6 fire retarded by red phosphorus.

Some oxidizing metal oxides were found to be beneficial with red phosphorus, probably because they facilitate interaction between red phosphorus and nylon. Here we report some new results on our mechanistic study of the fire retardant action of red phosphorus.

EXPERIMENTAL

Materials

The basic polymer used in this study was nylon 6 (Ny 6, Du Pont, Zytel 211). Red phosphorus [P_{red}, stabilized (Safest) and unstabilized] was supplied by Italmatch, Italy. Phenol-formaldehyde resin of novolac type (Durez 29295) was supplied by OxyChem. Ferric oxide (Fe_2O_3) and vanadium pentoxide (V_2O_5) were of reagent grade from Khimreaktiv, Russia.

Combustion and Thermal Decomposition

Combustion performance of the fire retardant nylon 6 was studied using the oxygen index (OI) test according to ASTM D 2863-77 or the UL 94 vertical test according to the protocol of Underwriters' Laboratory. In the oxygen index test, seven to ten specimens of each sample were tested at the threshold oxygen concentration, which usually gave standard deviation smaller than ±0.3. Thermal decomposition of the formulations was studied by thermogravimetry at a heating rate of 10°C/min in an argon flow of 60 cm^3/min. Solid products of thermal decomposition were characterized by infrared. Morphology of the chars collected after combustion was studied by electron scanning microscopy.

Effect of Ferric/Ferrous Oxides

Combustion

Table 1 shows the fire retardant performance of red phosphorus in nylon 6. Stabilized red phosphorus at the addition level of 10–15% wt. provides a V-2 rating in the UL94 test. At 15%, the flammability of the formulation increases as seen from the increase of the afterflaming time (t_2). Partial substitution of P_{red} with commercial Fe_2O_3 at a 5% wt. level leads to a non-dripping formulation with a V-0 rating.

Table 1. Fire retardant performance of nylon 6 with red phosphorus and Fe containing co-additives.

No.	Additive	P_{red}, wt%	Co-add. wt%	OI	UL94 t_1/t_2[b]	UL94 Dripping	UL94 Rank
1	P_{red}	10	—	24.3	5/2	D	V-2
2	P_{red}	15	—	24.3	1/20	D	V-2
3	P_{red} + Fe_2O_3 (commercial)	10	2	25.3	1/8	D	V-2
4	P_{red} + Fe_2O_3 (commercial)	10	5	24.8	1/3	N	V-0
5	P_{red} + Fe_2O_3 (fresh)	10	5	24.2	0/7	D	V-1
6	P_{red} + Fe_2O_3/Fe_3O_4 (4%)[a]	10	5	24.2	2/3	N	V-0
7	P_{red} + Fe_2O_3/Fe_3O_4 (43%)	10	5	23.1	0/1	N	V-0
8	P_{red} + Fe_2O_3/Fe_3O_4 (57%)	10	5	24.2	2/3	D	V-2
9	P_{red} + Fe_2O_3/Fe_3O_4 (61%)	10	5	22.8	0/0	N	V-0
10	P_{red} + Fe_2O_3/Fe_3O_4 (65%)	10	5	25.1	0/7	D	V-2
11	P_{red} + Fe_2O_3/Fe_3O_4 (91%)	10	5	24.2	0/1	D	V-2
12	P_{red} + Fe_3O_4 (100%)	10	5	24.7	2/7	D	V-2

[a]Percentage shows the content of Fe (II) relative to stoichiometric in Fe_3O_4.
[b]t_1/t_2 is an average afterflaming time after the first and the second ignitions respectively.

We believed that the synergistic effect of Fe_2O_3 might be a catalytic effect. One can assume that freshly prepared ferric oxide might have more active surface. Therefore, a series of intimate mixtures of Fe_2O_3/Fe_3O_4 was prepared by partial oxidation in air at 260°C of fresh Fe_3O_4 made by the co-precipitation of Fe (II) and Fe (III). To obtain fresh Fe_2O_3, Fe_3O_4 was oxidized by air for 1.5 hours at 260°C. The content of the components was estimated by X-ray diffraction analysis.

As Table 1 shows, upon increasing the Fe(III) content in the formulation with P_{red} + Fe_2O_3/Fe_3O_4, the OI goes through a minimum, whereas the UL94 rating goes through a maximum. The most robust V-0 with non-ignitable polymer was observed at the ratio Fe_2O_3/Fe_3O_4 = 2:3.

Morphology of the Char

Scanning electron micrographs of the char after self-extinguishment of Ny 6 + 10% P_{red} and the char after self-extinguishment of Ny 6 + 10% P_{red} + Fe_2O_3 are shown in Figures 1 and 2, respectively. The appearances of these two chars are very different: the char without Fe_2O_3 has smooth surface, but it contains craters from which combustible gases probably escaped, whereas Fe_2O_3 makes the char very rippled and uneven but unbroken as if it had solidified from a viscous melt. It is likely that the char produced in the presence of Fe_2O_3 is more protective because of its differ-

Figure 1. Scanning electron micrography of the surface of the char of self-extinguished specimen of Ny 6 + 10% P_{red}.

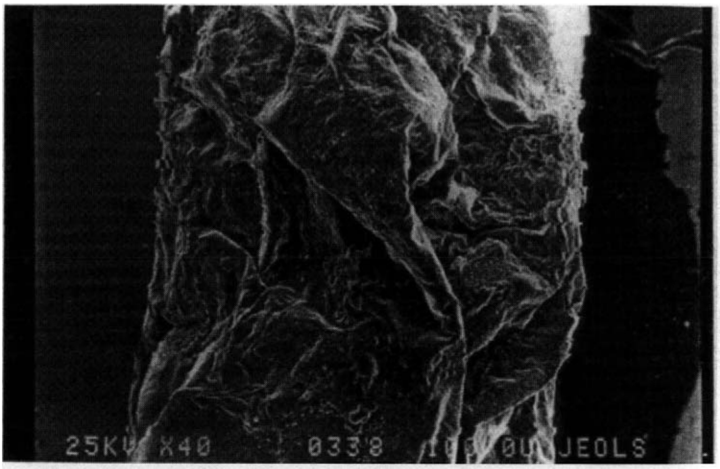

Figure 2. Scanning electron micrography of the surface of the char of self-extinguished specimen of Ny 6 + 10% P_{red} + Fe_2O_3.

ent morphology. A similar effect on char by iron oxides had been reported in an earlier study on nylon 4,6 [4].

The Effect of Particle Size and Its Distribution

It was believed that the synergistic effect between P_{red} and Fe oxides might be increased, and the phosphine-forming propensity decreased, if appropriate contact of the two components is achieved. First, we studied the effect of distribution of additives. A colloidal dispersion of Fe_3O_4 in a low boiling solvent was prepared. Several methods of blending the components before melt compounding were used: (a) after evaporation of the solvent, the fresh solid Fe_3O_4 was dry mixed with Ny-6 and unstabilized P_{red}, (b) the particles of unstabilized P_{red} were coated by Fe_3O_4 by evaporation of solvent from the suspension of unstabilized P_{red} in the colloidal dispersion; and (c) Ny-6 was coated by Fe_3O_4 by evaporation of the solvent from the colloidal dispersion into which Ny 6 was placed.

Table 2 shows the combustion performance of the three formulations prepared from the differently blended components. It is seen that the coating of P_{red} by Fe_3O_4 is more advantageous than the coating of the polymer or the dry mixing of all ingredients.

The data of Table 2 showed that the close contact of P_{red} and the Fe containing additive is desirable to maximize the synergistic effect. Encapsulation of P_{red} and Fe_3O_4 might help to keep them together. The encapsulation was done by phenol-formaldehyde resin (novolac) as follows:

Table 2. Oxygen index for the formulations nylon 6 + 10% P_{red} + 5% Fe_3O_4 prepared by different methods of blending.

No.	Method of Blending	OI
1	Dry mixture of Ny 6, P_{red} and Fe_3O_4	23.8
2	P_{red} coated by Fe_3O_4 mixed with Ny 6	24.8
3	Ny 6 coated by Fe_3O_4 mixed with Ny 6	24.1

1. encapsulation of P_{red}
2. encapsulation of P_{red} covered by Fe_3O_4
3. encapsulation of Fe_3O_4

The mixtures of P_{red} + Fe_3O_4 and P_{red} covered by Fe_3O_4 were used as references. Table 3 shows the data on combustion performance of the formulations with the encapsulated additives. As seen in terms of the UL94 rating, P_{red} covered by Fe_3O_4 and encapsulated with novolac is more beneficial compared to the other grades of the additives. In terms of the oxygen index test, just encapsulation with novolac seems to be better than using both Fe_3O_4 and novolac.

Stabilization against Phosphine Evolution

As mentioned above, the risk of phosphine evolution is one of the factors limiting wide application of red phosphorus. We thought that oxidizer-type co-additives might decrease phosphine evolution because

Table 3. Fire retardant performance of nylon 6 + P_{red} + Fe_3O_4 (encapsulated).

			UL-94		
No.	Additive	OI	Rank	Dripping	t_1/t_2[b]
1	7.5% P_{red}	24.0	V-2	D	15/9
2	7.5% P_{red} + 2.5% Fe_3O_4	24.9	V-2	D	9/5
3	7.5% P_{red}:nov = 40:1 (1)[a]	25.3	NC	D	17/burn
4	7.5% P_{red}:nov = 10:1 (1)[a]	25.6	V-2	D	13/8
5	7.5% P_{red} + 2.5% Fe_3O_4:nov = 10:1 (2)[a]	24.6	V-2	D	10/7
6	7.5% P_{red} + 2.5% Fe_3O_4:nov = 40:1 (2)[a]	24.6	V-1	N	10/5
7	7.5% P_{red} + 2.5% Fe_3O_4:nov = 20:1 (3)[a]	24.8	V-2	D	13/7
8	10% P_{red} covered by Fe_3O_4 = 3:1	24.5	V-2	D	8/11

[a]( )Method of encapsulation of the additive.
[b]t_1/t_2 is an average afterflaming time after the first and the second ignitions respectively.

they will be oxidized upon evolution. To check this hypothesis, the pieces of the specimens for the UL94 test (0.5 g) were placed into test tubes with one drop of water. Originally unstabilized red phosphorus was used to prepare these samples. The test tubes were closed by a cork to which a strip of filter paper impregnated by a water solution of $AgNO_3$ was suspended. All the test tubes were kept at room temperature in a dark place. The evolution of phosphine was detected by time of appearance of a black spot on the bottom edge of the paper strip.

Table 4 shows the relative stability of the various formulations in terms of phosphine evolution. It is seen that oxidizing agents are more efficient compared to acid scavengers ($Mg(OH)_2$). The strongest oxidizing agent (V_2O_5) provides the best stabilizing effect. It is even more advantageous when P_{red} is coated by the oxidizing agent (formulation 6).

Mechanistic Studies

Effect of Moisture

It is known that P_{red} can undergo reaction with humid air, which leads to phosphine and various phosphorus acids [5]. In the formulations with nylon, the sources of water might be absorbed moisture or water produced by the decomposition of primary amide chain ends. We checked if the absorbed moisture could affect the flammability. Thoroughly dried specimens of Ny 6 + 7.5%P_{red} (unstabilized) were kept in a desiccator at humidity of 100% for different periods of time. The water uptake was measured as an increase of the weight of specimens. As Table 5 shows, the fire retardant efficiency of P_{red} does not depend on (UL94) or decreases (OI) with increasing the amount of moisture absorbed by nylon 6.

Table 4. Times when evolution of phosphine was detected from different formulations.

No.	Additive	Time, min
1	7.5% P_{red}	25
2	7.5% P_{red} + 2.5% $Mg(OH)_2$	35
3	7.5% P_{red} + 2.5% Fe_2O_3	50
4	7.5% P_{red} + 2.5% V_2O_5	75
5	7.5% P_{red} + 2.5% Fe_3O_4 (fine powder)	45
6	10% P_{red} (coated by Fe_3O_4 = 3:1)	110

Table 5. Fire retardant performance of the formulations of Ny 6 + 7.5% P_{red} absorbed moisture.

Absorbed Water, %	OI	UL/94		
		Rank	Dripping	t_1/t_2[a]
Dried	24.3	V-2	D	15/3
1.8%	24.2	V-2	D	14/3
3.6%	23.1	V-2	D	15/2

[a] t_1/t_2 is an average afterflaming time after the first and the second ignitions, respectively.

Analysis of the Char for the Presence of H_3PO_4

Two modes of fire retardant action of P_{red} in the condensed phase were discussed in the literature: P_{red} is oxidized by oxygen from the atmosphere giving phosphoric acid which covers the surface of the burning polymer and promotes char [6,7], or P_{red} reacts with the oxygen-containing groups of the polymer [8–10] or other source of oxygen in the condensed phase [3].

After self-extinguishing Ny 6 + 10%P_{red} specimens, the char was scraped from the surface, ground and extracted by water. The extract was analyzed for H_3PO_4 by titration of the third proton after addition of $CaCl_2$ to precipitate $Ca_3(PO_4)_2$ with liberation of titratable HCl, a known method. In our previous work [3], we showed that the char on the top of self-extinguished specimens contained ca. 20 wt. % of phosphorus. Now it was established that about 4 wt. % from the total amount of phosphorus is in the form of H_3PO_4.

CONCLUSIONS

Combustion studies showed that ferric/ferrous oxides are synergistic with red phosphorus. Non-ignitable nylon 6 was obtained upon addition of red phosphorus in combination with F_2O_3/Fe_3O_4, especially at the ratio 2:3. Morphological study of the surface of the char on the self-extinguished polymer specimens showed that the char is rippled and uneven but not perforated in the presence of ferric oxide, whereas without ferric oxide, the char is smooth but contains craters for the escape of combustible gases. Close contact between ferric/ferrous oxide and red phosphorus helps to improve the synergistic action, whereas encapsulation of red phosphorus coated by iron oxides is even more advantageous. Nylon 6 formulations containing red phosphorus coated by Fe_2O_3 release phosphine 4.5 times more slowly than formulations containing plain red phosphorus.

Mechanistic studies of the fire retardant action of red phosphorus showed that the presence of moisture in the formulation, which might promote phosphorus oxidation, does not affect or even deteriorate the fire retardant effect. Only 4% of phosphorus found in the char is present in the form of phosphoric acid. These data disagree with the mechanism suggested in the literature [6,7], where red phosphorus was believed to oxidize by air to phosphorus oxide and provide a fire retardant effect because of the appearance of phosphoric acid on the surface. These data agree with the hypothesis that red phosphorus is oxidized by the oxygen presented in the polymer structure.

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