

Smoke Suppression by Ammonium Polyphosphate in Poly(acrylonitrile) Combustion

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Synopsis

The influence of ammonium polyphosphate (APP) on the smoke emission of poly(acrylonitrile) (PAN) has been examined, and its mechanism of action as a smoke suppressant agent has been investigated. Smoke density and corresponding residual char data, as a function of temperature, were obtained in order to characterize the smoke propensity of PAN. The amount of generated smoke, both in smoldering and flaming conditions, was considerably lowered by the presence of APP, and higher char yields were obtained. Beside the smoke suppression, flame inhibition effect of APP on PAN was evidenced. Thermogravimetry (TG), oxygen index (OI), and nitrous oxide index (NOI) experiments were also performed. On the basis of our data, APP appears to act as a char-forming agent in PAN combustion. Both smoke suppression and flame inhibition effects can be considered a consequence of this action.

INTRODUCTION

A large body of work has appeared in the open and patent literature concerning the problem of flame retardation of poly(acrylonitrile) (PAN).¹ Both the pyrolysis²⁻⁴ and the combustion^{1,5,6} of acrylic and modacrylic fibers have been studied extensively and self-extinguishing fibers have been commercialized by the fiber industry.¹ On the contrary, little work has been concerned with attempts to suppress the amount of smoke evolved in the PAN combustion. In fact, the introduction of ionic additives, such as KCN, or acid comonomer units, such as methacrylic acid or yet additives such as diphenylpicrylhydrazyl radicals, provoked only minor effects in the suppression of the smoke evolving from PAN.⁷

On the other hand, self-extinguishing acrylic resins (modacrylic fibers) do contain sizeable amounts of chlorine, and evolve high quantities of smoke when ignited.⁸ It appears, therefore, interesting to seek effective smoke-suppressant agents for PAN.

We report here a study of the influence of ammonium polyphosphate (APP) on the smoke emission of PAN. APP is widely used as a flame retardant additive for several polymers (polyolefins, PET, PMMA),⁹⁻¹¹ but scarce reports have appeared on the possible smoke suppressant action.

In a previous work¹¹ we have investigated the amount of smoke generated in the combustion of pure PAN at different temperatures, both in smoldering and flaming regions. Now, the effect of APP has been studied, and the results show that it causes a reduction of smoke emission in PAN. In fact, smoke density is

almost halved when 10 phr (parts per hundred resin) of APP are added to PAN.

The mechanism of action of APP as a smoke-suppressant agent has been studied, and the overall evidence shows that APP acts in condensed phase, causing a strong increment of char yield, with consequent reduction of volatile products and smoke density.

EXPERIMENTAL

Materials: Polyacrylonitrile (PAN) used in this study was a high purity commercial sample from Aldrich Chemical Co., with an inherent viscosity of 1.2. Ammonium polyphosphate (APP) was obtained from Hoechst (Exolit 263). Mixtures were prepared by combining PAN mechanically with finely ground APP in a porcelain mortar.

Smoke density measurements: The combustion apparatus used to perform measurements of smoke density has been described elsewhere.^{12,13} This apparatus permits experiments at any suitable temperature up to 1000°C, and the smoke evolved from burning materials can be measured in both the accumulation or dynamic method. The smoke amount, measured by accumulation method, is expressed in terms of the specific optical density (D_s) according to the equation

$$D_s = \frac{D_m \cdot V}{L \cdot W}$$

where D_m = maximum optical density (decibels), V = volume of the accumulation chamber (m^3), L = path length (m); W = initial weight of material (g). 200-mg pellets were used in this study. The specific optical density (D_s) is expressed in $ob \cdot m^3 \cdot g^{-1}$, where ob = obscura (unit that expresses smokiness of an ambient atmosphere when the measured light attenuation is one decibel per meter of smoke path).¹⁴

Char and phosphorous residue measurements: The amount of residual char was measured, after each combustion experiments in the furnace, drawing out the crucible after a fixed time; the crucible was rapidly cooled under N_2 (in order to avoid further decomposition or oxidation process) and then weighed. The P retained in these residues was determined by colorimetric measurements. The combustion residue was treated with HCl (1:3) and maintained under stirring at the boiling for 1 h, in order to convert phosphorous compounds in orthophosphoric acid soluble form. After cooling and filtration, the solution, opportunely diluted, was treated according to the ASTM D-515 method for the determination of P as phosphovanadomolibdic acid measuring the absorbance at 400 nm.

Oxygen index (OI) and Nitrous oxide index (NOI) measurements: Measurements were carried out on a Stanton-Redcroft apparatus (model FTA) in both oxygen and nitrous oxide atmosphere. We have used pressed pellets of the sample instead of molded rods since PAN cannot be molded. The pellets (~500 mg) were placed on a porcelain disc ($\phi 2.5$ cm) whose stem was fitted to the sample holder of the FTA instrument. The OI and the NOI were taken as the concentration of oxygen or nitrous oxide in the atmosphere sustaining the combustion of sample for 60 s after ignition (10 s) with a butane flame. These values, named by us oxygen index (OI) and nitrous oxide index (NOI), are not

to be confused with standard limiting oxygen index (LOI) and with the nitrous oxide index (NOI) measured with conventional rod-shaped samples.

Thermogravimetry: A Perkin-Elmer thermal analyzer TGS-2 was used to determine the weight loss during the thermal degradation of pure PAN and mixtures with APP. Experiments were carried out on 2 mg of the compression molded sample under N_2 or air flow (60 mL/min) and furnace heating rate of $200^\circ\text{C}/\text{min}$ up to 500°C or $10^\circ\text{C}/\text{min}$ up to 850°C .

RESULTS AND DISCUSSION

In order to characterize the effect of APP on the combustion of PAN, it seemed opportune to investigate the thermal behavior of a few APP—PAN blends by TG and flammability methods. In fact, an efficient smoke-suppressant agent, often, shows also a flame retardant action.

In Figure 1 is shown the thermal decomposition (TG under N_2 ; heating rate $10^\circ\text{C}/\text{min}$) of PAN. It exhibits two regions of major weight loss. In the first, the sample loses about 22% of its weight between 280°C and 350°C . This weight loss corresponds to loss of hydrogen cyanide and volatile nitrilic compounds generated by random decomposition of the main chain.²⁻⁴ In the second region, with maximum at 460°C , it loses about 40% of its weight, leaving a persistent residue (850°C) of 40%. In air flow, the first decomposition region occurs with a maximum at 300°C while the second is shifted at about 500°C and corresponds to the oxidative process of PAN.

Isothermal TG experiments were carried out at 500°C , both under nitrogen and air flow. Weight loss curves vs. time are shown in Figure 2. It can be noted that the residue increases as a regular function of the APP content in the mixture, both in N_2 or air flow experiments (Table I).

Under air flow, higher residues were recorded with respect to those in N_2 , but this beneficial effect of oxygen is not unexpected in the case of PAN. In fact,

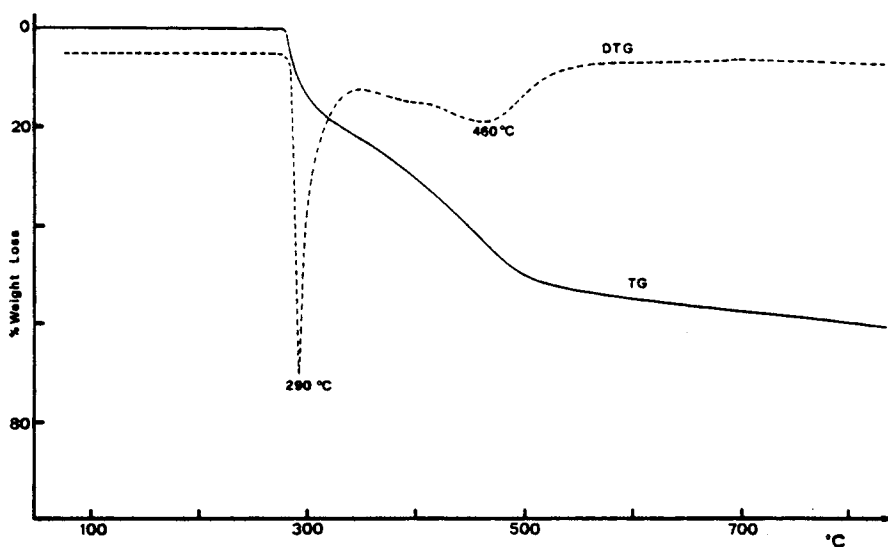


Fig. 1. TG: (—) % weight loss and (---) differential curves as a function of temperature for PAN, under N_2 atmosphere (60 mL/min) at a heating rate of $10^\circ\text{C}/\text{min}$.

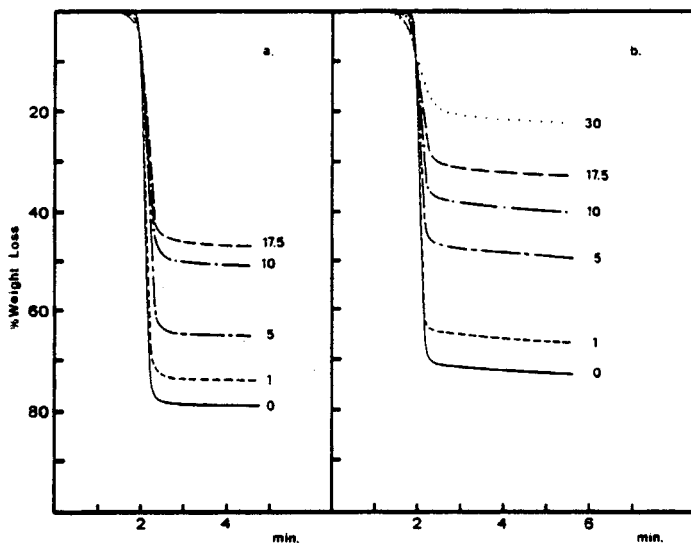


Fig. 2. Isothermal weight loss as a function of time [500°C, initial heating rate 200°C/min, flow rate 60 mL/min: (a) nitrogen; (b) air] for PAN mixtures with APP (phr).

in air atmosphere, the access of oxygen into the polymer surface causes chain oxidation promoting crosslinking reaction.³ These data suggest that APP reacts with the polymeric substrate acting as a char-forming agent. The high char increment, observed at add-on levels of 5 phr (Fig. 2, Table I), supports the view that a chemical interaction is taking place between APP and PAN. In general, the assumption of a condensed or gas-phase mode of action of an additive can be tested experimentally by using nitrous oxide instead of oxygen to burn the sample.¹⁵

In Figure 3 are reported the oxygen index (OI) and the nitrous oxide index (NOI) of PAN samples as a function of the APP amount in the mixture. Both OI and NOI increase linearly with APP content and, moreover, both plots have the same slope. Accordingly, it is most likely that the contribution to the fire retardancy properties of APP by flame inhibition in the gas phase is negligible. It should be noted that APP is a moderately efficient flame-retardant agent for PAN.

Coming now to the smoke density measurements, we have chosen to explore a wide range of combustion temperatures rather than confining ourselves to measurements of smoke density at one or two combustion temperatures. Therefore, a smoke density vs. temperature profile is obtained for each sample investigated in our experiments. This procedure is quite informative and has several advantages.^{12,13}

Smoke density vs. temperature plots for the pure polymer and for PAN containing 10 phr of APP are reported in Figure 4; pertinent values for mixtures with additive amounts in the range of 1–30 phr are collected in Table I. For both curves in Figure 4, smoke density increases linearly with temperature in the smoldering region up to 550–570°C. An abrupt reduction of smoke emission is observed at the self-ignition temperature, but beyond 600°C it increases again. APP causes a considerable smoke suppression over the entire range of the explored temperatures (Table I). Also the combustion residues of PAN are affected by APP presence.

TABLE I
Combustion Results for PAN and PAN Mixtures with APP

APP (phr)	OI ^a	NOI ^a	TG residue ^b						Combustion					
			500°C		400°C		500°C		700°C		800°C			
			Air	N ₂	D _s ^c	% R ^d	D _s ^c	% R ^d	D _s ^c	% R ^d	D _s ^c	% R ^d	D _s ^c	% R ^d
0	18.7	43	27.5	21	4.6	48	7.2	27	—	—	2.7	1	3.7	0
1	19.7	43.5	32.7	25.2	3.9	53	7	32	—	—	2.1	4	2.6	0
5	21.2	45.5	46.7	31.2	3.2	61	6	43	96	87	1.2	16	2.2	7
10	24	47	52.2	41	2.5	67	4.6	49	94	86	1.1	25	1.6	21
17.5	27	50	55.1	42	1.7	71	3.8	59	87	82	0.9	37	1.3	26
30	33	55	59.5	—	—	—	—	68	—	—	—	49	—	—

^a Measured using ignition of pressed pellets (see Experimental section).
^b TG wt % subtracted of the P₂O₅ amount corresponding to the APP contained in each mixture.
^c Specific optical density (ob·m²·g⁻¹).
^d % residue with respect to initial weight of sample, taken after 4 min of combustion.
^e % elemental phosphorus retained into residue.

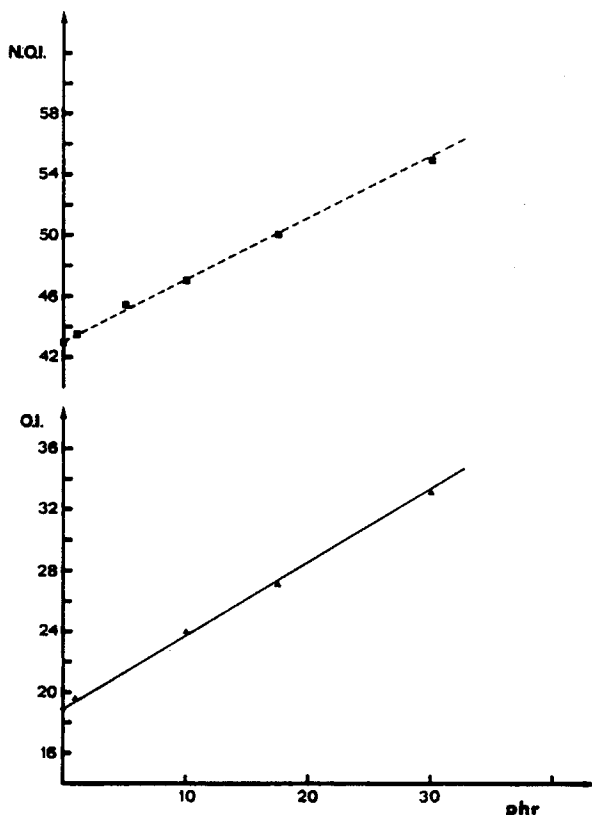


Fig. 3. (—) oxygen index (OI) and (- - -) nitrous oxide index (NOI) vs. APP content for PAN (pressed pellets).

In Figure 5 are reported the residue amounts, referred to the initial weight of sample, as a function of the combustion temperature, for PAN with different amounts of APP. In all cases (Fig. 5) the residue decreases with the increasing temperature. However, it can be noted that higher char residues were obtained for APP mixtures with respect to pure PAN (see also Table I).

In Figure 6 the effect of APP on the smoke emission is compared with its effect on the combustion residue. A linear correlation exists between the reduction of the smoke and the increment of the char yield in smoldering conditions (400 and 500°C).¹⁶

The correlation between smoke density and char residue is diagnostic, since it allows us to assess the mechanism of action of APP as a smoke-suppressant agent for PAN. In fact, APP promotes an increment in formation of char, reducing simultaneously the amount of smoke evolved. This is due, in turn, to the reduction of volatile products in the combustion of PAN.

This conclusion is consistent with TG and flammability data, which support a condensed-phase mechanism of action, and also with the fact that very little phosphorous volatilization was found in the combustion residues (Table I).

At last, Figure 7 shows an interesting correlation between the char residue increment in combustion at 500°C and the corresponding OI values for the mixtures investigated. A linear correlation exists up to 5 phr of APP, but at higher concentrations the slope of the curve increases dramatically. This effect

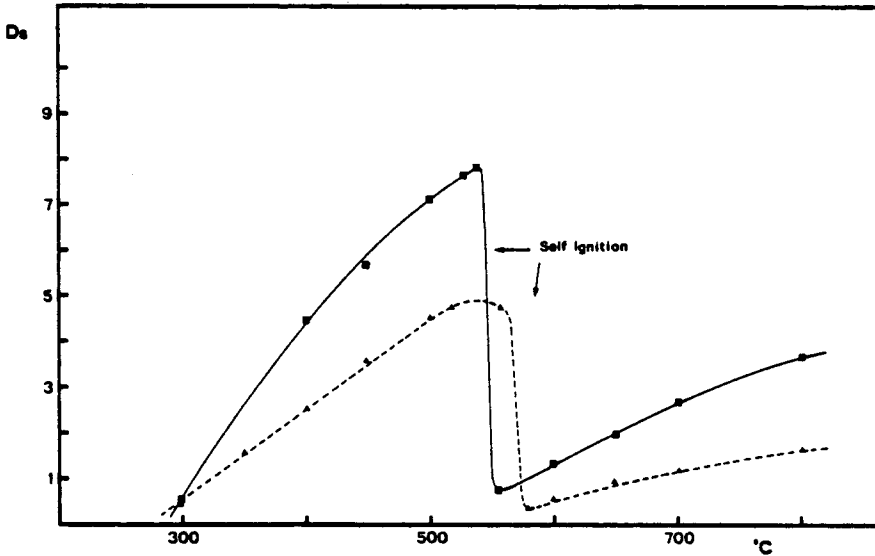


Fig. 4. Specific optical density (D_s) of evolving smoke vs. combustion temperature for (—) PAN and (- - -) PAN/APP 10 phr.

might be explained considering that, beyond 5–10 phr of APP, the total amount of fuel generated in the combustion is only a fraction of the initial sample weight. Under these conditions, little reduction of fuel causes large increments of OI. Alternatively, one might think that at higher add-on levels, APP may display also another mode of action, inhibiting physically the combustion of PAN.

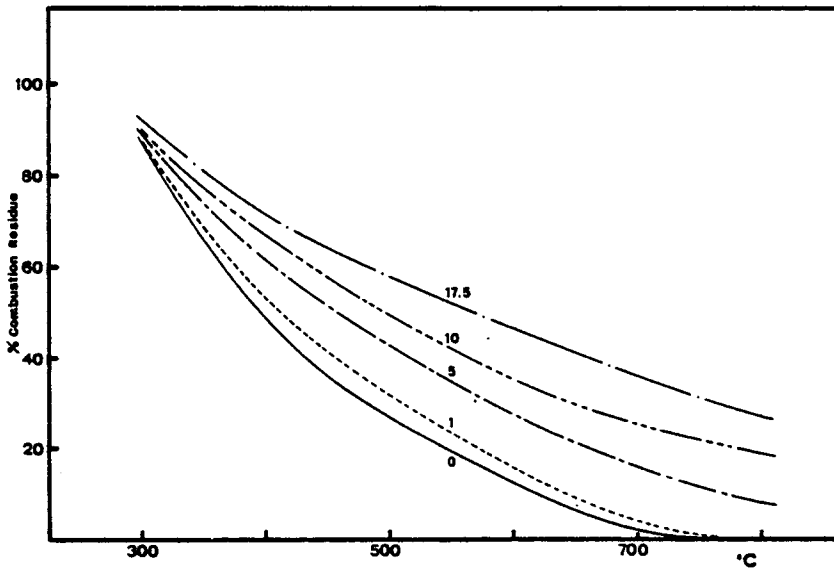


Fig. 5. % Residual char as a function of the combustion temperature for PAN mixtures with APP (phr).

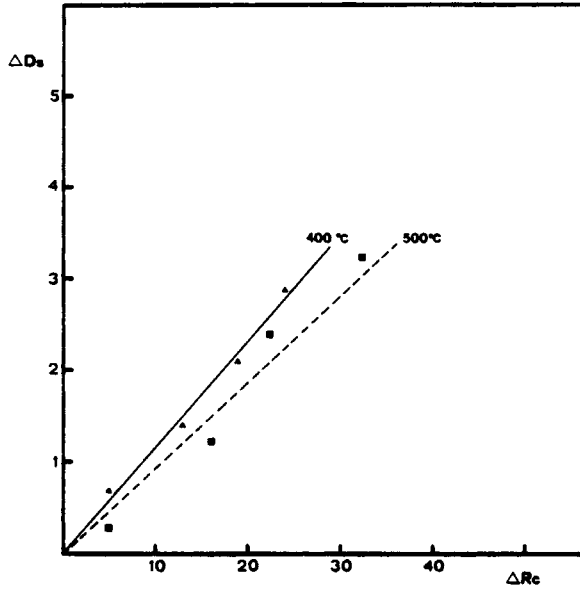


Fig. 6. Correlation between the reduction of smoke density (ΔD_s) and the increment of char yield (ΔR_c) as a function of the APP content in PAN (APP: 1, 5, 10, 17.5 phr; see Table I).

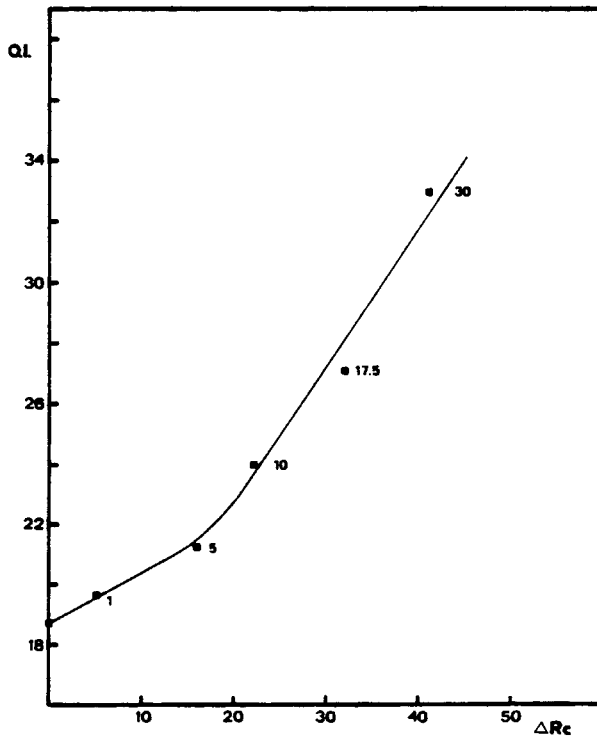


Fig. 7. Oxygen index (OI, pressed pellets) as a function of char yield increment (ΔR_c at 500 °C) for PAN mixtures with APP (phr).

CONCLUSIONS

In our opinion this study has provided evidence that APP acts as an efficient char-forming agent in PAN combustion. The smoke suppression and the flame inhibition actions can be considered a consequence of this effect. Evidence that the principal mechanism of the APP occurs in condensed phase consists of the following:

- (1) the correlation between smoke reductions and char increment;
- (2) the identical slope of the OI and NOI curves as a function of the increasing APP content;
- (3) the correlation between the increment of the char yields (combustion experiments) and OI increment;
- (4) almost all the APP added is retained into char.

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16. Smoke density data in flaming conditions show a linear behavior only up to an APP level of 5% (Table I). This may be due to particle size differences involved in the soot formation in flaming conditions when high levels of APP are added.

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