

# Intumescent Flame Retardants for Polymers. I. The Poly(acrylonitrile)-Ammonium Polyphosphate-Hexabromocyclododecane System

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## Synopsis

The influence of ammonium polyphosphate (APP) and hexabromocyclododecane (HBCD) as flame retardant (FR) on poly(acrylonitrile) (PAN) has been examined. The APP-HBCD system behaves as an intumescent flame retardant (IFR) formulation, APP being the char-forming agent and HBCD the blowing agent. A negligible gas-phase mode of action was ascertained for HBCD with this substrate. A synergism between the two FR agents was observed, corresponding to about 50% increased efficacy with respect to the separate effects of the two components. Thermogravimetry (TG), oxygen index (OI), nitrous oxide index (NOI) experiments and phosphorous residue measurements were performed to substantiate the conclusion that a condensed phase mechanism of action accounts for all the facts observed.

## INTRODUCTION

Research in the field of FR formulation for polymers has recently pointed toward the study and development of intumescent systems. However, intumescence is an ill-defined phenomenon, difficult to characterize otherwise than visually, and also in the composition of the intumescent recipes there is more craft than science. We have undertaken a systematic study of intumescent FR (IFR) for polymers in the attempt to correlate intumescence with some defined physical and chemical parameters.

In this first approach to the problem, we have chosen to describe an intumescent system with polyacrylonitrile (PAN) as polymeric substrate.

IFR formulations, first utilized in the painting industry, have been more recently applied to the fire stabilization of polymeric materials used in textiles, building, and transportation.<sup>1-3</sup>

A few intumescent recipes have been recently proposed,<sup>1,4-7</sup> and some of them have been introduced commercially.

IFR agents base their actions on the formation of a carbon layer at the burning surface. This layer inhibits heat and oxygen transfer into the undecomposed bulk and slows down diffusion of the fuel formed toward the atmosphere.

The typical formulation for an IFR agent to be used in painting recipes was made of four constituents: a binder, a carbonific, a catalyst and a blowing agent.<sup>1</sup> Modern intumescent formulations for polymeric materials must be much simpler since they have not to be spread over the surface of a fabricate, but have to be compounded with polymer in bulk.

Char-forming additives are selected on the basis of the chemical structure of the polymeric substrate.

Ammonium polyphosphate (APP) has been used as a charring agent in the case of intumescent formulations for polypropylene<sup>4-7</sup> and polystyrene.<sup>4</sup>

We have previously shown that APP acts as a charring agent also in the PAN combustion, although it was noted that APP is a moderately efficient FR agent for PAN.<sup>8</sup>

Accordingly, we have thought of interest to find a blowing agent capable of yielding an intumescent formulation for PAN, when coupled with APP. Hexabromocyclododecane (HBCD) was found suitable under this respect.

We have observed that, comparing the oxygen index (OI) measured on pressed pellets and on molded rods of the same sample, the values measured for pellets tend to be sensibly higher with respect to those of molded rods in the case of intumescent formulations.<sup>9</sup>

However, homopolymeric PAN cannot be moulded and therefore the experiments with this material ought to be confined only to pressed pellets. Although our earlier investigation<sup>8</sup> was concerned with PAN homopolymer, in the present work it became opportune to utilize a copolymer of PAN containing about eight mol % of methylacrylate (MA). This copolymer, which has the composition of several acrylic fibers currently marketed as "polyacrylonitrile fiber," can be molded, and, with respect to combustion, it behaves analogously to PAN homopolymer. In fact, the TG curves of PAN and PAN copolymer exhibit two regions of major weight loss. The first decomposition step, in the case of PAN, occurs with a maximum at about 300°C and corresponds to the loss of hydrogen cyanide and volatile nitrilic compounds generated by random decomposition of the main chain<sup>10</sup>; PAN copolymer evolves at the same temperature also methanol deriving from MA units. The second decomposition maximum for both occurs at about 460°C in nitrogen atmosphere and 500°C under air flow corresponding to the oxidative process of the residue.<sup>8</sup>

## EXPERIMENTAL

**Materials.** The copolymer of acrylonitrile with methylacrylate (PAN copolymer) was obtained by polymerization in water suspension and its composition was deduced from microanalysis and NMR.<sup>10</sup> Ammonium polyphosphate (APP) was obtained from Hoechst (Exolit 263). Hexabromocyclododecane (HBCD) was obtained from Great Lakes. FR mixtures were prepared by combining PAN copolymer mechanically with APP and/or HBCD.

**Thermogravimetry.** A Perkin-Elmer Thermal Analyzer TGS2 was used to determine the weight loss during the thermal degradation of PAN copolymer and mixtures with APP and/or HBCD. Experiments were carried out on about 2 mg of sample under nitrogen or air flow rate (60 mL/min) and furnace heating rate of 200°C/min up to 500°C.

**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. OI and NOI were measured for both molded rods and pressed pellets. In the last case, the pellets (about 500 mg) were placed on a porcelain disc ( $\phi = 2.5$  cm) whose stem was fitted to the sample holder of the FTA instrument. OI and NOI were taken as the concentration of oxygen or nitrous oxide in the atmosphere sustaining the combustion of sample for 3 min, in the molded rods case, and 60 s for pressed pellets, after ignition (10 s) with a butane flame.

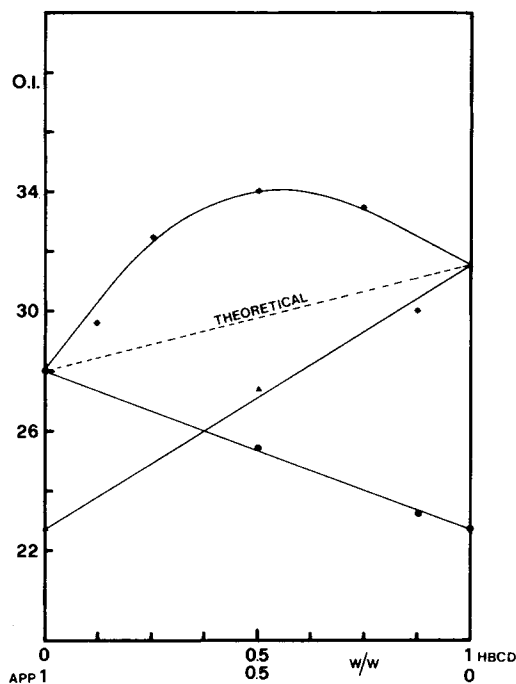


Fig. 1. Oxygen index (OI) for pressed pellets vs. composition of the APP-HBCD system in PAN copolymer at a total additive concentration of 10 phr [(●) only APP; (▲) only HBCD; (\*) APP-HBCD system].

**Phosphorous Residue Measurement.** The amount of P retained in the combustion residue of the mixtures studied here was determined by colorimetric measurements as described elsewhere.<sup>8</sup> The data obtained show that almost all P (90%) is retained into the combustion residue.

## RESULTS AND DISCUSSION

In order to characterize the effect of the APP-HBCD system on the combustion of PAN copolymer, it seemed opportune to investigate the thermal behavior of a few PAN copolymer/APP-HBCD blends by TG and flammability methods and, for comparison, also those of PAN copolymer/APP and PAN copolymer/HBCD systems.

In Figure 1 are reported the OI values, measured on a series of pressed pellets of PAN copolymer mixed with increasing amount of APP and HBCD, respectively, up to 10 phr level. Also shown in Figure 1 are the OI values calculated for mixtures containing a total amount of 10 phr of these two additives, assuming no interaction between them, and the experimental OI values determined for these mixtures. The difference between the calculated straight line and the experimental curve is a measure of the synergistic effect between APP and HBCD in the flame retardancy of the PAN copolymer.

It can be noted that the synergism is maximum for a 1:1 ratio of the two additives, and therefore our study has been performed on this composition which is referred to as APP-HBCD system.

In order to simulate the thermal shock in the combustion, isothermal TG ex-

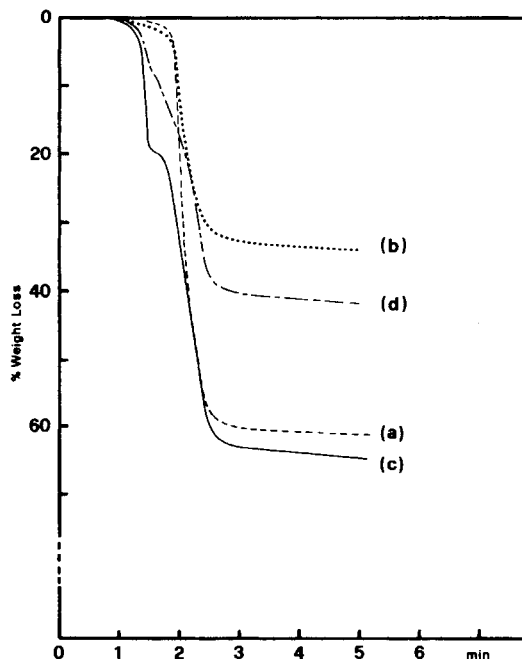


Fig. 2. Isothermal weight loss (500°C, air) as a function of time for: (a) (---) PAN copolymer; (b) (···) PAN copolymer/APP 20 phr; (c) (—) PAN copolymer/HBCD 20 phr; (d) (— · —) PAN copolymer/APP-HBCD (1:1) 20 phr.

periments (500°C, under air) were carried out with an initial heating rate of 200°C/min. Weight loss curves against time are shown in Figure 2.

It can be noted that the residue increases sensibly in the mixture containing APP, since the latter acts as a char-forming agent on this substrate.<sup>8</sup> A similar increment of residue is observed also in the case of the HBCD-APP blend, while this is no more true in the case of the mixture containing HBCD. The analysis of the differential TG curves (Fig. 3) shows that the HBCD mixture displays a volatilization step at shorter times with respect to the pure PAN copolymer. This early volatilization step corresponds to the thermal decomposition of HBCD to yield essentially HBr.<sup>11</sup> This accounts for the sensible degree of swelling (intumescence) that is visually observed during the combustion of PAN copolymer/APP-HBCD samples, indicating therefore that the HBCD component may act as a blowing agent, while APP acts as a char-forming one.

Since it is well known that HBCD behaves as a flame poison in the case of polyolefins and other polymeric materials,<sup>1</sup> it seemed of interest to investigate if a flame-poisoning effect might be active also in the present case.

In general, the assumption of a gas-phase or condensed-phase mode of action of an additive can be tested experimentally by using nitrous oxide instead of oxygen to burn the polymer sample.<sup>12</sup>

In Figure 4 are reported the OI and NOI values measured for pressed pellets of PAN copolymer as a function of the additive amount in the mixture. In the case of APP [Fig. 4(a)], both OI and NOI increase linearly with the additive content and, moreover, both plots have the same slope.

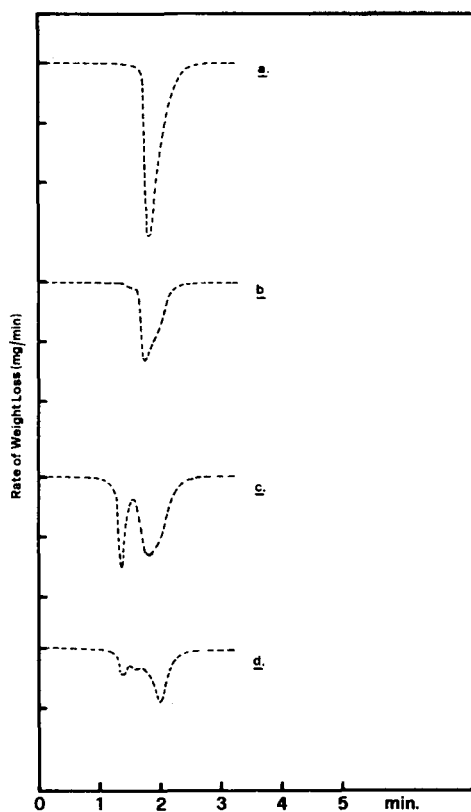


Fig. 3. Rate of weight loss (500°C) as a function of time for: (a) PAN copolymer; (b) PAN copolymer/APP 20 phr; (c) PAN copolymer/HBCD 20 phr; (d) PAN copolymer/APP-HBCD (1:1) 20 phr.

Accordingly, it is most likely that the contribution to fire retardancy properties of APP by flame inhibition in the gas-phase is negligible.<sup>8</sup>

In the case of HBCD [Fig. 4(b)], OI and NOI increase with about the same slope up to 10 phr content of HBCD, indicating that a condensed-phase mechanism of flame inhibition is taking place also here. However, at higher HBCD add-on levels, the NOI curve becomes flat while the OI curve increase steadily [Fig. 4(b)]. Contrary to the case of APP-containing mixtures, a sensible swelling of the burned pellets is observed in this case.

A possible explanation for this behavior is the following: at low HBCD content, the brominated gases evolving from the thermal decomposition of the latter (see TG data) are used mainly to blow the fluid mass of the decomposing polymer. This produces the formation of an expanded carbon layer at the burning surface of the pellet and slows down the diffusion of the fuel formed in the combustion towards the atmosphere. The fuel evolved becomes therefore too diluted to retain the flame-poisoning properties typical of concentrated brominated gases, and the preponderant FR effect originates in the condensed phase as a consequence of the carbon layer insulating effect. At higher HBCD content, the bromine concentration in the evolving gases increases, and a gas-phase effect is also observed.

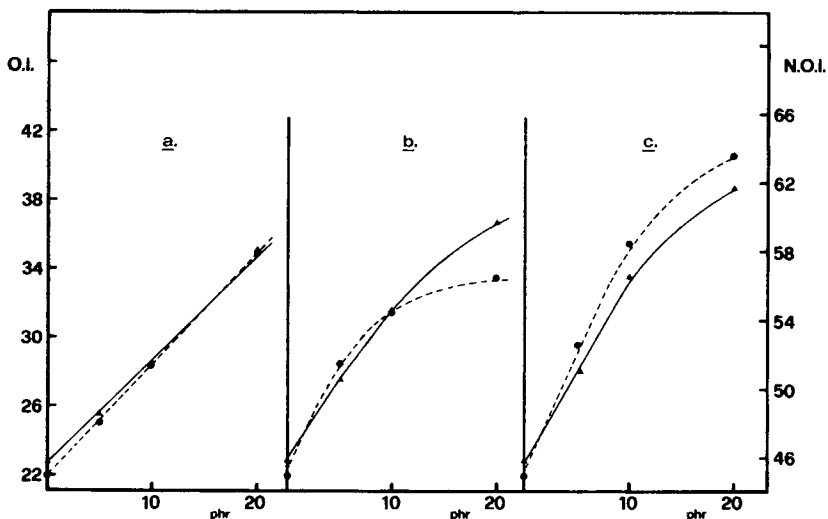


Fig. 4. (—▲—) Oxygen index (OI) and (---●---) nitrous oxide index (NOI) for pressed pellets vs. the additive amount in the mixture for: (a) PAN copolymer/APP; (b) PAN copolymer/HBCD; (c) PAN copolymer/APP-HBCD (1:1).

Remarkably, HBCD does not show any condensed-phase mode of action with polyolefins,<sup>1</sup> because these polymers burn without leaving combustion residue. Instead, the combustion of PAN generates a consistent residue<sup>8</sup> susceptible to be blown and swollen to yield an intumescent system.

In the case of the APP-HBCD system [Fig. 4(c)], the slopes of OI and NOI curves are again closely related at all add-on levels, and it can be concluded that this system acts mainly in the condensed phase. This is quite understandable since, even at 20 phr add-on level, the amount of HBCD in the mixture is only

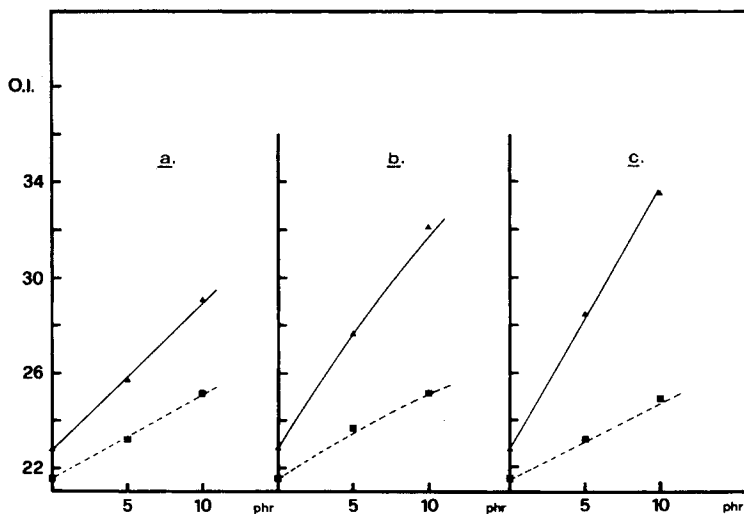


Fig. 5. Oxygen index (OI) for pressed pellets (—▲—) and molded rods (---■---) vs. the additive amount in the mixture for: (a) PAN copolymer/APP; (b) PAN copolymer/HBCD; (c) PAN copolymer/APP-HBCD (1:1).

10 phr. Furthermore, the presence of APP increases the charred residue of combustion, so that the blowing effect of HBCD is maximized. In fact, the APP-HBCD mixed pellets show the largest degree of swelling observed herein.

An attempt to evidenciate the intumescent effect otherwise than visually is reported in Figure 5, where we have compared the oxygen index measured on pressed pellets and on molded rods of the same sample. It can be noted that, for the three formulations investigated, OI values measured for pellets are always higher with respect to those measured for molded rods and that the difference between the two values becomes larger in the case of the APP-HBCD system.

Considering the different geometries of pellets and rods, it can be realized that the formation of a thick carbon layer at burning polymer surface it is likely to inhibit heat and oxygen transfer more efficiently in the case of pellets than in the case of rods.

The higher OI values measured for pellets (Fig. 5) reflect this situation. An OI difference ( $\Delta$ OI) of 1.5% is initially observed for the PAN copolymer, and it increases up to 3.5% at 10 phr APP content [Fig. 5(a)]. This  $\Delta$ OI increment is due to the charring effect of APP on the PAN copolymer, which causes the production of a higher amount of carbon residue in the combustion.

In the other two systems shown in Figures 5(b) and 5(c), respectively, the  $\Delta$ OI observed at 10 phr add-on levels are sensibly higher because now the carbon layer formed at the burning surface is blown in a cellular form, and it results therefore much more insulating.

Remarkably, in the case of the most efficient intumescent system, APP-HBCD [Fig. 5(c)], the  $\Delta$ OI value is about three times higher with respect to the value observed in the APP case [Fig. 5(a)], in which the carbon layer is in a compact form. Similar observations were made in our laboratory for a number of intumescent formulations, and in every case sensible differences in the OI measured for pressed pellets and molded rods were observed.<sup>9</sup> On the contrary, when the polymeric substrate tended to burn, leaving little combustion residue, the two OI values came quite close.<sup>9</sup>

## CONCLUSIONS

Summarizing our results, this study has provided evidence that APP-HBCD system behaves as a IFR formulation for PAN copolymer. APP is a char-forming agent for PAN, and HBCD acts as a blowing agent; their combined effect makes PAN copolymer self-extinguishing at the 20-phr add-on level. A synergism between APP and HBCD has been observed, corresponding to about 50% increased FR efficacy with respect to the effects of the separate components. This synergistic effect is probably due to the intumescence phenomenon. However, due to the peculiar thermal degradation behavior of PAN, the observed synergism by APP-HBCD mixtures is probably a special case that is confined to PAN as the matrix polymer. No gas-phase mode of action was ascertained for HBCD with this polymeric substrate, almost all P is retained into the combustion residue, and therefore the principal mechanism of FR occurs in condensed phase.

Finally, we have observed that it is possible to characterize the intumescent mixtures investigated here by comparing the difference of OI measured on pressed pellets and on molded rods, respectively.

Since this observation was made in the case of other intumescent formulations,<sup>9</sup> we would like to propose it, tentatively, as a criterion for determining the intumescent potential of a FR formulation.

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