

Intumescent Flame Retardant for Polymers. III. The Polypropylene–Ammonium Polyphosphate– Polyurethane System*

G. MONTAUDO and E. SCAMPORRINO, *Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, Viale A. Doria 6, 95125 Catania*, and C. PUGLISI and D. VITALINI, *Istituto per la Chimica e Tecnologia dei Materiali Polimerici, Consiglio Nazionale delle Ricerche, Viale A. Doria 6, 95125 Catania, Italy*

Synopsis

The action of some mixtures of ammonium polyphosphate (APP) and polyurethanes (PUr) as flame retardant (FR) agents for polypropylene (PP) was examined. The APP–PUr systems behave as intumescent flame retardant (IFR) formulations. The IFR action of these systems is described by the comparison of the oxygen index (OI) values measured on molded pellets and on molded rods, by measurements of the polymer temperature just below the burning surface and by visual observations. A strong synergism between APP and some polyurethanes, having piperazine units in the polymer chain, was ascertained with a maximum 3:1 ratio. Our results also indicate that only polyurethanes with specific structure, in combination with APP, are active as IFR agents on PP combustion.

INTRODUCTION

The flame-retardant additives used mainly for polyolefins are halogenated compounds, especially in synergistic combination with Sb_2O_3 .³

These systems have serious disadvantages because of the high add-on levels generally required and the remarkable amount of toxic, corrosive and obscuring smoke generated under conditions of fire.⁴

Research related to new solutions has been undertaken and promising results have been obtained with additives acting in condensed phase.⁵⁻⁷

Works concerning the use of intumescent fire-retardant (IFR) systems for polypropylene (PP) have been reported.^{4,8,9}

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

IFR systems, first used in the painting industry, have been applied to the fire stabilization of polymeric materials.^{1,2,10,11} The typical formulation of an IFR agent is made of four constituents: binder, carbonific, catalyst, and blowing agent.¹² Depending on the chemical structure of the polymeric substrate, it is often unnecessary to include all four constituents in the formulation²; for example, in polyacrylonitrile the addition of a blowing

* For Parts I and II, see Refs. 1 and 2.

agent and ammonium polyphosphate, as charring agent, is enough to produce intumescence.¹

The addition of APP does not induce an adequate char formation in the combustion of PP. However, when specific polyureas are mixed with APP, the formation of an intumescent carbon layer is observed.^{2,8}

Our previous study² allowed us to conclude that the interaction between the thermal degradation products originated from some polyureas and APP causes the formation of active species capable of inducing charring of PP.

The elucidation of the role of polyureas in the combustion mechanism² brought us to consider that other polymers, able to generate reactive species similar to those formed by polyureas, might act as FR agents for PP as well.

The thermal decomposition of some structurally related N—H and N-substituted polyurethanes and their mixtures with APP,¹³ indicate that the N—H polyurethanes undergo a quantitative depolymerization process with formation of compounds with hydroxylic and isocyanate end groups. To contrary, the thermal degradation of the N-substituted polyurethanes proceeds by different mechanism as a function of their chemical structure.¹³

There are accounts in the literature dealing with the mechanism of action of APP on the thermal decomposition of some polymeric substrates^{2-5,8,14,15} and it is generally agreed that APP, a precursor of polyphosphoric acid, is capable of affecting the thermal stability of these polymers, presumably because it promotes acid hydrolytic reaction of the substrates.²

Our results show that the addition of APP lowers the thermal stability of N-substituted polyurethanes, whereas in the other polyurethanes it results unaltered.¹³ Furthermore, it was found that APP often changes the nature of the pyrolytic products, sometimes inducing an hydrolytic cleavage of the polymeric chain, other times causing the formation of tertiary amines.¹³

Based on the similarity of thermal behavior between polyurethanes and polyureas with regard to temperature of maximum thermal degradation rate (PDT, see Experimental) and to the chemical nature of degradation products, we have investigated the possible FR action of some polyurethanes (listed in Table I) and APP mixtures on the PP combustion.

EXPERIMENTAL

Materials. Pure powdered isotactic polypropylene (PP) used in this study was obtained from Montedison.

Ammonium polyphosphate (APP) was obtained from Hoechst (Exolit 263).

Polyurethanes used in this study were synthesized by dispersion polymerization. In a typical procedure, in the container of a Waring Blender, precooled in a freezer, were placed 1.0 g (0.0116 mol) of piperazine and 2.46 g (0.0232 mol) of Na₂CO₃ in 25 mL of water. To the rapidly stirred system was added 2.72 g (0.0116 mol) of hydroquinone-bis-chloroformate in 20 mL of tetrahydrofuran, in one application. The mixture was stirred for 5 min and poured into 300 mL of cold water. After some hours, the polymer was filtered, washed with water and dried *in vacuo* at 70°C.

Inherent viscosities ($\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/dL) of polyurethanes were

measured by a Desreux Bishoff suspended level viscometer; temperature was maintained at $30.00 \pm 0.01^\circ\text{C}$. Pertinent values are collected in Table I.

All the polyurethanes were characterized by direct pyrolysis mass spectrometry. Data are reported elsewhere.¹³

Thermogravimetry. A Perkin-Elmer Thermal Analyzer TGS-2 was used to determine the thermal behavior of the samples. Experiments were carried out on about 2 mg of sample, under nitrogen flow (60 mL/min) and a furnace heating rate of $10^\circ\text{C}/\text{min}$ up to 800°C .

Temperatures of maximum thermal degradation rate (PDT) were taken on DTG (derivative thermogravimetry) curves in experiments carried out at $10^\circ\text{C}/\text{min}$. Pertinent values are listed in Table I.

In order to simulate the thermal shock in the combustion, isothermal TG experiments (under air flow) were carried out with an initial heating rate of $200^\circ\text{C}/\text{min}$ up to 290°C (temperature choice on the basis of the thermal behavior in air of PP).

Oxygen Index (OI) Measurements. Experiments were carried out on a Stanton-Redcroft apparatus (mod. FTA) in oxygen/nitrogen atmosphere. Measurements were performed both in molded rods and molded pellets. In the last case, the pellets (about 500 mg) were placed on a porcelain disc [diameter (ϕ) = 2.5 cm] whose stem was fixed to the sample holder of the FTA instrument.

The oxygen index (OI) represents the minimum oxygen concentration in the atmosphere capable of sustaining the combustion of sample for 3 min or 5 cm, in the molded rod case, or 60 s, in the molded pellet case, after ignition (10 s) with a butane flame.

Polymer Temperature Measurements. Measurements were taken on molded pellets (about 500 mg) placed on a porcelain disc (ϕ = 2.5 cm) and burned in air atmosphere with a butane flame maintained in a fixed vertical position on it for the duration of the experiment.

The temperature, measured by a chromel-alumel thermocouple (ϕ = 0.5 mm) placed in a fixed position inside the sample, was recorded as a function of time.

RESULTS

In Figure 1 are reported the OI values measured on two series of PP molded rods mixed with increasing amounts of APP and PUr I (see Table I), respectively, up to 20 phr (part per hundred of resin) level. Also shown in Figure 1 are the OI values measured for a third series of molded rods of PP containing a total amount of 20 phr of APP and PUr I, but with a different ratio of the two additives in each sample.

The difference between the straight line (Fig. 1), calculated by assuming no interaction between the two additives and the experimental curve, is a measure of the synergism between the two additives with respect to the flame retardant effect on the PP.

Data reported in Figure 1 show a strong synergist effect between APP and PUr I with a maximum for a 3:1 ratio of the two additives. This composition is referred in the following as APP-PUr system.

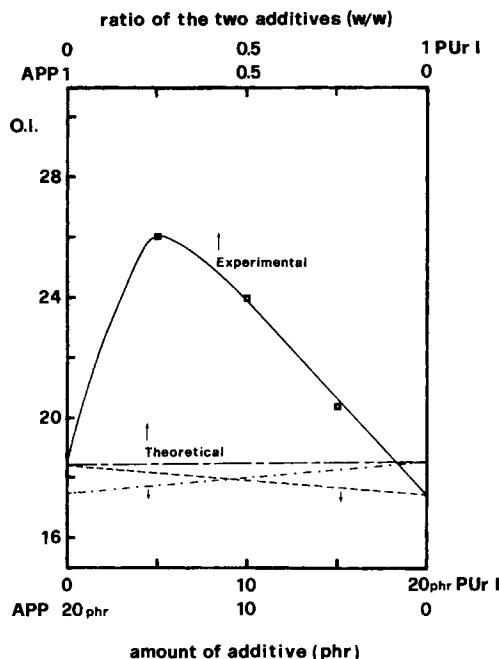


Fig. 1. Oxygen index (OI) values measured on three series of molded rods of PP mixed with APP and/or PUr I vs. amount (lower scale) or ratio (w/w) (upper scale) of the two additives: (—) PP/APP mixtures with increasing amounts of APP up to 20 phr; (- · -) PP/PUr I mixtures with increasing amounts or PUr I up to 20 phr; (—) PP/APP-PUr I mixtures with a total amount, 20 phr, of the two additives, but with different ratio (w/w) (APP/PUr I) in each sample (experimental curve); (---) calculated curve for PP/APP-PUr I mixtures, assuming no interaction between the two additives (theoretical curve).

To clarify the mechanism of action of an APP-PUr system on PP combustion, it seemed opportune to investigate the thermal behavior of PP/APP-PUr and, for comparison, PP/APP, PP/PUr blends by TG and flammability methods.

TG experiments under nitrogen flow and heating rate of 10°C/min were performed. The polymer degradation temperature (PDT; see Experimental) of samples investigated are collected in Table I.

The weight loss values at the end of the degradation step for PUr-APP mixtures are also reported in Table I.

In order to simulate the thermal shock in the combustion, isothermal TG experiments (290°C, under air flow) were carried out with an initial heating rate of 200°C/min. Weight loss curves against time for PP, PP/APP, PP/PUr I, and PP/APP-PUr I mixtures, which contain a total amount of 20 phr of additive, are shown in Figure 2. It can be noted that in the PP/APP-PUr I case, a higher yield of char residue is observed with respect to pure PP, PP/APP, and PP/PUr I cases.

PP, when ignited, burns with a hot smoke-free flame without leaving char residue and with dripping. Instead, visual observations (Fig. 3) of the combustion of the PP/APP-PUr I samples show a sudden formation of an expanded carbon layer at the burning polymer surface, which suggests the

TABLE I
Structure, Inherent Viscosity, Maximum of Polymer Degradation Temperature (PDT), and % Weight Loss of APP Mixtures of Polyurethanes Investigated

	Polyurethane structure	η_{inh}^a	PDT values ^b		% weight loss ^c
			Pure	With 10% APP	
PUr I		0.85*	455	370-460	74
PUr II		0.94*	370	370	86
PUr III		0.93*	460	400	87
PUr IV		0.26**	450	380-430	77
PUr V		0.20**	395	380	79

(Table continued on next page)

TABLE I (Continued from the previous page.)

	Polyurethane structure	η_{inh}^a	PDT values ^b		% weight loss ^c
			Pure	With 10% APP	
PUr VI	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---N---} \end{array} \text{Ph---CH}_2\text{---} \begin{array}{c} \text{CH}_3 \\ \\ \text{---C---} \end{array} \begin{array}{c} \text{CH}_3 \\ \\ \text{---C---} \end{array} \text{Ph---O---} \begin{array}{c} \text{O} \\ \\ \text{---C---} \end{array} \right]_n$	0.31**	490	400-450	72
PUr VII	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---N---} \end{array} \text{Ph---CH}_2\text{---} \begin{array}{c} \text{CH}_3 \\ \\ \text{---C---} \end{array} \begin{array}{c} \text{CH}_3 \\ \\ \text{---C---} \end{array} \text{CH}_2\text{---O---} \begin{array}{c} \text{O} \\ \\ \text{---C---} \end{array} \right]_n$	0.21**	480	380	80

^a $\eta_{inh} = \ln \eta/c$; $c = 0.5$ g/dL; (*) in phenol/tetrachloroethane 3:2 (v/v); (**) in dimethylformamide.

^b Temperatures of maximum thermal degradation rate (PDT) were taken on DTG curves obtained by experiments under nitrogen, gas flow rate of 60 mL/min, and heating rate 10°C/min.

^c % weight loss calculated at the end of the degradation step (experiments under N_2 at 10°C/min.)

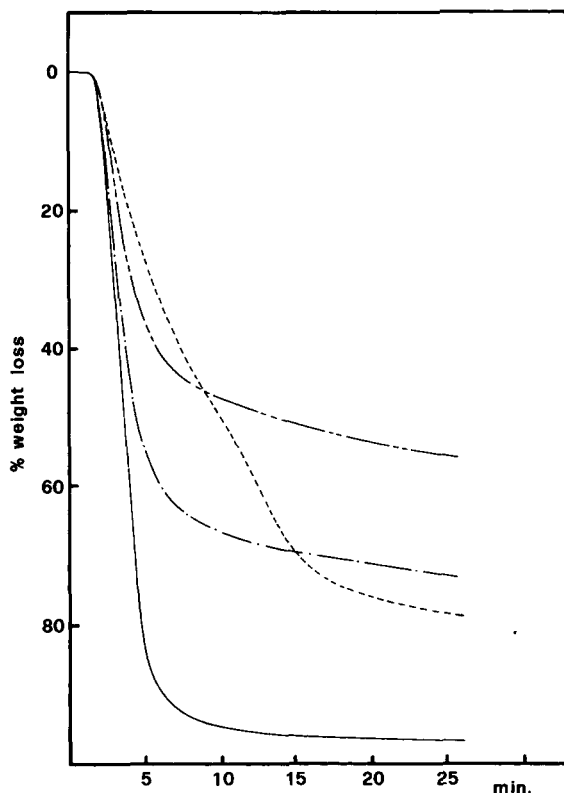


Fig. 2. Isothermal weight loss (%) as a function of the time (290°C, under nitrogen flow rate of 60 mL/min, initial heating rate 200°C/min) for: (—) PP; (- · -) PP/APP; (- - -) PP/PUR I; (- - - -) PP/APP-PUR I. Total additive amount 20 phr.

possible presence of an intumescent phenomenon.

In previous articles,^{1,2} we reported an attempt to define an intumescent effect otherwise than visually. In particular, two reproducible and simple methods have been described. Both methods exploit the inhibiting action of the expanded carbon layer at the burning surface towards heat transfer from the flame zone to the bulk.

The first method consist in a comparison between OI values measured on molded pellets and molded rods; the second one is based on the measure of the temperature just below the burning polymer surface.

In Figure 4 the OI values measured on molded pellets and molded rods for PP/APP-PUR I blends are reported as a function of the additive amount in the sample. It can be noted that for molded pellets higher OI values are observed than for molded rods.

These different values of flammability, measured on pellets and rods for a same system, are diagnostic of the occurrence of an intumescent phenomenon. In fact, considering the different geometries of pellets and rods, it is obvious that the formation of a carbon layer in a expanded cellular form at the burning polymer surface (intumescence) is likely to inhibit heat and oxygen transfer more efficiently for pellets than for rods.

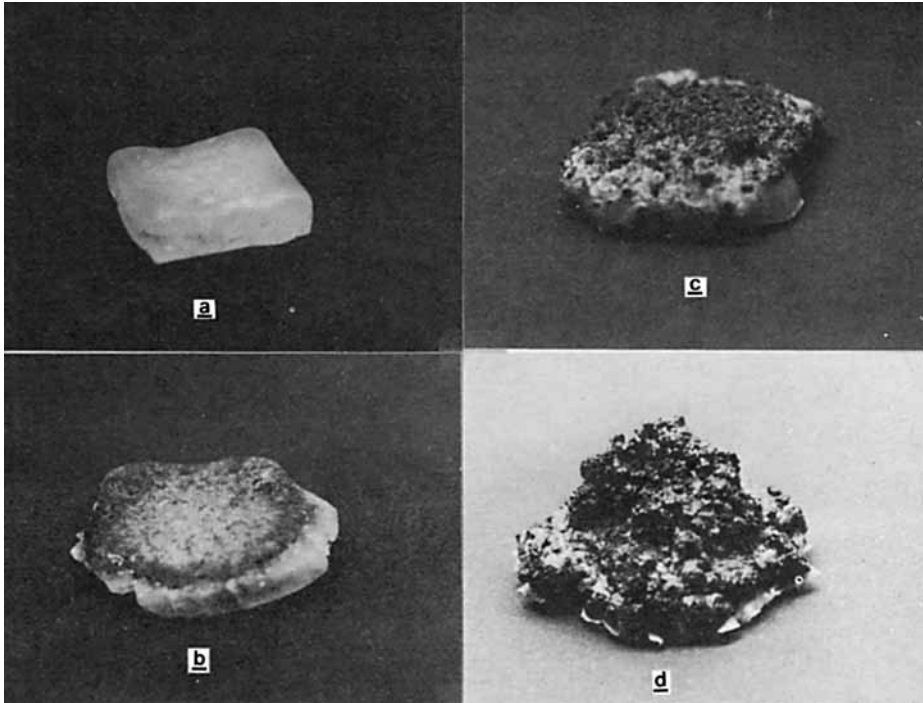


Fig. 3. Photograph of molded pellets after burning: (a) PP, (b) PP/APP, (c) PP/PUR I, (d) PP/APP-PUR I (amount of additive, 20 phr).

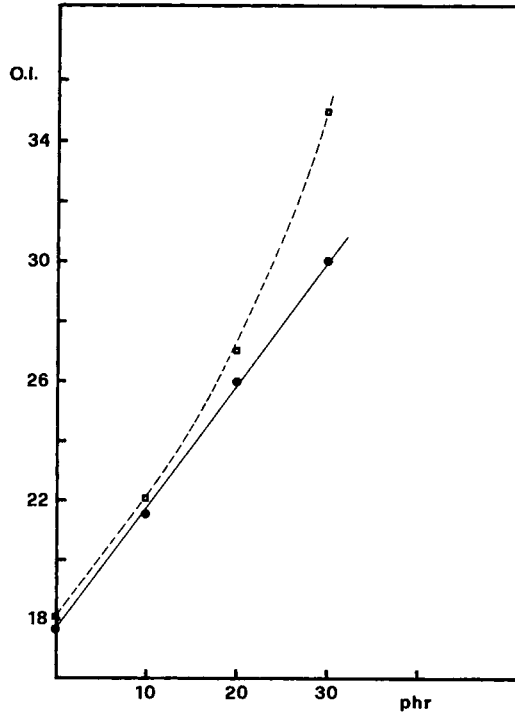


Fig. 4. Oxygen index (OI) for molded rods (—) and molded pellets (- - -) vs. the APP-PUR I amount (ratio 3:1) added to PP.

In Figure 5 the temperatures measured just below the burning polymer surface for PP, PP/APP, PP/PUR I, and PP/APP-PUR I samples are reported as a function of the combustion time.

It can be noted that for PP/APP-PUR I blend the sample temperature remains low also at long flame-exposition times, whereas for the other mixtures it quickly reaches high values in short time. Considering that the sample temperature measurements were carried out under forced combustion conditions, maintaining a pilot flame on the sample for all the experimental time, the temperature profiles reported in Figure 5 indicate clearly that an intumescent phenomenon is occurring. In fact, the expanded carbon layer formed at the burning surface acts as an heat insulating material, inhibiting therefore the heat transfer from the flame zone to the bulk. The low value of the sample temperature is diagnostic for the presence of the intumescent effect and allows to quantify the phenomenon.

In Figure 6 are reported the polymer surface temperatures of PP/APP-PUR I, PP/APP-PUR II, and PP/APP-PUR III blends and for comparison PP as a function of the combustion time. All the blends display temperature profiles typical for intumescent systems, but it can be noted that in the PP/APP-PUR II and PP/APP-PUR III cases higher temperatures are

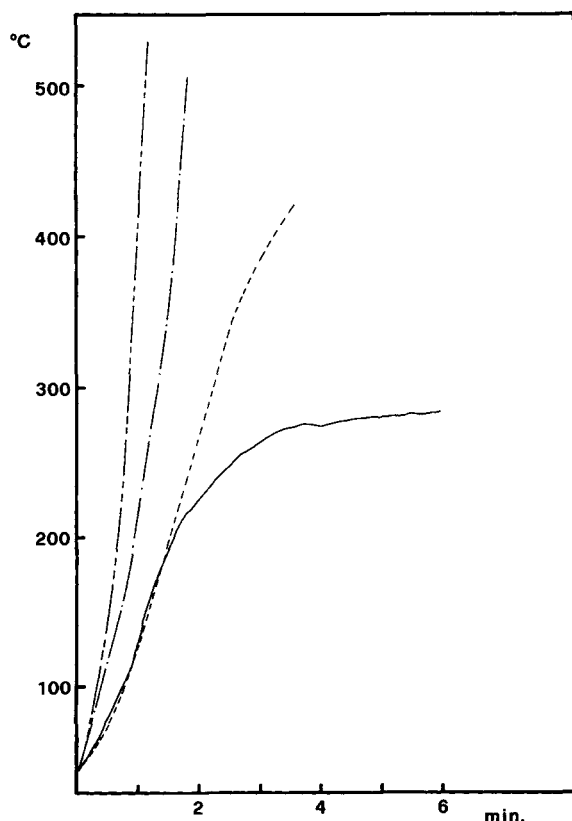


Fig. 5. Polymer temperature vs. combustion time for: (---) PP; (- · -) PP/APP; (- · -) PP/PUR I; (—) PP/APP-PUR I (amount of additive, 20 phr; APP/PUR I ratio, 3:1).

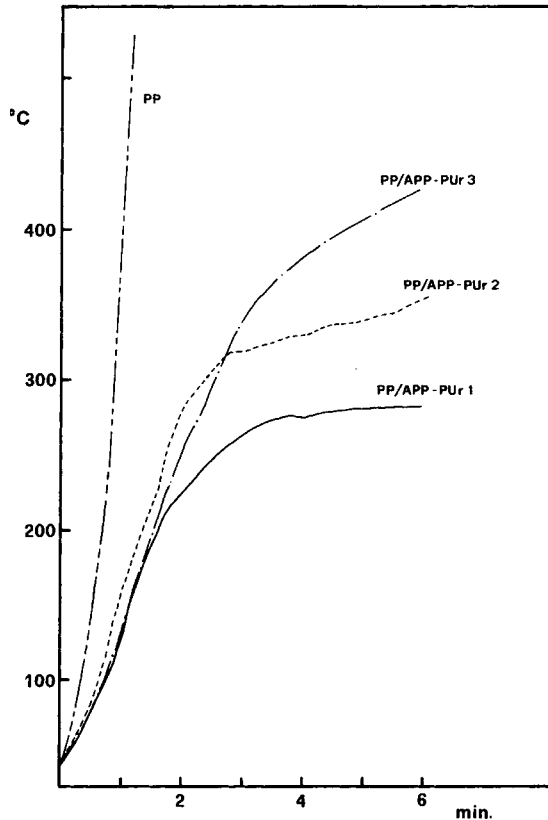


Fig. 6. Polymer temperature vs. combustion time for: (---) PP; (—) PP/APP-PUR I; (- - -) PP/APP-PUR II; (- · -) PP/APP-PUR III. Total amount of additive 20 phr APP/PUR ratio 3:1.

reached with respect to PP/APP-PUR I case. On the basis of this evidence, it can be concluded that the intumescent effect is greater in the last case, in agreement with the OI values reported in Table II.

Among the polyurethanes investigated, only PUR I, PUR II, and PUR III are efficient FR agents in combination with APP. OI data reported in Table

TABLE II
Values Measured on Molded Rods for PP and PP Added of 20 phr of APP-PUR Systems (Ratio 3:1)

Sample	OI
PP	17.5
PP/APP-PUR I	26.5
PP/APP-PUR II	25.5
PP/APP-PUR III	23.0
PP/APP-PUR IV	20.5
PP/APP-PUR V	18.5
PP/APP-PUR VI	20.5
PP/APP-PUR VII	20.0

II, regarding the remaining systems, show very little FR action. Accordingly, the sample temperature profiles of these systems indicate no presence of intumescent effect.

DISCUSSION

Data collected in Table II show that some APP-PUr mixtures are efficient flame retardant agents for PP. Sample temperature profiles obtained under actual forced combustion conditions (Figs. 5 and 6) and comparison between OI values measured on molded pellets and molded rods (Fig. 4) suggest that the flame-retardant effect is associated with an intumescent phenomenon.

Under these circumstances, it is important to clarify the role of each component of the ternary mixture (PP/APP-PUr) with respect to the mechanism of intumescence. The function of the polyurethane in promoting intumescence in PP combustion, might be associated with a mode of action as spumific, carbonific, or promotor of charring reactions.

Data in Table I show that the PDT values of the APP-PUr systems investigated fall in a narrow range of temperatures. Besides, TG data (Table I) show that the weight loss of these systems is comparable. Since only some APP-PUr systems are able to generate intumescence, the role of polyurethane in the IFR blend cannot be of blowing agent.

Only moderate amounts of polyurethane are present in the most efficient IFR blends (Table II) and a higher polyurethane content is harmful to the flame-retardant action (Fig. 1). These results suggest that polyurethane acts as initiator or promotor of char formation, rather than carbonific, in the IFR blends.

APP is unable to induce charring reactions in polyolefins like polypropylene,² although it behaves as charring agent for several polymers.¹⁴ However, in presence of little amounts of some compounds (like polyureas²), APP is able to promote char formation in the combustion of PP. Similar behavior is observed in the polyurethane case. For instance, a relevant yield of char residue is noted for PP/APP-PUr I blend in isothermal TG experiments (Fig. 2) with respect to PP alone, PP/APP, and PP/PUr I.

Under actual flame conditions, the gases generated by the thermal decomposition of PP act as spumific and cause the swelling of the carbon formed by interaction among PP, APP, and PUr.

The thermal decomposition of polyurethanes produces compounds with reactive end groups such as isocyanates and/or amines. In the presence of APP, isocyanates are quickly hydrolyzed to amines,¹³ which, presumably in the form of phosphate salts, are the active species towards PP.

The pyrolysis of PP has been thoroughly studied and an abundant formation of compounds with olefin end groups has been observed among other products.¹⁶ The PP, APP, and PUr interaction may therefore occur in a reaction between olefins and phosphate salts of the amines. However, other reactions may be proposed to account for the origin of active species capable to react with PP and to cause the formation of char.

Our data show that only polyurethanes having piperazine units in the polymeric chain (PUr I, PUr II, and PUr III; see Table I) are able to induce IFR effect (Table II), implying that a particular molecular structures of amine end groups is necessary.

This work was carried out under Contract 83.00312.95 of the Consiglio Nazionale Ricerche (Rome), Finalized Project of Fine and Secondary Chemistry.

References

1. A. Ballistreri, G. Montaudo, C. Puglisi, E. Scamporrino, and D. Vitalini, *J. Appl. Polym. Sci.*, **28**, 1743 (1983), Part I.
2. G. Montaudo, E. Scamporrino, and D. Vitalini, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 3361 (1983), Part II.
3. W. C. Kuryla and A. J. Papa, in *Flame Retardancy of Polymeric Materials*, Marcel Dekker, New York, 1973, Vols. 1-5.
4. G. Bertelli, O. Cicchetti, G. Landoni, R. Locatelli, and P. Roma, paper presented at the *3rd European Conference on Flammability and Fire Retardants*, June 28-29, 1979, Rome, Italy.
5. S. K. Brauman, *J. Fire Ret. Chem.*, **8**, 8 (1981).
6. J. C. W. Chien and J. K. Y. Kiang, *Macromolecules*, **13**, 280 (1980).
7. C. Savides, A. Granzow, and J. F. Cannelongo, *J. Appl. Polym. Sci.*, **23**, 2639 (1979).
8. G. Bertelli, P. Roma, and R. Locatelli, *Br. Pat.*, 1.568.581 (1980).
9. D. G. Brady, C. W. Moberly, J. R. Norell and H. C. Walters, *J. Fire Ret. Chem.*, **4**, 150 (1977).
10. M. Kay, A. F. Price, and I. Lavery, *J. Fire Ret. Chem.*, **6**, 69 (1979).
11. J. A. Rhis, *Fire Mat.*, **3**, 154 (1980).
12. C. F. Cullis and M. M. Hirschler, in *Combustion of Organic Polymers*, Clarendon, Oxford, 1981.
13. G. Montaudo, C. Puglisi, E. Scamporrino, and D. Vitalini, *Macromolecules*, **17**, 1605 (1984).
14. A. Ballistreri, G. Montaudo, C. Puglisi, E. Scamporrino, and D. Vitalini, *J. Appl. Polym. Sci.*, **27**, 3369 (1982).
15. N. Grassie and M. Zulfiqar, in *Developments in Polymer Stabilization—1*, G. Scott, Ed., Applied Science, London, 1979, Chap. 6, p. 197.
16. D. Deur-Sifter and V. Svob, *J. Chromatogr.*, **51**, 59 (1970).

Received January 27, 1984

Accepted August 6, 1984