

A THERMOGRAVIMETRIC STUDY OF THE FLAME RETARDANT SYSTEM CYAGARD® RF-1/AMMONIUM POLYPHOSPHATE

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ABSTRACT

The flame retardant Cyagard RF-1 {ethylene bis[tris(2-cyanoethyl)]phosphonium bromide} decomposes in a solid-state reaction by way of a Prout–Tompkins mechanism with HBr as the main gaseous decomposition product. The flame retardant synergist, ammonium polyphosphate, decomposes by a first-order process with the liberation of gaseous ammonia. Mixtures of Cyagard RF-1 and ammonium polyphosphate decompose at a lower temperature than the individual components.

Addition of a mixture of Cyagard RF-1 and ammonium polyphosphate retards the thermal decomposition of polypropylene, which suggests a flame retardant action via a condensed phase effect. In high-impact polystyrene, the thermal decomposition is retarded to a lesser degree. This is in agreement with the lower flame retardant activity of the Cyagard RF-1/ammonium polyphosphate system in this polymer.

INTRODUCTION

In recent years, flame retardation of organic polymers has become an important area of research. The inherent flammability of combustible polymers can be reduced by the incorporation of additives that act as flame retardants, among the most effective of which are organophosphorus compounds [1]. In thermoplastic polymers such as polypropylene (PP) or high-impact polystyrene (HIPS), additives are required that possess sufficient thermal stability to withstand the high processing temperatures required by these polymers. Phosphorus-based flame retardants that fulfil this stability requirement include many compounds that belong chemically to the classes phosphine oxides and phosphonium salts [2].

The flame retardant activity of some of these organophosphorus compounds is enhanced by the addition of ammonium polyphosphate (APP) [3]. The combined flame retardant effects of the organophosphorus compound and the APP exceed the sum of the effects of the individual components. Therefore, APP has to be considered as a true flame retardant synergist, if synergism is defined as the cooperative action of two flame retardants so that the total effect is greater than the sum of the two effects taken independently [4].

The mode of action of organophosphorus/APP combinations is believed to involve mainly reactions that occur in the condensed phase of the polymer/

flame retardant system: the flame retardant exerts its effect by changing the rate of formation and/or the composition of the combustible pyrolysis products that serve as fuel for the polymer flame.

In this report, we will show how thermogravimetry (TG) can be a tool in flame retardant research. TG analysis can determine the thermal stability of flame retardant additives, establish synergistic interactions, and determine the effect of flame retardants on the thermal decomposition of polymers. As an example, studies are reported on the phosphonium salt Cyagard RF-1 {ethylene bis[tris(2-cyanoethyl)]phosphonium bromide}, which in combination with APP has found commercial use, especially in the flame retardation of PP.

EXPERIMENTAL DETAILS

Materials

Cyagard RF-1 (American Cyanamid Company), ammonium polyphosphate (APP) (Phoschek[®] P 30, Monsanto), polypropylene (PP) (Profax[®] 6401, Hercules), and high-impact polystyrene (HIPS) (Impact Grade 825 TV, Cosden Oil Co.) were used in this investigation.

Procedures

Both the TGS-1 and TGS-2, thermogravimetric instrumentation manufactured by Perkin-Elmer Corporation, were used in this study. The instruments were calibrated with Curie point standards, as per the manufacturer's specifications. Sample sizes were of the order of 5 mg. A dynamic gas atmosphere was maintained by a 25 ml min⁻¹ stream of either dry air or dry argon. In the case of simultaneous dynamic thermogravimetry/derivative thermogravimetry (TG/DTG) runs, the heating rate was 5°C min⁻¹.

In the isothermal experiments, the furnace was preheated to 285°C and then placed in contact with the previously weighed sample. The recorder drive was started simultaneously.

RESULTS AND DISCUSSION

Thermal stability of the RF-1/APP system

As a general rule, a flame retardant additive has to be thermally stable at the processing temperature of the polymer in which it is to be incorporated. However, to be effective as a flame retardant, the additive has to decompose rapidly at temperatures corresponding to those that are encountered at the surface of the burning polymer. In other words, the activation energy of the thermal decomposition rate for the flame retardant has to be high. The

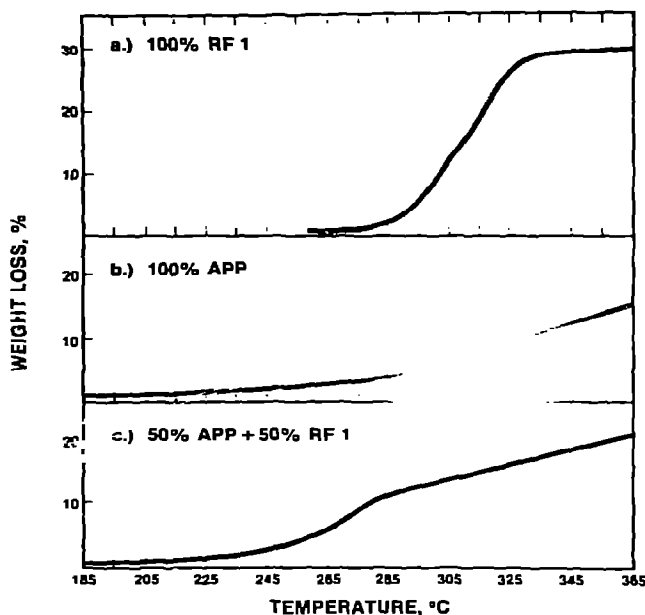


Fig. 1. TG curves of: (a) RF-1; (b) APP; and (c) RF-1 + APP (1 : 1 mixture). Heating rate $5^{\circ}\text{C min}^{-1}$; air atmosphere.

processing temperature for PP is $250\text{--}270^{\circ}\text{C}$, while that for HIPS is about 220°C and the temperature at the surface of the burning polymer is about 400°C . Therefore, flame retardants for these polymers should decompose ideally in the temperature range $275\text{--}400^{\circ}\text{C}$.

As shown in Fig. 1, the phosphonium salt, RF-1, is stable to about 275°C , while APP already shows a slow weight loss below this temperature. Interestingly, a mixture of 50% RF-1 and 50% APP exhibits an onset of volatilization at a lower temperature than either of the two components. This reduction of the thermal stability for the RF-1/APP mixture requires that the processing of PP containing RF-1/APP mixtures be carried out at about 250°C .

Kinetics of the dynamic thermal decomposition of RF-1 and APP

As shown in Fig. 1, the weight loss of RF-1 occurs in two distinct stages. Each step corresponds to a weight loss of 13.5%, and the total weight loss can be accounted for in terms of the consecutive release of 2 moles of HBr. Passing the pyrolysis gases through an aqueous solution of AgNO_3 established qualitatively the presence of Br^- . The decomposition curve is not affected by a change from an air to an argon atmosphere. The decomposition of APP occurs over a wide temperature range, and the main weight loss of 17% can be accounted for in terms of a release of NH_3 .

These decomposition processes are even more clearly reflected by the DTG curves shown in Fig. 2. The thermal curve for RF-1 shows two distinct peaks with maxima at 310 and 320°C . The peaks are of nearly equal height, corresponding to maximum rates of about $38\% \text{ min}^{-1}$; they are characterized by their width at half height of $12\text{--}15^{\circ}\text{C}$. In the case of APP, the main

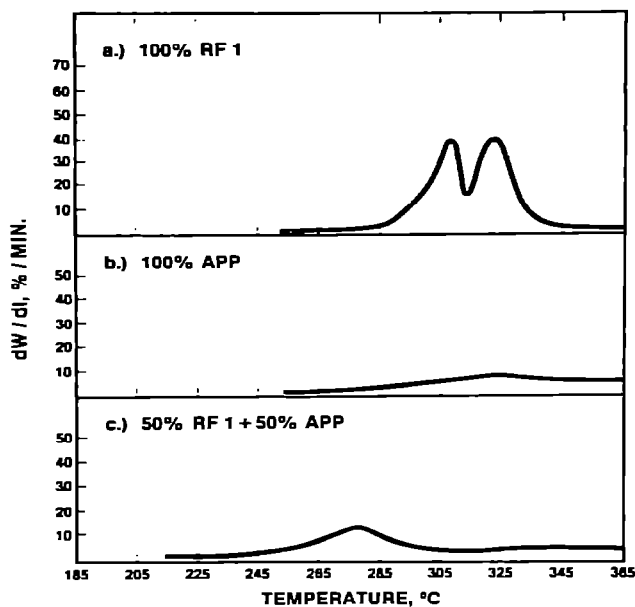


Fig. 2. DTG curves of: (a) RF-1; (b) APP; and (c) RF-1 + APP (1 : 1 mixture). Heating rate $5^{\circ}\text{C min}^{-1}$; air atmosphere.

weight loss occurs over a broad range of about 50°C , with a maximum rate of $8\% \text{ min}^{-1}$ at 325°C . For an RF-1/APP mixture, the maximum rate of $13\% \text{ min}^{-1}$ occurs at 280°C , with a width at half height of 28°C . If the two components of the mixture are placed in the same TG pan without intimate mixing, the resulting DTG curve is a simple superimposition of the DTG curves of the two components. Consequently, we conclude that the interactions that are responsible for the decrease of the decomposition temperatures of the RF-1/APP mixtures are not caused by volatile pyrolysis products but, rather, by solid-state reactions between the two components. These reactions are only possible in an intimate mixture of the two components.

Kinetics of the isothermal decomposition of RF-1 and APP

To obtain a more detailed picture of the decomposition kinetics for the individual components of the flame retardant mixture, the decomposition was followed isothermally. To prevent any interference by the atmosphere, the isothermal TG runs were performed in an argon atmosphere.

Figure 3 shows the decomposition curve for RF-1 at 285°C . As in the dynamic case, the final weight loss is 27%. The isothermal decomposition curve is sigmoidal, and the maximum volatilization rate occurs at about 50% conversion. This curve shape suggests that the decomposition occurs by way of an autocatalytic solid-state reaction that can be accommodated by a Prout-Tompkins mechanism [5]. The complexities of solid-state kinetics have to be kept in mind. Parameters such as particle size, particle size distribution, and purity of the sample may affect the thermal curve. A plot in the appropriate coordinates (Fig. 4) is linear over approximately 90% of the reaction, with a rate constant of $k = 6.6 \times 10^{-2} \text{ min}^{-1}$.

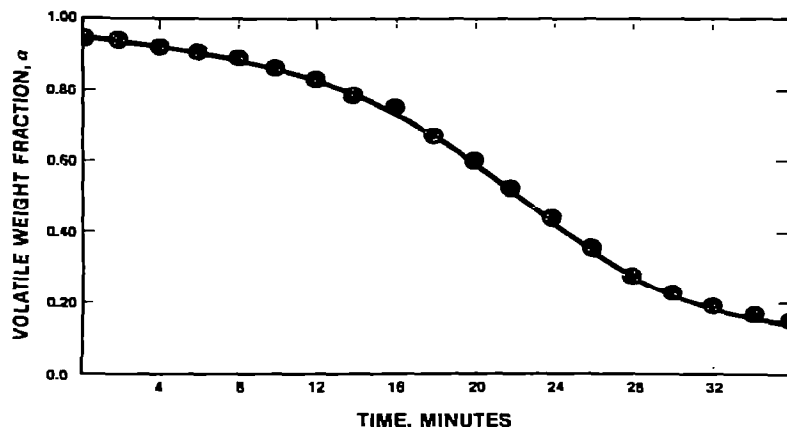


Fig. 3. Isothermal TG curve of RF-1. $T = 285^{\circ}\text{C}$; argon atmosphere.

Isothermal decomposition of RF-1/APP mixtures

While solid-phase interactions of RF-1/APP are qualitatively established using TG/DTG experiments, isothermal experiments are required to elucidate the nature of those interactions.

Figure 5 shows the isothermal TG curve of a mixture consisting of 50% RF-1 and 50% APP at 285°C ; no induction period is observed. The weight loss at infinite time equals the sum of the weight losses for the two components. This indicates that the overall stoichiometry of the decomposition remains the same, while the kinetics of the decomposition are changed.

The kinetic analysis for the decomposition of the mixture at 285°C is exemplified by Fig. 6, which shows the data of Fig. 5 in semilog coordinates. For long reaction times, this plot is linear, with a first-order rate constant of $3.0 \times 10^{-2} \text{ min}^{-1}$. Extrapolation to zero reaction time shows that 70% of the

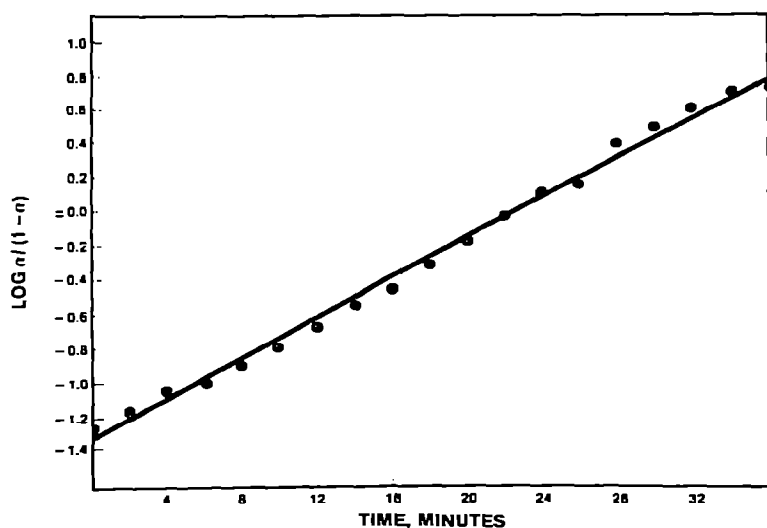


Fig. 4. Prout-Tompkins plot for the isothermal decomposition of RF-1. $T = 285^{\circ}\text{C}$; argon atmosphere.

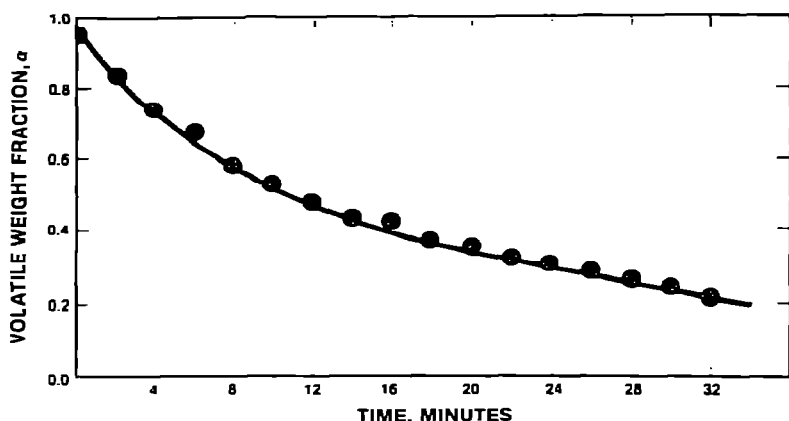


Fig. 5. Isothermal TG curve of a 1 : 1 mixture of RF-1 and APP. $T = 285^{\circ}\text{C}$; argon atmosphere.

total weight loss is accounted for by this process. This agrees with the calculated weight loss attributed to the RF-1 fraction in the mixture. The first part of the weight loss curve of the RF-1/APP mixture, therefore, represents the decomposition of APP. The rate constant for this process is obtained by subtracting from the total weight loss the part that is due to the decomposition of RF-1 and by plotting this difference vs. time in semilog coordinates.

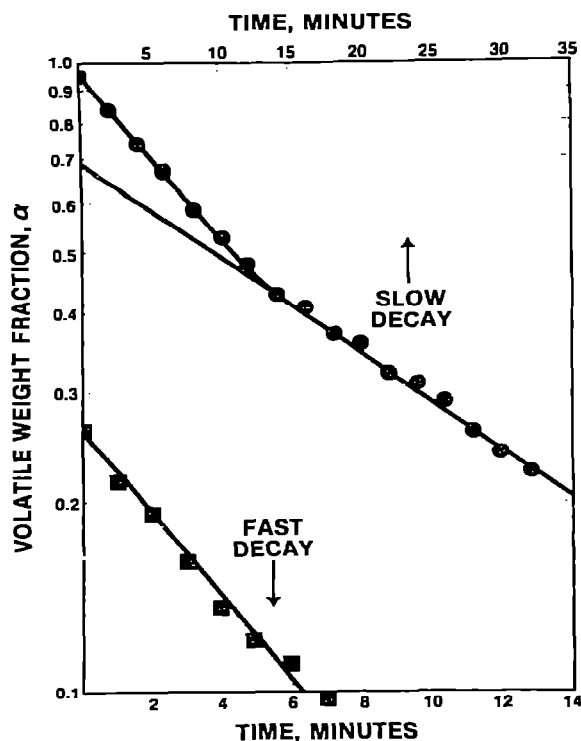


Fig. 6. Kinetic analysis of the isothermal TG curve of a 1 : 1 mixture of RF-1 and APP. $T = 285^{\circ}\text{C}$; argon atmosphere. ●, Evaluation of slow decay, top scale; ■, evaluation of fast decay, bottom scale.

This difference plot is linear and yields a rate constant of $k = 0.15 \text{ min}^{-1}$ for the decomposition of APP.

Effect of RF-1/APP mixtures on the volatilization of PP and HIPS

While these experiments afford an estimate of the thermal stability of the components of the flame retardant system and establish the type of synergistic interactions that occur between its components, they give no information regarding the volatilization of the polymer in the presence of the phosphonium salt/APP combinations. Figure 7 shows the temperature-programmed weight loss curves for PP and for PP containing 30% of a (1 : 1) mixture of RF-1 and APP. The onset of volatilization is shifted to a higher temperature in the case of the flame-retarded polymer, and the volatilization occurs over a wider temperature range. Since during actual combustion, the polymer has to be volatilized first to generate combustible pyrolysis products, this shift to higher decomposition temperature may account for the flame retardant effect of the phosphonium bromide/APP mixtures. Figure 8 shows the effect of the phosphonium salt/APP flame retardant on the thermal decomposition curve of HIPS. In the case of HIPS, the retarding effect of the flame retardant mixture on the volatilization of the polymer is much smaller than in the case of PP. This is in agreement with the much higher flame retardant concentrations that are required for the protection of HIPS; in PP, addition of 20% of the RF-1/APP mixture is sufficient to obtain a flame retardant formulation, while the corresponding formulation for HIPS requires a loading of 35% [6]. A similar retarding action of a flame retardant on the volatilization of a thermoplastic polymer has been observed previ-

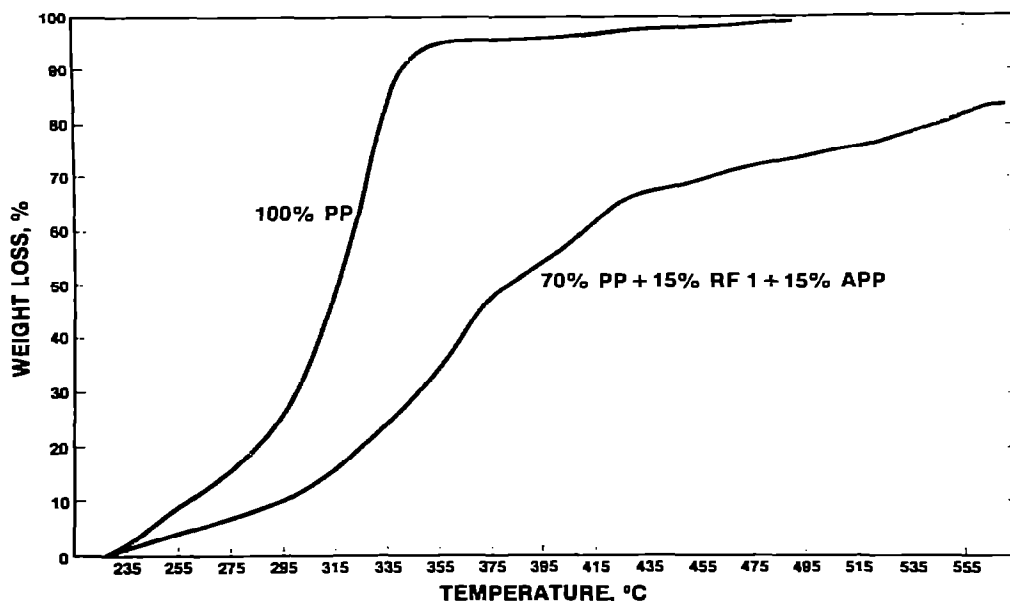


Fig. 7. TG curves for: (a) PP; and (b) 70% PP + 30% RF-1/APP (1 : 1 mixture). Heating rate 5°C min^{-1} ; air atmosphere.

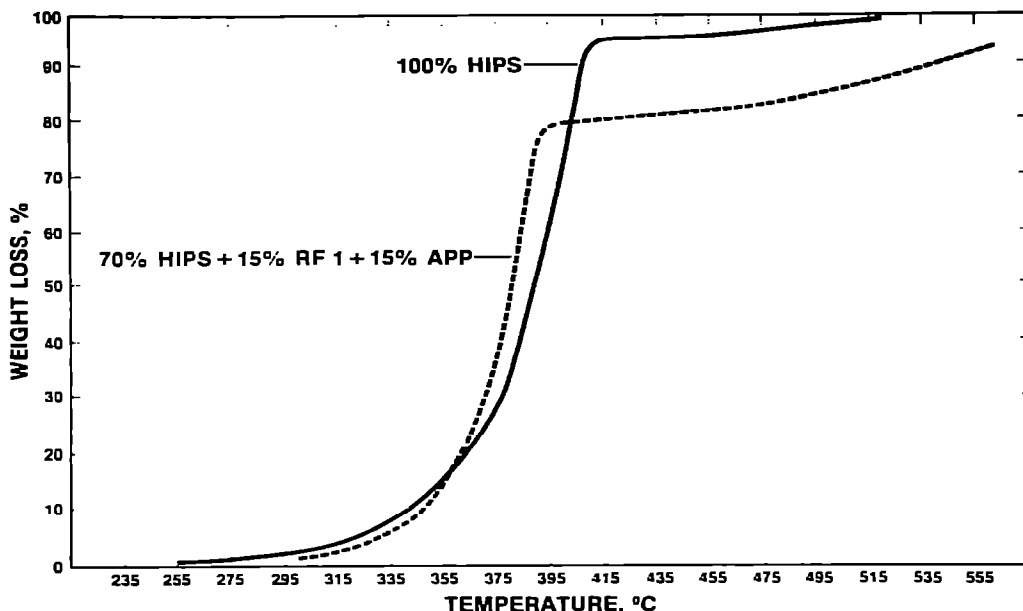


Fig. 8. TG curves for: (a) HIPS; and (b) 70% HIPS + 30% RF-1/APP (1 : 1 mixture). Heating rate $5^{\circ}\text{C min}^{-1}$; air atmosphere.

ously in the case of the poly(ethylene terephthalate)/red phosphorus system [7,8].

One should note that during the flaming combustion of polymers, the actual heating rates are of the order of 10^2 – $10^3^{\circ}\text{C min}^{-1}$. Therefore, the results of TG experiments performed at much lower heating rates may be applicable only qualitatively.

TG experiments and char formation

While the neat polymers, PP and HIPS, volatilize without residue under TG conditions, samples containing the RF-1/APP flame retardant mixture leave a nonvolatile pyrolysis residue. This residue formation is apparent in Figs. 7 and 8.

The residue formation under TG conditions can be compared with the char yield observed during the actual combustion of polymer samples containing RF-1/APP mixtures. The char yield is defined as the gravimetrically determined weight fraction of char residue obtained upon burning of a flame-retarded PP sample in an atmosphere containing sufficient oxygen to support flaming combustion. Figure 9 shows the char yields of PP samples containing 30% of RF-1/APP mixtures of different compositions, together with the corresponding residue yields observed under TG conditions. While the amount of TG residue is largely independent of the composition of the RF-1/APP mixture, the char yield shows a pronounced maximum for the mixtures containing about equal amounts of RF-1 and APP.

Likewise, maximum flame retardancy is obtained for mixtures containing about equal weights of RF-1 and APP. The degree of flame retardancy,

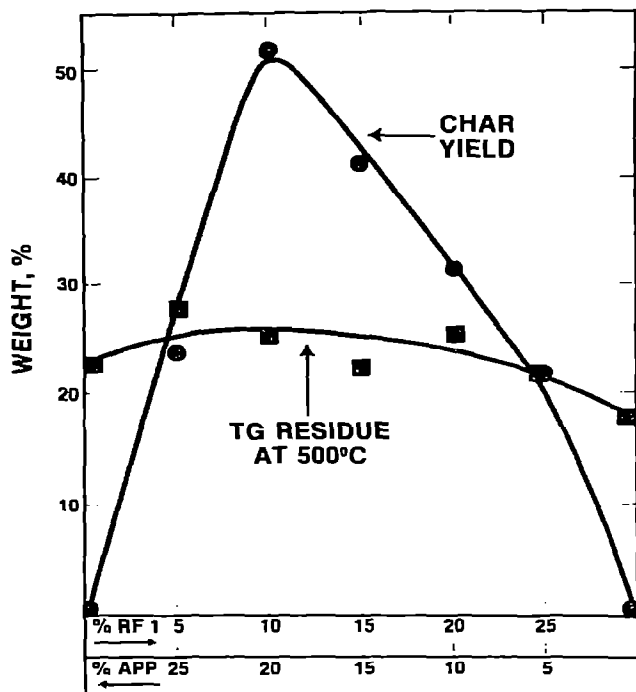


Fig. 9. TG residues and char yields for PP containing 30% RF-1/APP mixtures of different compositions. Conditions: TG residues — heating rate $10^{\circ}\text{C min}^{-1}$, air atmosphere; char yields — combustion in an atmosphere containing about 30% $\text{O}_2 + 70\%$ N_2 . ■, TG residue at 500°C ; ●, char yield.

therefore, correlates with the char yield [4,9], but not with the amount of TG residue. We therefore conclude that quantitative predictions of flame retardant performance based solely on TG experiments are generally not admissible.

CONCLUSIONS

(1) Flame retardant additives have to be stable at the processing temperature of the matrix polymer but must rapidly decompose at temperatures that are encountered during actual combustion of the polymer. The fulfilment of these criteria can be established with the help of TG experiments

(2) Synergistic interactions between flame retardant additives can be detected by TG experiments. The use of the DTG method is especially useful for the observation of small effects.

(3) The decomposition kinetics of a flame retardant can be elucidated only by means of isothermal TG runs, since rather complex processes are frequently encountered. In these cases, a kinetic analysis based on dynamic TG will lead to incorrect results.

(4) The influence of a flame retardant on the volatilization behavior of different polymer systems can be investigated by TG. However, it is not possible to simulate performance under actual fire conditions, since the high

heating rates that occur during combustion cannot be reproduced by the TG method.

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