Invariant Kinetic Parameters of Polymer Thermolysis. IV. Influence of Fire-Retardant Additives on Polypropylene Thermolysis

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SYNOPSIS

Analyzing the transformation-degree dependence of the effective activation energy, we have studied the thermolysis gross kinetics of polypropylene (PP)-based fire-resisting composition and a synergetic mixture of fire-retardant additives: antimony oxide and hexabrominecyclododecane (HBCD). The addition to PP of individual HBCD and in a mixture with antimony oxide increases the activation energy at the initial stage of thermolysis, which is attributed to the ability of fire-retardant additives to impede destruction initiated by oxidation. The investigation of the process proceeding in PP prior to the onset of decomposition in the presence of fire-retardant additives has shown that these additives stimulated crosslinking of polymer chains. The addition to PP synergetic mixture gives the greatest—compared to its individual components—content of the crosslinked fraction (10%), whose presence is likely to inhibit the proceeding of thermolysis by the oxidation mechanism.

INTRODUCTION

Our previous work[1] of this series was devoted to the investigation of the gross kinetics of thermolysis of polypropylene (PP) and PP-based fire-resisting composition containing 10% hexabrominecyclododecane (HBCD) as a fire-retardant additive. The nonisothermal thermogravimetric data were processed by the previously proposed (for analyzing the gross kinetics of complex processes) approach[2] based on the investigation of the shape of the transformation-degree dependence of the effective activation energy calculated by isoconversion method. The increasing dependence of activation energy on the transformation degree was explained by the competing character of the processes of oxidation-initiated thermodestruction and by PP pyrolysis. Thermolysis in the helium atmosphere leads to the suppression of oxidation and increases the effective activation energy at the initial stage of thermolysis.

A similar effect is attained by introducing HBCD into PP, which permits considering the ability of this additive to inhibit the oxidation process in the condensed phase as one of the causes of the fire-retardant activity.

In this work, we investigated the gross kinetics of PP thermolysis in the presence of organohalogen–Sb_2O_3 mixture, the fire-retardant potential of which is well known.[3,4] As the object of investigation, the fire-resisting composition containing 78% PP and 22% Sb_2O_3 + HBCD mixture revealing at the ratio of components 1 : 2.14 the synergetic fire-retardant properties[5,6] has been chosen. The aim of the work was to establish the gross kinetic of thermolysis of the fire-resisting composition and to elucidate the character of the effect of fire-retardant additives on the processes proceeding in the condensed phase of PP.

EXPERIMENTAL

For investigations, commercial isotactic PP was taken. As the components of the fire-retardant com-

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position, we used Sb_2O_3 and 1,2,5,6,9,10-HBCD, the gross formula — $C_{12}H_{18}Br_6$. The derivatograms were taken on a "MOM" derivatograph in stationary air atmosphere at heating rates 2.5, 5, 10, and 20 dg/min. Unlike the previous work,[1] the tests in inert atmosphere were not carried out because the real fire-resisting composition was investigated under conditions close to reality. The 250-mg samples were investigated in open platinum crucibles.

Figure 1 shows the transformation-degree dependencies of the effective activation energy calculated by the isoconversion method[2] for individual PP (1) and fire-resisting compositions: PP + HBCD (2) and PP–Sb_2O_3–HBCD (3). Dependencies (1) and (2) were obtained in our previous work.[1] It is seen from Figure 1 that unlike the monotonically increasing dependencies (1) and (2) characteristic parallel reactions,[2] dependence (3) goes through the minimum in the region of transformation degree near 0.2. As mentioned above, the increasing character of dependencies (1) and (2) is attributed to the competition of two main processes proceeding at PP thermolysis: the oxidation-initiated destruction and pyrolysis. Likewise, we can, perhaps, explain the character of dependence (3) in the range of transformation degrees 0.2–0.9, where it is similar in shape and position (taking into account the uncertainty in activation energy calculating; see Fig. 1) to dependencies (1) and (2). However, in the range of transformation degrees up to 0.2 the dependency obtained by us is decreasing.
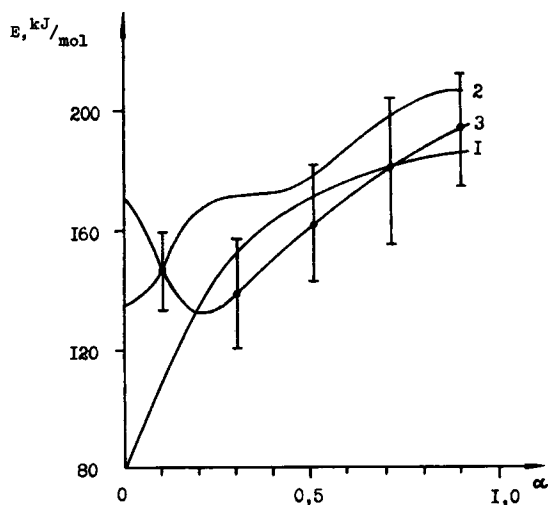
The difference in shape of the above dependencies is a source of useful information on the mechanism of the action of fire-retardant additives on the kinetics of PP thermolysis. So, in our case the observed difference points to different mechanisms of the action of the HBCD–Sb_2O_3 mixture and HBCD on PP thermolysis. At the same time, attention is attracted by the fact that the addition of both individual HBCD and its mixture with Sb_2O_3 causes an increase in the effective activation energy at the initial stage of thermolysis, i.e., when its rate is determined[1] mainly by the destruction initiated by oxidation. Therefore, the principles of the action of these additives are similar and, perhaps, are reduced to the inhibition of the PP destruction initiated by oxidation.

PP Transformations in the Region of the Decomposition Onset

The above results of kinetic investigations show that the cause of changes in the gross kinetics of thermolysis of the fire-resisting composition PP–HBCD–Sb_2O_3, as compared to the composition without Sb_2O_3, should be sought in the processes proceeding in the PP prior to the onset of decomposition registered by the mass loss—220–230°C. We therefore focused on the changes observed in PP in the presence of HBCD, Sb_2O_3, and their mixture before the onset (200°C) and at the very beginning of decomposition (250°C). The obtained data on the effect of the influence of the above fire-retardant additives on the process of PP chain crosslinking are given below.

To determine the quantity of the crosslinked PP fraction, the samples being investigated were dissolved, on heat treatment, by boiling in p-xylene in a Soxhlete apparatus. Then, the gel-fraction formed was dried at 100°C until its constant weight was reached. As the quantitative characteristic of the content of the crosslinked PP fraction, the mass percentage of the polymer going over to the gel fraction to its original mass was used. Chemical analysis of the PP mixture insoluble residue proved that HBCD and Sb_2O_3 are washed down completely by p-xylene.

The results of the investigation are given in Table I, from which it is seen that at 200°C in individual PP the processes of crosslinking are not observed. The addition of HBCD to PP leads to the formation at this temperature of crosslinked fraction whose maximum content (4%) is observed 2–3 min after. The addition of Sb_2O_3 to PP also stimulates the pro-

Figure 1 Dependence of the effective activation energy on the transformation degree for the samples studied. 1, PP; 2, PP–HBCD; 3, PP–Sb_2O_3–HBCD.

Table I Quantity of Crosslinked Fractions in PP in Presence of Fire-Retardant Additives

| Sample | Quantity (%) of Crosslinked Fractions by Temperature (°C) | |
	200	250
PP	—	12.0 ± 1.0
PP–HBCD	4.0 ± 0.5	0.7 ± 0.1
PP–Sb$_2$O$_3$	5.5 ± 0.5	6.0 ± 0.5
PP–Sb$_2$O$_3$–HBCD	10.0 ± 1.5	5.0 ± 0.4

cess of polymer crosslinking. The maximum content of the crosslinked fraction in this case is 5.5% and is attained within 2–3 min. The use of synergetic mixtures of fire-retardant additives HBCD and Sb$_2$O$_3$ leads to a considerable increase in the maximum content of the crosslinked fraction (10%), which is obtained in 4 min.

As the temperature is increased to 250°C, the character of the action of fire-retardant additives on PP is changed. So, while in individual PP the maximum content of the crosslinked fraction fixed after 10 min of heating is 12%, in a HBCD-containing sample no more than 0.7% of crosslinked fraction is formed during the same time. For Sb$_2$O$_3$-containing samples, the temperature rise does not practically lead to an increase in the maximum content of the crosslinked fraction, which constitutes 6% and is formed in 2–3 min. The synergetic mixture at this temperature also leads to the formation of a relatively small quantity of the crosslinked fraction (5%) after 10 min.

Thus, the fire-retardant additives used stimulate the process of polymer chain crosslinking taking place prior to the onset of PP decomposition. It should be noted that in individual PP prior to the onset of decomposition the crosslinked fraction is not formed. However, after the beginning of decomposition the fire-retardant additives produce the opposite effect on the process, which proceeds more violently in individual PP.

DISCUSSION

Thus, based on the investigations of the gross kinetics of fire-resistant composition thermolysis and the mechanism of the action of fire-retardant ad-

ditives on individual PP thermolysis, the following can be stated. Individual PP in which the crosslinked fraction is not formed prior to decomposition begins its transformation by the oxidation mechanism, i.e., at the initial stage the rate of its thermolysis is determined by oxidation-stimulated destruction. The addition to PP a mixture of fire-retardant HBCD and Sb$_2$O$_3$ leads to the fact that prior to the onset of decomposition the polymer contains a significant quantity of the crosslinked fraction, whose presence is likely to inhibit the processing of thermolysis by the oxidation mechanism. Anyhow, the high values of the effective activation energy given in Figure 1. [dependence (3)], at a transformation degree close to zero, are far more characteristic[1] of the PP pyrolysis rather than of the destruction by the oxidation mechanism. The decrease, with increasing temperature, of the quantity of the crosslinked polymer fraction in the presence of mixture of HBCD and Sb$_2$O$_3$ leads to the creation of favorable conditions for the PP thermolysis to proceed by the oxidation mechanism. As a result, we observe a gradual decrease in the quantity of activation energy with increasing transformation degree down to 0.2. Subsequently, the fire-resisting composition thermolysis occurs by the mechanism analogous to the individual PP thermolysis, i.e., to the competition the oxidative-stimulated destruction and pyrolysis.

Combining the obtained results with those of our previous work,[1] it should be noted that the addition to PP of HBCD or a mixture of HBCD–Sb$_2$O$_3$ inhibits, in some way or other, the process of oxidation-stimulated destruction, which, in the final analysis, impedes the polymer thermolysis. Considering the ability of fire-retardant additives to impede the thermolysis of PP in the condensed phase as one of the causes of their fire-retardant efficiency, it should be noted that these additives must prevent the polymer ignition since they are only effective in the region of relatively low temperature (up to 400°C), at which the thermolysis of fire-resisting composition is largely determined by the process of oxidation-stimulated destruction.

Summarizing the results, we wish to draw the reader's attention to the possibility of obtaining interesting information about the mechanism of complex processes and the character of the influence of various factors on them in terms of nonisothermal kinetics. The indispensable condition for realizing such a possibility is the use of adequate methods of kinetic data processing. Among them is a set of undiscriminating[7,8] methods for calculation of Arrhenius parameters and, in the first place, the iso-

conversion methods, the use of which forms the basis of approach[2] to the analysis of complex processes.

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