THERMOANALYTICAL STUDY OF NUCLEATING EFFECTS IN POLYPROPYLENE COMPOSITES
III. Intumescent flame retardant containing polypropylene

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Abstract

Engineering application of polypropylene requires the employment of flame retardants. Reactive compounding of ammonium-polyphosphate and synergist additives with polypropylene is an effective way for forming flame retardant polypropylene. Both the ammonium-polyphosphate and the additives used for improving its performance effect the crystallization and melting behavior of polypropylene. Encapsulation of flame retardant additives with appropriate elastomer, in order to improve their water resistancy, causes further changes in degree of crystallinity and consequently in the mechanical properties.

Introduction

Engineering and household application of PP requires for several areas high level of flame retardancy. Halogen containing flame retardants are widely used to ensure medium level of flame retardancy (V2 degree). A few type of them has been found to increase the spherulite growth rate in PP [1]. The fields of application and the degree of flame retardancy of halogen containing systems are limited. Ammonium-polyphosphate containing flame retardant formulations and other intumescent flame retardants meet the most severe requirements and avoid the usage of halogenated compounds, so their importance is increasing. In most cases different synergists are applied with the main flame retardant component. The most widely used ammonium-polyphosphate (APP), pentaery-thritol (PER), melamine (ME) system has been thoroughly studied [2–9]. The intumescent flame retardant systems (IFR) form a barrier char foam on the surface of polymers during ignition preventing its further burning. The dependence of the physical characteristics and structure of the foamed char on the composition has been analyzed earlier [10–13]. No attempt has been made, however, for determining the effect of APP on the crystallization of PP.

The presence of synergist additives may also effect this process. The role of interaction between these components in the formation of crystalline structure of PP, is one of the main questions to be solved in this important field.

Experimental

Materials

The polyolefin grades used in this study were:
Polypropylenes (PP): Tipplen H 377 homopolymer product of Tisza Chemical Works (Hungary), density: 0.9 g cm^{-3}, melt index: 8 g min^{-1} (21.6 N, 230°C).
Tipplen K793 ethylene-propylene copolymer, product of Tisza Chemical Works (Hungary), density: 0.9 g cm^{-3}, melt index: 4 g min^{-1} (21.6 N, 230°C).
Low density polyethylene (LDPE): Tipolen AE 1716 product of Tisza Chemical Works (Hungary), density: 0.921 g cm^{-3}, melt index: 7 g min^{-1} (190°C).
Ethylene-vinylacetate copolymer (EVA): EVA 3325 (ICI), Vac content: 33%, density: 0.98 g cm^{-3}, melt index: 28.8 g min^{-1} (21.6 N, 230°C).
Boron-siloxane elastomer was prepared according to the method described earlier [14].
Commercial samples of ammonium-polyphosphate (APP) (Hostaflam 422, Hoechst), pentaerythritol D/S (PER) (Degussa), and melamine (ME) (Reanal) were used as supplied. Their ratio in the intumescent flame retardant (IFR) additive system was APP:PER:ME = 1:0.2:0.2 if not stated otherwise.

Test methods

Mixing of the components was carried out using Brabender Plasti-Corder PL2000 (mixing chamber 350) with rotor speed 50 rpm.
Differential Scanning Calorimetry (DSC) measurements were performed using Setaram DSC 92, sample weight: 10 mg, heating rate: 10°C min^{-1}, atmosphere: air. The first melting of the samples was performed up to 230°C and then the crystallization and second heating curves were registered. Heat of fusion of polypropylene 207.1 J g^{-1} was assumed in calculation of degree of crystallinity [15].
Thermogravimetry (TG) measurements were performed using MOM 3427 Derivatograph, sample size: 100–200 mg, heating rate: 10°C min^{-1}, atmosphere: air.
Scanning Electron Microscopy (SEM) of the fractured surface of injection molded samples (broken in liquid nitrogen) micrographs were taken using Jeol JSM-35 instrument. Etching of samples was performed in hot heptane for 15 min.
The conductivity of 100 cm^3 extraction water after extraction of 3 g injection moulded samples (surface area: 13 cm^2 g^{-1}) were determined using a Radelkis (Hungary) conductometer.
The conductivity of the polymer samples were determined as reciprocal bulk resistance $(R_v[\Omega cm] = U/I \, A/d)$ according to ASTM D618 standard, using Hewlett Packard 4329A instrument.

Results and discussion

PP loaded with 18% APP does not meet the V0 degree of flame retardancy, but it is a normal loading level when it is used with synergists. We prepared therefore flame retardant PP mixtures of this concentration for the DSC experiments. The DSC results of this mixture compared with pure PP and intumescent flame retardant system (IFR=APP 18%+PER 5.5%+ME 5.5%+Zn-borate 1.5%) are given in Table 1.

Table 1 DSC data of flame retardant polypropylenes (T_C T_m: starting temperature of crystallization and melting respectively, T_C, T_m: temperature of crystallization and melting at top of peak)

Materials	$T_{cristallization}$ /°C		$\Delta H_{C,PP}$/	$T_{second\ melting}$ /°C		$\Delta H_{m,PP}$/
	T_{C_o}	T_C	J g^{-1}	T_{m_o}	T_m	J g^{-1}
Tipplen H 337	119.8	113.8	84.1	160.3	172.7	70.6
Tipplen H 337 +18% Hostaflam 422	129.9	123.4	92.9	165.7	176.9	94.5
Tipplen H 337 + IFR system	125.6	119.2	72.9	160.2	171.6	72.3
Tipplen H 337 + IFR system + 2% EVA	129	123.2	86.2	163.2	174.8	93.3
Tipplen H 337 + IFR system + 3.5% EVA	130.1	123.4	91.2	164.7	174.6	90.4

The increased ΔH_C and T_C of PP/APP mixtures indicates the nucleating activity of APP. The nucleating effect of this flame retardant additive is not surprising, if we consider that some organophosphorus salts are used as nucleating agent in PP [16].

APP is, however, never used in PP alone and the presence of synergists decrease its nucleating activity (see IFR system in Table 1). Application of ethylene-vinyl-acetate (EVA) copolymer elastomer in this system increases the measured ΔH values again. We attempted to determine the interactions that are responsible for these changes. ME and Zn-borate found to be inactive at the temperature of mixing, but PER is reported to react with APP under appropriate circumstances according to the following equation [9].
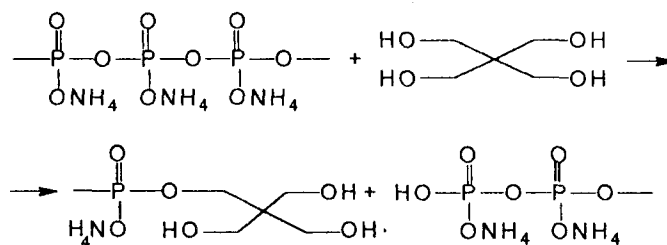
We tried to ascertain, that this reaction may occur under the circumstances of reactive compounding as well. Using PE matrix instead of PP, the mixing could be performed below (at 170°C) and above (at 230°C) temperature of reaction. The bonding of PER to APP is clearly shown by the series of DSC results in Fig. 1.
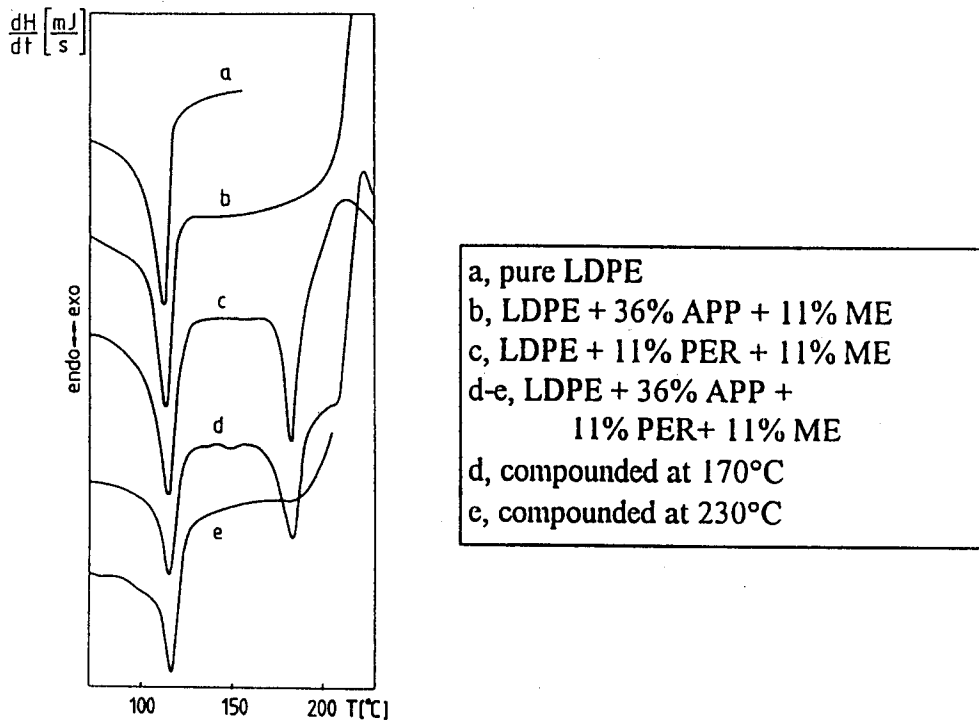

a, pure LDPE
b, LDPE + 36% APP + 11% ME
c, LDPE + 11% PER + 11% ME
d-e, LDPE + 36% APP +
          11% PER+ 11% ME
d, compounded at 170°C
e, compounded at 230°C

Fig. 1 DSC curves of LDPE mixed with IFR additives

The results in Fig. 1 prove, that the whole amount of PER and at least a part of APP participates in ester formation reaction, when the optimal parameters for reactive compounding are ensured. Consequently the partial reaction of APP with PER is the most probable reason of its decreased nucleating activity in IFR systems.

The IFR system is much more effective in retarding the burning process than APP alone and the TG results in Fig. 2 shows that the residual char is of highest value in case of IFR system as well.

Even if the conditions for APP-PER reaction are ensured, the resistance of the formed flame retarded polymers against water is very poor.

For decreasing the water sensitivity of the product, we tried to apply the method of encapsulation by elastomer during the mixing process. This method has been successfully applied earlier in filled polyolefins for improving the mechanical properties [17–19]. We applied the same method for surrounding the flame retardant particles and improving their resistance against water this way. For this purpose we
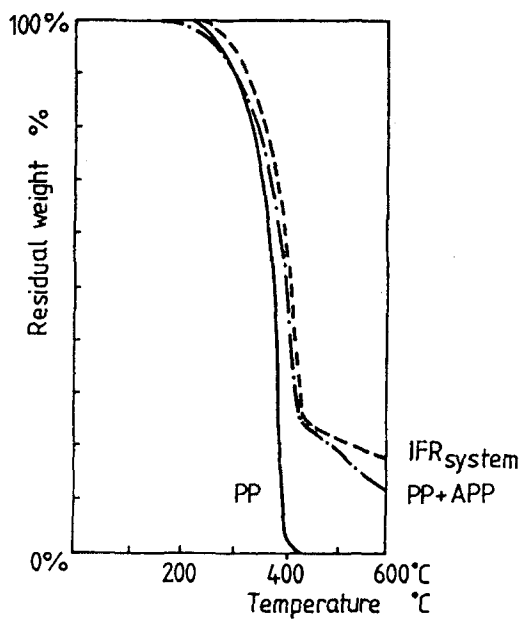
Fig. 2 TG results of PP and flame retardant PP systems

Fig. 3 SEM micrograph of 29% IFR containing PP sample after etching with heptane

applied an EVA type copolymer of high vinyl-acetate content in the PP/IFR system, as it is given in Table 1.

The structure of material formed in course of thermomechanical mixing of PP/IFR/EVA system has been studied by scanning electron microscopy (SEM). The surface of samples broken under liquid N_2 can be seen in Figs 3 and 4. After etching this surface with heptane, which is a good solvent for EVA, holes appear around the particles showing the original place of the elastomer in such a system. This is shown in Fig. 4. The smaller (probably PER) particles has been covered thoroughly while the larger (probably APP) particles only partly. For comparison the heptane treated surface of the same composition, but without EVA is shown in Fig. 3. In this case the white IFR particles are embedded into the polymer matrix.
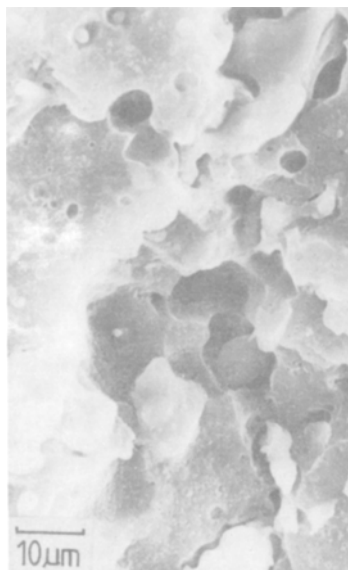
Fig. 4 SEM micrograph of 29% IFR and 3.5% EVA containing PP sample after etching with heptane

The SEM results prove that the encapsulating during compounding can be successfully used in case of IFR additives as well. In order to control the efficiency of the process, the conductivity of the flame retarded polymer samples and of the water used for the extraction of these samples has been investigated. The results are presented in the Fig. 5.

The solved molecules of flame retardants extracted from the surface of the samples highly increase the conductivity of extracting water (<40 μSiemens). The effect of elastomer is quite clear from both of measurements, the sensitivity to environmental humidity can be reduced this way substantially. The magnitude of effect depends on elastomer content in accordance with our earlier results concerning filled polymer: concentration lower than required to cover the particles may cause
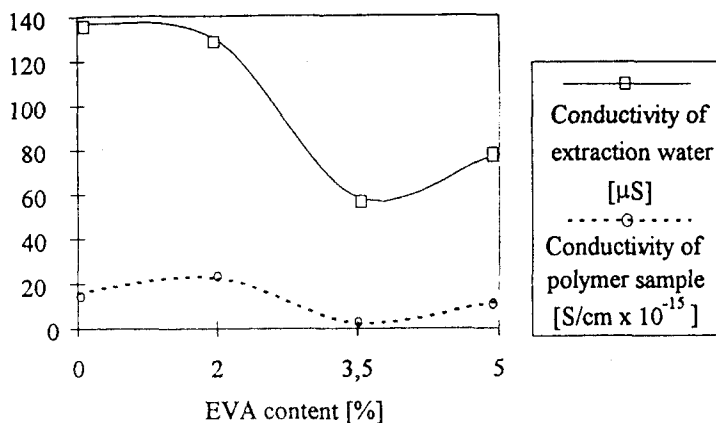
Fig. 5 Effect of EVA additive on the electrical conductivity of PP+34% IFR samples and of the extraction water after the extraction of these samples at 25°C for 1500 min

heterogeneous structure while above this level the surplus elastomer takes place in separate disperse phase [17].

The effect of EVA on the crystallization of PP/IFR system is given in Fig. 6. An increased crystallization temperature and crystallinity suggest that the reaction between PER and APP does not take place in this case, the nucleating activity of APP is unchanged. The surrounding of PER by EVA at the earlier stage of mixing restrict probably its reaction with APP.

The flame retarding efficiency of this system is decreased, at least 5% higher amount of IFR additive is required to achieve the V0 degree of flame retardancy in the presence of EVA.

In order to combine the advantageous effects of an elastomer with improvement of the efficiency of flame retardants, we applied a boron-siloxane elastomer instead
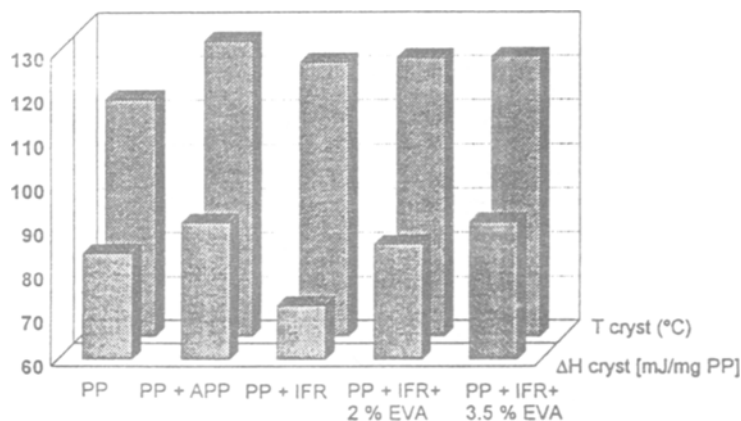

Fig. 6 Heath and temperature of crystallization of flame retardant PP compositions

of EVA for embedding the water sensitive additives [20]. The method is again a simple thermomechanical mixing, but during the process this component may react with the OH groups of the IFR additives. The scheme of the structure formed this way is shown in Fig. 7.

Recent conductivity and XPS investigations demonstrated, that this modification may reduce the water sensitivity of the product similarly to EVA and contribute to the effect of flame retardants due to its migration to the surface [20].

The most considerable effect of boron-siloxane elastomer is the increase of elongation at break, that becomes even higher than pure PP's, in spite of the high additive content (Fig. 8). DSC studies of the same samples has been performed, in order to determine the reasons for this improvement. The results in Fig. 8 suggest a
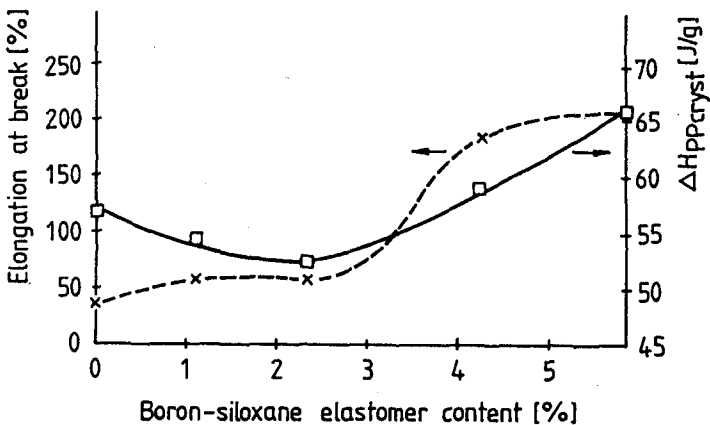

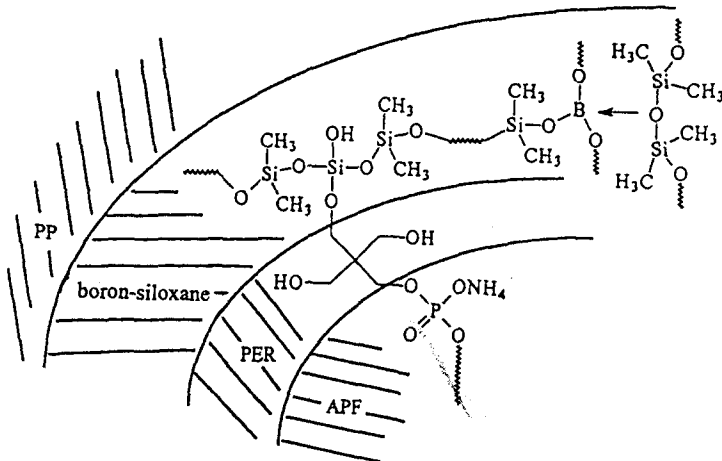Fig. 7 Scheme of the chemical structure of reactive compounded IFR additives in PP

Fig. 8 Heat of crystallization and elongation at break of PP copolymer samples containing 34% IFR additive and different amounts of boron-siloxane elastomer

direct relationship between the crystalline structure and stretching of the samples. A steep increase of elongation at break starts above a critical amount of boron-siloxane elastomer. Approximately the same critical ratio has been determined earlier by conductivity measurements [20] and it appears in the ΔH_C curve in Fig. 8 as well, suggesting that this is the amount required to cover the surface of the solid APP particles. The surplus elastomer is dispersed in the PP matrix separately from the solid particles and acts as plasticiser enhancing the mobility of PP macromolecules. The higher mobility during crystallization leads to higher degree of crystallinity. The increase of ΔH_C in Fig. 8 above the critical concentration can be explained by this effect. The same plasticiser action contributes to the increase of the elongation at break.

Conclusion

Ammonium-polyphosphate, an essential component of non-halogenated, intumescent flame retardant systems, acts as nucleating additive in PP. Increased temperature and enthalpy of crystallization indicate this effect in course of DSC measurements. Improved performance in intumescent flame retardants could be achieved by applying the optimal parameters for reactive compounding of ammonium-polyphosphate–pentaerythritol–melamine systems with PP. Pentaery-thritol used generally to increase the effectivity of flame retardant system may react with APP during melt mixing and decreases its nucleating effect this way. EVA elastomer acting as interface modifier decreases the sensitivity of flame retardant polyolefin system to environmental moisture significantly, but the degree of flame retardancy is decreased as well in this case. PER does not decreases the nucleating activity of APP in presence of EVA, while the reaction between the two component of flame retardant system is restricted. Boron-siloxane elastomer modifies the heat of crystallization of PP depending on its concentration and improves various properties of flame retardant PP system.

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