

The Mechanical Properties and Thermal Performances of Polypropylene with a Novel Intumescent Flame Retardant

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ABSTRACT: A novel intumescent flame retardant: tetra-spirophosphoryl-benzoguanamine (TSPB) containing three constituents was used as a new flame retardant for polypropylene to prepare flame-retardant materials, whose flammability and thermal behavior were studied by the limited oxygen index (LOI), thermogravimetric analysis (TGA), in addition whose mechanical properties were investigated in this work. It was found that when the addition of TSPB was 25 wt %, the LOI value of the PP could achieve to 29.5 and pass the UL-94 V-0 rating test. The TGA data showed that

TSPB could enhance the thermal stability of PP and effectively increase the char residue formation. The mechanical performance test showed that the addition of TSPB improve the mechanical performances of PP to some extent. Thus, the trinity intumescent flame retardant TSPB is good to modify PP. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2170–2177, 2010

Key words: intumescent flame retardant; polypropylene; thermogravimetric analysis; limited oxygen index; mechanical properties

INTRODUCTION

With the increasing concern about the health and environmental risks, flame retardants are required not only to have excellent flame retardancy, but also to reduce the evolution of toxic gases and to possess good effect on smoke inhibition when the flame retardant materials are combusting, simultaneously having little influence on the mechanical properties of flame retardancy material. Because many conventional flame retardants (especially for halogen-antimony system) have such disadvantages, they are confronted with austere challenges, which provide a favorable development opportunity for intumescent flame retardants. They will be one of the most popular research subject in flame-retardant field in the future, and they will be regarded as an effective way to realize halogen-free flame retardant.¹

In recent years, intumescent-flame-retardant (IFR) additives have been widely utilized in flame-retarding flammable polymers such as polypropylene due to their advantages such as low smoke and toxicity, and no corrosive gas generation, no flame dripping and halogen-free over the halogen-containing compounds.^{2,3} As well known, the formation of expanding charred crust is the

crucial requirement for an intumescent system. A typical intumescent flame retardant is generally made of three constituents: an essentially phosphorus-containing additive; a second additive, containing nitrogen, such as melamine, urea, urea-formaldehyde resins and polyamides, which serves as a foaming agent; and a third, carbon-containing additive, which acts as a carbon donor to allow an insulating cellular carbonaceous layer (char) to be formed between the polymer and flame.⁴ The phosphorus-nitrogen containing compounds mainly act as intumescent flame retardants resulting in a char layer in the condensed phase which can produce less toxic gas and smoke⁵ and the charred layer acts as a physical barrier which slows down heat and mass transfer between gaseous and condensed phase.

Polypropylene are widely used in many applications, such as housing materials, transport and electrical engineering, but it is easily inflammable due to chemical constitutions. To reduce its flammability, flame retardants are added.^{6–9}

In this article, tetra-spirophosphoryl-benzoguanamine (TSPB) which possesses three components: acid source, char former and blowing agent was combined with PP in different ratios. The mechanical, thermal and burnable properties of the flame-retardant PP were investigated by LOI, TGA, SEM and mechanical properties testing.

EXPERIMENTAL

Materials

TSPB was synthesized in my own laboratory, of which the synthesis method is going to be applied

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for patent and its chemical structure was showed in Scheme 1. PP powder (homopolymer, melt flow rate: 3.5 g/10 min) was supplied by Daqing Huake Company (Daqing, China)

Sample preparation

PP and TSPB were blended in different ratios (Table I) with a high-speed mixer (SHR, Zhangjiagang, China) and extruded using a counter-rotation twin-screw extruder (D:20 mm, L/D:32, Model: SLJ-20 Nanjing Jieya Chemical Engineering Equipment company, China). The temperatures from hopper to die at six different zones are 160, 175, 180, 190, 190, and 185°C respectively, and the screw speed is 160 rpm. The extrudate was cut into pellets and dried in an oven at 70°C for 6 h, then injection-molded (SJ-20×25, Harbin special plastic product company, China) at 210°C into various specimens for test and characterization.

Limiting oxygen index

Limited oxygen index (LOI) of all samples were tested on a JF-3 oxygen index instrument (Jiangning, China) at room temperature with sheet dimensions of 130 × 6.5 × 3 mm according to ASTM D2863-97. LOI is a parameter for evaluating flame retardancy and flammability of polymeric materials in the same conditions. It denotes the lowest volume concentration of oxygen sustaining candle-like burning of materials in mixing gases of nitrogen and oxygen.

UL-94 test

Vertical burning tests were conducted on a vertical burning test instrument (CZF-3, Jiangning, China) with sheet dimensions of 130 × 13 × 3 mm according to ASTM D3801.

Mechanical property test

Tensile and Bend strength tests were carried out according to ASTM D638 and ASTM D790 on a T-20A universal testing machine (Shenzhen, China) with a crosshead speed of 5 mm/min and 2 mm/min at room temperature respectively,^{10–15} and the results reported were the average from five samples. Izod impact tests were carried out on a XJC-5 notched impact tester (Chengde, China) according to ASTM D256, and the results reported were the average from ten samples.

Thermogravimetry analysis (TGA)

Thermogravimetry analysis (TGA) was performed on a Perkin-Elmer Pyris 1 Thermal Analyzer with platinum crucible sample holder. The samples were

examined under flowing high-purity nitrogen of 50 mL/min, at a constant heating rate of 10°C/min in the temperature range 50–800°C and the weight of all samples were kept within 3–5 mg.

Kinetic analysis

The application of dynamic TGA methods holds great promise as a tool for unraveling the mechanisms of the physical and chemical processes that occur during degradation of polymers and their composites. The thermal degradation kinetics of PP and flame-retardant PP composites are determined on the basis of TGA results. In TGA measurements, conversion, α , is defined as:

$$a = \frac{w_i - w_a}{w_i} \quad (1)$$

where w_a and w_i are the actual, and initial sample weights, respectively. Kinetic information can be extracted from dynamic experiments by various methods. All kinetic studies assume that the isothermal rate of conversion,¹⁶ $d\alpha/dt$, is a linear function of the reactant concentration loss and of the temperature-independent rate constant, k , and a temperature-independent function of conversion, that is:

$$d(\alpha)/d(t) = \beta(d\alpha/dT) = k(T)f(\alpha) \quad (2)$$

where $f(\alpha)$ and $k(T)$ are the functions of conversion and temperature, respectively, and $\beta = dT/dt$.

The temperature dependence of the kinetic constant (k) can generally be given by the Arrhenius equation:

$$k(T) = Ae^{-E/RT} \quad (3)$$

where E is the activation energy of the reaction, A is the frequency factor, T is the reaction temperature, and R is the gas constant.

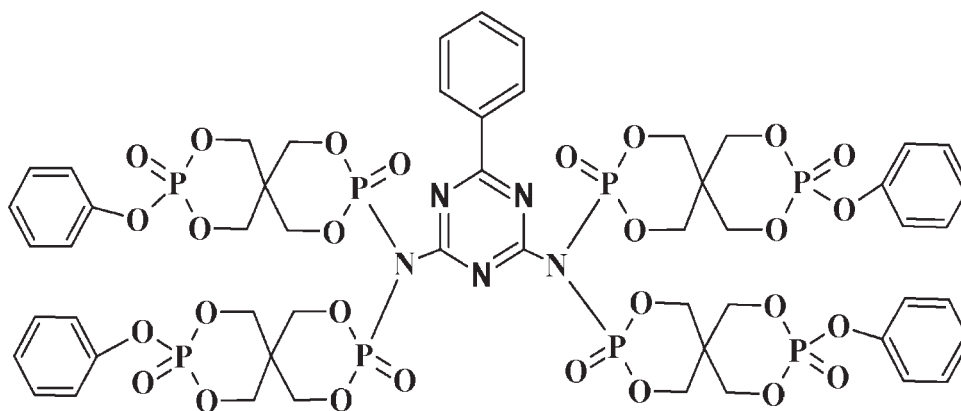
The $f(\alpha)$ depends on the particular decomposition mechanism. The simplest and most frequently given model in TGA data for $f(\alpha)$ is:

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

where $(1-\alpha)$ is the dimensionless amount of reactive remaining and n is the reaction order. The combination of eqs. (2), (3), and (4) gives the following equation:

$$d(\alpha)/d(t) = \beta(d\alpha/dT) = Ae^{-E/RT}(1 - \alpha)^n \quad (5)$$

Equation (5) is normally the fundamental base for kinetic analysis of a solid material from nonisothermal TGA experiments data. In the present study,



Scheme 1 The chemical structures of TSPB.

one method were used to analyze the nonisothermal kinetics of PP and flame-retardant PP composites.

The Flynn–Wall–Ozawa method^{17,18} is derived from the integral method. The standard eq. (5) can be given as follows:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{Ae^{-E/RT}}{\beta} dT \quad (6)$$

which is integrated with the initial condition of $\alpha = 0$ at $T = T_0$ to obtain the following expression:

$$F(\alpha) = \int_0^\alpha \frac{1}{(1-\alpha)^n} d\alpha = \frac{1}{\beta} A \int_{T_0}^T e^{-E/RT} dT \quad (7)$$

where $F(\alpha)$ is the integral function of conversion.

From eq. (7) and the Doyle approximation, the result of the integration can be simplified as:

$$\log \beta = \log \frac{AE}{R} - \log F(\alpha) - 2.315 - 0.457 \frac{E}{RT} \quad (8)$$

where β , A , E , and T are as already defined.

This is one of the integral methods that can determine activation energy without knowledge of the reaction order. The activation energy for different conversions can be calculated from a plot of $\log \beta$ versus $1000/T$. So this method was adopted in this article.

TGA of the PP and PP10 were performed under high-purity nitrogen of 50 ml/min, at heating rates of 5, 10, 15, 20, and 25°C/min to evaluate the degradation kinetics parameters. The Flynn–Wall–Ozawa method is probably the most general derivative technique,¹⁹ which is an integral method that is independent of the degradation mechanism. Using eq. (8), the activation energy values of pure PP and flame-retardant PP10 could be obtained from a linear fitting of $\log \beta$ against $1000/T$ for a fixed degree of conversion because the slope of such a line is given by $-0.457 E/RT$.

Scanning electron microscopy (SEM)

The fractured surfaces of sample PP25 and PP30 were investigated by means of scanning electron microscopy (SEM, QUANTA-200, FEI). Cryogenic fractured surfaces were obtained by immersing the unbroken samples into liquid nitrogen for several minutes and breaking them with the tap of a hammer, which is called brittle fracture. All the fracture surfaces were gold coated before SEM examination.

RESULTS AND DISCUSSION

Flame retardancy

LOI measurement and UL-94 test are widely used to evaluate the flame retardant properties of materials. Generally, LOI values describe a procedure for measuring the minimum concentration of oxygen that will just support flaming combustion in a flowing mixture of oxygen and nitrogen, essentially an “ease of extinction” test. The UL-94 test is used to determine the small scale ignition and flame spread of materials, and the results are classified by flammability ratings V-0, V-1, or V-2, where V-0 rating is the highest flame retardant rating for materials, corresponding to prevention of flame spread vertically upwards, and without sample dripping, the V-1 rating allows nonflaming drips and V-2 allows flaming drips.²⁰ Table I shows the LOI values, UL-94 rating and dripping behavior of all the specimens studied.

TABLE I
The Flame Retardancy of PP with Different Loading Levels TSPB

Sample	PP (wt %)	TSPB (wt %)	LOI	UL-94	Drip
PP	100	0	18.0	–	Heavily
PP10	90	10	20.6	–	Some
PP15	85	15	24.2	–	Some
PP20	80	20	26.3	V-1	Little
PP25	75	25	29.5	V-0	No
PP30	70	30	32.4	V-0	No

TABLE II
The Mechanical Properties of PP with Different Loading levels TSPB

Sample	Tensile strength (MPa)	Bend strength (MPa)	Tensile modulus (MPa)	Bend modulus (MPa)	Izod impact strength(KJ/m ²)
PP	24.732	36.990	162.907	1039.08	3.517
PP10	22.397	36.673	178.473	1296.27	4.482
PP15	25.120	38.753	170.237	1268.43	3.901
PP20	21.817	39.760	182.323	1301.92	4.355
PP25	21.377	41.957	164.073	1417.99	3.573
PP30	21.060	40.450	154.430	1362.52	3.626

PP is easy flammable and its LOI is only 18.0 and its UL-94 can't pass any rating with heavily dripping. It is obvious that TSPB has enhanced the flame retardancy of PP, whose LOI reaches 29.5 when addition of TSPB is 25 wt %, with LOI 32.4 at 30 wt % and whose UL-94 achieves V-0 rating without dripping when addition of TSPB is just 25 wt %. From Ref. 21 it can be seen that if have the same level of flame retardancy as the PP25 composite, the MH (Magnesium Hydroxide) concentration needed was 60% and the BR (Mixture of Brominated Phosphate Ester and Antimony Trioxide) concentration needed was 30%. When the loadings of flame retardance was 30%, the LOI values of PPAPP30, PPAPPER3/1, PPAPPER1/1, PPAPPER1/3, PPPER30, and PPMPP30 were: 20, 27.5, 28, 25, 20, and 30.5, and all of these samples could not achieve UL-94 V-0 rating.²² The LOI values of PP/PSiN-A and PP/PSiN-B were 26.0 and 24.0 (the concentrations of PSiN-A and PSiN-B were also 30%).²³ Therefore, TSPB used in flame retardant PP obtains a surprisingly good result.

From the above results, we can conclude that the halogen-free flame retardant TSPB has a significant and beneficial flame-retardant effect on PP. This novel flame retardant provides a good choice for preparing flame-retardant PP.

Mechanical properties

Table II gives mechanical properties of the flame retardant PP, whose formulation are based on Table I. Figure 1 shows the results of tensile tests, flexural tests and Izod impact tests. It can be seen that the tensile strength and tensile modulus have only tiny changes with the increasing of IFR loading level, in comparison with pure PP. The bend strength and bend modulus have comparatively obvious improvement. In addition, the Izod impact strength of specimens with various IFR loading level is nearly no change paralleling with pure PP. These results indicate that TSPB has good compatibility with PP which not only won't deteriorate the mechanical properties of PP as other intumescent flame retardants doing,²⁴⁻²⁹ but also improves them to a certain extent, which is because that the stereo-structure of

TSPB molecular might be spherical³⁰ which makes the nonpolar groups such as phenyl and spirocyclic be exposed and the polar groups enwrapped. The values of bend strength and bend modulus reach the maximum when TSPB content was 25 wt %, following tightly by 30 wt %. The values of tensile

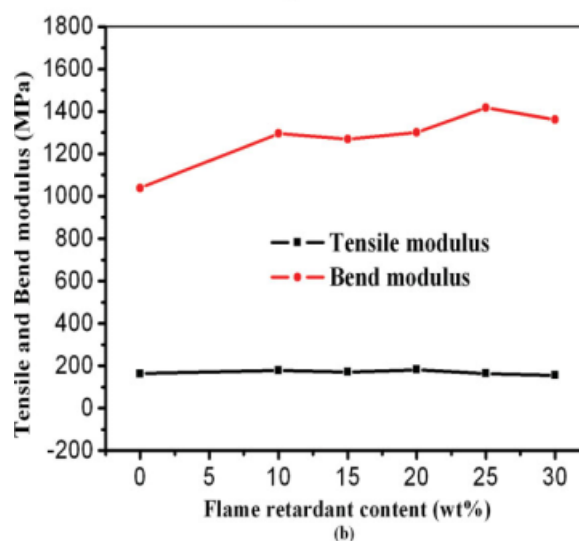
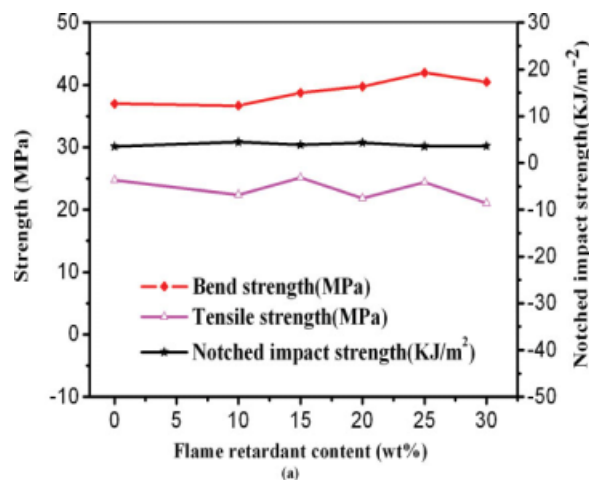


Figure 1 Mechanical property curves of IFR-PP specimens. (a) Tensile strength, Bend strength and Izod impact strength versus TSPB content, (b) Tensile modulus and Bend modulus versus TSPB content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

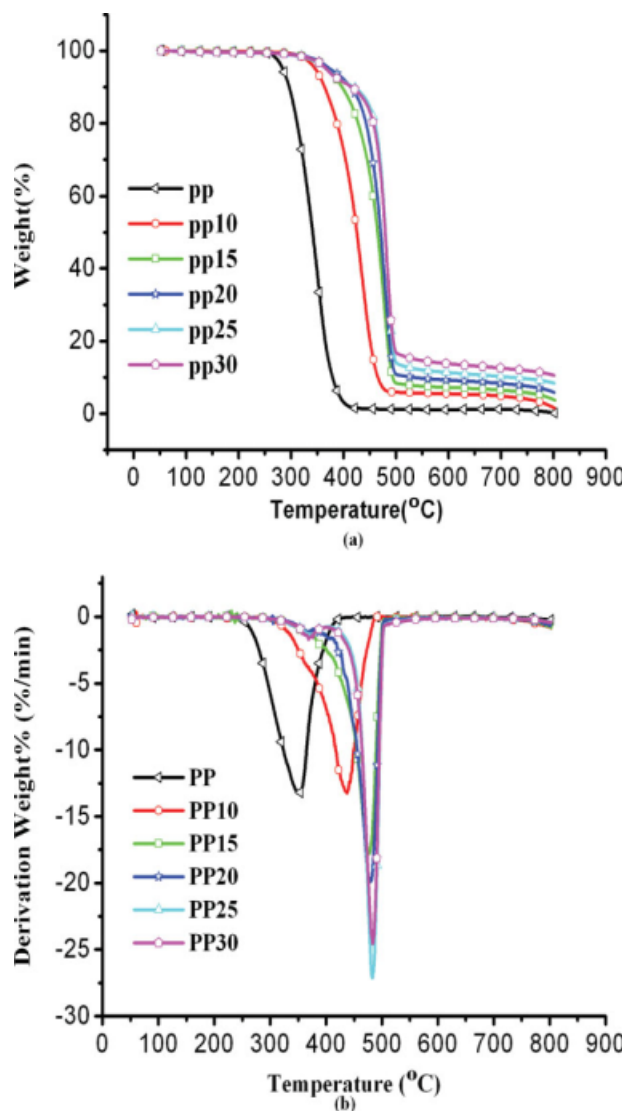


Figure 2 TG (a) and DTG (b) curves of various samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

modulus and izod impact strength of PP25 were almost the same as pure PP. Only the tensile strength had some decrease in comparison with

pure PP. Moreover, it is noted that PP25 and PP30 are classed V-0 in the UL-94 test (Table I).

Thermogravimetric analysis (TGA)

TGA can serve as a useful indicator of polymer decomposition and flammability behavior and it is the most favored technique for rapid evaluation in comparing and ranking the thermal stability of various polymers.^{31–33} Figure 2 shows the thermal decomposition behaviors of various specimens, and the test data are summarized in Table III, including the 5% weight loss temperature ($T_{5\%}$), the 50% weight loss temperature ($T_{50\%}$), the maximum-rate decomposition temperature (T_{\max}) and the char residues at 600°C (Y_1) and 800°C (Y_2).

It could be noted that all the data of sample IFR-PP are significantly higher than sample pure PP. From the data in Table III, it can be found that $T_{5\%}$, which is defined as the temperature at which weight loss is 5 wt %, is 284°C for pure PP, indicating that pure PP is relatively thermally stable below 284°C with a weight loss of less than 5%. When the temperature further increases, weight loss increases rapidly and a lot of volatile is produced until almost exhaust at 800°C. Meanwhile the $T_{5\%}$ raises to 346–374°C for IFR-PP with various loading of TSPB and the char residues at 600°C and 800°C increase gradually along with the increasing loading of TSPB. The char residues are from 1.127 to 13.764 (600°C) and from 0.023 to 10.598 (800°C), meanwhile, the maximum-rate decomposition temperature also increases from 351.3 to 483.2°C. PP25 and PP30 represent higher thermal stability and higher rate of char (600°C) in comparison with PP-PER-APP system,³⁴ PP-APP system,³⁵ PP-MH system³⁶ (The loading of the flame retardant were all 25 or 30%). It is mainly attributed to the phosphate-nitrogen group which has a major contribution to form the compact char to protect the PP specimens from further decomposition.^{37,38} In other words, the sample PP with higher TSPB content is more stable at high

TABLE III
Calculated Results from TG, DTG curves of Various Samples

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	$T_{50\%} - T_{5\%}$ (°C)	T_{\max} (°C)	R_{\max} (%/min)	Y_1 (%)	Y_2 (%)
PP	284.4	341.0	56.6	351.3	13.3	1.127	0.023
PP10	346.4	425.6	79.2	437.5	13.2	5.486	1.728
PP15	368.9	465.0	96.1	477.1	17.8	7.214	3.901
PP20	374.4	471.0	96.6	478.6	19.9	9.251	5.925
PP25	367.4	479.7	112.3	482.8	27.1	11.341	8.460
PP30	367.4	479.4	112.0	483.2	24.6	13.764	10.598

$T_{5\%}$, temperature of 5% weight loss.

$T_{50\%}$, temperature of 50% weight loss.

T_{\max} was the maximum-rate decomposition temperature.

R_{\max} was the maximum mass loss rate.

Y_1 was the residue at 600°C.

Y_2 was the residue at 800°C.

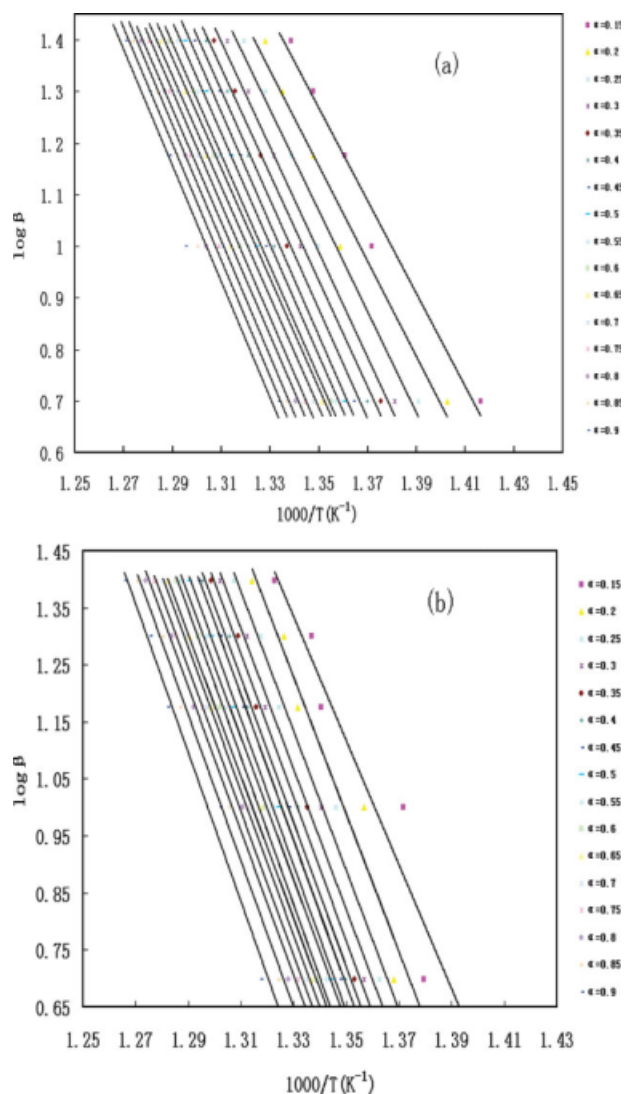


Figure 3 Ozawa plots of PP and PP10 at different conversion: (a) PP; (b) PP10. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature. It can also be verified by the changes of 50% mass loss temperature along with the different TSPB content showed in Table III. That the higher TSPB content specimen possess the greater difference values for $T_{50\%} - T_{5\%}$ evidently proves that the addition of TSPB slows down the decomposition of PP. That the specimen with more loading of TSPB have the higher T_{max} , which is closer and closer to 500°C, and R_{max} increase gradually except for PP30, lead to the momentary formation of protective char layer to prevent PP from further decomposition. That the peak width in DTG curves, corresponding to the major mass-loss stage, becomes more and more narrow along with the increase of TSPB content affirmed from Figure 2(b) indicate that the addition of TSPB shortens the degradation process of PP. Besides, plenty of volatile is generated in charring process, resulting in the increase of R_{max} in other words, the

TABLE IV
Activation Energy of PP obtained by Flynn-Wall-Ozawa Method

Conversion, α	Activation energy, E (kJ/mol)	Correlation coefficient, R^2
0.15	163.6544	0.977
0.20	168.8232	0.973
0.25	177.9414	0.975
0.30	185.276	0.979
0.35	186.914	0.979
0.40	192.738	0.973
0.45	197.106	0.980
0.50	196.378	0.982
0.55	196.560	0.982
0.60	194.012	0.976
0.65	195.104	0.976
0.70	198.926	0.974
0.75	200.200	0.982
0.80	203.476	0.971
0.85	204.568	0.971
0.90	204.932	0.960
Average	191.663	

speed of char residue formation is relative to the quantity of volatile materials produced and that is corresponding to the maximum mass loss rate (R_{max}).

Thermal degradation kinetics of PP and flame-retardant PP

From the Flynn–Wall–Ozawa analysis, we used conversion values in the range of 15–90% with this method, so α values of 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, and 0.9 were used. The results are given in Figure (3), which

TABLE V
Activation Energy of PP10 obtained by Flynn-Wall-Ozawa Method

Conversion, α	Activation energy, E (kJ/mol)	Correlation coefficient, R^2
0.15	198.113	0.907
0.20	218.613	0.945
0.25	222.564	0.979
0.30	224.348	0.979
0.35	229.300	0.987
0.40	230.519	0.987
0.45	231.739	0.994
0.50	232.959	0.994
0.55	227.170	0.991
0.60	234.798	0.994
0.65	226.350	0.992
0.70	229.864	0.996
0.75	229.427	0.993
0.80	230.155	0.987
0.85	233.177	0.991
0.90	237.711	0.979
Average	227.300	

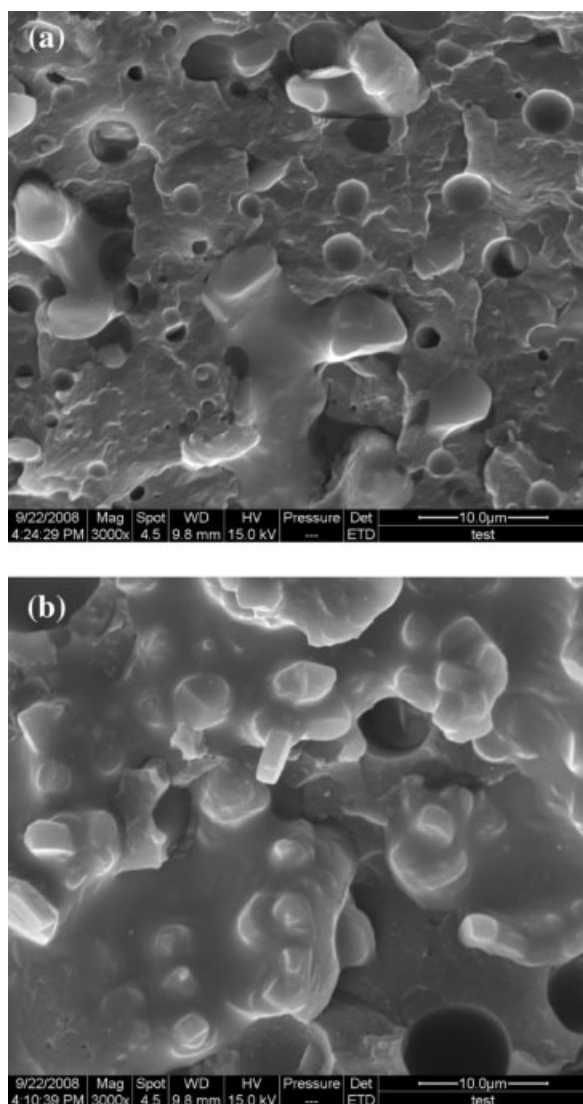


Figure 4 SEM micrographs of fracture surfaces of the samples ($\times 3000$): (a) PP25; (b) PP30.

shows the plots of $\log \beta$ versus $1000/T$ at varying conversion in nitrogen. The straight lines fitting the data are nearly parallel, this being an indication that the activation energies at the different degrees of conversion are similar. The activation energies (E) corresponding to the different rates of conversion are listed in Tables IV and V, which show that the pure PP and PP10 respectively, had an average activation energy of 191.663 and 227.300 kJ/mol respectively. It was clearly observed that the E of pure PP was much lower than that of PP10. In other words, TSPB could improve the thermal degradation of PP. The increase in the apparent activation energy of the polypropylene thermal degradation can interpret why the addition of TSPB slows down the decomposition of PP and why the maximum-rate decomposition temperatures of flame-retardant PP were higher than pure PP. In other words, flame retardant could improve the thermal stability of PP.

SEM analysis

The SEM micrographs of fractured surfaces of sample PP25 and PP30 are showed in Figure 4. It can be seen that the flame retardants at 25% content disperses more homogeneously than the flame retardants at 30% content. As seen from Figure 4(a), TSPB and PP matrix almost become one flesh, showing well comparability between flame retardants and PP matrix. Thus, it could lead to better mechanical properties, which is in common with anterior conclusion. It is worthwhile to point out that the TSPB particles in the PP30 specimen [Fig. 4 (b)] were significantly centralized than in the PP25 specimen [Fig. 4 (a)]. This indicated that the TSPB agglomerated for the specimen with higher flame-retardant filler content, and their aggregation decreased the dispersion of flame-retardant additives in the PP matrix. The poor dispersion of TSPB in the PP30 specimen could lead to their comparability with PP matrix bad in comparison with that in the PP25 specimen. The poor comparability between flame-retardant and matrix might not result in good mechanical properties.^{8,21} This also could interpret why the mechanical property of PP25 specimen is better than PP30 specimen.

CONCLUSIONS

The novel intumescent flame retardant, TSPB, exhibits extremely effective flame retardancy for PP, and the LOI is improved along with the increase of TSPB content. The addition of TSPB reinforces the mechanical performance in bend strength and bend modulus and makes the tensile strength and tensile modulus have only tiny changes. TGA curves show that the higher TSPB content can cause higher char residue and TSPB also promotes the thermal stability of PP. It could be noted that the addition of TSPB makes the maximum-rate decomposition temperature shift towards upper position obviously. But the improvement range is not significant when the loading of TSPB exceeds 25%. Moreover, the addition of TSPB improves the activation energy values of PP. So, that the trinity intumescent flame retardant TSPB is used to modify PP can obtain good effect and the optimum loading of TSPB is 25 wt %.

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