Effect of Boron-Containing Materials on the Flammability and Thermal Degradation of Polyamide 6 Composites Containing Melamine

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ABSTRACT: Three different boron-containing substances—zinc borate (ZnB), borophosphate (BPO_4), and a boron- and silicon-containing oligomer (BSi)—were used to improve the flame retardancy of melamine in a polyamide 6 (PA-6) matrix. The combustion and thermal degradation characteristics of PA-6 composites were investigated with the limiting oxygen index (LOI), the UL-94 standard, thermogravimetric analysis (TGA)/Fourier transform infrared (FTIR) spectroscopy, and differential scanning calorimetry (DSC). A slight increase was seen in the LOI values of a sample containing BSi (1 wt %). BPO_4 at high loadings showed a V0 rating (indicating the best flame retardancy) and slightly lower LOI values in comparison with samples with only melamine. For ZnB and BSi, glassy film and char formation decreased the dripping rate and sublimation of melamine, and this led to low LOIs. According to the TGA–FTIR results, the addition of boron compounds did not change the decomposition product distribution of melamine and PA-6. The addition of boron compounds affected the flame retardancy by physical means. The TGA data showed that boron compounds and melamine reduced the decomposition temperature of PA-6. According to the DSC data, the inclusion of boron compounds increased the onset temperature of sublimation of melamine and also affected the flame retardancy negatively. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2722–2727, 2010

Key words: flame retardance; polyamides; thermogravimetric analysis (TGA)

INTRODUCTION

Most polyamides are classified as V2 (worst flame retardancy rating) according to the Underwriters Laboratory UL-94 test. This means that polyamides are self-extinguishing to some extent because of extensive shrinkage and dripping during combustion. The flame retardancy of polyamides must be improved for more widespread applications despite their self-extinguishing properties.[1,2]

There are many different types of flame retardants, such as additives containing halogens, phosphorus, nitrogen, sulfur, boron, and silicon, that are used with polyamides to reduce their flammability. A flame-retardant additive operates by interfering with at least one of the individual stages of the burning process in a physical or chemical way. The end result of a flame-retardant additive is the retardation and final elimination of the burning-process mechanism. A synergistic effect exists among different types of flame retardants, so the combination of different flame retardants provides improved results. Synergistic reactions also make it possible to reduce the amounts of other flame-retardant agents employed.[1–6]

The most important nitrogen-containing flame retardants are melamine and its derivatives. Melamine, a white, crystalline solid, has a melting point of approximately 350°C. Melamine has three effects on individual stages of the burning process. At its melting point, melamine is known to vaporize or sublime rather than go through a traditional melting phase change. During sublimation, it absorbs a significant amount of heat (1965 kJ/mol) and thus acts as a heat sink in case of fire. Vaporized melamine also acts as an inert gas and dilutes the oxygen and fuel gases present at the point of combustion. Melamine destabilizes polyamide 6 (PA-6) and increases the dripping behavior of the polymer so the fuel source is removed from the combustion zone.[1,4,5]

Boron-containing compounds are used either alone or with other flame retardants to improve the flame retardancy of polymeric materials.[7,8] The main purpose of this work was to investigate the combustion characteristics and thermal degradation of flame-retardant PA-6 composites containing melamine with three different kinds of boron-containing additives: zinc borate (ZnB), borophosphate (BPO_4), and a boron- and silicon-containing oligomer (BSi). The combustion and thermal degradation characteristics

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TABLE I
Compositions of the Formulations and UL-94 Ratings

Sample	PA-6	Melamine	ZnB	BPO_4	BSi	UL-94
NM0	100	—	—	—	—	V2
NM1	80	20	—	—	—	V0
NM2	80	19	1	—	—	V2
NM3	80	17	3	—	—	V2
NM4	80	15	5	—	—	V2
NM5	80	19	—	1	—	V0
NM6	80	17	—	3	—	V0
NM7	80	15	—	5	—	V0
NM8	80	19	—	—	1	V0
NM9	80	17	—	—	3	V0
NM10	80	15	—	—	5	V2

were investigated with the limiting oxygen index (LOI), the UL-94 standard, thermogravimetric analysis (TGA)/Fourier transform infrared (FTIR) spectroscopy, and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

PA-6 (trade name Bergamid B65 Natur-TP) was purchased from Polyone (Fischbach, Luxembourg). Melamine (Melafine) was purchased from DSM (Geleen, the Netherlands). ZnB (ZB 467) was purchased from Great Lakes Chemical GmbH, a Chemtura company (Frauenfeld, Switzerland). A powder sample of BPO_4 was prepared by a solvothermal method with benzyl alcohol.[9] The characterization of BPO_4 particles was performed with X-ray diffraction, TGA, and scanning electron microscopy; the details are presented in our previous article.[10] BSi was synthesized through the condensation of boric acid with vinyltriethoxysilane at a relatively low temperature (150–160°C).[11] The characterization of the oligomers was performed with FTIR, gel permeation chromatography, and TGA. The details are again presented in our previous article.[10]

Preparation of the samples

The total concentration of the flame retardants (melamine and boron compounds) mixed with PA-6 was maintained at 20 wt %. The addition of boron compounds at concentrations of 1, 3, and 5 wt % corresponded to 5, 15, and 25% reductions in the amount of melamine, respectively. The compositions of the formulations and their UL-94 ratings are shown in Table I. PA-6 and flame retardants were mixed in a twin-screw extruder at 100 rpm and 230°C. PA-6 pellets were dried at 80°C for 24 h before mixing. The extrudate was cut into pellets, and they were compression-molded at 230°C into test bars for flammability testing.

LOI

LOI was measured with a Dynisco LOI analyzer (Akron, OH) on test bars ($130 \times 6.5 \times 3.25$ mm^3) according to the ASTM D 2863 standard oxygen index test.

UL-94 testing

The UL-94 rating [ranging from V0 (best flame retardancy) to V2 (worst)] was obtained according to ASTM D 3801. Bar specimens ($130 \times 13 \times 3.25$ mm^3) were tested.

TGA and FTIR spectroscopy

TGA–FTIR was carried out on a PerkinElmer Pyris 1 thermogravimetric analyzer (Massachusetts) and a PerkinElmer Spectrum 1 FTIR spectrometer (Massachusetts) at a heating rate of 10°C/min up to 600°C under a nitrogen flow of 50 mL/min.

DSC

DSC was carried out on a Mettler-Toledo DSC 1 Star System (Columbus, OH) at a heating rate of 10°C/min up to 400°C under a nitrogen flow of 50 mL/min.

RESULTS AND DISCUSSION

LOI and UL-94 rating

LOI and vertical burning ratings (UL-94) were determined to investigate the flame retardancy behavior of the PA-6 composites. As shown in Figure 1, the LOI value sharply increased from 22.5 to 31 when 20 wt % melamine was added to PA-6. Similar results can be found in the literature.[12,13] Except for a composite containing 1 wt % BSi, the addition of boron compounds reduced the LOI value with respect to NM1. The addition of 1 wt % BSi slightly increased the LOI value from 31 to 31.4. In the absence of any synergy, the LOI values decreased when the amount of the effective flame-retardant

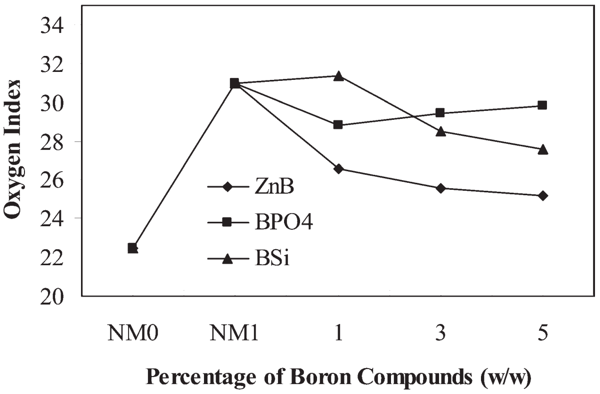

Figure 1 LOI values of the composites.

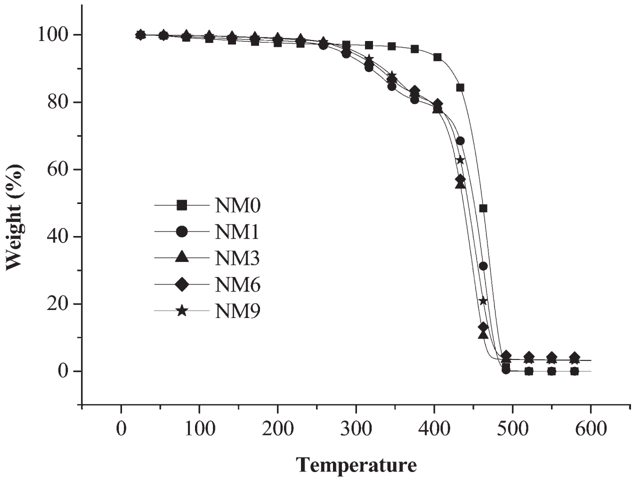

Figure 2 TGA curves of selected composites.

agent (melamine) was reduced. This general trend is shown in Figure 1. Another reason that a large reduction of the LOI values occurred for both BSi and ZnB was the capacity for glassy surface formation during combustion. This glassy structure that formed over the liquid combustion phase slowed the sublimation of melamine. The reduction of the rate of sublimation of melamine had two effects during combustion. First, the heat-sink action of melamine was reduced, and second, the dilution of combustible gases was reduced. Interestingly, the BPO_4-containing composites reached the minimum LOI value (28.8) when they contained 1 wt % BPO_4, and then the LOI value increased to 29.8 when the amount of BPO_4 reached 5 wt %. BPO_4 had a spherical shape with a high melting point (1000°C) and high thermal stability (up to 1200°C). The BPO_4 particles were stable and increased the dripping rate. The increase in the dripping rate of PA-6, which removed the fuel source from the combustion zone, led to the V0 rating and high LOI values. The dripping rate was also a function of the surface tension of the pendent drop hanging from the sample tip. BPO_4, stable in its solid form, did not change the low surface tension of PA-6 and melamine, whereas decomposing BSi and ZnB could increase the drop surface tension and give rise to reduced dripping rates. To understand the increase in the LOI trend at higher BPO_4 loadings, a composite with 10 wt % BPO_4 was prepared, and an LOI of 22 and a V2 rating were obtained. The trend, therefore, was reversed because of the inadequate amount of melamine.

According to the UL-94 test, the total burning time (the afterflame time after the first ignition plus the afterflame time after the second ignition) of all samples, except NM0, was less than 20 s. All BPO_4- and ZnB-containing samples had V0 and V2 ratings, respectively, at all tested concentrations. On the other hand, ZnB had the ability to form a glassy surface. This glassy layer slowed the flame-retarding mechanism of melamine, as mentioned previously.

TGA

TGA can serve as a useful indicator of polymer flammability. TGA curves of selected composites are shown in Figure 2. TGA data for all composites are listed in Table II. According to Figure 2 and Table II, the weight loss of pure PA-6 took place in a single step, with the maximum weight-loss rate at 471°C without any char residue at 600°C. Two weight-loss steps can be seen in the TGA curves of PA-6 containing melamine. The first step can be attributed to the sublimation of melamine, and the second step arose from the decomposition of PA-6.[12,13] The composite containing only melamine had no char residue at 600°C. According to previous research on melamine cyanurate, the addition of melamine cyanurate increased the char yield from 0% to 0.6%.[10] The inclusion of boron compounds increased the

TABLE II
TGA Data for the Composites

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_{max} (°C) Stage 1	T_{max} (°C) Stage 2	Char yield (%)
NM0	335	461	—	471	0.00
NM1	281	450	334	462	0.00
NM2	279	436	319	440	2.79
NM3	292	437	338	445	3.29
NM4	285	435	329	444	4.49
NM5	284	432	337	443	2.15
NM6	285	438	334	442	4.09
NM7	276	439	328	450	6.06
NM8	272	436	325	453	1.73
NM9	299	443	356	446	3.18
NM10	280	430	328	436	5.23

$T_{5\%}$ = 5% decomposition temperature; $T_{50\%}$ = 50% decomposition temperature; T_{max} = maximum decomposition temperature.

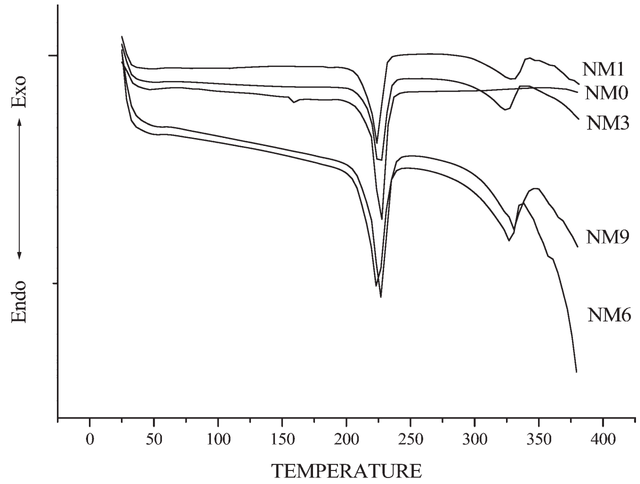

Figure 3 DSC curves of selected composites.

char yield. The char yield of BPO_4- and BSi-containing composites was higher than that of ZnB-containing ones because BPO_4 and BSi were thermally stable up to almost 600°C. From the 5% decomposition temperatures, we can see that melamine destabilized PA-6. Although the mechanism of destabilization of PA-6 is not clear, it may be interference with hydrogen bonding or a basic catalytic effect (aminolysis or ammonolysis by evolved ammonia).[1] The inclusion of boron compounds reduced the 50% decomposition temperature and the maximum decomposition temperature of PA-6, as shown in Table II.

DSC

DSC curves and data for selected composites are shown in Figure 3 and Table III. Two endothermic peaks were observed in the DSC curves, except for NM0 (PA-6). The first endothermic peak was attributed to the melting of PA-6 crystals, and the second peak resulted from the sublimation of melamine. The inclusion of melamine reduced the enthalpy of melting by nearly 3 J/g (with the lower PA-6 content being taken into account), whereas the inclusion of boron compounds increased the enthalpy of melting. This may have resulted from the heterogeneous nucleation role of boron compounds. The sublimation enthalpy of the ZnB-added sample was almost equal to that of melamine because of its endothermic decomposition. The other two boron compounds did not decompose significantly at these temperatures, so there was a drop in the enthalpy of sublimation with a decrease in the melamine percentage. It can be concluded that the addition of boron compounds did not affect the sublimation temperature of melamine.

Thermal degradation

The thermal degradation of the composites was investigated with TGA–FTIR spectroscopy to examine variations when melamine and boron compounds were added under an N_2 atmosphere. FTIR spectra of the decomposition gases of selected composites at 350 and 450°C are presented in Figures 4 and 5, respectively.

According to Figure 4, CH_2 groups (2939 cm^{-1}) and lactam absorption (1713 cm^{-1}) showed that PA-6 started to decompose at 350°C.[12] The characteristic peak of melamine can be seen at 1601 (NH_2 scissoring and ring stretching) and 1440 cm^{-1} (ring and side-chain CN stretching). These peaks show that melamine started to sublime. The peak at 2350 cm^{-1} resulted from the formation of CO_2. Herrera et al.[14,15] studied TGA–FTIR data for PA-6 under a nitrogen atmosphere and in air. CO_2 formation was much greater in air than in a nitrogen atmosphere. The formation of CO_2 increased under a nitrogen atmosphere when BPO_4 was added to a sample composition. Kılınç[16] studied the decomposition product distribution of BPO_4 with mass spectroscopy and showed that the decomposition products were BPO_4, BPO_3, BPO^-, PO_4, and O_2. It can be speculated that the small amount of O_2 formation during the decomposition of BPO_4 (NM6) gave rise to the formation of CO_2 observed around 2350 cm^{-1}. According to these results, BPO_4 can be a source of oxygen and favors the formation of CO_2 under a nitrogen atmosphere at a given temperature.

In Figure 5, the peaks at 2939 (CH_2 group), 1713 (lactam absorption), and 930 and 965 cm^{-1} (NH_3) show that PA-6 decomposed with the formation of ε-caprolactam. The characteristic peak of melamine (1601 and 1440 cm^{-1}) shows that the sublimation of melamine still continued at 450°C. There are a lot of small peaks, which may have resulted from the compounds containing CN and NH_2 end groups and can be observed between 1120 and 1350 cm^{-1}.[17–21] According to the TGA–FTIR results, the boron compounds used in this study did not change gaseous products that formed during the decomposition of melamine and PA-6. The products that formed in the condensed phase may have been different.

TABLE III
DSC Data for Selected Composites

Sample	T_m (°C)	ΔH_m (J/g)	T_{sub} (°C)	ΔH_{sub} (J/g)
NM0	227.5	54.0	—	—
NM1	226.0	40.0	330	21.3
NM3	226.0	42.0	330	21.5
NM6	224.5	44.3	329	20.5
NM9	228.0	44.5	331	20.2

ΔH_m = enthalpy of melting; ΔH_{sub} = enthalpy of sublimation; T_m = melting temperature; T_{sub} = sublimation temperature.

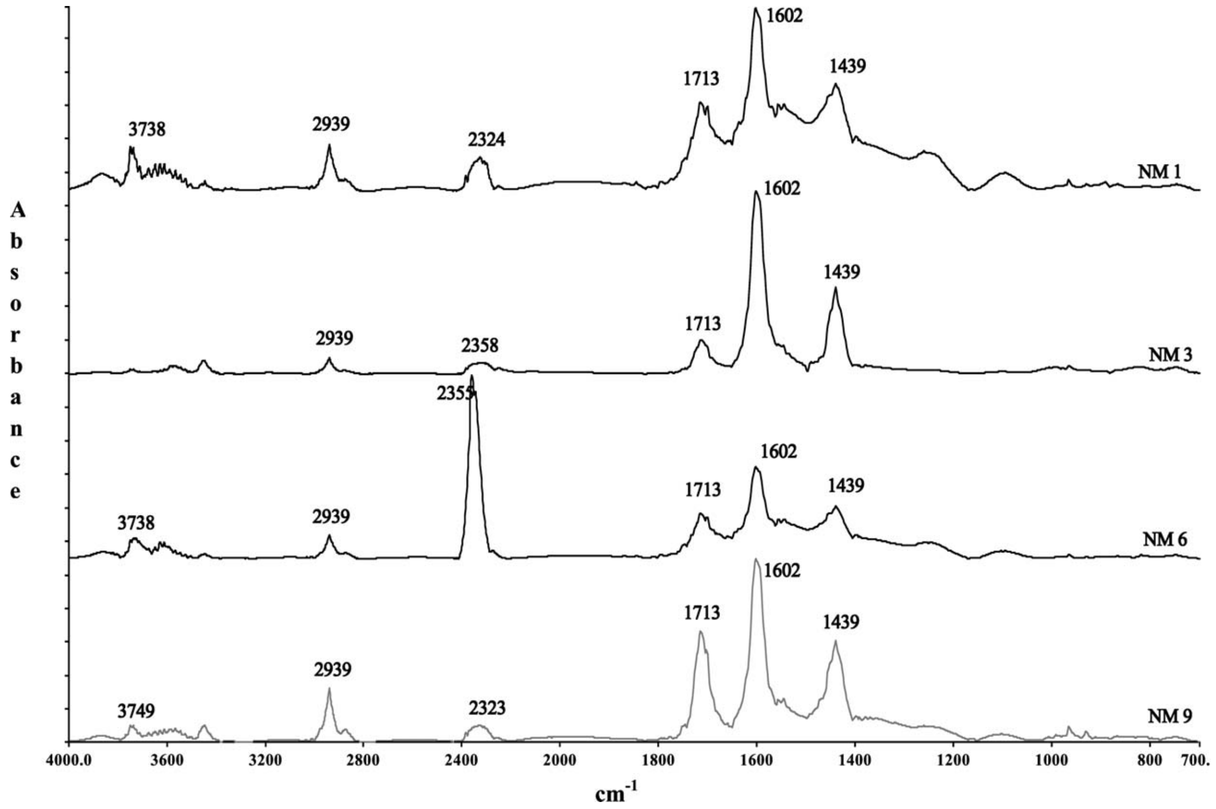

Figure 4 FTIR spectra of decomposition gases of selected composites at 350°C.

CONCLUSIONS

We studied the flame-retardant behavior of PA-6 with the addition of melamine and three different boron-containing substances. The effect of the addition of boron compounds on the UL-94 rating and LOI was studied. TGA–FTIR and DSC investigations were also performed for an understanding of the relevant basic mechanisms. According to the results, the addition of 20 wt % melamine was enough to

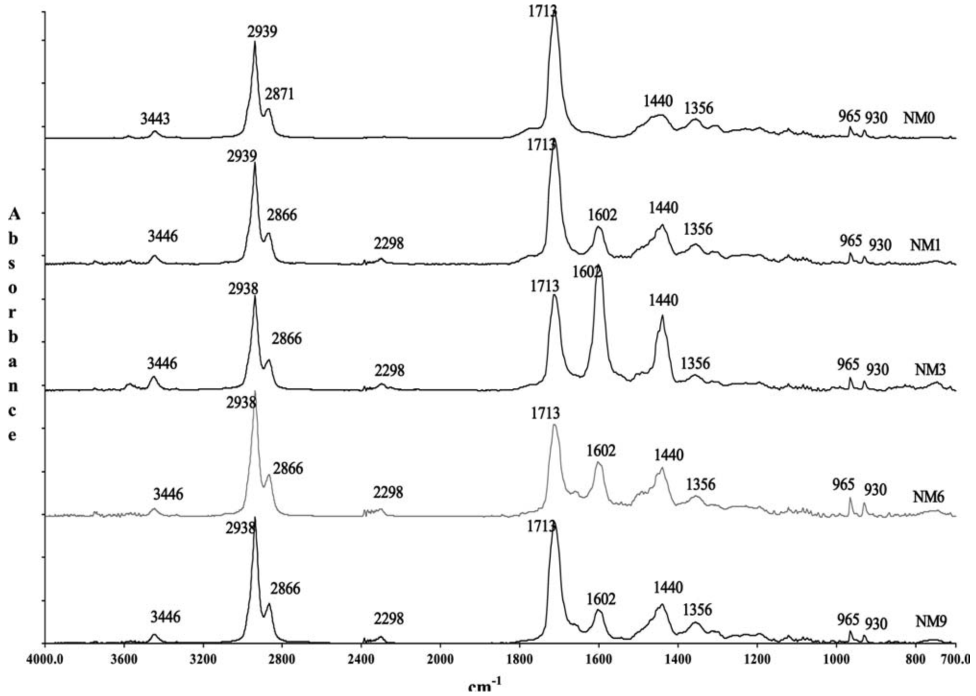

Figure 5 FTIR spectra of decomposition gases of selected composites at 450°C.

obtain a V0 PA-6 compound. According to the LOI test, there was a synergistic effect between BSi (1 wt %) and melamine. BPO_4-containing samples showed promising results when the amount of BPO_4 reached 3 or 5 wt %, but they still had lower LOIs than a sample with only melamine. This improvement was due to an increase in the dripping rate, which seems to be one of the important flame-retarding mechanisms in these systems. According to the TGA–FTIR results, the boron compounds did not change the degradation path of the melamine-containing composites and reduced the decomposition temperature of PA-6.

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