# Thermal Polymerization of a Brominated Flame Retardant in a Glass-Fiber-Reinforced Polypropylene—Quantitative Analysis

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**ABSTRACT:** Pentabromobenzylacrylate (PBBA) is a possible candidate for use as a fire retardant (FR) in polypropylene (PP) composites. While PBBA imparts FR properties to the PP composite, it also affects adversely its mechanical properties. The FR may undergo thermal polymerization or grafting to the PP chains during processing. To study the effect of the different forms of FR (monomer, polymerized, or grafted) on composite properties, we have quantified the extent of FR polymerization and extent of grafting onto the PP chains. Fourier transform infrared microscopy was used in this work to determine the extent of polymerization and the spatial distribution of the FR. The latter was found to be homogeneous throughout the composite. Thermal polymerization of the FR during extrusion is varied mainly by the addition of an antioxidant. The grafting process of the FR onto PP depends on the degree of thermal polymerization, and therefore on the addition of antioxidant. The limiting value for grafting achieved at full polymerization is ~10% w/w. The grafted FR was found to have a significant effect on PP crystallinity, and hence it is expected to affect the mechanical properties as well. Bromine analysis indicates the FR has reacted with filler surfaces as well. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1506–1515, 2003

**Key words:** poly(propylene) (PP); thermal properties; flame retardance

## INTRODUCTION

Pentabromotoluene is an excellent flame retardant but suffers from a major disadvantage by undergoing sublimation during heating. Pentabromobenzylacrylate (PBBA) is a derivative of the latter with an acrylic group in order to achieve better thermal properties. PBBA is a crystalline monomer classified as a vapor-phase active flame retardant whose activity is achieved through a halogen radical mechanism. Its chemical structure is shown in Figure 1(a). This type of flame retardant (FR) interferes with the chemical process of combustion. The FR either quenches combustion-enhancing radicals such as oxygen radicals, or competes with them in the reaction with fuel fragments. Therefore, the heat flux formed during combustion is reduced as result of the less energetic reaction of the halogen radicals. This, in turn, reduces the amount of flammable gas fumes that fuel the combustion process.[1–3] PBBA is capable of polymerizing by radical polymerization of its unsaturated acrylic group. This polymerization may be initiated thermally during reactive extrusion to produce poly(pentabromobenzylacrylate) (PPBBA), whose structure is shown in Figure 1(b).[4]

Polypropylene (PP) is one of the most versatile and cost-effective polymers available today. Isotactic PP is a semicrystalline (~60% crystallinity) polymer ($T_m$ = 160°C, $T_g$ = $-8 \sim -11$°C), which exhibits good mechanical properties with acceptable physical properties such as low density, good water, and chemical resistance. Like most commercial polymers, PP is highly flammable. Therefore, it requires the incorporation of a FR in order to reach flame resistance. PP is stable up to ~240°C. At high extrusion temperatures (above 240°C), tertiary carbo-cations may form on the PP backbone, which in turn may undergo oxidation or $\beta$-scission.[5,6] Thus, PBBA may react with PP during extrusion either to form PP grafted PPBBA (PP-g--PPBBA),[4] or to be attached as an end group to low molecular weight PP chains.

The nonpolar nature of the PP hinders its interaction and adhesion to common polar fillers such as magnesium hydroxide [Mg(OH)$_2$] or glass fibers. Various types of surface treatments exist for these fillers in order to improve their compatibility with PP and thus the mechanical properties of the mixture.[7] The grafting of PBBA may be expected to increase the polarity of the PP and thus enhance its adhesion to polar

(a)



(b)
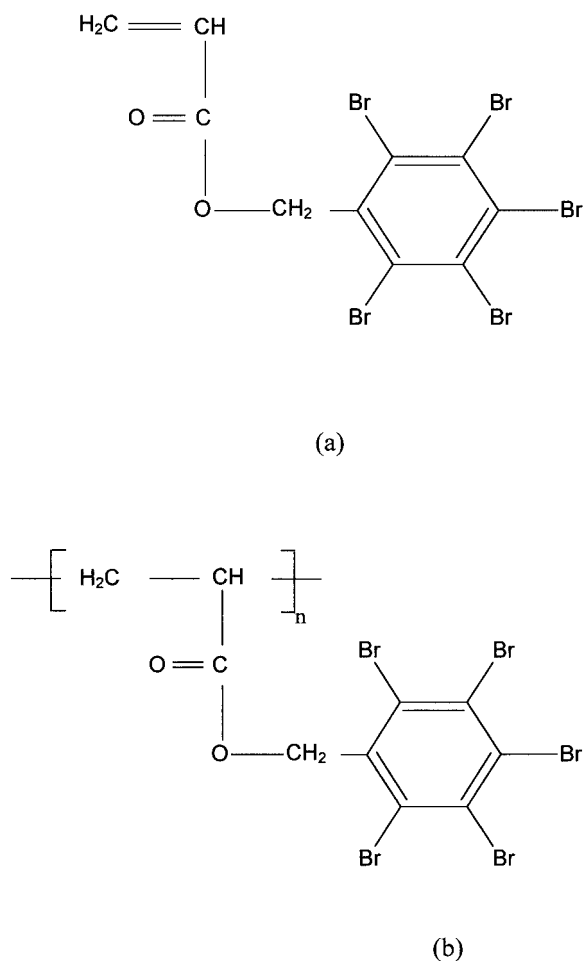
**Figure 1** Chemical structure of the FR: (a) monomer (PBBA) and (b) polymer (PPBBA).

fillers[4,8] a role that presently is assigned to modifiers such as maleic anhydride. $Mg(OH)_2$ acts as a FR with excellent smoke suppression ability.[9] Therefore, the addition of $Mg(OH)_2$ as a secondary FR may reduce the amount of PBBA required to meet FR demands.[10,11] Although the addition of PBBA imparts FR properties to the PP composite and possibly improves its compatibility as discussed above, it also affects adversely the mechanical properties of the composite. However, the monomeric and the polymeric forms of the FR may differ in their effect on the mechanical and FR properties of the composite. Thus, it is of practical importance to investigate the distribution of the FR in the PP composite, to determine the extent and nature of its polymerization during extrusion, and the effect of other components on the polymerization in order to better understand its role in the system.

In our previous article, we developed a technique for qualitative determination of the spatial distribution of the FR in the matrix. The technique allowed the visualization of the FR in PP composites and the identification of the monomeric and polymeric forms of this FR by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) coupled with energy-dispersive spectrometry (EDS).[12] In this article, we quantify the extent of FR polymerization and grafting onto the PP chains. In the following section, the materials and experimental techniques employed in this work are described. Next, the extent of polymerization and the homogeneity of the FR distribution in the composite are determined by means of Fourier transform infra red (FTIR) microscopy. The adequacy of PBMMA to serve as FR for PP-based composites is verified by means of thermal property analyses [differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)]. Thermal analysis is also used to determine changes in PP crystallization as result of compounding. Swelling is used to identify the factors responsible for these changes in PP crystallization. Finally, the extent of grafting of the FR onto PP is estimated by means of solvation, and its attachment to different fillers is determined by titration.

## EXPERIMENTAL

### Materials

The materials are all technical grades commercially available, and were used as received. A typical formulation was prepared by compounding the following materials:

PP (3120MN1, Appryl-Atofina, Lavera, France): the basic polymer matrix.

PBBA (FR1025M, DSBG Beer Sheva, Israel): a primary FR.

Antimony trioxide, masterbatch of 80% $Sb_2O_3$ and 20% low density poly(ethylene), characteristic diameter 1.5 $\mu$m (L0112 Kafrit, Kfar Aza, Israel): a FR-synergistic additive that enhances the FR properties via a different radical mechanism. For optimal FR activity,[7,13] it is added in a 1:3 ratio antimony to PBBA.

Irganox (B225, blend of Irganox 1010-hindered phenol type and Irgafos 168-phosphate type, Ciba Specialty Chemicals, Basel, Switzerland): an antioxidant, used to prevent PP oxidation during compounding (the commercial PP, as received, already contains ~800 ppm of this antioxidant).

Magnesium hydroxide, (FR20, DSBG, Israel) coated with 2% stearic acid: a filler with FR properties, a secondary FR.

Chopped glass fibers characteristic length 4.5 mm and characteristic diameter ~10 $\mu$m, $d$ = 2.6g/ $cm^3$ (P355, Vetrotex, Chambery, France): a primary filler, in order to improve mechanical properties. The fiber surface is treated with silane-

**TABLE I**
**Formulation of Polypropylene Composites (in wt %) and Flame Retardant Properties of Composites**

|  | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 | Sample 7 | Sample 8 |
|---|---|---|---|---|---|---|---|---|
| Polypropylene | 60 | 60 | 73.5 | 43.5 | 46.5 | 38.5 | 38.5 | 38.5 |
| PBBA | 30 | 29.7 |  | 14 | 14 | 15 | 12.5 | 14.63 |
| Antimony oxide | 10 | 10 |  | 4.6 | 4.6 | 5 | 4.15 | 4.87 |
| Antioxidant (Irganox B225) |  | 0.3 | 0.3 | 0.3 | 0.3 | 0 | 0.15 | 0.3 |
| Glass fibers |  |  | 25 | 25 | 20 | 25 | 25 | 15 |
| Magnesium hydroxide |  |  |  | 11.4 | 13.4 | 14.8 | 18.5 | 24.5 |
| PP graft maleic anhydride |  |  | 1 | 1 | 1 | 1.5 | 1 | 2 |
| PE wax |  |  | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| UL94 VB | V0 | V0 | Nonrated | Nonrated | Nonrated | V0 | V1 | V1 |
| LOI (limiting oxygen index) (LOI, PP ≈ 18) |  |  |  | 24–24.5 | 23.5–24 | 25–25.5 | 25–25.5 | 26.5–27 |
| $X_c$ (crystallization degree) |  |  |  |  |  | 44.5 | 46.6 | 40 |
| Extent of polymerization (%) | ≈100 | ≈33 |  | ≈28 | ≈45 | ≈85 | ≈49 | ≈36 |

based coupling agent for better compatibility with PP.

PP graft maleic anhydride (Exxelor VM42E, Exxon Mobile, Houston, TX) $d = 0.9 g/cm^3$: used as a compatibilizer, grants the PP a somewhat polar nature.

Poly(ethylene) wax (AC-6A, Allied, Morristown, NJ): added in order to lower sheer stresses developed during extrusion.

Methanol, analytical grade (EIL, Haifa, Israel).

Xylene, high performance liquid chromatography (HPLC) grade (Aldrich, St. Louis, MO).

Bromobenzene, analytical grade (Aldrich).

## Formulation

All formulations were compounded and pelletized at 250°C in a corotating twin-screw extruder, Berstorff ZE25, open vent, length/diameter = 32. The angular velocity of the screws rotation was 350 rad/min. The pellets obtained were dried overnight. The formulated compounds were injected by means of Arburg Allrounder 320S injection molding machine into "dog bones." A Nozzle temperature of 240°C and an injection pressure of 1300 bar were employed. The formulations are detailed in Table I. Samples 1 and 2 contain PP with the FR and its synergistic component, but sample 2 also contains an antioxidant in order to examine the role of the latter in the system. Sample 3 contains none of the FRs, but does contain glass fibers as a representative of the best formulation for mechanical properties. The rest of the samples contain varying amounts of all of the components, which form a typical PP composite formulation. Approximately 25 additional samples with varying compositions (given elsewhere[14]) were prepared, and used in the FTIR and thermal analysis experiments.

## FTIR microscopy

The samples were cut into ~40 $\mu$m thick strips by means of a Microm HM355 rotary microtome (feed range of 0.25–500 $\mu$m) at room temperature. The samples were examined in transmission mode in 600–4000 cm$^{-1}$ range using a Bruker FTIR microscope (Equinox 55 spectrometer, IR scope II microscope with 15× magnification, IR objective, and Mercury Cadmium Teluride (MCT) detector, liquid $N_2$ cooled). Interferograms were collected by OPUS FTIR software. Interferograms were deciphered and examined using OMNIC FTIR software.

## DSC measurements

The samples were examined under argon using a Mettler Toledo system TA 8000, DSC 820 CELL. Each sample examined weighed between 10 and 20 mg. The method of operation: heating rate, 5°C/min; cooling rate (max uncontrolled rate), ~20°C/min; temperature range, 50–230°C. Two consecutive runs were carried out on each sample.

## TGA measurements

The samples were examined under argon using a Mettler Toledo system TA 8000, TG 50. Each sample examined, weighed between 10 and 20 mg. The method of operation: heating rate, 10°C/min; temperature range, 50–500°C.

## Swelling–deswelling

The samples were cut into accurately weighed ($w_0$) cubes of ~2mm edge size. Five solvent mixtures, 100 mL each, composed of xylene [solubility parameter = 8.8 (cal/cm$^3$)$^{0.5}$], a good solvent for PP [solubility parameter = 9.2 (cal/cm$^3$)$^{0.5}$], and methanol, a poor solvent for PP [methanol solubility parameter = 14.5 (cal/cm$^3$)$^{0.5}$],[15] were prepared. The compositions used were 20, 40, 60, 80, and 100% wt xylene in methanol, respectively. In swelling experiments the cubes were placed in the solvent mixtures in sequentially increasing solvent quality starting with the poorest solvent
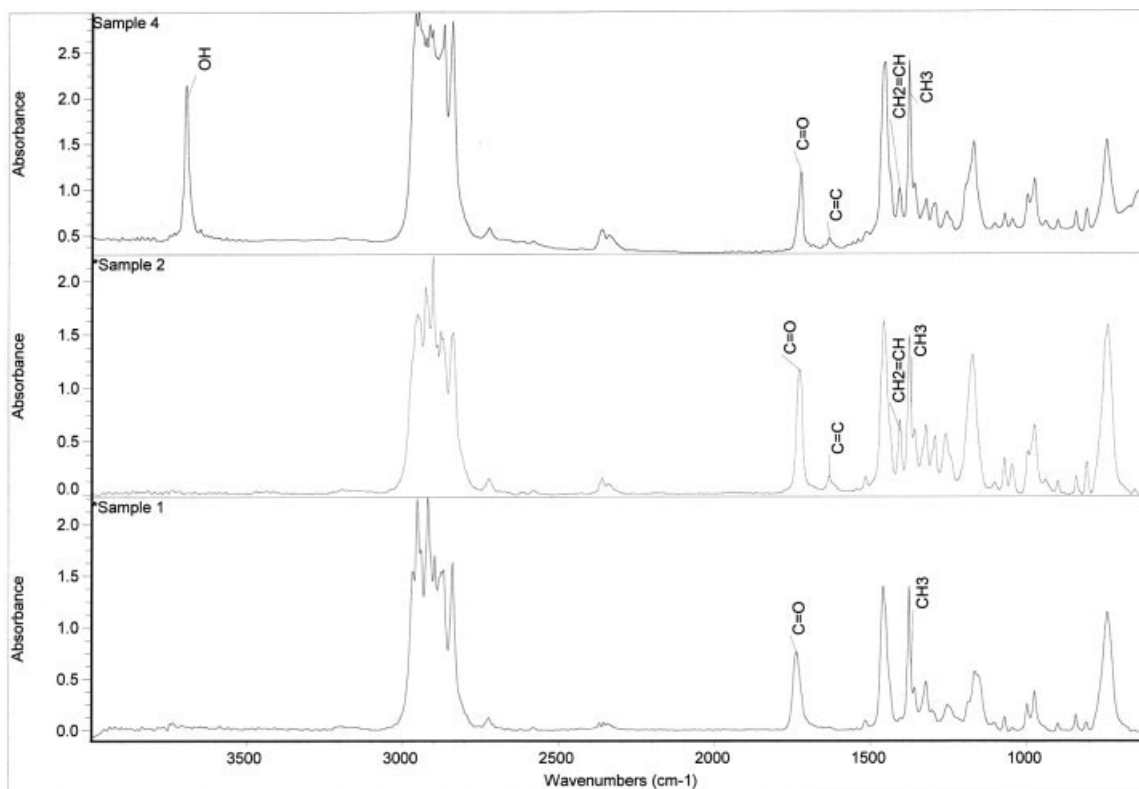
**Figure 2** Interferograms of samples 1, 2, and 4. Assignments for the main peaks are indicated.

and ending with the best solvent, allowing at least 24 h at room temperature in each mixture. The solvents were collected and analyzed by FTIR for dissolved composite components. Upon reaching maximum swelling, the samples were removed from the solvent, excess solvent was wiped off their surface with a paper tissue, and the samples were accurately weighed ($w_{eq}$). The samples were placed in clean xylene and the xylene/methanol sequence was reversed for deswelling. At the end of the deswelling experiment, excess solvent was wiped off the surface with a paper tissue and the deswollen cubes were weighed ($w_d$). The fraction of soluble material extracted from the sample $w_s$ and the swelling factor $Q$ were obtained from

$$w_s = 1 - (w_d/w_0) \qquad (1)$$

$$Q = (w_{eq}/w_d) - 1 \qquad (2)$$

**Solvation**

Five grams of each sample were cut into cubes of ~2 mm edge size and extracted in a sohxlet extraction system. The extraction was carried out with boiling bromobenzene in a Munktell filter thimble (size 33 × 80mm) that was placed in a Tector module Soxtec system HT2 with 1045 extraction unit and 1046 service unit as a heat bath at 180°C.

**Bromine titration**

The solid polymer samples were subjected to a sodium peroxide fusion in a Parr bomb following standard procedures.[16] Initially, 100–150 mg of accurately weighed sample are mixed with about 1.1–1.2 g of sucrose and $KNO_3$ mixture (1:2.5 weight ratio) and placed in the parr bomb capsule. Excess of $Na_2O_2$ (one Parr-bomb spoon) was added and the entire mixture was sealed off in the 22 mL capsule. The sample was allowed to oxidize following the Parr bomb procedure. The products were dissolved in 45 mL of a 1:1 water/$HNO_3$ solution. The amount of Bromine was determined by means of potentiometric titration with $AgNO_3$.

## RESULTS AND DISCUSSION

**FTIR measurements**

The extent of polymerization of the FR during processing is determined by means of FTIR spectroscopy. Figure 2 depicts three interferograms: the first two represent samples containing mostly the polymer and FR (samples 1 and 2) and the third one is typical of a complete composite formulation (sample 4). The presence or absence of the double bond distinguishes between the otherwise chemically identical units of PBBA and PPBBA.[12] For quantitative conversion calculations, two peaks were chosen in the interefero-

grams: one, which remains unchanged in both species, and the other, which is characteristic of the double bond. Namely, the carbonyl stretching-mode peak at about 1720 cm$^{-1}$ remains untouched by the polymerization reaction, whereas the vinyl stretching-mode peak at ~1405 cm$^{-1}$ is representative of the monomeric species. Their relative magnitude is reduced with increasing extent of polymerization. It was found that absolute peak sizes varied with change in sample variables such as thickness and flatness, but the ratio of areas under different peaks was found to be independent of the sample surface and thickness, and dependent only on its composition. In order to calculate the degree of polymerization and the amount of residual monomer, calibration was required. It was obtained by using a series of reference samples of mixtures of predetermined amounts of PBBA and PPBBA. Based on this calibration and the ratio of the areas under the two selected peaks, the extent of polymerization and the amount of residual monomer were determined for the 30 samples examined. These values are specified in Table I for the seven FR-containing samples. The data for the remaining samples and the FTIR interferograms obtained are given elsewhere.[17] A typical composite contains initially between 10 and15% wt PBBA in order to meet V0 level according to the UL94 standard (i.e., FR requirement). Based on the FTIR measurements, we have determined that the conversion of PBBA to PPBBA varies between ~30 and 85% depending on the composite makeup. The primary factor in determining the conversion is the antioxidant, Irganox, which is a radical scavenger and therefore interferes with the polymerization of the FR. As may be observed by comparing the interferograms for samples 1 and 2 in Figure 2, the vinyl peak (1405 cm$^{-1}$) has completely disappeared in sample 1, whereas it has decreased only slightly for the case of sample 2. Hence, PBBA has polymerized completely during compounding of sample 1 but only 33% conversion has been achieved in sample 2 (cf. Table I). Similarly, composite samples 6–8 of almost identical composition but with 0, 0.15, or 0.30% Irganox, show 85, 49, and 36% PBBA conversion, respectively. Similar results have been observed in all other compositions not shown here.[17] We may conclude that increasing Irganox concentration results in a reduction in PBBA polymerization. These results are supported by our previous visualization study in which we also determined that FR polymerization is catalyzed by Sb$_2$O$_3$.[12] Thus, in some instances antimony oxide counteracts the effect of Irganox. There is no clear indication to what extent any of the other components such as Mg(OH)$_2$ or glass fibers have a significant effect on the polymerization reaction.

Additional experiments have been carried out to determine the homogeneity of the FR distribution and the extent of polymerization throughout the sample. A cross-sectional cut of the "dog bone" formed from a typical sample was examined. FTIR spectra have been collected at 20 points, 0.5 $\mu$m apart along two separate lines stretched from the sample center to the centers of two adjacent edges. At each point the ratio between the vinyl (1405 cm$^{-1}$) and carbonyl (1720 cm$^{-1}$) peaks (which is equivalent to the PBBA/total FR ratio), and the ratio between the vinyl (PBBA) peak and a peak corresponding to the PP (—CH$_3$ symmetrical deformation mode at 1370 cm$^{-1}$), were measured (cf. Fig. 1). At all points except for the edge point, the ratios gave identical readings within the experimental error (±5%). The edge point differed significantly from the other points, but this may be the result of inaccurate measurement at the edge due to surface irregularities or due to oxidation that may occur on the surface, yielding an artificial increase in the carbonyl peak. Based on these experiments, we may conclude that the FR is evenly distributed in the PP matrix and the extent of polymerization is identical throughout the sample.

### Thermal studies

The DSC thermogram of the monomeric FR (Fig. 3) shows two endothermic peaks at ~120°C, which correspond to the melting of two polymorphic crystals, followed by an exothermic thermal polymerization process, which peaks around 139°C. The heating cycle is followed by cooling of the now polymeric FR, which is then followed by a second heating cycle. No discernible features are observed in the latter cycle, indicating that the FR shows no sign of thermal degradation or first order phase transitions up to 230°C.

PP composite processing is carried out at 250°C. Based on Figure 3, PBBA is in the molten state during compounding (i.e., not a solid filler) and may aid the processing by lowering the viscosity of the composite extrudate. We may observe also that the thermal polymerization is carried out during processing.

The TGA analysis of pure PP indicates a thermal stability up to 240°C followed by an accelerated breakdown until 450°C, at which temperature the entire sample is consumed. The processing of PP was performed deliberately at 250°C (generally 210–250°C) in order to generate radicals that may promote PBBA grafting.

The TGA analyses of PBBA and PPBBA indicate thermal stability up to 290°C followed by a steep breakdown up to 370°C. The maximal consumption rate is at 330°C. There is a total of 87% consumption of sample within the tested temperature range. Due to its thermal stability at PP processing temperatures, and its degradation at temperatures concurrent with degradation of PP, PBBA is suitable for use as a FR for PP composites.[2]
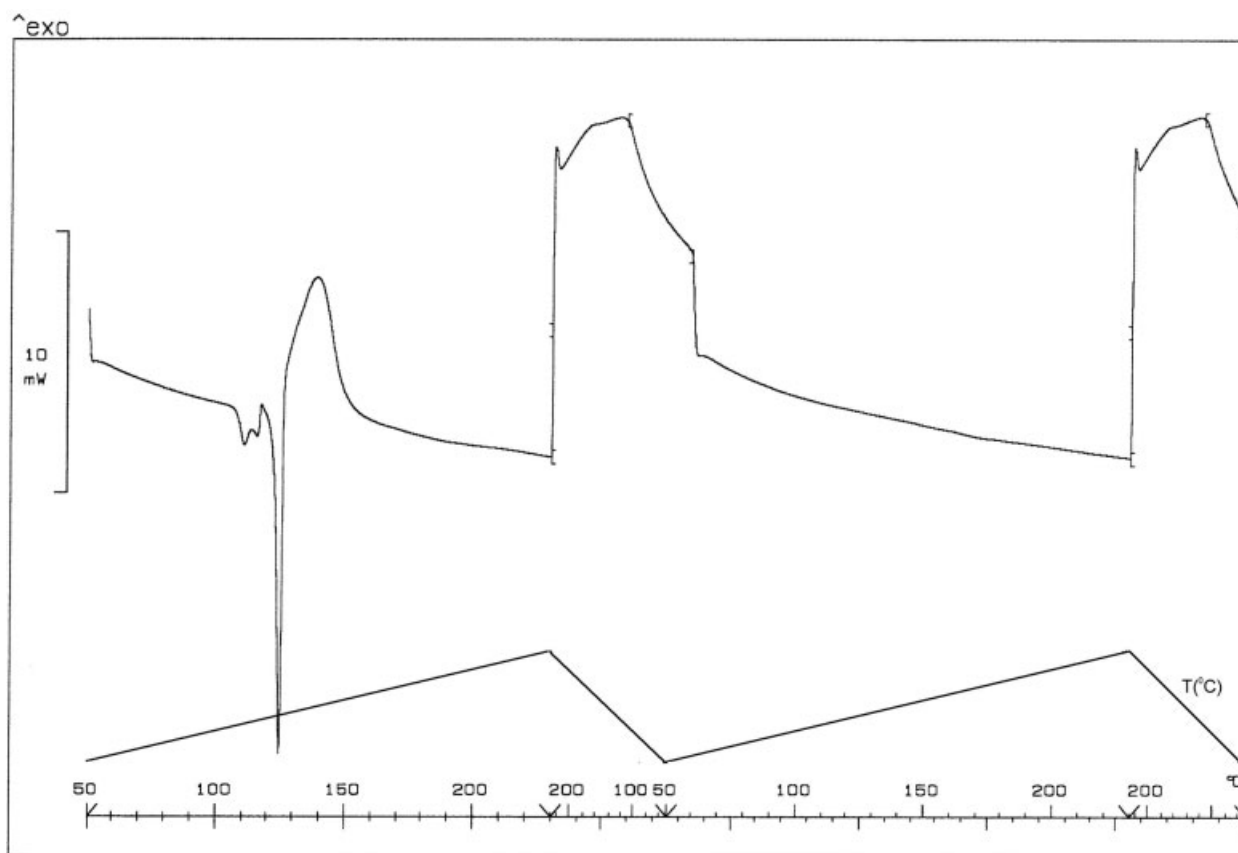
**Figure 3** Thermal properties of PBBA. The DSC thermogram describes a heating cycle (at 5°C/min) from 50 to 230°C, fast quench back to 50°C, followed by a second heating cycle. In the first cycle two melting endotherms (110, 123°C) followed by a polymerization exotherm (onset 125°C) are observed. In the second cycle no features are detected.

The TGA analysis of Mg(OH)$_2$ indicates thermal stability up to 340°C followed by accelerated breakdown until 440°C. There is 30% water release within this temperature range. Due to its thermal stability at the processing temperatures of PP, and its degradation at temperatures concurrent with degradation of PP, Mg(OH)$_2$ is suitable for use as a FR and smoke suppressant for PP composites.

A thermal gravimetric analysis of a typical composite shows that the breakdown of PP, PBBA, and Mg(OH)$_2$ in the composite are identical to their individual degradations in the pure samples. The relative peak sizes in the DTG analysis shown in Figure 4 are proportional to the initial amounts of these components in the sample. Based on the initial composition of the sample and the measured amount of residues at the end of the TGA experiment, we concluded that Sb$_2$O$_3$, which was added to PBBA in a ratio 1:3, has been fully consumed. In other experiments, not reported here using different Sb$_2$O$_3$:PBBA ratios, not all of either the Sb$_2$O$_3$ or PBBA has been consumed. Hence, we conclude that at this ratio, Sb$_2$O$_3$ acts as a perfect synergist to PBBA.[7]

DSC experiments were carried out for the 30 samples mentioned above and the results are given else-

where.[17] The thermogram depicted in Figure 5, corresponding to sample 8, is typical of the thermograms obtained for PP composites. The value of $X_c$ (degree of crystallinity) given in Table I is computed from the area under the endotherm peak corresponding to the melting of PP in the first heating cycle. It should be noted that the size of the melting peak in the second heating cycle is different from the first since crystallization has been carried out under different thermal and flow histories. The value of $X_c$ was determined using the following relationship[18]:

$$Xc = 100 \ (\Delta H / \Delta H_0) \tag{3}$$

where $\Delta H$ is the specific heat of fusion of PP (normalized for the amount of PP in the composite) obtained from the integration of the endotherm peak in the DSC thermogram and $\Delta H_0$ is the heat of fusion of 100% crystalline PP. A value of $\Delta H_0 = 190 \ \text{J g}^{-1}$ was used in all present calculations. As has been shown above, PBBA has reached 36% conversion in sample 8 based on FTIR measurements. This fact is confirmed by the presence of a small PBBA melting peak at ~120°C. In contrast, the thermogram for sample 6 (not shown here) does not show a PBBA melting peak, in agree-
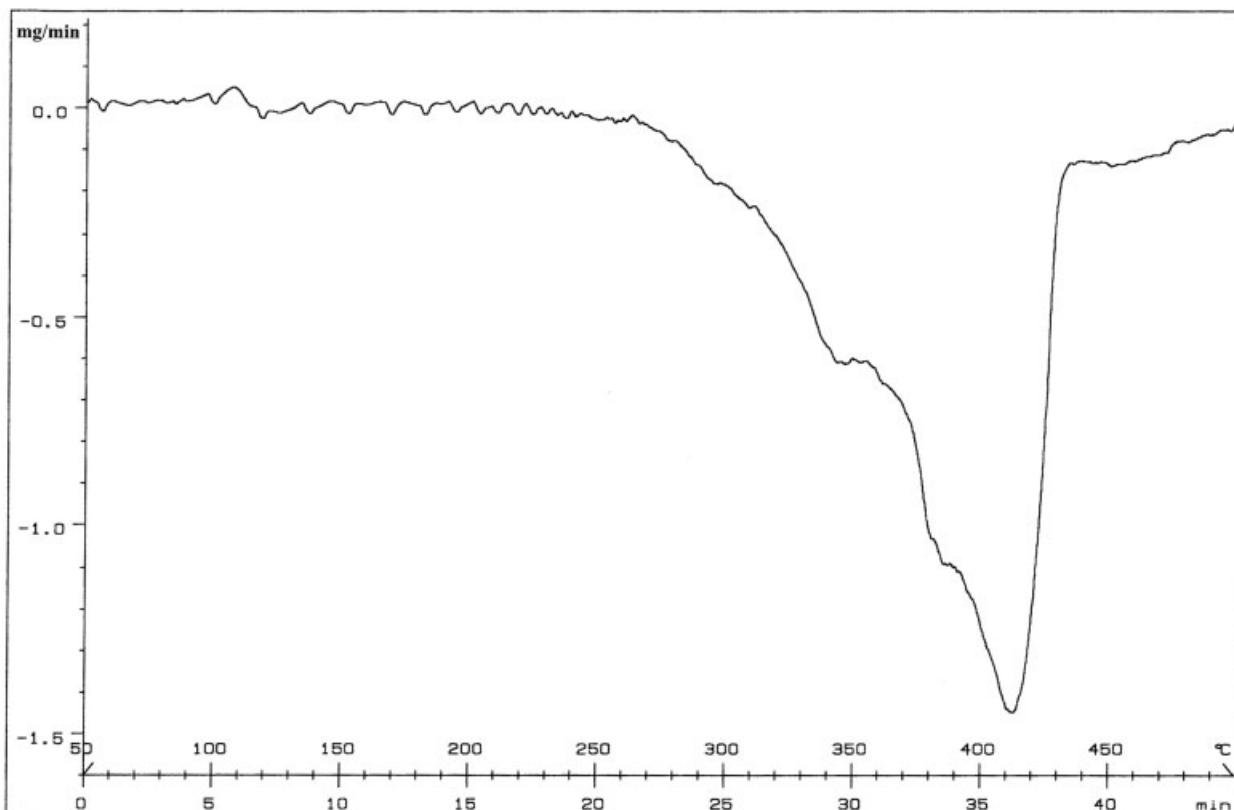
**Figure 4** DTG analysis of a typical formulation. The figure depicts mass-loss rate as function of temperature (heating rate 10°C/min).

ment with the measured 85% conversion determined by FTIR. We have used statistical analysis of the 30 samples tested[14,17] to investigate the factors that affect PP crystallinity in the composite. This analysis shows that maleic anhydride modified PP, being used as a compatibilizer between PP and polar fillers, is the primary factor affecting $X_c$: an increase in the maleic anhydride content results in a lower $X_c$. As opposed to all the other additives in the composite, which are either macroscopic in size or undissolved in PP, maleic anhydride is grafted onto the PP chains and thus interferes with the crystallization of PP by hindering the structural order of the lamellae. It is expected that grafted FR may have a similar effect for identical reasons on PP crystallinity. This issue is further considered in the next section.

**Swelling experiments**

Swelling experiments are usually conducted on crosslinked polymers yet; we may consider crystalline PP as physically crosslinked where the crosslink zones are the PP spherulites. Support for this hypothesis may be obtained from the fact that xylene is a good solvent for PP, capable of dissolving it only above PP melting temperature. The PP may be viewed as a macromolecular network in which the crystals cannot

be solvated while the PP chains in the amorphous part between the crystallites may adopt an extended or collapsed conformation according to the nature of the solvent. During the swelling process, the unattached PP chains are leached out of the network. The amount of the leached material, which includes these chains as well as brominated FR, was found to vary between 1 and 15%. Careful examination and spectral analysis of the extract showed that none of the other components present in the composite leached out. We have carried out a second cycle of swelling/deswelling experiments on the same samples. No measurable amounts of material were extracted in the repeat experiments, ruling out degradation as the source of extractable material. The swelling measurements were performed on the samples shown in Table II. The first column in the table shows the amount of extractable material $w_s$. The measured values of the swelling factor $Q$ are shown in the second column of Table II.

For most samples we observe only small degrees of swelling (small $Q$ values) corresponding to a large degree of crystallization. We may anticipate that as the degree of crystallinity is increased, the apparent distance between "crosslinks" is decreased. Examining Table II, we finds that the results may be arranged into three groups: the first group with $Q$ values around 0.05 includes pure PP and sample 2, the second group
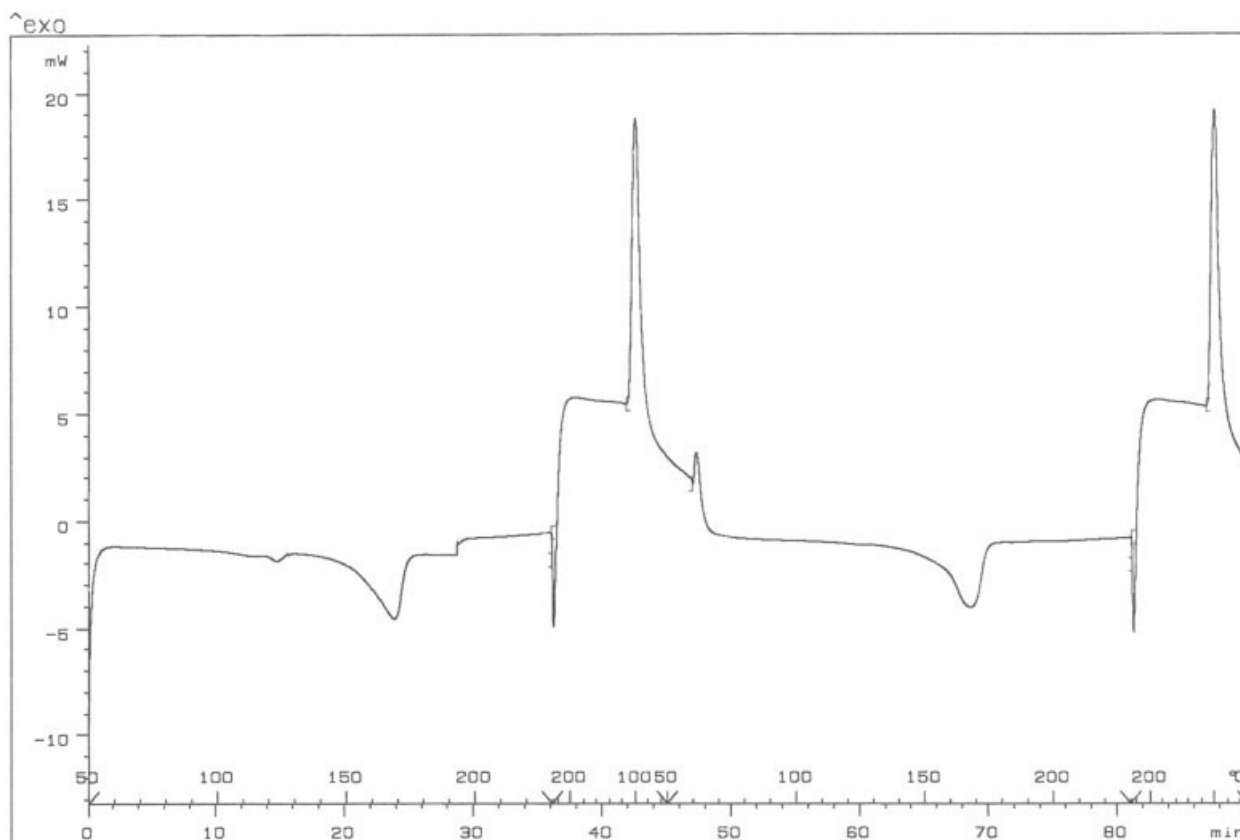
**Figure 5** DSC thermogram of sample 8. The thermogram describes the heating cycle (at 5°C/min) from 50 to 230°C, fast quench to 50°C, followed by a second heating cycle. In the first cycle, two melting endotherms correspond to residual FR monomer and PP, respectively. In the second cycle, only melting of PP is observed.

with $Q$ values around 0.1 consists of sample 3 and 4, and the last one with the largest $Q$ value (0.27) includes only sample 1. Sample 2 contains only PBBA and Irganox. As has been shown above based on FTIR results, the addition of Irganox prevents PBBA polymerization. Since the FR in its monomeric form is insoluble in PP, it remains dispersed in the matrix with no effect on PP crystallization, explaining the similarity in $Q$ of pure PP and sample 2.

In the second group, sample 3 contains only glass fibers whereas sample 4 is a complete composite formulation with relatively large amount of glass fibers (25%). Based on FTIR measurements we have determined that the degree of polymerization of PBBA is low in sample 4, i.e., the FR is mostly in its monomeric

### TABLE II
### Results of Swelling Experiments

| Composite | $w_s$ | $Q$ |
|---|---|---|
| PP | 0.013 | 0.06 |
| Sample 3 | 0.01 | 0.09 |
| Sample 4 | 0.06 | 0.1 |
| Sample 1 | 0.15 | 0.27 |
| Sample 2 | 0.1 | 0.04 |

form. As already mentioned above, the monomeric FR has no effect on PP crystallization explaining the similarity between samples 3 and 4. The increase in $Q$ of this group relative to the first one may be attributed to the presence of the glass fibers. Possibly, glass fibers may affect the kinetics of PP crystallization by hindering PP chain movement resulting in lower degree of crystallization or higher $Q$. The largest change in $Q$ is observed in sample 1. Sample 1 contains PBBA with no Irganox, resulting in complete polymerization of PBBA, and shown below, also a high degree of grafting of the FR onto PP chains. The former is confirmed by the absence of any traces of PBBA in the extracts. Grafted chains tend to sterically hinder the crystallization process. A similar effect has been observed for the case of maleic anhydride chains described in the Thermal studies section. We may conclude that the thermal polymerization of PBBA in the composite results in a lower degree of crystallinity, which in turn may be the cause for inferior mechanical properties.

Finally, we would like to address the values of extractable material ($w_s$) for the different samples. Pure PP and sample 3 (which contains only glass fibers and Irganox), extract almost the same amount of

**TABLE III**
**Amount of grafted FR in PP-g-PBBA**

| Sample | Grafted FR (%w/w) |
|--------|-------------------|
| Sample 4 | $\approx$0.5 |
| Sample 6 | $\approx$8.5 |
| Sample 1 | $\approx$10.5 |

dangling PP chains. In sample 4, which is a complete formulation, there is an increase in $w_s$ due to the additional extraction of PBBA that has polymerized only to a small extent (cf. Table I). Sample 2,which contains mostly PP and monomeric FR (which has not polymerized due to the presence of Irganox, cf. Table I), shows almost a twofold increase in $w_s$ relative to sample 4. This increase is attributed to the twofold larger amount of PBBA in the formulation of sample 2 relative to sample 4. The highest value of $w_s$ is observed in sample 1, which contains mostly polymerized FR (cf. Table I). The large extent of FR polymerization has been achieved as discussed below, by the absence of antioxidant, which in turn increases PP degradation. We attribute the higher amount of extractable material to the degraded PP.

### Solvation

The solvation experiments were mainly conducted in order to quantify the portion of PBBA that grafts onto the backbone of PP. Higher degree of grafting will force concurrent flow of PP and PBBA, which should result in better flame retardancy properties. The solvent in the Sohxlet process was bromobenzene, which is a common solvent for PP (at elevated temperatures) and the FRs (either in monomeric or polymeric form). Therefore, this solvent is capable of extracting PP, PBBA, PPBBA, and PP-g-PBBA. The residue in the thimble will contain the nonsoluble solids such as glass fibers, $Mg(OH)_2$, and $Sb_2O_3$. After extraction the solvent was cooled in order to further separate the insoluble pp PP-g-PBBA from the soluble FRs. Two distinct layers are formed upon cooling. The upper layer contains PP and PP-g-PBBA, whereas the lower layer is a solution of the FRs. The upper layer of PP and PP-g-PBBA is removed and further refluxed in xylene in order to wash out residual bromobenzene. Finally, the xylene is evaporated and the dried sample is examined for Br content by Br titration. The amount of Br found in the PP corresponds to grafted PBBA; these values are shown in Table III.

Samples 4, 6, and 1 have reached (cf. Table I) 28, 85, and 100% conversion of PBBA to PPBBA, respectively. These differences have been attributed to the effect of Irganox on the thermal polymerization. As clearly shown by Table III, the degree of polymerization is highly correlated with the degree of grafting. Irganox

is a radical scavenger that is added to PP to prevent oxidation. By the same mechanism it reduces the possibility of polymerization and grafting onto the PP backbone. In the absence of Irganox, the formation of a free radical on the PP backbone is possible and subsequently a radical grafting of the FR. Sample 1 contains only PP and PBBA/$Sb_2O_3$. Since 100% conversion of PBBA is reached and the amount of FR is high relative to complete formulations it is expected that this sample illustrates optimal conditions for grafting. Thus, the value of $\sim$10% grafting is apparently the maximum achievable level of grafting in fully compounded composites.

### Bromine titration

The residue left in the thimble from the solvation process contains the insoluble solids such as glass fibers, $Mg(OH)_2$, and $Sb_2O_3$. Bromine titration has been used in order to determine whether the FR or PP interact with any of these sizing agents. The surface modification of $Mg(OH)_2$ is stearic acid and that of the glass fibers is not known to us, but is claimed by the manufacturer to be suitable for PP. Initially, $Mg(OH)_2$ was physically separated from the glass fibers by means of a sieve with an appropriate mesh size. This process yields two separate fractions: the first contains $Mg(OH)_2$ with $Sb_2O_3$ and the second glass fibers contaminated with considerable amount of $Mg(OH)_2$. The separation of the glass fibers from the $Mg(OH)_2$ residue cannot be achieved chemically because sized $Mg(OH)_2$ is insoluble in either acid or organic solvents, especially so if it is covered by the FR layer, which is highly resistant to chemical reactions. The separation was achieved by placing the solid mixture in a water/oil (decane)/surfactant (AOT) mixture, which caused $Mg(OH)_2$ to float at the interface from which it was easily removed.

Bromine titration of the glass fibers showed $\sim$0.2% w/w Br content. This indicates that a certain fraction of the FR has reacted on the surface of glass fibers. Electron microscopy combined with EDS experiments[12] have shown that PPBBA is adsorbed to the glass fibers, confirming our present findings. In some cases the polymeric form is attached to the fiber and serves as anchor to attachment of either PBBA or PP.

Based on bromine titration, we have determined that the extracted $Mg(OH)_2$/$Sb_2O_3$ contains $\sim$0.5% w/w Br. This again confirms our previous findings[12] of the presence of FR on the surface of $Sb_2O_3$ and $Mg(OH)_2$.

### CONCLUSIONS

The thermal stability of PBBA and $Mg(OH)_2$ at temperatures above PP-composite processing tempera-

tures and their concurrent breakdown with respect to PP in pyrolysis temperatures prove that these materials are adequate to serve as FRs in high-loading PP composites.

It was shown that PBBA is in the molten state at processing temperatures and that it undergoes thermal polymerization during extrusion. The extent of polymerization is mainly governed by the addition of an antioxidant since the latter may inhibit the radical polymerization. It was found that the FR is homogeneously distributed in the final composite.

Thermal polymerization of the FR may also result in grafting to the PP backbone, the extent of which is governed by the amount of antioxidant. The upper limit for the extent of grafting of the FR onto PP chains is achieved at ∼100% conversion of the polymerization reaction and is approximately 10% w/w. By elemental analysis, we have also determined that the reactive FR reacts with filler surfaces.

The addition of maleic anhydride to a PP composite causes a reduction in PP crystallinity. Grafted FR has a similar effect and causes a reduction in PP crystallinity as well, via a similar mechanism.

Although the monomeric and polymeric forms of the FR are evenly distributed in the composite, there is a major difference between the behavior patterns of the two types. Most pronounced is the effect during swelling: the monomeric FR is insoluble in the PP chains and leaches out of the network during swelling whereas the polymeric form is retained in the swollen sample. This observation may serve as an explanation to the blooming phenomena commonly observed with PBBA in PP composites and its disappearance upon thermal polymerization.

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