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BULK REACTION OF TRIGLYCIDYLISOCYANURATE WITH BORIC ACID BY DIFFERENTIAL SCANNING CALORIMETRY AND ROLE OF REACTION PRODUCTS ON POLYMER THERMAL STABILITY

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The bulk reactions between triglycidylisocyanurate (TGI) and boric acid, at molar ratios from 5:1 to 1:2 have been studied by Differential Scanning Calorimetry (DSC). The obtained materials were used as additives of polyolefins and the added polymers were investigated by Thermogravimetry (TG) in air in order to observe the variations of their thermal stability with varying the boric acid content. The additives show to increase the degradation temperature of polypropylene, polyethylene and polystyrene.

Keywords: bulk reaction, polymers, thermal stability

Introduction

In previous papers [1, 2] we have described the reactions between TGI and orto phosphoric or polyphosphoric acids and studied the course of the reaction by DSC and TG. The obtained products have high thermal stability and an intrinsic flame retardant property.

We used these products as additives; in fact they mixed with polypropylene, produce materials which are classified as V0 according to UL 94 test when the additives are present at a content as low as the 20% in the polymer.

TGI is a trifunctional epoxy compound having the formula

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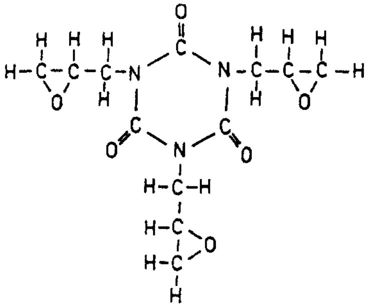


Fig. 1 Structure of triglycidylisocyanurate

The epoxy groups of TGI can react with carboxyl acids [3], aniline or aliphatic polyamines [4], melamine [6] and phosphoric acids [1]. In this last case we have also suggested a probable structure of the products obtained by the reaction [2].

Boric acid is mainly used with borax as flame retardant for wool and cotton since the past century and applications of ester of this acid are now known [5].

In this paper we report about the bulk reaction between TGI and boric acid in order to investigate if the obtained product could have thermal stabilizing and flame retardant properties and to compare the properties of a containing boron products with those ones of a product containing phosphorous.

We have used DSC as an investigation tool to follow the bulk reaction between TGI and boric acid according to our previous papers [1, 2].

Experimental

Chemicals

Triglycidylisocyanurate was Araldite PT 810 from Ciba Geigy and boric acid was obtained from Fluka, polypropylene was Moplen FLF20 from Himont, polystyrene (Edistyr) and high density polyethylene (Eraclene) were Enichem Polimeri products. These chemicals were used without further purification.

Mixtures of TGI and boric acid at chosen molar ratios were prepared by mixing their powders in closed bottles.

The TGI/H_3BO_3 additives were obtained by heating their mixtures in oven at 473 K for 2 hours.

Analysis

DSC curves were obtained on a DSC-2C Perkin Elmer instrument equipped with Thermal Analysis Data Station 3600. Samples of 3 – 5 mg were weighted in closed aluminium pans. Measurements were carried out with a scanning rate of 20 deg·min^{-1} in a nitrogen atmosphere.

Thermogravimetry was carried out by means of a Perkin Elmer TGS-2 Thermogravimetric Analyzer with platinum pans with a scanning rate of 20 deg·min^{-1} in air and in nitrogen atmosphere with a flow rate of 30 ml/min.

DSC curves are reported as differential heat flow to the sample and reference, d*Q*/d*t*, in function of increasing temperature in Kelvin degrees.

d*Q*/d*t* values for each DSC curve are given in mcal/s.

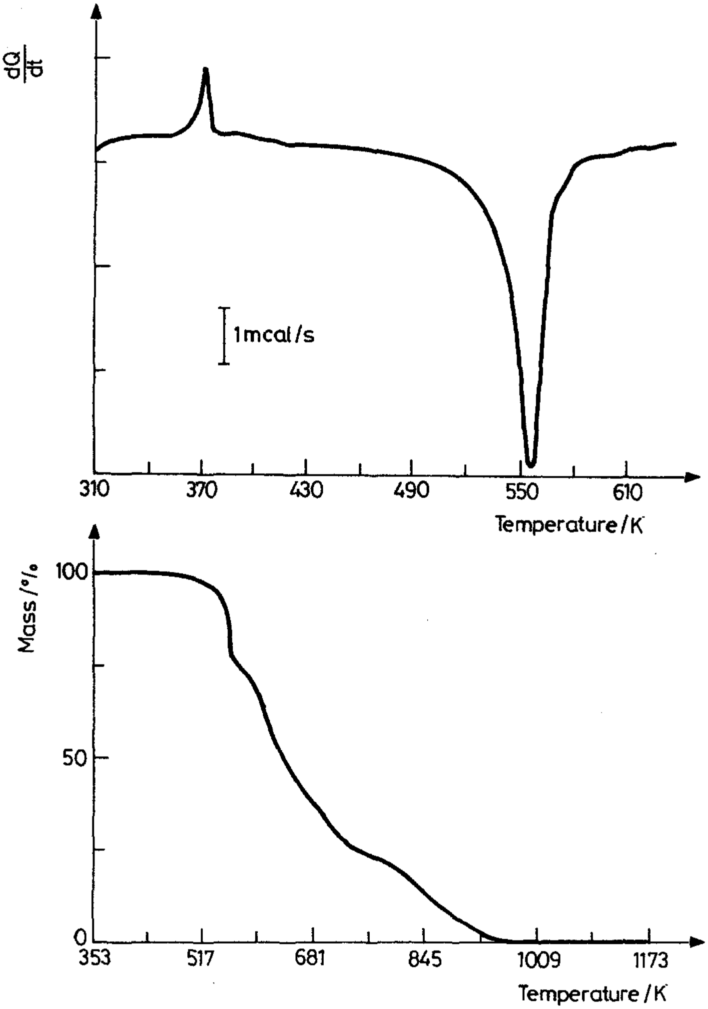


Fig. 2 Differential scanning calorimetry and thermogravimetric analysis for TGI as a function of the temperature

Results

TGI, a cristalline epoxy compound, shows at DSC measurements a melting peak at about 373 K and an exothermic peak at 558 K over a large range of temperature from 523 to 593 K due to the TGI homopolymerization [1].

TG analysis in air shows a loss of weight, beginning at 523 K, which becomes complete at 973 K without any residue. Figure 2 shows DSC and TG curves for TGI. A residue at higher temperature is indeed observed when TG analysis of TGI is carried out in nitrogen atmosphere.

It has been noticed in Fig. 2 that TG curves of TGI show a first weight loss of about 25% both in air and nitrogen on the same temperature range when TGI homopolymerizates. Thermal behaviour of boric acid is well known [5].

As the temperature increases, boric acid loses water in two stages between 370 and 470 K according to the relationship

$$H_3BO_3 \xrightarrow{-H_2O} HBO_2 \xrightarrow{-\frac{1}{2}H_2O} \frac{1}{2}B_2O_3$$

obtaining above 523 K a 'vitreous' glassy residue of B_2O_3, the 55% of the starting acid, which can act against fire at the surface of polymers as an intumescent coating, as reported in literature [5].

Figure 3 shows DSC and TG curves of the boric acid.

We have carried out DSC measurements on TGI/H_3BO_3 physical mixtures with known molar ratios ranging from 5:1 to 1:2, in order to know their thermal behaviour and to reach the best conditions for a complete reaction between TGI epoxy groups and boric acid protons.

The thermal behaviour of TGI/H_3BO_3 mixtures, at molar ratios 2:1, 1:1 and 1:2 are reported in Fig. 3.

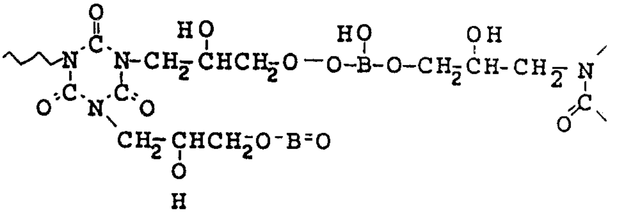
On heating our mixtures we notice three exothermic heats.

ΔH_1 at 378 K, ΔH_2 at 473 K and ΔH_3 at 573 K.

Because ΔH_3 occurs at the same temperature of the homopolymerization of TGI [1] and it decreases up to their complete desappearence as well as the boric acid content in the mixtures increases, we think that this is the heat due to TGI homopolymerization. ΔH_1 and ΔH_2, never seen before, are heats reasonably due to the reaction of TGI with H_3BO_3. We think that some amount of HBO_2 is also present in the mixture, together with H_3BO_3, due to the partial loss of water that appears in the curves of Fig. 4.

When the homopolymerization heat becomes zero we suppose that occurs only the reaction between TGI and boric acid.

This compound, in analogy with the results obtained by pyrolysis studies on TGI/H_3PO_4 reaction [2], could have the following general formula:



The TGI reaction heats ΔH_1, ΔH_2 and ΔH_3 calculated from DSC as a function of the H_3BO_3 content are quoted in Table 1.

Reaction enthalpy of -63 kJ·mol^{-1} for bulk reaction of TGI and H_3BO_3 at 1:1 molar ratio is less than that of TGI and H_3PO_4 at 1:1 molar ratio quoted as -89 kJ·mol^{-1} in [1]. The difference could be connected to different strength of the two acids. The reaction is more exothermic with the more strong acid.

From the data it is evident that the TGI addition with boric acid occurs at around 473 K. As it is shown in Fig. 4, the bulk reaction with mixture at 1:1 molar

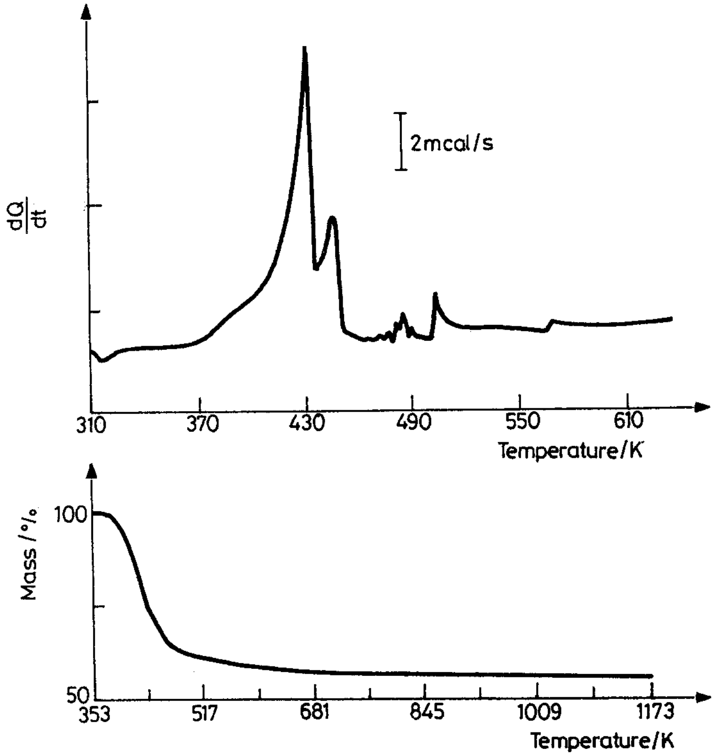


Fig. 3 Differential scanning calorimetry and thermogravimetric analysis for boric acid as a function of the temperature

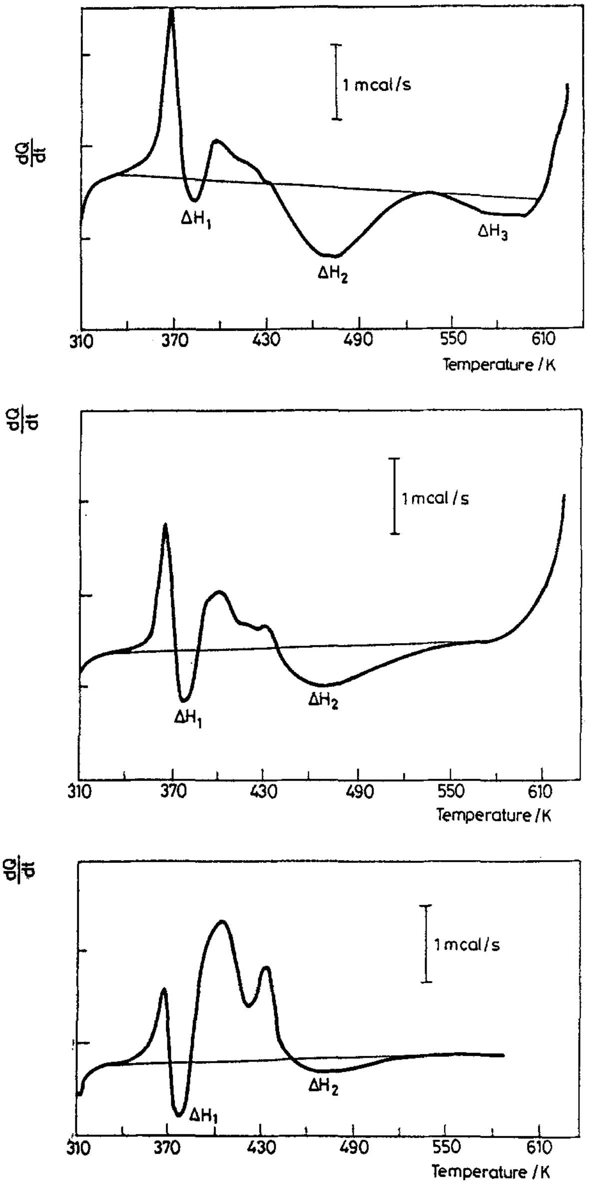


Fig. 4 Comparison, from up to down, of the differential scanning calorimetric behaviour respect to the temperature for TGI/H_3BO_3 mixtures having TGI/H_3BO_3 molar ratios ranging from 2:1 to 1:2

Table 1 Enthalpies for TGI/H_3BO_3 bulk reactions

Sample	TGI/H_3BO_3	$-\Delta H_1$ /kJ·mol^{-1}	T_1/K	$-\Delta H_2$ /kJ·mol^{-1}	T_2/K	$-\Delta H_3$ /kJ·mol^{-1}	T_3/K
A	1/0	–	–	–	–	285	558
B	5/1	–	–	38	478	66	580
C	3/1	–	–	46	475	19	575
D	2/1	1	383	47	471	4	577
E	1/1	12	379	51	467	–	–
F	1/2	17	378	17	478	–	–

ratio shows already the whole lack of TGI homopolymerization at about 580 K and the reaction between the two compounds seems to be complete.

This last DSC curve is very similar to that for 1:1 molar TGI/H_3PO_4 mixture reported in [1].

Fourier transform infrared absorbance spectra of the reaction products, see Fig. 5, indicate the lack of the absorption bands of the epoxy groups at 920 cm^{-1}

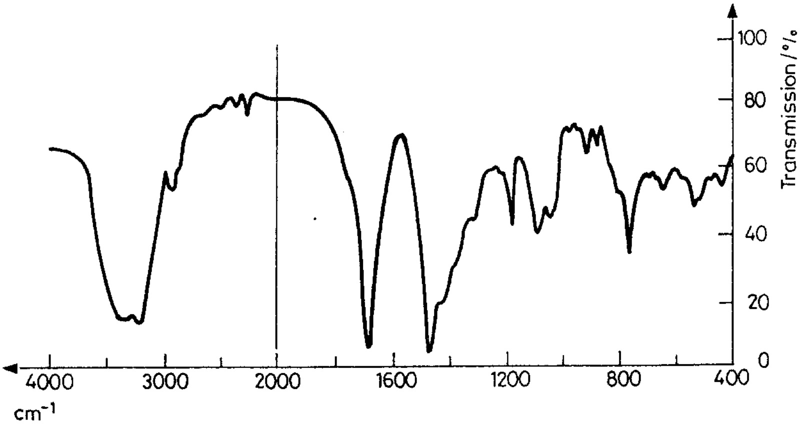


Fig. 5 Infrared spectrum of TGI/H_3BO_3 mixture at 1:1 molar ratio after heating for 1 hour at 473 K

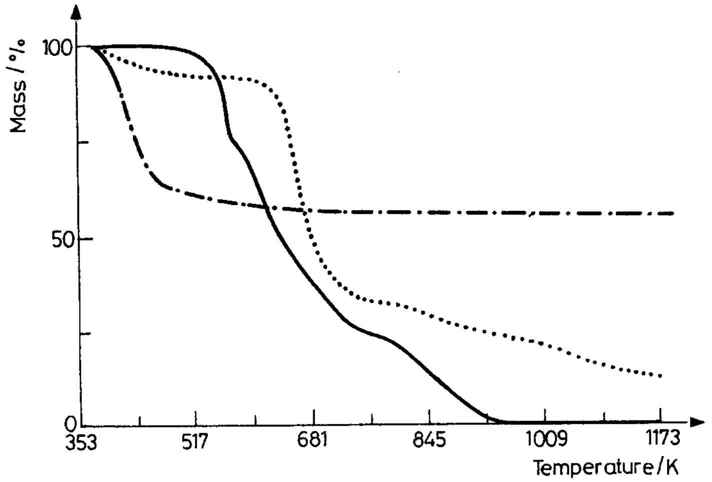


Fig. 6 Thermogravimetric analysis in air of the mixture TGI/H_3BO_3 at 1:1 molar ratio (····) in comparison with those of parent products TGI (—) and boric acid (– · –)

while the absorbance peaks of isocyanurate ring present at 1680 and 1450 cm^{-1} confirm the thermal stability of the heteroatom ring.

Stretching absorbance of group B–O appears at 1200 cm^{-1}.

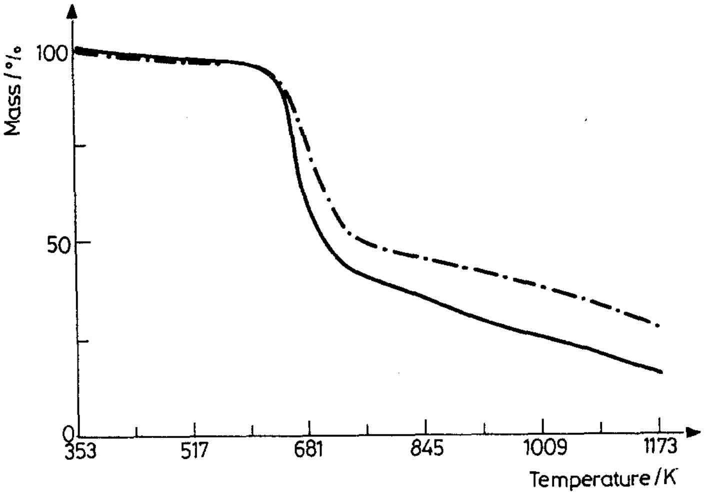


Fig. 7 Comparison of weight stability to the temperature of the two additives having molar ratios 1:1 (—) 1:2 (– · –)

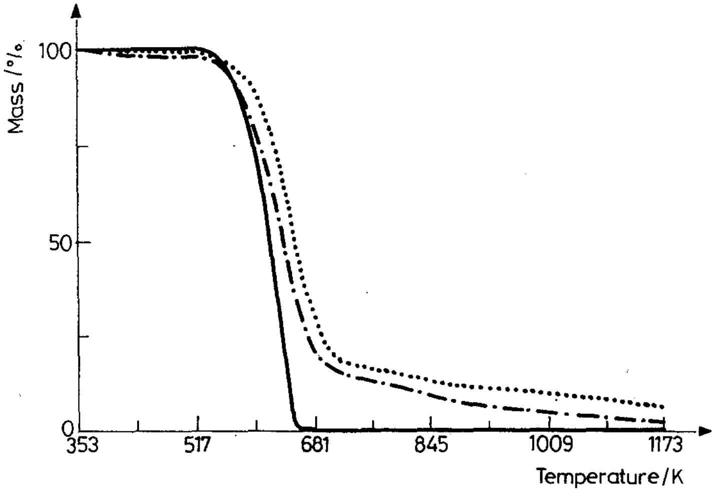


Fig. 8 Increment of degradation temperature of PP (—) added with fire retardants having decreasing TGI/H_3BO_3 molar ratios from 1:1 (– · –) to 1:2 (····)

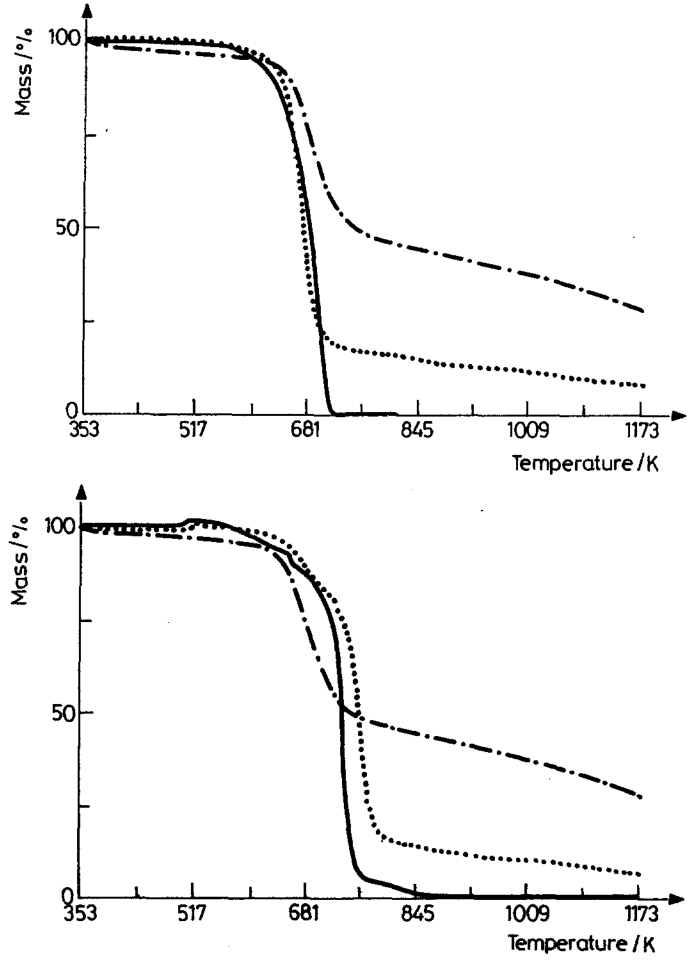


Fig. 9 Thermogravimetric behaviour of pure PS (—) (above) and HDPE (below) respect to TGI/H_3BO_3 1:2 molar ratio additive (– · –) and added polymers(·····)

It is known [7] that TG allows us to know the thermal behaviour of materials and to distinguish how an additive increases thermal stability of polymers. In analogy of what we found in the case of phosphoric acid, we are inclined to suppose that an increase of thermal stability of such a compound is generally strictly related with an increase also of the flame retardant properties of the products.

As a matter of fact, we compare in Fig. 6 the TG findings for TGI, H_3BO_3 and the mixture TGI/H_3BO_3 at 1:1 molar ratio by using a heating rate of 20 deg·min^{-1} The TG of the mixture shows that its weight stability covers a temperature range much wider than that of TGI up to 643 K.

Furthermore, a resistent residue to higher temperature, up to 1173 K, is noticed.

This thermal stability, better than that of parent products, indicates that we have likely obtained a new product with flame retardant property.

Samples of TGI/H_3BO_3 mixtures at 1:1 and 1:2 molar ratios have been heated for 2 hours at the temperature of 473 K, where DSC curves of the TGI/H_3BO_3 mixtures indicate highest polymerization rate. The obtained materials have been examined by TG according to our experimental conditions.

Figure 7 shows TG curves in air of two materials coming from TGI/H_3BO_3 mixtures at molar ratio 1:1 and 1:2. Both compounds have a wide weight stability up to the temperature of 643 K, then a degradation occurs until 723–753 K and at the end a large residue remains. They are resistent to temperature above at 1170 K and their amounts are respectively 18% and 29% of the starting weight. These values are much bigger than those calculated by their stoichiometric B_2O_3 contents. The char increment at 1173 K in nitrogen is only a few percent higher than the value found in air.

We have tested these products as additives and we have examined the thermogravimetric behaviour of polypropylene containing 30% of the product made with TGI/H_3BO_3 at molar ratios of 1:1 and 1:2. The results are in Fig. 8 in comparison with the TG of the pure polymer.

The initial degradation temperatures of the added polypropylene samples are the same of virgin one but the degradation curves are stressed towards higher temperatures as much as the used additives are able to give higher char content. Better results are obtained by using the additive having TGI/ H_3BO_3 molar ratio of 1:2.

Furthermore, we have added 30% of the additive with 1:2 molar ratio of TGI/H_3BO_3 to polystyrene and to high density polyethylene and we have carried out TG in air of the samples. These TG curves are reported in Fig. 9 together with TG curves of the pure polymers and of the pure additive.

All these added polymers show a certain char amount coming from the additive but polypropylene and high density polyethylene show a significant increment of the degradation temperature.

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Zusammenfassung — Mittels DSC wurde die Reaktion zwischen Triglycidylisocyanurat (TGI) und Borsäure bei Molverhältnissen von 5:1 bis 1:2 untersucht. Die erhaltenen Substanzen wurden als Zusatzstoffe von Polyolefinen verwendet und die so erhaltenen Polymere wurden in Luft mittels TG untersucht, um die Änderung ihrer thermischen Stabilität als Funktion des Borsäuregehaltes zu erhalten. Die Zusatzstoffe scheinen die Zersetzungstemperatur von Polypropylen, Polyethylen und Polystyrol anzuheben.