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TG-MSを用いた臭素系難燃剤を含む耐衝撃性ポリスチレンの熱分解挙動の検討
Investigation of the thermal decomposition of flame retarded high-impact polystyrene by TG-MS

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The degradation of several samples of high-impact polystyrene (HIPS) containing the flame retardants decabromo diphenylether (DPE) and decabromo dibenzyl (DDB), respectively, was investigated by thermogravimetry coupled with mass spectroscopy (TG-MS). Additionally, the effect of antimony oxide (Sb_2O_3) was examined. Various brominated compounds were observed during the degradation of the flame retardant. Brominated benzenes, phenols, and dibenzofurans were obtained from DPE, while brominated toluenes were detected in the presence of DDB. 1-Bromo-1-phenylethane as a addition product of HBr and styrene was present in any sample. The rise in the formation of radicals caused a change in the mechanism of the polystyrene degradation.

Key Words: HIPS, Brominated Flame retardant, Polybrominated dibenzofurans, Polybrominated phenanthrenes

1. Introduction

Flame retardants are a necessary additive for many plastic applications. Brominated flame retardants are often used for this purpose. During recycling, however, they impose a high risk of releasing hazardous compounds when thermally treated. Carcinogen substances, such as brominated dibenzodioxins and dibenzofurans, are released. Furthermore, the degradation pathway of the polymer is changed, altering the product composition.

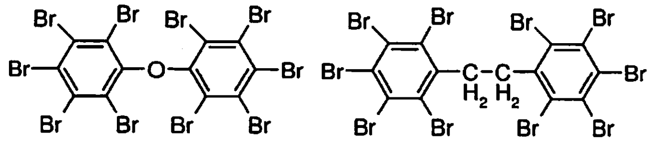
In this work, we investigated the effect of the flame retardant on the pyrolysis behavior of high-impact polystyrene (HIPS), and the degradation of the flame retardants decabromo diphenylether (DPE) and decabromodibenzyl (DDB) in the presence and in the absence of antimony oxide (Sb_2O_3).

2. Experimental

For these experiments, HIPS was blended with DPE and DDB, respectively (Fig. 1). Sb_2O_3 was also added to some samples. The composition of the samples used is shown in Table 1.

The TGA measurement was performed with a Seiko TG/TDA6200 over a temperature range of between 50 and 700°C at a heating rate of 5 K min^{-1}, using 10 mg of sample. The helium flow was set to 200 ml min^{-1} in order to avoid corrosion, caused by the diffusion of HBr, released during the decomposition of flame retarded HIPS. The gas was analyzed by MS (HP5973). TG and MS were connected by a 5 m stainless steel capillary (Frontier Labo, UADTP-5M) with an inner diameter of 0.25 mm, heated at 300 °C.

Evolving products were identified by pyrolysis experiments carried out in a quartz glass reactor, using 500 mg of sample. The same heating program was used as for the TGA-experiments. The product oil was qualitatively analyzed by GC/MS (HP6890/HP5973) and quantified by GC-FID (GL Science GC390). Brominated compounds were analyzed by GC-ECD (HP6890). The same type of column (GL Science Inert Cap 5MS/Sil) was used for all GC analyzes.



Decabromodiphenylether (DPE) Decabromodibenzyl (DDB)

Fig. 1. Flame retardants used in these experiments

Table 1. Sample composition

Sample	Flame retardant	Synergist
DPE-Sb(0)	DPE 13wt%	-
DPE-Sb(5)	DPE 13wt%	Sb_2O_3 5 wt%
DDB-Sb(0)	DDB 13wt%	-
DDB-Sb(5)	DDB 13wt%	Sb_2O_3 5 wt%

3. Results and Discussion

The thermal degradation the Sb_2O_3 free samples DPE-Sb(0) and DDB-Sb(0) started at about 300 °C (Fig. 2). The degradation proceeded in two steps, visible by the shoulder attached to the main degradation step. The degradation of the Sb_2O_3 containing samples DPE-Sb(5) and DDB-Sb(5) started at about the same temperature, however, the degradation rate was in the beginning strongly accelerated, resulting in an early maximum at 330 °C and a second maximum at about 400 °C, which might be identical to first degradation step of the Sb_2O_3 free samples. The presence of Sb_2O_3 resulted in an accelerated degradation of both the flame retardant and HIPS. A closer look at the degradation of DPE-Sb(5) at a heating rate of 5 K min^{-1} by TG-MS reveals that styrene and its dimers and trimers were

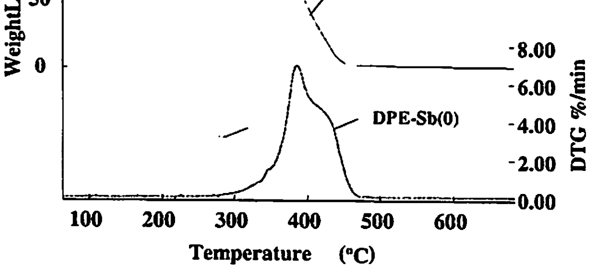


Fig. 2. TGA/DTG of HIPS and flame retarded HIPS

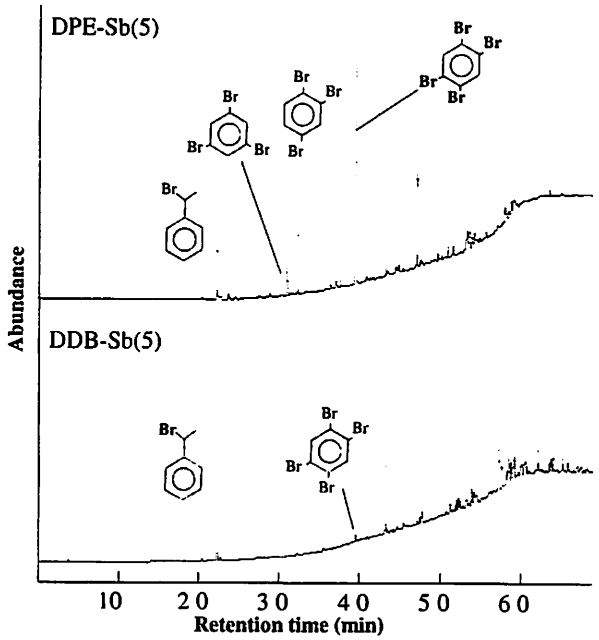


Fig. 3. GC-ECD of the degradation products of flame retarded HIPS containing Sb_2O_3

produced during the whole degradation range. Hydrogen bromide as an indicator for the degradation of the flame retardant was only released during the first stage of the degradation. Obviously, the presence of Sb_2O_3 triggered the decomposition of the flame retardant at a lower temperature releasing high concentrations of HBr, $SbBr_3$, and water.[1] The degradation of the flame retardant proceeded by a radical mechanism, and bromine radicals were released in high concentrations. Radical transfer reactions with the polystyrene chain resulted in HBr and polystyrene tertiary macroradicals. The chain fission resulted in a secondary marcoradical, releasing styrene by a zipper mechanism, and a polymer chain with an unsaturated chain end, which might not undergo degradation immediately, but being the source of the increased production of by-products due to the odd chain end.

Besides styrene, styrene dimers and trimers, which are common products of the polystyrene degradation, by-products in high yields were observed during the degradation of flame retarded HIPS. Products, such as toluene, α-methylstyrene, 1,3-diphenylpropane, and methyl-phenyl-naphthalene can also be found under the degradation products of polystyrene, but their formation were strongly enhanced. Products, such as cumene, 1,3-diphenylbutane, diphenylpentadiene, and triphenylpentane, are less common for the degradation of polystyrene, but can be explained by the extraordinary conditions in the presence of a flame retardant.

GC-ECD revealed the presence of various brominated organic compounds present in the product oil of flame retarded HIPS after the thermal degradation (Fig. 3). DPE released more brominated compounds in the presence of Sb_2O_3 than in its absence. When DDB was used as a flame retardant, the vice versa effect was observed. According the different structures of the flame retardants used, the chromatograms showed significant differences. While DPE formed brominated phenols and dibenzofurans, brominated phenanthrenes were observed from the degradation of DDB. α-Ethylbenzene, however, was found as a product of both DPE and DDB containing HIPS, since it is not derived directly from the decomposition of a flame retardant, but resulted from the reaction of HBr with styrene.

The pathway of the degradation of flame retarded HIPS differs strongly from that of polystyrene (Fig. 4). Polystyrene undergoes a chain fission in the first step, followed by the unzip-mechanism as the main reaction pathway.[2,3] To some extent, back-biting reactions take place, resulting in dimers and trimers. In the presence of a flame retardant, the mechanism changes due to the high concentration of free bromine radicals. After the degradation of the flame retardant molecule, the resulting bromine radicals transfer the radical to the polymer chain, forming HBr. Since the secondary macroradical is more stable than the primary one, it can be assumed that solely the secondary macroradical is formed, which can decompose by the unzip-mechanism. The other side of the chain is stabilized as an alkene and does not undergo a further degradation until another radical transfer takes place. Each radical transfer leaves an odd chain end, which results in products different to those obtained from the degradation of pure HIPS.

4. References

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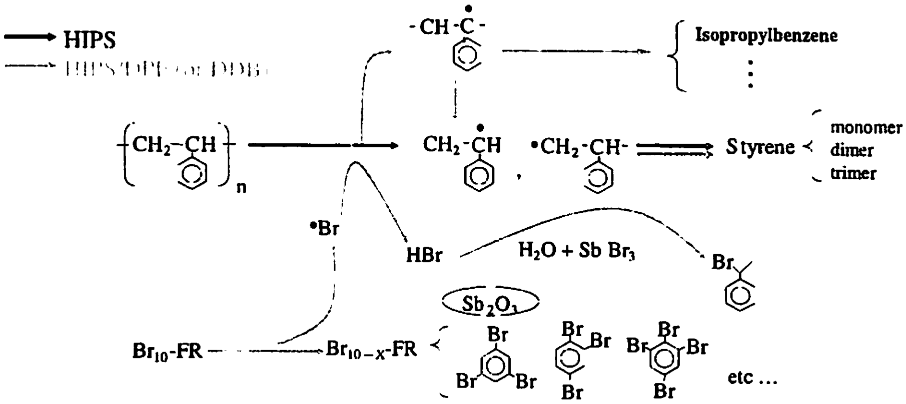

Fig. 4. Degradation pathway of HIPS and flame retarded HIPS