Interaction Between Polybrominated Flame Retardants and High Impact Polystyrene

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SYNOPSIS

Mixtures of two crystalline brominated aromatic flame retardants with a surrounding polymer were studied by differential scanning calorimetry, dynamic mechanical analysis (DMA), wide angle X-ray scattering, and solid-state NMR spectroscopy. 1,2-Bis(tetrabromophthalimide)ethane (I) and decabromodiphenyloxide (II) were evaluated in high impact polystyrene (HIPS). Additive I exhibits all the properties of an inert filler. The crystalline structure with respect to the pure material remains unchanged within the polymer. Concerning the HIPS matrix, a slight rise in the melt viscosity and a reduced impact strength as compared to the base resin was observed. In contrast, additive II is miscible with the HIPS matrix and dissolves completely. This leads to an increase of the glass transition temperature of the polybutadiene phase as revealed by solid-state NMR spectroscopy and DMA. The impact resistance of the HIPS matrix is less affected by additive II than by additive I. No interactions were noted with the PS phase at temperatures up to the glass transition. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

High impact modified polystyrene (HIPS) is widely used for numerous applications in our daily life. For many applications, in particular transportation and electrical appliances, fire safety regulation rules apply and flame retardants are used to improve the ignition resistance of polymers.[1,2] For HIPS, polybrominated aromatic compounds are the most efficient polymer additives. For a long time, crystalline decabromodiphenyloxide (DBDPO) has been the additive of choice.[3]

Moreover, flame retardancy is just one important aspect of the performance of such polymer additives. Other aspects include thermal and UV stability, effects on physical properties of the polymer matrix, processability, and the compatibility with polymers. In applications requiring resistance to UV light, 1,2-bis(tetrabromophthalimide)ethane (I) has been found to perform admirably. Resistance to discoloration as shown by a tristimulus color change after

300 h of xenon light exposure were measured as dE = 11.4 for unmodified HIPS, 54.9 for flame retarded HIPS using DBDPO, and 6.3 using I. Addition of hindered amine light stabilizer and pigments gave value of under one with I a very desirable value for a HIPS resin.[4]

Little is known and found in the literature about the behavior of a flame retardant within a polymer matrix, in particular HIPS. For the most investigated flame retardant, DBDPO, however, it is reported that this compound dissolves within the HIPS matrix at temperatures above 520 K and recrystallizes on cooling.[5] This is revealed by light transmission measurements that are sensitive on the micron length scale, therefore an understanding on the molecular level is not achieved here. On the other hand, an intimate mixing for this system is proposed on the basis of dynamic mechanical analysis (DMA) measurements,[6] but experimental evidence is still not conclusive. The interaction of the crystalline brominated aromatic species with a surrounding polymer is of interest in understanding the physical properties of these mixtures.

The subjects of our investigation are two different species, 1,2-bis(tetrabromophthalimide)ethane (I)

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and DBDPO (II), which are mixed as flame retardants in HIPS. The chemical structures and melting points for both additives are given in Table 1. The rheology as well as the impact behavior differ, however, between HIPS mixtures of I and II. Blends containing 12 wt % I show the behavior expected for inclusion of an inert solid: a slight rise in viscosity and a reduction in impact properties. Blends containing 12 wt % II in contrast, have a lower viscosity than the base resin and a smaller decrease in impact strength than observed using species I. In the present work, these two mixtures were chosen for a comparative study. More insight into the quite different behavior is obtained by combination of differential scanning calorimetry (DSC), DMA, solid-state NMR, and wide angle X-ray scattering (WAXS) measurements.

EXPERIMENTAL

Sample Preparation

Additives I and II were mixed with a commercially available HIPS using a Werner and Pfleiderer 30-mm corotating twin screw extruder. Additives were added to the throat with the HIPS at a combined rate of 8 kg/h. Screw speed was held at 150 rpm and the compound temperature was 493 K. The pelletized extrudate was then molded using a Battenfield BSKM 100/40 injection molder to give the samples investigated in this study. Cylinders used for the NMR experiments were lathe cut from the molding sprues.

DMA Measurements

The DMA measurements were performed with a Rheometrics RMS 800 instrument equipped with a rectangular torsion sample fixture. The measuring frequency was 10 rad/s and the heating rate 2 K/min.

DSC Measurements

The DSC measurements were performed with a Mettler DSC 30 instrument using a heating rate of 10 K/min. The sample weight was between 5 and 10 mg.

NMR Measurements

The temperature-dependent static ^{1}H-NMR experiments were performed with a Bruker ASX 500 spectrometer equipped with a standard Bruker static double resonance probe operating at a frequency of 500.13 MHz for protons and a standard Bruker temperature unit.
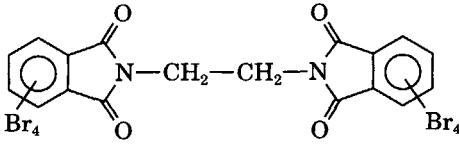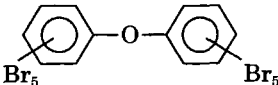
WAXS Measurements

The WAXS data were obtained in a range for $2\theta = 1°-50°$ in steps of 0.02° on a Siemens Kristalloflex Diffractometer with a collimator width of 0.3 mm and scintillation-based detection. The wavelength of the Cu-K$_\alpha$ radiation was 0.154 nm.

CHARACTERIZATION OF PURE HIPS MATERIAL

First, the exact composition of the pure HIPS matrial is checked by high-resolution NMR using CDCl$_3$. In this solvent, the PS component dissolves completely. The rubber component, however, is insoluble due to crosslinks but it swells. This swelling leads to a sufficient increase of the molecular dynamics that high-resolution liquid-state NMR can be performed. The composition of the sample is evaluated by integration of the aromatic proton res-

Table I Chemical Structure and Melting Point for Additives I and II

Name	Structure	Melting Point
I: 1,2-bis(tetrabromophthalimide)ethane		725 K
II: Decabromodiphenyloxide		575 K

onances at 6.55 and 7.05 ppm characteristic for PS and the olefinic proton resonances at 5.0 and 5.4 ppm characteristic for polybutadiene. In this way, the rubber content of the HIPS material is calculated to about 8 mol %, corresponding to 4.3 wt %.

Furthermore, the polybutadiene microstructure is checked by ^{13}C single pulse solid-state NMR spectroscopy.[7] This reveals that the rubber consists of about 5 mol % of 1,2 adduct and to 95 mol % of 1,4 adduct. The 1,4 adduct exists to equal amounts in the *cis* and *trans* configurations.

RESULTS AND DISCUSSION

Investigation of HIPS Matrix

Interaction between a polymer additive and the polymer matrix is expected to influence the dynamic behavior of both components. In particular, this can result in changes in the polymer glass transition temperature, T_g. For the HIPS material, both components, the rubber, and the PS phase can be affected, which should be detectable by DSC measurements. Using this technique, the glass transition of PS is detected at 369 K for all samples, the pure HIPS material as well as the samples containing additives **I** and **II**. Thus, the DSC glass transition of the PS phase is not affected by the presence of the flame retardants.
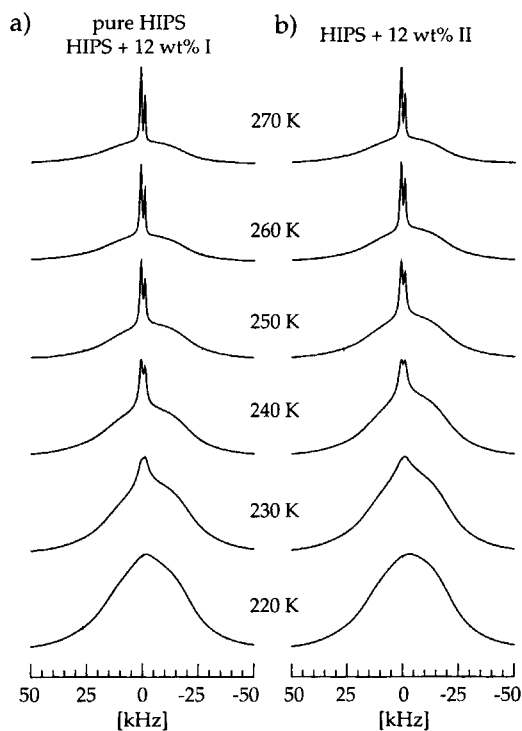
The glass transition of the rubber phase is not detected in DSC measurements due to the low polybutadiene content of 8 mol %. Because of the strong influence of the polybutadiene phase on the mechanical properties of the HIPS material,[8] DMA is applied to investigate the glass transition temperature of the polybutadiene. The plots of G'' and tan δ versus temperature are shown in Figure 1(a) and (b), respectively. The data are obtained at a frequency of 10 rad/s and the G'' maximum is used for the determination of the glass transition temperature. The curves for the pure HIPS material and the sample containing additive **I** are nearly identical, but the curve for the sample containing additive **II** is shifted to higher temperatures in contrast. The glass transition temperatures of the rubber phase within the pure HIPS material and the one containing species **I** are identical at 190 K, whereas T_g is increased by 8 K in the blend containing species **II**. It is important to note that additive **II** decreases the mobility of the rubber component leading to the observed shift of the glass transition to higher temperatures. This result suggests that the DBDPO (**II**) is at least partly soluble in the polybutadiene phase

a)

b)
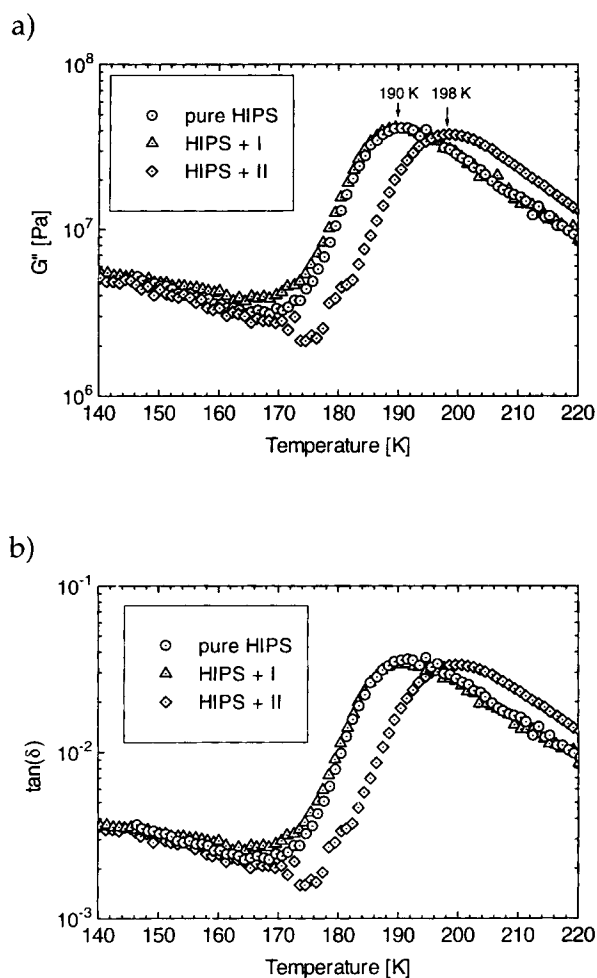
Figure 1   Dynamic mechanical data for the pure HIPS sample and the mixtures containing additive **I** and **II** acquired at a measuring frequency of 10 rad/s and a heating rate of 2 K/min. (a) G'' and (b) tan δ.

of the HIPS material. In the rubber phase the additive **II** acts as an antiplasticizer. At this point, no statement can be made about the behavior of additive **I** within the HIPS matrix.

The influence of the DBDPO **II** on the dynamics of the polybutadiene component can also be directly monitored by solid-state NMR spectroscopy.[9] Therefore ^{1}H one-pulse experiments are performed on the pure HIPS material and samples containing 12 wt % of the additives in the temperature range from 188 to 293 K. The spectra are plotted in Figure 2. No difference could be detected between the spectra of pure HIPS and the material with 12 wt % **I**. Therefore the spectra of Figure 2(a) are representative of both samples. They display the transition from a broad line at 188 K to a motionally narrowed spectrum at 248 K due to the dynamic glass transition. The ^{1}H-NMR line shape is most sensitive to

a) pure HIPS
HIPS + 12 wt% I

b) HIPS + 12 wt% II

270 K

260 K

250 K

240 K

230 K

220 K

50 25 0 -25 -50   50 25 0 -25 -50
[kHz]   [kHz]

Figure 2 ^{1}H one pulse solid-state NMR spectra recorded in the temperature range from 188 to 248 K. (a) Spectra representative for the pure HIPS and the HIPS containing 12 wt % **I**. (b) Spectra of the HIPS material containing 12 wt % **II**. The decreasing line width shows the increasing mobility of the polybutadiene phase within the HIPS material. The line narrowing for the spectra recorded for the sample containing 12 wt % DBDPO (**II**) (b) occurs at higher temperatures as compared to the pure HIPS material and the sample containing 12 wt % **I** (a).

temperature in the region from 218 to 238 K. Here, differences between HIPS [Fig. 2(a)] and the mixture with additive **II** [Fig. 2(b)] can be detected, indicating a slight immobilization of the blend rubber phase. In particular, the onset of the line splitting, visible for the pure HIPS at T = 228 K, is apparent in the mixture only at T = 238 K.
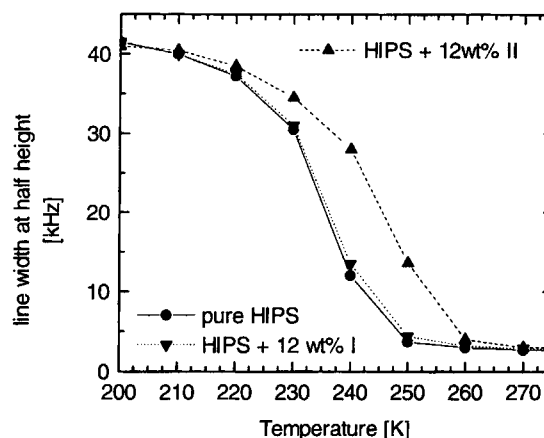
The molecular mobility of the polybutadiene is reflected in the line width at half-height of these spectra. This is plotted versus the temperature for the pure HIPS material as well as for the blend in Figure 3. Here, the shift to higher temperatures of the spectra recorded from the blend is clearly demonstrated. A quantitative determination of the T_g shift would require a thorough line shape analysis. From a visual inspection of Figures 2 and 3 we estimate 5 K $< \delta T_g <$ 10 K. Thus, in complete agreement with the DMA data, solid-state NMR shows that the dynamic behavior of the rubber phase is decreased at low temperatures by the presence of

the additive **II**. Because this effect is observed for the bulk material, it can be concluded that the flame retardant **II** is mixed with the rubber phase on a molecular level. At room temperature, however, well above T_g, essentially the same dynamic behavior is observed for the pure HIPS material and the blend containing **II**.

Investigations on Structure of Polymer Additive

Up to this point, the investigations focused on the influence of the polymer additives on the mechanical properties and the dynamic behavior of the polymer matrix. We will now consider the structure of the additives within the HIPS material itself. Due to the low content of **I** and **II** in the blends and because of the strong dipolar coupling between the ^{79}Br and the ^{81}Br isotopes to the ^{13}C nuclei, the additives can hardly be detected by solid-state ^{13}C-cross polarization/magic angle spinning (CP/MAS) NMR spectroscopy. In the spectrum of the blend containing 12 wt % **I** (not shown here), only the carbonyl peak of the phthalimide structure can be detected with great effort. Unfortunately, no information can be extracted from this weak signal concerning the crystallinity and the influence of the environment compared to the pure material.

Because both components **I** and **II** are crystalline materials in bulk, X-ray scattering is best suited to investigate the additives even within the polymer matrix. Figure 4(a) shows the WAXS pattern obtained from pure crystalline 1,2-bis(tetrabro-

line width at half height
[kHz]

40

30

20

10

0

200 210 220 230 240 250 260 270
Temperature [K]

----▲---- HIPS + 12wt% II

---●--- pure HIPS
----▼---- HIPS + 12 wt% I

Figure 3 Plot of the line width at half height from the spectra shown in Figure 1 versus temperature. Clearly seen is the temperature shift of the polybutadiene glass transition temperature of about 8 K of the rubber phase within the blend containing 12 wt % DBDPO (**II**) as compared to the rubber within the pure HIPS material and the sample containing 12 wt % **I**.
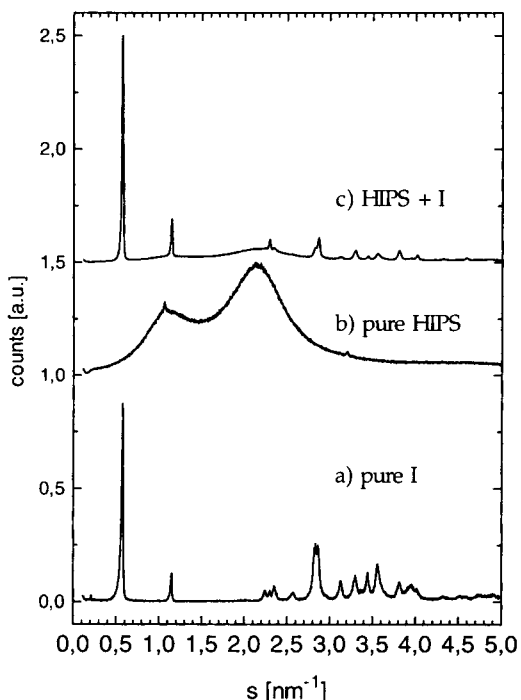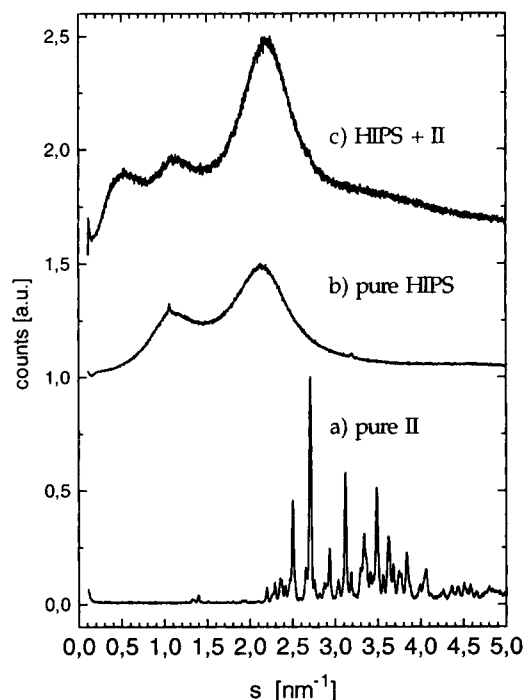
Figure 4   Wide angle X-ray scattering (WAXS) curves: (a) scattering pattern of the pure additive I revealing its crystallinity; (b) scattering pattern of the pure HIPS material showing its completely amorphous state; (c) scattering pattern of the blend containing 12 wt % of species I showing a superposition of curves (a) and (b) revealing the crystalline nature of I within the HIPS even after processing.

mophthalimide)ethane (I) in the range from 2θ = 1°–45°. It exhibits sharp reflections as expected from such a crystalline compound. A quantitative analysis is beyond the scope of this study. In contrast, the scattering pattern for the pure HIPS material is depicted in Figure 4(b) and shows only two amorphous halos and no indication for crystallinity. The scattering pattern of the blend, shown in Figure 4(c), consists of a superposition of the X-ray spectra of the pure HIPS and the pure I. All major signals of I are found in the blend as well, revealing that the crystal structure of I remains unchanged even within the polymer matrix. This gives evidence that additive I shows all the properties known for an inert filler without interaction with the polymer matrix, that is, no effect on the glass transition of the matrix material. Small changes in the scattering pattern of I in the blend compared to the pure sample [Fig. 4(a)] are attributed to orientational effects. Due to the extrusion during blend processing a preferential order is introduced, not only for the polymer matrix, but also for the anisotropically shaped additive crystals (V. Enkelmann, Pers. commun.).

The results are quite different for the blend containing additive **II**. The WAXS pattern for the pure flame retardant depicted in Figure 5(a) shows its crystalline nature in bulk. However, in the blend, shown in Figure 5(c), no indication for crystallinity is observed anymore. This reveals that additive **II** is completely dissolved in and miscible with the HIPS matrix. Thus, the structural data obtained with X-ray scattering completely corroborates our conclusion about the different dissolution behavior of additives **I** and **II**, based on dynamical measurements.

Interesting is the appearance of a broad low angle peak in the WAXS pattern at s = 0.5 nm^{-1} shown in Figure 5(c). Its molecular origin, however, is not clear.

The lack of crystallinity found in the X-ray spectra of mixtures **II** and HIPS is surprising in that phase separated additive can be noted in the HIPS optically. A less involved blending study in unmodified PS indicated that approximately 5 wt % **II** can be dissolved in PS without visual indication of phase separation. DSC measurements did not reveal a

Figure 5   Wide angle X-ray scattering (WAXS) curves: (a) scattering pattern of the pure additive **II** revealing its crystallinity; (b) scattering pattern of the pure HIPS material showing its completely amorphous state; (c) scattering pattern of the blend containing 12 wt % of species **II**. No crystallinity is detected here, revealing the solubility and compatibility of **II** with the HIPS material. However, an additional peak at s = 0.5 nm^{-1} is observed.

meaningful shift in glass transition. These observations are consistent with the earlier light scattering study.

CONCLUSIONS

Two flame retardants, 1,2-bis(tetrabromophthalimide)ethane (**I**) and DBDPO (**II**) are compounds used as additives in HIPS. It is shown that additive **I** exhibits all properties of an inert filler. No interaction with the polymer matrix is observed. The crystallinity of **I** remains unchanged even after processing at a high temperature of 490 K. However, the presence of solid particles with a median size of about 2.5 μg in bulk influences the impact properties of the HIPS matrix and leads to an embrittlement. In contrast, polymer additive **II** is miscible with the polybutadiene phase and dissolves completely during the extrusion process. After cooling, no recrystallized domains are found. Therefore the HIPS material containing **II** exhibits good performance concerning its impact behavior, despite a slightly increased T_g of the rubbery phase. This result is in accordance with investigations from Sprenkle and Southern who investigated the dissolution behavior of DBDPO in HIPS by thermal optical analysis, which is based on turbidity measurements. They found that the solution process of DBDPO starts at a solubilization temperature T_s, which is reported at 522 K here, and increases with temperature and time.[5] However, they also observed a phase separation on cooling.

According to Chang et al., the different behavior of the two polymer additives can be related to the different melting points of the flame retardant.[6] Important here is the relation between the melting point, T_m, of the crystalline additive to the processing temperature, T_p, during extrusion. The closer both temperatures are, the more likely is the solubilization of the flame retardant within the matrix polymer. In our case the two melting points differ by 150 K, where T_m of **I** is around 725 K and T_m of **II** is around 575 K. Fortunately T_p must not necessarily exceed the melting point of the additive because T_m is often higher than the decomposition temperature of the polymer matrix. The processing temperature for the samples studied here was around 493 K, $\delta T = T_m - T_p$ is then 82 K for the blend containing species **II** and 232 K for the blend containing species **I**. The distinct behavior of both samples can therefore be ascribed to the differences in the melting point.

Furthermore, the chemical structures of the flame retardant and the polymer matrix have to be taken into account for evaluating if miscibility can be achieved or not. The phthalimide structure incorporated in additive **I** is much more polar than the DBDPO **II**. In addition, it is presumed that the crystal lattice energy of **I** is much higher as compared to **II** due to favorable dipolar interactions between the carbonyl units. Therefore, it is more likely that **II** is more miscible with the apolar hydrocarbon polymers PS and polybutadiene than the additive **I**. This explains further the performance differences of the blend containing **II** as compared to the blend containing **I**. The same polarity that gives **II** its extreme thermal stability and its blends in styrenics a high heat distortion temperature, leads to immiscibility in these polymers.

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