Determination of a Polymeric Hindered Amine Light Stabilizer in Polypropylene Formulated with Magnesium Hydroxide Flame Retardant by Reactive Thermal Desorption-Gas Chromatography

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A polymeric hindered amine light stabilizer (HALS), Tinuvin 622 (MW $\approx$ 4000), in PP materials formulated with a magnesium hydroxide flame retardant was determined by reactive thermal desorption (RTD) gas chromatography (GC). Two kinds of the HALS components that were formed through the RTD in the presence of tetramethylammonium hydroxide [(CH₃)₄NOH, TMAH] were clearly observed in the chromatograms of the PP samples, with negligible interference from the other additives and the PP substrate. Here, the coexisting flame retardant was proved to affect significantly the RTD process of the occluded HALS. As a result, the recovery of the HALS components in the RTD-GC chromatograms of the PP samples increased with increase in the content of the flame retardant. This enhancement of the HALS recovery is attributed mainly to the preferential exposure of the HALS on the surface of the ground PP sample through the interaction between the polymeric HALS and the flame retardant in the molten PP during kneading. In spite of such a considerable action of the flame retardant, the observed intensities of the characteristic peaks of HALS by RTD-GC showed a good linear relationship with the HALS content in the PP samples with constant content of the flame retardant (50 phr); this relationship could be used as the calibration line for the determination of the polymeric HALS in the PP materials containing the flame retardant.

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Introduction

Hindered amine light stabilizers (HALSs) are commonly added to various polymer materials in outdoor uses as excellent radical scavengers in the order of 0.1% or less for the prevention of the photodegradation of the materials.^{1,2} HALSs in polymer materials have been generally analyzed by means of gas chromatography (GC) or liquid chromatography (LC) after their extraction from the substrate materials.^{3,4} However, the extraction process is often tedious and time-consuming especially for the oligomeric or polymeric HALSs, which are often employed in practical use because the amount that bleeds out from the substrate materials is low. Moreover, the quantitative recovery of the higher molecular weight components in the HALS is not thoroughly attained by ordinary solvent extraction because of their lower solubility and possible decomposition during the extraction process.

Recently, the authors have developed a novel method to determine a polymeric HALS in polypropylene (PP) materials using reactive thermal desorption-gas chromatography (RTD-

GC) in the presence of an organic alkali, tetramethylammonium hydroxide [(CH₃)₄NOH, TMAH].^{5,6} This technique allowed the rapid and highly sensitive determination of the polymeric HALS in the PP samples on the basis of its methylated fragments in the resulting chromatograms without using any sample pretreatment such as solvent extraction and subsequent derivatization.

Meanwhile, polymer materials in practical uses are generally formulated with a variety of additives and ingredients as well as HALSs. For example, flame retardant is one of the most important additives for various polymer products. Until now, halogenated flame retardants have been widely used because of their extremely high flame retardancy. However, the formulations of these retardants might cause the formation of toxic compounds such as dioxin relatives during combustion.⁷ Therefore, various non-halogenated flame retardants have been used for polymer materials in recent years.⁸ Among these, the metal hydroxide flame retardants are added to polymer substrates in large quantities (~60 wt%) to exert the sufficient flame retardancy. As for the polymer samples formulated both with HALS and the considerable amounts of the inorganic flame retardant, the RTD-GC process of the occluded HALS components could be appreciably affected by some catalytic action induced by the metal hydroxide. In this work, the change in the RTD behavior of a polymeric HALS, Tinuvin 622, caused

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Fig. 1 Chemical structure of Tinuvin 622.

by the coexisting magnesium hydroxide ($\text{Mg}(\text{OH})_2$) flame retardant in the PP materials was investigated in detail. The determination of the HALS contents in the PP samples was then examined by RTD-GC while considering the influence of the formulated inorganic flame retardant.

Experimental

Materials

In this work, Tinuvin 622 [Ciba Specialty Chemicals (Basel, Switzerland), MW $\approx$ 4000] was used as the polymeric HALS to be formulated in the PP samples. Figure 1 shows the chemical structure of Tinuvin 622 given by the manufacturer. This HALS has been increasingly utilized for miscellaneous polymer materials in recent years because of its long-lasting stabilization effect. Fine Mag MO-T [TMG (Tokyo, Japan)] was employed as a magnesium hydroxide flame retardant; its surface was treated with fatty acid to improve the miscibility with the polymer substrates. PP substrate in powdered form was a commercial product with melt flow index of 1.0 without containing any additives. This combination of the HALS, the flame retardant and the PP is a model for waterproof PP sheet products in outdoor uses. The model PP composite samples containing the polymeric HALS and the $\text{Mg}(\text{OH})_2$ flame retardant were prepared in a similar manner to that explained in our previous paper.⁶ Before the PP samples were prepared, the antioxidants Irganox 1010 (Ciba Specialty Chemicals) and Irgafos 168 (Ciba Specialty Chemicals) were each added in the powdered PP substrate by 0.1 phr (parts per hundred parts of resin) to prevent thermal degradation of PP during kneading. Weighed amounts of PP (10–30 g) thus blended with the antioxidants (Irganox 1010 and Irgafos 168) in powder form were kneaded at 180–190°C for 5 min. Then the $\text{Mg}(\text{OH})_2$ flame retardant was added to the molten PP and the material was kneaded again for 5–10 min. After the flame retardant was well mixed with PP, the polymeric HALS was promptly added to the mixture and this mixture was further kneaded for 3 min. Table 1 shows the formulation of two series of the PP samples thus prepared. In the A series samples, the contents of the $\text{Mg}(\text{OH})_2$ flame retardant were varied between 0 and 250 phr while fixing the HALS content at 0.50 phr. On the other hand, the B series samples contain the constant concentration of the flame retardant (50 phr) and various amounts of the HALS ranging from 0.05 to 5.0 phr. Prior to RTD-GC measurements, thus formulated PP samples were powdered in a freezer mill [Spex (Metuchen, NJ, USA) Model 6750] at liquid nitrogen temperature both to homogenize the composite materials and to improve the reactive thermal desorption efficiency of the additives in the presence of TMAH.

RTD-GC measurement

The main RTD-GC system employed in this work is basically the same as that in our previous work;⁵ it consists of a vertical microfurnace pyrolyzer [Frontier Lab (Koriyama, Japan) Model PY-2020D], and a gas chromatograph [Hewlett Packard

Table 1 Amounts of HALS and the flame retardant in prepared PP samples

Sample code	Content of additives (phr) ^a	
	Tinuvin 622	Fine Mag MO-T ^b
A-0	0.50	0
A-1	0.50	5
A-2	0.50	10
A-3	0.50	25
A-4 ^c	0.50	50
A-5	0.50	100
A-6	0.50	250
B-1	0.05	50
B-2	0.10	50
B-3	0.25	50
B-4 ^c	0.50	50
B-5	1.0	50
B-6	2.5	50
B-7	5.0	50

a. Parts per hundred resin.

b. Magnesium hydroxide flame retardant treated with fatty acid.

c. Identical sample.

(Avondale, PA, USA) Model 6890 plus] equipped with a metal capillary separation column (Frontier Lab, Ultra ALLOY+-5, 30 m $\times$ 0.25 mm i.d., coated with 5% diphenyl 95% dimethylpolysiloxane in 0.25 μm film thickness). About 150–500 μg of the PP samples, corresponding to 150 μg net weight of the PP substrate, and 2 μL of a methanol solution (25 wt%) of TMAH (Aldrich) taken in a small platinum cup were introduced into the continuously heated center of the pyrolyzer at 300°C. The thermochemical decomposition of the target compounds (HALS) at 300°C is known to finish within a short time in the presence of TMAH. The specific components thus formed from HALS were rapidly swept from the pyrolyzer to the separation column by a flow of 50 mL min^{-1} helium carrier gas. The carrier gas flow was then reduced to 1 mL min^{-1} at the entrance of the capillary separation column by means of a splitter. The column temperature was programmed from 50 to 300°C at a rate of 5°C min^{-1} and then maintained for 20 min at 300°C.

Identification of the characteristic peaks on the resulting chromatograms was mainly performed by a GC/MS system [JEOL (Akishima, Japan) AUTOMASS 150] with an electron impact ionization (70 eV) source to which the same pyrolyzer was directly attached.

Results and Discussion

Figure 2 shows the chromatograms of (a) Tinuvin 622 alone and (b) the mixture of Tinuvin 622 and the $\text{Mg}(\text{OH})_2$ flame retardant in weight ratio of 1:10, obtained by RTD-GC at 300°C, along with the structures of the characteristic products assigned by GC-MS. Under the given RTD conditions, the ester linkages in Tinuvin 622 should be selectively hydrolyzed during the RTD procedure. The carboxyl groups thus formed were quantitatively derivatized to produce methyl esters, while the hydroxyl ones were partly underivatized. As a result, dimethyl succinate (peak 1) and three kinds of products (one dimethylether and two types of monomethylethers), reflecting the tetramethylpiperidine moiety (peaks 2–4), were

Fig. 2 Chromatograms obtained by reactive thermal desorption-GC in the presence of TMAH at 300°C: (a) Tinuvin 622; (b) the mixture of Tinuvin 622 and the magnesium hydroxide flame retardant (1/10 weight ratio). FAME: fatty acid methyl ester.

characteristically observed in both chromatograms. In addition, C₁₆ and C₁₈ fatty acid methyl esters that originated from the flame retardant were observed in the chromatogram of the mixture (b). Moreover, the intensity of dimethyl succinate (peak 1) considerably decreased in chromatogram (b) probably because of its absorption on Mg(OH)₂, and the formation of the underivatized tetramethylpiperidine component (peak 5) was promoted due to some catalytic effect of the retardant. Observed intensities of peaks 2–4, however, were almost identical in both the chromatograms. This result suggests that the Mg(OH)₂ flame retardant itself has little effect on the yields of the main HALS components containing tetramethylpiperidine unit in RTD-GC measurement.

Figure 3 shows the observed RTD-GC chromatograms of the PP samples (a) A-0 containing HALS alone (0.50 phr) and (b) A-4 formulated with HALS (0.50 phr) and the flame retardant (50 phr). As for the sample A-0, partially expanded chromatogram around 22–27 min is also indicated. The compounds 2 and 3 derived from Tinuvin 622 were commonly observed along with the products from the antioxidants (peaks a, b and c) and the propylene oligomers desorbed from the PP substrate, although peak 2 slightly overlapped with peak b. Moreover, C₁₆ and C₁₈ fatty acid methyl esters that originated from the retardant were additionally observed in chromatogram (b). It is interesting to note that the relative peak intensities of the main HALS components 2 and 3 to those of the products from the antioxidants and the PP substrates were apparently much higher for A-4 (b) than those for A-0 (a), in spite of having the same contents of the polymeric HALS in A series samples.

Here, the recoveries of the HALS components 2 and 3 desorbed from the PP composite samples and observed in the chromatograms were calculated on the basis of the corresponding peak intensities obtained by the RTD-GC measurement of the intact HALS. The recoveries of the HALS thus estimated for A-0 and A-4 were *ca.* 20% and *ca.* 60%, respectively. Figure 4 shows the relationship between the recovery of the HALS components observed in the RTD-GC chromatogram and the contents of the inorganic flame retardant for the A series samples. In this case, the observed recovery of

Fig. 3 Chromatograms of PP composite samples obtained by RTD-GC: (a) PP composite A-0 without flame retardant; (b) PP composite A-4 containing flame retardant (50 phr). a, b and c: from antioxidants added in PP composites.⁵ *: propylene oligomers originated from PP substrate.

Tinuvin 622 monotonously increased with the increase in the contents of the flame retardant, and almost quantitative recovery was attained when the comparable or greater amount of the flame retardant was added to the PP substrate (A-5 and A-6). Moreover, as for the PP composite sample that contained 50 phr of the reagent grade $\text{Mg}(\text{OH})_2$ instead of the flame retardant, the observed recovery of Tinuvin 622 was almost identical to that for the PP sample containing the same amounts of the retardant (A-4). These results suggest that the reactive thermal desorption of the occluded polymeric HALS components in the PP materials was significantly promoted by the co-existing $\text{Mg}(\text{OH})_2$.

The following tests were carried out to verify the effect of the flame retardant enhancing the recovery of the HALS components from the PP materials during RTD. At first, a physical blend of PP material containing the HALS and the $\text{Mg}(\text{OH})_2$ flame retardant was prepared using the freezer mill through co-grinding the PP sample A-0 containing no retardant and the retardant itself in 1:1 weight ratio corresponding to the formulation of A-5; this sample was subjected to the RTD-GC measurement. The observed recovery of the HALS components for the physical blend sample, however, was only about 30%, while the corresponding molten mixture sample A-5 gave almost quantitative recovery of HALS under the same RTD conditions as shown in Fig. 4. This result suggested that the contact between the flame retardant and HALS (and/or PP substrate) might have little effect chemically on the RTD process.

Next, the RTD-GC recovery of the HALS components was correlated to the particle size of the PP sample; this should show an inverse relation to the surface area of the sample exposed to the alkaline reagent. Here, PP sample A-0 freezer-milled in various period was examined by RTD-GC. The recovery of the

Fig. 4 Relationship between the content of the magnesium hydroxide flame retardant in PP and the recovery of Tinuvin 622 obtained by RTD-GC.

Fig. 5 Speculated localization state of Tinuvin 622 in PP materials before and after grinding: (a) PP material without flame retardant; (b) PP material containing flame retardant.

HALS components slightly increased with increase in the grinding time. This result suggests that RTD efficiency might be improved by enlargement of the exposed surface of the sample. However, the observed recovery (up to 30% for sample A-0) was far from a quantitative value even after the longer grinding. This limitation probably came from the fact that the minimum particle size of the PP sample was restricted to around 30 μm in diameter because of its elasticity.

On the basis of these observations, the effect of $\text{Mg}(\text{OH})_2$ flame retardant to RTD of the polymeric HALS occluded in the PP material was discussed. Figure 5 shows the speculated localization state of Tinuvin 622 in (a) PP material without the flame retardant and (b) that containing the flame retardant before and after grinding. In the absence of the flame retardant (a), the polymeric HALS was still occluded mainly in the material even after grinding, because of high compatibility of the HALS with the PP substrate. Since TMAH reacted mostly with the HALS molecules exposed on the sample surface, the observed recovery of the HALS components in the chromatogram by RTD-GC measurement was fairly low (ca. 20%). On the other hand, in the PP material containing the $\text{Mg}(\text{OH})_2$ flame retardant (b), it is presumed that the polymeric HALS was chiefly localized at the interface between the flame retardant and the PP substrate during kneading, due to the polar

Fig. 6 RTD-GC chromatograms of PP samples containing different quantities of HALS with constant content of $\text{Mg}(\text{OH})_2$ flame retardant: (a) B-4 (HALS content: 0.5 phr); (b) B-6 (HALS content: 2.5 phr).

Fig. 7 Relationship between HALS content in PP samples containing 50 phr of $\text{Mg}(\text{OH})_2$ flame retardant and peak intensities of the products from HALS.

nature of the HALS. Furthermore, the PP material might be preferentially broken at this interface during the grinding, causing the predominant exposure of the HALS on the surface of the powdered sample. As a result, the RTD efficiency of the HALS in the PP samples should be highly enhanced in the presence of the flame retardant.

Finally, the polymeric HALS contents in the PP samples (B series) with a fixed amount of the flame retardant (50 phr) were estimated by RTD-GC. Figure 6 shows the observed RTD-GC chromatograms of the B series PP samples containing different amounts of HALS: (a) B-4 (0.5 phr) and (b) B-6 (2.5 phr). The peak intensities of the components 2 and 3 were much higher for B-6 containing a larger amount of HALS. Figure 7 shows the relationship between the sum of the peak intensities of the components 2 and 3 normalized by the net weight of the PP substrate and the contents of the polymeric HALS in B series PP samples. Here, the peak intensities were calculated after the molar sensitivity correction for the GC detector using the effective carbon number concept.⁹ A linear relationship was obtained for the whole range of the HALS content with a good reproducibility; the relative standard deviation (RSD) for the corrected peak intensities (2 + 3) for the PP sample containing 0.5 phr of the HALS (B-4) was ca. 5% for three repeated runs. These results demonstrate that the content of the polymeric

HALS in PP materials containing a constant amount of $\text{Mg}(\text{OH})_2$ flame retardant can be precisely determined by RTD-GC on the basis of such calibrations, although the $\text{Mg}(\text{OH})_2$ content has to be separately estimated for an unknown composite. In the case of a specific $\text{Mg}(\text{OH})_2$ flame retardant such as Fine Mag MO-T used in this work, its content needs to be also determined based on the peak intensities derived from the surface treating agents, as observed in the RTD-GC chromatogram.

In conclusion, our research revealed that the apparent recovery of the polymeric HALS, Tinuvin 622, from the PP composite samples in the RTD-GC measurement was strongly affected by the presence of the $\text{Mg}(\text{OH})_2$ flame retardant. Even for such PP materials, the RTD-GC method was proved to be useful for the rapid and precise determination of the polymeric HALS occluded in the PP samples with a constant amount of the flame retardant.

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