

Volatility of Additives from Polymers. Concentration Dependence and Crystallinity Effects

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SYNOPSIS

The evaporation of 2-hydroxy-4-methoxybenzophenone (HMB) from polypropylene was studied by an isothermal method at different concentrations of HMB ranging from 0.3 to 1.2 wt %. The evaporation of the additive was correlated according to first-order kinetics, and rate constants of evaporation were calculated. A linear dependence of the rate constants of volatility on the initial concentration of the additive in the polymer was observed. This result suggests that in the given system, volatility is governed by evaporation from the polymer surface. Volatility of HMB from polypropylene depends on the degree of crystallinity of polypropylene. Samples with different degrees of crystallinity were prepared by quenching of the polymer blends and subsequent annealing at 423K. Isothermal measurements at 383 and 423K yielded higher rate constants for annealed samples than for quenched samples. The rate constant of evaporation at 383K was 20% higher for the annealed sample, whereas at 423K it was 27.5% higher. These results are interpreted on the basis of the concentration changes occurring during annealing. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It has been recently concluded that the physical loss of stabilizers from polymers plays an important role in polymer stabilization.^{1,2} The present theory of the physical loss of additives from polymers introduced by Billingham and Calvert^{2,3} is actually similar to that for loss of heat from solids. Two processes simultaneously occur here. First, the additive must be removed from the surface of a polymer (the parallel for this process is surface emissivity), and second, additive must migrate from bulk to the surface to replace the lost additive (the parallel for this process is thermal conductivity).

Thus the mathematical modelling requires two constants: a mass transfer parameter characterizing transfer across the surface, and a constant characterizing mass transfer within the bulk of a polymer. According to Billingham and Calvert^{2,3} the first process is described by equation 1:

$$V = V_0 C_s / S_p = H C_s \quad (1)$$

where V is the rate of volatilization of the additive from unit surface area of a polymer, V_0 is the rate of evaporation of pure additive under the same conditions, C_s is the surface concentration of the additive, S_p is the solubility of the additive in the polymer, and H is a mass transfer constant.

The mass transfer within a polymer is usually described by Fick's laws of diffusion. Hence, the rate constant of the process is a diffusion coefficient. The solution of Fick's laws for various cases and sample geometries has been described by Crank.⁴

In the preceding paper we have studied the temperature dependence of the stabilizer's loss from polypropylene and the effect of phase transitions of the polymer and stabilizers.⁵ In the present report the results of the studies of the stabilizer concentration dependence and the effect of the degree of crystallinity of the polymer on the thermal loss of 2-hydroxy-4-methoxybenzophenone from polypropylene are presented.

EXPERIMENTAL

Materials and Sample Preparation

The polymer used in this study was commercial polypropylene powder Tatren HPF (Slovnaft Bratislava, Czechoslovakia) which has a melt flow index MFI = 5.24 g/10 min. 2-Hydroxy-4-methoxybenzophenone (HMB) (Cyasorb UV-9, Ciba-Geigy) was used as a light stabilizer. The mixture of polypropylene with the HMB was homogenized for 5 min at 463K, 12.7 MPa, and 60 rpm in the mixing chamber of a Plastograph Brabender (Duisburg, Germany). The stabilized polypropylene sheets with thickness of 0.5 mm were prepared from this blend by pressing at 463K and 12.7 MPa for 5 minutes. The prepared samples were quenched at 197K in an ethanol-dry ice mixture and stored at this temperature in a Dewar flask. The nonstabilized articles were prepared in the same way. Discs of diameter 3 mm and weight ca. 4 mg were cut from the sheet for measurements. The annealing of the samples was performed in sealed pans of a differential scanning calorimetry (DSC) instrument at 423K for 20 min.

Thermogravimetric Measurements

Thermogravimetric measurements were performed using a thermobalance TGS-1 (Perkin Elmer) in isothermal mode. Experiments were carried out in dry nitrogen atmosphere. The time period of one measurement was about 30 minutes. The final form of the plot was an average of at least 5 measurements. For the calibration, the calibration weights of the M class, tolerance of which is ± 0.005 mg for 1–50 mg were used, and for temperature calibration Alumel and Nickel were used. Thermal measurements were performed by means of a differential scanning calorimeter DSC-1B (Perkin Elmer). Thermal calibration was conducted on the basis of known heats of fusion of indium and a set of high-purity Fischer Thermic standards.

Stabilizer Determination

The polypropylene foil was cut into small pieces, weighed, and dissolved in hot toluene. After cooling, the precipitated polymer was filtered off and the solute was transferred into a volumetric flask and the volume was adjusted to the mark. The stabilizer concentration was measured by ultraviolet (UV) spectroscopy (Carl Zeiss Jena, Germany) at 328 nm. The content of HMB was determined from the calibration plot of the pure HMB in toluene. In the

concentration range used in the present studies, the plot of concentration vs. absorption was linear.

RESULTS AND DISCUSSION

Concentration Dependence

The volatility of additives from polymers is, according to the present theory,^{2,3} governed by two processes. The first, interfacial mass transport between the polymer and surrounding medium is described by eq. (1). It follows from this equation that the loss of an additive is dependent on the surface concentration of the additive and this dependence should be linear according to first order kinetics. The second process is diffusion of an additive from the bulk of a polymer to the surface. Diffusion processes are also concentration dependent,⁶⁻⁹ especially in systems where diffusion of a low molecular weight species in a polymer proceeds.⁸ In this case the concentration dependence of the diffusion coefficient is not usually linear, and downward or upward curvatures appear in diffusion coefficient vs. concentration plots.^{7,9} It was therefore interesting to study the thermal loss at different concentrations of a stabilizer in a polymer.

The samples with the content of HMB 0.3, 0.5, 0.7, 1.0, and 1.2 wt % were prepared from nonstabilized polypropylene powder. The rate of the stabilizer loss was measured by isothermal gravimetry at 423K. This temperature is lower than the temperature of fusion of the polymer. On the other hand, it enables fast measurements of the stabilizer loss. In the control experiments, we have observed that under our experimental conditions the weight of pure PP is unaffected. This means that the weight changes describe the loss of stabilizers.

Figure 1 shows the weight decrease of the specimens with the concentration of HMB ranging from 0.3 to 1.2 wt %. It is evident from the figure that the rate of weight loss increases with increasing stabilizer concentration, and total loss is approximately equal to the stabilizer concentration. These curves were correlated according to first-order kinetics [eq. (2)].

$$-\ln \frac{c_0 - c}{c_0} = kt \quad (2)$$

where c_0 is the initial amount of additive in the polymer (wt %), c is the amount evaporated from the polymer (wt %) in time t , and k is the rate constant of the process.

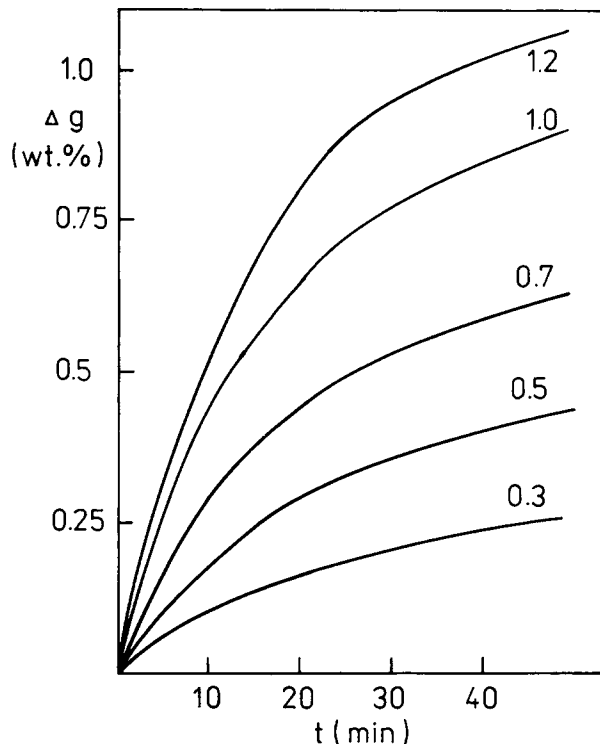


Figure 1 Time dependence of the weight loss, Δg , of 2-hydroxy-4-methoxybenzophenone from polypropylene at 423K for different initial concentrations of additive.

This dependence is in agreement with our previous results⁵ as well as with the results of Matsumoto¹⁰ for the loss of phenolic antioxidants from polyethylene. Using the coordinates, $\ln(c_0$

$-c)/c_0$ vs. t , these curves yield straight lines as seen in Figure 2. The rate constants calculated from the slopes of the respective lines for different concentrations of HMB are in Table I.

If we consider a concentration dependence of the evaporation of an additive from a polymer, we can write:

$$k = f(c_0) \quad (3)$$

and the final form of this dependence follows from the plot c_0 vs. k . As is shown in Figure 3, this dependence yields a straight line obeying the linear relationship:

$$k = k_0 c_0 + q \quad (4)$$

where k_0 and q are the slope and intercept of the linear dependence. For our system, the calculated values are $k_0 = 1.78 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$, and $q = 6.44 \times 10^{-4} \text{ s}^{-1}$. This confirms, in accordance with Angert,¹¹ that the rate constant of evaporation of an additive from a polymer is linearly dependent on the initial concentration of the additive in a polymer. The appearance of the linear dependence of the evaporative loss of HMB from polypropylene would suggest that for the given system, the rate controlling step is surface evaporation of the stabilizer from polypropylene.

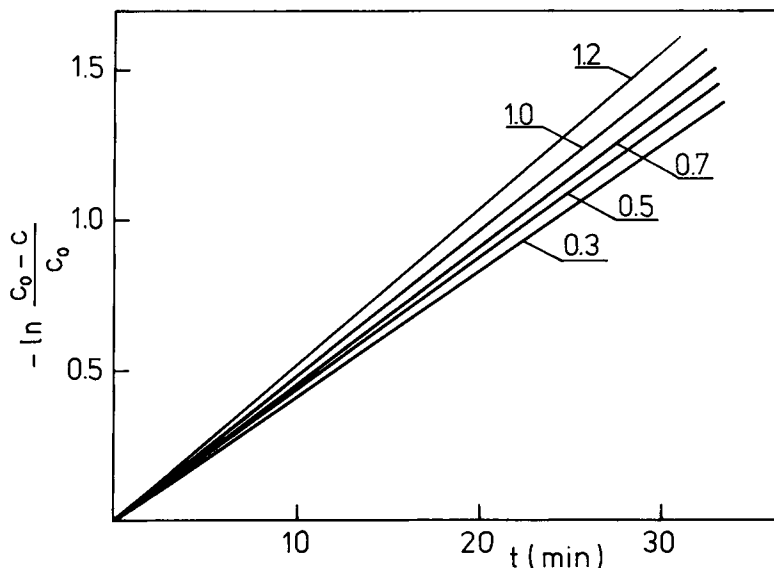


Figure 2 First-order plot of time dependence of weight loss of 2-hydroxy-4-methoxybenzophenone from polypropylene at 423 K for different initial concentrations of additive.

Table I The Effect of Initial Concentration of 2-Hydroxy-4-Methoxybenzophenone on the Rate Constant of Evaporation from Polypropylene at 423 K

c_0 (wt %)	0.3	0.5	0.7	1.0	1.2
$k \times 10^4$ (s ⁻¹)	7.0	7.4	7.6	8.1	8.7

Crystallinity Effects

In another approach we tried to obtain some information on the effect of the supermolecular structure of the polymers on the volatility of HMB from polypropylene. The effect of crystallinity and morphology on the solubility and diffusion of antioxidants in polypropylene have been already described.¹²

Therefore, we used two methods of sample preparation. The samples with low degree of crystallinity were prepared from virgin polymer as well as from polymer with 1 wt % HMB by rapid cooling of the blends at 197K in an ethanol-dry ice mixture. The samples with higher degree of crystallinity were prepared by annealing of rapidly cooled samples at 423K in sealed pans in a DSC instrument for 20 min. The thermal characteristics of these samples are given in Table 2, together with the calculated degree of crystallinity. The degree of crystallinity was calculated on the basis of heats of fusion data. The value $\Delta H_f = 188 \text{ J} \cdot \text{g}^{-1}$ for fusion of pure isotactic polypropylene^{13,14} was used.

It is evident from Table II that the melting temperature (T_m) of the virgin as well as the stabilized polymer is only slightly affected by different regimens of the sample preparation, and is lower than

Table II Melting Temperatures (T_m), Enthalpy of Fusion (ΔH_f), and Degree of Crystallinity of Virgin and Stabilized Polypropylene Samples

n	Sample	T_m (K)	ΔH_f (J/g)	Degree of Crystallinity (%)
1	PP ^a	436	98.84	52.6
2	PP ^b	437	109.26	58.1
3	PP + 1 wt % HMB ^a	435	88.22	46.9
4	PP + 1 wt % HMB ^c	439	111.74	59.5

^a PP quenched in ethanol-dry ice mixture.

^b Pure PP freely cooled to room temperature.

^c Stabilized PP quenched in ethanol-dry ice mixture and annealed 20 minutes at 423 K.

that of the pure isotactic polypropylene ($T_m = 443\text{K}$).¹⁵ The highest T_m has been obtained by annealing the stabilized polymer below T_m . The effect of sample preparation on crystallinity is easily visible in terms of the enthalpy of fusion. Rapid cooling of the polymer below T_g results in a lower degree of crystallinity for both virgin and stabilized polymers. The presence of the stabilizer in rapidly cooled samples decreases the degree of crystallinity in comparison with the pure polymer. The difference is more than 5% (10 J/g), which reflects the influence of the additive molecules on the course of the crystallization process. The more pronounced increase of the degree of crystallinity was observed after annealing of the samples at 423K. In this case, the difference between the two samples is as high

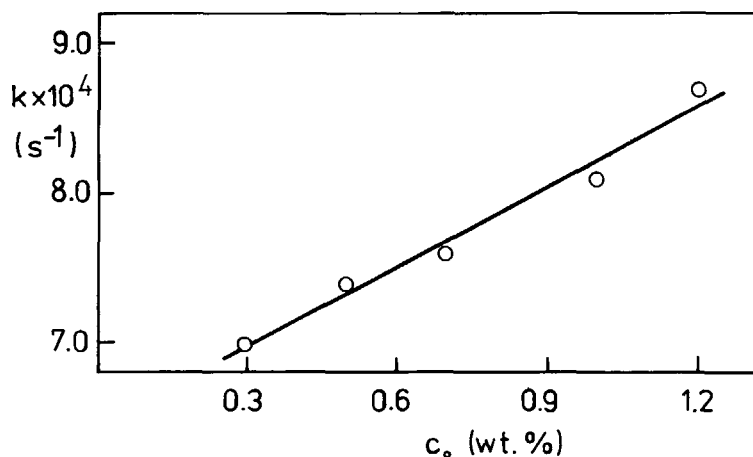


Figure 3 Dependence of the rate constants of evaporation of 2-hydroxy-4-methoxybenzophenone from polypropylene on initial concentration of the additive in polypropylene at 423 K.

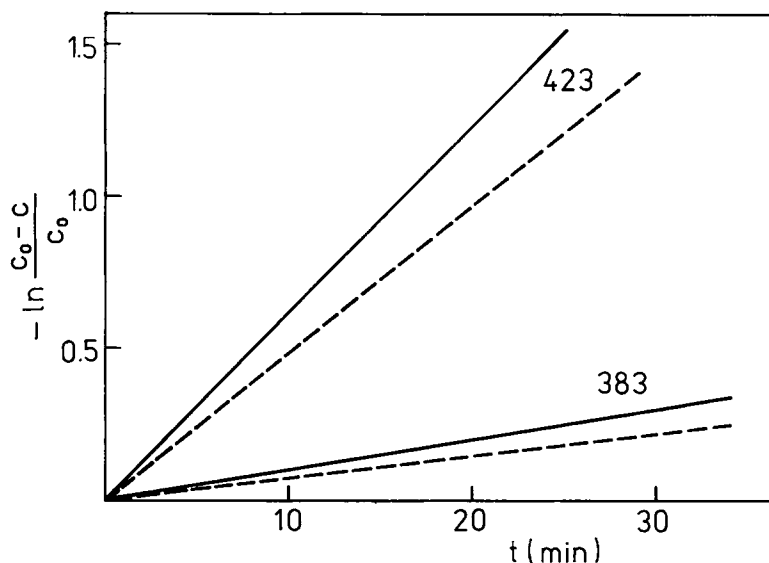


Figure 4 First-order plot of time dependence of weight loss of 2-hydroxy-4-methoxybenzophenone from polypropylene at 383 K and 423 K for quenched (---) and annealed (—) samples.

as 12.6% (23.5 J/g) and the crystallinity of the annealed, stabilized sample is higher than that of the freely cooled, nonstabilized sample.

The volatility of HMB was measured on samples which had the same thermal history as the samples given in Table II. The volatility was measured at 383 and 423K. Measurements at 423K have shown that the total weight loss corresponds to the initial concentration of HMB for both quenched and annealed articles. This means that during annealing in sealed pans the concentration of HMB does not change. The weight loss was correlated according to first order kinetics [eq. (2)]. First order plots (Fig. 4) produced the rate constants of the evaporation of HMB from polypropylene shown in Table III.

It is evident from Table III that the effect of annealing reflects itself in the increase of the rate constants of evaporation. For the lower temperature (383K), k is 20% higher for the annealed sample while for the higher temperature (423K) the increase is 27.5%. The reasonable explanation of this phenomenon follows from the thermal history of the samples and subsequent structural changes in the polymer matrix.

It has been mentioned in the previous part that the crystallinity of the polypropylene changes during annealing (see Table II). Also the supermolecular structure is different. While fast cooling of polypropylene results in a spherulite average diameter smaller than 10 microns, annealing results in the growth of spherulites up to 300–500 microns.¹² It

follows from these facts that the distribution of an additive in the polymer has to change as well. It has been previously proved^{12,16–21} that the distribution of additives in semicrystalline polymers is not uniform. The low molecular weight compounds are rejected from growing crystallites and tend to accumulate in the amorphous phase between the spherulites and in noncrystalline regions of the spherulites. At the same time, the additives remain sufficiently mobile to equilibrate to a uniform concentration in the amorphous regions after crystallization. The redistribution processes have been observed experimentally, and the mathematical modelling of the additive distribution was in excellent agreement with experimental results.^{19–21}

Table III Rate Constants of Volatility of 2-Hydroxy-4-Methoxybenzophenone (1 wt %) from Polypropylene Sheets at 383 K and 423 K

n	Sample	T [K]	$k \cdot 10^4$ [s ⁻¹]
1	Quenched ^a	383	1.50
2	Annealed ^b	383	1.80
3	Quenched ^a	423	8.10
4	Annealed ^b	423	10.33

^a Quenched at 197 K in ethanol–dry ice mixture.

^b Annealed at 423 K for 20 minutes.

In our case, we can expect similar processes. During annealing, when the growth of spherulites proceeds and the amount of crystalline phase increases, redistribution of HMB produces changes in its local concentration. The stabilizer concentrates in the amorphous phase and in less ordered parts of spherulites. Correspondingly, an increase in the crystalline phase results in a decrease in the amount of polymer matrix available for dissolution of the additive. This results in an increase of the concentration of HMB in noncrystalline parts of the polymer. Therefore, the concentration dependence of the volatility of additives explains the faster evaporation of HMB from the annealed polypropylene samples.

CONCLUSIONS

The evaporation of HMB from polypropylene is a first-order process. This process is concentration dependent. A simple, first-order dependence was observed between the rate constants of evaporation and initial concentration of HMB in polymer. This result suggests that in the given system the volatility is governed by evaporation of the additive from the polymer surface.

The effect of the degree of crystallinity of polypropylene on volatility of HMB was observed. For quenched polymer samples the rate of evaporation is lower than for annealed samples with higher degree of crystallinity. These observations are interpreted on the basis of concentration changes which proceed as a consequence of redistribution of an additive during annealing of polymer.

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