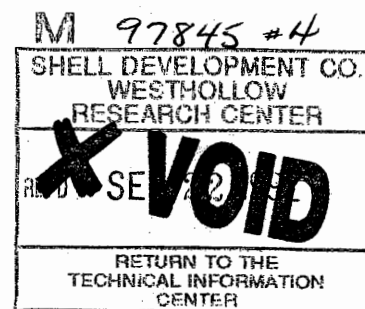# The Behavior of Additives in Polyketone

Solubility, Diffusivity, and Evaporative Loss

R. N. French

Technical Progress Report **WRC 347-91**

Project No. 62181

The Behavior of Additives in Polyketone

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CARILON® Polymer Stabilization

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

ABSTRACT

We measured the sorption of various additives into polyketone films from 130 to 210°C. From these data, we derived solubilities and diffusion coefficients for additives covering a wide range of molecular weights. These results were related to additive effectiveness and used to model evaporative loss of additives at oven-aging conditions.

TECHNICAL PROGRESS REPORT WRC 347-91

THE BEHAVIOR OF ADDITIVES IN POLYKETONE: SOLUBILITY, DIFFUSIVITY, AND EVAPORATIVE LOSS

BY

R. N. FRENCH

SUMMARY

Limitations in melt and long-term heat stability reduce the commercial potential of CARILON® polymer. Development of an effective additive package is a high priority of the CARILON Polymer project. Additive effectiveness often depends upon its mobility in and compatibility with the host polymer. Therefore, we have measured the sorption of antioxidants and UV-stabilizers into polyketone from 130 to 210°C to generate solubility and diffusion data.

The solubilities of two commonly used antioxidants, Irganox 1330 and 1076, are below the concentrations at which these additives are typically loaded. This may account for the lower effectiveness of these additives relative to Naugard 445 and XL1, which are more soluble by an order of magnitude. Solubility generally increases with increasing temperature.

Diffusion coefficients in polyketone are at least two orders of magnitude lower than in polyolefins or polyurethanes, but are comparable to those we have measured in a Nylon 66 polymer. The lower mobility of additives in polyketone relative to polyolefins suggests that evaporative loss should also be lower. However, this low mobility may compromise the effectiveness of additives to react with radical sites in the polymer.

Using the diffusion data, we have modeled the evaporative loss of additives from polyketone under oven-aging conditions. Our results suggest that low molecular weight additives may be completely lost from the polymer on the time scale of the oven-aging tests. For high molecular weight additives, significant depletion near the surface may occur, although high levels in the bulk may be maintained.

Strategies to minimize evaporative loss include the use of additives with very low vapor pressures or the use of "polymeric" additives. Generally, additives with high melting points are expected to have lower vapor pressures, although such additives also have low solubilities. If vaporization from the polymer surface becomes the rate-limiting step for additive loss, then a layer of neat additive will be maintained on the surface. This will remove the driving force for net diffusion to the surface. Alternatively, the functional groups responsible for antioxidant and UV protection could be incorporated into polymers that are compatible with polyketone. Such additives would be highly resistant to evaporation or extraction.

In principle, a dispersed second phase, highly loaded with additive, could act as a "controlled release reservoir" to circumvent compatibility and evaporative loss problems. However, a second phase with the appropriate mass transport characteristics will be difficult to find.

INTRODUCTION

Improvements in melt and long-term heat stability will greatly expand the commercial potential of CARILON polymer. Most commercial polymers contain low molecular weight additives which act as antioxidants or UV stabilizers. Development of the optimal additive package is a high priority of the CARILON Polymer project.

Antioxidants and stabilizers must be uniformly well dispersed to inhibit the initiation of degradation and/or provide competitive chain termination. High solubilities ensure good dispersions even at high additive loadings. If a stabilizer is added at levels above saturation, phase separation may occur through "blooming" or additive crystallization.

Of particular importance is the temperature dependence of solubility. Most additives are added to polymer melts. However, at end-use temperatures, solubility is generally much lower. Above an additive's melting point, its heat of solution into the polymer defines the temperature dependence of its solubility. Below its melting point, an additive's heat of fusion contributes to its solubility behavior and greatly steepens its temperature dependence. For additives with high melting points, solubility can decrease by one to two orders of magnitude between polymer melt and 25°C.

Knowledge of the diffusion coefficients of additives in polymers is important (a) to assess the potential for loss through diffusion to the surface and subsequent evaporation and (b) to relate the mobility of the additive within the polymer matrix to its effectiveness. The loss of additives from polymers by evaporation or extraction into a fluid limits the effective lifetime of the additive in the polymer. These processes require diffusion of the additive to the polymer surface and subsequent vaporization or dissolution. Diffusion is often, but not always, the rate-determining step.

In a recent review,[1] Billingham summarizes the importance of solubility and diffusion to antioxidant effectiveness in polymers. While much is known about the behavior of additives in polyethylene and polypropylene, minimal data exist for additives in polar polymers such as polyketones. Most work on diffusion and loss of polymers relates to polyolefins. Increasingly, high molecular weight additives or additives grafted onto polymers are being used to minimize evaporative and extractive loss.[2] Such additives have lower diffusion coefficients and vapor pressures than their lower molecular weight counterparts. However, they often have lower solubilities as well. An additive with low mobility may have limited ability to react with free radical sites in sufficient time to protect its host polymer. This aspect has been raised but not investigated in the literature.

SORPTION EXPERIMENTS

We measured the sorption by weight change of additives into polyketone films. Polyketone films were prepared from packaging grade material (89/022) which contains 0.2%wt of the lubricant glycerol monostearate and 0.2%wt of the phenolic antioxidant Irganox 1330. Films were either 4x4 or 5x5cm,[2] 0.42mm thick, and weighed between 0.7 and 1.3g. The additives used are listed in Table 1, and their structures are shown in Figure 1.

Powdered additive was placed between two films to form a sandwich which was wrapped tightly in aluminum foil. The sandwiches were held in an oven at 130, 150, 180, or 210°C and removed at specified times. The oven was purged with nitrogen but oxygen was not rigorously excluded. Upon removal, the films were immediately quenched in dry ice to halt sorption. Excess additive was washed off with octane and cold acetone before weighing.

Table 1

ADDITIVE SOLUBILITY IN POLYKETONE/WEIGHT PERCENT

Additive	M.W.	Melting Point/°C	130°C	150°C	180°C	210°C
BHT	220	70	1.9	2.0	2.2	2.6
Tinuvin P	225	130		5.2	9.0**	13.5**
Cyasorb UV531	326	48	2.1	2.2	2.7	2.9
GMS	344	57	3.0	2.2	1.9	1.3
Naugard 445	405	95		2.9	3.6	3.8
Tinuvin 234	456	139		1.6	2.2	1.8*
Irganox 1076	530	52		0.4	0.3*	~0.1
Tinuvin 144	682	148			>0.7*	
Naugard XLl	697	180			2.6	>1.5*
Irganox 1330	774	244		≤0.2	≤0.2	≤0.2
Irganox 1010	1177	118			>0.7*	

*Probably not at saturation.
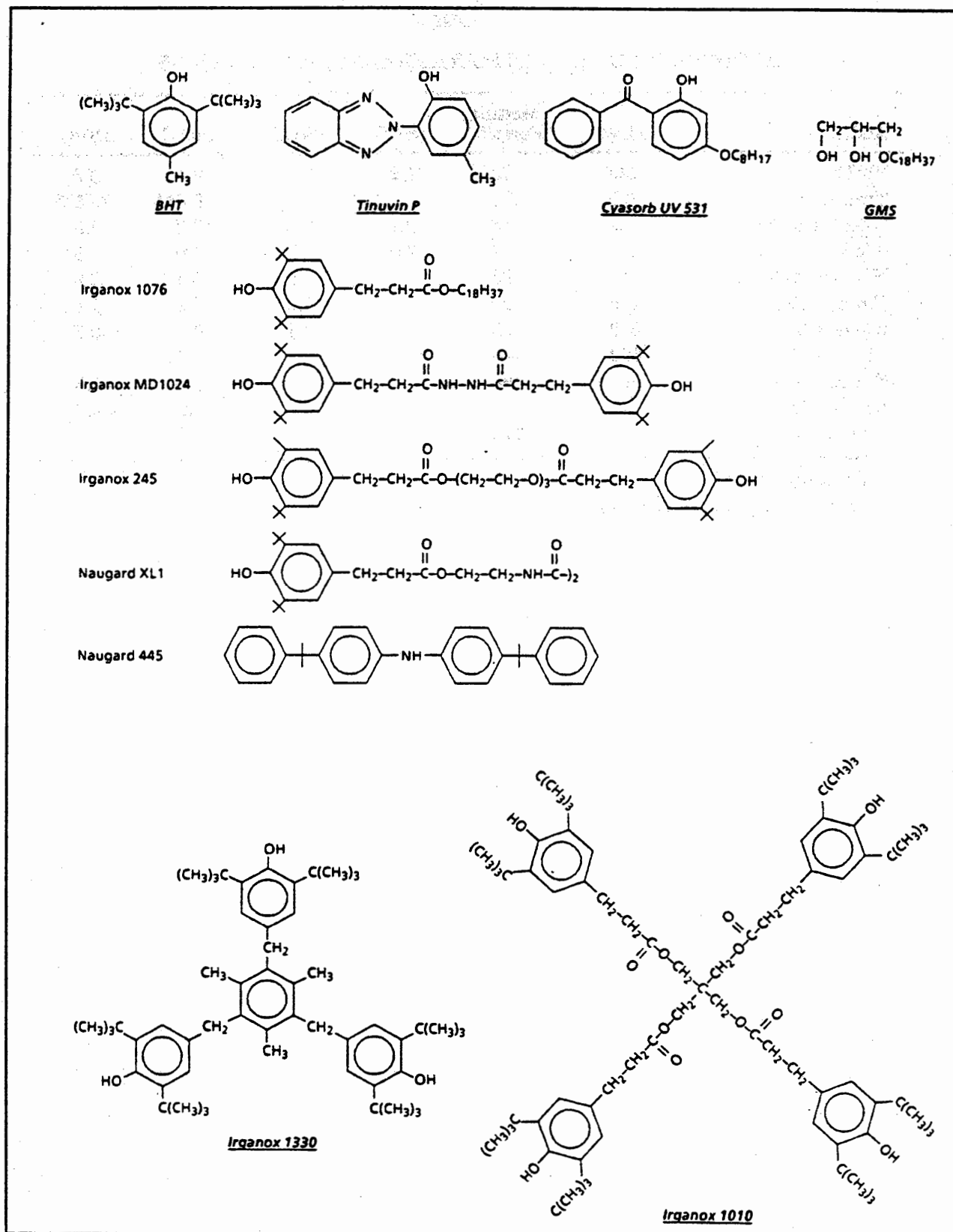**Larger than usual uncertainty.

Fig. 1 — Additive structures.

Sorption was determined by the net weight gain of the film following correction for the weight loss of neat polyketone films under identical conditions. This correction was typically between 0.5 and 1%wt and presumably represented moisture loss.

Most experiments were performed above the melting points of the additives. The melted additives flowed around the films and provided a continuous coating.

We tested this procedure by measuring the solubility of Cyasorb UV531, a UV stabilizer, in polypropylene. Concentrations estimated from weight gains were in good agreement with those determined by extraction and subsequent HPLC analysis by Ron Skelton of Analytical. The saturation concentration was in reasonable agreement with solubilities reported by Billingham.[3]

Polyketone is a semicrystalline polymer and we assume additives are soluble only in amorphous regions. The percent crystallinity may change during the sorption experiments as a result of annealing and/or degradation. At long times, some samples showed significant degradation, presumably from oxidative degradation. We measured the densities of several films following sorption to identify changes in the material.[4] Control films showed a density increase which leveled off at long times. Films in contact with additives generally showed small density decreases which leveled off at long times. It is not possible to analyze these results further as there are numerous scenarios which can lead to small density changes.

Recently, we have demonstrated how an FTIR microscope can be used to determine diffusion coefficients of an additive in polypropylene.[5,6] Samples for this technique are prepared from sorption experiments run much the same way as the polyketone work reported here. With the FTIR analysis we see that the washing step following sorption may extract additive from the near-surface region. This suggests that the weight gains measured from sorption experiments may be slightly underestimated. Fortunately, this effect is probably minimized in tests with polyketone due to its high solvent resistance.

SOLUBILITY

Sorption curves (weight gain versus time) at 150, 180, and 210°C are shown in Figures 2, 3, and 4. The weight uptakes at early times are generally below saturation levels. We will use this information in the next section to estimate diffusion coefficients. All but the heaviest additives appeared to reach saturation during our experiments. Table 1 summarizes the solubility values estimated from the sorption experiments and uncorrected for crystallinity. We make the following observations from the data:

1. Two commonly used antioxidants, Irganox 1330 and 1076, have been added to polyketone at concentrations near or above their saturation level. This is consistent with observations of blooming during processing of polymer containing high levels of 1330.*

2. Naugard 445 and XL1 have significantly higher solubilities than Irganox 1330 and 1076. This may account for their higher effectiveness.

3. Solubility generally increases with increasing temperature; GMS appears to be an exception.

4. Relative solubilities in polyketone at high temperature generally agree with relative solubilities at 25°C in acetonyl acetone,[7] a low molecular weight analog of polyketone. This relationship is demonstrated in Figure 5.

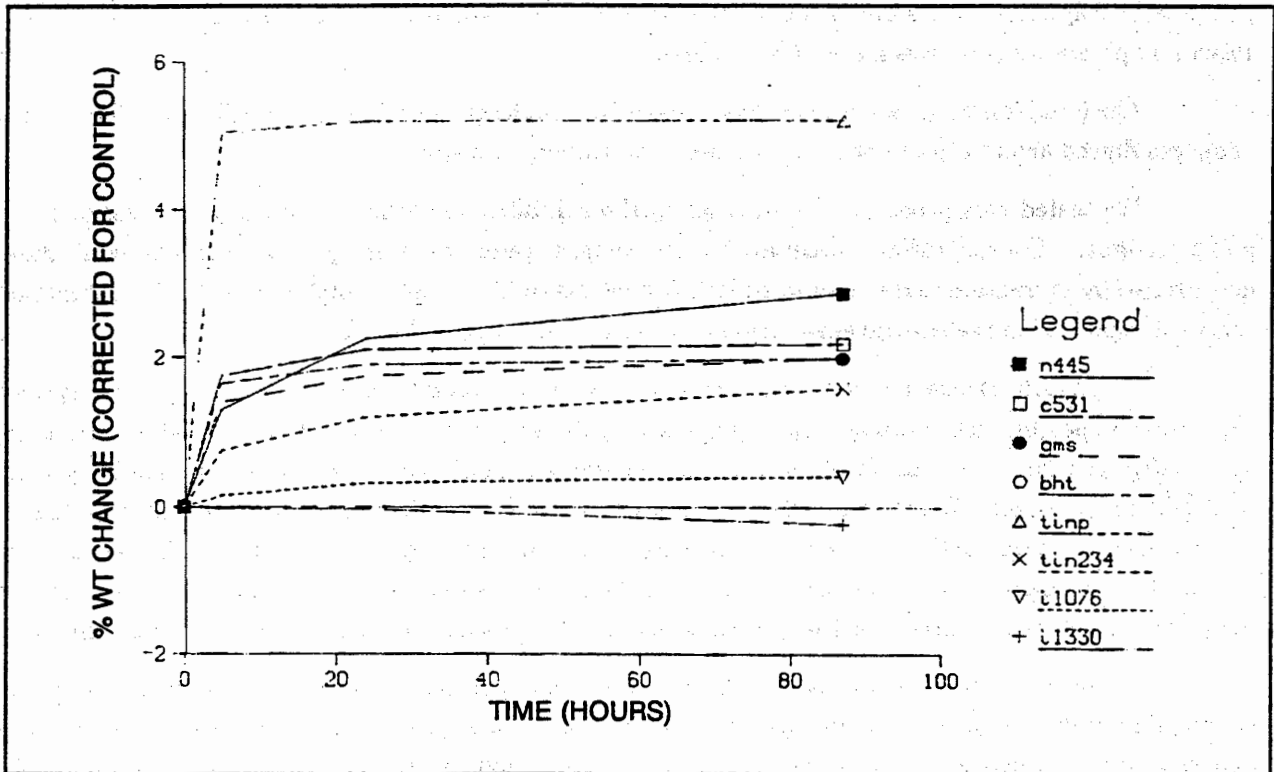*J. R. Kastelic, Westhollow Research Center (personal communication)
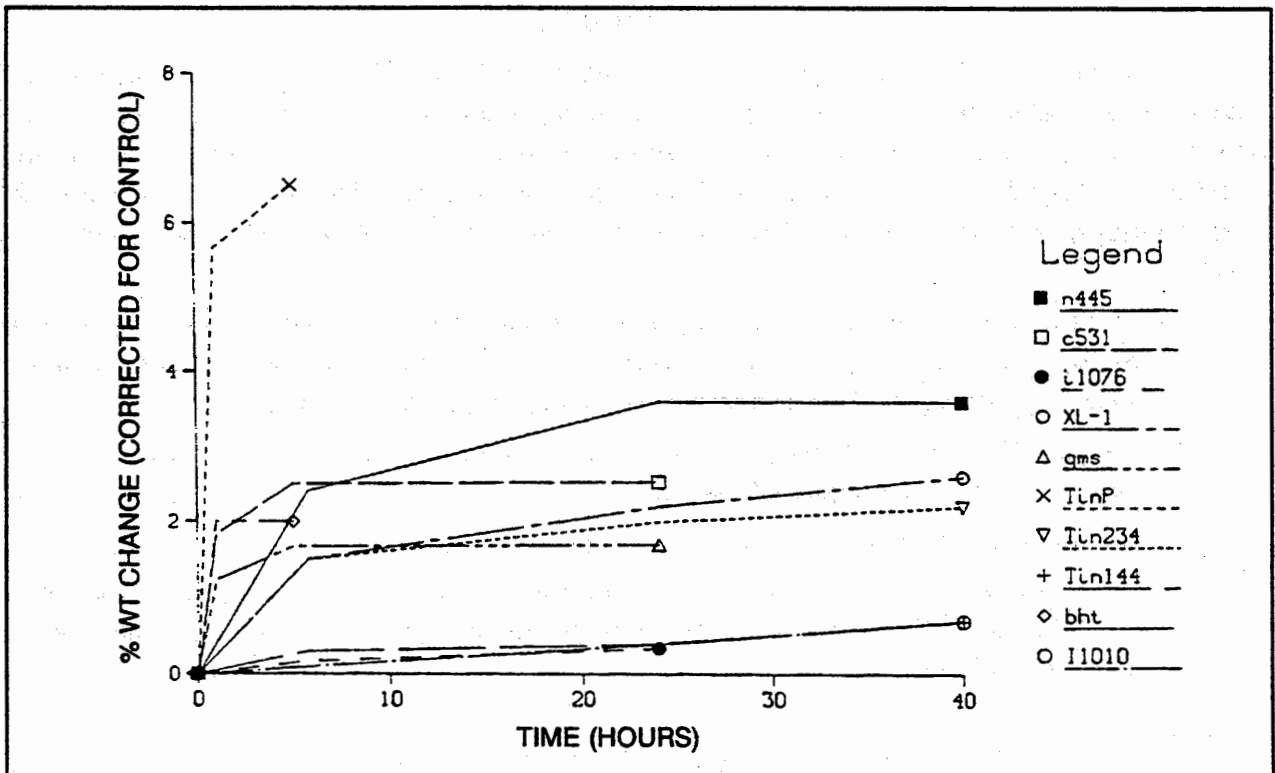
Fig. 2 — Sorption curves at 150°C.

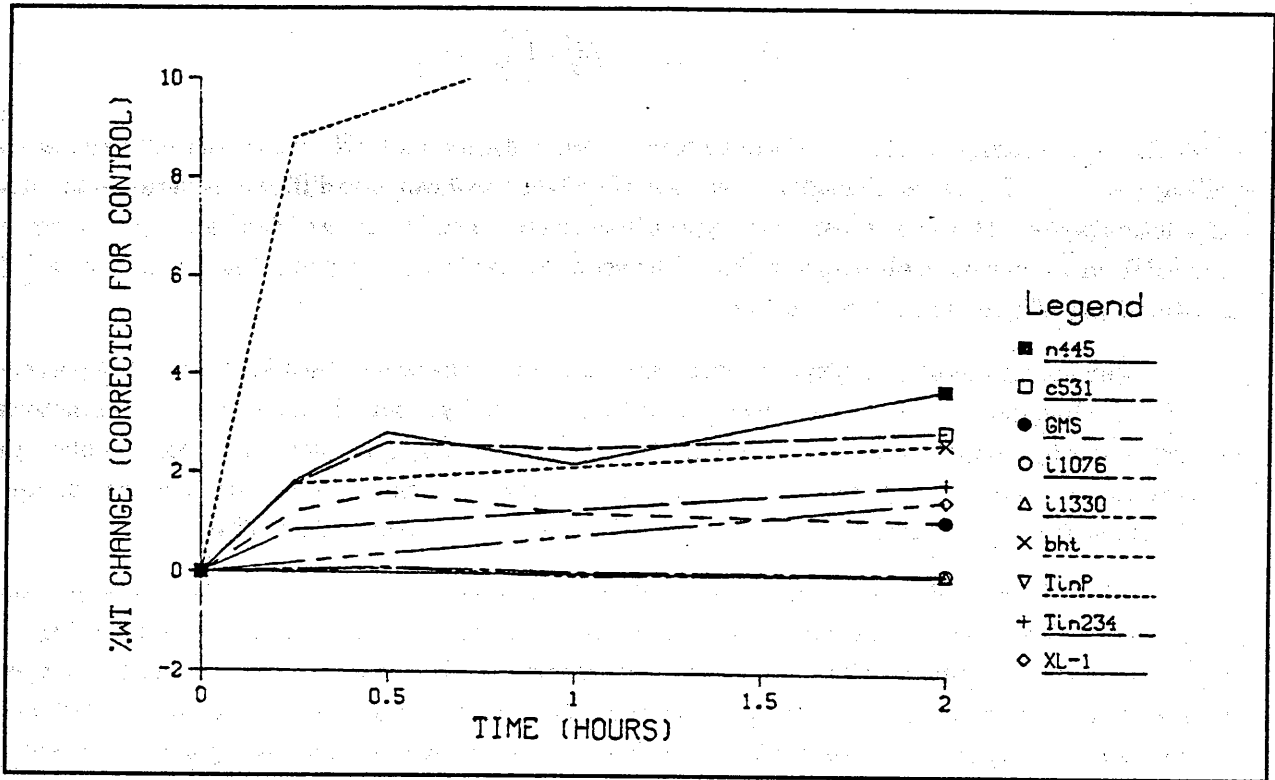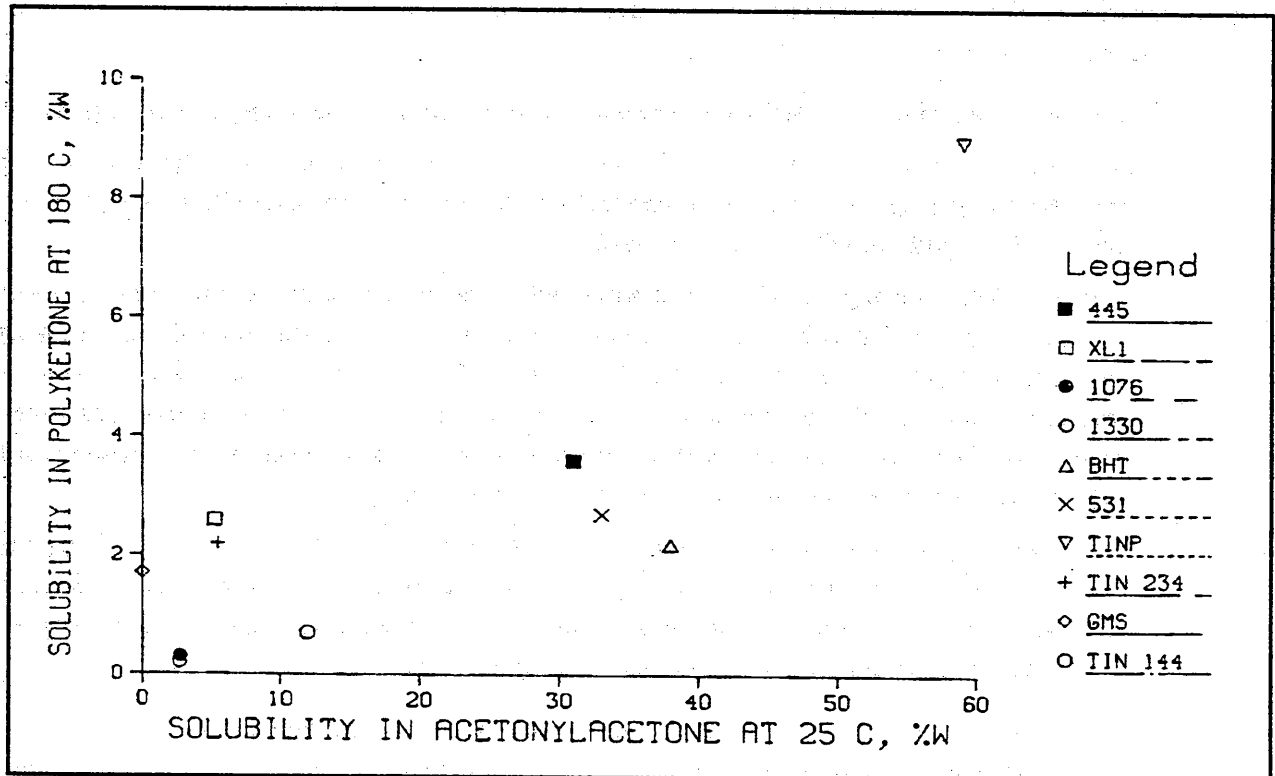Fig. 3 — Sorption curves at 180°C.

Fig. 4 — Sorption curves at 210°C.

Fig. 5 — Solubility of additives.

From a thermodynamic analysis, the weight fraction solubility of an additive in a polymer is given by

$$\ln\frac{1}{W_2} = \ln\Omega_2 + \frac{\Delta H^f}{RT_m}\left(\frac{T_m}{T} - 1\right) , \qquad (1)$$

where Ω_2 is the activity coefficient of the additive in the polymer, and ΔH^f is the heat of fusion at the melting point, T_m. Equation (1) neglects two terms involving heat capacity differences between the solid and solution phases. However, these terms typically cancel to a large extent and can be ignored unless far removed from the normal melting point. For additives above their melting point, the second term on the right-hand side of Equation (1) disappears.

The activity coefficient depends upon the interactions between the additive and the polymer. The Flory−Huggins model can be used to estimate activity coefficients from a combinatorial entropy-of-mixing term and a residual energy term expressed through the χ parameter. Unless the additive has functional groups which can interact favorably with the polymer through, for example, dipole−dipole forces or hydrogen-bonding, the χ parameter will be large and positive.

Billingham and coworkers have analyzed additive solubilities in polypropylene using Equation (1). They find that the heat of fusion and melting point of the additive often play as big or a bigger role than compatibility with the polymer in determining solubility. Increased solubility is favored by a lower heat of fusion and a lower melting point for the additive. Asymmetric structures, which have lower melting points, are more soluble than highly symmetric molecules. Increasing alkyl substitution increases solubility in polyolefins through increasing compatibility with the polymer and by decreasing melting point. The equilibrium solubilities of most additives in polyolefins are low, but increase rapidly with temperature. Therefore, many common additives are readily soluble at melt conditions, but become supersaturated at use and/or testing conditions.

Additive solubilities in polyketone are important primarily in three temperatures regions:

1. At processing conditions, near 250°C. This determines how well the additive is initially dispersed in the polymer. Since this is above the melting point for most additives, only the most incompatible additives will not disperse well.

2. At oven-aging, typically 125°C. This is where additives are screened for effectiveness. Since polyketone is semicrystalline, actual additive concentrations in the amorphous phase are significantly higher than the nominal additive level. Solubilities will be lower than at processing, particularly for additives with high melting points. If concentrations exceed saturation, then "blooming" is possible and evaporative loss may be enhanced. These effects may be manifested as low effectiveness against degradation.

3. At ambient or end-use conditions. Since almost all additives will be below their melting point, solubilities will be much lower. Undoubtedly, some additives will be supersaturated and at increased risk for "blooming" and/or evaporative loss. This can lead to much shorter lifetimes than predicted from accelerated aging tests at high temperature.

The data in Table 1 pertain mostly to oven-aging and processing conditions. However, "ballpark" extrapolations to low temperatures can be made using heats of fusion and melting point data.

DIFFUSION

We need diffusion coefficients to evaluate the loss mechanism and mobility of additives in polyketone. These can be derived from the sorption measurements used to obtain solubility values. For each additive, we have data corresponding to concentrations below saturation. Diffusion coefficients can be back-calculated from a model of sorption for a well-defined sample geometry and experimental conditions.

We neglect edge effects and model the polyketone films as infinite sheets of thickness 2l. At low additive levels, we assume a concentration-independent diffusion coefficient, D. We need a solution to Ficks law for these initial and boundary conditions:

$$\left(\frac{\partial C}{\partial t}\right) = D \left(\frac{\partial^2 C}{\partial x^2}\right) \tag{2}$$

$$C = 0, \text{ for } l > x > -l, \text{ at } t = 0 \tag{3}$$

$$C = C_0, \text{ for } x > l, \; t > 0 \tag{4}$$

Crank[8] has given a solution to this case:

$$\frac{C_t}{C_\infty} = 1 - \sum \frac{8}{(2n+1)^2\pi^2} \exp\left[-D\left(n+\frac{1}{2}\right)^2\pi^2\frac{t}{l^2}\right] \tag{5}$$

where C_t/C_∞ is the degree of saturation, expressed as the concentration at time t relative to the concentration at saturation. Crank presents a smooth curve for C_t/C_∞ as a function of $\sqrt{(Dt/l^2)}$. D can be calculated for individual points. The main objective of the sorption experiments was to obtain solubilities, not to derive highly accurate diffusion coefficients. However, they are sufficiently reliable to interpret trends and to compare to diffusion in other polymers.

Table 2 lists the estimated diffusion coefficients at 150, 180, and 210°C. Figure 6 shows D as a function of molecular weight for additives representing a variety of chemical types. Figure 7 shows the temperature dependence of D in an Arrhenius-type plot. From these data, we can make order-of-magnitude estimates of D for most additives in polyketone over a range of relevant temperatures.

Table 2

DIFFUSION COEFFICIENTS OF ADDITIVES IN POLYKETONE

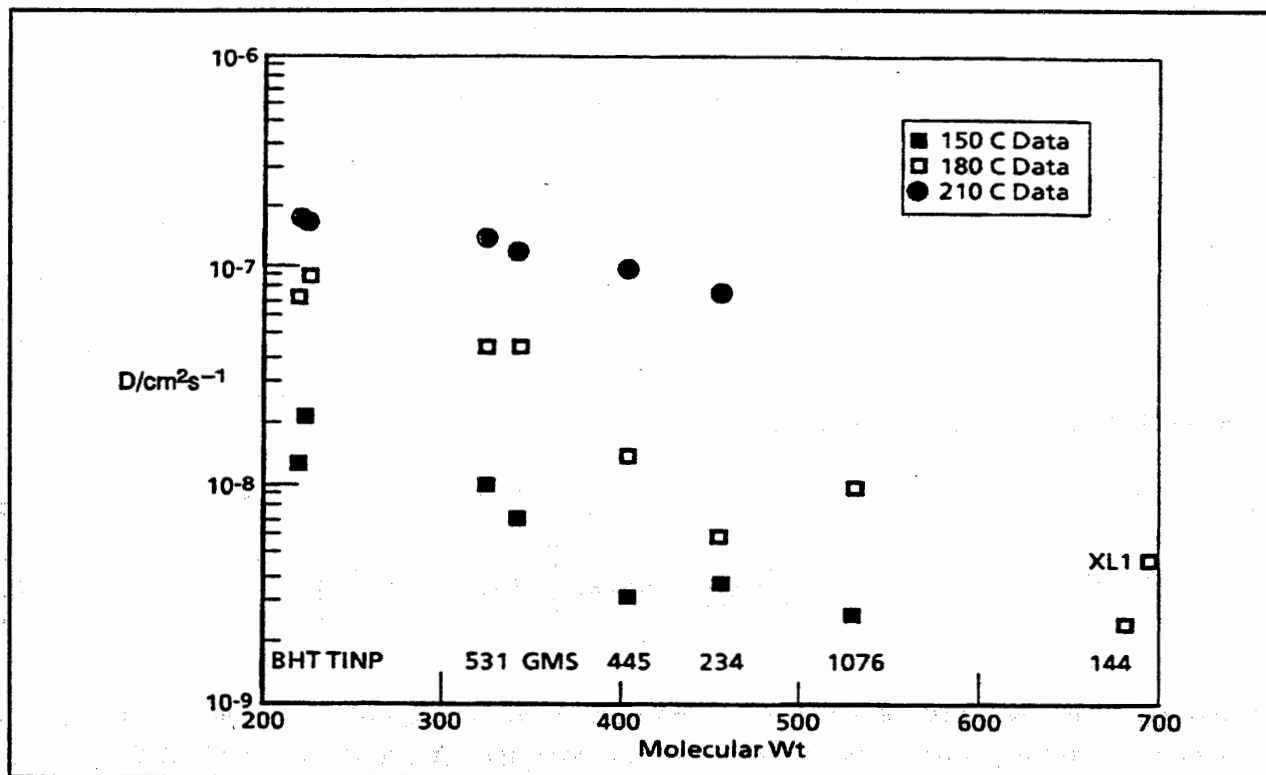|	$D/cm^2 sec^{-1}$			
Additive	130°C	150°C	180°C	210°C
BHT		1×10^{-8}	7×10^{-8}	2×10^{-7}
Tinuvin P		2×10^{-8}	9×10^{-8}	2×10^{-7}
Cyasorb UV531	6×10^{-9}	1×10^{-8}	4×10^{-8}	1×10^{-7}
GMS		7×10^{-9}	4×10^{-8}	1×10^{-7}
Naugard 445		3×10^{-9}	1×10^{-8}	1×10^{-7}
Tinuvin 234		4×10^{-9}	6×10^{-9}	8×10^{-8}
Irganox 1076		3×10^{-9}	3×10^{-8}	——

Fig. 6 — Diffusion coefficient in polyketone as a function of molecular weight.
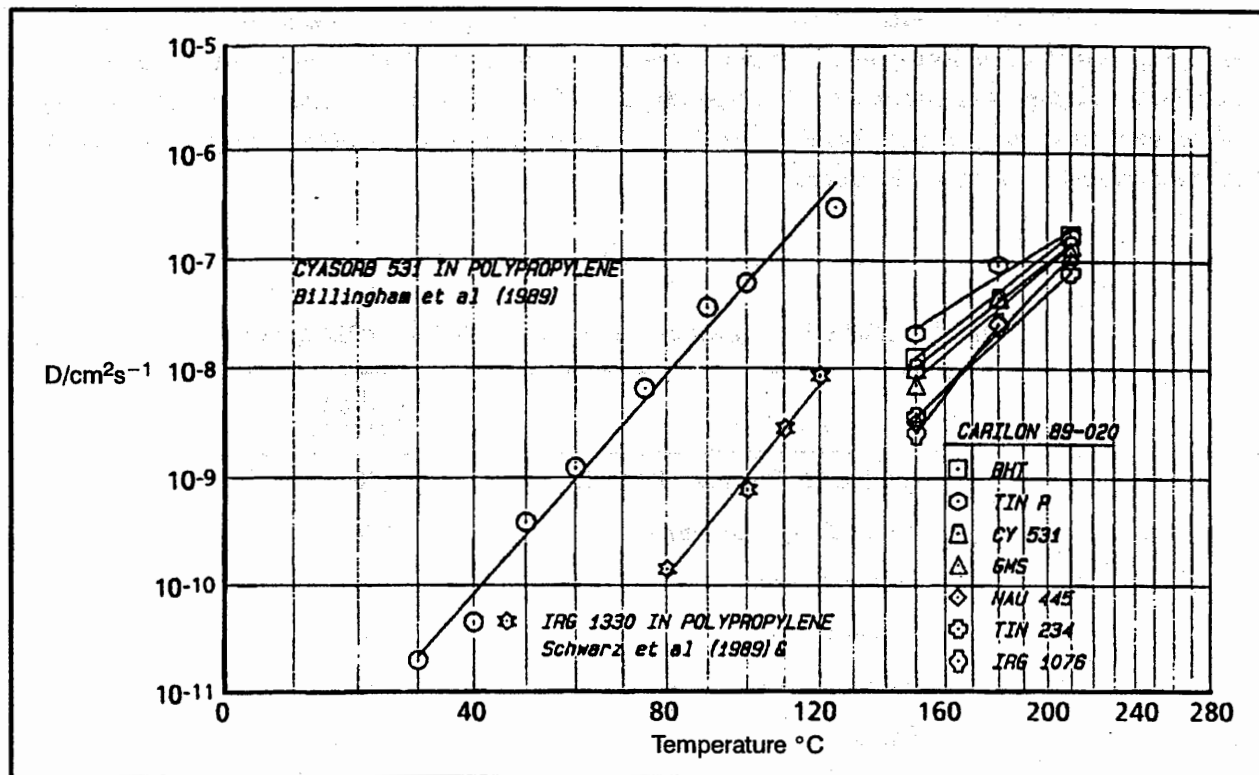
Fig. 7 – Diffusion coefficient in PP and in CARILON EP.

For comparison, Figure 7 includes D values in polypropylene for one light[9] and one heavy stabilizer.[10] Diffusion in polyketone appears to be lower by a factor of 100 than in polypropylene. Therefore, evaporative loss for a given additive should be slower in polyketone than in polyolefins. However, effectiveness may be diminished by the decreased mobility.

We were interested in how diffusion in polyketone compared to diffusion in other engineering thermoplastics. To address this, we measured the sorption of Cyasorb UV531 and Irganox 1076 into Zytel 101, a nylon 66. Solubility and diffusion coefficients are in Table 3. Estimated D values in the nylon fall in the same range as those in polyketone. Interestingly, the conventional additives play only a small role in heat-stabilizing nylon. A complex system involving copper and iodide salts is usually used.

Table 3

SOLUBILITY AND DIFFUSION IN ZYTEL 101 VS POLYKETONE AT 180°C

Additive	Solubility/%wt		Diffusion Coefficient/cm^2 sec^{-1}	
	Polyketone	Zytel 101	Polyketone	Zytel 101
Cyasorb UV531	2.7	1.5−2.0	$3-6 \times 10^{-8}$	$3-5 \times 10^{-8}$
Irganox 1076	0.3*	0.6	$1-4 \times 10^{-8}$	$\sim 1 \times 10^{-8}$

*Probably not at saturation.

The diffusion coefficient of Cyasorb UV531 has also been measured in polycarbonate,[11] polyurethanes,[12] and polyethylenes.[13] Since these studies covered different temperature regions, it is not possible to compare D values at a given temperature in all these polymers. However, in Table 4, are given the temperatures at which $D = 5 \times 10^{-8}$ cm^2 s^{-1} for eight polymers. Clearly, polyketone stands out as having extremely low mass transport.

<u>Table 4</u>

DIFFUSION OF CYASORB UV531 IN VARIOUS POLYMERS

Polymer	T/°C at which D= 5×10^{-8} cm^2 sec^{-1}
CARILON Polymer (89/022)	180
Zytel 101 (Nylon 66)	180
Polycarbonate	170
Polypropylene	100
High-Density Polypropylene	80
Polyurethane	75−80
Low-Density Polypropylene	70

MODELING EVAPORATIVE LOSS

Oxidative degradation limits the long-term heat stability of polyketone. Identification of an appropriate additive package to minimize or offset this degradation is a high priority of the CARILON Polymer project. Oven-aging tests are used to screen additives for effectiveness. Test strips approximately 30mils thick are aged at 125°C. Effectiveness is evaluated as the number of days until cracking occurs when the strip is folded in half. These results can be extrapolated using an Arrhenius expression to estimate performance at lower temperatures.

We have used our diffusion coefficients to model the evaporative loss of typical antioxidants from polyketone under oven-aging conditions. We assume the diffusion coefficients are concentration independent. This is reasonable for low concentrations of additives in a polymer far from its glass transition temperature.

Evaporative loss occurs by migration to the surface followed by volatilization from the surface. For an additive to migrate to the surface from the bulk of the polymer, its concentration at the surface must be lower than in the bulk. If such a concentration gradient exists, the additive migrates to the surface at a rate governed by its diffusion coefficient in the polymer. Volatilization from the surface depends upon the additive vapor pressure and how quickly the additive diffuses through the air layer above the surface. The overall evaporation rate may be governed by either diffusion through the polymer or volatilization from the surface. Practical examples of both cases are known.

Evaporative loss of antioxidants is a serious problem in polyolefins.[14,15] Billingham and coworkers have devoted much attention to this area and have developed a model of evaporative loss:[16,17]

$$D\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{dM_t}{dt} = H\,(C-C_s)\ . \tag{6}$$

The bulk polymer is modeled as a semi-infinite solid with boundary and initial conditions:

$$C = 0,\ x = 0,\ \text{for all}\ t \tag{7}$$

$$C = C_0,\ x>0,\ \text{at}\ t=0 \tag{8}$$

This results in the following solution for relative concentration as a function of depth and time:

$$\frac{C}{C_0} = \text{erf}\left(\frac{x}{\sqrt{4Dt}}\right) + \exp\left[\frac{Hx}{D} + \frac{H^2t}{D}\right]\text{erfc}\left[\frac{x}{\sqrt{4Dt}} + H\sqrt{\frac{t}{D}}\right]. \tag{9}$$

The mass transfer coefficient, H, is defined by the rate of volatilization of the pure additive, V_0, and the solubility of the additive, S:

$$H = \frac{V_0}{S} \tag{10}$$

Billingham and coworkers arbitrarily define failure of a sample as corresponding to loss of 90% of the original amount of additive. They have compared the loss behavior for various sample geometries using actual additive properties. The rate-determining step for loss depends not only on the relative magnitudes of the mass transfer and diffusion coefficients, but also on the thickness of the sample.

Unfortunately, we do not have sufficient volatility data for our additives to apply the full model to polyketone. Therefore, we have assumed rapid volatilization from the surface, and hence, a diffusion-limited evaporation rate. This corresponds to using only the first term on the right-hand side of Equation (9). This assumption will be tested in the next section on desorption experiments.

Our results are shown in Figures 8, 9, and 10 for BHT (mol wt = 220), Naugard 445 (mol wt = 405), and Naugard XL1 (mol wt = 697), respectively. The calculated concentration of additive relative to initial concentration is shown as a function of distance from the center of the strip. Curves are given for 2 hours, 24 hours, and 7 days. Table 5 gives the times to lose 10, 50, and 90% of the initial additive amount during oven-aging.
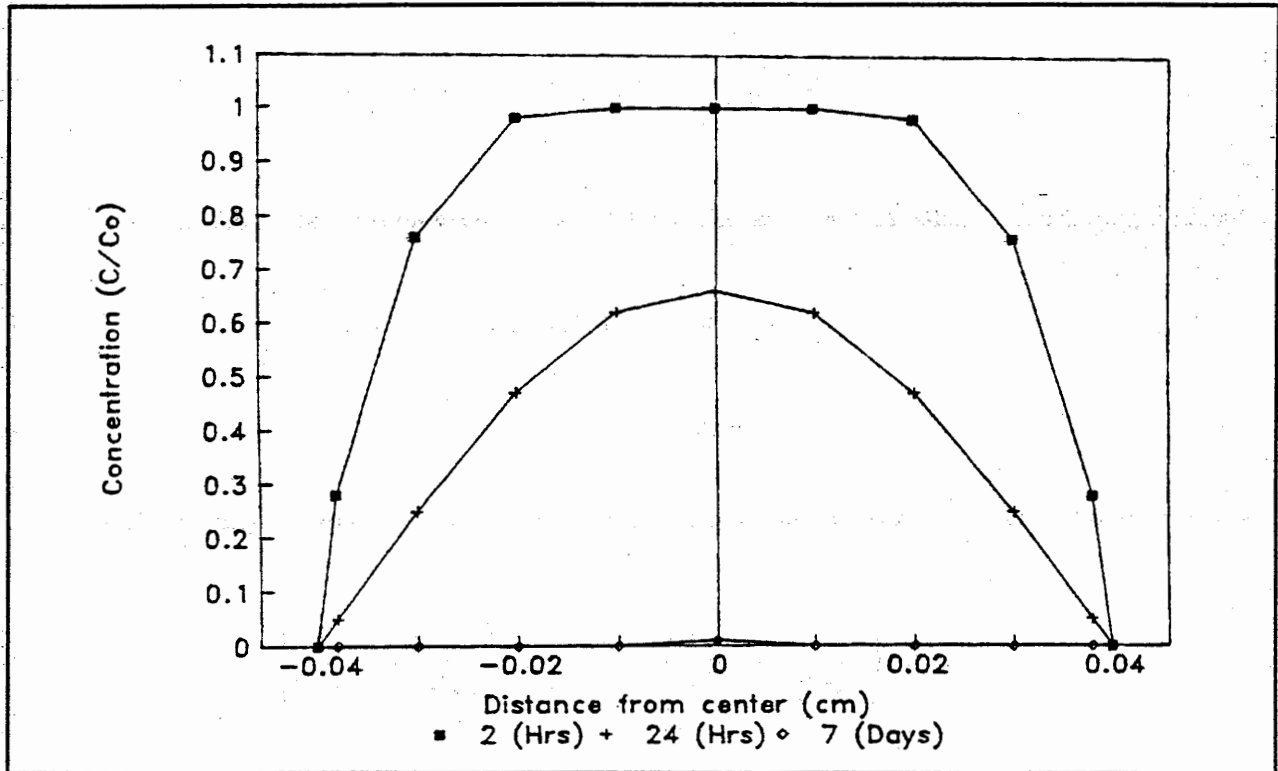
Fig. 8 — Model of evaporative loss of BHT from polyketone under oven-aging conditions.
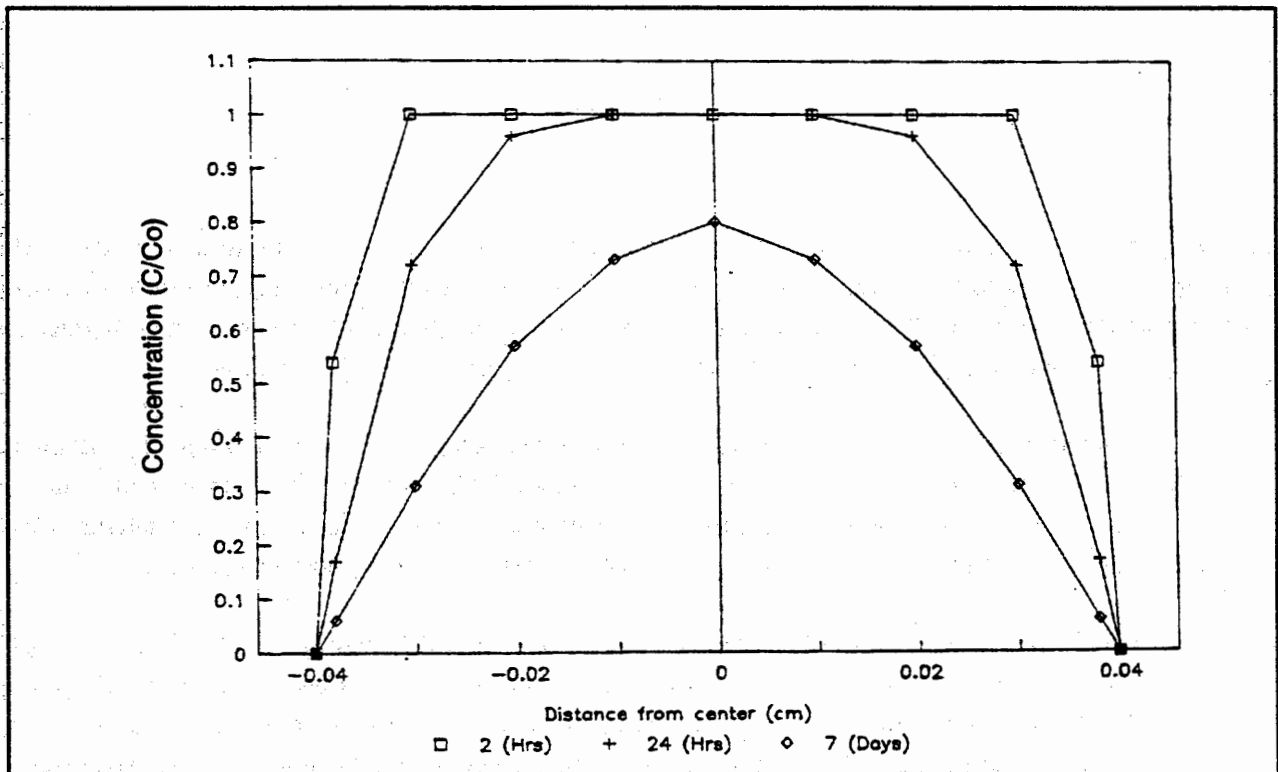

Fig. 9 — Model of evaporative loss of Naugard 445 from polyketone under oven-aging conditions.
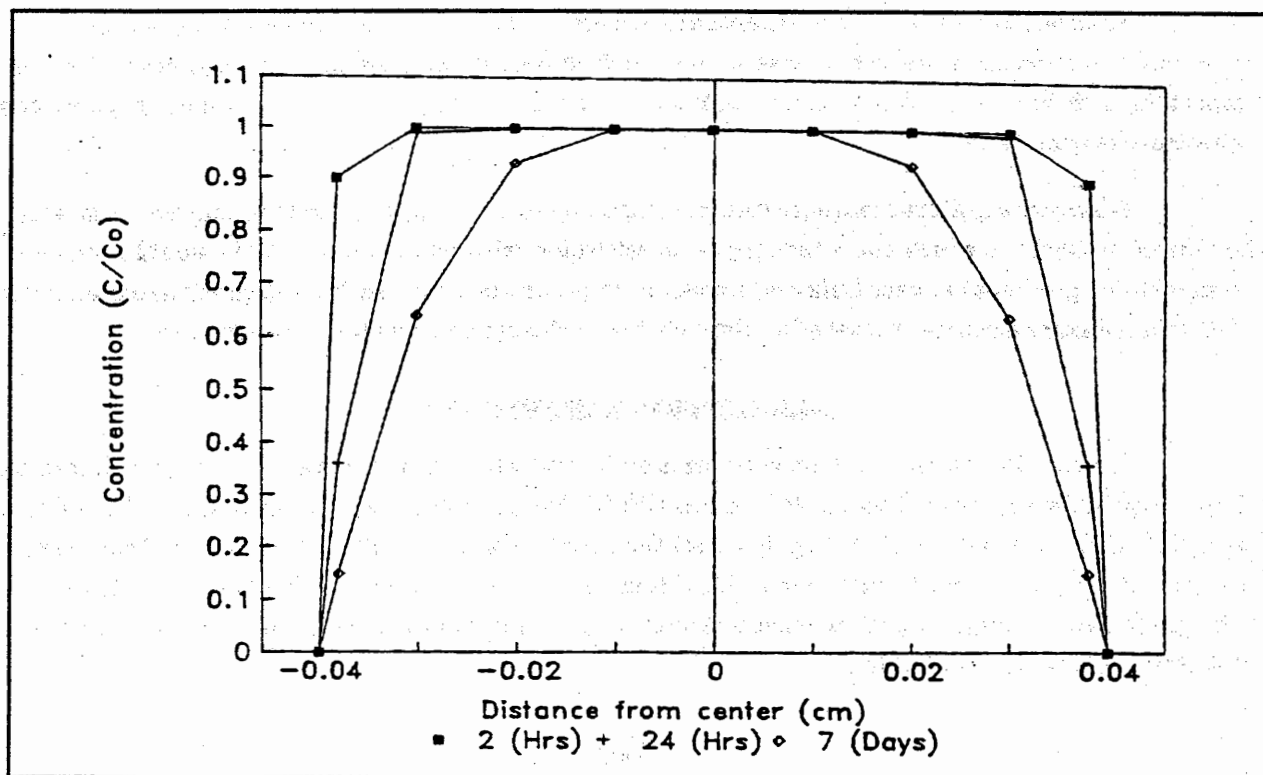
Fig. 10 – Model of evaporative loss of Naugard XL1 from polyketone under oven-aging conditions.

BHT is significantly depleted from the surface within two hours. Within one day, depletion from the center occurs. Virtually all additive disappears within one week, leaving the polymer unprotected. This is well below the time to failure shown by many relatively "good" additives (3 weeks). Lifetimes must be extended significantly further than this to obtain a desirable high-temperature UL index.

Table 5

EVAPORATIVE LOSS TIMES DURING OVEN-AGING[a] OF POLYKETONE[b]

	Time to Lose		
Additive	10%	50%	90%
BHT	53 min	21 hr	4 days
Naugard 445	6.5 hr	6.5 days	28 days
Naugard XL1	26 hr	26 days	114 days

[a] T=125°C, 30 mil samples.
[b] Modeled assuming surface concentration=0 for
   all t (fast evaporation), D's extrapolated to 125°C.

Naugard XL1 will stay in the polymer significantly longer than BHT or Naugard 445. However, the region near the surface will become depleted rapidly, although the bulk concentration remains high.

Since additive diffusion coefficients are at least one hundred times smaller in polyketone than in polyolefins, we expect evaporative loss to be much slower in polyketone. Nevertheless, for many important additives, evaporative loss is sufficiently rapid to impact their effectiveness in polyketone during oven-aging tests.

To ensure a uniform concentration of a highly mobile, rapidly evaporating additive, tests should be run in an oven in which the vapor phase is saturated with the additive. This would remove the concentration gradient between bulk and surface polymer and preclude additive migration to the surface. This would ensure a constant level of a relatively fast-diffusing additive for the entire test.

DESORPTION EXPERIMENTS

To evaluate diffusion versus volatilization in controlling evaporative loss, we ran a desorption test for five additives, BHT, Tinuvin P, Cyasorb UV531, Naugard 445, and Naugard XL1. The additives were sorbed in our usual fashion into polyketone films for five hours at 180°C. After removal of the excess additive on the surface, we hung the individual films in an oven at 180°C for five hours. A high level of nitrogen flowed through the oven to ensure that vapor concentration was kept close to zero. The per cent of additive lost is given in Table 6.

Table 6

DESORPTION OF ADDITIVES AT 180°C FOR FIVE HOURS[a]

Additive	% of Additive Lost
BHT	100
Tinuvin P	100
Cyasorb UV531	100
Naugard 445	60
Naugard XL1	1

[a] Under high nitrogen flow. Samples prepared by sorption experiment at 180°C for five hours.

Since the times for sorption and desorption were equal, we expect to see 100% loss for diffusion-controlled desorption. This is the case for the three lightest additives, BHT, Tinuvin P, and Cyasorb UV531. The heaviest additive, Naugard XL1, lost only 1%wt. This indicates that volatilization is rate-limiting for this additive. This effect probably arises from a very low vapor pressure for the high-melting XL1. Naugard 445 falls in between these two behaviors, and it appears that diffusion and volatilization are competitive.

Workers at KSLA compared "surface" (approximately 0.2mm thick) to bulk properties after aging polyketone at 120°C in air versus nitrogen. For the sample aged in air, they found significant loss of Irganox 1076 and 1330 from the surface region. However, under nitrogen, no depletion was noted. In these tests, additive which has reacted is not detected. Therefore, the apparent depletion in the sample aged in oxygen may reflect a significant amount of additive "consumed" by reaction, rather than through evaporative loss. Model calculations for these conditions indicate that under diffusion-limited

evaporative loss, both additives should be significantly depleted. Therefore, we suspect that volatility limited evaporative loss in these experiments.

In general, both diffusion coefficient and volatility decrease with increasing molecular weight. However, structural effects can also play an important role in these properties. For example, we find that BHT (mol wt = 220) and Tinuvin P(mol wt = 225) have equivalent diffusion coefficients in polyketone. However, the vapor pressure of BHT is more than 20x greater than that of Tinuvin P at 150°C.

ADDITIVE BEHAVIOR IN A HETEROGENEOUS SYSTEM

Sequestering an additive in a second polymer phase has been suggested as a way to reduce diffusion-limited evaporative loss and overcome compatibility problems in polyketone. In principle, a second phase, well dispersed throughout the polyketone, and loaded with a high level of additive, could act as an additive reservoir. This concept resembles the controlled release technology often used for drugs.

To model the mass transport of additive from a dispersed phase, P_1, to a matrix, P_2, we must satisfy the following two boundary conditions:

$$\frac{C_{P_1}}{S_{P_1}} = \frac{C_{P_2}}{S_{P_2}} \tag{11}$$

$$D_{P_1}\left(\frac{\partial C_{P_1}}{\partial x}\right) = D_{P_2}\left(\frac{\partial C_{P_2}}{\partial x}\right) \tag{12}$$

where C_{P_i} is the concentration, S_{P_i} is the solubility, and D_{P_i} is the diffusion coefficient of additive in P_i. The first boundary condition expresses the equilibrium partitioning of the additive between the two phases. The second condition represents a net zero flux across the interface between the two phases.

To see a significant advantage via this approach, mass transfer from the dispersed to matrix phase must be slow compared to loss of additive from the matrix. Otherwise, if rapid equilibrium is achieved between dispersed and matrix phases, then there is no benefit to the initial placement of the additive.

Factors which would minimize mass transfer between dispersed and matrix phases are

1. A high partition coefficient. It is unlikely that there could be more than an order-of-magnitude difference in solubility between the two polymers.

2. A lower diffusion coefficient in the dispersed phase relative to the matrix. This would be difficult to achieve for polyketone because diffusion coefficients of additives in polyketone are already quite low. Most rubbery polymers will have D values 1 to 2 orders of magnitude higher than in polyketone. The best prospect would probably be a glassy polymer. However, at high loadings, the additive would probably plasticize the dispersed polymer, thereby increasing D. Perhaps additive loaded into a subsequently cured resin would provide sufficiently slow diffusion.

3. Large domain size, minimum surface to volume ratio, and a sharp interface. However, these properties are inconsistent with a good dispersion of a second phase.

4. Use of crystalline additive as the second phase would eliminate difficulties with other polymers. Mass transport from the "reservoir" to polyketone would depend upon the dissolution kinetics of the additive crystals. This is an area which has not been well addressed in the literature. Achieving a good dispersion of crystalline additive would present problems. Most additives crystallize at polymer surfaces, not in the bulk phase.

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