

PREDICTION OF HEAT STABILIZER CONSUMPTION IN PE, PP, PS AND PVC BY FLUORESCENCE REFLECTOMETRY

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Introduction

Interest in the study of the fluorescence in synthetic polymers is increasing and the technique is beginning to be used to monitor degradation (1). In particular, thermally degrading polyolefines, polystyrenes and PVC were shown to become strongly fluorescent in the visible region when irradiated with UV light. This phenomenon, related to the oxidation of the polymers (2) can easily be exploited to obtain useful information on their heat stability and how it is affected by the quality and quantity of stabilizers used in polymer compounds.

Principle

A continuous representation of the time dependent, heat stability related fluorescence is obtained by first exposing a series of long polymer strips to heat in a dynamic testing oven maintained at constant temperature, from which they are progressively removed as to generate a degradation gradient over their whole length, and then by scanning them on a Fluorescence Reflectometer where each sample passes at a constant speed under a UV light source centered at 365nm. The fluorescence radiation emitted by the sample is immediately collected by a photosensor adjusted to receive the band centered at 490nm where most of the polymers investigated were found to emit light (3).

This fluorescence analysis is visualized by a recorded emission intensity curve, each point of which corresponds to the position of the sensor as it scans the length of the sample. Each expression of emission intensity thus obtained is therefore directly related to the duration of exposure of the polymer in the oven. Such a typical fluorescence curve is illustrated in Fig. 1.

One way to express the notion of resistance to oxidation is to measure the induction period preceding the appearance of fluorescent species (t_i) and - as these species tend to accumulate progressively (from x_1 to x_2) - the time (t_2) it takes to reach near maximum concentration (x_2). These two time parameters are indicative of the stabilizer's ability (or lack thereof) to prevent or retard the degradation until the fluorescence species disappear (t_3).

The shape of the fluorescence curve thus depends on the polymer's resistance to oxidation - with antioxidants present or not - and on the temperature. A temperature increase or a poorer resistance to oxidation generally causes the curve to evolve as illustrated in Fig. 2. As the temperature increases:

- t_i , t_2 and t_3 decrease. The induction period (t_i) shortens as illustrated in Fig. 3.

- the concentration ratio (x_2-x_1) increases as the quantity of fluorescent species increase, and

- the time difference (t_2-t_1) shortens as the speed of formation of fluorescent species increases.

The last two points are illustrated in the case of unstabilized polystyrene in Fig. 4.

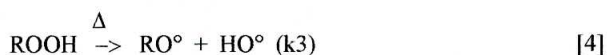
Theoretical approach

After the cause of fluorescence in degrading PVC was established experimentally (4) and attributed to the accumulation of short chain conjugated polyenes during the early stages of thermal degradation (5), an attempt was recently made to elucidate the cause of fluorescence occurring similarly in polyolefines. By examining a number of model compounds for their inherent fluorescence or the influence they have on the fluorescence of the polymers, reasonable evidence was found for attributing the cause of fluorescence in polyolefines to the initial formation of α,β -unsaturated carbonyl species bound to the polymer, followed by the build-up of short chain conjugated polyenes similar to those encountered during the degradation of halogenated vinyl compounds (6)(7).

The examination of the fluorescence curves of the many polymers we have investigated suggests that the fluorescent species are transitory and disappear as they form non fluorescing chromophores while thermal oxidation progresses. This implies that during oxidation there is an accumulation of these fluorescent species (hereafter referred to as "E") but also that the consecutive formation of ever more predominant chromophores - which play the role of either masking agents during excitation or quenchers during emission - favors the yellowing of the polymer.

Regardless of the exact structure of the fluorescent species in a given polymer undergoing thermal degradation, a simplified reaction mechanism shows that fluorescence reflectometry is a suitable method for evaluating the relative stability of a polymer and for determining the amount of stabilizer(s) necessary and sufficient to achieve it. If we accept a general scheme of hydroperoxide reactions as ruling the early phase of thermo-oxidation,





In an excess of oxygen and assuming that the amount of reactive sites (RH) is constant, a proposed kinetic analysis (8) shows that one could expect a period of time of degradation after which a quasi stationary state of formation and disappearance of hydroperoxides is reached. In that case, the quantity of light emitted according to the simplified fluorescence mechanism:



$$\text{as: } \frac{d\{h\nu_2\}}{dt} = g_2 \{\text{E}\}^* - g_3 \{\text{Q}\} (h\nu_2) \quad [9]$$

$$= g_1 (h\nu_1) \{\text{E}\} - g_3 \{\text{Q}\} (h\nu_2) \quad [10]$$

would tend to progress as a function of time along an asymptotic curve as illustrated in Fig.5.

However, contrary to the initial hypothesis, the amount of reactive sites $\{\text{RH}\}$ decreases as the degradation progresses and the concentration of quenchers $\{\text{Q}\}$ increases. This explains the downward inflexion of the fluorescence curve once the stabilizer is no longer able to retard the formation of the quenching polyenic chromophores. This trend is particularly evident in the thermal degradation of PVC where initial oxidation is quickly followed by rapid dehydrohalogenation (9).

Fluorescence barely arises in unstabilized PVC because nothing prevents the degradation from progressing rapidly beyond the formation of polyconjugated trienes and tetraenes known to be fluorescent (10). Such short sequences of conjugated double bonds can only exist if the allylic chlorine atoms are being replaced by stabilizer residues and it is likely that the strong fluorescence observed in stabilized PVC is caused by the presence of the relatively stable reaction products between the polyenic species and the stabilizer. The build-up of units of this nature in the polymer is supported by the UV absorption spectra of tin- or zinc stabilized PVC samples heated in air or under nitrogen. Application of Woodward's Rules to estimate the position of the main absorption band for the system $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CHX}-\text{CH}_2-$ gives a value close to the 224-236nm observed for all PVC samples examined.

In light of the above, the fluorescence appears to be closely related to the amount of stabilizer consumed by the polymer during the early stage of thermal decomposition. This was

found to be the case for a variety of thermo-oxidizable polymer products of different structures.

While thermal degradation in PVC proceeds throughout the bulk of the sample exposed to heat in the dynamic oven, the microscopic examination of polyolefine samples reveals that these polymers are essentially oxidized at the surface (a few μm) exposed to air. The oxidized polymer then seems to act as a barrier preventing further diffusion of oxygen, which would explain the slow kinetics of the thermo-oxidation reaction.

An examination of the oxidized surface of polyethylene and polypropylene samples by FTIR confirms the formation of carbonyl species represented by a band centered at about 1715cm^{-1} . In Fig.6 and Fig.7 we have plotted the concentration of these species $\{\text{R}\}$ in two different Ziegler polyethylenes. The factor R is defined as the ratio between the optical density at 1715cm^{-1} and the sum of this optical density plus the optical density at 2920cm^{-1} representing the $-\text{CH}_2-$ groups in the polymer.

When these concentration curves are superimposed to the fluororelectrometric curves of the same two polyethylene samples, we observe the close similarity between fluorescence and R-concentration, particularly when put in relation to the induction period. This suggests that the fluorescent short conjugated polyenes are most likely to be polyconjugated carbonyl species stemming from the α,β -unsaturated ketones mentioned earlier.

Practical results

The experimental procedure leading to significant and useful results consists generally in:

- blending a polymer formulation if necessary
- casting, molding or otherwise preparing long test samples
- exposing the film, sheet, powder, paste or pellets to heat in a dynamic testing oven, and
- analyzing each sample by fluorescence reflectometry.

Depending on the nature of the polymer, its resistance to thermo-oxidation is conveyed by the time of induction (t_i) leading to the first appearance of the fluorescent species. This time is expressed in hours, minutes or seconds and is influenced by temperature, as we have seen. It is also affected by the speed at which the samples come out of the dynamic oven as illustrated in Fig.8 for PE at three different levels of protection.

The oven-exit-speed parameter superimposes on the thermo-oxidation kinetics a test duration kinetics, and this for each point of the sample at the oven temperature. The higher the exit speed, the shorter the residence time in the oven of each point on the sample and the lesser advanced the thermo-oxidation. Therefore, an increase of the induction period (t_i) is to be expected as the exit speed increases.

This implies that polymer compounds can only be compared at the same exit speed and evidently at the same temperature.

Beyond the induction period, the relative concentration of fluorescent species (x_2-x_1) over a time of accumulation (t_2-t_1) is an indication of how the stabilizer not only retards the onset of thermo-oxidation but also becomes chemically active in preventing the short polyenic fluorescent species from growing into the long, light absorbing chromophores which cause the extensive yellowing of the polymer (see again Fig.6 and Fig.7).

The near maximum concentration value (t_2) set on the reflectometer for a given sample used as a reference is generally indicated as an absolute light intensity in arbitrary units. It can be compared to another (t_2) value only within a same "family" of comparable samples and it is always the total fluorescence of the whole sample which should be measured. Both the chemical structure and the amount of stabilizer present in the compound influence the profile of the fluorescence curve where $h\nu=mV$.

In order to show that the method is reliable for the assessment of polymer quality, we have evaluated its precision and reproducibility by considering as essential parameters for stabilized- (t_i = long) and unstabilized polymers (t_i = short):

- the press molding or extrusion of the samples. Polymer samples were generally prepared from molded plaques or extruded sheet under carefully controlled conditions. This allowed to control the reproducibility of the test in regard to the processing equipment and the polymer.

- the batch. Several batches of 5 samples of the same polymer compound were tested. This allowed to control the reproducibility of the testing equipment.

- the position of the sample in the dynamic oven. There are five positions numbered 1 to 5 from one of the oven's inner side to the other. This parameter allowed to evaluate the lateral distribution of the temperature in the heated enclosure.

The mean deviation of (t_i) values for samples of the same polymer exposed to heat while at either one of these five positions are on the order of 2min. Therefore, the results of a comparative test only make sense if the difference between the (t_i) values of various polymers is greater than 2min for a test duration of one hour. The test temperature and the oven exit kinetics should of course be chosen according to the nature of the polymer and the efficacy of the stabilizer formulation it may contain.

Moreover, it is most important to test a polymer batchwise (5 samples). The induction time (t_i) for that polymer is then the mean value obtained for the 5 readings on the reflectometer. Since deviations for reference readings on the reflectometer do not exceed 30s, the typical deviation for this measure should remain below 2min. If the deviation is greater than 2min, the test is not significant, either because of a non homogeneous temperature distribution in the oven, poor sample preparation conditions or a heterogeneous polymer. In the latter case, the method can in fact be used for measuring the degree of homogeneity of the product.

As for the significance of the test in the evaluation of the

resistance to thermo-oxidation, it is particularly evidenced by the fact that the induction time is so much longer for stabilized than it is for unstabilized polyethylene (26min vs. 14min).

We have successfully applied the fluorescence reflectometry method to the evaluation of the following polymers:

Polymer	°C (oven)	Duration	(t_1)	(t_2)	(t_2-t_1)	(x_2-x_1)
PVC (stab.)	200°	30mn	14,	20,	6mn	5,2mV
PVDF	290	60	39	44	5	7,7
LDPE (stab.)	230	60	26	32	6	15,3
LDPE (unstab.)	230	60	14	21	7	6,9
HDPE	230	60	17	22	5	20
PP (stab. A)	250	90	35	44	9	12,3
PP (stab. B)	250	90	31	38	7	12
EPR	230	60	16	23	7	10
E/DA/MAH	250	60	24	28	4	11
PS (unstab.)	250	60	15	38	25	35
PS (stab.)	250	60	20	50	30	37

However, for useful as it may be, the method has its limitations. It is not suitable for evaluating products containing structural features or additives that annihilate the fluorescence as, for example, highly unsaturated polymers such as polybutadiene and high concentrations of carbon black, titanium dioxide or yellow pigments. Also products which degrade via mechanisms other than thermo-oxidation such as PMMA cannot be evaluated by using this technique.

Conclusions

The method of progressive exposure to heat in a dynamic testing oven followed by reflectometric fluorescence analysis provides a simple, fast, and practical quality control test for determining, on representative sample sizes, the resistance of polymers to thermo-oxidation.

The results obtained in this investigation indicate that the rate at which stabilizers or decomposition products become chemically involved during the process of thermal degradation in PE, PP, PS, PVC and others can easily be monitored.

Since the fluorescence is remanent, it can be measured long after the completion of the thermal exposure. Such measurements, carried out on test compounds in the laboratory, enable to predict the behavior of these same compounds and their needs for specific quantities of stabilizers as they are to be exposed to heat in various industrial processing equipments.

References

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Illustrations

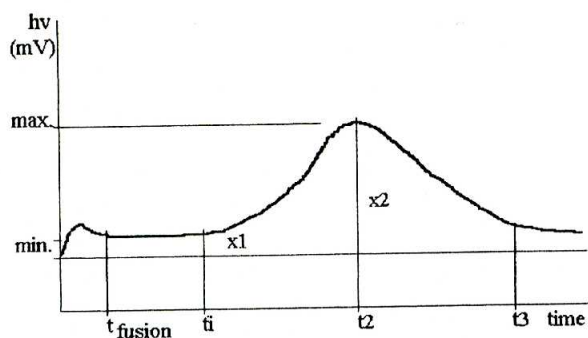


Fig.1- Typical fluorescence curve of a polymer strip after exposure to heat in a dynamic oven.

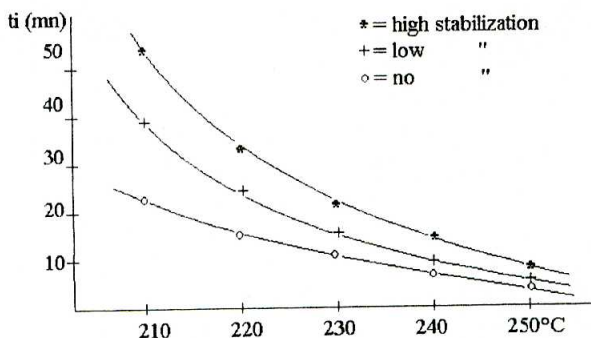


Fig.3- Evolution of the induction time in LDPE with the increase of temperature

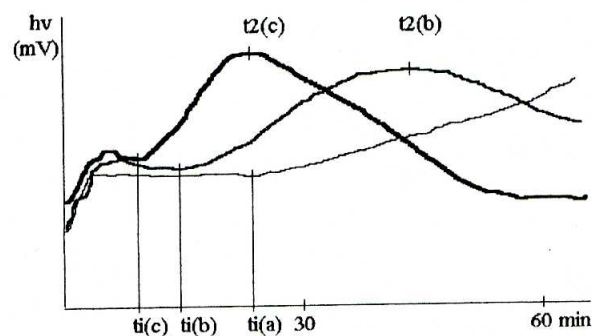


Fig.4- Evolution of fluorescence in unstabilized PS at three different temperatures: a=220, b=240 and c=260°C.

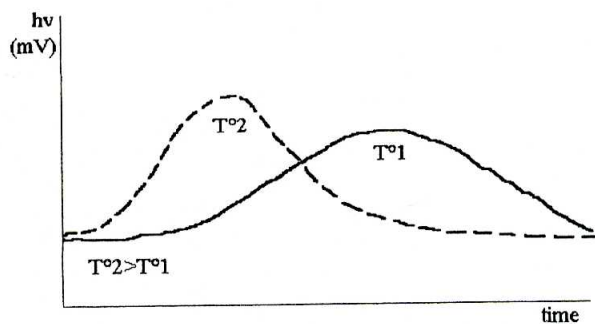


Fig.2- General evolution of the fluorescence when the temperature increases.

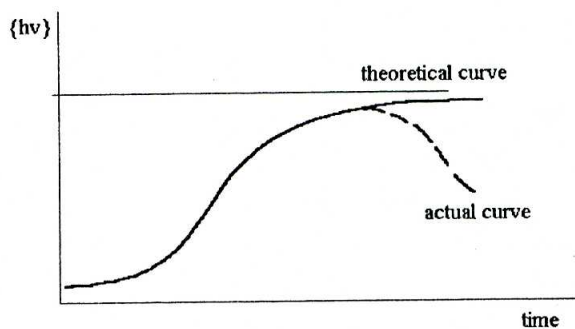


Fig.5- Curve bending caused by the decrease of reactive sites {RH} and the increase of quenchers {Q}.

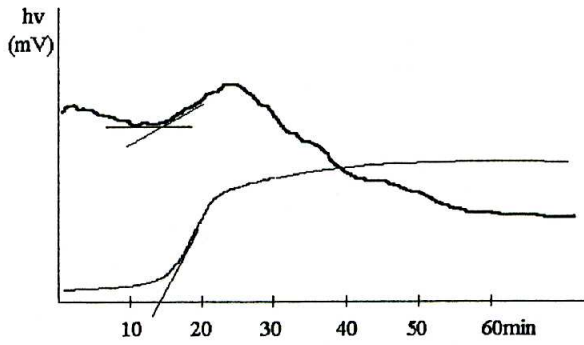


Fig.6- Fluorescence vs. carbonyl concentration in Ziegler polyethylene protected by stabilizer A

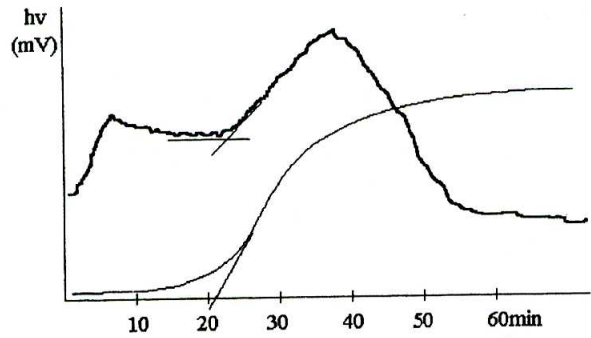


Fig.7- Fluorescence vs. carbonyl concentration in Ziegler polyethylene protected by stabilizer B

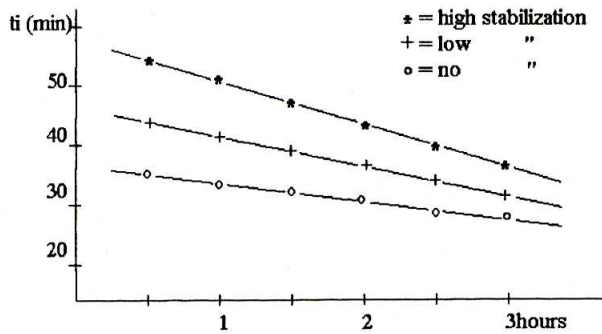


Fig.8- Evolution of the induction time in LDPE with the increase of residence time in the oven.