

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

P. Bréant
Elf Atochem/Cerdato, Serquigny, France
and
C.H. Stapfer
Metrastat PSD, Düsseldorf, Germany

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,



