Thermochimica Acta, 99 (1986) 37–42
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF SOME EXPERIMENTAL PARAMETERS ON THE OXYLUMINESCENCE CURVES OF SELECTED MATERIALS

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(Received 14 August 1985)

ABSTRACT

The effects of changes of sample particle size, oxygen flow rate, heating rate, and diluent on the OL curves of various polymers are described. The experimental changes all affect the T_{max} and/or intensity of the OL curve peaks in a manner similar to other thermal analysis techniques. Thus, the technique of OL in the non-isothermal mode may be considered as another thermal analysis method.

INTRODUCTION

The oxyluminescence (OL) of polypropylene was first described by Ashby [1] in 1961. Many other substances, including polymers, exhibit this phenomenon when heated from 150 to 300°C in an air or oxygen atmosphere [2–11]. It has been found that OL is a general phenomenon that applies to numerous organic and polymeric substances. Wendlandt [12] has recently reviewed many of the applications of OL to polymeric materials.

Most of the early work on OL was in the isothermal mode with light emission measurements being determined as a function of time at a constant temperature. Wendlandt and co-workers have made extensive use of the non-isothermal mode where the light emission of a substance is obtained as a function of temperature, as the material is heated at a fixed rate of temperature increase. Thus, the OL process can be considered as another thermal analysis technique [13] and as such, the effect of experimental variables on the light emission curve must be known. The effects of sample particle size, furnace gas atmosphere flow rates, and other parameters on the OL curves are described in this investigation. It was found that OL curves in the non-isothermal mode could be made reproducible to within ±2–3% of each other.

0040-6031/86/$03.50

EXPERIMENTAL

The OL apparatus was the same as previously described [14–16]. A Bascom-Turner Model 8110-4 data center recorder permitted subtraction of the background radiation from the OL curve as well as mathematical manipulation of the data. A plot of the corrected light emission, I_c, versus temperature constitutes an OL curve. Sample sizes ranged in mass from 0.05 to 14 mg. These samples were heated at a heating rate of 12°C min^{-1} in an oxygen atmosphere (flow rates of 20–40 ml min^{-1}).

The polymer samples were obtained from Scientific Polymer Products, Inc., Webster, New York.

Sample containers were pressed from aluminum foil and were washed with toluene and acetone and dried at 150°C before use.

RESULTS AND DISCUSSION

The OL curves for Nylon 6, which illustrate the effect of particle size on the OL curve shape, are given in Fig. 1. It is clearly seen that the smaller the particle size, the sharper the peak is, and the lower the characteristic peak temperature. In each case, identical amounts of sample were used for each particle size studied. The lowering of the curve peak temperature is similar to that observed in DSC or DTG and is due to the increase in surface area of the sample. Since OL originates from the reaction of oxygen with active sites

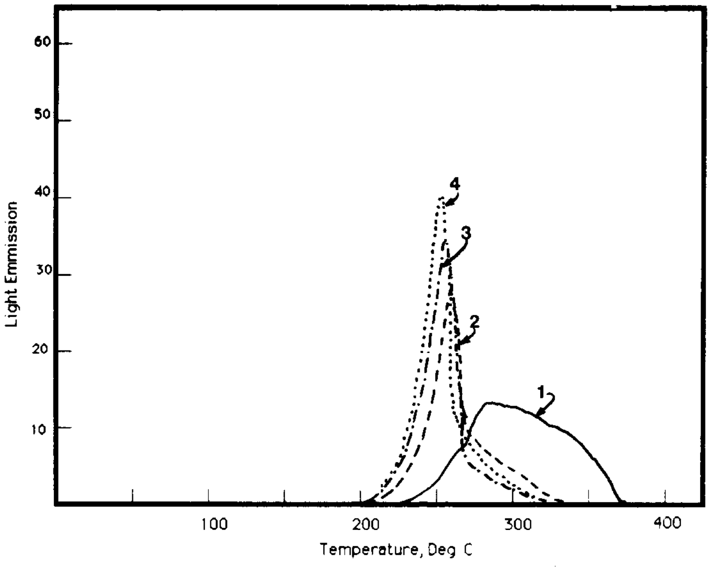

Fig. 1. Change of Nylon 6 OL curve peak shapes with particle size. (1) single pellet; (2) 15–25 mesh; (3) 30–40 mesh; (4) 45–55 mesh; all samples were 14.0 mg.

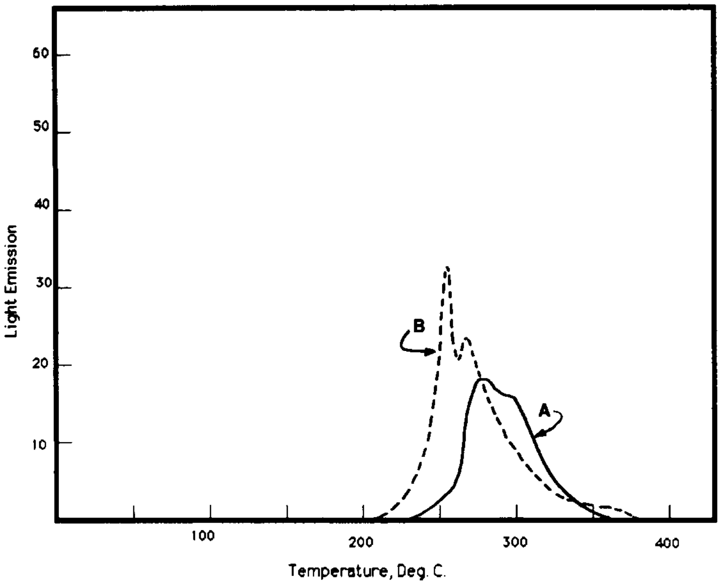

Fig. 2. Effect of particle size on resolution between overlapping peaks in the OL curve of Nylon 6/12. (A) single pellet, 10 mg; (B) powdered sample, 30–40 mesh, 10 mg.

on the polymer surface, a large surface area should result in the generation of light emission at a lower temperature. A decrease in particle size thus increases the apparent reaction rate giving peak maxima at lower temperatures.

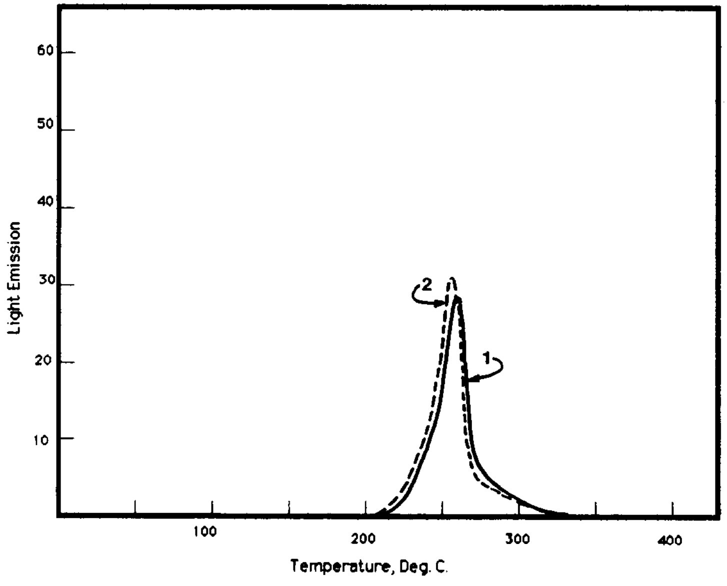

Fig. 3. Effect of oxygen flow rate on the OL curve peaks of Nylon 6. (1) 20 ml min^{-1}; (2) 40 ml min^{-1}; sample mass, 14.0 mg.

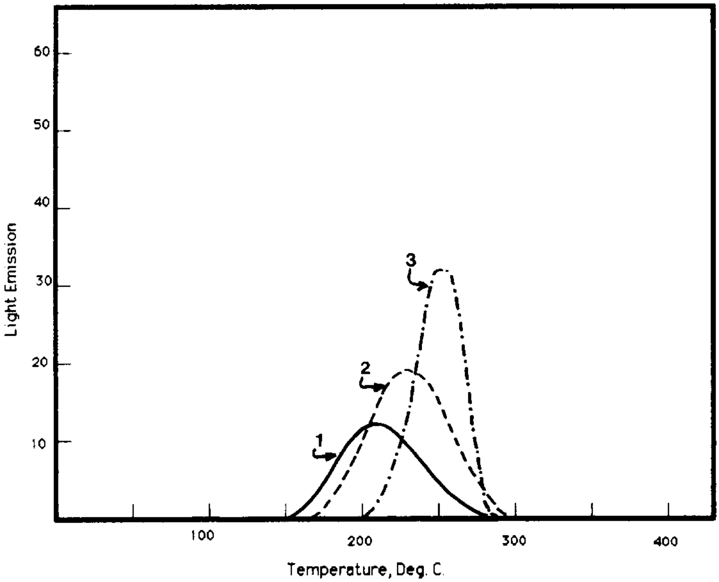

Fig. 4. Effect of heating rate on T_{max} in the OL curves of poly(vinyl stearate). (1) 2.5°C min^{-1}; (2) 5.0°C min^{-1}; and (3) 10°C min^{-1}.

A change in particle size of the sample also affects the adjacent curve peak resolution. This is illustrated in Fig. 2 where a powdered (30–40 mesh) sample of Nylon 6/12 is compared with a solid pellet of the sample, both of the same mass. The powdered sample gives two peak maxima in the 200–300°C temperature range while the OL curve of the pellet contains only one broad peak maximum at a higher temperature. For the powdered sample, peak maxima temperatures were 255 and 265°C, while the solid pellet sample had a peak maximum temperature of 275°C.

The effect of oxygen flow rate on the OL curve appeared to be slight. As shown in Fig. 3, the OL curve peaks for Nylon 6 changed very little on varying the oxygen flow rate from 20 to 40 ml min^{-1}. Admittedly, this is not a very drastic change of flow rates and perhaps higher flow rates, say in the l min^{-1} range, would cause more of an effect.

The effect of changing heating rate on a sample is shown by the OL curves of poly(vinyl stearate) in Fig. 4. As the furnace heating rate is increased from 2.5 to 10°C min^{-1}, the curve peak maximum shifts to higher temperatures. The shift in T_{max} at the different heating rates is 215°C at 2.5°C min^{-1}; 225°C at 5.0°C min^{-1}; and 245°C at 10°C min^{-1}. Observing the change in T_{max} with heating rate is the basis of a method for determining the kinetics of OL processes [17].

In the apparatus described here, only a small amount of the emitted light is actually detected. Due to the sample holder geometry, some of the emitted light is absorbed by the sample container, the glass enclosure, and so on. The

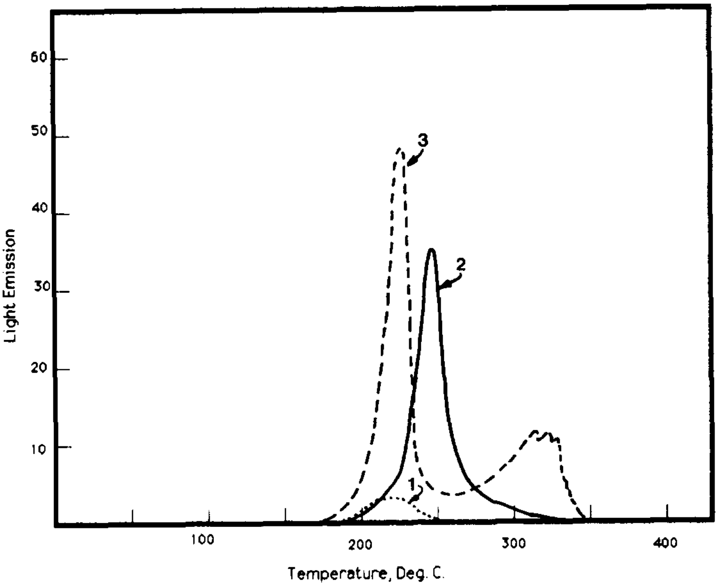

Fig. 5. Effect of various diluents on the OL curve peaks of Nylon 6/9. (1) 10 mg sample + 5 mg carbon block; (2) 10 mg sample; (3) 10 mg sample + 10 mg glass micro-beads.

resulting light emission that is detected is due to direct emission and reflectance from the aluminum sample container and the walls of the sample holder. In order to improve the detection efficiency, the sample was diluted with various matrices such as glass micro-beads. Figure 5 illustrates the effect of various matrices on the OL curve peaks of Nylon 6/9. Glass micro-beads increase the light emission of the sample, as expected, while the carbon block decreases it. The latter matrix absorbs most of the emitted light resulting in a very small OL curve peak. Glass micro-beads, on the other hand, increase the internal reflection of the sample-matrix mixture, giving a slightly greater increase in the OL curve peaks.

ACKNOWLEDGMENT

The financial support of this work by the Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged.

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