

Oxyluminescence of Polymers.

II. Effect of Temperature and Antioxidants

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Synopsis

The oxyluminescence of polypropylene and polyethylene stabilized with various amounts of 4,4'-thiobis(3-methyl-6-*tert*-butylphenol) were studied and compared with oxygen uptake data. It was found that there was a correlation, although not linear, between the two methods. In the case of the stabilized polypropylenes, a pronounced aging effect was noticed. The oxyluminescent behavior of stabilized polyethylene was somewhat different from that of stabilized polypropylene. The temperature coefficients of the oxyluminescence of polypropylene, polyethylene, nylon 6, polystyrene, polyurethane and polymethyl methacrylate were obtained. From these data the apparent activation energies for the light-emitting reaction were calculated. For the olefin polymers, these values are close to the activation energies of the oxidative degradation reaction obtained by other means. Both polyethylene and polymethyl methacrylate have different activation energies below their transition points as compared to higher temperature, indicating a different mode of reaction in the solid state from that occurring in the melt. An interesting transition luminescence, which was more pronounced in the absence of oxygen, was observed in the case of polyethylene.

INTRODUCTION

In the previous paper¹ some of the general oxyluminescent characteristics of polymers, such as effect of atmosphere and time dependency of maximum luminosity, were investigated, and results were correlated qualitatively with oxygen absorption data. The polymers investigated were also divided into classes having strong, medium or weak luminous intensity upon heating in oxygen. The present paper describes further studies of the effects of temperature, antioxidants, and aging on the luminescent behavior of various polymers.

Ashby² has used oxyluminescence as a screening test to determine the effectiveness of antioxidants. It was therefore decided to compare the luminescent effects of polymers containing antioxidants with another method of evaluating oxidative stability such as oxygen absorption.

The earlier results¹ on unstabilized polymers indicated the build-up of the light-emitting species to be very rapid after oxygen is admitted to the system. The species causing this initial luminescence are apparently those formed during the initial phases of the oxidative degradation. If the mode of action of a stabilizer is that of inhibiting the initial reactions which

lead to the formation of these species, then the light emission should be suppressed for a period of time which is dependent on the stabilizer concentration.

The oxyluminescent effect also has great promise as a means of studying the fundamental nature of the oxidative degradation of polymers. For instance, when the species causing the luminescence are identified, the kinetics of these initial phases of degradation can be established. Moreover, the apparent activation energies of those parts or branches of the series of reaction occurring in the oxidation of polymers which result in the emission of light should be obtainable by studying the effect of temperature on the luminosities of polymers in the presence of oxygen. These may not necessarily have the same values as those obtained from induction period data or rate studies where the overall reaction is under consideration.

EXPERIMENTAL PROCEDURE

The oxyluminescence studies were carried out in the apparatus described previously.¹ The luminosities were recorded as the resulting anode currents generated in the 1P21 photomultiplier tube operating with an anode potential of 1000 v. Unstabilized commercial polymers were used except where noted. Stabilized polypropylene samples were prepared by thoroughly dry-blending a powdered, highly crystalline polypropylene sample having a melt flow rate of 3.0 at 230°C. with the desired amounts of 4,4'-thiobis(3-methyl-6-*tert*-butylphenol). These mixes were then compression-molded into sheets 15 mils thick. The stabilized polyethylene was a commercial material made from the same base polymer as the unstabilized low density polyethylene but containing 0.1% of 4,4'-thiobis(3-methyl-6-*tert*-butylphenol). After placing a sample in the apparatus, it was kept under nitrogen until the test temperature was reached. The nitrogen was then replaced by oxygen. A temperature of 150°C. was used throughout for the constant temperature studies. The temperature coefficients were determined during both the heating and cooling of the sample in the presence of oxygen after the sample had reached a steady state emission. The rate of heating and cooling for these initial experiments was fixed by the heating and cooling capacity of the apparatus. For the temperature range of 150°C. to 40°C., the heating rate was approximately 4.4°C./min., and the cooling rate 4.1°C./mm.

RESULTS AND DISCUSSION

Effect of Stabilizers and Aging

The oxyluminescent behavior of a typical polypropylene, having a melt flow rate of 3.0 at 230°C., a heptane insolubility of 93% and stabilized with varying amounts of 4,4'-thiobis(3-methyl-6-*tert*-butylphenol) is shown in Figure 1A. It will be noted that the light emission was delayed for a short period of time after the admission of oxygen to the system to an

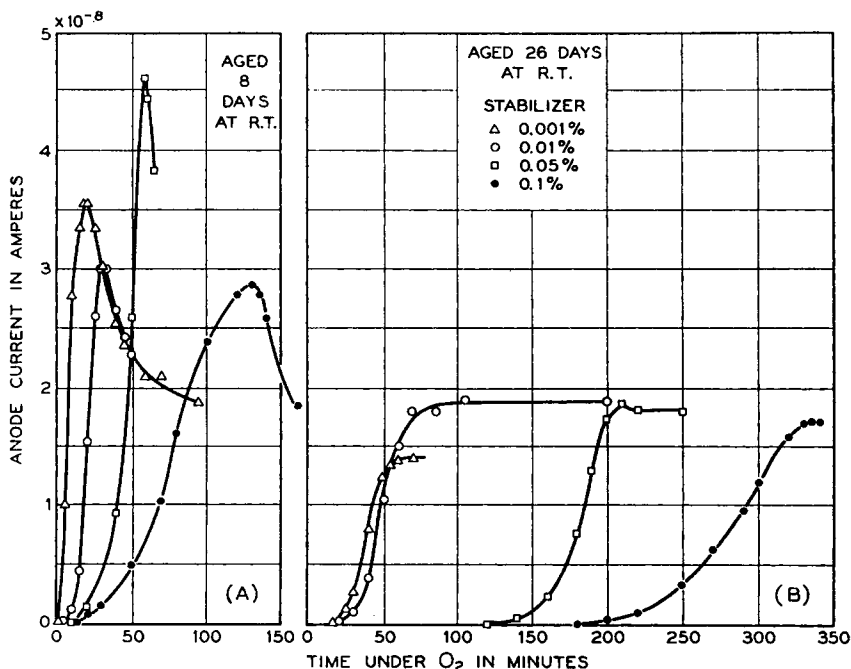


Fig. 1. Oxyluminescent behavior of polypropylene stabilized with 4,4'-thiobis(3-methyl-6-*tert*-butylphenol).

extent depending on the stabilizer concentration. Following this initial period, the luminosity rose to a maximum then dropped off. The rate of rise appeared to vary inversely as a function of the stabilizer concentration. These curves were obtained 8 days after the samples had been prepared. When samples of the same sheets, which had been kept under nitrogen, were tested after 26 days, the curves shown in Figure 1B were obtained. It will be noted that with this series, the time period for start of detectable emission was much longer, and the rate of increase in intensity was slower. Moreover, there was no maximum, and all samples gave about the same steady state intensity of luminosity with the exception of the sample containing 0.001% stabilizer. It is also interesting that the steady-state intensity levels were about the same as the unstabilized polypropylene which was used to prepare the stabilized samples.

The changes in the oxyluminescent behavior with time of aging of these samples containing antioxidants might have been caused by morphological changes in crystal structure with aging which resulted in a slightly larger crystalline fraction. Similar effects have been observed in the case of polypropylene-insulated wire samples which showed slightly longer induction times after a week or two of aging than if tested immediately after preparation. Earlier work by Hawkins, Matryek, and Winslow³ has shown that the oxidation and chlorination of polyethylene takes place

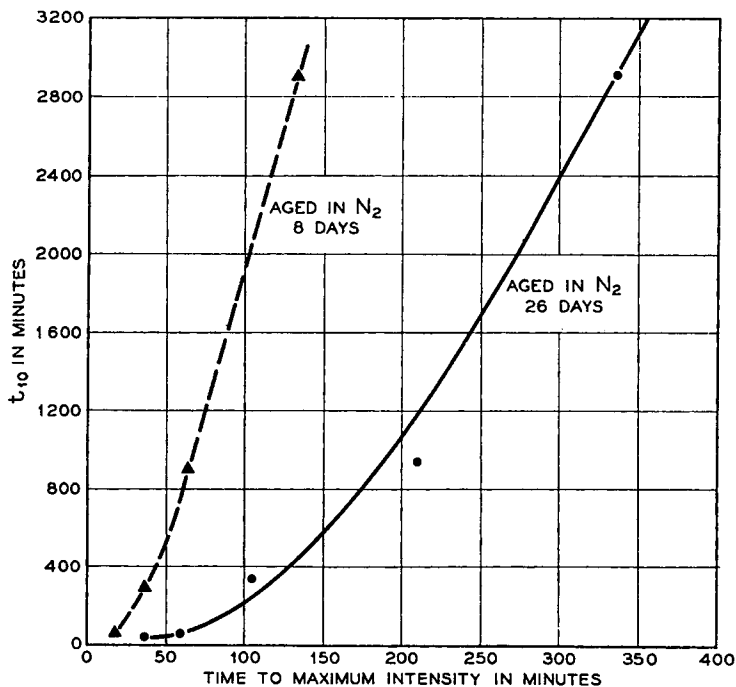


Fig. 2. Oxyluminescence vs. t_{10} at 150°C. for stabilized polypropylene.

preferentially in the amorphous areas. Moreover antioxidants would tend to migrate to, and concentrate in, the amorphous areas resulting in greater overall protection of the susceptible regions. This latter explanation still does not answer the disappearance of the initial maximum observed after oxygen is added to the system and it is obvious more study of this system is required.

The results of oxygen absorption studies on stabilized polymers are shown in Table I in terms of the t_{10} values (time required for absorption of 10 ml. of oxygen per gram of polymer) for polypropylene with various stabilizer concentrations and for polyethylene with and without stabilizer. The data for the samples which had been aged only 8 days compared to oxygen uptake data are shown in Figure 2 (dotted line). The oxygen uptake values were obtained about a month after the samples had been prepared. Experience indicates that although there might be some change with aging in the values of t_{10} , this change would be small compared to the change noticed in oxyluminescence of the same samples aged 26 days (solid line). The rather large differences noticed in these two curves indicate that the age of these samples had a greater influence on the oxyluminescence of these samples than upon their oxygen uptake. Preliminary data which will be reported in a subsequent paper also indicate that the shapes of these curves will be different for different base polymers as well as for different stabilization systems. If such factors as these

TABLE I
Effect of Stabilizer on Oxyluminescence and t_{10} at 150°C.^a

Polymer	Aged 8 days		Aged 26 days		t_{10} min.
	Max. intensity, amp × 10 ⁸	Time to max. intensity, min.	Max. intensity, amp. × 10 ⁸	Time to max. intensity, min.	
Polypropylene (PP), no stabilizer	1.9	37	1.9	37	49
PP + 0.001% stabilizer	3.55	17.5	1.4	60	65
PP + 0.01% stabilizer	3.0	29	1.8	105	354
PP + 0.05% stabilizer	4.6	58	1.85	210	945
PP + 0.1% stabilizer	2.9	130	1.7	335	2,920
Low density polyethylene (L.D.PE.), no stabilizer ^b	—	—	0.067 ^c	>120	108
L.D.PE + 0.1% stabilizer ^b	—	—	0.0069	0.5	20,460

^a Stabilizer used: 4,4'-thiobis(3-methyl-6-*tert*-butylphenol).

^b Aged 3 months in N₂ at room temperature.

^c Value obtained after 2 hr. in oxygen at 150°C.

are kept in mind, curves for the various antioxidant systems could be constructed which would permit a rapid means of evaluating stabilizer protection. These aging effects are not as clear cut in the case of unstabilized polymers and a study of this phenomenon is continuing.

Preliminary studies also show that the effect of stabilizers upon the oxyluminescence of polyethylene is quite different from that in polypropylene. Here the time to maximum intensity is of little value, since with 0.1% stabilizer present the maximum intensity is achieved almost instantaneously. The magnitude of intensity varies inversely with stabilizer concentration, however, and may be correlated with oxygen uptake data. This difference in behavior of polyethylene compared with polypropylene again emphasizes that each polymer system must be considered separately, even with two closely related polymers such as these. One would hazard a guess that the 4,4'-thiobis(3-methyl-6-*tert*-butylphenol) acts differently, at least in the initial phase of oxidation, when used to stabilize polyethylene than when used in polypropylene. Another explanation could be that the two polymers have different reaction paths upon oxidation.

Effect of Temperature

The apparent energies of activation of the light emitting reactions listed in Table II for the various polymers were obtained from the Arrhenius plots of the light intensities measured at various temperatures. These plots for several polymers are shown in Figure 3. Comparing these energies with the relative steady state or maximum luminosities which are also shown in Table II, it can be seen that there was no relation be-

TABLE II
Apparent Activation Energies of Oxyluminescence

Polymer	E , kcal./mole	Max. intensity at 150°C., amp. $\times 10^9$
Polypropylene	23.3	19.0
Polyethylene (L.D.) (above transition)	19.7	0.67
Polyethylene (L.D.) (below transition)	7.4	—
Nylon 6	15.4	7.8
Polystyrene	12.1	0.069
Polyurethane	11.2	0.29
Polymethyl methacrylate	20.5	0.95
Polymethyl methacrylate (below transition)	6.4	—

tween the apparent activation energy of light emission and the intensity of emission. Thus, although polypropylene requires a higher energy (23.3 kcal./mole) than polyethylene (19.7 kcal./mole) to undergo reaction, the former has a much greater intensity of light emission. This indicates that in polypropylene there is a much higher concentration of the active species which are responsible for light emission than in polyethylene. This could be connected with the greater number of tertiary hydrogen atoms, or possibly a different reaction path.

Polymethyl methacrylate shows a sharp change in slope, and hence different values for the activation energies, at 100°C., which is quite close to its glass transition temperature at 105°C. These data also show that the emission intensities may change relative to each other depending upon the temperature, as, for instance, nylon 6 and polypropylene.

These plots are the averages of the data obtained during cooling and heating the polymer. There was some slight separation of the two lines, although the slopes in the case of a given polymer were essentially the same. This was undoubtedly due to the fact that both heating and cooling rates may have been too rapid to allow the true equilibrium or steady state emissions to be obtained at a given temperature. The use of programmed temperature control is being planned in the future which will allow more precise data to be obtained.

The results for the low density polyethylene (Fig. 4) are particularly interesting. It was found that this polymer exhibits a form of transition luminescence⁴ between 87.5 and 97.5°C., which is about the temperature where the major changes in crystallite structure occur in such polyethylenes. This luminescent effect consisted of a burst of photon emission upon cooling, while a reduction in luminosity was observed in this temperature region on heating. This effect was most pronounced in a nitrogen atmosphere and was partially quenched by oxygen. Hence, this was distinctly different from oxyluminescence. This phenomenon has been observed at

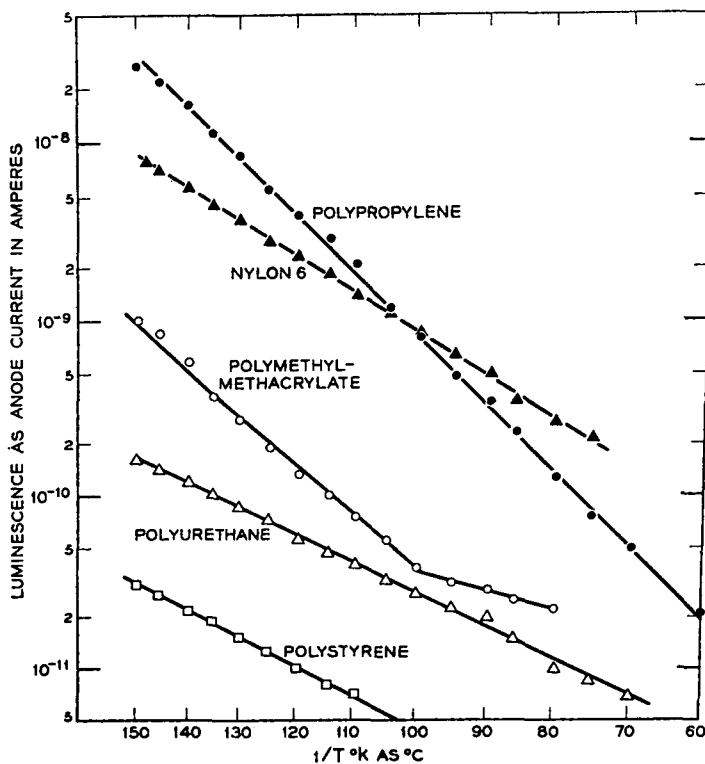


Fig. 3. Temperature dependence of luminescence of various type polymers.

the transition points of a number of organic compounds and will be reported in more detail at a later date. Above and below this transition region, the slopes of the lines and consequently the activation energies are different, thus providing some additional evidence that the morphological state of a polymer may affect its reactivity. The reduced temperature dependence at the lower temperatures would result if there were two competing reactions with different activation energies. A homogeneous reaction would usually have a higher activation energy and hence be favored at high temperatures, whereas a heterogeneous reaction would predominate at lower temperatures. There also may be strain effects (triboluminescence) associated with the solid state which may alter the oxyluminescence.

The average value of 23.3 kcal./mole found for the unstabilized polypropylene is reasonably close to the 26–27 kcal./mole for the oxidation of both isotactic and amorphous polypropylenes found by Hawkins and his co-workers.^{3,5} This value is even closer to the 24–25 kcal./mole that Manyasek et al.⁶ found for the energy of activation of peroxide formation in atactic polypropylene. Their value for the activation energy of the decomposition of these peroxides was 27 kcal./mole. This value of 23.3

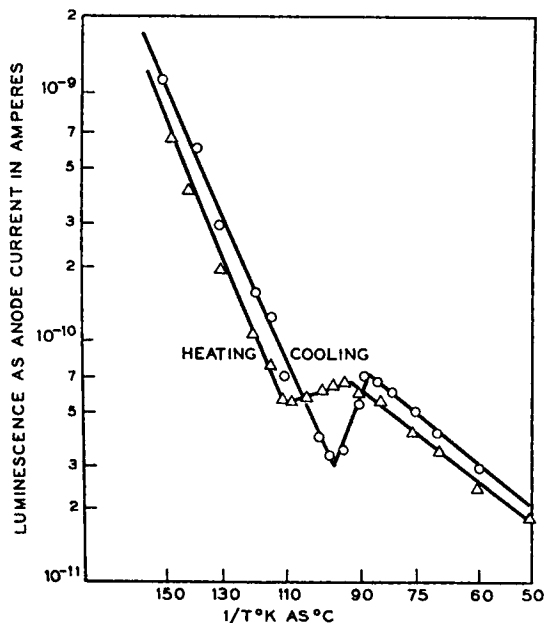


Fig. 4. Temperature dependence of luminescence of low density polyethylene.

kcal./mole could, therefore, be interpreted as supporting the theory that light is emitted by reactions of the $\text{ROO}\cdot$ radicals which was proposed by Vasil'ev and his co-workers.⁷

For the low density polyethylene the average value of 19.7 kcal./mole obtained above the transition region is close to the 21.6 kcal./mole reported by Hawkins, Matryek, and Winslow³ and the value of 18 kcal./mole found by Gilroy⁸ in studies of melt flow behavior on oxidation. Below the transition point, polyethylene resembles polymethyl methacrylate, as it has a much lower energy of activation (7.4 kcal./mole) than it does at temperatures above this point. The methacrylate, however, does not show transition luminescence, but rather the two lines intersect in the neighborhood of 100°C.

Nylon 6, which undergoes an autoretardant type of reaction,¹ has a lower energy of activation for oxyluminescence than do the polyolefins. Both polystyrene and polyurethane showed lower luminescent activation energies although both are basically more stable than the polyolefins. Here again it appears that although the active centers are more easily formed with these more stable polymers, their number is smaller than in the polyolefins.

CONCLUSIONS

Examination of the data obtained during these studies of polymer oxyluminescence shows that this method is very useful for studying the

effects of antioxidants and the mechanisms of polymer degradation. The times required for stabilized samples of polypropylene to reach steady-state oxyluminescence are related to the induction periods obtained by absorption studies, although not in a linear manner. One interesting effect noted was the change in the shape of the light emission versus time curves for these polymers. It appears therefore that for a given system oxyluminescence could be used to estimate stabilizer effectiveness, providing careful attention is paid to sample aging and other test conditions.

The effect of stabilizer in polyethylene was somewhat different and manifested itself mainly as a significant lowering of oxyluminescent intensity.

Oxyluminescent studies can also provide a great deal of information on oxidative degradation of polymers. The dependence of light emission upon temperature is very easily obtained in a short time, and from these data the apparent energies of activation for the light-emitting phase of the degradation reaction can be calculated. These energies of activation for polyethylene and polypropylene are in the neighborhood of values found for the oxidation of these materials by other methods.

Two of the polymers studied, polyethylene and polymethyl methacrylate, had different activation energies above the transition point from those below. Moreover, polyethylene showed a sudden increase in light emission when cooled through its transition point. This transition luminescence was different from oxyluminescence and was most pronounced in the absence of oxygen.

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Résumé

L'oxyluminescence du polypropylène et du polyéthylène stabilisés avec de différentes quantités de 4,4'thiobis-(3-méthyl-6-*tert*-butylphénol) a été étudiée et comparée avec les données de fixation d'oxygène. On a trouvé qu'il y a une corrélation, bien que non-linéaire, entre des deux méthodes. Dans le cas de polypropylènes stabilisés, on a remarqué un effet de cisaillement prononcé. Le comportement de l'oxyluminescence du polyéthylène stabilisé était un peu différent de celui du polypropylène stabilisé. On a obtenu les coefficients de température de l'oxyluminescence du polypropylène, polyéthylène, nylon-6, polystyrène, polyuréthane et du polyméthacrylate de méthyle. A partir de ces données, on a calculé les énergies d'activation apparentes pour la réaction d'émission de lumière. Pour les polymères oléfiniques, ces valeurs sont très rapprochées des énergies d'activation de la réaction de dégradation oxydative, obtenues par une autre

manière. Le polyéthylène et le polyméthacrylate de méthyle ont des énergies d'activation différentes en dessous et au-dessus de leurs points de transition, ce qui indique que la réaction dans l'état solide est différente de la réaction dans la masse fondue. Dans le cas du polyéthylène on a observé une intéressante luminescence de transition, qui était plus prononcée en absence d'oxygène.

Zusammenfassung

Es wurde die Oxyluminiszenz von Polypropylen und Polyäthylen, die mit verschiedenen Mengen von 4,4'-Thiobis-(3-Methyl-6-*tert*butylphenol) stabilisiert waren, untersucht und mit der Sauerstoffaufnahme verglichen. Es besteht eine, allerdings nicht lineare, Beziehung zwischen den beiden Methoden. Im Falle des stabilisierten Polypropylens wurde ein ausgeprägter Alterungseffekt beobachtet. Das Oxyluminiszenzverhalten von stabilisiertem Polyäthylen war von demjenigen von stabilisiertem Polypropylen etwas verschieden. Es wurden die Temperaturkoeffizienten der Oxyluminiszenz von Polypropylen, Polyäthylen, Nylon-6, Polystyrol, Polyurethan und Polymethylmethacrylat bestimmt und daraus die scheinbare Aktivierungsenergie für die Lichtemissionsreaktion berechnet. Diese Werte lagen bei den Olefinpolymeren nahe der auf anderem Wege ermittelten Aktivierungsenergie des oxydativen Abbaus. Sowohl Polyäthylen als auch Polymethylmethacrylat haben unterhalb und oberhalb ihrer Glasumwandlungstemperatur verschiedene Aktivierungsenergien. Das weist auf einen unterschiedlichen Reaktionsablauf im festen und im geschmolzenen Zustand hin. Im Falle des Polyäthylens wurde eine interessante, in Abwesenheit von Sauerstoff besonders ausgeprägte Umwandlungsluminiszenz beobachtet.

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