

**Estimation of Shelf Life of Unstabilized Polyolefins
from Thermal Oxidation Data**

INTRODUCTION

Numerous attempts have been made to correlate outdoor weathering of plastics with accelerated aging (e.g., ref. 1). Generally, such correlations have been reported to be poor due to the many factors involved in the natural and artificial photochemical aging processes. Besides photochemical oxidation, various workers have employed thermal oxidation.

Thus, Grieveson and co-workers² investigated the effect of air oxidation of unstabilized high-density polyethylene at 120°C on physical properties. They indicated that, although very little oxygen had been absorbed at the end of the induction period, considerable changes in intrinsic viscosity and flex value had occurred. For all practical purposes, therefore, it seemed that at the end of the induction period the polyethylene sample had reached also the end of its useful life. Oswald and Turi³ studied the effect of oxidative degradation on the deterioration of physical properties of unstabilized isotactic polypropylene (in 100% oxygen at 75°C). They found that the absorption of only 1.1 mg oxygen per gram isotactic polypropylene (IPP) resulted in a 20% loss in properties, e.g., in the impact index. Further, these workers indicated that extrapolation of elevated temperature data to ambient temperatures was unsafe (as judged by changes in physical properties). Thus, utilizing an apparent activation energy of 30–32 kcal/mole, a life expectancy of six years for IPP in air at 25°C was calculated as compared with the experimental value of approximately 16 months (based on viscosity changes).

The purpose of this report is to present a semiempirical expression which, in conjunction with carbonyl formation data at elevated temperatures, may be used for extrapolation to obtain useful lifetime values of unstabilized polyolefins [IPP, atactic polypropylene (APP), and atactic polybutene-1 (APB)] at ambient temperatures.

RESULTS AND DISCUSSION

Based on theoretical considerations previously presented (e.g., ref. 4), the following expression may be written for rate of carbonyl formation, ρ_{CO} , during polyolefin oxidation:

$$\rho_{CO} \approx CR_i t \quad (1)$$

where $C = k_3 k_6 / (k_3 + k_4)$; k values denote rate constants; t = times; and R_i denotes initiation rate and is equal to $k_i [RH][O_2]$ where, in turn, k_i = initiation rate constant; $[RH]$ = concentration of reactive hydrogen on polymer main chain; and $[O_2]$ = oxygen concentration in per cent. [In the derivation of eq. (1), it was assumed that the term $At \ll 1$ (see ref. 5)]. Upon integrating eq. (1), there is obtained

$$[CO] = Ck_i [RH][O_2] \frac{t^2}{2} \quad (2)$$

Now, if we assume that at $t = \theta$ (an induction time) eq. (2) is still valid, this equation becomes

$$[CO]_{ind} = Ck_i [RH][O_2] \frac{\theta^2}{2} \quad (2a)$$

where $[CO]_{ind}$ = carbonyl concentration during induction time θ . When $[CO]_{ind}$ is maintained constant, the Arrhenius relation is employed, and it is assumed that $(k_3 + k_4)/k_3$ is approximately constant at various temperatures (see ref. 6), then

$$\ln \{\theta^2 [O_2]\} = \ln K + \{(E_i + E_6)/RT\} \quad (3)$$

where $K = 2 [\text{CO}]_{\text{ind}}(k_3 + k_4)/k_2 [\text{RH}]Z_iZ_0$; Z values are frequency factors; E values denote activation energies; R = gas constant; and T = temperature.

In order that $[\text{CO}]_{\text{ind}}$ be approximately constant in eq. (3), we arbitrarily let $\theta = 0.4 t_m$, where t_m = time at which the maximum rate of carbonyl formation is reached (see Fig. 1). At this value of θ , $[\text{CO}]_{\text{ind}}$ should be very low and approximately equal at various values of $[\text{O}_2]$ and temperature. Further, at this value of θ , the deterioration of physical properties of the polymers may not be too severe as yet.

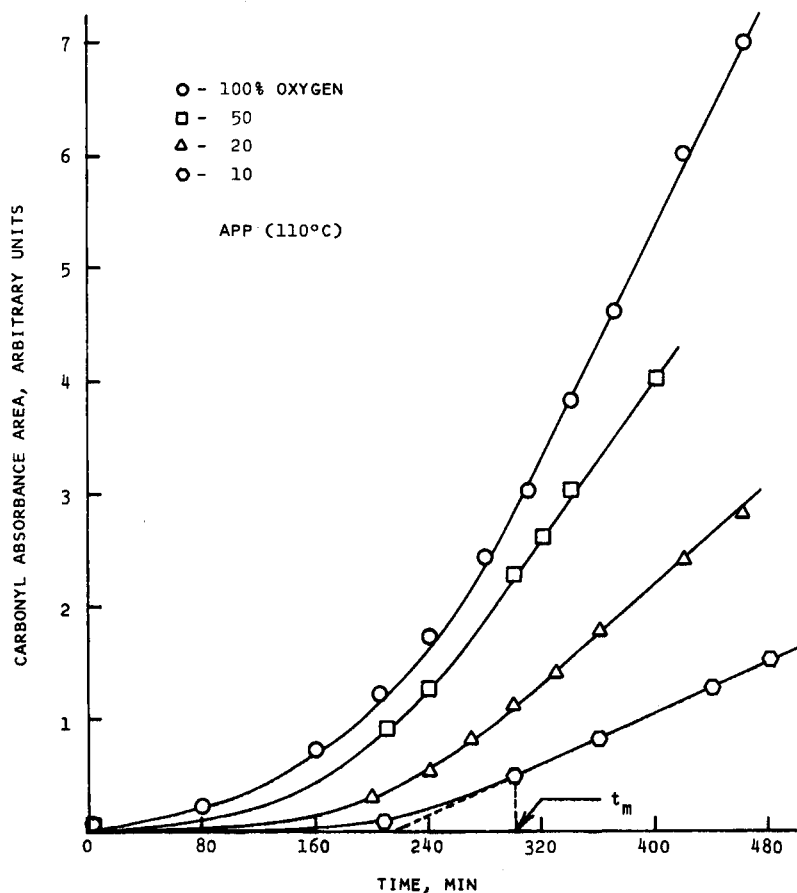


Fig. 1. Carbonyl absorbance area vs. time during oxidation of atactic polypropylene at 110°C.

Figures 1 and 2 depict plots of carbonyl absorbance area (from infrared measurements and in arbitrary units⁷⁻⁹ versus time for the oxidation of APP and IPP at various temperatures and oxygen concentrations. From such typical plots were obtained values of $(\theta_2[\text{O}_2])$ at various temperatures and oxygen concentrations for APP, IPP, and APB. In Figures 3A and 3B are shown plots of average values of $\log (\theta_2[\text{O}_2])$ versus $1/T$ (reciprocal temperature) for APP, IPP, and APB. In the plots for APP and IPP (Fig. 3A), the derived data virtually coincide. (This may be due to the equal reactivity of amorphous regions in APP and IPP, which results in a similar time interval for obtaining maximum

carbonyl formation). Using the mean deviations for values of $\log(\theta^2[\text{O}_2])$, upper and lower limits were drawn (Fig. 3A) for the data, and the intermediate linear relation was obtained from a least-squares analysis (the linear correlation coefficient possessed a value between 0.98 and 0.99). The values of the apparent activation energies [see eq. (3)] (going from the lower limit to the upper limit) were 32, 37, and 42 kcal/mole.

From the lower limit plot, a value of $\theta = 6.3$ hr can be calculated for $[\text{O}_2] = 100\%$ and 75°C . Data of Oswald and Turi (Figs. 8, 11, 12, and 13 of ref. 3) indicated that at 75°C and $[\text{O}_2] = 100\%$ and $\theta = 6.3$ hr, the change in intrinsic viscosity was relatively small, and there was 85–100% retention in the impact index and in the ultimate tensile strength and ultimate elongation of the unstabilized polypropylene film used (which was 25 mil thick). Further, from the lower limit and the linear regression line (Fig. 3A), the values of θ were, respectively, 50 and 100 days at 22°C , and $[\text{O}_2] = 20\%$. Oswald and Turi observed that marked changes in intrinsic viscosity commenced when unstabilized poly-

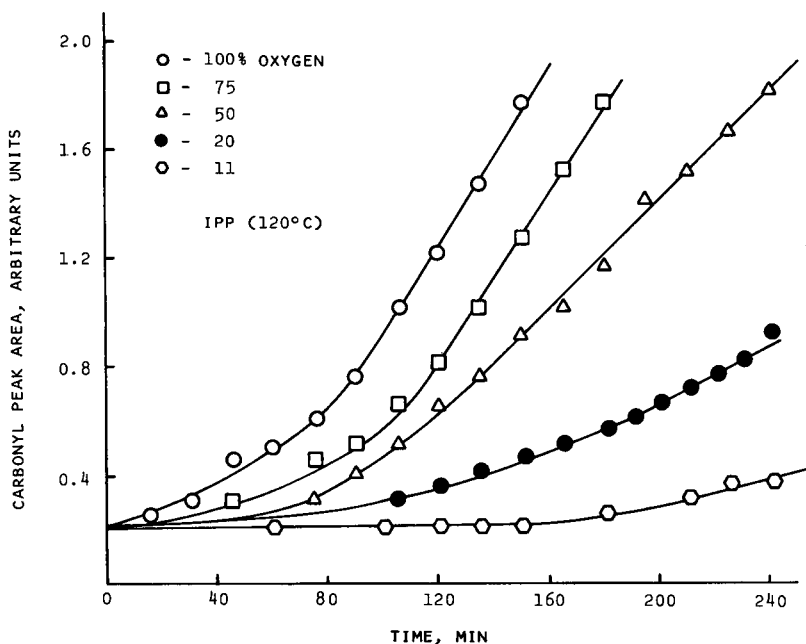


Fig. 2. Carbonyl absorbance area vs. time during oxidation of isotactic polypropylene at 120°C .

propylene powder was shelf stored at ambient temperature in air for approximately 450 days. In this respect, it may be remarked that relatively large changes in mechanical properties undoubtedly occurred long before the marked change in intrinsic viscosity took place (see Figs. 8 and 12 of ref. 3). Thus, the lower limit line may provide a fairly safe prediction of the maximum time that unstabilized polypropylene should be shelf stored (or maintained at higher temperatures) before its mechanical properties would degrade considerably. However, it should be noted here that much more data on shelf-life stability of unstabilized polypropylene is needed before any definite conclusions can be drawn.

Figure 3B depicts a plot of $\log(\theta^2[\text{O}_2])$ versus $1/T$ for APB. The lower limit and least-square lines afforded values of activation energies of, respectively, 46 and 55 kcal/mole (a

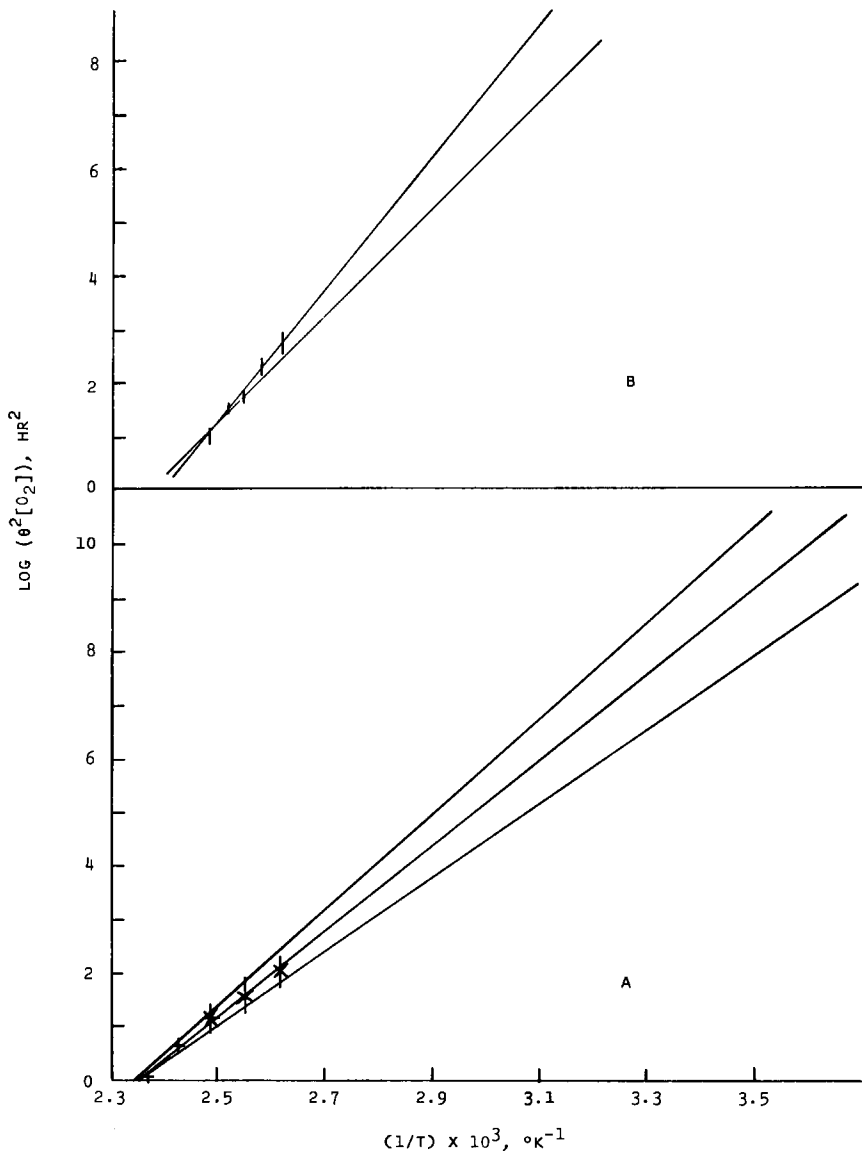


Fig. 3. (A) $\text{Log } (\theta^2[\text{O}_2])$ vs. reciprocal temperature for atactic and isotactic polypropylenes; (B) $\text{log } (\theta^2[\text{O}_2])$ vs. reciprocal temperature for atactic polybutene-1.

value of $E_i + E_6 = 43$ kcal/mole has been reported¹⁰). However, due to lack of appropriate data on unstabilized APB shelf life, no extrapolations to ambient temperature were made. Nevertheless, it would appear from a comparison of Figures 3 A and 3B that unstabilized APB would provide a longer shelf life than APP or IPP.

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