

Kinetics of Wet Oxidation of Nylon 66

D. W. SUNDSTROM, A. J. LUCIANO, and H. E. KLEI, *Department of Chemical Engineering, The University of Connecticut, Storrs, Connecticut 06268*

Synopsis

The kinetics of the aqueous phase oxidation of nylon 66 was studied at temperatures up to 190°C. The nylon 66, in the form of a cylindrical disc, was attached to the shaft of a variable-speed drive inside the reactor. With a rotating disc geometry, the chemical kinetics of the surface reaction can be separated from the mass transfer effects. By measuring the reaction rates at different temperatures, pressures, and disc rotational speeds, a kinetic rate expression was developed relating nylon degradation to dissolved oxygen concentration and temperature. The order of reaction with respect to dissolved oxygen concentration was 0.6, and the activation energy was 42 kcal/g-mole.

INTRODUCTION

Organic compounds can be oxidized chemically in an aqueous system by heating under pressure in the presence of dissolved oxygen. When applied to the disposal of aqueous organic wastes, the technique is called wet oxidation or wet combustion. Plastic waste materials exceed 6 billion pounds per year and are often resistant to biodegradation by bacteria or fungi. Since wet oxidation is a chemical rather than a bacterial oxidation and can give high reaction rates, it is a promising method for degrading polymeric wastes. In this study, the kinetics of the aqueous phase oxidation of nylon 66 was explored using a rotating disc geometry.

The degradation of nylon 66 in vacuum, inert gas, and air has been examined by several investigators.¹⁻⁵ Most studies have emphasized the effect of thermal exposure on structure and properties rather than kinetics. Valko⁴ determined the activation energy and rate constants for the elimination of amine end groups in air near 150°C, and Goldstein⁵ derived a rate equation for the pyrolysis of nylon in air between 200° and 600°C.

Aqueous phase studies of nylon degradation have been largely restricted to temperatures below 100°C. Mikolajewski et al.⁶ exposed undrawn nylon 66 to water for several days at temperatures from 50° to 90°C. An extensive analysis of products was made to aid in determining the causes of degradation. Vachon et al.⁷ measured changes in chemical and physical properties of nylon 66 filaments in oxygenated aqueous systems at 60° to 80°C. They postulated a mechanism for the autoxidation of nylon involving hydroperoxides as initiators.

The previous studies on aqueous phase oxidation of nylon were conducted

at low temperatures with little emphasis on reaction kinetics. In this study, the kinetics of wet oxidation of nylon 66 will be determined at temperatures near 175°C.

ROTATING DISC GEOMETRY

Wet oxidation of a solid polymer is a heterogeneous reaction between dissolved oxygen in the water and the polymer at the solid-liquid interface. Since the oxygen must diffuse to the surface before reacting, the overall reaction rate is governed by both mass transfer and chemical kinetics considerations. To obtain a kinetic rate expression, it is necessary to measure the chemical kinetic contribution for a system in which both surface reaction and mass transfer may be significant.

The kinetic term can be calculated by using a rotating disc geometry, which consists of a cylindrical disc of solid polymer with only its lower surface exposed to the oxygenated liquid. The concentration profile is independent of radial position on a rotating disc, ensuring that the reaction rate will be uniform over the surface of the disc. Since the reacting area remains essentially constant, problems associated with changing particle sizes in other geometries are eliminated.

The rotating disc offers a well-defined hydrodynamic situation where an exact solution of the equations of continuity and motion are possible. With the known velocity profile on the boundary layer, chemical kinetics can be extracted from overall rate data. The rotating disc also has the experimental advantage that it does not require pumping large quantities of high-velocity liquid over a surface to attain a low diffusional resistance. The water need only be fed rapidly enough to supply fresh dissolved oxygen and to remove reaction products from the vicinity of the surface.

THEORY OF ROTATING DISC

A cylindrical disc rotating in a quiescent fluid draws fluid axially toward its surface and pushes it outward away from the center. The three-dimensional flow pattern can be described by the Navier-Stokes equations for the axial, radial, and circumferential directions:

$$v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial Z} = -\frac{1}{\rho} \frac{\partial p}{\partial z} + \nu \left[\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r} \frac{\partial v_z}{\partial r} + \frac{\partial^2 v_z}{\partial Z^2} \right] \quad (1)$$

$$v_r \frac{\partial v_r}{\partial r} + v_z \frac{\partial v_r}{\partial Z} - \frac{v_\phi^2}{r} = -\frac{1}{\rho} \frac{\partial p}{\partial r} + \nu \left[\frac{\partial^2 v_r}{\partial r^2} + \frac{\partial}{\partial r} \left(\frac{v_r}{r} \right) + \frac{\partial^2 v_r}{\partial Z^2} \right] \quad (2)$$

$$v_r \frac{\partial v_\phi}{\partial r} + \frac{v_r v_\phi}{r} + v_z \frac{\partial v_\phi}{\partial Z} = \nu \left[\frac{\partial^2 v_\phi}{\partial r^2} + \frac{\partial}{\partial r} \left(\frac{v_\phi}{r} \right) + \frac{\partial^2 v_\phi}{\partial Z^2} \right]. \quad (3)$$

The boundary conditions at the surface of the disc and in the bulk fluid remote from the disc are

At $Z = 0$:

$$v_r = 0, v_z = 0, v_\phi = \omega r \quad (4)$$

At $Z = \infty$:

$$v_r = 0, v_\phi = 0, v_z = -u_\infty \quad (5)$$

where ω = rotational velocity, sec^{-1} ; and u_∞ = axial velocity toward disc, cm/sec . These equations have been solved numerically by Levich⁸ to yield the pressure and velocity distributions. The solution shows that the thickness of the boundary layer is constant over the entire surface of the disc.

The concentration profile is obtained from the mass transfer equation:

$$v_r \frac{\partial C}{\partial r} + \frac{v_\phi}{r} + \frac{\partial C}{\partial \phi} + v_z \frac{\partial C}{\partial Z} = D \left[\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial Z^2} + \frac{1}{r^2} \frac{\partial^2 C}{\partial \phi^2} \right]. \quad (6)$$

In the bulk fluid, the boundary condition is

At $Z = \infty$:

$$C = C_\infty. \quad (7)$$

If the reaction is assumed to follow n th order irreversible kinetics, the boundary condition at the surface of the disc is

$$J_0 = D \left(\frac{\partial C}{\partial Z} \right)_{z=0} = kC_0^n \quad (8)$$

where J_0 = flux of oxygen to surface of disc, mole/sec . Thus, the chemical kinetic term enters the model as a boundary condition to the mass transfer equation.

Solution of the mass transfer equation results in an implicit expression for the flux of oxygen:

$$J_0 = k(C_\infty - 1.61 D^{-2/3} \nu^{1/6} \omega^{-1/2} J_0)^n. \quad (9)$$

In the experiments, the rate of reaction of nylon was measured instead of the rate of consumption of oxygen. If the moles of oxygen consumed per mole of nylon reacted is essentially constant, then the fluxes are related by

$$J_0 = J_n S \quad (10)$$

where J_n = flux of reacted nylon, moles of nylon repeat units/sec; S = stoichiometric factor, moles O_2/mole nylon repeat units reacted. The mass flux equation in terms of nylon is given by

$$J_n S = k(C_\infty - 1.61 D^{-2/3} \nu^{1/6} \omega^{-1/2} J_n S)^n. \quad (11)$$

Evaluation of the constants k , n , and S requires data on nylon flux as a function of rotational velocity.

The previous equations are valid for the general case where the overall rate of reaction is governed by both diffusional and kinetic resistances. If the rotational velocity of the disc is decreased, the flux of fresh dissolved oxygen to the surface is reduced. At very low speeds where C_0 approaches zero, the flux equation becomes

$$J_n S = \frac{D^{2/3} \nu^{-1/6} \omega^{1/2} C_\infty}{1.61}. \quad (12)$$

In this region, the flux is proportional to the square root of the rotational velocity, and the rate of reaction is controlled by diffusion.

If the rotational speed is increased, the flux of dissolved oxygen to the surface reaches a magnitude where C_0 approaches C_∞ and the flux equation reduces to

$$J_n S = kC_\infty^n. \quad (13)$$

At high speeds, then, the flux is independent of the rotational velocity, and the rate of reaction is controlled by chemical kinetics.

EXPERIMENTAL

The major purpose of the apparatus shown in Figure 1 is to contact dissolved oxygen with the lower surface of a rotating disc at a controlled temperature and pressure. The reactor itself is a 1-liter stainless-steel autoclave equipped with a variable-speed magnetic drive agitator. To permit close temperature control of the contents, the reactor has a continuous heater to compensate for normal heat loss and a controlled heater to provide incremental energy.

A separate 2.5-liter contactor with controlled heaters is used to contact the air and water. Air is bubbled continuously through the water to saturate it with dissolved oxygen at the contactor temperature and pressure. During a run, the oxygenated liquid is pumped from the contactor into the bottom of the reactor by a variable-output positive-displacement pump. To attenuate the pulsing action of the pump, a surge tank is installed immediately downstream of the pump. Appropriate instrumentation is installed to measure temperatures, pressures, and flow rates.

The polymer is machined into the form of 2-in. diameter discs, dried in an oven, weighed accurately, and inserted into a holder which attaches to the drive shaft of the agitator. The holder assembly is designed so that only the lower surface of the polymer disc is exposed to the liquid. The rotational velocity of the disc is controlled by the variable-speed drive and measured with a tachometer.

At the beginning of a run, the temperature, pressure, flow rates, and disc speed are set at the desired levels. Before flow is started to the reactor, air is bubbled through the water in the contactor for about 2 hr to reach saturation with dissolved oxygen. The oxygenated water is then circulated through the reactor for the duration of the run. Since the rotating disc theory applies to a quiescent fluid, the volumetric flow rate of water to the reactor is set at the

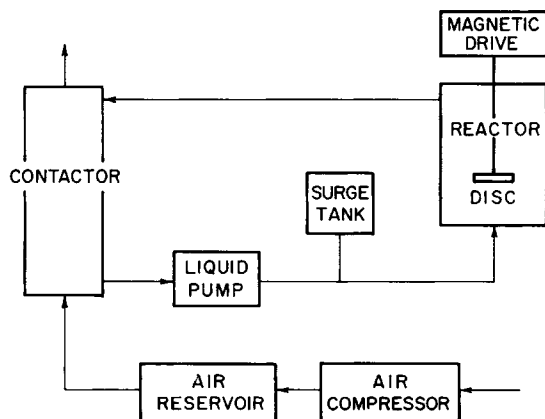


Fig. 1. Schematic diagram of wet oxidation apparatus.

theoretical rate required for the pumping action of the disc. This flow rate provides a basically quiescent fluid and maintains a fresh supply of dissolved oxygen at the reacting surface. At the end of the run, the system is cooled rapidly and the disc is removed, dried, and weighed.

RESULTS

To analyze weight loss data by the rotating disc theory, the material should conserve a flat smooth surface at the conditions of oxidation. Nylon 66 was observed to react with dissolved oxygen at reasonable rates for temperatures between 160° and 190°C without swelling, melting, or distortion of the surface. At temperatures below 160°C, the rate of reaction was too slow for a practical degradation process. When temperatures exceeded 190°C, the heat of reaction was sufficient to raise the surface temperature of the disc several

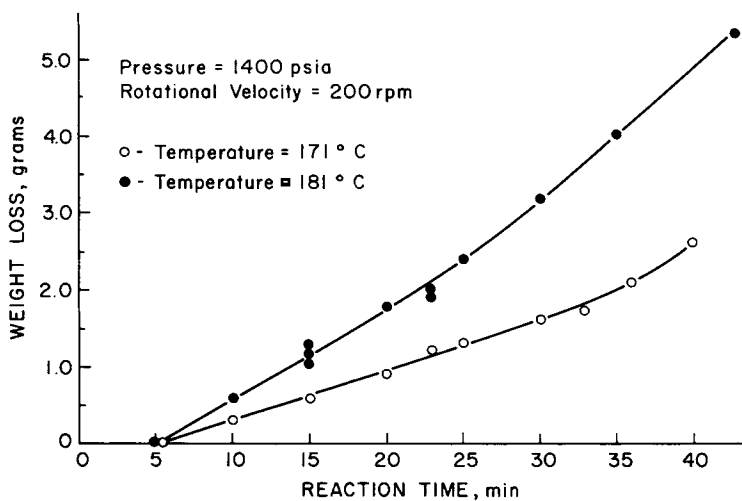


Fig. 2. Effect of time on weight loss of nylon discs.

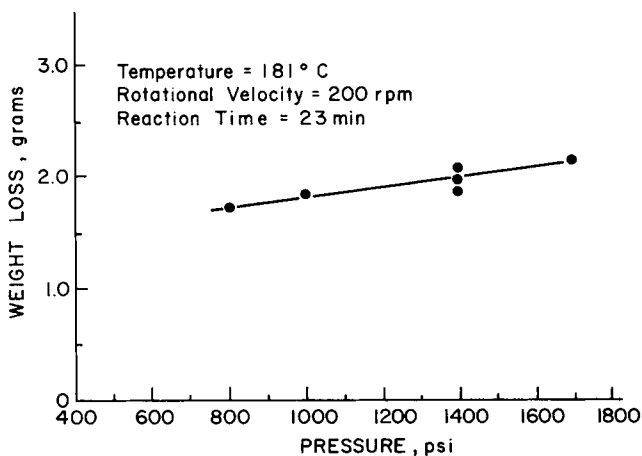


Fig. 3. Effect of pressure on weight loss of nylon discs.

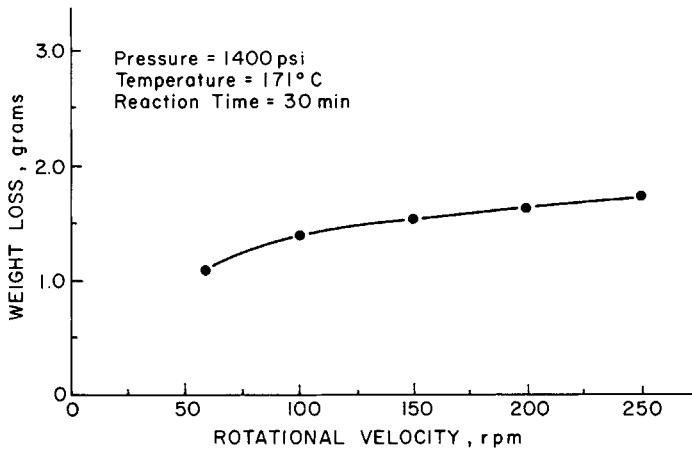


Fig. 4. Effect of rotational velocity on weight loss at 171°C.

degrees above the water temperature, which complicated analysis of the data. Thus, the experiments were restricted to a range of conditions where reaction rates were of convenient magnitude and the rotating disc theory was applicable.

The effect of reaction time on weight loss at two temperature levels is shown in Figure 2. After an induction period, the amount of nylon degraded increases linearly with time until about 2.5 g are lost. Above this value, the rate of weight loss increases because of an increasing surface area associated with the gradual appearance of spiral grooves. The formation of a spiral surface pattern is characteristic of rotating discs in the laminar flow regime. The delay of about 5 min before the onset of weight loss results from the induction period of the reaction plus the time for the oxygenated water to reach the disc after flow is started to the reactor. For all subsequent runs, the reaction times were restricted to the region where weight loss varied linearly with time.

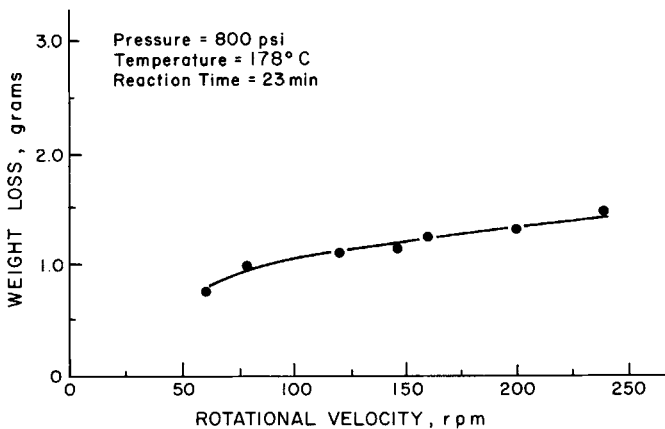


Fig. 5. Effect of rotational velocity on weight loss at 178°C.

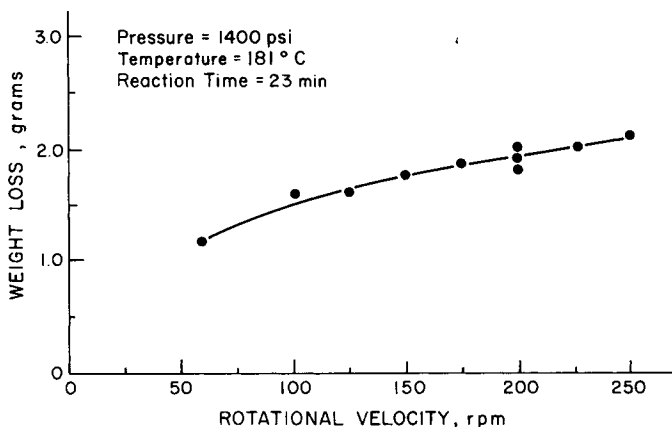


Fig. 6. Effect of rotational velocity on weight loss at 181°C.

Figure 3 shows that the rate of reaction increases gradually as reactor pressure is raised from 55 to 115 atm. The main cause of the pressure effect is the increase in the solubility of oxygen, C_{∞} , with increasing pressure.

The effect of disc rotational velocity on weight loss was studied at three temperature levels (Figs. 4, 5, and 6). Reaction rates increase with increasing rotational velocity, but the slopes of the curves decrease. The slopes of these curves are typical of the intermediate reaction region where both mass transfer and chemical kinetics are important.

The maximum rotational velocity is determined by the critical Reynolds' number at which the transition to turbulent flow occurs. For the conditions of this study, the critical Reynolds' number corresponded to a disc speed of about 600 rpm. Turbulence was evidenced by a rough pitted surface instead of a smooth spiral pattern. To avoid the turbulent region, the maximum rotational velocity used in the experiments was limited to 300 rpm.

ANALYSIS OF RESULTS

The rate constant k , order of reaction n , and stoichiometric factor S were evaluated by applying eq. (11) to the data shown in Figures 4, 5, and 6. If an n th order rate expression is applicable over the range of conditions used, the reaction should have the same order and stoichiometric factor at each temperature level. To facilitate processing of the data, a computer program was written to calculate corresponding values of S and n from the measurements of nylon weight loss versus rotational velocity. At $S = 1.15$ moles oxygen/mole nylon, a common value of $n = 0.60$ was found for each set of data. In addition, these values of S and n minimized the standard deviation between experimental and predicted nylon fluxes for each temperature level. Thus, $S = 1.15$ and $n = 0.60$ represent the best values of these constants for all data combined.

The rate constant k is dependent upon temperature level. Using the best values of S and n , the rate constants were calculated to be 3.0×10^{-4} (g-mole) $^{0.4}$ /sec (cm) $^{0.2}$ at 171°C, 6.0×10^{-4} (g-mole) $^{0.4}$ /sec (cm) $^{0.2}$ at 178°C, and $8.1 \times$

$10^{-4} (\text{g}\cdot\text{mole})^{0.4}/\text{sec} (\text{cm})^{0.2}$ at 181°C . The rate constants were correlated with temperature by the Arrhenius equation:

$$k = Ae^{-E/RT}. \quad (14)$$

By plotting $\ln k$ versus $1/T$ (Fig. 7), a straight line was obtained with a slope of $-E/R$. From Figure 7 and eq. (14), the activation energy E and frequency factor A were found to be 42 kcal/g-mole and $1.3 \times 10^{17} (\text{g}\cdot\text{mole})^{0.4}/\text{sec} (\text{cm})^{0.2}$, respectively.

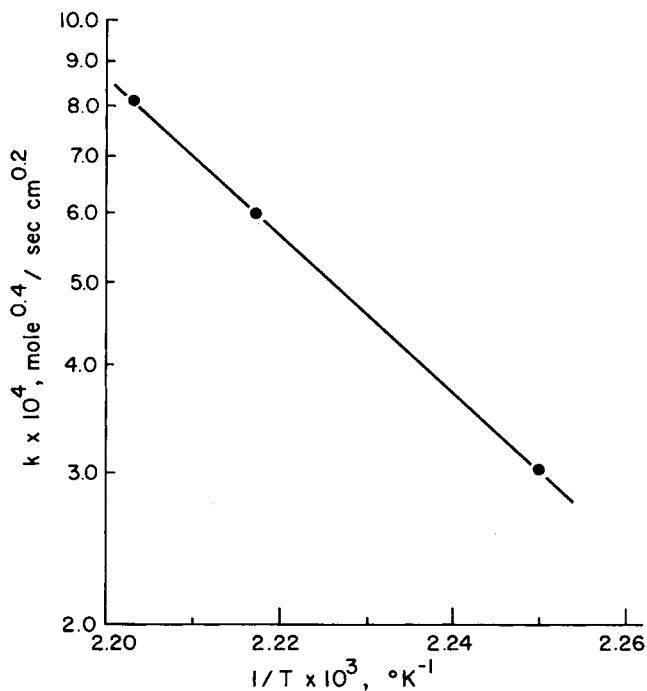


Fig. 7. Arrhenius equation plot of $\ln k$ vs. $1/T$.

The final kinetic expression for the aqueous phase oxidation of nylon 66 is therefore given by

$$J_n = \frac{k}{S} C^n = \frac{A}{S} e^{-E/RT} C^n = 1.13 \times 10^{17} e^{-42,000/RT} C^{0.6}. \quad (15)$$

As noted in the literature survey, previous studies on wet oxidation of nylon have been restricted to lower temperatures with little emphasis on reaction kinetics. Vachon et al.,⁷ for example, evaluated the changes in properties of nylon 66 filaments in oxygenated water at temperatures below 100°C . Based on measurements of intrinsic viscosity of the degraded nylon, they estimated an activation energy of 20 kcal/mole. Because of the different measure of degradation and the lower temperatures, comparison of results with the present study is difficult. Valko⁴ exposed nylon 66 to air at temperatures of 136° to 215°C and found the activation energy for the elimination of amine endgroups was 40 kcal/mole. Although this value compares favorably with

the present study, the environment was air and the measure of degradation was endgroups rather than weight loss.

The mechanism for the oxidation of nylon was not investigated but probably involved free-radical reactions. Vachon et al.⁷ found that their data were consistent with a mechanism in which trace amounts of hydroperoxides were formed and acted as initiators for the autoxidation of nylon. Emmanuel et al.⁹ discuss kinetic mechanisms for the liquid-phase oxidation of hydrocarbons. For free-radical reactions proceeding by initiation, propagation, and termination steps, they show that the order of reaction for dissolved oxygen is usually between 0 and 1, depending upon the relative magnitudes of the kinetic constants for the various steps. The value of $n = 0.6$ determined in this study thus falls within the range commonly observed for free-radical oxidation reactions.

Nomenclature

A	frequency factor in Arrhenius equation
C_0	concentration of dissolved oxygen at solid surface, moles/l.
C_∞	concentration of dissolved oxygen in bulk liquid, moles/l.
D	diffusivity of oxygen in water, cm^2/sec
E	activation energy for reaction, kcal/mole
J_n	mass flux of degraded nylon from surface, moles of nylon repeat units/ $\text{cm}^2 \text{ sec}$
J_0	mass flux of dissolved oxygen to surface, moles/ $\text{cm}^2 \text{ sec}$
k	rate constant for reaction, $\text{mole}^{0.4}/\text{sec cm}^{0.2}$
n	order of reaction
p	pressure in reactor, dynes/ cm^2
r	radial distance from center of rotating disc, cm
R	gas constant, cal/mole $^\circ\text{K}$
S	stoichiometric factor, moles O_2 reacted/mole nylon repeat units degraded
T	temperature in reactor, $^\circ\text{K}$
u_∞	velocity of liquid toward surface, cm/sec
v_r	radial component of velocity, cm/sec
v_ϕ	angular component of velocity, cm/sec
v_z	axial component of velocity, cm/sec
Z	axial distance from surface of rotating disc, cm
ρ	density of liquid, g/cc
ϕ	angular position on rotating disc
ν	kinematic viscosity of liquid, cm^2/sec
ω	rotational velocity of disc, radian/sec

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