

Polymer Dissolution Experiment for **Chemical
Engineering Laboratory**

Zhihua Cao, Suphan Kovenklioglu, Dilhan M. Kalyon, Rahmi Yazici
Stevens Institute of Technology

Introduction

Polymer dissolution is increasingly becoming important in pharmaceutical applications such as controlled release, polymer fractionation, microlithography and in the recovery and recycle of energetic materials where the polymeric binder which encapsulates other components of the energetic material must first be dissolved. Polymer dissolution rates can also be fairly accurately described by semi-empirical film models which chemical engineers extensively use in describing rate processes where the flow is typically turbulent. The experiments can be easily performed in a three hour laboratory period by using a glass bottle with a magnetic stirrer or by using an autoclave stirred with an impeller. The glass bottle offers the unique advantage of being able to monitor the dissolution process with a camera where one can observe how the changes in flow dynamics affect the rate of dissolution.

Experimental System

Schematics of the experimental set-up is shown in Figure 1. The glass (pyrex) bottle in which the dissolution experiments are to be carried out is heated electrically to control the temperature. The polymeric binder can be shaped into a sphere and suspended in the glass bottle at the end of a hooked wire. The solvent is heated to the desired temperature in the autoclave pressurized by an inert gas and transferred to the glass bottle. Agitation is achieved with a magnetic stirrer. Samples are to be collected at regular time intervals and analyzed by infrared spectroscopy using an FTIR. Collection of samples is done by opening the valve on the same line which is used for transferring the solvent under pressure into the glass bottle.

The polymeric binder is BAMO/AMMO (12% BAMO) thermoplastic elastomer which is obtained from the polymerization of BAMO (3,3-bis (azidomethyl)oxetane) and AMMO (3-azidomethyl-3 -methyloxetane) monomers. This binder is available from Thiokol Corporation. BAMO is a crystalline homopolymer forming the hard block and AMMO is an amorphous homopolymer forming the soft block of the energetic thermoplastic elastomer. THF and ethyl acetate are both effective solvents for the BAMO/AMMO polymer. However, the characteristic azide peak of 2100 cm^{-1} for this polymer is masked if ethyl acetate is used as the solvent. Hence if the IR technique is to be used to determine the binder concentration, it is necessary to use THF. We would like the students to use FTIR to gain experience with this increasingly important analytical tool. Refractive index measurements can also be used both with ethyl acetate and THF as solvents, however, these measurements are not accurate at low binder concentrations. If the dissolved binder is not recovered, it is important to work at low binder concentrations due to the high cost of the binder.



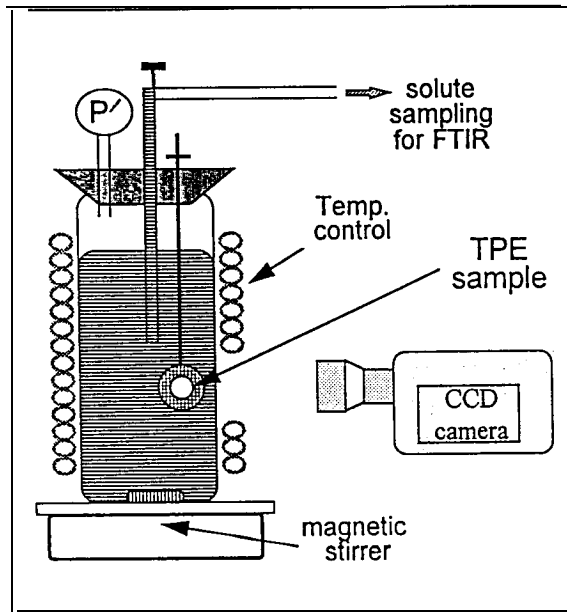


Figure 1. Experimental Setup for Dissolution Studies

Mathematical Analysis of the Dissolution Process

The mathematical analysis of the dissolution process is based on the film theory of interracial mass transfer(1). Film theory assumes that a stagnant film the thickness of which depends primarily on the system hydrodynamics exists near every interface. This hypothetical film also called the “unstirred layer” presumes that transport processes in the film occurs by diffusion alone with the concentration varying linearly across the film. Since the film is assumed to be very thin, the quantity of solute within the film would be small relative to the amount passing through it so that **the concentration gradient** would be set up quickly. The molar flux (N) of the solute across the film is then written as a product of mass transfer coefficient (k) and the concentration difference across the film ($C_i - C_b$). Here N is the flux relative to the solid-fluid interface and C_i and C_b are interracial and bulk concentration in the fluid. In chemical engineering practice there is a large body of empirical correlations for mass transfer based on film theory to determine mass transfer coefficients where typically the Sherwood number is expressed as a function of Reynolds and Schmidt numbers. Film theory has ben found to be satisfactory for predicting interracial mass transfer rates and is often preferred due to its simplicity than the more rigorous boundary layer models. Hence it will be used here to model the dissolution process.

Here the polymeric sample is of spherical shape where the surface area $A(t)$ is progressively shrinking. The molar diffusion flux of the solvated polymer in the film is given by

$$N = k(C_i - C_b) \quad (1)$$

where k is the mass transfer coefficient and C_i and C_b are the interracial and bulk concentrations in the fluid.

Also, since the film is presumed to be very thin, there would be no mass accumulation in the film and the mass diffusion flux through the film can be taken to be equal to the rate of dissolution (r_d) based on the external surface area $A(t)$ of the dissolving particle and represented by

$$N.M_w = r_d = -(1/A(t))dW_s/dt \quad (2)$$

Combining Equations (1) and (2) and assuming that the interracial concentration (C_i) will be equal to the equilibrium concentration (C_e) at the solid-liquid interface (2) one obtains

$$-(1/A(t))dW_s(t)/dt = k M_w (C_e - C_b) \quad (3)$$

Here it will be assumed that the sphere retains its shape during dissolution and $C_b=0$ at the low concentrations for which the data were collected. If the density of the polymer during dissolution process can be assumed to stay constant, then the surface area $A(t)$ can be expressed in terms of the weight of the dissolving sample, $W_s(t)$. Eq. (3) can then be integrated and with $W(t) = W_o - W_s(t)$ and rearranged to yield

$$W(t)/W_o = 1 - (1 - k' W_o^{-1/3} t)^3 \quad (4)$$

where

$$k' = k C_e M_w (4\pi/3\rho^2)^{1/3} \quad (5)$$

The definitions of the parameters appearing in the above equations are summarized below:

- C_b = bulk concentration of the dissolved polymer
- C_e = concentration of the dissolved polymer in solution in equilibrium with the solid polymer
- C_i = interfacial concentration of the dissolved polymer
- k = mass transfer coefficient
- k' = constant defined by Eq. (5)
- M_w = molecular weight of the dissolving polymer
- N = molar flux of the dissolving polymer
- t = time
- $W_s(t)$ = weight of the polymer at time t
- $W(t)$ = weight of the dissolved polymer in solution at time t
- W_o = initial weight of the polymer particle
- ρ = density of the polymer

One would note that Eq. (4) should be used up to

$$t = W_o^{1/3} / k' \quad (6)$$

at which time all of the polymer will have dissolved in the solution. Also C_e is treated as constant with the assumption that solubility is not significantly influenced in the temperature range at which the data were collected.



Testing of the Mathematical Model with Data

The ability of the model to correlate the data can be tested by fitting data for the dissolution of the polymeric binder samples to Eq. (4) and evaluating k' at different temperatures.

Sample experimental data are represented in Figures 2 and 3 in the temperature range of 34-67 °C. The weight of the binder dissolved into the THF solution were calculated by using the calibration curve (Figure 4) where the absorbance of the azide peak at 2100 cm are plotted as function binder concentration" in solution. The curves in Figures 2 and 3 are obtained based on the best fit using Eq. (4). The k' obtained at different temperatures are plotted as a function of temperature in the Arrhenius form in Figure 5. This information can be used to determine the activation energy of the dissolution process.

In a single laboratory session it is suggested that students working in groups of two collect dissolution data at one temperature and use the additional data provided here. This would allow time for the camera observation of the dissolution process. The following questions are suggested for analysis.

1. Plot the normalized weight $W(t)/W_0$ of the polymer dissolved in solution as a function of time at the specified temperature ($W(t)$ is obtained from FTIR measurements using the calibration curve in Figure 4). Using Equation (4) which was derived earlier obtain the best k' by curve fitting. Comment on whether the fit is satisfactory.
2. Using k' values which have been similarly obtained at other temperatures and assuming that k' is an Arrhenius function of temperature plot $\ln k'$ vs $1/T$ and determine the activation energy.
3. In polymeric substances, before dissolution can occur, the solvent would penetrate a certain distance into the polymer (internal diffusion). Typically, there will be some swelling in the layer penetrated by the solvent. Internal diffusion as well as external diffusion i.e., diffusion of the solvated polymer from the polymer-solvent interface into the bulk solvent affect the overall dissolution rates. If internal diffusion is very slow relative to the external diffusion, the penetration thickness will be small and dissolution rate can be said to be controlled by internal diffusion. On the other hand for rapid internal diffusion relative to external diffusion, the penetration thickness will be large and external diffusion controls the overall dissolution rate. The activation energy associated with internal diffusion is typically larger than external diffusion.

In view of the above discussion, is there any evidence in the $\ln k'$ vs $1/T$ data that the diffusion regime maybe changing as the temperature is increased? If so which regime appears to be rate controlling at the higher temperatures?

Effect of Agitation on Dissolution Rates

It is possible to observe the effect of agitation on dissolution by carrying out dissolution at different levels of agitation and observing the solid-liquid boundary with a video camera. When there is no agitation the dissolution rate is low. In this case the solvated polymer dragging down along the sides of the sample form long strips at the bottom of the sample which thin out and eventually snap, slowly disappearing into solution. Increasing the RPM of magnetic stirrer significantly enhances the dissolution rates. It is suggested



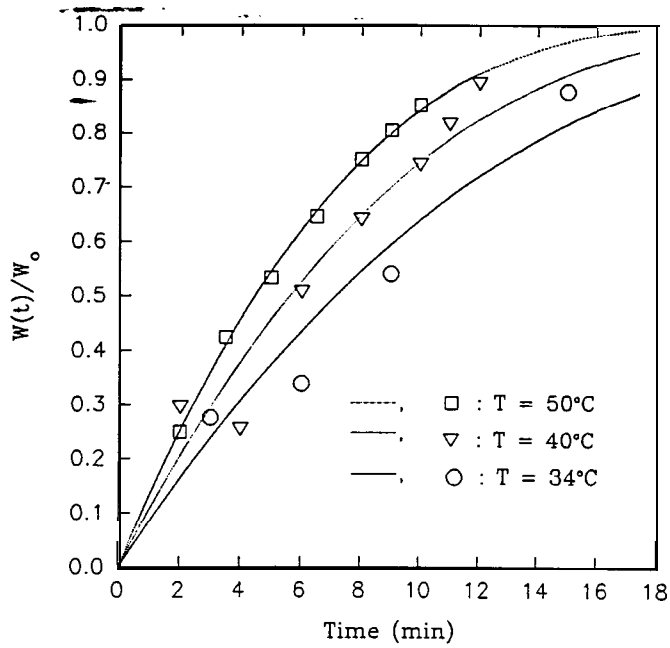


Figure 2. Dissolution Data in the Temperature Range 34–50°C

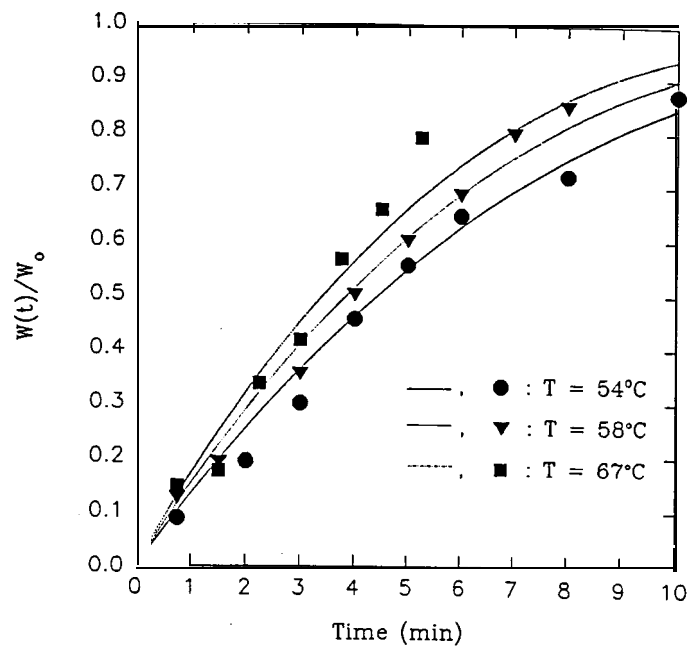


Figure 3. Dissolution Data in the Temperature Range 54–67°C

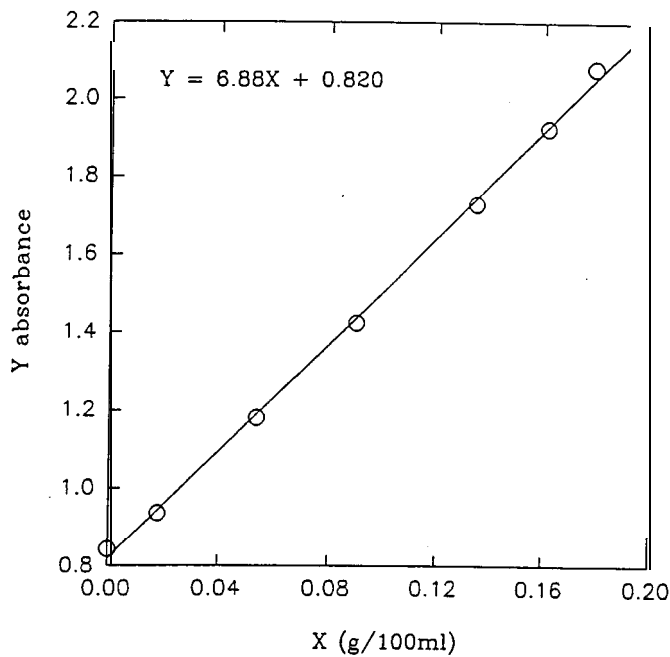


Figure 4. Calibration Curve for FTIR Absorbance vs. Binder Concentration

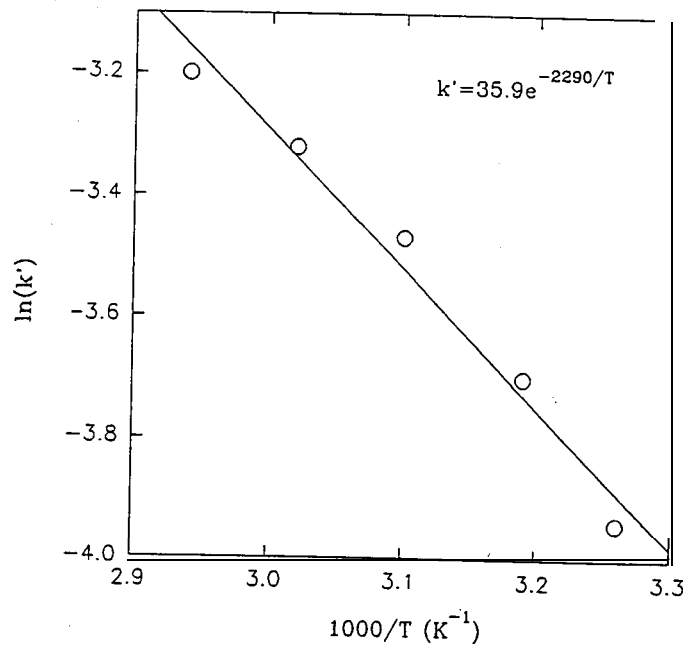


Figure 5. Variation of Velocity Constant with Temperature

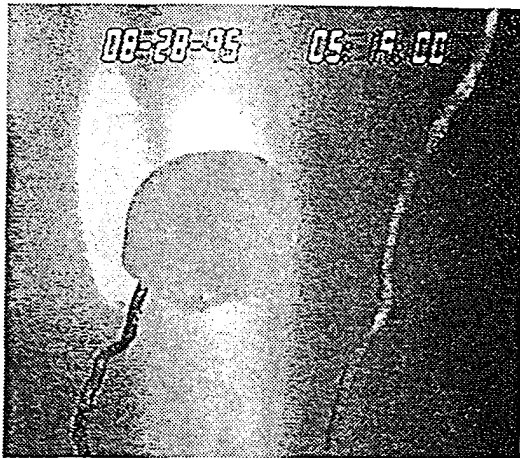
that students perform such experiments at several stirrer speeds and observe how the shape of the sample changes with time. An example of how the sample looks before and three minutes into the dissolution process is shown in Figure 6. However, the figure does not give any indication of the velocity field around the polymer sample.

Observation of the progress of dissolution and the velocity field around the particle with a video camera is much more revealing. Sample questions relevant to this observations are as follows:

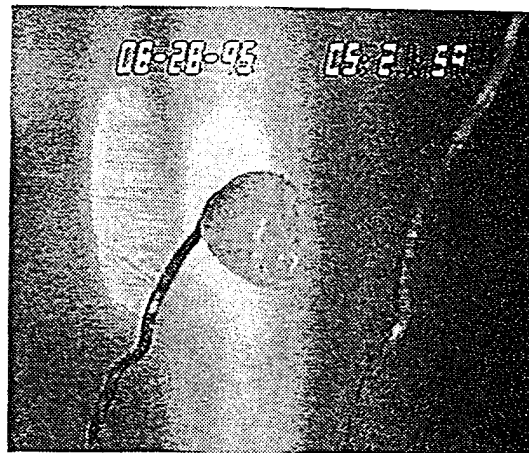
1. As the dissolution progresses the spherical sample does not retain its shape. Explain why the sphere does not shrink uniformly.
2. In view of the nature of the velocity field you have observed around the particle, how would you reevaluate the assumption of constant mass transfer coefficient k used in the mathematical model?
3. Consider the dissolution where there is no stirring. Do you observe any effect due to gravity? In the absence of gravity describe how the sample will look like as dissolution proceeds.

References

1. Lewis and Whitman, Industrial and Engineering Chemistry, Vol .16, p.1215 (1924).
2. Treybal, Mass Transfer Operations, McGraw Hill, New York (1 987).



a) beginning of dissolution;



b) after 180 seconds of dissolution.

Figure 6. Progress of Binder Dissolution



ZHIHUA CAO

Zhihua Cao is a graduate student in the chemical engineering program at Stevens Institute of Technology. He is a graduate of East China University of Chemical Technology. Currently he is working on his doctoral research area of dissolution and recovery of energetic materials.

DILHAN M. KALYON

Dilhan M. Kalyon is a professor in the Chemical Sciences and Engineering Program at Stevens Institute of Technology and Director of Highly Filled Materials Institute. His research is in the area of polymer engineering and science.

SUPHAN KOVENKLIOGLU

Suphan Kovenklioglu is a professor in the Chemical Sciences and Engineering Department at Stevens Institute of Technology. His research area is in reaction engineering and catalysis.

RAHMI YAZICI

Rahmi Yazici is a senior scientist at the Highly Filled Materials Institute at Stevens Institute of Technology. His research area is in material science and engineering.

