




Dissolution Rates of Oxetane Thermoplastic Elastomer for Dissolution Based Recycling of Elastomeric Formulations

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INTRODUCTION

Polymer dissolution has long been receiving attention for its importance in applications such as microlithography, controlled drug delivery and, more recently, in the recycling of polymers. Early work established the main features of polymer dissolution where a swollen layer forms during the induction period followed by the quasi-stationary dissolution period (1,2). Various models which have addressed polymer dissolution include: a) polymer disassociation where the polymer goes from gel-like entangled phase to free state in the liquid solution (3), b) relaxation controlled dissolution where the stress-relaxation rate is controlled by the reptation time (4), c) reptation controlled dissolution (5), d) a chain disentanglement model where the disentanglement time was taken to be in the order of the reptation time (6).

The focus of the present work is the dissolution of an oxetane thermoplastic elastomer which is being used as a binder in various energetic material formulations. The oxetane binder is an alternating block copolymer obtained from the polymerization of monomers. BAMO (bis(3-

azidomethylene)oxetane) crystalline homopolymer forming the hard block and AMMO ((3-azidomethylene-3-methyl)oxetane amorphous homopolymer forming the soft block. It is manufactured by the Thiokol Corporation under the trade name Poly(BAMO/AMMO) and is 25% BAMO. The oxetane binder was characterized using X-ray diffraction, differential scanning calorimetry and thermogravimetric analysis in our laboratories (7).

EXPERIMENTAL

Solubility Studies

Equilibrium solubilities of the oxetane binder in ethyl acetate were determined in the temperature range of 20-95 °C. Measured amounts of the oxetane binder and ethyl acetate were mixed in 10 ml graduated cylinder. The mixture was kept at constant temperature in a hot water bath for at least 24 hours. Formation of a sharp boundary between the solvent rich phase and polymer rich phase enabled determination of the volumes for both phases at equilibrium. Samples were taken from the solvent rich phase and analyzed by UV spectrophotometry.

Oxetane Binder Dissolution Experiments

The dissolution experiments were carried out in a transparent vessel shown in Figure 1. The transparent vessel consisted of a 500 ml pyrex bottle which is heated electrically from outside and equipped with temperature controller. The oxetane binder of about 0.4 g was shaped into a sphere and suspended at the end of a hooked wire in the transparent vessel. 400 ml of ethyl acetate was heated in an autoclave and delivered to the transparent vessel at the desired temperature and agitated at 300 rpm.

In the experiments described above solid/solvent contact surface area decreases with time and the oxetane binder concentration in solution is low throughout the dissolution process. Another set of experiments were performed by using larger quantities of the oxetane binder in order to achieve binder concentrations in solution approaching the solubility values. The as-received oxetane binder comes in lumps of irregular shape. About 40 g of the oxetane binder was first placed in the transparent vessel and heated above its melting temperature of 80 °C followed by overnight cooling to ambient temperature. This process molds the oxetane binder to a cylindrical shape at the bottom of the vessel and generates a flat and smooth surface on the top making it possible to accurately determine the solid/solvent contact area. In these experiments the solid/liquid surface area (which is equal to the inner cross-sectional area of the transparent vessel) remains constant during dissolution. The oxetane binder was heated to the desired temperature and the solvent was introduced at the same temperature from the autoclave in order to ensure temperature uniformity at the beginning of the dissolution process. At high viscosities magnetic stirrer is ineffective, hence in those cases agitation was achieved by placing the transparent vessel in a shaker apparatus.

The dissolution experiments indicated that the time associated with the swelling and

disentanglement of the polymeric chains i.e., the induction time was less than five seconds. In both sets of experiments samples were collected at regular time intervals and analyzed by a UV spectrophotometer.

Mathematical Model

Since the induction time was found to be less than 5 seconds, a quasi-stationary dissolution model is used. The quasi-stationary dissolution of the oxetane binder can be represented by a material balance for the oxetane binder where the rate of dissolution of the binder based on the solid/liquid interfacial area is equal to the rate of mass transfer of dissolved binder across the solid/liquid boundary layer:

$$-\frac{dm}{A dt} = k(C_e - C) \quad (1)$$

Here, m is the mass of the binder and A is the external surface area. Based on the film theory assumption, k is the mass transfer coefficient, C_e is the dissolved concentration on the liquid side of the solid/liquid film and C is the concentration in the bulk solution. The concentrations are based on the mass of the binder per unit solvent volume. The left hand side of Eq. 1 can be expressed in terms of binder concentration in solution by observing $-dm/dt = d(CV)/dt$ where V is the volume of the solvent. For constant solvent volume Eq. 1 can be written as follows

$$\frac{VdC}{A dt} = k(C_e - C) \quad (2)$$

When the mass transfer area A stays constant, Eq. 2 can be rearranged and integrated to give

$$C = C_e \left(1 - e^{-\frac{A}{V} kt} \right) \quad (3)$$

For experiments where the dissolving binder is of spherical shape, the mass transfer area decreases during the progress of dissolution. On the other hand, C always remains small enough to be neglected with respect to C_e . In order to integrate Eq. 2, the external surface area must be expressed in terms of concentration. This can be done by first expressing the external surface area in terms of the mass of the binder

$$A = \frac{4 \pi m^{2/3}}{\left(\frac{4}{3 \pi \rho}\right)^{2/3}} \quad (4)$$

The relationship between the mass of the oxetane binder and its concentration in solution i.e., $m = m^0 - CV$, can then be substituted into Eq. 4 to obtain

$$A = \frac{4 \pi (m_o - CV)^{2/3}}{\left(\frac{4}{3 \pi \rho}\right)^{2/3}} \quad (5)$$

Finally Eq. 5 can be substituted into Eq. 2 followed by integration with the initial condition that $C=0$ at $t=0$ to yield

$$C = \frac{m_o}{V} - \left[\left(\frac{m_o}{V} \right)^{1/3} - k^* t \right] \quad (6)$$

where:

$$k^* = \left(\frac{4 \pi}{3 V \rho^2} \right)^{1/3} C_e k \quad (7)$$

Eq. (6) is applicable until $t = (m^0/V)^{1/3}/k^*$ at which time all the oxetane binder is dissolved and the concentration of the dissolved binder in the solution is at the maximum level of m^0/V .

RESULTS AND DISCUSSION

Results of Solubility Experiments

Table 1 shows the equilibrium solubilities (C_e) as grams oxetane binder per 100 ml solvent. The temperature dependence of equilibrium solubility is not very strong with the equilibrium solubility increasing 25% in the temperature range of 20-95 °C. Equilibrium solubility values were determined from UV spectrophotometry where the characteristic absorbance of the dissolved oxetane binder at 254 nm was found to be a linear function of concentration. The volume fraction of solvent in the solid phase (ϕ_s) in equilibrium with the solvent phase was determined from material balance and is also shown in Table 1. The solvent volume fraction in the solid phase was about 1%.

Results for the Oxetane Binder Dissolution

a) Low Oxetane Binder Concentration, Spherical Sample

The results of the dissolution experiments of the oxetane binder shaped into a single sphere and contacted with ethyl acetate are summarized in Figure 2. Here the dissolved binder concentration is plotted as a function of time in the temperature range of 24-75 °C. The driving force for mass transfer in all these experiments is constant since the concentration of the dissolved oxetane binder is negligible relative to the equilibrium solubility value at the solid/liquid interface. Hence the leveling off in the oxetane binder concentration with time is due to diminishing surface area of the dissolving particle. The dissolution process was also monitored with a video camera which indicated that the extent of swelling is very small.

In polymer dissolution disentanglement rates are typically much faster than diffusion rates. Hence the dissolution rate data are either controlled by the diffusion of the solvated binder from the boundary layer into the bulk solvent or by the diffusion of the solvent into the dissolving binder. The activation energy was obtained from the Arrhenius plot of $\ln k$ vs. $1/T$ and was found to be 3.4 kcal/mole. This low activation energy would be compatible with a diffusion controlled process. In obtaining the mass transfer coefficient k , k^* (defined by Eq. 7) was first determined at each temperature from the best fit of the experimental data (Fig. 2) to the mathematical model given by Eq. 6. Eq. 7 was then used to calculate the k where the C_e were taken from the equilibrium solubility data at the prevailing temperature and the polymer density was taken to be constant at 1.26 g/cm³. The curves in Fig. 2 are based on Eq. 6 using the k^* values determined on the basis of best fit.

b) High Oxetane Binder Concentration, Constant Surface Area

In the second set of dissolution experiments the oxetane binder was melted and molded into cylindrical shape at the bottom of the vessel with a flat smooth constant surface area of contact with the solvent. Other features which are different than those carried out with the spherical binder are: a) oxetane binder to solvent ratio is much higher so that the solubility equilibrium is reached before all the binder is dissolved, b) agitation is achieved by placing the transparent vessel in a shaker apparatus where the resulting hydrodynamics are different than those with the spherical oxetane binder where a magnetic stirrer was used. Figure 3 summarizes the experimental data collected over the temperature range of 21-94 °C. The curves were obtained from the best fit of the mathematical model represented by Eq. 3 to the experimental data. In obtaining the best fit the equilibrium solubility (C_e) was treated as an unknown parameter, along with the mass transfer coefficient (k). Table 2 summarizes the k and C_e values obtained from the best fit where the C_e values are within 1% of the C_e values obtained from equilibrium solubility experiments (Table 1). The activation energy was calculated from the Arrhenius plot of $\ln k$ vs. $1/T$ and found to be 3.1 kcal/mole, which again implies diffusion control. The mass transfer coefficients here are about 20-30% lower than in experiments involving the spherical sample

where a magnetic agitator was used. In earlier work we observed that for Reynolds numbers higher than those obtained here with the magnetic stirrer the dissolution rates were a strong function of the agitation rate (7). Hence for both sets of dissolution experiments here it appears that the dissolution rate is controlled by the diffusion of the dissolved binder across the boundary layer rather than the diffusion of the solvent into the binder.

Results of Structural Characterization

The oxetane thermoplastic elastomer materials were characterized before and after dissolution experiments in order to assess the viability of the recycling methods by dissolution and precipitation (7). The FTIR measurements indicated no change in polymer structure. The x-ray diffraction measurements showed no measurable difference in the degree of crystallinity of the BAMO domains which was also confirmed by DSC results on melt transition energies.

CONCLUSIONS

Dissolution studies were carried out in the temperature range of 20-95 °C for an oxetane thermoplastic elastomer (binder) in well agitated vessels with ethyl acetate as the solvent. It was found that the induction period was less than 5 seconds. Monitoring of the dissolution process with a video camera also indicated that the extent of swelling was very small.

The dissolution rate data was correlated with a pseudo-stationary model based on the film theory. The assumption of solubility equilibrium at the solid/liquid interface was validated by comparing the equilibrium solubility parameters obtained from the model on the basis of best fit to the experimental equilibrium solubility values where the difference was found to be at most 1%. The mass transfer coefficients for the two different sets of experiments were also obtained on the basis of the best fit from Equations 3 and 6 and the corresponding activation energies were found to be 3.1 and 3.5 kcal/mole indicating that dissolution is diffusion controlled.

These results suggest that it would be possible to selectively dissolve and recover the oxetane thermoplastic elastomer from energetic material formulations where the oxetane is used as the binder. Selective dissolution of the oxetane binder must be the first step in separation and recovery of all ingredients in the energetic material formulation since the binder encapsulates these ingredients. Once the oxetane binder is removed recovery of other ingredients can proceed. The rate data provided here would facilitate design and scale-up of the equipment necessary to carry out the selective dissolution of the oxetane binder.

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Table 1. Equilibrium Solubility Data for Oxetane Binder in Ethyl Acetate

Temperature (°C)	Ce (g/100ml)	ϕ^s (ml/ml)
20	33.1	0.0123
40	35.0	0.0125
60	37.1	0.0128
80	39.6	0.0131
95	41.8	0.0133

Table 2. Parameter Estimation for Oxetane Binder Dissolution in Ethyl Acetate (High Concentration)

Temperature (°C)	Mass Transfer Coefficient (cm/min)	Solubility (g/100ml)
21	0.032	33.5
43	0.051	35.3
66	0.070	37.0
80	0.073	40.0
94	0.094	42.1

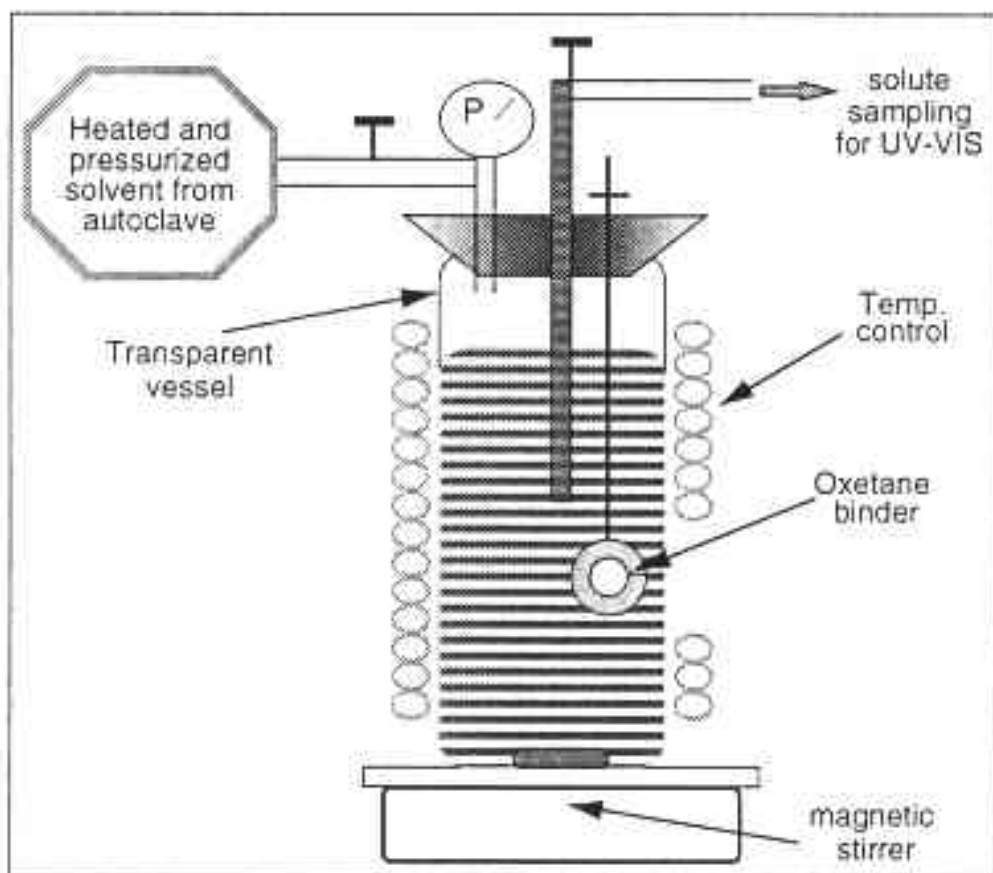


Figure 1. Experimental Apparatus for Dissolution Studies

