Polymerization with Redox Initiators

INTRODUCTION

It has been established through studies in our laboratories that hazardous wastes can be encapsulated and immobilized in a polyester matrix.[1-9]

There are two key steps in the polyester encapsulation process. In the first step, emulsification of the aqueous waste with the neat polyester resin is carried out. Various techniques for emulsion formation have been evaluated. A basic study has been done on the quality of the emulsion in terms of applied shear, droplet size distribution, viscosity, and the corresponding leach characteristics of the encapsulated waste.

The second step is the solidification of the emulsion. The polymerization reaction, which involves the crosslinking of the resin matrix, is exothermic and a peak exotherm is associated with the curing of the emulsion. This exothermicity could be coupled with curing reaction kinetic parameters to simulate, on the computer, cure temperature profiles, which would help decide on optimum length/diameter ratios for commercial size containers. In order to simulate these profiles, some basic kinetic data, not available in the literature, have been developed in our laboratories and these are described here.

BACKGROUND

In the polyester encapsulation process, an unsaturated polyester resin, composed of three basic types of structural units—unsaturated acids, saturated acids, and glycols—and dissolved in a solvent such as styrene, is used for the emulsification. A commercial water-extensible polyester resin, Aropol WEP 661-P (Ashland Chemical Co., Div. of Ashland Oil, Inc., Columbus, Ohio 43216), which contains 60% styrene, has been used in all the laboratory and pilot plant runs. A water-in-oil emulsion is formed by dispersing the waste solution as micron-sized droplets in the continuous resin phase. WEP 661-P contains proprietary emulsifying agents which considerably lower the energy requirements[10] for forming a stable "water-in-resin" emulsion. During the curing, styrene serves to crosslink the polyester chains, thus forming a rigid three-dimensional structure.

As opposed to thermal cleavage of peroxides, a reduction–oxidation (redox) system enables free-radical polymerization to take place at room temperature. An example of a redox system useful for the polymerization of Aropol WEP 661-P is a dimethyl aniline (DMA) and methyl ethyl ketone peroxide (MEKP). Once a free radical is generated—from whatever source—subsequent reactions follow the traditional free-radical polymerization kinetics.[11] The rate of polymerization in the (MEKP-DMA)-initiated system is then given as

$$R_p = -\frac{dM}{dt} = \left[\left(\frac{k_p}{2k_t} \right)^{1/2} f k_d \right]^{1/2} (ab)^{1/2} (M) \tag{1}$$

where k_p is the propagation rate constant, k_t is the termination rate constant, k_d is the dissociation rate constant (for peroxide), f is the initiator efficiency ($f = 1.0$ implies each initiator molecule which decomposes will produce one growing polymer chain and a lower number indicates lower initiator efficiency), a is the concentration of promoter (DMA), b is the concentration of peroxide (MEKP), and M is the concentration of monomer.

The WEP 661-P contains 60% styrene monomer (Technical Data on Aropol WEP-661-P, Ashland Chemical Co.) and as such the curing reaction can be approximated well by the polymerization of styrene to form polystyrene which crosslinks the polyester chains. Since the resin composition is proprietary, precise numbers for the promoter concentration are not available. Realistic approximate figures based on the published literature[12] have been used in computations discussed elsewhere.[5]

The other parameters that need to be determined for the computations are k_p, k_t, k_d, and f. The k_p has been evaluated[13] for styrene and is not likely to change for the resin reaction. Values for the termination constant k_t have also been reported for bulk styrene but k_t is a strong function of viscosity[11] of the styrene (Trommsdorff effect). High viscosity hinders the diffusion of polymer chains and termination is reduced. It is estimated that typical k_t values for bulk styrene polymerization
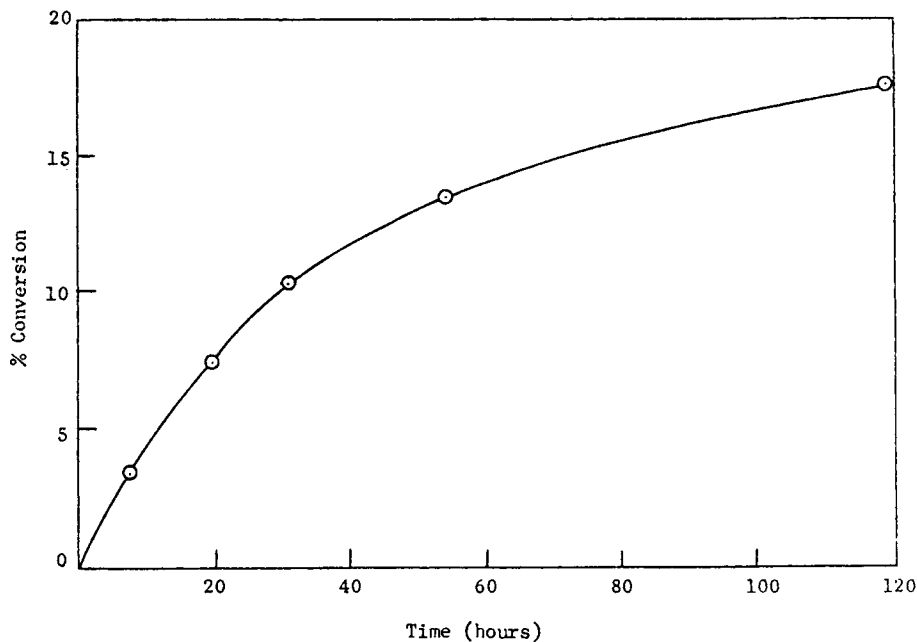
Fig. 1. Plot of conversion vs. polymerization time.

are reduced by several orders of magnitude for viscosities encountered during the curing of the waste-in-resin emulsion. Values for f and the dissociation constant k_d for the system MEKP-DMA-cobalt naphthenate (cobalt naphthenate is a commercial term; its major component is a cobaltous salt of 2-ethyl hexanoic acid) are not available in the literature. Laboratory experiments were, therefore, performed based on the procedure described by O'Driscoll.[14] Equation (1) differs from the one used by O'Driscoll[14] by a factor of 2. The reason for this (ref. 11, p. 191) is that one peroxide molecule yields only one radical capable of initiating polymerization.

EVALUATION OF k_d AND f

O'Driscoll and McArdle[14] have developed a general method for describing the course of polymerization when a redox system is used. When the extent of polymerization is measured as a function of time, sufficient data are then available to determine the second-order decomposition rate constant and the overall catalyst efficiency in initiating polymerization chains.

In eq. (1), k_p^2/k_t has been measured for styrene.[13] Equation (1) can be integrated to obtain explicit solutions for the catalyst concentrations a and b as functions of time. With a_0 and b_0 as the initial concentrations of promoter and initiator, respectively, and based on the second-order rate expression and stoichiometry, a final expression of the form

$$\frac{M_\infty}{M_t} = \left[\frac{(a_0/b_0)^{1/2} \exp[k_d t(a_0 - b_0)/2] - 1}{(a_0/b_0)^{1/2} \exp[k_d t(a_0 - b_0)/2] + 1}\right]^{(fk_p^2 k_d/2k_t)^{1/2} \cdots} \tag{2}$$

is obtained, where M_∞ is the limiting conversion; from this, k_d can be determined.

EXPERIMENTAL PROCEDURE

Styrene, as supplied by the manufacturer, was first stripped of its inhibitor by washing several times with 10% sodium hydroxide solution. The styrene was then dried over anhydrous sodium sulfate and doubly promoted[12] with (1) 0.1% by weight of 6% cobalt naphthenate, and (2) 0.05% by weight of DMA to approximate promoter concentrations in WEP 661-P.

The promoted styrene (75 g) was transferred to each of five conical flasks. Nitrogen was passed over the liquid in each flask to displace the air and provide a nonoxidizing atmosphere. The flasks were then sealed with serum stoppers and 0.5 ml MEKP [this is about 0.6% by weight ratio of initiator to styrene or 1% by weight ratio initiator to WEP 661-P resin (as used in the immobilization runs)]
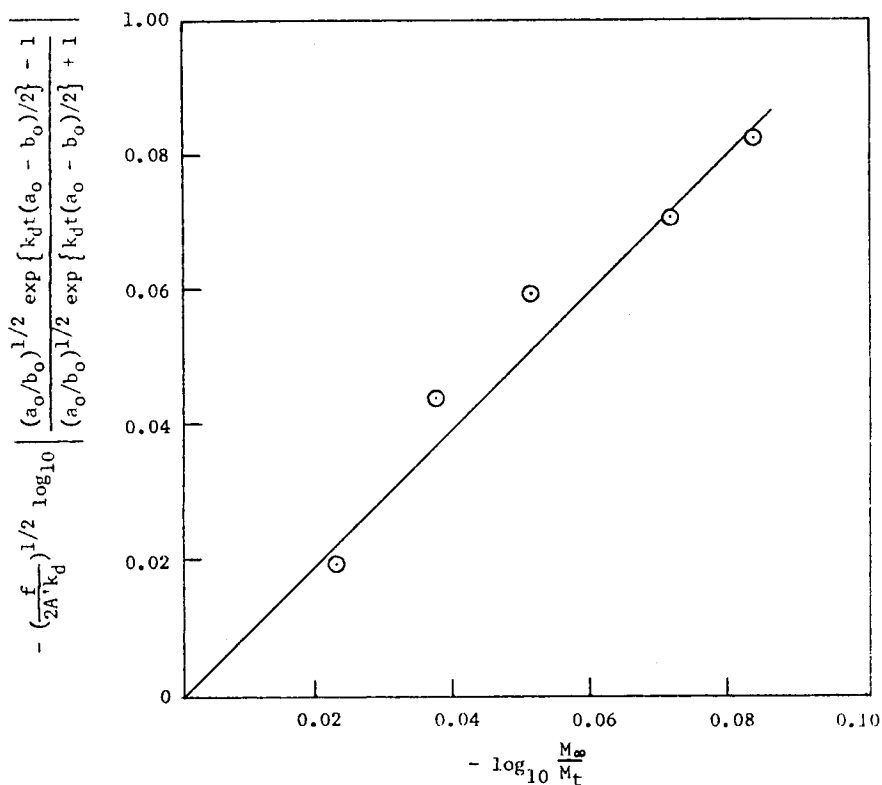
Fig. 2. Plot of eq. (2).

injected into the flasks by a hypodermic needle. The flasks were placed in a constant temperature water bath at room temperature (21°C).

To measure the conversion, the reaction was stopped by adding a pinch of hydroquinone to the contents of the flask. The polystyrene was then precipitated in excess methanol. The bulk of the precipitate was placed on a watch glass, allowed to dry to constant weight at 32°C, and then weighed.

RESULTS

$$DMA[C_6H_5HO(CH_3)_2] = 0.004 \text{ mole/liter}$$

$$\text{Cobalt naphthenate } [Co(C_8H_{15}O_2)_2] = 0.00019 \text{ mole/liter}$$

$$\text{MEKP (60.5\% by weight of } C_8H_{16}O_4) = 0.021 \text{ mole/liter}$$

$$M_0 = 10.56 \text{ mole/liter}$$

TABLE I
Conversion Versus Polymerization Time

Time, sec	% Conversion	M (mole/liter)	$\log_{10}(M_t/M)$
0	0.0	$M_0 = 10.6$	0.084
27,000	2.9	10.3	0.071
70,200	7.2	9.8	0.051
111,600	10.3	9.5	0.036
194,400	13.4	9.2	0.022
428,400	17.5	$M_\infty = 8.7$	0

Figure 1 shows a plot of degree of conversion versus time. The ordinate in Figure 2, which is the log of the right-hand side of eq. (2), is calculated (an average value of $k_p^2/k_t = 7000$ liter/mole sec has been used) for various combinations of values of f and k_d. A straight line is then fit by linear regression between these values and the corresponding values on the last column in Table I. The best fit is obtained (Fig. 2) for $k_d = 4.0 \times 10^{-4}$ liter/mol hr and $f = 0.28$.

References

1. R. V. Subramanian and R. A. V. Raff, "Immobilization of Low-Level Radioactive Wastes," AIChE 80th National Meeting, Boston, MA, 1975.
2. M. Juloori, M. S. thesis, Chemical Engineering, Washington State University, Pullman, WA, 1976.
3. W. P. Wu, M. S. thesis, Materials Science and Engineering, Washington State University Pullman, WA, 1978.
4. P. K. Jain, M. S. thesis, Chemical Engineering, Washington State University, Pullman, WA, 1978.
5. R. K. Biyani, M. S. thesis, Chemical Engineering, Washington State University, Pullman, WA, 1978.
6. R. Mahalingam, M. Juloori, R. V. Subramanian, and W. P. Wu, "Pilot Plant Studies on the Polyester Encapsulation Process for Hazardous Wastes," Proceedings of the National Conference on Treatment and Disposal of Industrial Wastewaters and Residues, Houston, TX, 1977.
7. R. V. Subramanian, W. P. Wu, R. Mahalingam, and M. Juloori, see ref. 6.
8. "Polyester Process for Immobilization of Hazardous Wastes," Workshop, Washington State University, Pullman, WA, 1977.
9. R. V. Subramanian and R. Mahalingam, Stabilization/Solidification Options for Hazardous Waste Disposal, R. B. Pojasek, Ed., Ann Arbor Science, Ann Arbor, MI, 1978.
10. "Aropol WEP Resins for Casting," Tech. Bull. 1166-1, Ashland Chemical Co., Div. of Ashland Oil, Inc., Columbus, OH 43216.
11. G. Odian, Principles of Polymerization, McGraw-Hill, New York, 1970.
12. "Ketone Peroxides," Product Bulletin, Form #020176-5M, Lucidol Div., Pennwalt Corp., NY.
13. C. Walling, Free Radicals in Solution, Wiley, New York, 1957.
14. K. R. O'Driscoll and A. R. McArdle, J. Polym. Sci., 11, 557 (1959).

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