《報 文》

界面重合反應器內에서의 破裂現象分析

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Breakage Phenomena in a Interfacial Polymerization Reactor

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Abstract

Breakage phenomena observed in a novel interfacial polymerization reactor was characterized by a breakage parameter (t_b/t_m) which can be interpreted to be the ratio of the breakage time divided by the mean residence time. This parameter was calculated from the equation relating the mean fibrid sizes in the product and the initial streams. The usefulness and validity of the analysis were checked bycomparing the calculated variance of the product distribution against experimental data. The breakage parameters obtained from the 25 gallon unit data were also related to the reactor volume and r. p. m. by nonlinear regression analysis.

When an interfacial polymerization is carried out in an agitated vessel, a suspension of unusual fibrous material results. This pulplike synthetic material is called fibrids (Ref. 1, 2). More precisely, fibrids are defined as nonrigid wholly synthetic polymeric particles which are capable of forming paperlike structures on a paper-making machine (Ref. 2).

These fibrids are normally not uniform in size and this nonuniformity often is undesirable in terms of practical application of the product. This work is concerned with the mathematical simulation of the breakage that takes place within the reactor to minimize the variance of the fibrid size distribution. The work was also intended to obtain a sound scale-up technique for this unsual polymerization system.

Experimental

A schematic diagram of the condensation polymerization system is shown in Figure 1. As indicated, an aqueous solution of reactant whose main constituent is an amine compound is pumped into the system before the start-up. After the reactor content is at a desired level, the high speed agitator is turned on to provide a turbulent vortex. Then the second reactant B which is a polymeric solution with active isocyanate group is introduced streamwise onto the vortex. The fibrids are normally formed instantaneously upon contact and swept into the center of the vortex. The fibrids then undergo some internal recirculation before leaving the reactor. A periodic sampling of the product showed that the fibridator reaches a steady state in 3-4 mean residence times, as expected from well-stirred reactor theory.

Figure 1 also shows a U loop in the reachant B stream which was charged with reactant B with red pigment. The content of the U tube was injected into the system by manipulating the valves after the system came to steady state. The normal flow of re-

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actant B which gives white fibrids resumes after the almost instantaneous injection of the pigmented reactant B. The resulting red fibrids among the normal white fibrids were collected at regular time intervals to trace the history of fibrid break-up. The first gr-

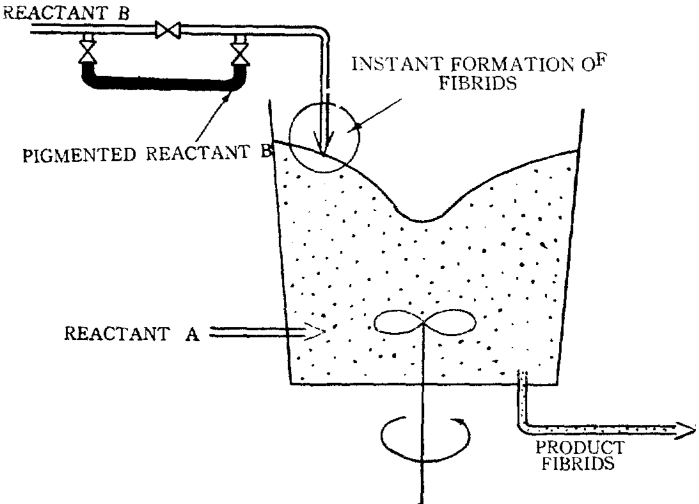

Fig. 1. Interfacial Polymerization Reactor

oup of red fibrids which appeared at the outlet were collected and classified into five fractions according to size by means of Clark classifier used in the paper industry. The distribution thus obtained was used as a good estimate of the initial distribution of fibrids which were formed at the first conact of two reactants A and B. The justification of the above method was based on the fact that a small portion of an incoming fluid into a well-stirred reactor always shows up immediately at the outlet without any internal circulation.

Of course, the other pigmented fibrids were also found among the regular white fibrids continuously for the next 3 to 4 mean residence times and these were sampled at regular intervals for a transient study. The main concern, however, is to predict the steady state distribution of the fibrids from the knowledge of an initial distribution. This is the subject of this work.

Mathematical Analysis

The strategy of the analysis, however, was to represent the system with a single characteristic variable. This approach was motivated by the belief that a simulation with a single parameter is usually clear cut and easier to manupulate than the multivariable model.

Consider now an agitated tank with a continuous feed and a continuous product removal. We assume the tank to be well mixed so that the size distribution in the product slurry is identical to that of the reactor tank. As mentioned earlier, the fibrids are formed instantaneously on the surface of the vortex as the two reactants A and B, come into contact. These fibrids then undergo a size reduction either due to the turbulent shear field or by coming into an actual conact with the high speed blade. To represent the system mathematically, we let

$I(\mathrm{m})$=Fraction of fibrids in the size range (m, m+dm) as they form instantly upon contact of reactants A and B.

$R(\mathrm{m})$=Fraction of fibrids in the the size range (m, m+dm) in the reactor and the product slurry.

n_i, n_o=Input and output rates of fibrids, respectively.

N=Total number of fibrids in the reactor

$g(\mathrm{m})$=Net rate of fibrid generation with respect to the particular size range under consideration, i. e., (m, m+dm).

With the above quantities defined, we can write the following number blance for a steady state operation. It should be noted that the balance is written for fibrids of a particular size range (m, m+dm) only. The size balance equation is:

$$n_i I(\mathrm{m}) - n_o R(\mathrm{m}) + g(\mathrm{m}) = 0 \qquad (1)$$

(Input) (Output) (Generation)

In order to define $g(\mathrm{m})$ more precisely, we will assume the following.

1. All fibrids, regardless of the size, are broken up at the same break-up frequency of $(1/t_b)$. The quantity, t_b, is therefore the time required for the fibrids to break up.

2. Each fibrid breaks into two smaller fibrids of equal size.

Needless to say, the above simplification is highly idealized. Under the stipulation, the generation term becomes:

$$g(\mathrm{m})=\frac{N}{t_b}2R(2\mathrm{m})-\frac{N}{t_b}R(\mathrm{m}) \qquad (2)$$

(Appearance of 2 fibrids of size m) (Disappearance of 1 fibrid of size m)

The equation balances the breakage of a large fibrid of size 2m and the disappearance of a fibrid m which occurs simultaneously. Combination of (1) and (2) then gives the desired number balance below:

$$n_i I(\mathrm{m})-n_o R(\mathrm{m})+\frac{N}{t_b}[2R(2\mathrm{m})-R(\mathrm{m})]=0 \quad (3)$$

The above equation is applicable for any size m either large or small. A similar balance on the entire fibrids, on the other hand, simply is:

$$n_i-n_o+\frac{N}{t_b}=0 \qquad (4)$$

Next, the elimination of n_o from equations (3) and (4) gives:

$$n_i I(\mathrm{m})-(n_i+\frac{N}{t_b})R(\mathrm{m})+\frac{N}{t_b}[2R(2\mathrm{m})-R(\mathrm{m})]=0 \qquad (5)$$

The rearrangement of (5) then gives:

$$(1-\alpha)I(\mathrm{m})-R(\mathrm{m})+\alpha R(2\mathrm{m})=0 \qquad (6)$$

Where:

$$\alpha=\frac{2(\frac{N}{n_i})}{t_b+2(\frac{N}{n_i})}=\frac{2}{(\frac{t_b}{t_m})+2} \qquad (7)$$

In the above equation, t_m is defined to be (N/n_i) which is the average residence time of the fibrids in the reactor. Note that α is a function of the single ratio (t_b/t_m) and that the breakage phenomena is characterized entirely by this ratio. We will now attempt to obtain a solution to the governing equation (6).

Recall that the breakage process, under the hypothesis, is such that the resulting particle size is half of the original one before breakage. This suggests the following transformation of variable.

$$m=m_o\frac{1}{2y} \qquad (8)$$

or

$$y=-\frac{ln(\frac{m}{m_o})}{ln2} \qquad (9)$$

It should be noted the value of fibrid size m is normalized with respect to the longest fibrid size expected so that its numerical value is always less than 1.0. The value of y, in turn, therefore is always larger than zero. Application of this transformation to the governing equation (6) then yields the following linear difference equation:

$$(1-\alpha)I'(y)-R'(y)+\alpha R'(y-1)=0 \qquad (10)$$

Where primes are added to emphasize the independent variable change of m to y.

The solution of this equation can be obtained by applying a z-transform which is definned by:

$$\bar{I}(z)=\sum_{y=0}^{\infty}z^{-y}I'(y),\quad y=0,1,2,3\ldots\ldots \qquad (11)$$

This is the discrete data counterpart of the more common Laplace transform. First, multiply $\sum_{y=0}^{\infty}z^{-y}$ to all the terms of (10):

$$(1-\alpha)\sum_{y=0}^{\infty}z^{-y}I(y)-\sum_{y=0}^{\infty}z^{-y}R(y)+\sum_{y=0}^{\infty}z^{-y}R(y-1)=0 \quad (12)$$

But recall that $R(y)=0$ for $y<0$ since none of the fibrids get bigger than m_o. The last term of (12) therefore can be altered to give the following two equations:

$$(1-\alpha)\sum_{y=0}^{\infty}z^{-y}I(y)-\sum_{y=0}^{\infty}z^{-y}R(y)+\alpha z^{-1}\sum_{y=0}^{\infty}z^{-(y-1)}R(y-1)=0 \qquad (13)$$

$$(1-\alpha)\sum_{y=0}^{\infty}z^{-y}I(y)-\sum_{y=0}^{\infty}z^{-y}R(y)+\alpha z^{-1}\sum_{y=0}^{\infty}z^{-y}R(y)=0 \qquad (14)$$

In the transform notation, this becomes

$$(1-\alpha)\bar{I}(z)-\bar{R}(z)+\alpha z^{-1}\bar{R}(z)=0 \qquad (15)$$

$$\therefore\ \bar{R}(z)=\frac{(1-\alpha)\ \bar{I}(z)}{1-\alpha z^{-1}} \qquad (16)$$

The above equation relates the input and output distribution of fibrids in the transformed notation. In our case, we found that all the fibrids were initially of unit size. Therefore

$$I(m)=\begin{pmatrix}1, & \text{if } m=m_o\\ 0, & \text{otherwise}\end{pmatrix} \qquad (17)$$

or

$$I'(y)=\begin{pmatrix}1, & \text{when } y=0\\ 0, & \text{everywhere else}\end{pmatrix} \qquad (18)$$

Even with this limiting narrow distribution initially, a broad product distribution is created.

The transform is simply

$$\bar{I}(z)=1 \qquad (19)$$

Substitution of (19) to (16) then gives

$$\overline{R}(z)=\frac{(1-\alpha)}{1-\alpha z^{-1}}=(1-\alpha)\sum_{y=0}^{\infty}\alpha^{y}z^{-y} \tag{20}$$

But by definition

$$\overline{R}(z)\equiv\sum_{y=0}^{\infty}z^{-y}\ R'(y) \tag{21}$$

Therefore comparison of (20) and (21) gives

$$R'(y)=(1-\alpha)\ \alpha^{y} \tag{22}$$

where $m=m_o\frac{1}{2^y}$, $y=0, 1, 2.$

The resultant product fibrid distribution $R'(y)$ then can be plotted either against y or m. More concisely, however, one can compute the average size and the variance of the distribution. The mean of the fibrid distribution which is the flrst moment of distribution can be stated as

$$\mu\equiv M_1\equiv\sum_{y=0}^{\infty}m(y)\ R'(y) \tag{23}$$

Inserting the result of (22)

$$\begin{aligned}\mu=M_1&=m_o(1-\alpha)\sum_{y=0}^{\infty}2^{-y}\alpha^{y}\\&=m_o(1-\alpha)\sum_{y=0}^{\infty}\left(\frac{\alpha}{2}\right)^{y}\\&=m_o(1-\alpha)\left(\frac{1}{1-\frac{\alpha}{2}}\right)\end{aligned} \tag{24}$$

Equation (24) can be used to calculate α. The breakage parameter t_b/t_m, which can be interpreted as the ratio of the breakage time divided by the fibrid mean residence time then can be computed from Equation (7).

The consistency of the analysis is then checked by comparing the calculated variance of distribution against the experimental data. To derive the equation for the variance of the distribution, however, we will show how the moments of distributions are related to the z-transform. By definition, kth moment of distribution is defined as

$$\begin{aligned}M_k&\equiv\sum_{y=0}^{\infty}R'(y)\ [m(y)]^k\\&=m_o^k\sum_{y=0}^{\infty}R'(y)\ (2^{-y})^k\\&=m_o^k\sum_{y=0}^{\infty}R'(y)\ (2^k)^{-y}\end{aligned} \tag{26}$$

Recall that the z-transform of the product was defined as

$$\bar{R}(z)\equiv\sum_{y=0}^{\infty}R'(y)z^{-y} \tag{26}$$

Comparison of equations (25) and (26) then gives the following simple relation between the moments of distribution and the z-transform

$$M_k=m_o^k\overline{R}(z)\,|_{z=2^k} \tag{27}$$

Thus, the mean of the product fibrid distribution can be simply obtained by substituting 2^k for z in equation (20) multiplied by m_o which yields identical result shown in equation (24).

Similarly, the second moment of distribution is

$$M_2=m_o^2\frac{1-\alpha}{1-\alpha(\frac{1}{4})} \tag{28}$$

Furthermore the variance of distribution is related to the moments by

$$\sigma^2=M_2-(M_1)^2 \tag{29}$$

In our case, the variance of the distribution can be predicted by

$$\sigma^2=\left[\frac{1-\alpha}{1-\frac{\alpha}{4}}-\left(\frac{1-\alpha}{1-\frac{\alpha}{2}}\right)^2\right]m_o^2 \tag{30}$$

The experimental data, t_b/t_m calculated by equation (24) and experimental values of variances are shown in Table. 1. These values are plotted against the theoretical curve of equation (30) in Figure 2. It can be seen that the agreement is good, verifying the usefulness of our model.

Table 1. Experimental Data and Mathematical Analysis of 25-Gallon Fibrid Reactor

Run	Reactor Volume, Gal.	Agitator Rpm.	Average Size of Product Fibrids (Inches)	Variance of Product Fibrid Distribution	Breakage Parameter (t_b/t_m)
345	20	3500	0.0365	0.812	2.38
346	15	3500	0.0336	0.815	2.14
347	15	3500	0.0280	0.709	1.80
348	16	3500	0.0280	0.734	1.80
349	20.5	3500	0.0396	0.761	2.70
350	15	3500	0.0311	0.736	1.98
351	20	3500	0.0338	0.785	2.16
352	15	3500	0.0305	0.765	1.94
353	20.5	3500	0.0320	0.750	2.03
356	16.5	2330	0.0382	0.762	2.54
357	21	2330	0.0392	0.878	2.65
358	14.3	2330	0.0375	0.829	2.47
359	15	2330	0.0404	0.849	2.78
360	20.4	2330	0.0381	0.833	2.54
361	20.6	2330	0.0426	0.837	3.08
362	14.0	2330	0.0430	0.820	3.15
363	20.8	2330	0.0353	0.837	2.27

Notes: (1) Initial distribution of fibrids was found to be sharp around the mean size of 0.063 inches for all runs.
(2) Product flow rate was 2.8 gallons/minute.

Along with the mathematical analysis, we have also subjected the factorially designed experimental

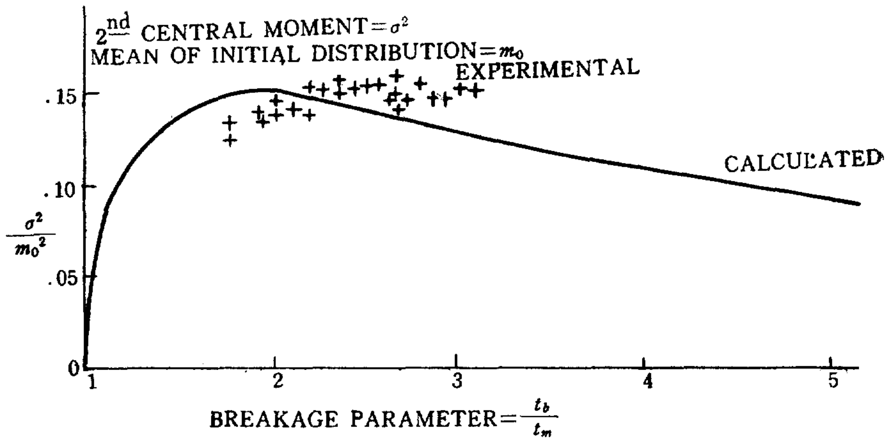

Fig. 2 Product Variance Related to the Breakage Parameter Data for 25-Gallon Unit.

results to the nonlinear regression analysis. The examination of the curve fitting by comparing the standard deviation against the residual standard deviation indicated that the breakage parameter is a function of reactor volume and the agitator speed. The response contour curve of this dependence is shown in Figure 3. This plot can be used to select process conditions. For example, Figure 2 indicates that the breakage parameter should be close to 1.0 if fibrids of uniform size are desired. Figure 3 then indicates how readily such condition can be realized.

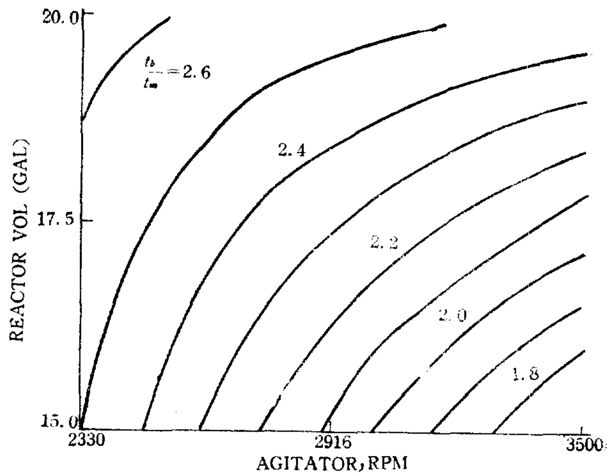

Fig. 3 Breakage Parameter, (t_b/t_m) as a Function of Operating Variables.

Conclusion

The work thus far conducted suggests that the breakage parameter, (t_b/t_m), can be used successfully to represent the breakage phenomena occuring in an interfacial polymerization reactor. The analysis also gave indications of the difficulty of producing fibrids of uniform size in a large reactor. It is believed that the approach can be applied in analyzing many other unit operations where breakage or size reduction plays an important role.

Acknowledgements

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References

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Nomenclature

$I(m)$=Fraction of fibrids in the size range $(m, m+dm)$ in the initial distribution.

$R(m)$=Fraction of fibrids in the size range $(m, m+dm)$ the reactor and in the product slurry.

$I'(y)$ and $R'(y)$=Function $I(m)$ and $R(m)$ with change in independent variable according to (9)

n_i, n_o=Input and output rates of fibrids.

N=Total number of fibrids in the reactor.

$g(m)$=Net rate of fibrid generation with respect to the size range $(m, m+dm)$.

t_b=Time required for the flbrid to break up.

t_m=Average fibrid residence time in the reactor, (N/n_i), approximated by (Q/V).

α =Defined by Equation (7).

y =Defined by Equation (9).

z =z-transform parameter.

β =Parameter in the Pascal distribution.

D=Parameter in the Poisson distribution.

M_k=kth moment of distribution.

k =A parameter in the mements of distribution.

μ =Mean the product distribution.

δ^2 =Variance of the product distribution.

V =Reactor volume.

Q =Product flow rate.

t_b/t_m=Breakage parameter.

m_o=Reference fibrid size which can be taken to be the largest size expected.

Appendix

1) **Initial distribution of Pascal type**

In this case,

$$I(y)=(1-\beta)\beta^y$$

where (31)

$$m=m_o2^{-y},\quad y=0, 1, 2, \ldots\ldots$$

For simplicity, also assume $m_o=1$. The z-transform of the above distribution is

$$\overline{I}(z)=\frac{1-\beta}{1-\beta z^{-1}} \tag{32}$$

The transform of the product distribution obtained by substituting (32) into (16) which gives

$$\overline{R}(z)=\frac{(1-\alpha)\ (1-\beta)}{(1-\alpha z^{-1})\ (1-\beta z^{-1})}$$

$$=(1-\alpha)\ (1-\beta)\sum_{y=0}^{\infty}z^{-y}\{\sum_{k=0}^{y}y\ \ ky-k\}$$

$$=\frac{(1-\alpha)(1-\beta)}{\frac{\beta}{\alpha}-1}\sum_{y=0}^{\infty}z^{-y}[\beta^y-\alpha^y] \tag{33}$$

where we have expanded the transform and evaluated the sums. By inspection, the desired product distribution can be seen to be

$$R'(y)=\frac{(1-\beta)\ (1-\alpha)}{\frac{\beta}{\alpha}-1}(\beta^y-\alpha^y) \tag{34}$$

$$m=2^{-y},\quad y=0, 1, 2\ldots\ldots$$

2) **Initial distribution of Poisson type**

$$I(y)=\frac{e^{-D}D^y}{y\,!} \tag{35}$$

$$m=2^{-y},\quad y=0, 1, 2\ldots\ldots$$

The z-transform is

$$\overline{I}(z)=e^{-D}e^{D/z} \tag{36}$$

Using equation (16),

$$\overline{R}(z)=\frac{(1-\alpha)e^{-D}e^{D/z}}{(1-\alpha_z^{-1})} \tag{37}$$

Expanding (37) and identifying the coefficients of z^{-y}, we get the desired inverse of

$$R(y)=(1-\alpha)e^{-D}\sum_{i=0}^{y}\frac{d^y\alpha^{y-i}}{i\,!} \tag{38}$$

$$m=2^{-y},\quad y=0, 1, 2, 3\ldots$$

Both cases are realistic examples of possible cases in practice.