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A Kinetic Model for the Acid-Catalyzed Decomposition of Delrin

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SUMMARY

A kinetic model is derived for the acid-catalyzed decomposition of Delrin, an acetal-formaldehyde resin. The kinetic model proposed assumes the hydrolysis of Delrin to form polyformaldehyde and the subsequent decomposition of polyformaldehyde to formaldehyde.

The kinetic model is tested for a Delrin-citric-acid system. A nonlinear regression analysis is used to predict the experimental thermograms between 25 and 300°C and for a 10-fold range of the initial citric acid concentration (2-20% by weight).

In the model the hydrolysis reaction is first-order in Delrin and half-order in citric acid, and the decomposition of polyformaldehyde is zero-order in polyformaldehyde.

The model successfully predicts the thermograms with a maximum error of 5%.

INTRODUCTION

Delrin is an acetal-formaldehyde resin with many industrial uses. In aerospace research it may have application because it decomposes to a simple pyrolysis gas, formaldehyde, with no residual char. Both of these properties help to simplify analysis of ablation phenomena where chemical

Fig. 1. Cahn balance thermogravimetric analyzer.

decomposition is coupled with mass and heat transfer. One of the inputs to such an analysis of ablator performance is the kinetics of the decomposition of the ablator. Therefore, in order to analyze the performance of an ablator, its decomposition must be analyzed.

A number of high-melting-point organic acids, including citric acid, catalyze the decomposition reaction of Delrin. Isophthalic and tartaric acid are two others that can be used successfully. The citric acid-Delrin system was chosen for kinetic analysis because it is under study in our ablation facilities. Pure Delrin decomposes at about 300°C. With acid as a catalyst, Delrin can be decomposed to formaldehyde at lower temperatures and its rate of decomposition can be controlled. Thus, the kinetic effects in ablation performance can be controlled systematically over a wide range of physical conditions.

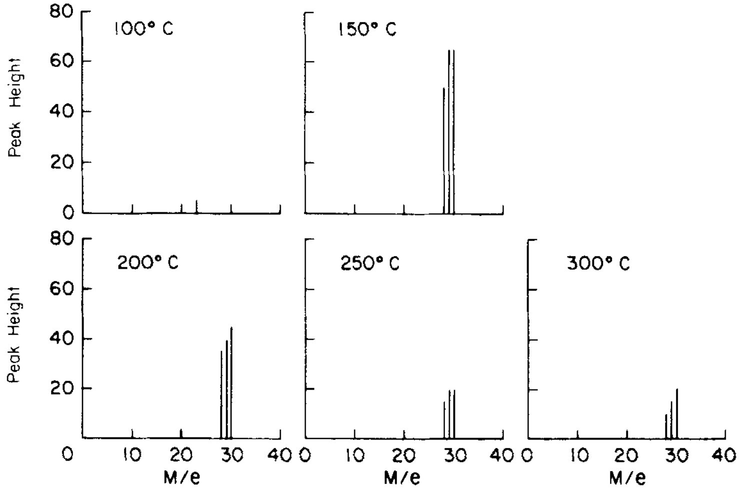


Fig. 2. Mass spectrometer analysis (70 eV) of 5% by weight citric acid-Delrin mixture.

EXPERIMENTAL PROCEDURE

Mixtures of powdered Delrin 150 obtained from the du Pont Corporation and citric acid obtained from the Matheson Corporation were made up containing 2-20% by weight citric acid. Samples of these mixtures were placed in a Cahn thermogravimetric analyzer and heated at 3°C/min under a nitrogen atmospheres (see Fig. 1). Residual weight versus temperature was recorded. Samples of these mixtures were also pyrolyzed and analyzed in a Bendix time-of-flight mass spectrometer. A sample of mixture was heated in a pyrolysis chamber connected directly to the mass spectrometer. The sample in the chamber was heated to 100°C and was kept at this temperature for 10 min; then the remaining sample was heated to 150°C and was kept at this temperature for 10 min. The same procedure was repeated at 50°C intervals until 400°C was reached. At each of the temperature levels the pyrolysis gases were analyzed with the mass spectrometer.

RESULTS AND DISCUSSION

From observation of the solids in a melting point apparatus, it was found

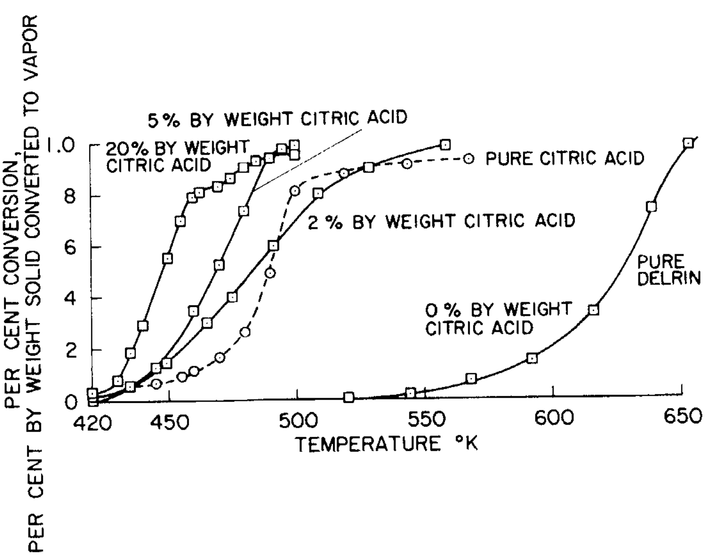


Fig. 3. Decomposition of Delrin-citric acid mixtures.

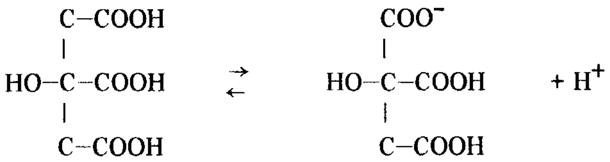
that pure Delrin melts at 175°C; pure citric acid melts at 154°C. Mixtures of citric acid and Delrin melt at about 150°C. From these observations and the TGA's it can be concluded that the decomposition reaction occurs in the molten phase. Figure 2 shows a typical result from the mass spectrometer analysis. The major peaks at all the pyrolysis temperatures are at a M/e of 28, 29, and 30. These are attributable to formaldehyde (see *API Mass Spectral Data,* Serial 84). Thermograms for 2, 5, and 20% by weight citric acid-Delrin mixtures are shown in Fig. 3. The thermograms are plots of weight % solid lost, or converted to vapor, vs. temperature.

As the starting concentration of citric acid increases, the temperature at which decomposition occurs is lowered. Also presented in Fig. 3 is a TGA for pure Delrin. As can be seen from the figure, all mixtures containing citric acid decompose at lower temperatures than does pure Delrin. For the TGA representing the case for an initial concentration of citric acid of 20% by weight, a plateau is reached at 80% conversion (80% weight loss). This represents the point at which all the Delrin has decomposed and just the citric acid remains. On increasing the temperature of this mixture the remaining citric acid also decomposes. A TGA for the decomposition of pure citric acid is shown in Fig. 3. From Fig. 3 it can be seen that in the temperature range of interest the kinetic model must include the thermal decomposition of citric acid.

MODEL DERIVATION

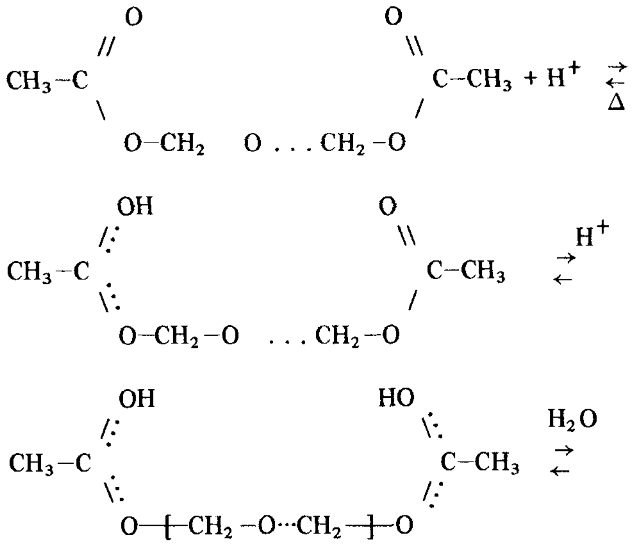
The following sequence of chemical steps is assumed as the basis for the kinetic model:

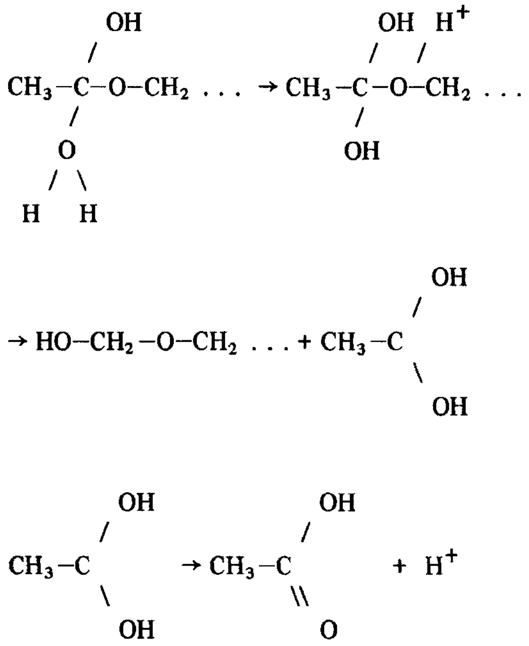
1. Ionization of citric acid



$$\begin{array}{c} \mathrm{C{-}COOH} \\ | \\ \mathrm{HO{-}C{-}COOH} \\ | \\ \mathrm{C{-}COOH} \end{array} \rightleftarrows \begin{array}{c} \mathrm{COO^-} \\ | \\ \mathrm{HO{-}C{-}COOH} \\ | \\ \mathrm{C{-}COOH} \end{array} + H^+$$

2. Acid hydrolysis of Delrin



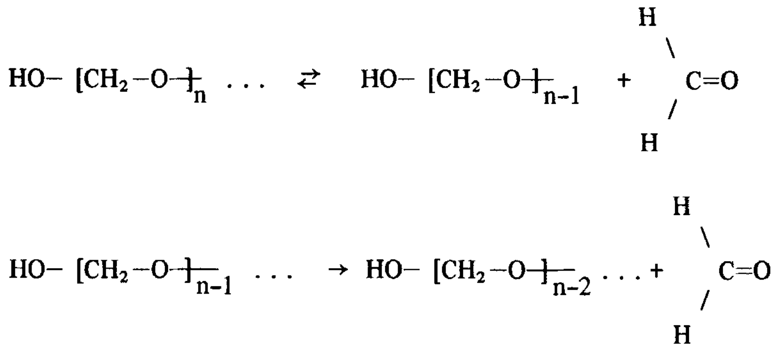


$$CH_3-\underset{\underset{H\quad H}{O}}{\overset{OH}{C}}-O-CH_2\ldots \rightarrow CH_3-\underset{OH}{\overset{OH}{C}}-\overset{H^+}{O}-CH_2\ldots$$

$$\rightarrow HO-CH_2-O-CH_2\ldots + CH_3-C\begin{matrix}OH\\OH\end{matrix}$$

$$CH_3-C\begin{matrix}OH\\OH\end{matrix} \rightarrow CH_3-C\begin{matrix}OH\\ \| \\ O\end{matrix} + H^+$$

3. “Unzipping” of polyformaldehyde



$$HO-[CH_2-O]_n\ldots \rightleftarrows HO-[CH_2-O]_{n-1} + \begin{matrix}H\\H\end{matrix}C=O$$

$$HO-[CH_2-O]_{n-1}\ldots \rightarrow HO-[CH_2-O]_{n-2}\ldots + \begin{matrix}H\\H\end{matrix}C=O$$

and so on.

The rate-determining step in the acid hydrolysis is assumed to be the first step in the reaction scheme, the protonation of the carbonyl group. The over-all reaction may then be represented as:

Delrin + citric acid → polyformaldehyde → formaldehyde

KINETIC RATE EQUATIONS

The following kinetic rate equations are used to describe the aforementioned chemical reactions. Where possible, kinetic constants are obtained independently from experiments with pure substances. Therefore, these constants for pure substances are independent of the experiments for the over-all Delrin-citric acid reaction.

Ionization of citric acid:

$$HC \rightleftarrows H^+ + C^- \qquad [H^+] = K_{eq}^{1/2}\ [HC]^{1/2} \tag{1}$$

Decomposition of citric acid:

$$HC \xrightarrow{K_D} X \qquad \frac{d[HC]}{d\theta} = -K_D[HC] \tag{2}$$

Acid hydrolysis of Delrin:

$$D + [H^+] \xrightarrow{K_H} P \qquad \frac{d[D]}{d\theta} = -K_H\ [D]\ [H^+] \tag{3}$$

Substituting Eq. (1) in Eq. (3):

$$\frac{d[D]}{d\theta} = -K_H\ K_{eq}^{1/2}\ [D]\ [HC]^{1/2}$$

"Unzipping" of polyformaldehyde:

$$P \xrightarrow{K_Z} F$$

$$\frac{d[P]}{d\theta} = -K_Z \qquad \text{(zero order)} \qquad (4)$$

Net rate of polyformaldehyde production:

$$D + H^+ \xrightarrow{K_H} P \xrightarrow{K_Z} F$$

$$\frac{dP}{d\theta} = K_H\,Keq^{1/2}\,[D]\,[HC]^{1/2} - K_Z \qquad (5)$$

Net weight loss:

$$[P] > 0 \qquad \frac{dw}{d\theta} = -MWTp(K_Z) - MWThc\,[K_D(HC)] \qquad (6a)$$

$$[P] \sim 0 \qquad \frac{dw}{d\theta} = -MWTp\left[K_H\,Keq^{1/2}\,[D]\,[HC]^{1/2}\right] - MWThc\left[K_D\,[HC]\right] \qquad (6b)$$

where MWTp is the average molecular weight of polyformaldehyde ~75,000 and MWThc is the molecular weight of citric acid ~210.

Let:

$$K_T = K_H\,Keq^{1/2} \text{ in Eq. (6b); then}$$

$$\frac{dw}{d\theta} = -MWTp\left\{K_T[D]\,[HC]^{1/2}\right\} - MWThc\,[K_D(HC)] \qquad (7)$$

Equation (6a) represents the condition where polyformaldehyde concentration controls the weight loss of the sample, because the decomposition reaction of polyformaldehyde is zero-order. Equation (6b) represents the condition where the polyformaldehyde decomposes much faster than it is produced from Delrin, and therefore the rate-controlling step for the weight loss is the acid hydrolysis reaction. The experimental data used are nonisothermal data; therefore, the Arrhenius form of the rate constants is used. This form is:

$$K_i = Ai\ e^{-Ei/RT} \tag{8}$$

If the Arrhenius form is substituted in Eqs. (6a) and (6b),

$$\frac{dw}{d\theta} = -MWTp\left(Az\ e^{-Ez/RT}\right) - MWThc\left(Ad\ e^{-Ed/RT}\ [HC]\right) \tag{9a}$$

$$\begin{aligned}\frac{dw}{d\theta} = {} & -MWTp\left(At\ e^{-Et/RT}\quad (D)\ (HC)^{1/2}\right)\\ & -MWThc\left(Ad\ e^{-Ed/RT}\quad (HC)\right)\end{aligned} \tag{9b}$$

If the heating rate used in the TGA's is HETA (°C/min), the rate equations can be converted from a time to a temperature variable. The rate equations (9a) and (9b) become:

$$\frac{dw}{dT} = \left(-MWTp\left(Az\ e^{-Ez/RT}\right) - MWThc\left(Ad\ e^{-Ed/RT}\right)(HC)\right)/HETA \tag{10a}$$

$$\begin{aligned}\frac{dw}{dT} = \Big(& MWTp\left(At\ e^{-Et/RT}\right)(D)\ (HC)^{1/2}\\ & - MWThc\left(Ad\ e^{-Ed/RT}\right)(HC)\Big)/HETA\end{aligned} \tag{10b}$$

From independent experiments with pure citric acid the constants Ad and Ed are found using the same type of nonlinear regression technique described later for the acid-catalyzed decomposition reaction.

From the rate equations (10a) and (10b) a maximum of four constants must be obtained–Az, Ez, At, and Et. They represent the kinetic constants for the acid hydrolysis and the "unzipping" reaction. Four constants are necessary if any of the composition or temperature regions are such that both mechanisms (6a) and (6b) occur.

NONLINEAR REGRESSION ANALYSIS

The Arrhenius constants are obtained by a nonlinear regression technique. Constants are chosen such that the sum of the squares of the difference between predicted TGA's and experimental TGA's are minimized. First, in order to obtain a predicted TGA, the set of five rate equations have to be simultaneously numerically integrated. These five equations are:

$$\frac{d[HC]}{dT} = -Ad\, e^{-ED/RT}\, (HC)/HETA$$

$$\frac{d[D]}{dT} = -At\, e^{-Et/RT}\, (D)\, (HC)^{1/2}/HETA$$

$$\frac{dP}{dT} = \left[+At\, e^{-Et/RT}\, (D)\, (HC)^{1/2}\ -Aze^{-Ez/RT} \right] /HETA$$

$$\frac{dw}{dT} = \text{Eq. (10a) or (10b)}$$

The numerical integration technique used was the Runge-Kutta method. This was modified so that the temperature interval of integration could be varied according to how large the constants were in the Runge-Kutta technique; i.e., where the thermogram was changing rapidly, the temperature increment was reduced and vice versa. When a thermogram was predicted it was compared with the experimental thermogram, and the sum of the squares of the difference between thermograms was calculated. The regression analysis to correct the thermogram was performed with a modified form of a computer program available in the literature (SHARE General Program Library ER NLR(PA) 3146). This program varied the kinetic constants so that the sum of the squares of the difference between predicted and experimental thermograms was minimized. The results from the computer analysis are shown in Figs. 4, 5, and 6 for TGA's for 2, 5, and 20% citric acid, respectively. In Figs. 7, 8, and 9 are plotted the predicted concentrations of the various species predicted by the model. In

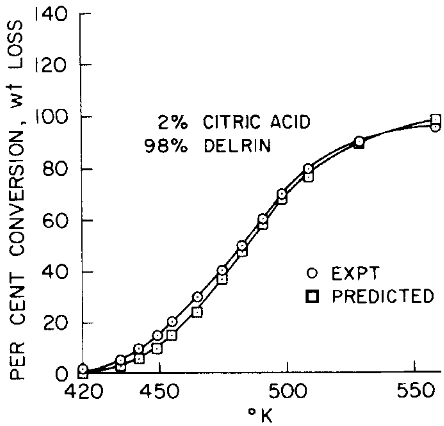


Fig. 4. Comparison of experimental and predicted data; 2% citric acid, 98% Delrin.

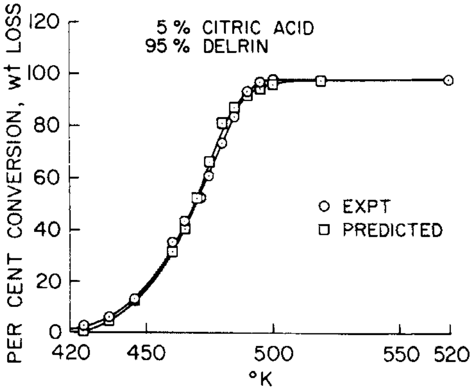


Fig. 5. Comparison of experimental and predicted data; 5% citric acid, 95% Delrin.

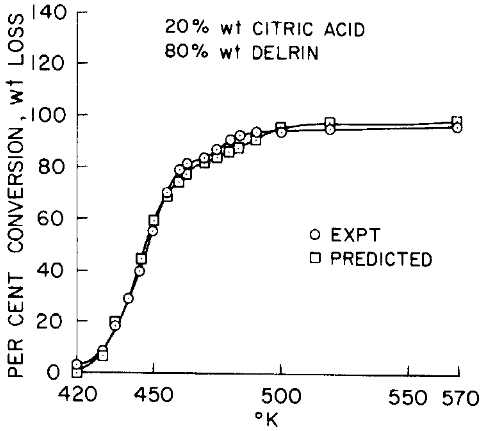


Fig. 6. Comparison of experimental and predicted data; 20% wt citric acid, 80% wt Delrin.

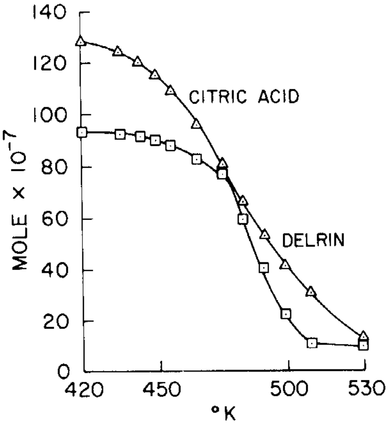


Fig. 7. Model prediction; 2% citric acid, 98% Delrin.

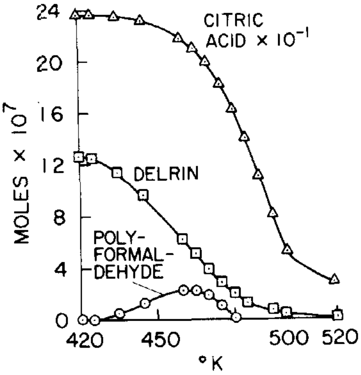


Fig. 8. Model prediction; 20% citric acid, 80% Delrin.

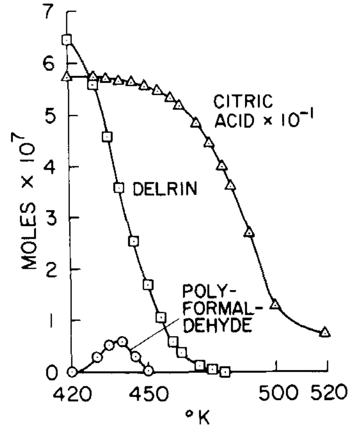


Fig. 9. Model prediction; 5% citric acid, 95% Delrin.

Figs. 5, 6, 8, and 9 the model predicts a small concentration of polyformaldehyde in the mixtures. In these regions of concentration and temperature the rate-determining step for weight loss of polymer is dependent only on the decomposition of polyformaldehyde, because polyformaldehyde is predicted to exist and its decomposition is zero-order in polyformaldehyde. For Figs. 4 and 7 and concentration and temperature regions in Figs. 5, 6, 8, and 9 where polyformaldehyde is predicted to be negligible, the acid hydrolysis determines the loss of weight of the polymer. The kinetic

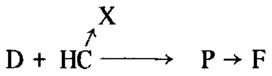
Table 1

At		1.2750	±	0.1425 (10^8)
Et		17.833	±	0.691 kcal/mole
Az		0.1245	±	0.0122
Ez		16.286	±	0.518 kcal/mole
Ad	=	2.698 (10^{11})		
Ed	=	31.402 kcal/mole		

constants derived from this analysis, and their standard deviations, are shown in Table 1. The activation energy and pre-exponential factor for the acid hydrolysis calculated by the regression analysis, At and Et, are over-all constants. From Eq. (7) these kinetic constants represent a combination of the equilibrium constant for citric acid ionization and the protonation of the carbonyl group in Delrin. The kinetic constants are accurate between ±3 and 11%.

CONCLUSION

Mixtures of Delrin and citric acid melt at approximately 150°C. In this molten phase the acid-catalyzed decomposition of Delrin to formaldehyde can be adequately described with an accuracy of 5% by a model representing the acid hydrolysis of Delrin to polyformaldehyde and subsequent "unzipping" of polyformaldehyde to formaldehyde. The sequence of chemical reactions for a citric acid-Delrin system are:



$$D + HC \xrightarrow{} P \rightarrow F, \quad HC \nearrow X$$

where D represents Delrin; HC, citric acid; X, citric acid decomposition products; P, polyformaldehyde, and F, formaldehyde.

For concentrations of citric acid greater than 2% the loss of weight of the mixture is due to the "unzipping" reaction of polyformaldehyde and citric acid decomposition. At citric acid concentrations of less than 2%, the rate-determining step is always the acid hydrolysis of Delrin and the decomposition of citric acid. The kinetic constants for this complex reaction scheme can be obtained from TGA data by use of a nonlinear regression analysis. This analysis is applied to rate equations as follows:

$$\frac{d(HC)}{dT} = -Ad\, e^{-Ed/RT}\, [HC]/HETA \quad \text{pure citric acid decomposition}$$

$$\left.\begin{aligned}
\frac{dw}{dT} &= \Big(-MWTp\,\big(Az\, e^{-Ez/RT}\big) \\
&\qquad -MWThc\, Ad\, e^{-Ed/RT}\, (HC)\Big)/HETA \\
\frac{dw}{dT} &= -\Big(MWTp\,\big(At\, e^{-Et/RT}\big)\,(D)\,(HC)^{1/2} \\
&\qquad -MWThc\, Ad\, e^{-Ed/RT}\, (HC)\Big)/HETA
\end{aligned}\right\}\ \begin{array}{l}\text{residual}\\ \text{weight}\\ \text{equations}\end{array}$$

The constants based on this model have an estimated accuracy of ±3-11%.

NOMENCLATURE

HC	citric acid concentration
K_{eq}	citric acid ionization constant
X	citric acid decomposition products
D	Delrin concentration
H^+	hydrogen ion concentration
P	polyformaldehyde
F	formaldehyde
K_D	citric acid decomposition constant
K_H	Delrin hydrolysis constant
K_Z	polyformaldehyde decomposition constant
W	weight
θ	time
MWTp	average molecular weight of polyformaldehyde
MWThc	molecular weight of citric acid
T	temperature
Az	pre-exponential factor for polyformaldehyde decomposition

Ez	activation energy for polyformaldehyde decomposition
Ad	pre-exponential factor for hydrolysis reaction
Ed	activation energy for hydrolysis reaction
HETA	thermogravimetric constant heating rate (TGA)

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