POLYMER SOLUTIONS

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Polyester Resin Calculations
Beta version

Commonly used polyester variable calculations used in the Resin Industry

A. Excess Polyol

Excess polyol refers to the presence of polyol added over and above the stoichiometric quantity required to react with an acid.
There is no internationally uniform method of calculating this value, and the following formulations are used:

1. $$\text{Excess Polyol} = \frac{\text{Mass polyol over stoichiometric amount}}{\text{Total Mass of polymer}} * \frac{100}{1}$$

2. $$\text{Excess Polyol} = \frac{\text{Percent polyol over stoichiometric amount}}{\text{Total Mass of polymer}} * \frac{100}{1}$$

B. Average Functionality

The overall Functionality of a system (F_{AV}) is calculated as follows:

$$\text{Fav} = \frac{\text{Total Equivalents}}{\text{Total Moles}} = \frac{\boldsymbol{e_o}}{\boldsymbol{m_o}}$$

C. Carothers Gel Point Equation

If:
N_o = Number of monomer molecules initially present and
N_r = Number of molecules after reaction

Then:
The number of functional groups initially present: $F_o = N_o * Fav$

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The number of functional groups lost (2 functional groups per reaction are lost): $F_l = 2(N_o - N_r)$

The extent of the reaction (ρ) is given by:

$$p = \frac{2(No - Nr)}{No * Fav}$$

The fractional degree of polymerisation (x):

$$x = \frac{No}{Nr}$$

Thus, substituting $No = x * Nr$

$$p = \frac{2(x * Nr - Nr)}{x * Nr * Fav}$$

$$p = \frac{2x * Nr - 2Nr}{xNr * Fav}$$

$$p = \frac{2 * \cancel{xNr}}{\cancel{xNr} * Fav} - \frac{2\cancel{Nr}}{x\cancel{Nr} * Fav}$$

$$p = \frac{2}{Fav} - \frac{2}{xFav}$$

As x increases towards the gel point the equation can be reduced to:

$$Pg \approx \frac{2}{Fav}$$

Where *Pg* is the polymer gel point (most commonly referred to as "*PGel*").
A value of 1 indicates the polymer will gel (i.e., equal equivalents of acid and base).

However, this equation only works when there are equal equivalents of both acid and base (polyol).
In most resins, an excess of polyol is used in hydroxy terminated resins although in acid terminated resins the acid is in excess quantities.

Thus, for this equation to be more useful, one must use only the equivalent amounts of polyol and acid reacted. Depending on the formulation (polyol or hydroxy terminated) the minimum equivalents of polyol or acid must be used, hence disregarding the excess of one or the other. i.e.

$$Fav' = \frac{2Em}{Total\ moles}$$

Where Minimum Equivalents (Em) is the total equivalents of acid, in a polyol terminated resin, or the total equivalents of polyol, in an acid terminated resin.
The revised formulation for PGel is thus:

$$\boldsymbol{Pg \approx \frac{2}{Fav'}}$$

D. Patton's Gelation Constant ('K' Value')

Patton starts off by using Carothers' Gel Point

$$\boldsymbol{Pg \approx \frac{2}{Fav} = 2m_o/e_o}$$

And goes on to argue that the Carothers equation assumes that both acid and base are charged at equal equivalents, which is rarely the case.
Based on the 'norm' of adding excess base to a resin, the reaction will terminate when all the acid is reacted. For a hydroxy terminated resin, the excess remains and reduces the effective functionality of the of the molecule. Hence the effective number of 'reacting equivalents' of the resin is $\boldsymbol{2\varepsilon_a}$
Thus, the correct way of determining the Pg would be to only use the acid equivalents by substituting $\boldsymbol{\varepsilon_0}$ with $\boldsymbol{2\varepsilon_a}$:

$$\boldsymbol{Pg \approx \frac{2m_o}{2e_a} = \frac{m_o}{e_a} = K\ Value}$$

E. Flory Gel Point Equation

Carothers' definition of gel point assumes an infinite 'Number Average' molecular mass corresponds to gelation.
Flory (and others) developed their theories of gelation on the 'Mass Average' molecular weight approaching infinity at the gelation point.

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The derived equation from this standpoint is:

$$Pa\ (gel) = \sqrt{\frac{\varepsilon}{2(1-\lambda)}}$$

Where:

$$\varepsilon = \frac{Equivalents\ of\ Hydroxyl}{Equivalents\ of\ Acid}$$

And

$$\lambda = \frac{Equivalents\ of\ Acid\ from\ monobasic\ acid}{Total\ equivalents\ of\ acids}$$

In practice, neither the Carothers nor Flory equations are useful in designing resins from theoretical considerations alone as they disregard 'side reactions' that can take place such as:

- Intramolecular esterification
- Etherification reactions
- Assumptions that all reacting groups are of equal reactivity.
- Branch growth of polymers, with ingredient functionalities of over 2, produce '3 dimensional molecules' whose 'mobility' is sterically hindered giving extremely high viscosity polymers at low conversion rates (i.e., low 'degrees of polymerisation').

Where these calculations are of use is in amending the formulation of a resin which has prematurely gelled.

F. Controlling polyol functionality utilising monobasic acids

Monobasic acids, such as Benzoic Acid, can be used to control the functionality of a polyol. For example, a 1:1 molar composition of Benzoic acid (E_a = 1) and Glycerine (E_b = 3) would (theoretically) result in a polyol functionality of 2 (E_b - E_a = 3-1)

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G. Calculating water of esterification

$$\boldsymbol{Water\ Off = 18 * Equivalents\ of\ Acid + 9 * Equivalents\ of\ Anhydride}$$

This equation assumes:

a. The reaction is carried to completion (i.e., no residual acidity)
b. The resin is hydroxy terminated.

Correcting for residual acidity the equation becomes:

$$\boldsymbol{Water\ Off = 18 * Equivalents\ of\ Acid + 9 * Equivalents\ of\ Anhydride - \frac{18 * AN}{56,100}}$$

Where *AN* is the residual acid number

Where the resin is acid terminated the equation becomes:

$$\boldsymbol{Water\ Off = 18 * Equivalents\ of\ base - \frac{18 * OHV}{56,100}}$$

Where *OHV* is the residual hydroxyl value

H. Calculating Yield

The yield of an esterification reaction (*Y*) may be calculated as follows:

$$\boldsymbol{Y = Charge\ Mass - Water\ Off}$$

I. Calculating % Excess Hydroxyl

The percentage excess hydroxyl (*%XSOH*) is calculated according to the following equation:

$$\%XSOH = \frac{(Hydroxyl\ equivalents - Acid\ equivalents)}{Acid\ Equivalents} * \frac{100}{1}$$

Or:

$$\boldsymbol{\%XSOH = \left(\frac{Hydroxyl\ Equivalents}{Acid\ Equivalents} - 1\right) * \frac{100}{1}}$$

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J. Calculating Hydroxyl Number

The hydroxyl Number (*OHN*) is calculated according to the following Equation:

$$\boldsymbol{OHN = \frac{(Hydroxyl\ Equivalents - Acid\ Equivalents) * 56,100}{Yield} + AN}$$

K. Calculating Hydroxyl Equivalent Mass

The Hydroxyl Equivalent Mass (*OHEM*) is calculated according to the following equation:

$$\boldsymbol{OHEM = \frac{56,100}{OHN}}$$

L. Calculating Molecular Mass

There are two methods used to calculate the Molecular Mass of a polymer mixture of known polymer molecular masses.

The Number Average Molecular Mass ($\overline{M}_n$) is calculated according to the following equation:

$$\boldsymbol{\overline{Mn} = \frac{\sum_{i=1}^{n} N_i M_i}{\sum_{i=1}^{n} N_i}}$$

$$\boldsymbol{\overline{Mn} = \frac{\sum_{i=1}^{n} w_i}{\sum_{i=1}^{n} \frac{w_i}{M_i}}}$$

However, $\boldsymbol{\sum_{i=1}^{n} w_i = 1}$

$$\boldsymbol{\overline{Mn} = \frac{1}{\sum_{i=1}^{n} \frac{w_i}{M_i}}}$$

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The Mass Average Molecular Mass ($\overline{M}_w$) is calculated according to the following equation:

$$\overline{Mw} = \frac{\sum_{i=1}^{n} N_i M_i^2}{\sum_{i=1}^{n} N_i M_i}$$

However, $N_i = w_i / M_i$

$$\overline{Mw} = \frac{\sum_{i=1}^{n} w_i M_i}{\sum_{i=1}^{n} w_i}$$

However, $\sum_{i=1}^{n} w_i = 1$

$$\overline{Mw} = \sum_{i=1}^{n} w_i M_i$$

N_i = Number of Moles of monomer(i)
M_i = Molecular mass monomer(i)
w_i = Mass Fraction of monomer = $M_i * N_i$
However, with resins we are dealing with a mixture of monomers that have yet to be polymerised. As such, the above equations cannot be used.

The Mass Average Molecular Mass ($\overline{M}_{av}$) is calculated according to the following equation:

M_o = Initial total number of acid and base molecules in formulation
W = Total Mass of the formulation
e_a = Total number of initial acid equivalents in the formulation
AN = Acid Number (Acid Value) at the completion of reaction
Man = Remaining acid molecules after reaction to the final Acid Number (assuming hydroxy termination)
$\overline{M}_{av}$ = Average polymer molecular mass

$$Unreated\ Acid\ Equivalents = \frac{W * AN}{56,100}$$

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$$Acid\ equivalents\ reacted = Total\ Inital\ Acid\ Equivalents - Unreated\ Acid\ Equivalents$$

$$\boldsymbol{Acid\ equivalents\ reacted = e_a - \left(\frac{W * AN}{56,100}\right)}$$

$$\boldsymbol{M_{an} = Initial\ total\ number\ of\ molecules} - \textbf{Acid equivalents reacted.}$$

$$\boldsymbol{M_{an} = m_o - \left(e_a - \frac{W * AN}{56,100}\right)}$$

$$\boldsymbol{M_{an} = (m_o - e_a) + \left(\frac{W * AN}{56,100}\right)}$$

$$\boldsymbol{\bar{M}_{av} = \frac{W}{M_{an}}}$$

$$\boldsymbol{\bar{M}_{av} = \frac{W}{(m_o - e_a) + \left(\frac{W * AN}{56,100}\right)}}$$

Please note, I wrote these notes a number of years ago and need to revise at some stage. If anyone finds any major errors, please email me.