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Relationships between glass transition temperature and conversion

Analyses of limiting cases

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SUMMARY

The Couchman approach to the expression of the compositional variation of glass transition temperature (or the Di-Benedetto equation) can be used to evaluate the effect of molecular weight on T_g for a stepwise linear polymer. An expression for the K_L constant in the Fox-Flory equation is proposed. It is also possible to estimate the T_{gL} corresponding to the hypothetical linear structure defined in a three-dimensional network. For different epoxy-diamine systems, we have found a good concordance with the results obtained previously using an additive law.

INTRODUCTION

We have recently shown [1] that an extension of Couchman's approach [2] for the expression of the compositional variation of the glass transition temperature, T_g, enabled us to derive the following relationship between T_g and conversion, x, for a thermosetting polymer :

$$\frac{T_g - T_{go}}{T_{g\infty} - T_{go}} = \frac{\lambda x}{1 - (1 - \lambda)x} \quad \text{or} \quad T_g = T_{go} + \frac{(T_{g\infty} - T_{go})\,\lambda x}{1 - (1 - \lambda)\,x} \qquad (1)$$

where $\lambda = \Delta C_p / \Delta C_{po}$ is the ratio of the isobaric heat capacities of the fully reacted and the initial system ($\lambda < 1$), and T_g and T_{go} are the glass transition temperatures of the completely reacted system and the initial solution of monomers, respectively.

Equation (1) is also called the Di Benedetto equation after the original report by Nielsen [3,4]. The reliability of Eq. (1) when applied to epoxy-diamine systems has been shown by comparing experimental values of and independent measurements of ΔC_p / ΔC_{po} ratios [1,5]. A good agreement was found for every case.

Our intention now is to analyze the following limiting cases derived from Eq. (1) :

i) particular case of $\Delta C_p\, T_g$ = constant [6] ;
ii) stepwise polymerization of difunctional monomers leading to a linear polymer ;
iii) determination of the glass transition temperature, T_{gL}, corresponding to the linear structure defined in a three-dimensional network [7] (T_{gL} is the limiting value of T_g when the crosslink density tends to zero).

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Case of $\Delta C_p\, T_g$ = constant

For this particular case,
$$\lambda = \frac{\Delta C_{p\infty}}{\Delta C_{po}} = \frac{T_{go}}{T_{g\infty}} \qquad (2)$$

The possibility of estimating λ by Eq. (2) has been shown for several (but not all) epoxy-amine systems [1,5].

Substituting the expression for Eq. (2) into Eq. (1) and rearranging, we get :

$$\frac{1}{T_g} = \frac{x}{T_{g\infty}} + \frac{(1 - x)}{T_{go}} \qquad (3)$$

The simple rule of mixtures, similar to the Fox equation [8], may be used for a rough estimation of the T_g vs x relationship using reported values for T_{go} and $T_{g\infty}$. Due to the fact that there are few ΔC_p values reported in the literature, this equation Eq. (3) can be very useful.

Linear stepwise polymerization

For the homopolymerization of an A_2 monomer and for the copolymerization of an A-B monomer or a stoichiometric $A_2 + B_2$ mixture, the number average degree of polymerization, $\overline{DP}_n$, varies with conversion as follows :

$$\overline{DP}_n = \frac{1}{1 - x} \qquad (4)$$

By introducing Eq. (4) into Eq. (1) and rearranging, we get :

$$T_g = T_{g\infty} - \frac{T_{g\infty} - T_{go}}{1 + \lambda\,(\overline{DP}_n - 1)} \qquad (5)$$

The applicability of Eq. (5) has been tested for different epoxy prepolymers (Figure 1) with different molecular weights. Dynamic differential scanning calorimetry (DSC) runs, carried out at 10 K/min under an argon atmosphère, showed that $\Delta C_p(1.03)$ = 0.55 J/gK for a prepolymer with $\overline{DP}_n$ = 1.03 ($\bar{n}$ = 0.03) and $\Delta C_p(81)$ = 0.30 J/g/K for a polymer with $\overline{DP}_n$ = 81 ($\bar{n}$ = 80). Since ΔC_p decreases when $\overline{DP}_n$ increases, it may be stated that :

$$\lambda = \frac{\Delta C_{po}}{\Delta C_{p\infty}} < \frac{\Delta C_p\,(1.03)}{\Delta C_p\,(81)} = 0.55 \qquad (6)$$

Table I shows experimental values of T_g (onset values determined by DSC at 10 K/min), for several commercial epoxy prepolymers.

TABLE I. Comparison of experimental and predicted T_g values for several commercial epoxy prepolymers

Commercial name	$\bar{n}$	$\overline{DP}_n$	T_g (K) (exp.)	T_g Eq. (3) (λ = 0.6)		T_g Eq. (3) (λ = 0.5)
DGEBA	0	1	-	252	(T_{go})	252.5
DER 332 (DOW)	0.03	1.03	254	254		254
Lopox 200 (CdF Chimie)	0.14	1.14	257	260		259
Araldite 6Y280 (Ciba)	0.74	1.74	277	284		280
Lopox 440 (CdF Chimie)	1.26	2.26	289	296		292
Lopox 810 (CdF Chimie)	3.94	4.94	322	324		321
PKHH (Union Carbide)	80	81	353	353		353
polyphenoxy	$\to \infty$	$\to \infty$	-	355	($T_{g\infty}$)	355.5

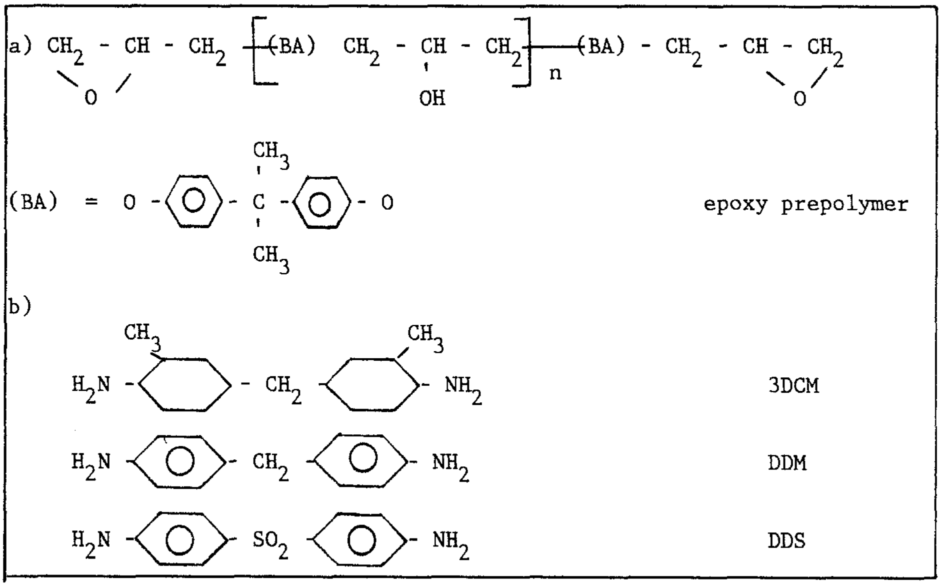

Fig.1. Structural formulae of the epoxy prepolymers and diamines used

Two values of λ were selected to use in Eq. (5), λ = 0.6 and λ = 0.5. In each case, Eq. (5) was written for $\overline{DP}_n$ = 1.03 and $\overline{DP}_n$ = 81, and values of T_{go} and $T_{g\infty}$ obtained as shown in Table I.

Then Eq. (5) was used to predict the other glass transition temperatures. A good agreement with experimental results is shown for $\lambda = 0.5$. Even though the reliability of Eq. (5) must be validated with different systems, it may be regarded as a general relationship between T_g and $\overline{DP}_n$ for linear polymers obtained by a stepwise mechanism, independent of any consideration about the value of $\overline{DP}_n$.

It is also interesting to take the specific case of $\overline{DP}_n \gg 1$, which transforms eq. (5) into :

$$T_g = T_{g\infty} - \left(\frac{T_{g\infty} - T_{go}}{\lambda} \right) \cdot \frac{1}{\overline{DP}_n} \qquad (7)$$

Therefore, Eq. (5) contains the Fox-Flory equation [9] as a particular case, with constant K_L :

$$K_L = \left(\frac{T_{g\infty} - T_{go}}{\lambda} \right) \cdot \frac{1}{\overline{M}_{n,o}}$$

($\overline{M}_{n,o}$ is the average molecular weight of the monomer mixture)

We must remark that for a chainwise polymerization, the treatment leading to Eq. (5) is not possible because a direct relationship between $\overline{DP}_n$ and x does not exist.

Determination of T_{gL}

Predicting the glass transition temperature, T_g, of crosslinked copolymers from the knowledge of their chemical structure is of great interest from a theoritical as well as from a practical point of view. Many predictive methods based on physical or empirical approaches have been developed and recently reviewed by Bellenger et al. [7]. These authors conclude that, for epoxy-amine systems, the T_g can be expressed by the following equation, established by Di Marzio[10] and based on the theory of configurational entropy:

$$T_{gL} = T_g \left(1 - K_{DM} \times F \times n\right) \qquad (9)$$

where,

- K_{DM} is the Di Marzio constant, n, the crosslink density and F a flex parameter,

- and T_{gL} is the glass transition temperature of a hypothetical linear copolymer in which the constitutional (or monomeric) repeating units (CRU) contain all the difunctional constitutional units (CU) of the network with the same molar ratio.

T_{gL} represents the "copolymer effect" and can be calculated using an additive law [7,11]. We now propose to estimate T_{gL} with another experimental approach.

Using Eq. (1) for a particular thermosetting system leads to the prediction of the increase in T_g with conversion, x. A simple statistical analysis assuming that no intramolecular cycles are present in the pregel stage, leads to a relationship between $\overline{DP}_n$ and x. Thus a relationship between T_g and $\overline{DP}$ results. Therefore we define :

$$T_{gL} = \lim_{\overline{DP}_n \to \infty} T_g \tag{10}$$

The procedure will be illustrated with a particular epoxy-diamine system. Let us consider the polymerization of an epoxy prepolymer DGEBA (n = 0.03) with 4,4' diamino 3,3' dimethyldicyclohexyl methane, 3DCM, (Figure 1). The following parameters have been obtained for this particular system [1,12] : $\lambda = 0.464$, $T_{go} = 241$ K and $T_{g\infty} = 453$ K. For an $A_4 + B_2$ polymerization, the evolution of the number average molecular weight is given by :

$$\overline{M}_n = \frac{\text{total mass}}{\text{total number of moles}} = \frac{A_4 M_{A4} + B_2 M_{B2}}{A_4 + B_2 - 4\ A_4} \tag{11}$$

where it has been assumed that every time that an amino-hydrogen (or an epoxide) reacts, the number of molecules is reduced by one unit (no intramolecular cycle).

For a stoichiometric epoxy-diamine system, $B_2 = 2\ A_4$. Then from Eq. (11) we get :

$$\overline{DP}_n = \frac{\overline{M}_n}{\overline{M}_{n,o}} = \frac{1}{1 - 4/3\ x} \tag{12}$$

From Eqs. (1) and (12), it arises that for an epoxy diamine system, T_{gL} may be estimated by :

$$T_{gL} = \lim_{\overline{DP}_n \to \infty} T_g = T_{go} + \frac{\lambda\ (T_{g\infty} - T_{go})}{\lambda\ + 1/3}$$

and for the case considered we get $T_{gL} = 364.4$ K.

But from the authors' point of view, this value represent an overestimation of T_{gL}. In fact, after the gel point, $\overline{DP}_n$ has no physical sense. For the epoxy-diamine system studied here, gelation arises for $x_{gel} = 0.60$. [12] Then, values of $\overline{DP}_n$ have physical sense in the range x = 0 - 0.6 or $\overline{DP}_n$ = 1-5. The estimation of T_{gL} from Eq. (13) takes into account the contribution of the crosslinks formed after the gel point.

Thus substituting Eq. (12) and reported values for λ , T_{go} and $T_{g\infty}$ into Eq. (1) we obtain :

$$T = 241 + \frac{73.776\ (1 - 1/\overline{DP}_n)}{0.598 + 0.402\ (1/\overline{DP}_n)} \tag{14}$$

Figure 2a shows a representation of Eq. (14) in the range of physical sense, from $1/DP_n$ between 0.2 and 1. Plotting the tangent at the last experimental point, $1/DP_n = 0.2$, we determine a lower value than previously obtained, $T_{gL} = 356$ K.

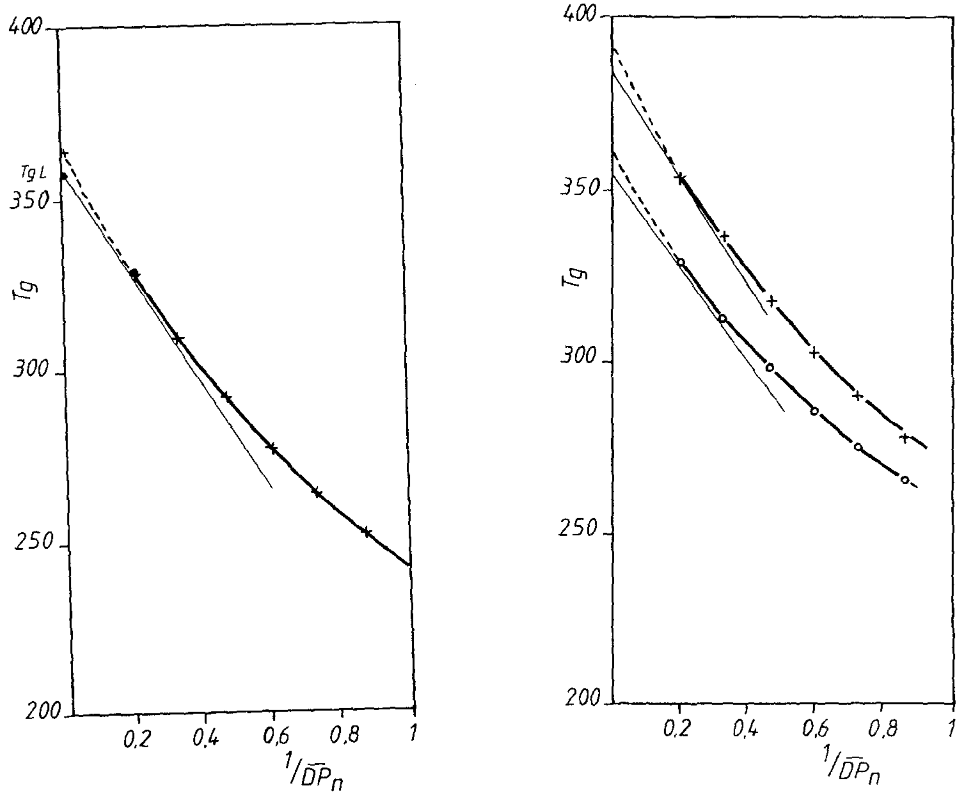

Fig.2. Increase in the glass transition temperature as a function of the number average degree of polymerization of the epoxy system of DGEBA $n = 0.03$ reacted up to the gel point. a) with 3DCM ; b) -o- with DDM, -+- with DDS

This theoretical treatment has also been applied to two other systems using the values for λ, T_{go} and $T_{g\infty}$ given in Table II [1,5]. The results are represented in Figure 2b, and extrapolated T_{gL} values are reported in Table II. These values are always higher but very close to the values arizing from the use of an additrive law [7,13] (Table II).

TABLE II - T_{gL} values for different epoxy-diamine systems. a) from extrapolated curves (Figures 2 a and b) ; b) from an additive law [7,9]

System	λ	T_{go}	$T_{g\infty}$	T_{gL} a)	T_{gL} b)
DGEBA-3DCM	0.464	241	453	356	354
DGEBA - DDM	0.39	257	451	355	350
DGEBA - DDS	0.38	268	491	384	364

CONCLUSION.

We have shown that the Couchman approach for the expression of the compositional variation of glass transition temperature can be useful to analyse the evolution of T_g during stepwise polymerizations, because in this case there is a direct relationship between the conversion, x, and the number average molecular weight, $\overline{M}_n$.

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