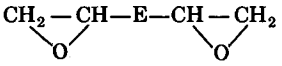
Packing Density of Nonstoichiometric Epoxide-Amine Networks

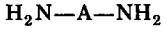
When epoxides, such as diglycidyl ether of bisphenol A (DGEBA), are cross-linked by diamines, such as metaphenylene diamine or diaminodiphenyl methane, practically no side reactions occur and the maximum value of the glass transition temperature T_g is reached when the reactants are in stoichiometric ratio. In certain cases, it has been observed that the density of the cured samples decreases when the amine concentration increases from 70–80% to 100% of its stoichiometric value. This result was interpreted in terms of free volume creation or, more generally, decrease of packing density when the cross-link density increases.[1] Our aim is to demonstrate that changes of van der Waals volume linked to the epoxide-amine addition can be also involved in these density variations.

CALCULATION OF THE PACKING DENSITY OF A NONSTOICHIOMETRIC DIEPOXIDE-DIAMINE NETWORK

Let us consider a system based on 2 mol diepoxide,



(molar weight M_e), and $(1 - x)$ moles ($x < 0.3$) of diamine;



(molar weight M_a). The molar weight of the resulting network structural unit is (by definition):

$$M = 2M_e + (1 - x)M_a = M_s - xM_a \tag{1}$$

where M_s is the molar weight of a stoichiometric network unit.

Assuming that all the amine groups have reacted with epoxide groups, the van der Waals volume is

$$V_w = 2V_w(E) + (1 - x)V_w(A) + 2(1 - x)V_w(N)$$

$$+4(1 - x)V_w\left(-CH_2-\underset{\underset{OH}{|}}{CH}-\right) + 4xV_W\left(-CH-\underset{O}{CH_2}\right)$$

which can be rewritten

$$V_w = V_{ws} - x(V_w(A) + 2V_w(N) + 4\delta V_w) \tag{2}$$

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where V_{ws} is the van der Waals volume of a stoichiometric network unit and $V_w(E)$, $V_w(A)$, and $V_w(N)$ refer to the groups —E—, and —A— and to the tertiary nitrogen atom, respectively.

$$\delta V_w = V_w\left(-CH_2-\underset{\underset{OH}{|}}{CH}-\right) - V_w\left(-\underset{\diagdown\,O\,\diagup}{CH}-CH_2\right)$$

Equations (1) and (2) give

$$\frac{V_w}{M} = \frac{V_{ws}}{M_s}\frac{1 - x(V_w(A) + 2V_w(N) + 4\delta V_w)/V_{ws}}{1 - xM_a/M_s} \tag{3}$$

Since $M_a < M_s$, for low values of x ($x < 0.3$),

$$\frac{V_w}{M} = \frac{V_{ws}}{M_s}(1 - Rx) \tag{4}$$

where

$$R = \frac{4\delta V_w}{V_{ws}} - \left(\frac{M_a}{M_s} - \frac{V_w(A) + 2V_w(N)}{V_{ws}}\right) \tag{5}$$

The packing density is

$$\rho^* = \frac{V_w}{V} = \rho\frac{V_w}{M}$$

where ρ is the density and V the molar volume of a structural unit. Thus, the eq. (4) can be written

$$\frac{\rho^*}{\rho_s^*} = \frac{\rho}{\rho_s}(1 - Rx) \tag{6}$$

where ρ_s^* is the packing density of a stoichiometric network.

DETERMINATION OF VAN DER WAALS VOLUMES

All the van der Waals volume group contributions except that of epoxide groups are given by Bondi.[2] For δV_w, the following estimation can be made. First,

$$V_w\left(-CH_2-\underset{\underset{OH}{|}}{CH}-\right) = 25.05 - \lambda \quad \text{cm}^3/\text{mol}$$

where λ is a correction for hydrogen bonding by the hydroxyl group. λ can be estimated from the hydrogen bond distance[2] and this latter from the OH infrared peak wave number ν_{OH}.[3] In our case, $\nu_{OH} = 3400\ \text{cm}^{-1}$, which gives $r = 2.8 - 2.9$ Å, and finally $\lambda = 1\ \text{cm}^3/\text{mol}$. That is, $\lambda < 2\ \text{cm}^3/\text{mol}$. Second, $V_w(-\underset{\diagdown\,O\,\diagup}{CH}-CH_2) = V_w(-\underset{|}{CH}-CH_2-O-) - \lambda' = 20.71 - \lambda'$ (cm^3/mol)

where λ' is a correction due to the cyclic structure of the epoxide group. λ' is unknown, but by analogy to other cyclic molecules ($\lambda' = 1.13$, 1.20, and 1.70 cm^3/mol for cyclohexyl, cyclopentyl, and dioxane,[2] respectively), it can reasonably be supposed that $\lambda' \geq \lambda$. Thus, a value of 4.3 cm^3/mol for δV_w does not seem to be overestimated.

APPLICATION TO THE CASE OF THE DGEBA-METAPHENYLENE DIAMINE (PDA) SYSTEM

For a DGEBA of $DP_n = 0.15$ ($M_e = 383$) and when PDA is used as hardener, the characteristics of the stoichiometric network are $M_s = 873$ g/mol and $V_{ws} = 486$ cm^3/mol. Taking $V_w(A) = 43.32$ cm^3/mol, $V_w(N) = 4.33$ cm^3/mol, and $M_a = 108$ g/mol, we obtain

$$\frac{4\delta V_w}{V_{ws}} \simeq 35 \times 10^{-3}$$

and

$$\frac{M_a}{M_s} - \frac{V_w(A) + 2V_w(N)}{V_{ws}} \simeq 17 \times 10^{-3}$$

Thus, $R \simeq 18 \times 10^{-3}$. From the recent results of Gupta et al.,[1,4] it can be estimated that $\rho_s = 1.209$ (stoichiometric ratio, 14.5 parts by weight of PDA per 100 parts by weight of DGEBA), and $\rho(x = 0.3) = 1.213$ (weight fraction of PDA = 10 parts per 100 parts of DGEBA). Thus, for small variations of ρ, we can write

$$\frac{\rho}{\rho_s} = 1 + 11 \times 10^{-3}x$$

Equation (6) becomes

$$\frac{\rho^*}{\rho_s^*} = (1 + 11 \times 10^{-3}x)(1 - 18 \times 10^{-3}x) = 1 - 7 \times 10^{-3}x \tag{7}$$

The number of cross-link points in the monomer unit is

$$N = N_t - N_f$$

where $N_t = 2(1 - x)$ is the overall number of nitrogen atoms per structural unit and $N_f = 4x$ is the number of nitrogen atoms connected to a free chain end, for example, to an unreacted epoxide. Thus the cross-link density is

$$n = \frac{N}{M} = \frac{2 - 6x}{M_s - xM_a} = \frac{2}{M_s}\frac{1 - 3x}{(1 - xM_a/M_s)} \tag{8}$$

Since $2/M_s$ is the cross-link density of the stoichiometric network and since $xM_a/M_s \ll 1$, eq. (8) can be written

$$\frac{n}{n_s} = 1 - 2.88x$$

which leads to

$$\frac{\rho^*}{\rho_s^*} = 997.6 \times 10^{-3} + 2.4 \times 10^{-3}\frac{n}{n_s}$$

Thus, the packing density is found to increase with the cross-link density, whereas the density decreases owing to the increase of van der Waals volume resulting from the epoxide-amine addition reaction. It can be concluded that density variations in nonstoichiometric epoxide-amine systems cannot be directly assimilated by variations in the degree of molecular packing.

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