

## Molecular Packing in Nonstoichiometric Epoxide–Amine Networks

Some studies on a difunctional, diglycidyl ether of Bisphenol-A (DGEBA) type epoxy resin, viz., Epon 828 of shell cured with different amounts of a tetrafunctional curing agent, viz., metaphenylene diamine (mPDA) [Fig. 1(b)] had shown<sup>1,2</sup> that the sample cured with stoichiometric amount of curing agent, i.e., 14.5 parts of mPDA by weight per hundred parts of resin (phr), had the highest crosslink density and the highest glass transition temperature ( $T_g$ ). However, this sample had the smallest bulk density at room temperature compared to the densities of the nonstoichiometric samples studied. It was suggested that, among other reasons, this could arise because the crosslink site did not provide a suitable environment for close packing of molecules and, therefore, when a sample was cooled from the final curing temperature to room temperature, the molecular packing in the sample with the highest crosslink density was relatively poor. Support for this observation has also come from wide angle X-ray scattering studies on these samples,<sup>3</sup> which showed that the average intermolecular distance was the largest in the most highly crosslinked samples. Poor molecular packing in highly crosslinked samples cured with stoichiometric amounts of curing agent in relation to those cured with nonstoichiometric amounts has been inferred from their low bulk density in other epoxide systems also.<sup>4,5</sup>

Recently, Bellenger et al.<sup>6</sup> have published the results of their calculations of the Van der Waals Volumes ( $V_w$ ) and packing coefficients for one of the nonstoichiometric samples reported in the earlier studies,<sup>1,2</sup> viz., the sample cured with 10 phr of mPDA and also for the stoichiometric sample (14.5 phr). They found on analysis of the data for these two samples that the packing density increases with crosslink density and concluded that the bulk density variations cannot therefore be directly assimilated by variations in the degree of molecular packing as they could arise from the changes in  $V_w$  as a result of the epoxide–amine addition reaction. The purpose of the present communication is to show that the above analysis is very sensitive to the values of  $V_w$  used by the authors.

$V_w$  values for the network were calculated by Bellenger et al.<sup>6</sup> from the group contribution values given by Bondi in his book,<sup>7</sup> which suggests a value of 3.7 cm<sup>3</sup>/mol for oxygen. In an earlier publication,<sup>8</sup> Bondi discussed the approximations involved in calculating  $V_w$  which result from the assumptions that have to be made in obtaining bond distances, bond angles, and contact distances. As regards the group contribution of oxygen, Bondi has emphasized the lack of good contact distance data. He has further stated that as a result of being too deeply buried within the molecule for frequent (or any) collision with neighboring molecules, the “effective volume” occupied by ether oxygen differs from molecule to molecule. In ethylene oxide, on the other hand, the ether oxygen is sufficiently exposed to yield a value of  $V_w = 5.5$  cm<sup>3</sup>/mol. In alkyl ethers, especially polyethers,  $V_w = 3.7$  cm<sup>3</sup>/mol and in polyphenylene ethers, it is 3.2 cm<sup>3</sup>/mol. In certain polyalkanes the value of  $V_w$  for the oxygen atom can be 5.2 cm<sup>3</sup>/mol, according to Bondi. With reference to the chemical structure of the epoxide resin used [Fig. 1(a)], it is clearly seen that the epoxide group oxygen is relatively more exposed than the oxygen attached to the phenylene ring. Therefore, as suggested by Bondi for ethylene oxide, the epoxide oxygen will be expected to have a higher  $V_w$ , say around 5.5 cm<sup>3</sup>/mol. It is interesting to note at this stage that Van Krevelen in his survey<sup>9</sup> of a number of group contributions to  $V_w$  of bivalent groups as proposed by Bondi<sup>7,8</sup> and Slonimskii et al.<sup>10</sup> notes that in general the values mentioned by the two authors show good correspondence except for oxygen in which case Slonimskii et al.’s value (5.8 cm<sup>3</sup>/mol) is larger and more realistic than Bondi’s value (3.7 cm<sup>3</sup>/mol).

In view of the above, the Van der Waals volumes have been recalculated using the method suggested by Bellenger et al.,<sup>6</sup> with the following two sets of values for oxygen:

Scheme A:  $V_w = 5.5$  cm<sup>3</sup>/mol for epoxide oxygen and 3.2 cm<sup>3</sup>/mol for phenylene oxygen

Scheme B:  $V_w = 5.5$  cm<sup>3</sup>/mol for epoxide oxygen and 5.2 cm<sup>3</sup>/mol for phenylene oxygen

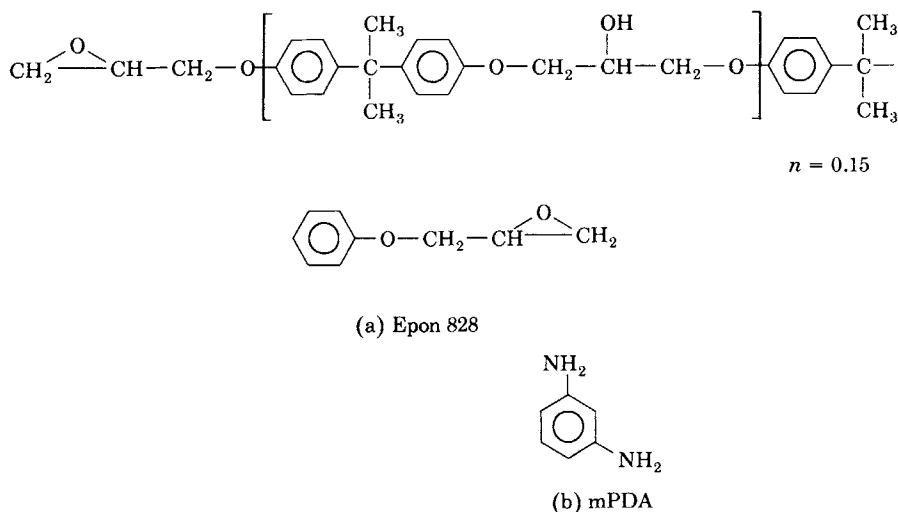


Fig. 1. The structures of the starting materials.

### THE PACKING COEFFICIENT

The packing coefficient,  $\rho^*$ , is defined as  $\rho^* = \rho \cdot (V_w/M)$ , where  $\rho$  is the measured density and  $M$  the molar weight.

Bellenger et al. have shown<sup>6</sup> that, for the epoxide-amine system considered, their analysis leads to the following relationship:

$$\rho^*/\rho_s^* = 0.9976 + 0.0024n/n_s \quad (1)$$

where  $\rho^*$  and  $\rho_s^*$  are the packing coefficients of the off-stoichiometric sample with an amine concentration of 70% of the stoichiometric value and stoichiometric sample, respectively, and  $n$  and  $n_s$  their respective crosslink densities. The packing coefficient is thus found to increase with increase in crosslink density.

The relationships between packing coefficient and crosslink density were derived with the  $V_w$  values as per schemes A and B and the following results were obtained:

$$\text{Scheme A: } \rho^*/\rho_s^* = 1.0025 - 0.0025n/n_s \quad (2)$$

$$\text{Scheme B: } \rho^*/\rho_s^* = 1.0034 - 0.0034n/n_s \quad (3)$$

In both the above schemes, the packing coefficient decreases with increasing crosslink density.

The packing coefficients obtained for the two samples are shown in Table I and it is noteworthy that the stoichiometric sample has now lower packing coefficients in both cases.

### THE BULK DENSITY

The total volume of the sample may be assumed to be the sum of the occupied or Van der Waals volume and the empty volume. In Table II, the measured specific volume<sup>1,2</sup> (reciprocal of measured density), the calculated value of  $V_w/M$  and the total empty volume ( $V_E$ ) which is equal to (specific volume -  $V_w/M$ ) are shown as per schemes A and B. It is observed that the decrease of density is due to the increase of empty volume and not due to the increase of  $V_w$ , as is the case in the analysis of Bellenger et al.<sup>6</sup>

TABLE I  
The Packing Coefficients

Sample (phr)	Scheme A	Scheme B	Ref. 6
10.0	0.670	0.684	0.671
14.5	0.669	0.682	0.672

TABLE II  
 $V_w$  and Empty Volume Data

Sample (phr)	Specific volume ( $\text{cm}^3/\text{g}$ )	Scheme A		Scheme B		Ref. 6	
		$V_w/M$	$V_E$	$V_w/M$	$V_E$	$V_w/M$ ( $\text{cm}^3/\text{g}$ )	$V_E$
10.0	0.824	0.553	0.271	0.564	0.260	0.553	0.271
14.5	0.827	0.553	0.274	0.564	0.263	0.556	0.271

From the above discussion, it is apparent that the conclusions regarding the bulk density and packing coefficients of epoxide networks are very sensitive to the  $V_w$  values used. It cannot therefore be concluded without reservation that the changes in bulk density cannot be directly assimilated by variations in the degree of molecular packing.

### References

1. V. B. Gupta, L. T. Drzal, and M. J. Rich, *J. Appl. Polym. Sci.*, **30**, 4467 (1985).
2. V. B. Gupta, L. T. Drzal, C. Y.-C. Lee, and M. J. Rich, *Polym. Eng. Sci.*, **25**, 812 (1985).
3. Satish Kumar and W. W. Adams, *Polymer*, **28**, 1497 (1987).
4. R. J. Morgan, F. M. Kong, and C. M. Walkup, *Polymer*, **25**, 375 (1984).
5. I. Perepechko, *Acoustic Methods of Investigating Polymers*, Mir, Moscow, 1978, Chap. 8.
6. V. Bellenger, W. Dhaoui, and J. Verdu, *J. Appl. Polym. Sci.*, **33**, 2647 (1987).
7. A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Glasses*, Wiley-Interscience, New York, 1968, pp. 450-468.
8. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
9. D. W. Van Krevelen, *Properties of Polymers: Correlations with Chemical Structure*, Elsevier, Amsterdam, 1972, pp. 50-52.
10. G. L. Slonimskii, A. A. Askadskii, and A. I. Kitaigorodskii, *Vysokomol. Soyed*, **A12**, 494 (1970).

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