Packing Density of Amine Cross-Linked Epoxy Networks

It has been observed[1-4] that in some cross-linked networks prepared by curing of epoxy resins based on Bisphenol-A with different amines, the sample density decreases with increasing crosslink density. It was suggested[1] that this could arise in the system studied viz. Epon 828 which is based on diglycidyl ether of Bisphenol-A (DGEBA) cured with m-phenylene diamine (m-PDA), due to poor molecular packing in samples having high crosslink density, as the crosslink site does not provide a suitable environment for the molecules to come close to each other. Bellenger et al.[5] have recently studied a number of epoxy resins which were cured with stoichiometric amounts of different amines. Based on results of their own work and also from the literature, they have concluded that epoxy-amine networks are densely packed and their packing density increases mainly with hydrogen bonding (or cohesive energy density) and also with the crosslink density, which seems to have a "specific influence" on T_g. In view of this they have put forward an alternative explanation to account for the decrease of sample density with increase in crosslink density. The purpose of the present communication is to show that the explanation based on the free volume concept is still valid.

The first point made by Bellenger et al.[5,6] is that a density decrease is not necessarily lacking in consistency with a packing density decrease in the case of DGEBA-mPDA system, as the decrease in density can be attributed to increase in Van der Waals volume (V_m) on curing. It has already been shown[7] that if more appropriate values of V_w are used for group contribution of oxygen, the Van der waals volume explanation cannot account for the density decrease. Thus, a density decrease for the DGEBA-mPDA system could still arise from free volume increase in the highly cross-linked sample, as had been postulated earlier.[1]

The second point made by Bellenger et al. in support of their earlier postulate is that for homologue series, based on completely cross-linked systems, in which the crosslink density is varied by using diepoxides differing in their degree of polymerization,[8] or aniline as a chain extender,[9] the sample density increases with crosslink density. Both these cases are considered below.

CASE I

In the first case,[8] the resins used were various Epon grades based on DGEBA having molecular weights between 352 to 1996. These were completely cured with stoichiometric amounts of methylene dianiline. The sample density decreased as the molecular weight between crosslinks (M_c) increased.

In this context, it is worthwhile recalling the work reported on incompletely cured stoichiometric networks based on two different epoxy resins cured with amines; the first studied by Enns and Gillham,[2] who found a decrease in sample density with increase in crosslink density and the second by Chang et al.[10] who found that sample density increases with crosslink density. The difference between the samples of Enns and Gillham[2] and Chang et al.[10] was that while the former used a rigid Bisphenol-A based epoxy prepolymer, the latter used a flexible butanediol based prepolymer. Since there is no other major difference between the two studies, it apparently appears that the degree of rigidity of the prepolymers plays an important role in addition to crosslink density in determining the packing density of the cured sample. In case I cited by Bellenger et al.,[5] the samples were based on a combination of prepolymers with varying molecular weight homologues.[8] The cured samples with higher homologues have a higher number of Bisphenol-A groups per unit length. These bulky and rigid groups can create free volume and thereby density can decrease with increasing M_c. Work done by Hata and Kumanotani[11] supports this view. Thus the free volume approach also offers a valid explanation for this case.

CASE II

In the second example, cited by Bellenger et al., the samples contained aniline as chain extender.[9] Using the more appropriate V_w group contribution values given by Slonimskii et al.,[12] as shown in

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TABLE I
Calculated Van der Waals Volumes for the Samples of Reference 9

Epoxy system	Specific volume cc/gm	Van der Waals volume cc/gm	Empty volume cc/gm
E_1	0.827	0.584	0.243
E_2	0.830	0.587	0.243
E_3	0.832	0.589	0.243

Table I the decrease in sample density in this case can be attributed to the higher V_w of phenyl groups of the aniline.

The third point made by Bellenger et al. is based on the work done by Fox and Loshaek.[13] They polymerized methyl methacrylate with dimethacrylates[14] and correlated the decrease in volume during polymerization with the degree of polymerization. It has been reported that increasing dimethacrylate concentration resulted in decreasing polymerization and so less volume reduction. Since some of the results published[1-4] suggest that higher crosslink density need not result in lower free volume, specific volume data on the above said acrylate copolymer systems cured to different extents should be obtained and compared before concluding that the reduction in volume is directly related to the degree of polymerization and crosslinking.

In order to gain a more definitive and unambiguous understanding of this problem, Araldite GY250, which is equivalent to Epon 828, was cured with stoichiometric amount of m-PDA (viz. 14.5 phr) at 75°C for 1, 1.5, and 2 h. Another set of samples was prepared by curing at 75°C for 2 h and further curing at 125°C for 0.5, 1, 1.5, and 2.0 h. Sample density was found to increase from 1.203 g/cc for 75°C 1 h cured sample to 1.205 g/cc for 75°C 2 h cured sample and on subsequent curing at 125°C, the density decreased to 1.204 g/cc after 0.5 h and then remained constant till 2 h of curing.

IR spectral analysis on these samples reported elsewhere[15] suggests that all the primary amines are exhausted during 75°C curing and unreacted secondary amines react during 125°C curing. Initial reaction of primary amine with the epoxy groups proceeds relatively rapidly and requires little heat. So during the second stage of curing no primary amine is left. When primary amine reacts, long chains are formed by epoxy ring opening and covalent bond formation which brings the small prepolymer molecules closer and this increases sample density during the first stage of curing. Secondary amine reaction at 125°C leads to crosslinking which results in a decrease of sample density. This observation supports the view that the crosslinking site can be a source of free volume.

In lightly cross-linked rubbers with M_c in the region of 10,000 or so, the molecules are known to come closer on crosslinking and as a result the density increases. Also vulcanised rubbers are close to their equilibrium state at room temperature. On the other hand, in the highly cross-linked rigid epoxy systems with M_c of around 300 or so, as after curing the sample is brought to room temperature (which is below the glass transition temperature), the molecules cannot come close to each other due to steric factors arising from the large number of crosslinks and rigidity of the prepolymer and the system is not in equilibrium as a consequence. The freezing of excess free volume in a glass, which is not in equilibrium, is a well-known physical phenomenon. In such cases the T_g is generally higher for a sample of high specific volume or low density.

Thus, it can be stated that decrease of sample density with crosslink density in Bisphenol-A based epoxy resin systems can arise from increase in free volume due to the high crosslink density and also due to the rigidity of the bulky Bisphenol-A groups.

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