Crosslink distribution of epoxy networks studied by small-angle neutron scattering

S. J. Bai
Research Institute, University of Dayton, Dayton, Ohio 45469, USA
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Crosslink distribution of epoxy networks of diglycidyl ether of bisphenol A (DGEBA) cured with stoichiometric amounts of *meta*-phenylene diamine (*m*PDA) was examined by small-angle neutron scattering (SANS). A monodisperse DGEBA resin with the smallest molecular weight was used to enhance the crosslink density and to simplify the network structure for deuterium-labelling. *Meta*-phenylene-d_4 diamine (*m*PDAd_4) was applied to label definitively the crosslinks. SANS measurements covered a reciprocal space range from 0.016 to 0.220 Å^{-1} or, equivalently, real-space distances from 400 to 30 Å. Application of SANS on the deuterium-labelled epoxy networks consistently produces a constant excess intensity over the unlabelled epoxy networks. Since the scattering intensity from total correlation of the network was negligible, as evident from measurements of SANS on the unlabelled epoxy networks and small-angle X-ray scattering on the epoxy networks, the constant excess SANS intensity can only be attributed to a uniform spatial distribution of the amine curing agent. In other words, the crosslinks are distributed uniformly throughout the epoxy network.

(Keywords: epoxy network; crosslink; small-angle neutron scattering; deuterium-labelling; spatial correlation)

INTRODUCTION

Epoxy resins are generally reacted with curing agents to form thermoset networks which are widely used in structural applications primarily as a matrix in advanced composite materials. The microstructure of the epoxy networks has attracted considerable interest. Extensive investigations have focussed on the existence of heterogeneities in and the distribution of crosslinks throughout the epoxy network[1-13].

Many studies have been reported on epoxy networks where a distinct second phase or heterogeneity has been detected. Small-angle X-ray scattering (SAXS)[1], nuclear magnetic resonance (n.m.r.)[2], electron paramagnetic resonance (e.p.r.)[3], and glass transition temperature (T_g)[4] measurements reveal a second phase which is attributed to a heterogeneous microstructure in the 100 to 1000 Å range. Direct imaging of the epoxy network by electron microscopy (*EM*) of ultramicrotomed sections[5], replicas of sections[6], unetched and etched fracture surfaces[7-9], shows a distinct nodular structure which is 100–600 Å in size. *EM* examinations of selectively reacted networks, either by plasma-etching of the fracture surface or by chemical staining, have further identified the nodules as being comprised of high crosslink density with a broad size distribution, predominantly in the 100 to 300 Å range, in a matrix of relatively low crosslink density. A most recent detailed *EM* study[10] of an epoxy network of diglycidyl ether of bisphenol A cured with metaphenylene diamine produces further evidence for the existence of these heterogeneities. It demonstrates that the size of these heterogeneities varies with the system stoichiometry and cure conditions. The stoichiometric amine–epoxy composition produces the smallest heterogeneity with the size increasing with either an excess of amine or epoxy.

Equally convincing, there is another school of evidence which suggests that the cured epoxy networks are homogeneous and do not have aggregations of crosslinks into nodules. It is considered that evidence of inhomogeneity in the network from SAXS, n.m.r. and e.p.r. fails to correlate the inhomogeneities with aggregations of crosslinks because either the technique (SAXS) is inadequate to identify the crosslink aggregations or the techniques (n.m.r., e.p.r.) examine only the local molecular behaviour instead of larger scale nodular morphology. Measurements of T_g may be explained by the nonequilibrium character of the thermodynamic properties, and not necessarily by the formation of heterogeneities of crosslinks[11,12]. Nodular morphology of the epoxy network obtained from *EM* is also questioned. Mainly, similar inhomogenetities have been observed by *EM* on bulk atactic polystyrene and poly(methyl methacrylate) which are linear polymers and contain no crosslinks[13].

In this study, we focus our efforts on the crosslink distribution of a selected epoxy network of high crosslink density and on the existence of the nodular morphology which was reported to have a size predominantly in the 100 to 300 Å range[10]. Our approach is to apply neutron scattering on an epoxy network cured stoichiometrically with isotope-labelled curing agents (this network reportedly generates the smallest nodules)[10]. We believe that this application of neutron scattering provides a unique nondestructive means to study definitively the distribution of crosslinks in the epoxy network.

NEUTRON SCATTERING

Scattering of neutrons is due to neutron–nucleus interactions. The neutron scattering cross sections of nuclei vary in a non-systematic manner, unlike X-ray scattering cross sections which increase with atomic number. A good example is the distinct difference in neutron cross sections of ^1H and ^2D. Hence, neutron scattering on isotope-labelled system where ^1H is substituted with ^2D (which preserved *identical* chemical characteristics of the system)

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provides a unique approach in the study of hydrogen-containing systems, such as polymers.

Neutron scattering intensity, like all other scattering intensities, is related to a simple spatial correlation function in the following manner. The elastic intensity:

$$I^{\mathrm{el}}(Q) \propto \left\langle \left| \sum_{\mathrm{j}} a_{\mathrm{j}} e^{\mathrm{i}\underline{\mathrm{Q}} \cdot \underline{\mathrm{r}}_{\mathrm{j}}} \right|^{2} \right\rangle = \left\langle \sum_{\mathrm{i,j}} a_{\mathrm{i}} a_{\mathrm{j}} e^{\mathrm{i}\underline{\mathrm{Q}} \cdot (\underline{\mathrm{r}}_{\mathrm{i}} - \underline{\mathrm{r}}_{\mathrm{j}})} \right\rangle \qquad (1)$$

where a_{i} is a quantity related to the scattering power of the i-th scattering unit at $\underline{\mathrm{r}}_{\mathrm{j}}$; $\mathrm{Q} \equiv \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)\hat{Q}$ for elastic scattering, where θ is the scattering angle; the bracket indicates ensemble average over all the accessible states of the system. Akcasu *et al.*^{14} and Williams *et al.*^{15} have formulated the coherent intensity, $I^{\mathrm{el}}_{\mathrm{coh}}$, of Equation (1) for a deuterium-labelled system, which can be described as:

$$I^{\mathrm{el}}_{\mathrm{coh}}(Q,C) \propto NC(1-C)|b_{\mathrm{D}} - b_{\mathrm{H}}|^{2} S_{\mathrm{S}}(Q) + A(C) S_{\mathrm{T}}(Q) \qquad (2)$$

where

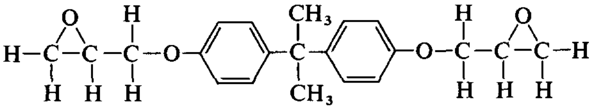
$$S_{\mathrm{S}}(Q) \equiv \frac{1}{N} \left\langle \sum_{\mathrm{k,l}} e^{\mathrm{i}\underline{\mathrm{Q}} \cdot (\underline{\mathrm{r}}_{\mathrm{k}} - \underline{\mathrm{r}}_{\mathrm{l}})} \right\rangle$$

$$S_{\mathrm{T}}(Q) \equiv \left\langle \sum_{\mathrm{i,j}} e^{\mathrm{i}\underline{\mathrm{Q}} \cdot (\underline{\mathrm{r}}_{\mathrm{i}} - \underline{\mathrm{r}}_{\mathrm{j}})} \right\rangle$$

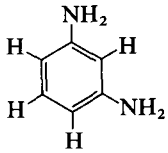
and C is the percentage of labelling, N is the number of the labelling component, b_{D} and b_{H} are the coherent scattering lengths (their values will be given later) of deuterated unit and of protonated unit, respectively. $S_{\mathrm{S}}(Q)$ is the form factor of the spatial correlation of the labelling component only (k and l sum over *the units of the labelling component*). $|b_{\mathrm{D}} - b_{\mathrm{H}}|^{2}$ is called the contrast factor resulting from the deuterium–hydrogen substitution. $A(C)$ is a constant which is related to the percentage of labelling in the *whole* system. $S_{\mathrm{T}}(Q)$ is the form factor of the total correlation of the system (i and j sum over *the whole system*). For X-ray scattering the isotope labelling concentration C is considered to be zero or one, the scattering intensity is actually a measurement of $S_{\mathrm{T}}(Q)$.

NETWORK PREPARATION

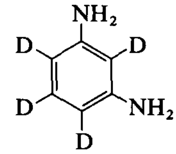
In order to maximize the possible aggregation and the amount of crosslinks per unit volume, we elected to use the smallest molecule of te epoxy resin based on the diglycidyl ether of bisphenol A (DGEBA) having the following chemical structure:



Samples of the DGEBA resin were obtained as EPON 825 from Shell Chemical Co. and a recrystallized resin designated as X-22. Liquid chromatographic analyses have shown that both resins are monodisperse in molecular weight. They are liquids of high viscosity at room temperature with an epoxide equivalent of 170. The curing agent was *meta*-phenylene diamine (*m*PDA), an aromatic amine which is a solid at room temperature with a melting point of 68°C. For neutron measurements in determining crosslink distribution of a cured epoxy network, we used *meta*-phenylene-d$_4$ diamine (*m*PDAd$_4$) as the labelled component. With complete deuterium labelling on the phenylene of *m*PDA we can (1) preserve identical curing kinetics of the amine–epoxy reaction, (2) provide a definitive labelling for neutrons to examine the distribution of crosslinks in the epoxy network. The chemical structures of the curing agents are given below:



meta-phenylene diamine
(*m*PDA)



meta-phenylene-d$_4$ diamine
(*m*PDAd$_4$)

The epoxy resin and the curing agent were heated or melted separately in an oven at 75°C. The curing agent was then mixed with the epoxy resin and deaerated. At the same time vigorous mixing took place. The mixture was cast in silicon rubber moulds into discs of 2 cm diameter. A thermal curing cycle of two hours at 75°C followed by two hours at 125°C was then applied. The cured samples were cooled slowly to room temperature by ambient conditions. In order to determine the crosslink distribution, by measuring $S_{\mathrm{S}}(Q)$ in equation (1), we have prepared independently two sets of samples of EPON 825 and X-22 each cured with stoichiometric amounts of curing agent. Use of two epoxy resins with identical chemical structure was designed to demonstrate the reproducibility of our sample preparation and the consistency of the measurement data. The stoichiometric amount for *m*PDA is 15.88 and for *m*PDAd$_4$ is 16.47 weight fraction of curing agent per hundred parts of DGEBA resin (phr). The curing agent compositions were *m*PDA at 15.8 phr (i.e. $C = 0.0$) and a mixture of *m*PDA and *m*PDAd$_4$ at half of their respective stoichiometric amounts to have the DGEBA resin still cured with stoichiometric amount of the amine curing agent, but with half of the curing agents deuterium-labelled (i.e. $C = 0.5$). Infra-red absorption spectroscopy has established that the epoxy networks have degree of cure above 94%.

Neutron scattering intensity difference between the labelled network and the unlabelled network should be an indication of the distribution of the labelling component. In this case, it is precisely the distribution of crosslinks in the epoxy network.

SMALL-ANGLE NEUTRON SCATTERING MEASUREMENTS

As shown in equation (1), the scattering intensty is related to the ensemble average of all the accessible states of the system. Because of the nature of the neutron–nucleus interactions in neutron scattering, the ensemble average over all the accessible nuclear spin states will generate incoherent scattering intensity I_{incoh}. The total intensity of scattered neutrons can be written as

$$I = T_{\mathrm{n}} K (I_{\mathrm{coh}} + I_{\mathrm{incoh}}) + \text{system noise} \qquad (3)$$

where T_{n} is the transmission factor of the sample; $K \equiv I_0 \cdot \Delta\Omega \cdot \Delta t \cdot \varepsilon(Q)$; I_0 is the incident neutron flux; $\Delta\Omega$ is

Table 1 Neutron scattering factors for the cured epoxy network of DGEBA/*m*PDA

Nucleus	Spin	b (10^{-12} cm)	σ^{coh} (barn)	σ^{inc} (barn)
^1H	1/2	−0.347	1.76	79.24
^2D	1	0.667	5.59	2.01
^{12}C	0	0.665	5.95	–
^{14}N	1	0.936	11.01	0.46
^{16}O	0	0.580	4.23	–

Table 2 Neutron scattering measurement configurations applied for the DGEBA/*m*PDA networks at the Oak Ridge National Laboratory (ORNL) and the National Bureau of Standards (NBS). ^{3}He position sensitive detectors (PSD) were used

	ORNL–NCSASR	NBS
λ	4.75 Å	5.10 Å
SDD	2.00 m, 4.30 m	3.60 m
DET	PSD (64×64 cm^2) $0.016 < Q < 0.220$ Å^{-1}	PSD (64×64 cm^2) $0.020 < Q < 0.200$ Å^{-1}

the solid angle of a detector element; Δt is the exposure time; and $\varepsilon(Q)$ is the efficiency of the detector element, which is a function of λ and θ.

For small-angle neutron scattering (SANS) on a deuterium-labelled system, the elastic coherent scattering intensity given in equation (2) is an adequate expression. The coherent scattering intensity, I_{coh}, is then written as:

$$I_{coh}(Q,C) = NC(1-C)|b_D - b_H|^2 S_S(Q) + A(C)S_T(Q) \quad (4)$$

The incoherent scattering intensity can be simply expressed as the sum of contributions from each nucleus,

$$I_{incoh}(C) = \frac{1}{4\pi}\left\{\sum_i \sigma_i^{inc}\right\} \quad (5)$$

where σ_i^{inc} is the incoherent scattering cross-section of the i-th nucleus. It should be noted that σ_i^{inc} is a constant and the incoherent intensity is distributed uniformly over 4π solid angle. In *Table 1*, we list the scattering factors for all the nuclei of the network of DGEBA/*m*PDA. It is obvious that in the network ^{1}H is the predominant contributor in scattering neutrons incoherently. It should also be pointed out that when *m*PDA in the network is substituted with *m*PDAd$_4$ to definitively label the crosslinks the incoherent intensity decreases, i.e. $I_{incoh}(0.5) < I_{incoh}(0.0)$.

For long wavelength neutrons, the phenylene of *m*PDA can be treated as a point scatterer. The coherent scattering length b is the sum of coherent scattering lengths of the atoms in the scattering unit. For the labelling component of the epoxy network,

$$b_D = 6.658 \times 10^{-12}\ \text{cm}$$

$$b_H = 2.602 \times 10^{-12}\ \text{cm}$$

and the contrast factor $|b_D - b_H|^2 = 16.45$ barn/*m*PDA. Then, N is the number of curing agent molecules or, equivalently, of crosslinks in the epoxy network.

SANS measurements were performed at the National Center for Small-Angle Scattering Research (NCSASR) at the Oak Ridge National Laboratory (ORNL). Two independent sets of network samples were measured on two spectrometer configurations (one before and one after the reblanketing of the High Flux Isotope Reactor that happened in 1983) with sample to detector distances (SDD) of 2.0 m and 4.3 m. This was designed to cover an angular region equivalent to a real-space distance up to 400 Å to encompass the crosslink aggregations which have been claimed by electron microscopic evidence. Even though we are going to report only the neutron scattering results taken on the NCSASR facility, it should be mentioned that one set of the network samples was also sent to the National Bureau of Standards (NBS) for preliminary measurement purposes. The measurement configurations for all SANS on epoxy network are summarized in *Table 2*. The system noise of each measurement configuration was determined and subtracted. The T_nK factor was removed with measured transmission values and with SANS measurements of H_2O which scatters neutrons incoherently. As shown in Equation (3), the net intensity is then composed of contributions only from $(I_{coh} + I_{incoh})$.

RESULTS AND DISCUSSIONS

In the application of SANS on isotope-labelled systems, it is necessary to address the problem of 'isotope segregation', i.e. the deuterium-labelled component aggregates together and is not distributed statistically. This kind of phase separation casts serious doubt on measured $S_S(Q)$ and the interpretation extracted from it. This is particularly true in systems involving co-crystallization of the labelled and the unlabelled components. One of the well-known examples is SANS on polyethylene[16–18]. It becomes necessary to demonstrate that similar concern is not warranted for our epoxy networks.

Figure 1 is a wide-angle X-ray scattering (WAXS) intensity profile for the labelled EPON 825 network, which shows an intense signal at $\theta \sim 19°$ (with CuKα radiation) and is attributed to be the diffuse 'halo' of scattering from a typical amorphous system, like atactic

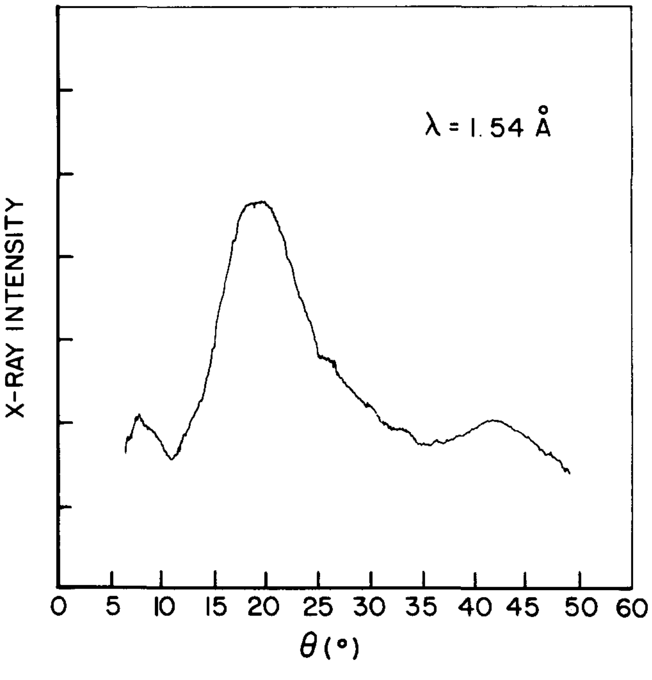


Figure 1 Wide-angle X-ray scattering on epoxy network of EPON 825 cured with a mixture of half of the stoichiometric amounts of *m*PDA and *m*PDAd$_4$

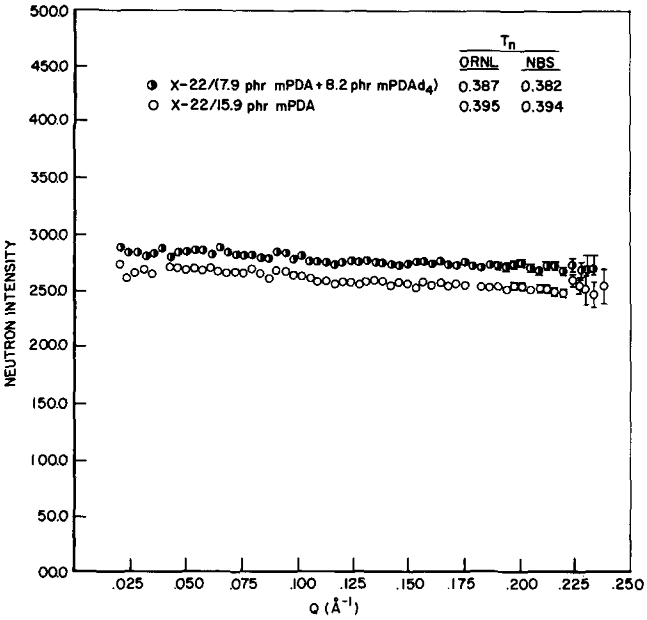


Figure 2 Small-angle neutron scattering on labelled (◑) and unlabelled (○) epoxy networks of X-22 cured with stoichiometric amounts of amines. Results were obtained on the ORNL 30 m neutron scattering facility with a sample to detector distance (SDD) of 2.0 m

polystyrene. However, unlike the ones from semicrystalline polyethylene, this WAXS spectrum does not have any lattice diffraction intensity which is related to the existence of crystalline structure. Because no lattice structure has been detected, the known amorphous nature of the cured epoxy network is proven here for our particularly labelled DGEBA/*m*PDA networks. Therefore, a large degree of isotope segregation of *m*PDA and *m*PDAd$_4$ is unlikely to have happened. It is reasonable to consider that the labelled *m*PDAd$_4$ is distributed statistically throughout the network like other labelled components in completely amorphous systems[14,19].

Net SANS intensities of two different sets of DGEBA/*m*PDA networks are presented in *Figures 2* and *3* for the two measurement configurations at NCSASR for a combined Q-region from 0.016 to 0.220 Å^{-1} which is equivalent to real-space distances from 400 to 30 Å. The two measurement configurations were also selected to overlap an extended Q-region to resolve better the low-Q behaviour of SANS intensities in *Figure 2* and to show the consistency of the measurements. Within experimental error, the general feature of the intensities can be approximated as being constant over the entire Q-region, and the labelled networks indeed have excess intensity, i.e. $I(Q, 0.5) > I(Q, 0.0)$.

The reduction of these net SANS intensities, of $I_{\mathrm{coh}} + I_{\mathrm{incoh}}$, in obtaining $S_S(Q)$ can be described as follows:

(1) I_{coh} contains contributions from $S_S(Q)$, from the correlation of the labelling component only, and $S_T(Q)$, from the total correlation of the whole system. As indicated before $S_T(Q)$ can be obtained by X-ray scattering. We have examined the epoxy networks with SAXS using a pin-hole camera and a high resolution slit-source Kratky camera. The X-ray intensities over an extended Q-region ($0.005 < Q < 0.40$ Å^{-1}) are negligible. This shows an insignificantly small $S_T(Q)$. In addition, our particular labelling scheme, by replacing half the stoichiometric amount of *m*PDA with *m*PDAd$_4$, and the use of monodisperse DGEBA molecules allow us to consider the network that on the average (as *m*PDAd$_4$ is distributed statistically) one of the 28 ^{1}H in the *repeat unit of the network* was replaced by ^{2}D. Moreover, the substitution was done precisely on the phenylene of *m*PDA to reflect the distribution of crosslinks throughout the epoxy network. This slight modification in the repeat unit of the network suggests that $A(0.5) \simeq A(0.0)$. Consequently, in considering the excess of coherent intensity between labelled and unlabelled networks, the contribution from total correlation of the network is negligible, i.e. $A(0.5)S_T(Q) - A(0.0)S_T(Q) = 0$. In other words, the net SANS intensity of the unlabelled network is $I_{\mathrm{inc}}(0.0)$.

(2) As shown in *Table 1*, the substitution of ^{1}H by ^{2}D should decrease the incoherent scattering intensity which is independent of θ, i.e. $I_{\mathrm{incoh}}(0.0) > I_{\mathrm{incoh}}(0.5)$. For the network of monodisperse DGEBA molecules cured with stoichiometric amounts of *m*PDA, it can be calculated that in substituting one of the 28 ^{1}H by ^{2}D in the repeat unit of the network, the incoherent scattering intensity decreases by about 3.5% which is within the uncertainty of the SANS measurement and means experimentally $I_{\mathrm{incoh}}(0.0) \simeq I_{\mathrm{incoh}}(0.5)$.

Owing to insignificant contribution from $A(C)S_T(Q)$ and similar contributions for I_{incoh}, we can say certainly that the difference in net intensity of $I(Q,0.5) - I(Q,0.0)$, as shown in *Figures 2* and *3*, can only be attributed to $S_S(Q)$ and can be approximated as a positive constant. The interpretation of $S_S(Q) = c > 0.0$ is straightforward, that the spatial distribution which is a Fourier transform of $S_S(Q)$ is required also to be a *positive constant* over a region from 30 to 400 Å. Since $S_S(Q)$ is due to the excess intensity from the labelling component, this further shows that the labelling component is distributed uniformly throughout the space. The deuterium-labelling has been selectively applied on the phenylene of the amine curing agent and is a true reflection of the crosslinking sites, we thus establish that the crosslinks are uniformly distributed throughout the network.

In summary, WAXS demonstrates that the deuterium-labelled networks of DGEBA/*m*PDA is a completely amorphous system. SANS on the unlabelled networks and SAXS on the networks over an extended Q-region show negligible intensity. In other words, the intensity due

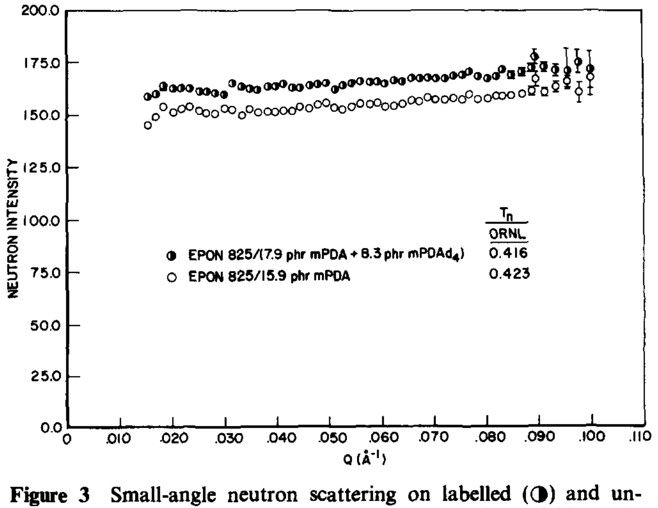


Figure 3 Small-angle neutron scattering on labelled (◑) and unlabelled (○) epoxy networks on EPON 825 cured with stoichiometric amounts of amines. Results were obtained on the ORNL 30 m neutron scattering facility with a sample to detector distance (SDD) of 4.3 m

to total correlation of the system is zero, and no significant heterogeneities have been observed. Application of SANS on epoxy resins cured with deuterium-labelled *m*PDA does have a constant excess intensity over the unlabelled epoxy network. This constant excess intensity can only be attributed to a constant spatial correlation of the labelling component (i.e. the amine curing agent) over a range of 30 to 400 Å. Owing to the unique and definitive deuterium-labelling of the phenylene of the *m*PDA curing agent, we can say that within experimental error the crosslinks are distributed uniformly throughout the epoxy network. The network morphology of aggregation of crosslinks into domains, of sizes predominantly in the 100 to 300 Å range, needs to be reexamined.

CONCLUSIONS

Crosslink distribution of the network was studied by SANS on epoxy resins cured with deuterium-labelled curing agent. A complete deuterium–hydrogen substitution was applied precisely on the phenylene of the *m*PDA curing agent. Deuterated and protonated *m*PDA was cured with a monodisperse DGEBA resin with the smallest molecular weight to enhance the crosslink density. The labelled networks do produce a constant excess SANS intensity which can only be attributed to the uniform distribution of the labelling component of the network, i.e. the amine curing agent. Consequently, this nondestructive approach clearly demonstrates that the crosslinks are distributed uniformly throughout the epoxy network.

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REFERENCES

1 Takahama, T. and Geil, P. H. *Die Makromol. Chemie, Rapid Commun.* 1982, **3**, 389
2 Morgan, R. J. and O'Neal, J. E. *J. Mater. Sci.* 1977, **12**, 1966
3 Yamini, S. and Young, R. J. *J. Mater. Sci.* 1980, **15**, 1823
4 Kreibich, U. T. and Schmid, R. J. *J. Polym. Sci.* (*Polym. Symp.*) 1975, **53**, 177
5 Oberlin, A., Ayache, J., Oberlin, M. and Guigon, M. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 579
6 Aspbury, P. J. and Wake, W. C. *Br. Polym. J.* 1979, **11**, 17
7 Racich, J. L. and Koutsky, J. A. in 'Chemistry and Properties of Crosslinked Polymers', (Ed. S. S. Labana), Academic Press, Inc., New York, 1977
8 Racich, J. L. and Koutsky, J. A. *J. Appl. Polym. Sci.* 1976, **20**, 2111
9 Mijovic, J. and Koutsky, J. A. *Polymer* 1979, **20**, 1095
10 Gupta, V. B., Drzal, L. T. and Adams, W. W. *J. Mater. Sci.* in press
11 Petrie, S. E. B. *J. Macromol. Sci.* (*Phys.*) 1976, **B12**, 225
12 Tonelli, A. E. *Macromolecules* 1971, **4**, 653
13 Dusek, K., Plestil, J., Lednicky, F. and Lunak, S. *Polymer* 1978, **19**, 393
14 Akcasu, A. Z., Summerfield, G. C., Johshau, S. N., Han, C. C., Kim, C. U. and Yu, H. *J. Polym. Sci. Polym. Phys. Edn.* 1980, **18**, 863
15 Williams, C. E., Nierlich, M., Cotton, J. P., Jannink, G., Boue, F., Daoud, M., Farnoux, B., Picot, C., de Gennes, P. G., Rinando, M., Moan, M. and Wolff, C. *J. Polym. Sci. Polym. Lett. Edn.* 1979, **17**, 379
16 Yoon, D. Y. and Flory, P. J. *Faraday Discuss.* 1979, **68**, 288
17 Summerfield, G. C., King, J. S. and Ullman, R. *J. Appl. Crystallogr.* 1978, **11**, 548
18 Spells, S. J. and Sadler, D. M. *Polymer* 1984, **25**, 739
19 Tangari, C., Summerfield, G. C., King, J. S., Berliner, R. and Mildner, D. F. R. *Macromolecules* 1980, **13**, 1546