Are cured epoxy resins inhomogeneous?

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The alternating mechanism of network formation in the curing of epoxy resins from bisphenol A diglycidyl ether (BADGE) and amine curing agents does not offer any special opportunity for the formation of inhomogeneities caused by partial segregation or inhomogeneous crosslinking. Etched fracture surfaces of resins cured with 4,4'-diaminodiphenylmethane, hexamethylenediamine and hexahydrophthalic anhydride at various initial ratios of BADGE, studied by electron microscopy, reveal globular structures 20—40 nm in size. However, similar structures are observed with etched surfaces of amorphous polystyrene and poly(methyl methacrylate). The small-angle X-ray scattering curves for cured epoxy resins do not differ in principle from those of common amorphous polymers; swelling in a solvent of a lower electron density does not lead to an increase in scattering within the particle size range $10-10^2$ nm. It is pointed out that the physical structure of simple cured epoxy resins does not essentially differ from that of common amorphous polymers. With more complicated systems, a more pronounced inhomogeneity might be caused by thermodynamic incompatibility or by non-alternating mechanisms of the curing reaction.

Cured epoxy resins are usually reported in the literature as inhomogeneous[1-4]; this view is supported by a number of arguments, the most important of which seem to be the following.

(1) The electron microscopy (e.m.) of unetched and etched free and fracture surfaces reveals a distinct nodular structure (see, for example, refs 2, 5 and 6). (2) Epoxy resins annealed below the glass transition temperature have an endothermic d.s.c. peak, which is explained by the separation of the resin into more or less independent and more and less crosslinked domains[4]. (3) The extractable (sol) fraction is much higher than with rubber vulcanizates having a lower crosslinking density[1].

Shapes of the mechanical loss maxima in the main transition region, which would indicate a two phase structure, can be seen only exceptionally with systems possessing a limited compatibility of components[1], or those in which the extent of reaction has not reached 100%. In a number of other cases (see refs 10 and 11), the loss maxima are symmetrical, unless any chemical reaction takes place during the measurement. Using an analysis of viscoelastic measurements, Kaelble[12] has inferred that 'the bulk properties of epoxide resins conform to general propositions in the physics of amorphous polymers'.

The main cause of inhomogeneous structure is usually seen in inhomogeneous crosslinking, i.e. in the ability of the reacting system to form more or less segregated domains with higher and lower crosslinking density (higher or lower concentration of the polyfunctional component)[1-4].

However, some of the indications of inhomogeneity, e.g. (1) and (2), are also common for linear amorphous polymers in the glassy state. Electron microscopy (e.m.) of such polymers, e.g. polystyrene or poly(methyl methacrylate), always reveals an inhomogeneous (nodular) structure, and the d.s.c. curves of annealed samples show endothermic

effects. A recent symposium on the physical structure of amorphous polymers[13] dealt in detail with problems of non-uniform structure in the amorphous glassy state. A number of sensitive methods, such as neutron scattering, small-angle X-ray scattering, light scattering, magnetic birefringence, stress birefringence of crosslinked polymers, etc. did not reveal significant density fluctuations or local order of dimensions of $10-10^2$ nm. E.m. methods always yield nodular structures, even with low molecular weight organic and inorganic glasses. Enthalpic effects observed with annealed glasses may also be explained by the non-equilibrium character of the glassy state and may thus be connected with the excess thermodynamic properties, and not necessarily with the formation of a structure other than ordering in liquids (Petrie[13], Tonelli[14]). If e.m. observations reflect a certain structural feature of polymeric glasses, it would involve probably the formation of noduli during the transition from melt (rubbery state) with a structure of randomly entangled coils into the glassy state with chain-folded structures (Boyer[13]). Such folding would of course be difficult with strongly branched irregular structures, e.g. cured epoxy resins.

In this paper we attempt neither a full elucidation of the physical structure of cured epoxy resins, nor to contribute to the characterization of the structure of the amorphous state; the latter problem has been dealt with in detail at the conference mentioned above[13] and in a number of other papers. In referring to the inhomogeneity of epoxy resins, it has become a habit to regard this inhomogeneity as being distinctly higher than and different from the possible inhomogeneity of common amorphous polymers. This is probably due to the fact that the main cause of inhomogeneities is seen in inhomogeneous crosslinking connected with the segregation of differently crosslinked domains.

This is why we made it the objective of this paper only to

analyse the course of the curing reaction with respect to possible causes of formation of inhomogeneities and to compare the results obtained by e.m. and small-angle X-ray scattering (SAXS) for a number of the simplest cured epoxy resins and for amorphous linear polystyrene and poly(methyl methacrylate).

EXPERIMENTAL

Sample preparation

Samples of epoxy resins were prepared from bisphenol A diglycidyl ether (BADGE) (99.2%), hexamethylene-diamine (HMDA) (98.9%), 4,4'-diaminodiphenylmethane (99.2%) and hexahydrophthalic anhydride (HHPA). The initial ratio of epoxide:amine or epoxide:anhydride functional groups was chosen to be 1:1, 1:1.5 and 1:2; diepoxide was regarded as bifunctional and amine as tetra-functional (curing with amines), or diepoxide was regarded as tetrafunctional and dianhydride as bifunctional (curing with anhydride). Samples in the form of plates were pre-pared in Teflon-coated moulds by heating at 80°C for 5 h and at 160°C for 7 h.

Electron microscopy

The internal structure was detected by using surface etching in high frequency plasma in air. The etching appara-tus has been described elsewhere[15]. To rule out the effect of the surface of casting moulds, fracture surfaces were etched. Fairly smooth fracture surfaces needed in the preparation of replicas were obtained by bending so as to make the fracture start at the narrower side of samples with rectangular cross-section. The etching time (30 min) was chosen so as to re-move the crazed layer from the fracture surface[16]. Samples for the transmission electron microscopy were prepared by preshadowing with a Pt–Pd alloy at 30° and by perpendi-cular deposition of the carrier carbon film. The replicas were peeled off by means of poly(vinyl alcohol), the film of which had been formed on the sample by evaporation of its solution in water.

X-ray scattering

Small-angle scattering curves were recorded with a Kratky camera (CuKα radiation, monochromatization with Ross filters, recording by proportional counter). Collimation corrections were made according to the method of Glatter[17]. Diffraction curves in the wide-angle region were measured with an automatic diffractometer, Syntex P2$_1$ (CuKα radia-tion, graphite monochromator, proportional counter).

RESULTS AND DISCUSSION

Possibility of formation of inhomogeneities as a consequence of the curing reaction

In the preparation of crosslinked (especially rather den-sely crosslinked) polymers one frequently observes the for-mation of inhomogeneities, mainly as a result of (a) strongly developed cyclization reactions or a preferential reaction of a polyfunctional crosslinking agent, accompanied sometimes by the formation of globular (microgel) domains having a higher crosslinking density, and (b) partial segregation on approaching the limit of the thermodynamic stability of the

system (χ and υ microsyneresis[18,19]). The cause (a) is characteristic of crosslinking chain polymerization[20], for which strong cyclization is a typical feature. At a higher content of the crosslinking agent, strongly crosslinked par-ticles are formed already at the beginning of the reaction[21]. Experimental conversions at the gel point are higher by a factor of $10-10^2$ than the theoretical value in the absence of cyclization[22]. The possibility of a thermodynamically controlled partial segregation (b) can be detected by a small change in such parameters as temperature, crosslinking den-sity and in some cases diluent concentration, which then leads to a thermodynamic instability of the system and to the easily detectable formation of a two phase structure.

In the case of curing of the epoxy resins, we shall analyse simple systems with amine curing agents, and particularly the curing of the bifunctional bisphenol A diglycidyl ether, BADGE, with tetrafunctional amines: 4,4'-diaminodiphenylmethane (DDM) and hexamethylenediamine (HMDA). If there are no epoxide groups in excess, the only reaction involved is the alternating reaction of amine and epoxide groups[23–25]. This is why polyfunctional molecules of diamine (crosslinking agent) cannot be bound with each other directly, but only through molecules of diepoxide (BADGE). From this viewpoint, the formation of domains having a higher and lower degree of crosslinking is far less likely than in the case of the crosslinking copolymerization, or in the crosslinking of primary chains. Cyclization can be neglected in the systems just mentioned[24]. Owing to the dif-ferent functionality of BADGE and diamines, there may exist some differences in composition: large molecules or the gel fraction may contain a somewhat larger amount of the tetra-functional component, while small molecules or sol are richer in the bifunctional diepoxide. In addition, if there existed an unfavourable large thermodynamic interaction between the components, partial segregation could not be ruled out.

An investigation of the course of curing of BADGE with DDM and HMDA[21,22] has shown that the critical conversion at the gel point agrees for a broad range of molar ratios of the epoxy and amino groups, with a purely chemical control of the reaction. This conclusion is also supported by measurements of the gel content and of the concentration of elastically active chains in the network. Also there is a good agreement between the ratios of the rate constants of the reaction of the primary and secondary amino groups with the epoxide group during curing and in the model re-action of monoepoxide with monoamine[25]. Thus, the results just described do not indicate a non-homogeneous course of the curing reaction. If partial segregation did take place at the stoichiometrically equivalent ratio of the components, these microregions probably would have an excess of either functional group and no full conversion of the functional groups could therefore be achieved in the alternating course of the reaction. The results indicate, however, that a vir-tually 100% conversion can be attained, if curing occurs at a temperature sufficiently above T_g.

Also argument (3), namely a higher amount of sol than in the vulcanization of rubber, need not indicate a non-homogeneous process of curing. Owing to the much higher functionality of rubbers (10^2-10^4) the sol fraction decreases much more steeply with increasing crosslinking density than in the alternating reaction of the bi- and tetrafunctional monomers. In the case of an incomplete curing reaction, caused by a deviation from the stoichiometrically equivalent ratio, or the presence of a major amount of monofunctional compounds, the cured system may contain a rather conside-rable quantity of sol.
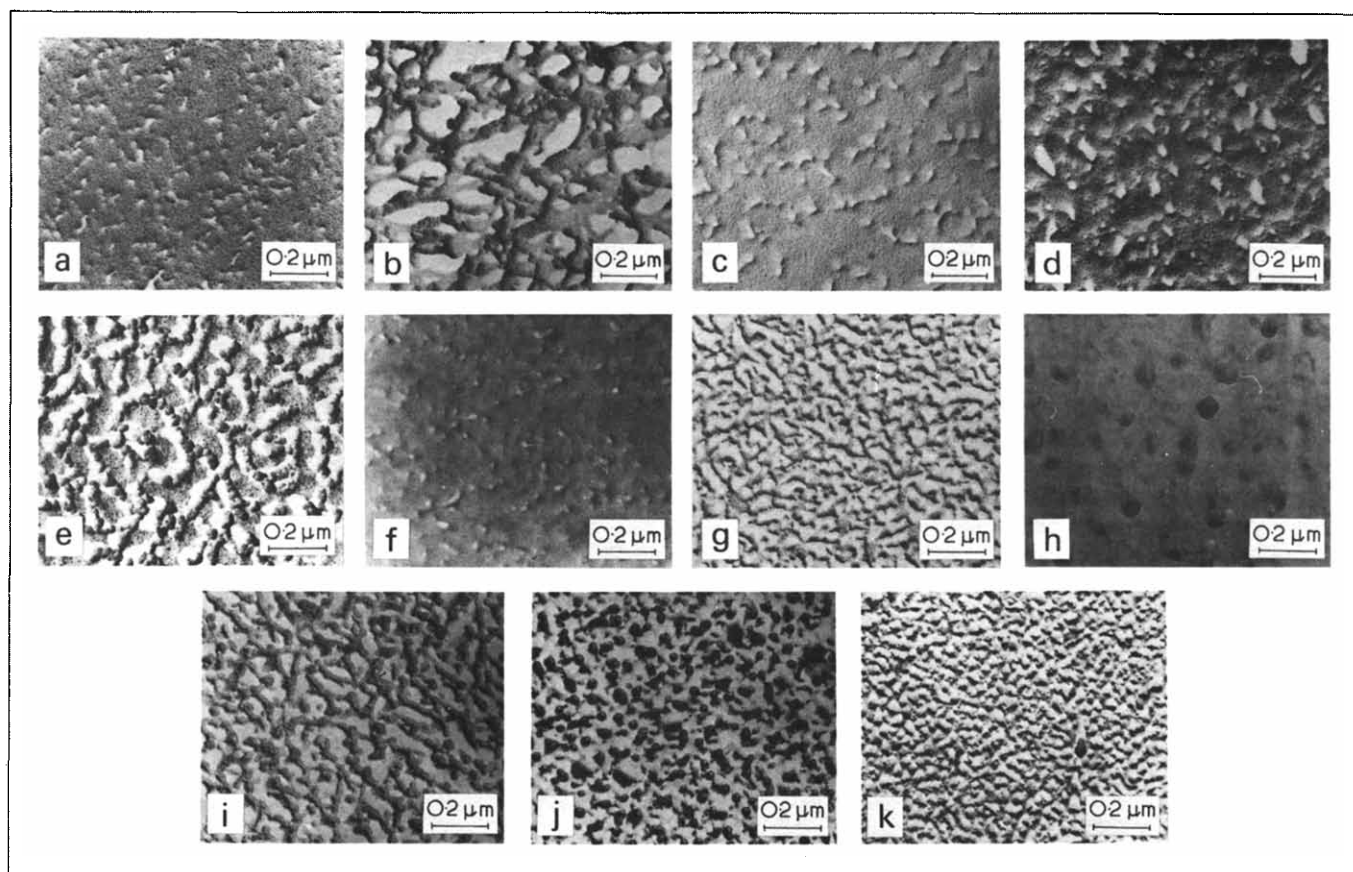
Figure 1 Electron micrographs of etched surfaces (samples denoted (a)–(k) correspond to samples 1–11 in *Table 1*). Bar scale represents 0.2 µm

Electron microscopy

Electron micrographs of the unetched free surfaces of all samples under investigation possess a relatively smooth structure, which probably corresponds to the surface of the polymerization moulds. Unetched fracture surfaces exhibited a characteristic oriented structure.

After plasma high frequency etching of the fracture surfaces, a globular (nodular) structure appears in all samples of cured epoxy resins prepared from BADGE, DDM or HHPA (*Figure 1*), with globule size 20–40 nm. The structures of etched surfaces of the individual samples differ in detail, so that one cannot say that the observed structure is an artefact arising only from the abrasive–chemical effects of ions. Consequently, the structure of the etched surface is determined by a certain property or by a complex of properties of the material: no clear-cut relationship between the structure observed and the composition of samples has been detected. Similar results were obtained by an electron microscopic investigation of etched epoxy films cast on the mercury surface at the stoichiometrically equivalent ratio or with amine in excess[26]. Some more pronounced differences appeared only when epoxide was present in excess. An important finding towards the aim of this work is that the structures of the etched surface of poly(methyl methacrylate) (PMMA) and of polystyrene (PS) are also similar, the size of the globules being 25–50 and 20 nm, respectively. The structure remained the same with the PS and PMMA samples containing 0.5% of ethylene dimethacrylate (cross-linking agent).

Hence, from e.m. results it can be concluded that the cured epoxy resins investigated here do not differ from amorphous PMMA or PS to any considerable extent.
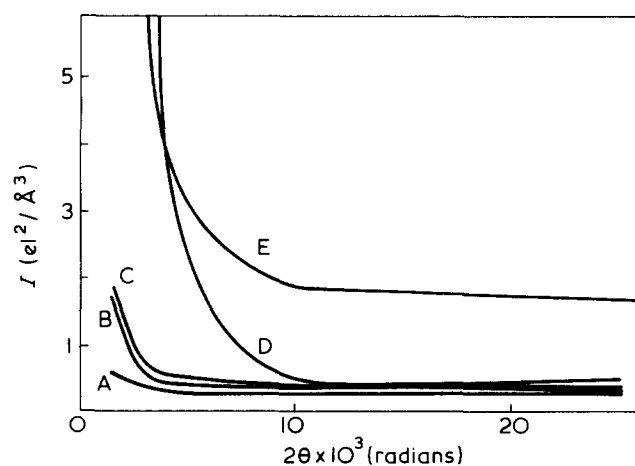

Figure 2 Small-angle scattering curves corrected for collimation effects (samples denoted as in *Table 1*) A, PS; B, PMMA; C, 4; D, 8; E, 8–THF

X-ray scattering

Small-angle scattering curves (examples see *Figure 2*) recalculated to the same intensity of the primary beam, absorption and sample thickness have the same shape for all samples of the epoxy resins. First, they decrease with increasing scattering angle 2θ, are roughly constant in the range $2\theta = 0.010–0.025$ rad, increase again and assume their maximum value at 0.10 rad. The rise in intensity at larger angles is due to the contribution of the wide-angle scattering. This part of the curves could not be reliably corrected for the primary beam length and is therefore not given in *Figure*
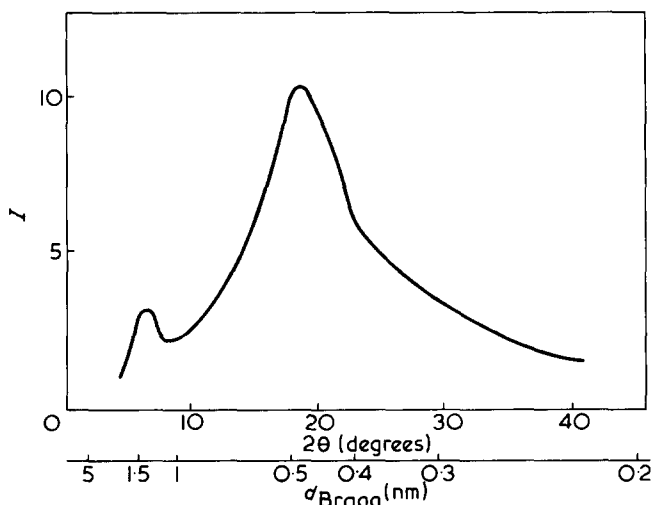
Figure 3 Schematic wide-angle scattering curves of epoxy resins BADGE–DDM

2. The curve of PMMA has a similar shape. With amorphous PS, the increase in intensity in the region $2\theta < 0.004$ rad is very small. The scattering curves of samples of BADGE–HMDA (1:1.5 and 1:2) swollen to equilibrium in tetrahydrofuran exhibit higher intensities in the angular range $2\theta = 0.003-0.05$ rad and decrease monotonically with increasing angle. For $2\theta > 0.01$ rad, their angular dependence is very weak, similar to that of the dry samples.

In the wide-angle region ($2\theta = 4°-40°$), two comparatively wide maxima can be distinguished in the diffractograms (*Figure 3*), with positions corresponding to Bragg distances 1.5 and 0.48 nm for the samples BADGE–DDM and 1.35 and 0.51 nm for BADGE–HHPA. The position of maxima in the individual series depends little on the amine–epoxide molar ratio. The samples do not contain any detectable amount of the crystalline phase but have a certain short range intra- or intermolecular ordering. Similar maxima in the same angular range can also be observed with PS or PMMA[27].

The small-angle scattering intensity in the range $2\theta = 0.010-0.025$ rad varies for dry samples of resins from 200 to 430 el²/nm³, and is in fair agreement with the intensity values calculated from isothermal compressibilities of amorphous polymers (see refs 28 and 29 and chapters by Fischer Harget and Uhlmann in ref 13). Hence, the scattering in this range can be assigned to the influence of local electron density fluctuations (in domains smaller than 1–2 nm). To characterize the magnitude of these fluctuations, *Table 1* presents the average intensity values for $2\theta = 0.010-0.025$ rad, I_{av}.

The increase in intensity at the smallest angles above the intensity of radiation scattered by local electron density fluctuations may be assigned to the scattering from heterogeneities of colloid dimensions up to the size of an order of magnitude of 100 nm. Their number may be estimated using the mean square electron density fluctuation $\langle(\Delta\rho)^2\rangle$ determined from the scattering curves[30]. For a two-phase system with the volume fractions of phases v_1 and $1-v_1$ and with the difference of electron densities $\Delta\rho = |\rho_1 - \rho_2|$ we have:

$$\langle(\Delta\rho)^2\rangle = (\Delta\rho)^2 v_1(1-v_1)$$

If $\Delta\rho$ corresponded to the value usual for semicrystalline polymers (~ 0.05 mol/cm³), the order of magnitude of the volume fraction of inhomogeneities would be 10^{-3}. In the

case of comparable phase volumes (which would correspond to the structures 'seen' by e.m.) the difference in electron densities would have to be lower than 0.005 mol/cm³ in all cases, i.e. the difference in densities smaller than 0.01 g/cm³. The dependence on the sample composition and crosslinking density has no pronounced trend. A correlation with the results obtained by electron microscopy, which records inhomogeneities in the same size range, is difficult.

An important finding for our analysis is that the intensity of scattering at low angles is generally low and does not indicate segregation; there is no essential difference between the epoxies investigated by us and amorphous PMMA or PS.

The objection may be made, of course, that the possible regions with a different crosslinking density could have very similar electron densities[2]. In this case, however, the differences could be increased or created by swelling the resin in a solvent with a different electron density. The result of swelling of samples 8 and 9 [with a relatively higher $\langle(\Delta\rho)^2\rangle$] in tetrahydrofuran (the electron density of which is much lower than that of resin) gives an answer. Absorption of 40–50% by volume of tetrahydrofuran caused a considerable increase in the local fluctuations (size range up to 1–2 nm, probably aggregates of several molecules of the solvent) but the scattering from inhomogeneities with dimensions of tens of nm did not increase. This is at variance with the view of partial segregation or of inhomogeneous crosslinking.

CONCLUSIONS

The analysis of network formation in the curing of simple epoxy resins with amines shows that the mechanism of crosslinking does not offer any special opportunity for inhomogeneous crosslinking or partial segregation. Neither do experimental results obtained in the curing of BADGE with HMDA and DDM indicate an inhomogeneous course of the reaction. The etched fracture surfaces of BADGE cured with HMDA, DDM and HHPA exhibit globular structure with globule size 20–40 nm; however, a similar structure is also characteristic of the etched surfaces of amorphous PS and PMMA. The

Table 1 Sample composition, mean square electron density fluctuation determined from SAXS, $\langle(\Delta\rho)^2\rangle$; SAXS intensities averaged in the range $2\theta = 0.010-0.025$ rad, I_{av}

Sample	Curing agent	a_0/b_0	$\langle(\Delta\rho)^2\rangle \times 10^6$ (mol/cm³)²	I_{av} (el²/nm³)
1	DDM	1	8	320
2	DDM	1.5	4	330
3	DDM	2	5	300
4	HHPA	1	4	430
5	HHPA	1.5	1	340
6	HHPA	2	1	290
7	HMDA	1	7	300
8	HMDA	1.5	4	330
9	HMDA	2	8	200
10	PMMA		1	290
11	PS		0	250
8–THF			3	1600
9–THF			9	2800

a_0/b_0 initial molar ratio of amine or acid functionalities: DDM, 4,4'-diaminodiphenylmethane; HHPA, hexahydrophthalic anhydride; HMDA, hexamethylenediamine; PMMA, poly(methyl methacrylate); PS, polystyrene; 8–THF and 9–THF samples 8 and 9 swollen to equilibrium in tetrahydrofuran, weight fractions of the polymer in the swollen resin 0.63 (8) and 0.56 (9)

SAXS curves of the samples do not differ in principle from those of amorphous PMMA and PS; swelling in a solvent with a considerably lower electron density does not lead to any change in the shape of the scattering curves that would correspond to a contrasting of possible inhomogeneities $10-10^2$ nm in size.

It seems, therefore, that simple cured epoxy resins in the glassy state do not exhibit any considerably higher inhomogeneity than amorphous glassy PS and PMMA. Hence, the inhomogenous structure is not an inherent property of the cured epoxy resins. It cannot be ruled out, of course, that inhomogeneity may appear in some more complicated epoxy system due to the effect of thermodynamic incompatibility or to pronounced non-alternating mechanisms of the curing reaction.

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