



INFLUENCE OF CHEMICAL STRUCTURE ON FREE VOLUME IN EPOXY RESINS: A POSITRON ANNIHILATION STUDY

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(Received 19 March 1993; accepted 27 April 1993)

Abstract—Positron annihilation lifetime (PAL) measurements are reported on a series of chemically different cured epoxy resin systems. Analysis of PAL data yields indicates the effects of changes in the cure temperature and chemical structure on the average molecular free volume size. A comparison of PAL with conventional density measurements on samples exhibiting different values of the glass transition temperature (T_g) indicates the importance of microscopic voids on the physical properties of epoxy resins. This study gives new insights into the effects of structural changes in thermosets on their T_g behaviour.

INTRODUCTION

Changes in chemical structure and cure temperature have profound effects on the physical properties of thermoset materials [1–4], and in hydrophilic systems influences the diffusion rates and equilibrium water uptake values. Changes in cure conditions lead to significant variation in the glass transition temperature [T_g] related as a result of differences in the type of network generated during the initial stages of cure. Studies of the microscopic free-volume can provide a basic understanding of the mechanical and physical properties of polymers and glasses [5], and the positron annihilation lifetime (PAL) method provides a molecular probe of the void structure of polymers and glasses [6–11]. The high sensitivity of PAL arises from preferential trapping (localization) of the positronium atom (Ps, a positron–electron bound state) in atomic scale voids—free volume holes. Ps can exist in two spin states, *para* positronium (*p*-Ps; spin allowed) with a lifetime of the order of 0.125 nsec and *ortho* positronium (*o*-Ps; spin forbidden) with a lifetime of the order of tens of nanoseconds. In organic media the lifetime of *o*-Ps is determined by the probability of electron exchange between itself and the surrounding matrix and is directly related to the mean size of the void in which it is thermalized.

PAL studies of epoxy resins have shown that the free volume distribution changes both with temperature and pressure and has values in the range 1–4 Å at room temperature [10, 12–18]. In this study, the effects of change in the chemical structure and cure temperature will be explored and the results of these investigations compared with bulk density measurements.

EXPERIMENTAL PROCEDURES

Materials

The epoxy resins investigated are summarized in Table 1. The resin was accurately weighed into a tall glass vial. The hardener was added in the required stoichiometric ratio. The sample was stirred in a preheated oil bath until a homogeneous mixture was obtained, times and temperatures used for mixing depended upon the hardener. The sample vial was placed in a vacuum oven to degas the mixture prior to placing it in the mould for the final cure process. The mould was constructed from two plates of glass separated by a PTFE/glass fibre spacer. The glass plates, 6 cm × 6 cm × 6 mm, were cleaned initially using water and then finally with acetone. The mould face of the plates was then coated with a fine layer of Rocol M. R. S. Advanced Non-Silicone Dry Film Spray. The plates were heated and then cooled before the surfaces were lightly wiped to remove any excess powder. The moulds were preheated to the initial curing temperature before the liquid sample was carefully pipetted into the top and allowed to slowly fill the mould. The curing schedules used are summarized in Table 1.

Positron annihilation lifetime (PAL) measurements

Positron annihilation measurements were performed using a conventional fast slow method as described previously [8]; the positronium source, 25 μm Ci of $^{22}\text{NaCl}$ (Aldemaston) was constructed by depositing the material onto a Kaptan foil and sealing the sandwich with epoxy resin. The ^{22}Na source emits a 1.28 MeV gamma ray which was used as a prompt signal and annihilation was marked by the coincident emission of two 0.511 MeV gamma rays. Samples were thermostated using an Oxford Instruments DN704 cryostat equipped with a DTC2 controller and over the temperature range 300–400 K, the precision of measurement was ±0.1 K. The time resolution of the equipment was determined using a ^{60}Co source and found to be 300 psec.

PAL spectra can be expressed as a convolution (*) of the instrument resolution function and a finite number (n) of negative exponentials:

$$y(t) = R(t) * \left(N_t \sum_{i=1}^n \alpha_i \lambda_i e^{-\lambda_i t} + B \right) \quad (1)$$

where $y(t)$ is an experimental raw datum, $R(t)$ is the instrument resolution function, N_t is the normalized total

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Table 1. Cure schedules and properties of the epoxy resins

Epoxy resin system	T_g (K)	phr	Cure schedule
DEGBA(MY750)/TETA	383	14	2 hr at 333; 16 hr at 373
DGEBA(EPON825)/DDM	459	29	30 min at 373; 3 hr at 353
DGEBA(EPON825)/DDS	490	36	3 hr at 403; 2 hr at 473
TGDDM(MY721)/DDM	536	47	18 hr at 358; 5 hr at 433; 2 hr at 453
TGDDM(MY721)/DDS	548	59	1 hr at 423; 5 hr at 450
TGAP(ERLA0510)/DDM	512	54	2 hr at 378; 1 hr 15 min at 503
TGAP(ERLA0510)/DDS	540	67	3 hr at 403; 1 hr at 453; 1 hr at 503
DGA/ <i>m</i> -DAB	429	26	17 hr at 353; 6 hr at 433
TFMDGA/ <i>m</i> -DAB	426	20	17 hr at 353; 6 hr at 433
DGEBA(EPON825)/NMA/0.5% DBA	432	105	2 hr at 373; 20 hr at 423
XD7342/DDS	481	40	17 hr at 423
	496	40	17 hr at 423; 5 hr at 453
	524	40	17 hr at 423; 5 hr at 453; 16 hr at 473
	551	40	17 hr at 423; 5 hr at 453; 16 hr at 473; 2 hr at 493; 2 hr at 513; 2 hr at 543

count, B is the background, λ_i is the inverse of the i th lifetime component (τ_i) and $\alpha_i \lambda_i$ is its intensity. Practically the number of resolvable terms is limited and in the case of annihilation in organic solids is best modelled in terms of three processes [19]. The experimental spectrum is least squares fitted to equation (3) to obtain lifetimes $\tau_i (= 1/\lambda_i)$ and the corresponding intensities. In epoxy resin samples with $n = 3$ fits with $\chi^2 < 1.1$ were obtained using the commercial computer code POSITRONFIT and RESOLUTION [20]. The spectrum consists of three components; two short time processes corresponding to the annihilation of free positron and *para*-positronium with lifetimes of respectively 0.125 and 0.4 nsec and a longer *ortho*-positronium component with a lifetime of the order of several nanoseconds. The average error in the lifetime was ± 0.03 nsec and $\pm 0.5\%$ in the intensity for the *ortho*-positronium component.

Density measurements

The density of the epoxy resins was determined by mixing a light (decane) and dense non-solvent (tetrachloroethane) and determining the composition in which the sample has the same density as the liquid mixture which was, in turn, measured using an Antoon Paar digital densimeter.

RESULTS AND DISCUSSION

A range of chemically different types of epoxy resins were examined and correspond to those investigated earlier by Johncock *et al.* [1–4], in their studies of water diffusion. The main objectives of this investigation are to determine whether significant changes in the free volume occur with variation of the chemical structure and cure temperature.

In PAL, the positron annihilation rate λ is defined by the integral of the positron $\rho_+(r)$ and electron density $\rho_-(r)$;

$$\lambda = \phi \int \rho_+(r) \rho_-(r) dr \quad (2)$$

where ϕ is a normalization constant related to the number of electrons involved in the annihilation process and τ , the annihilation lifetime is the reciprocal of the annihilation rate λ . In the pickoff model used to describe free volume processes [21], *o*-Ps is confined in a void between molecules. In most polymers, where no Ps quenching functional groups exist, the *o*-Ps (triplet state) will have a lifetime directly related to the hole size. A simple "particle in a

spherical box" approach leads to the following relationship [22, 23];

$$\tau_{o-Ps} = \frac{1}{\lambda_3} = \frac{1}{2} \left\{ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right\}^{-1}$$

where τ_{o-Ps} and R the hole radius are expressed in nanoseconds and angstroms respectively, R_0 equals $R + \Delta R$, where ΔR is the electron layer thickness ($\Delta R = 1.66 \text{ \AA}$). Although the above equation is based on a crude quantum model, a more accurate theoretical model [24], leads to a very similar result.

Data analysis for epoxy resins-redux 312/5

Positron annihilation data for the Redux 312/5 (DEGBA/DDM film adhesive) cured at 393 K are presented in Fig. 1. The lifetimes for the free positron and *p*-Ps remain virtually constant at 0.4 and 0.125 nsec respectively and are independent of temperature. In contrast, the *o*-Ps increases steadily with temperature whereas the intensity decreases. Average molecular void dimensions can be calculated using the relationship:

$$\tau_{o-Ps} = 6.98V + 1.30 \text{ nsec.} \quad (3)$$

where V is the volume in nm^3 and τ_{o-Ps} is the lifetime in nsec. Variation in the equivalent spherical cavity diameter calculated from the above data is from 0.36 to 0.42 nm over the temperature range 300–400 K. A variety of arguments have appeared in the literature concerned with the calculation of the void distribution from positron annihilation data [15–18]. Whilst it is clear that the use of a single value to describe the void size is not strictly correct, it is apparent that such a mean value is a good indication of the shortest radius for the cavity. In real system the voids are unlikely to be spherical, an assumption implicit in the current theories and it is therefore more correct to consider the size from the positron measurement as reflecting the minimum cavity dimension. Molecular models of the components of a typical epoxy resin would indicate that the bridging diphenyl will generate chevron type structures resulting in boomerang or oblate spheroid shaped voids. In this paper the simple exponential analysis is adopted as an indication of the minimum free volume size in epoxy resins. More sophisticated models are not

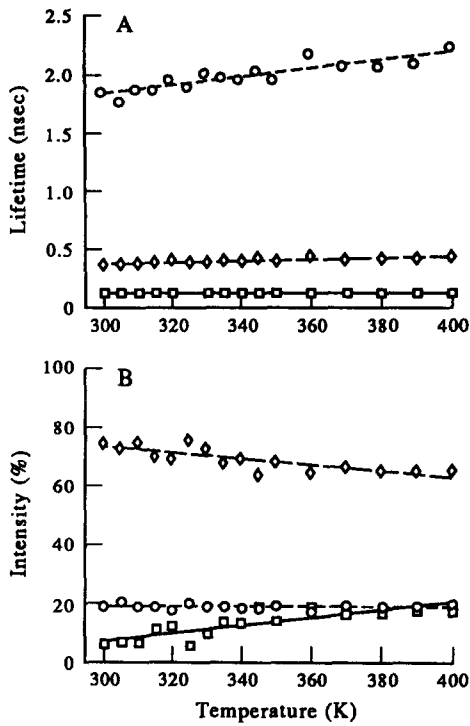


Fig. 1. Positron annihilation data for Redux 312/5 as a function of temperature; (A) lifetime (τ) data; (B) intensity data. \square , p -Ps; \diamond , free positron; \circ , o -Ps.

considered to be realistic because of the highly oblate nature of the voids expected in this system [26].

Effect of cure temperature of positron annihilation measurements

Samples of DGEBA/DDS cured at different temperatures were studied over the temperature range 300–400 K, Fig. 2. Lifetime and intensity data show scatter indicative of uncertainty in the fit of the longer lifetime component. Instead of using a single exponent a Weibull distribution [$\exp\{t/\tau\}^\beta$] could have been adopted [15, 16]. A detailed investigation indicated that the quality of the data was insufficient to justify determination of β with any degree of precision and the single exponential fit was adopted throughout this study. Lifetime data are very similar indicating that change in temperature of cure does not significantly influence the mean free volume size. In epoxy resins the bridge diphenyl methylene structure in the DGEBA and the diphenyl sulphone structure in the DDS lead to the oblate spheroid structures discussed above. The mean void diameter of 0.4 nm is comparable with that obtained from equation (3) in which values of the diameter of between 0.26 and 0.398 nm are obtained. In contrast, the intensity data which is related to the number density of voids capable of trapping the positronium reduces with increasing cure temperature. However, the differences in intensity observed at the higher temperatures are of the order of the precision in the measurements. The data implies that there is densification of the resin at the higher cure temperatures consistent with a loss in the free volume and a higher observed glass transition temperature.

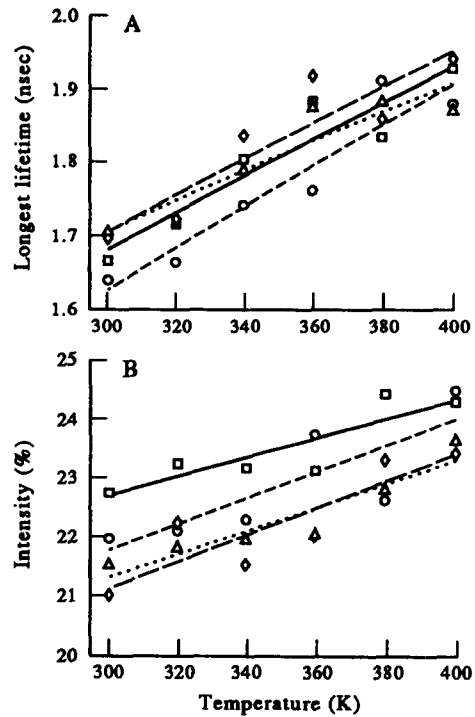


Fig. 2. XD7342/DDS cured resin as a function of temperature. \square , $T_g = 481$; \diamond , $T_g = 496$ K; \circ , $T_g = 524$ K; \triangle , $T_g = 551$ K.

The bulk density data, Fig. 3 indicate that as the cure temperature is increased so the bulk density is reduced. This apparent contradiction results from the lack of sensitivity of PAL measurements for voids $> 6 \text{ nm}^3$. Larger voids will be unable to trap the o -Ps but could make a significant contribution to the bulk density. Electron microscopic examination of epoxy resins has indicated that sub micron size voids do exist in fully cured materials and these lead to the observed reduction in the bulk density.

Influence of chemical structure on free volume size in cured epoxy resins

Intensity and lifetime data for the o -Ps component were measured for four systems as a function of

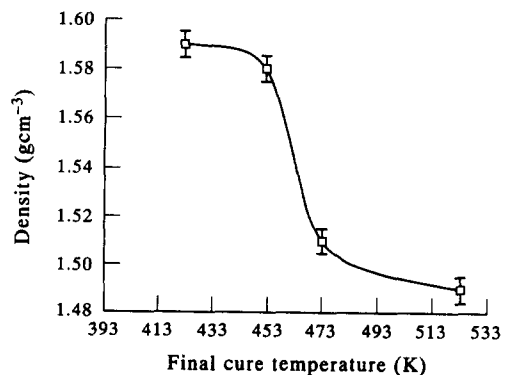


Fig. 3. Variation of density with cure temperature for XD7342/DDS.

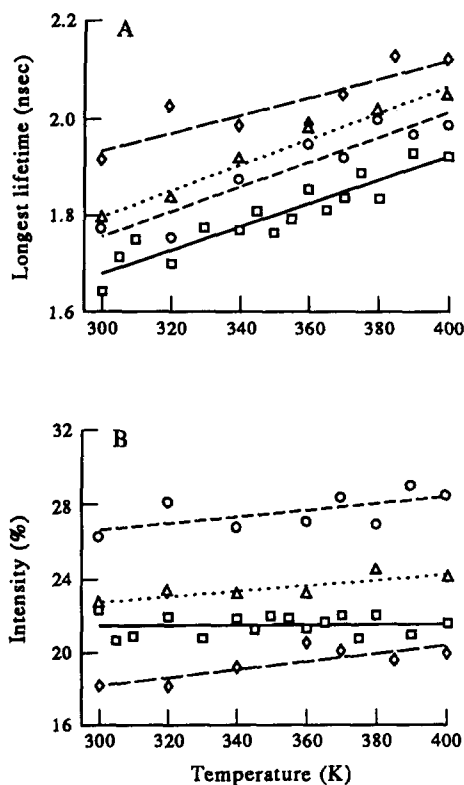


Fig. 4. Variation of positron lifetime (A) and intensity (B) data for TETA, anhydride, DDM and DDS/DEGBA cured epoxy resin systems as a function of temperature. \square , TETA ($T_g = 383$ K); \diamond , anhydride ($T_g = 432$ K); \circ , DDM ($T_g = 459$ K); \triangle , DDS ($T_g = 490$ K).

temperature, Fig. 4. The resins were cured using the schedule indicated in the Appendix. The smallest void size was observed with the lowest glass transition temperature material, TETA, and reflects the greater ability of the flexible chains to achieve good packing. Values obtained for this system are close to those reported for dibutylamine cured epoxy resins [14–16]. The volume in the case of DDS and DDM cures are comparable reflecting the close similarity in their molecular structures and anticipated void structure. In both cases the linked diphenyl bridge structure will inhibit the formation of a close packed structure. The differences observed in both lifetimes and intensities are greater than experimental error. The total free volume is the product of the lifetime {void size} and the intensity {number density of voids} and leads to the following void volumes:

System	Void size (nm ³)	Radius (nm)	Intensity (%)
Anhydride (DGEBA)	0.0873–0.111	0.275–0.298	18–19
DGEBA/DDM	0.0859/0.108	0.273–0.295	26–27
DGEBA/DDS	0.0714/0.0787	0.265–0.266	22–24
DGEBA/TETA	0.050–0.0703	0.248–0.256	22–20

The lower volume in the case of TETA reflects the greater mobility of the monomers in the gelation phase to adopt a minimum energy close packed state. In this case whilst the individual volumes are small, the number reflected in the intensity is large. In

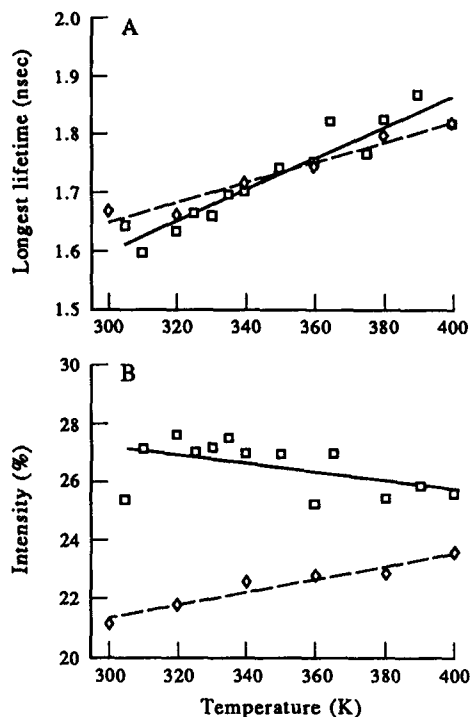


Fig. 5. Variation of positron lifetime (A) and intensity (B) data for TGDDM cured with DDM ($T_g = 535$ K) and DDS ($T_g = 548$). \square , DDM; \diamond , DDS.

contrast, the anhydride cure which will involve reaction of DGEBA with other DGEBA units produces a more hindered and hence larger unit volume, but there are a smaller number of such voids. DDM and DDS having similar molecular structures lead to similar void volumes, however the stronger intermolecular interactions generated as a consequence of the polar sulphone group leads to a more closely packed structure with a smaller volume and number of voids.

Comparison of TGDDM, TGAP and DGEBA based systems

Di-functional DGEBA reacts initially to produce a thermoplastic (linear polymer), whereas in the case of tetra-functional TGDDM a branched chain network structure is formed and can influence the final topography of the cured system. The lifetime and intensity data for TGDDM and TGAP systems are presented in Figs 5 and 6 and those for DGEBA in Fig. 4. In the case of TGDDM, the lifetimes and temperature dependences are not markedly influenced by change of hardener, however the TGDDM/DDS system with a T_g of 548 K has a lower I_{o,p_s} value (21–23%) than that observed in the case of the TGDDM/DDM system with a T_g of 535 K and I_{o,p_s} values of 29–26%.

Results for the equivalent TGAP, trifunctional epoxy system, Fig. 3, indicate that the void sizes are significantly smaller in the case of DDM and are comparable with those observed with the TGDDM system cured with DDS. In contrast, a significant lowering in the I_{o,p_s} is observed, consistent with the trifunctional epoxy forming a more densified network. The stresses generated in forming a highly

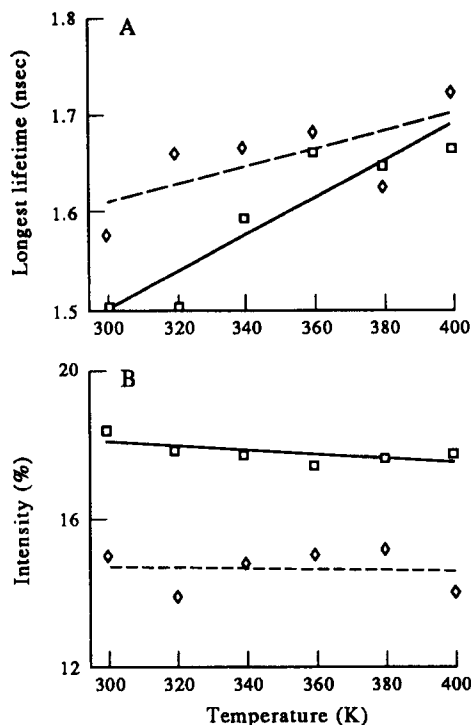


Fig. 6. Variation of positron lifetime (A) and intensity (B) data for TGAP cured with DDM [$T_g = 509$ K] and DDS [$T_g = 540$ K]. \square , DDM; \diamond , DDS.

crosslinked network lead to a less stable structure than when the diphenyl bridge structure is incorporated and a corresponding reduction in the T_g is observed.

Fluorinated vs non fluorinated epoxy resins

Cure of *m*-DAB was carried out using DGA and TFM-DAB, and the resulting materials have very comparable values of T_g , and the positron annihilation data are presented in Fig. 7. The value of τ_{o-Ps} for the fluorinated material is much greater than that for the non-fluorinated material, indicative of a larger molecular free volume as a consequence of weaker inter-chain interactions. These materials have similar values of T_g , although on the basis of the lifetimes alone one may have expected the fluorinated material to have a lower value of T_g as a consequence of the larger void volumes reflected in the values of τ_{o-Ps} . However, a marked decrease in the intensity implying a smaller number of voids in the fluorinated compared with the non-fluorinated material and in part explaining the similarity in values of the T_g .

CONCLUSIONS

Changes in the chemical structure do have a profound effect upon the number and size of molecular free volumes in the epoxy resin material. Comparison of the positron and density for XD7342 emphasizes the problem of understanding the water absorption data in terms of a simple molecular free volume model. The apparent discrepancies between PAL and bulk density data reflect the dominant role that microscopic voids with dimensions in the range

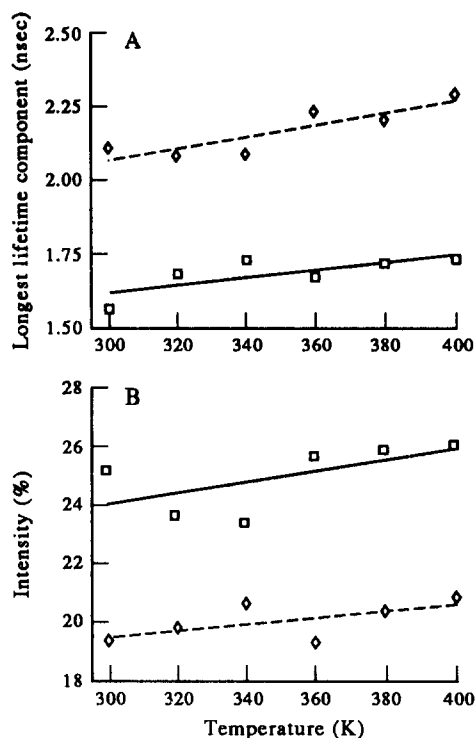


Fig. 7. Variation of positron lifetime (A) and intensity (B) data with temperature for DGA cured with *m*-DAB ($T_g = 429$ K) and TFM-DAB ($T_g = 433$ K). \square , DGA/*m*-DAB ($T_g = 429$ K); \diamond , TFM-DAB/*m*-DAB ($T_g = 433$ K).

0.1–1 μm play in determination of the physical properties of thermoset systems. These latter voids are probably a consequence of the network topography generated during the early stages of cure and the generation of holes as a consequence of stresses produced during the vitrification of the resin. The existence of such holes and their effect on bulk density has been discussed previously [25] and has important effects on the moisture transport coefficients for film coatings.

Acknowledgements—KJ wishes to thank the Royal Aerospace Establishment at Farnborough for the provision of an EMR studentship for the period of this work. The authors wish to thank Dr P. Wilford for his support and helpful discussions during the course of this research.

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APPENDIX 1

Code for Resins

Code	Supplier/Trade name	Chemical name
DGEBA	Ciba Geigy MY750 Shell Epon 825	Diglycidylether of Bisphenol A Diglycidylether of Bisphenol A
TETA	Aldrich	Triethylenetetramine
TGDDM	Ciba Geigy MY721	Bis[<i>N,N</i> -bis(2,3-epoxypropyl)- 4-aminophenyl]methane
TGAP	Ciba Geigy ERLA0510	<i>O</i> -(2,3-epoxypropyl) <i>N,N</i> -(2,3- epoxy-propyl)-4-aminophenol
DGA		<i>N,N</i> -bis(2,3-epoxypropyl)aniline
M-TFDMA		<i>m</i> -Trifluoromethyl <i>N,N</i> -bis (2,3-epoxypropyl)aniline
TGPM	Dow XD7342	Tris[<i>O</i> -(2,3-epoxypropyl)phenyl] methane isomers
DDM	Ciba Geigy HT972	Bis[4-aminophenyl]methane
DDS	Ciba Geigy HT976	Bis[4-aminophenyl]sulphone
DAB	Aldrich	<i>m</i> -Diaminobenzene
NMA	Aldrich	Nadic methyl anhydride.
DBA	Aldrich	<i>N,N</i> -Dimethylbenzylamine

Mixing Conditions

Hardener	Temperature (K)	Time of mixing (min)
DDM	373	5 min
DDS	403	10 min
NMA	333	5 min
<i>m</i> -DAB	353	5 min