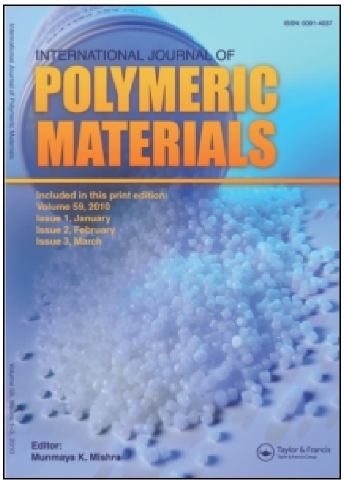

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Influence of Aniline Addition on the Cure, Mechanical Properties and Water Absorption Characteristics of Amine Cured Epoxy Resins

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Curing, dielectric, gravimetric, dynamic mechanical, infrared and density measurements are reported on the effect of the incorporation of mono and bi-functional amines on the water absorption and mechanical properties of diglycidyl ether of bisphenol A (DGEBA), MY720 (Ciba Geigy) cured with diaminodiphenylmethane, (DDM), HT972, (Ciba Geigy) and diaminodiphenylsulphone, (DDS), HT976, (Ciba Geigy). Resin samples were prepared with incorporation of mono/bi-functional amines of different ratios from 0% through to 60%. Analysis of these materials showed little difference in the water uptake properties of DGEBA cured with DDM than with DGEBA cured with DDS. The DDS cured material showed slightly better resistance to water uptake with a reduced water uptake and diffusion coefficient. The addition of aniline and *N*-ethylaniline increased the cure time of the resin due to hindrance of the network formation. Gravimetric water absorption measurements showed an increase in the diffusion coefficient and equilibrium water content on addition of *N*-ethylaniline due to more free volume in the system as confirmed by dynamic mechanical results. Addition of aniline showed an initial increase in the diffusion coefficient and then a decrease at greater than 20% aniline which is reflected by a corresponding increase in the glass transition temperature as shown by dynamic mechanical measurements.

Keywords: Epoxy resin; aniline; cure; mechanical properties; water absorption

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INTRODUCTION

Epoxy resins are traditionally seen to be brittle materials and there have been a number of attempts to improve their fracture properties [1–3]. Two approaches have been extensively pursued: addition of an amorphous glassy thermoplastic such as poly(ether sulphone) or the addition of a rubbery phase such as carboxyl terminated butadiene acrylonitrile. Both of these systems rely on the phase separation of the amorphous material to impart the additional toughness of the material. In this paper we are investigating the possibility of changing the basic chemistry of the epoxy resin system so as to increase its ability to dissipate energy and this in principle should increase the fracture toughness and would also influence other physical properties which rely on the dynamics of the matrix. We have previously shown [4–5] that the ability to absorb water depends on the glass transition temperature of the material and can be related to the presence in the system of binding sites in the form of hydroxyl groups and also the occurrence of microcavities which arise as a consequence of the curing procedure. An alternative mechanism for the toughening of epoxy systems have been proposed by Daly *et al.* [6–7] in which the toughening is achieved by modification of the chain topography. In this study we replace a proportion of the tetrafunctional hardener with a bi-functional amine which will produce a linear chain structure and a mono-functional amine which will lead to chain termination, but the end group potentially has the ability to act as an internal plasticiser. This study attempts to explore the effects which these variations have on the overall chain topography and its effect on the physical properties. A comparison was made of the properties of DGEBA with DDM and DDS. DDM is no longer extensively used due to safety aspects and the use of DDS was necessary during this study. A comparison is then made between systems cured with both amines with the addition of aniline to explore its toughening properties. The toughening properties of *N*-ethylaniline and bromo-aniline are also investigated for the system cured with DDM. Bromo-aniline being investigated because of its properties as a fire retardant.

EXPERIMENTAL

Materials

The investigation was based on the cure of diglycidyl ether of bisphenol. A (DGEBA) (Araldite MY750) with either 4,4′-diaminodiphenyl sulphone (DDS) (Ciba Geigy HT976) or 4,4′-diaminodiphenyl methane (DDM) (Ciba Geigy HT972) with the incorporation of varying amounts of aniline (Aldrich Ltd.), *N*-ethylaniline (Aldrich Ltd.) and bromo-aniline (Aldrich Ltd.). All materials were used as supplied without further purification. The components were degassed at 130°C under vacuum after mixing. Measurements were taken on solutions or films which were prepared from a homogeneous mixture. The cure cycles were determined on the basis of the results of the rheological experiments and were 3 hrs at 180°C for the DDM systems and 6 hrs at 200°C for the DDS cured systems.

Rheological Measurements

A curometer, designed at Strathclyde was used to monitor changes in the viscosity as a function of time and allow determination of the real and imaginary parts of the shear modulus at 2 Hz [8]. Samples of ~2 ml were placed in a glass vial and measurements were performed isothermally at 110°C for DDM and 160°C for DDS.

Infrared Measurements

Samples of the initial liquid mixtures were spread between two KBr disks. Infrared spectra were recorded using a Mattson 5000 FTIR spectrometer [4000–400 cm^{-1}] at a temperature of 110°C for DDM and 160°C for DDS, with measurements being taken every 30 minutes.

Density Measurements

Densities were measured at 30°C using a neutral buoyancy method. Samples of dimensions 10 mm×10 mm×2 mm were placed in a saturated solution of potassium bromide. Water was added while stirring until the density of the sample matched the density of the solution. Surface tension problems were removed by adding a small amount of surfactant. The density of the solution was then measured using a Anton Paar DMA 60 density meter connected to a DMA 601 density measuring cell.

Differential Scanning Calorimetry

Heat capacity measurements were performed using a Du Pont Model 9900 Calorimeter. In all cases a sample of ~10 mg was used at a heating rate of 10°C min^{-1} over a temperature range of −50 to 300°C.

Dynamic Mechanical Thermal Analysis

Measurements of the modulus and tan δ for polymer films were performed using a Polymer Laboratories Dynamic Mechanical Thermal Analyser MKII operating at a frequency of 1 Hz, a strain of×4 and a scanning rate of 3° per minute using samples 20 mm×10 mm×0.5 mm. The clamping torque in the single cantilever arrangement was 30 N. Measurements were performed from 0°C to above the T_g. Careful attention was given to problems of clamping of the sample with the more brittle materials.

Thermally Stimulated Depolarisation

TSD measurements were performed as described previously [9]. Samples were cast into a circular brass mould placed on top of a glass plate coated with a mould release agent, Rocol MRS advanced non-silicon dry film spray, and heated until gelation occurs. The flat disks obtained were sandwiched between copper electrodes in a parallel plate configuration. The samples were heated to just above T_g and poled using a field of 500 V/cm for 15 minutes after which the sample was rapidly cooled to room temperature with liquid nitrogen. Once at room temperature the voltage was removed and the sample reheated at 3°/min. and the discharge current measured using a Keithly Instruments 610°C solid state electrometer. This process was repeated to determine changes in the dielectric properties of the material as a function of the cure process.

Gravimetric Measurements

Water uptake measurements were performed on cured films of typical weight 2 g and approximately 2 mm thick. Films were then immersed in deionised water at 25°C. The weight of the films was determined periodically using a Mettler M5 balance [±0.00001 g]. The samples were removed from the water and wiped to remove excess water, after 2 minutes the samples were weighed and reimmersed after 3 minutes total out of water.

Low Frequency Dielectric Measurements 10^{-2} to 10^5 Hz

Water absorption was monitored using a dielectric method which involved performing electrical measurements over the frequency range 10^{-2} to 10^5 Hz on a sandwich construction [10] formed by silver coating two surfaces of the thin cured film. A 50 nm thick film of silver is completely permeable to water yet is sufficiently coherent to form a conducting film which acts as one of the electrodes. The reverse electrode is coated with 100 nm of silver and is impermeable to water and is also covered with silicone sealant. After the first 18 hrs of measurement the change in dielectric response was slow enough to be measured down to 10^{-3} Hz.

RESULTS AND DISCUSSION ASSESSMENT OF CURE

The differences in the reactivity of the various amines in the mixtures will be expected to have an influence on the rate at which cure proceeds. The cure process has been studied extensively using a variety of methods. One of the most characteristic changes to occur in the system is the increase in the viscosity. Rheological measurements have been previously reported on the DEGBA/DDS system [11], however the effects of the addition of aniline and its derivatives has not been explored. The cure time was calculated for DGEBA/DDM with the addition of *N*-ethylaniline and DGEBA/DDS with aniline, Table I and Figure 1. Addition of both aniline and *N*-ethylaniline have the effect of reducing the cure time of the resins presumably as a result of increasing the content of the linear epoxy fraction in the curing

TABLE I Cure times from Curometer and FTIR measurements on addition of aniline and *N*-ethylaniline

Resin	*Cure time (seconds) (curometer)*	*Cure time (seconds) (FTIR)*
DGEBA/DDS	5940	2280
DGEBA/DDS/10% aniline	6720	3540
DGEBA/DDS/20% aniline	8160	3720
DGEBA/DDS/30% aniline	9660	3660
DGEBA/DDS/40% aniline	15420	3660
DGEBA/DDS/50% aniline	25500	–
DGEBA/DDM/10%*N*-ethylaniline	8000	–
DGEBA/DDM/20%*N*-ethylaniline	12500	–
DGEBA/DDM/30%*N*-ethylaniline	32000	–

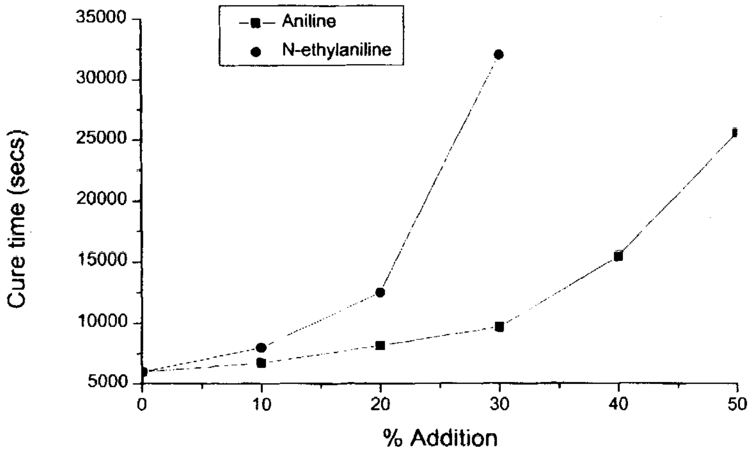

FIGURE 1 Cure time on addition of aniline and *N*-ethylaniline.

material. *N*-ethylaniline has the greater effect on cure time and on 40% addition no gel point was observed. It has been shown in a study of epoxy amine kinetics [12] that DDS and DDM are slower in reacting than other amines and it is likely that the aniline and *N*-ethylaniline are reacting preferentially with the epoxide groups and hence reducing the cure rate.

The effect of aniline on the cure of the DGEBA/DDS system was determined by monitoring the intensity of the infrared epoxide band absorption at 916 cm^{-1} using FTIR. The point at which the absorption level became asymptotic to the time axis was taken as the cure time for the materials. As the amount of aniline is increased so the 'cure time' increases, Table I, paralleling the observations from the curometer study.

PHYSICAL PROPERTIES

The extent of polymer – polymer packing is reflected in the density of a cured resin. The addition of *N*-ethylaniline as a crosslink inhibitor would be expected to reduce the density which was observed in the results, Table II. Addition of Bromine in the form of bromo-aniline should increase the density of the samples which was seen to occur, but the addition of aniline which would have been expected to produce more free volume also increased the density. The density results can be seen in Figure 2.

TABLE II Density, Glass transition temperature and Gravimetric diffusion coefficient for addition of aniline, *N*-ethylaniline and bromoaniline

Resin	*Density*	*T_g (°C) (DCS)*	*T_g (°C) (DMTA)*	*Diff. Coeff. ($\times 10^{10}$ cm^2/s)*
DGEBA/DDM	1.97	177	194.8	720
DGEBA/DDS	–	–	73.2	140
DGEBA/DDS/10% aniline	–	–	65.7	320
DGEBA/DDS/20% aniline	–	–	78.0	500
DGEBA/DDS/30% aniline	–	–	77.0	350
DGEBA/DDS/40% aniline	–	–	73.3	350
DGEBA/DDS/50% aniline	–	–	–	450
DGEBA/DDM/10% aniline	2.20	149	102	–
DGEBA/DDM/20% aniline	2.46	126	122	–
DGEBA/DDM/30% aniline	2.62	118	112	–
DGEBA/DDM/40% aniline	2.83	106	101	–
DGEBA/DDM/50% aniline	3.05	99	60	–
DGEBA/DDM/10% *N*-ethylaniline	1.95	142	149	860
DGEBA/DDM/20% *N*-ethylaniline	1.90	111	119	1050
DGEBA/DDM/30% *N*-ethylaniline	1.91	90	103	1270
DGEBA/DDM/40% *N*-ethylaniline	1.89	65	88	1830
DGEBA/DDM/50% *N*-ethylaniline	1.77	57	68	2870
DGEBA/DDM/10% bromoaniline	2.35	86	92	–
DGEBA/DDM/20% bromoaniline	2.60	87	105	–
DGEBA/DDM/30% bromoaniline	2.60	105	119	–
DGEBA/DDM/40% bromoaniline	2.96	112	130	–
DGEBA/DDM/50% bromoaniline	3.17	77	94	–

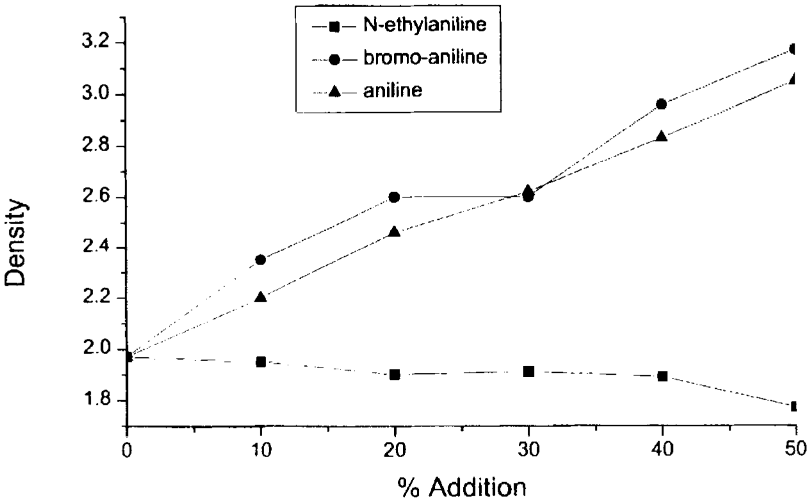

FIGURE 2 Density of DGEBA/DDM on addition of aniline, *N*-ethylaniline and bromoaniline.

An important characteristic of a thermoset resin is its glass-rubber transition temperature, T_g. A simple way to monitor changes in the physical properties of epoxy resins is to measure the changes in the glass transition temperature. The glass transition temperature was obtained from a scan of the cured materials by DMTA and compared to glass transition temperature obtained by DSC. The DMTA results for the addition of the different amines are shown in Table II and Figure 3. Results showed that the addition of *N*-ethylaniline has the effect of lowering the glass transition temperature of the resin. For the addition of aniline and bromo-aniline this trend is not observed. These results showed an initial drop in the T_g followed by an increase and a further lowering on addition of amine. The maximum T_g occurred at 20% addition of aniline and 40% addition of bromoaniline. The DSC results obtained for the addition of *N*-ethylaniline and bromoaniline are in agreement with observations from DMTA. The addition of aniline however did not show the expected trend with the T_g continually falling on addition of aniline, with the increase at 20% not being observed. This could result from DSC not being as sensitive a technique for determining the T_g of epoxy systems. Results are shown in Table II.

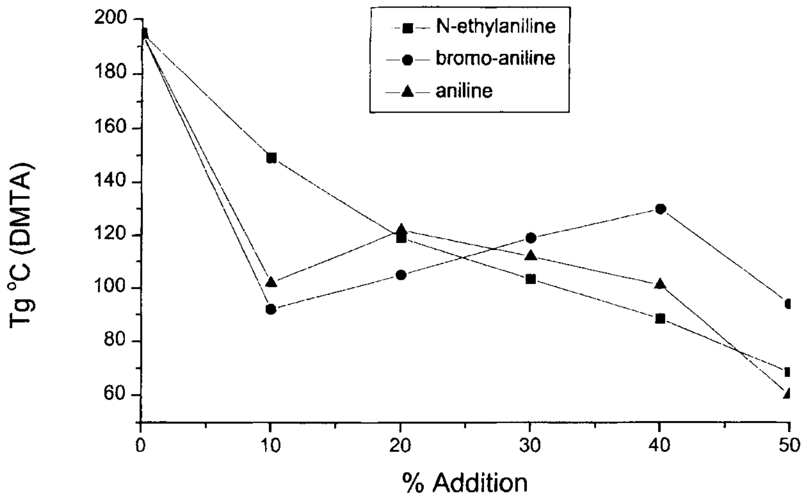

FIGURE 3 Glass transition temperature of DGEBA/DDM on addition of aniline, *N*-ethylaniline and bromoaniline.

TSD measurements were performed on the cure of samples with the incorporation of *N*-ethylaniline to again confirm DSC results and the values obtained are shown in Figure 4 and Table III. The relaxation obtained from TSD measurements should give an approximation to the glass transition process. It has been shown previously [9] in epoxy resin systems that the observed relaxation is a combination of the glass transition process, conductivity and the space charge peak. The poling temperature was 200°C for the pure resin and 160°C for other samples. For the results from 0–20% *N*-ethylaniline the glass transition process is masked by these other processes and a value cannot be obtained. The values obtained for 30–50% *N*-ethylaniline give values which

TABLE III Maximum peak temperature from TSD measurements on addition of *N*-ethylaniline

% N-ethylaniline	*Maximum peak temp.*
0	121
10	120
20	121
30	100
40	92
50	72

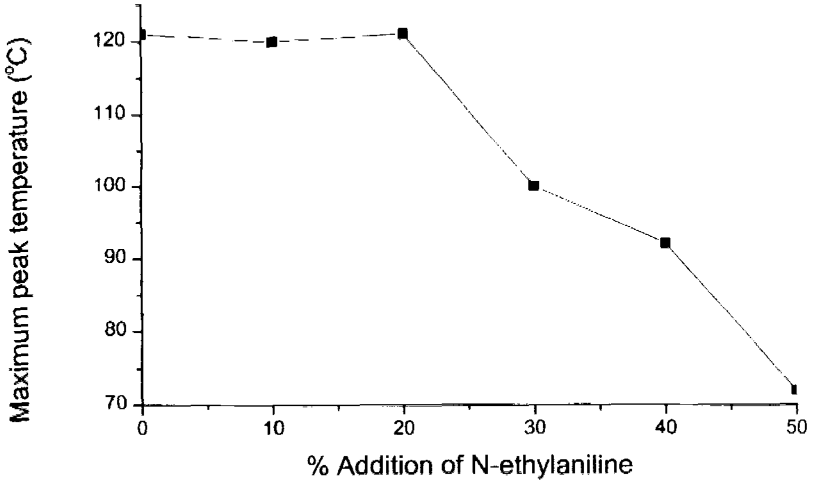

FIGURE 4 TSD maximum peak temperature on addition of *N*-ethylaniline.

follow the same trend as DSC measurements, but could still give incorrect values due to overlap of processes.

WATER ABSORPTION

Once the properties of the modified resins have been measured the next step is to monitor their water uptake properties. Although the sorption processes of liquids and vapours in glassy polymers follow complex mechanisms, water diffusion in epoxy resin matrices has been frequently represented by a Fickian behaviour [13–15] and has the following features [16]:

i) the sorption curves are linear in the initial stages.
ii) above the linear portion both absorption and desorption curves are concave to the abscissa. For absorption the linear region extends to over 60% or more of the region studied.
iii) when a series of reduced absorption curves are plotted for films of different thickness the curves are superimposable. If a plane polymer sheet is exposed to a fluid, the change of the concentration (C) of a diffusing substance as a function of time (t) and position

(x) is given by Fick's second law [15];

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

where D is the diffusion coefficient. If the material has a uniform initial diffusant concentration (C_0) and the surface is kept at a constant concentration $C_{\max}$, the solution of Eq. (1) is [14];

$$\frac{C - C_0}{C_{\max} - C_0} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\exp[-D(2n+1)^2\pi^2 t/h^2] \cos\frac{(2n+1)\pi x}{h} \tag{2}$$

The concentration of a substance diffusing in to the polymeric material (M) as a function of time is given by the integral of Eq. (2) across the thickness (h):

$$\frac{M}{M_{\max}} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-D(2n+1)^2\pi^2 t/h^2] \tag{3}$$

where $M_{\max}$ is the maximum quantity of the diffusing substance at infinite time. A simplified form of Eq. (3) for values of $M/M_{\max}$ lower than 0.6 [15] has the form;

$$\frac{M}{M_{\max}} = \frac{4}{h\sqrt{\pi}}\sqrt{Dt} \tag{4}$$

For gravimetric analysis, Eq. (4) is a valid representation of the time dependence of the water uptake.

Analysis of the water absorption data allows determination of the maximum weight gain M_∞ and the diffusion coefficient D. A log scale is used to present the data so as to enable all the data to be displayed in the same figure. The curves can be split into two regions; the initial absorption which follows a pseudo Fickian behaviour and can be analysed using Eq. (4). Subsequent absorption leads to a much slower rate of weight increase and following Johncock [17] the value of M_∞ was obtained by extrapolation of the second curve back to zero. The second region is a reflection of the changes which occur in the matrix as a result of the stress relaxation of the resin. Gravimetric measurements were carried out for samples with the addition of aniline and *N*-ethylaniline and the results are shown in Figure 5 and the values given in Table II. The addition of *N*-ethylaniline shows an increase in the diffusion coefficient and an increase in the water uptake of the samples. Which would indicate that the *N*-ethylaniline is producing free volume in the system by reducing the cross link density. This confirms the results obtained by DSC and DMTA which showed a decrease in the T_g, consistent with an increase in free volume, as confirmed by density measurements. The results for the addition of aniline show an interesting trend with the diffusion coefficient increasing to a maximum at 20% aniline and then falling before rising again at 50% aniline. This is consistent with mechanical results and suggests an increase in free volume up to 20% due to the aniline producing a more open network structure. The subsequent decrease in the diffusion coefficient as well as an increase in the T_g is consistent with densification of the matrix, possibly as a result of relaxations

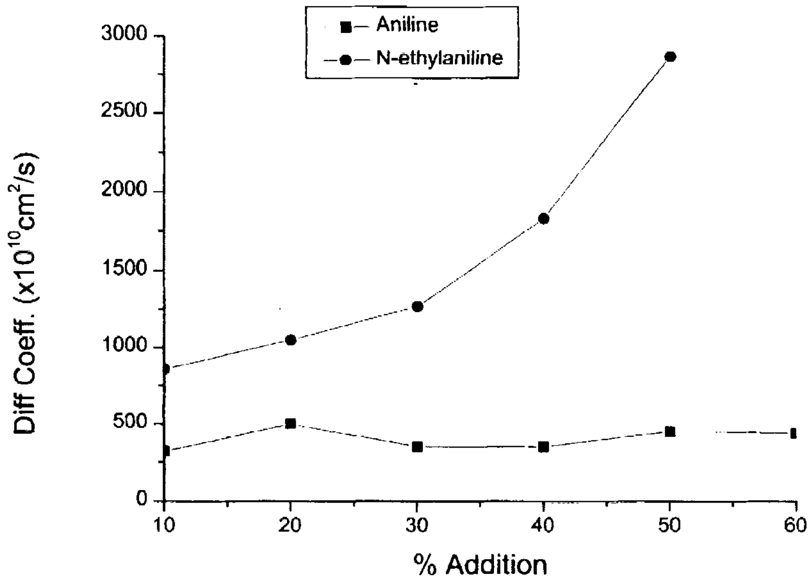

FIGURE 5 Gravimetric diffusion coefficient on addition of aniline and *N*-ethylaniline.

taking place to reduce the free volume. The fact that the equilibrium water concentration decreases with addition of aniline also suggests densification of the matrix.

Once the gravimetric results have been calculated the water uptake process is monitored by using dielectric relaxation to provide a more in depth analysis of the absorbed water in the base resins. The theory of the analysis of monitoring water uptake by dielectric analysis, which is a modification of gravimetric analysis, has been extensively reported previously [4–5, 18]. Samples of both DGEBA cured with DDM and with DDS were prepared and their water uptake properties measured to look at the comparison between DDM and DDS as curing agents. Measurements were performed over the frequency range 10^{-3}–3×10^9 Hz over a period of 2 weeks. An initial rapid increase in the dielectric permittivity and loss for all of the samples is observed after which the profile becomes almost constant. It may be assumed that the variation of the dielectric permittivity measured at 10 Hz reflects the total relaxation spectrum of the water molecules in the matrix and hence is correlated with the total sorption process. Water molecules in the matrix are in general bound to the hydroxyl group generated during the ring opening process and hence contribute to the relaxation process located at about 10^5 Hz at room temperature. Measurements above 10^6 Hz will reflect only water molecules which are loosely bound in the matrix and are designated 'free' water. Analysis of the dielectric permittivity variation at these frequencies will be used to discuss the difference between 'free' and 'bound' water in the matrix. The permittivity of free water is 80.4 at 293 K and apparent discrepancies between prediction and theory have been reported [19–22]. The water molecules may be assumed to be either clustered, in which case the dielectric increment should closely correlate with the value for water, or be bound to the matrix, in which case a lower value may be expected. Studies of the DGEBA/DDM and DGEBA/DDS systems indicate that the calculated diffusion coefficients are not significantly changing with the different amines. The diffusion coefficient and amount of bound water are lower for the DDS system which would suggest that the sulphone group slightly inhibits the water molecules in the network, probably due to closer packing of the network. The results are presented in Table IV.

TABLE IV Dielectric diffusion coefficient and % bound and free water for DGEBA cured with DDM and with DDS

Resin	*% Free water*	*% Bound water*	*D* $(\times 10^{10}\,cm^2/s)$
DGEBA/DDM	84.5	15.5	5.88
DGEBA/DDS	88.4	11.6	4.20

CONCLUSIONS

Dielectric results have shown that there is little difference between the water uptake properties of DGEBA cured with DDS compared to DGEBA cured with DDM. The resin cured with DDS shows a slightly lower diffusion coefficient and amount of bound water indicating that the sulphone group slightly reduces the rate of water uptake and inhibits the water molecules binding to the resin. Curing results showed that the addition of aniline and *N*-ethylaniline both lead to an increase in the curing time of the resin with increase in their concentration as was confirmed by FTIR measurements. Also on the addition of 50% *N*-ethylaniline no gel point is observed and network formation is prevented. Gravimetric water uptake measurements for increasing amounts of *N*-ethylaniline show an increase in the diffusion coefficient and equilibrium water uptake suggesting more free volume in the system. Increasing the amount of aniline shows an initial increase in the diffusion coefficient, the decrease at >20% aniline suggests densification of free volume in the system. DMTA, DSC and density measurements confirm this observation with the glass transition temperature falling on the addition of the bi functional amine and then rising again as a result of reduction of free volume in the system. TSD measurements proved to be unsuitable for monitoring the cure of these systems due to overlap of the observed processes.

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