Water absorption in a rubber-modified epoxy resin; carboxy terminated butadiene acrylonitrile-amine cured epoxy resin system

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Abstract

Gravimetric and dielectric measurements of water uptake by a series of carboxy terminated butadiene acrylonitrile (CTBN) -amine cured epoxy resin systems are reported. The amount of water absorbed and rate of diffusion increases up to approximately 15 w/w\% CTBN content. Anomalous behaviour is observed around a composition of approximately 20\% CTBN which is coincident with the occurrence of a co-continuous phase structure in the resin. Dynamic mechanical analysis and atomic force microscopy studies provide evidence for phase separation and inversion of phase structure at 20\% CTBN. The increase in the water uptake with increasing CTBN content reflects the ability of the highly polar acrylonitrile group to bind water. The general increase in the diffusion coefficient is consistent with CTBN being initially dispersed in the epoxy matrix tending to a lowering of the effective segment density inhibiting mobility of the water molecules. In the co-continuous region subtle effects of mutual solubility of components and generation of a long percolation path leads to the observed anomalous behaviour. Dynamic mechanical thermal analysis (DMTA) indicated that water absorption surprisingly leads to an increase in the glass transition temperature and is associated with a densification of the matrix structure. Atomic force microscopy measurements reveal that the surface roughness changes with composition with a marked increase in the surface roughness at 20\% CTBN. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Rubber-modified epoxy resin; Dynamic mechanical thermal analysis; Carboxy terminated butadiene acrylonitrile

1. Introduction

The inherent fragile nature of epoxy resins can be improved by the introduction of a second component which is capable of phase separation such as carboxy terminated butadiene acrylonitrile (CTBN)\cite{1–3} or polyethersulphone (PES). An attraction of CTBN as a modifier is its solubility in the base epoxy resin with the formation initially of a homogeneous solution. On cure the CTBN becomes insoluble in the increasing molar mass resin and phase separates to form usually occluded spherical domains. Previous studies of the dielectric behaviour of these systems indicates that phase separation occurs in the initial stages of cure before the matrix has been converted into the gel phase structure \cite{4–6}. This behaviour is in contrast to the simpler phase separation behaviour observed with the high temperature thermoplastic PES systems \cite{7–10}. In both systems the co-continuous phase exhibits interesting properties. At this composition a morphology is observed which is a superposition of ribbon-like structures formed from the two components. Because of the low levels of solubility of one component in the other, the two phases are not pure and will contain small amounts of the other component. Incorporation of PES in the epoxy matrix results in water uptake properties dominated by the epoxy phase and deviations for a simple compositional variation were observed in the co-continuous region. The phase separation process is manifested at the surface by an increased level of roughness detected by atomic force microscopy studies. A greater level of initial water uptake and rate of diffusion was observed around this composition in the case of PES modified epoxy systems and is believed in part to be associated with the unevenness of the surface topography. It is also of interest that the optimum mechanical characteristics occur around the co-continuous region. This study explores the effects of the addition of CTBN to the matrix on the water uptake properties.

2. Experimental

2.1. Materials

The system investigated was based on the cure of
Table 1
Gravimetric and dielectric diffusion coefficients, bound and free water contents and aged and unaged values of $T_g$ for CTBN–epoxy systems

<table>
<thead>
<tr>
<th>Resin system</th>
<th>Gravimetric water uptake (%)</th>
<th>Dielectric diffusion coefficient ($D \times 10^{-10}$ cm$^2$s$^{-1}$)</th>
<th>Gravimetric diffusion coefficient ($D \times 10^{-11}$ cm$^2$s$^{-1}$)</th>
<th>% Bound</th>
<th>% Free</th>
<th>$T_g$ unaged (°C)</th>
<th>$T_g$ aged in water (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA/Pipiredine + 0% CTBN</td>
<td>1.15</td>
<td>0.62</td>
<td>0.44</td>
<td>32</td>
<td>69</td>
<td>79.7</td>
<td>82.58</td>
</tr>
<tr>
<td>DGEBA/Pipiredine + 5% CTBN</td>
<td>1.31</td>
<td>0.96</td>
<td>0.50</td>
<td>57</td>
<td>43</td>
<td>80.6</td>
<td>85.14</td>
</tr>
<tr>
<td>DGEBA/Pipiredine + 10% CTBN</td>
<td>1.54</td>
<td>0.88</td>
<td>0.44</td>
<td>72</td>
<td>28</td>
<td>80.1</td>
<td>82.82</td>
</tr>
<tr>
<td>DGEBA/Pipiredine + 15% CTBN</td>
<td>1.55</td>
<td>0.65</td>
<td>0.57</td>
<td>98</td>
<td>2</td>
<td>84</td>
<td>83.6</td>
</tr>
<tr>
<td>DGEBA/Pipiredine + 20% CTBN</td>
<td>1.69</td>
<td>1.61</td>
<td>0.57</td>
<td>99</td>
<td>1</td>
<td>81.3</td>
<td>82.06</td>
</tr>
<tr>
<td>DGEBA/Pipiredine + 25% CTBN</td>
<td>1.54</td>
<td>1.90</td>
<td>0.95</td>
<td>97</td>
<td>3</td>
<td>85.2</td>
<td>80.36</td>
</tr>
<tr>
<td>DGEBA/Pipiredine + 30% CTBN</td>
<td>2.26</td>
<td>1.23</td>
<td>0.44</td>
<td>96</td>
<td>4</td>
<td>84.9</td>
<td>79.06</td>
</tr>
<tr>
<td>DGEBA/Pipiredine + 40% CTBN</td>
<td>4.39</td>
<td>2.46</td>
<td>1.93</td>
<td>95</td>
<td>5</td>
<td>77</td>
<td>71.9</td>
</tr>
</tbody>
</table>
diglycidylether of bisphenol A (DGEBA), Araldite MY750 (Ciba Geigy Polymers) with piperidine (Aldrich Ltd) incorporating varying amounts of carboxy terminated butadiene acrylonitrile (CTBN), (Hycar 1300X13). The epoxy resin and hardener were used as supplied in stoichiometric ratio of 100:5 (w/w) epoxy: hardener and samples were prepared with CTBN concentrations from 0% to 40%. The samples were produced by mixing the CTBN and DGEBA at 373 K until the mixture was homogeneous. The mixture was then degassed under vacuum and piperidine then added to the mixture. The blend was then poured into an open mould (dimensions 14 × 10 cm), which had been preheated to 413 K, and degassed for 30 min under vacuum to remove trapped air. The samples were then cured at 413 K for 4 h and allowed to cool to room temperature over night.

2.2. Gravimetric measurements

Thin films, weight typically 0.2 g, approximately 0.2 mm thick were immersed in deionised water at 298 K and weighed periodically using a Mettler M5 balance capable of measuring to ± 0.00001 g. The samples were removed from the water and wiped to remove excess water and left for 2 min to equilibrate before being weighed and then re-immersed. The total period for which the sample was out of water was approximately 3 min.

2.3. Low frequency dielectric measurements $10^{-2}$ to $10^5$ Hz

Dielectric measurements, from $10^{-2}$ to $10^5$ Hz were carried out on a sandwich construction [11] formed by silver

![Graph](image1)

**Fig. 1.** Gravimetric diffusion coefficients measurements for varying CTBN contents. The error bars for the diffusion coefficient measurements are calculated from the standard deviation of the fit of the diffusion curves.

![Graph](image2)

**Fig. 2.** Gravimetric equilibrium water uptake for varying CTBN contents. The error bars are calculated from the balance accuracy.
coating two surfaces of a thin film. One of the surfaces was coated with a 50 nm film and the other with a film thicker than 100 nm and this latter acts as an impermeable active electrode. Previously it was found that a 50 nm thick film of silver is completely permeable to water, yet forms a sufficiently coherent conducting film to act as a good electrode. The active electrode was further covered with silicone sealant and made effectively impermeable to water ingress. After the first 18 h of measurement the change in dielectric response was slow enough to be measured down to $10^{-3}$ Hz.

2.4. Dynamic mechanical thermal analysis

A Polymer Laboratories Dynamic Mechanical Thermal Analyser MKIII was operated at a frequency 1 Hz, a strain of $\times 4$ and a scanning rate of 3 K per minute using samples $20 \times 100 \times 5$ mm. The clamping torque in the single
cantilever arrangement was 30N. Measurements were performed from 273 K to above the $T_g$. With the softer materials careful attention was given to problems of clamping of the sample.

2.5. Atomic force microscopy

Micrographs of small sections of the resin sheets were recorded with a Burleigh ARIS-3300 Personal AFM. A standard Burleigh AFM probe was used for the measurements. The cantilever shape was rectangular with a length of 10–15 μm and a silicon pyramidal tip with a spring constant of $\sim 0.05$ N m$^{-1}$. Surfaces were imaged at a constant force of 5 nN. The sample was moved in the $x$-$y$ plane and a voltage was applied which moved the piezo driver over the $z$-axis in order to keep the probing force constant, resulting in a 3D height image of the examined surface.
3. Results and discussion

3.1. Water sorption studies

3.1.1. Gravimetric measurements

The sorption of water for samples with varying rubber content were investigated. Although the sorption processes of liquids and vapour in glassy polymers follows complex diffusion mechanisms in epoxy resin matrices, their behaviour has frequently been found to approximate to Fickian diffusion [12–14]. The characteristics of Fickian diffusion have been described by Fujita [15]:

1. The sorption curves are linear in the initial stages.
2. 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.
3. 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 in the concentration \(C\) of a diffusing substance as a function of time \(t\) and position \(x\) is given by Fick’s second law [14]:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]

(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 \(C_{\text{max}}\), the solution of equation (1) is [13]:

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

(2)

where \(n\) is an integer from 0 to \(\infty\). The total amount of substance diffusing in the polymeric material \(M\) as a function of time is given by the integral of equation (2) across the thickness \(h\):

\[
\frac{M}{M_{\text{max}}} = 1 - \frac{8}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} \exp\left[-D(2n + 1)^2 \frac{\pi^2 t}{h^2}\right]
\]

(3)

A simplified form of equation (3) for values of \(M/M_{\text{max}}\) lower than 0.6 has the form:

\[
\frac{M}{M_{\text{max}}} = 1 - \frac{8}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)^2} \exp\left[-D(2n + 1)^2 \frac{\pi^2 t}{h^2}\right]
\]

(4)

For gravimetric analysis equation (4) is a valid representation of the time dependence of the water uptake. The calculated diffusion coefficients are presented in Table 1 and are shown in Fig. 1. Results showed a similar trend to those obtained previously by the DERA [17] with the calculated diffusion coefficient going through a small but distinct maximum at 20%–25% CTBN, before increasing to a very high value. The equilibrium water uptake increased with addition of CTBN and data are presented in Table 1 and shown in Fig. 2.

3.1.2. Dielectric measurements

The dielectric measurements were performed over the frequency range \(10^{-3}\) to \(10^5\) Hz over a period of 2 weeks at 298 K, Fig. 3. The dielectric measurements reflect the increased permittivity and loss associated with the motion of water dipoles in the matrix. In amine cured epoxy resins the water binds almost exclusively to the hydroxyl groups produced during the cure process. The observed increase in the dielectric loss at low frequencies is associated with a combination of plasticisation shifting the \(T_g\) process to higher frequency and an enhancement of processes associated with polarisation phenomena ascribed to blocking electrode effects. The initial slow increase in the permittivity observed with the pure resin system is typical of water uptake. After approximately \(2 \times 10^5\) s there is the appearance of a large peak which because of its large amplitude must be ascribed to polarisation phenomena. In the case of the CTBN modified materials these polarisation phenomena appear more quickly and reflect the fact that the occluded phases can lead to additional polarisation process associated with restriction of the free migration of charges by the CTBN layer. In certain systems, for example in the 10% CTBN system there is a clear shift of the low frequency dielectric loss behaviour. This effect is most noticeable around 20% CTBN, where the co-continuous phases occur. The initially cured matrix will contain stresses left in the matrix due to the elevated temperature used in the cure process. Plasticisation allows the chains to move and is consistent with a shift to higher frequencies of the dielectric loss. The increase in local mobility will however allow both densification and or further reaction...
leading to an increase in $T_g$ and a reduction in the conductivity and associated polarisation loss processes.

By examining the water uptake plots, Fig. 3, and taking the value of $\varepsilon^{\prime}\infty$ as the measurement at $10^5 \text{Hz}$ for the initial ‘dry’ permittivity reading it is possible to evaluate the affects of water absorption. Variation of the dielectric increment $\Delta \varepsilon^{\prime}$ at 10 Hz with time reflects the effects due to an increased quantity of both the ‘bound’ and ‘free’ water in the system. The difference between the two increment values at 10 Hz and $10^5 \text{Hz}$ gives a measure of the amount of water which is intimately bound to the hydroxyl groups generated during the curing of the epoxy system. The water bound to these groups leads to an increase in the dielectric loss in this region without significant shift in the locus of the relaxation process and the calculated values for the ‘bound’ and ‘free’ water were obtained, Table 1. The contribution from ‘free’ water is associated with dipolar relaxation processes occurring above $10^5 \text{Hz}$ and located around $10^{11} \text{Hz}$ [18–21]. The occurrence of ‘free’ water in an epoxy system is associated with the occurrence of micro voids in the epoxy phase resulting from the build up of the three dimensional network structure and reflects the temperature used in the cure process. The higher the cure temperature the larger the void content. The water segregated into the voids will exhibit a dipolar process characteristic of free water. The micro voids are believed to have dimensions of

Fig. 4. Dielectric diffusion coefficients for varying CTBN contents. The error bars for the diffusion coefficient measurements are are calculated from the standard deviation of the fit of the diffusion curves.

Fig. 5. Glass transition temperatures for 0%–40% CTBN addition, dry and on exposure to water. The error bars are $\pm 1^\circ\text{C}$. 
~0.01 μm or less. As the CTBN content is increased there is a dramatic reduction in the amount of ‘free’ water with all the water being bound to the matrix at high CTBN levels.

Evolution of the dielectric permittivity with time is directly related to the diffusion of water into the capacitor structure and hence can be used to estimate the diffusion coefficient. Starting from equation (4), it is necessary to derive an equation which describes the situation used in the experiments. The cell used for the dielectric study allows diffusion from one side only, the edges and reverse side being sealed with silicone rubber and a silver electrode respectively. The theory describing the gravimetric measurements involves the concentration of the water molecules whereas the dielectric experiment measures the change in the permittivity of the media. Under isothermal conditions the increase in the permittivity observed during water diffusion ($\epsilon'$) is proportional to the number of water dipoles present in the system [20,21]. Therefore, a linear relationship between $\epsilon'$ and the water concentration in the polymer is expected. It is assumed that the thickness ($h$) does not change with water concentration. It has however been pointed out previously [13,20,22] that there is observed a discrepancy between the observed increment and that predicted on the basis of the amount of water absorbed. The permittivity of free water is 80.4 at 293 K and that predicted on the basis of the amount of water is observed a discrepancy between the observed increment however been pointed out previously [13,20,22] that there ($\epsilon'$) is the value of the dielectric permittivity at $t_0$ and the water concentration in the polymer is expected. It is assumed that the thickness ($h$) does not change with water concentration. It has however been pointed out previously [13,20,22] that there is observed a discrepancy between the observed increment and that predicted on the basis of the amount of water absorbed. The permittivity of free water is 80.4 at 293 K and that predicted on the basis of the amount of water is observed a discrepancy between the observed increment however been pointed out previously [13,20,22] that there is observed a discrepancy between the observed increment and that predicted on the basis of the amount of water absorbed. The permittivity of free water is 80.4 at 293 K and that predicted on the basis of the amount of water is observed a discrepancy between the observed increment however in the case of the CTBN samples with ratios $20\%–25\%$ CTBN, the apparent discrepancies between predicted and theory have been reported [20–23]. 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 observed. In the case of the dielectric analysis the diffusion can be modelled according to the following equation;

$$\frac{\epsilon' e_0}{\epsilon_{\text{max}} e_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left[-D(2n+1)^2 \pi^2 t / h^2 \right]$$

where $\epsilon'_{\text{max}}$ is the maximum value of the dielectric permittivity achieved by the water diffusing into the polymer matrix and $\epsilon'_0$ is the value of the dielectric permittivity at $t=0$. In this case the diffusion coefficient ($D$) can be estimated by considering only the first term in equation (5) (i.e. $n=0$) and by plotting the root of time ($t^{1/2}$) against the normalised dielectric permittivity: $\epsilon' e_0 / \epsilon_{\text{max}} e_0$, with the condition that $\exp[-D \pi^2 t / h^2] \approx 1$. Thus;

$$D = -\frac{h^2}{t^{1/2}} \ln \left[ \frac{\pi}{8} \right]$$

Further, equation (6) can be written in the approximate form:

$$D = 0.0947h^2 t^{1/2}$$

It has been previously observed that measurements of the diffusion permittivity at different frequencies leads to different values of the apparent diffusion coefficient [22], lower apparent values being observed at higher frequencies. It is 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.

The dielectric diffusion coefficients were calculated from the dielectric permittivity at 10 Hz using the method as described by Johncock [16] and are shown in Table 1 and Fig. 4. The diffusion coefficients which were obtained are similar to those obtained from gravimetric results with the $20\%–25\%$ CTBN samples having high diffusion coefficients. The experiments were performed in duplicate confirming the validity of these results. The initial high value of the dielectric permittivity on exposure to water would be consistent with there being a contribution to the polarisation due to the presence of a porous structure next to the electrode associated with the co-continuous structure of the material. The dielectric measurement reflects the top 10 nm of the sample next to the electrode which reaches equilibrium in the first few minutes. These observations are consistent with the increased roughness of these samples in the co-continuous region. Once diffusion has started the effects of these surface anomalies are lost and the change in the dielectric profile with time takes on a more normal form. Subsequent changes will be controlled by the same diffusion processes that control the mass variation with time and hence at longer times the dielectric curves assume a more expected form.

3.2. Physical properties

3.2.1. Dynamic mechanical analysis

DMTA measurements were performed for the initial dry samples and samples stored in deionised water for 21 days for each stoichiometric ratio of DGEBA/CTBN. The values of the glass transition temperatures, $T_g$, are presented in Table 1 and Fig. 5. In general water absorption leads to a broadening of the $T_g$ peak with a lowering of its value, however in the case of the CTBN samples with ratios $0\%–15\%$ the $T_g$ appears to increase indicative of the effects of physical ageing and densification of the matrix. For the ratios $20\%–25\%$ CTBN, the $T_g$ after water absorption is unchanged, which is consistent with the co-continuous phase being a rubbery CTBN matrix and stress relaxation might be expected to occur rapidly in this material and hence the release of internal stress on plasticisation by water of the matrix is not relevant in these materials. The co-continuous phase however will still contain frozen in stressed regions which are able to relax when plasticised and the apparently anomalous behaviour observed in these systems is probably a reflection of the fact that the matrix is initially a mixture of relaxed and unrelaxed regions. For
higher values of CTBN and water content the expected shift to lower values of $T_g$ is observed.

3.2.2. Atomic force microscopy

Two-dimensional surface images of epoxy with varying amounts of CTBN were examined. Changing the amount of rubber causes a change in the surface texture which parallels closely with observations on similar resins with the incorporation of thermoplastic. The AFM study not only allows imaging of the surface but also an estimation of the surface roughness. Although the samples look smooth; the AFM reveals that changes in the composition produce variations in surface texture. In the low concentration range, the dispersed phase is the CTBN and differences in surface tension and mechanical forces present during cure leads to very small pores being present when the occluded phase breaks the surface. Similarly above 25%, the surface texture reflects the phase separation of the epoxy phase. At 20% CTBN, the system exists as a co-continuous phase and the surface morphology is much rougher as a consequence of the differences in surface energy and the larger size of the occluded structures involved. The surface indentations for the 20% sample are typically ~ 40 nm and whereas for the other compositions the indentations are ~ 10–20 nm or less. The surface profiles for the samples can be seen in Fig. 6. The observed behaviour is once more a manifestation of the fact that the matrix contains relaxed CTBN and unrelaxed epoxy regions.

4. Conclusions

This study shows that increasing the amount of rubber in an epoxy system has the effect of increasing the amount of water sorption in the system. Dielectric analysis of the absorbed water has shown that although addition of rubber increases the amount of water in the resin system the amount of free water is dramatically reduced. The value of the glass transition temperature on exposure to water was greater for the compositions where the epoxy is the dominant phase indicating densification of the matrix. The $T_g$ in the co-continuous region was unaffected by water absorption, with the $T_g$ reducing when the rubber is the dominant phase. Gravimetric results showed diffusion coefficients which were consistent with previous results with the diffusion coefficient going through a maximum at about ~ 25% thermoplastic. The equilibrium water uptake confirmed that increasing the amount of CTBN increased the water uptake and showed an anomaly at 25% CTBN. This could be a reflection of the CTBN plasticising the epoxy up to 20% and allowing the epoxy to uptake more water. As phase inversion occurs the epoxy phase densifies reducing its water uptake. The exact water distribution between the phases is not known, but the results shows that the delicate balance of factors which control the final phase structure also influence the distribution between the phases present. Analysis of the dielectric results showed that as water was adsorbed plasticisation and advancement of cure are continually shifting the $T_g$ process, but the overall effect is one of plasticisation. Dielectric diffusion coefficients were consistent with gravimetric results with a high diffusion coefficient at ~ 25% rubber which indicated the presence of a porous structure next to the electrode. This was confirmed by atomic force microscopy results which showed an uneven morphology of this composition compared with the other compositions. Compared with previous systems with the incorporation of thermoplastic, these systems exhibit similar characteristics with the increase in the diffusion coefficient at the co-continuous phase occurring in gravimetric measurements. The anomalous behaviour may be ascribed to the fact that in the matrix before exposure to water the epoxy phase will be unrelaxed whereas the CTBN phase will have relaxed. Plasticisation allows relaxation of the epoxy with subsequent densification, apparent reduction in water uptake and lower diffusion coefficients.

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