Physical ageing of an epoxy resin/polyethersulphone blend

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An epoxy resin was blended with polyethersulphone. The enthalpy relaxation data obtained after annealing the neat cured resin and the blends at 180°C have been curve fitted to an equation which uses the Kohlrausch–Williams–Watts function. Such an approach may enable the prediction of the long term effects of ageing on the engineering properties of such materials.

(Keywords: physical ageing; epoxy resin; polyethersulphone; enthalpy relaxation; curve fitting)

Introduction

There has been great interest in recent years in molecular relaxation or physical ageing of non-crystalline and semicrystalline organic polymers[1]. Much of the experimental relaxation data have been curve fitted to equations which utilize a semi-empirical function due to Kohlrausch[2] and revived by Williams and Watts[3], referred to as the Kohlrausch–Williams–Watts (KWW) function[4]. Using the KWW function is a useful first step in data analysis and enables tentative conclusions to be drawn with regard to relaxation times and the distribution of relaxation times of a material. This may enable approximate predictions to be made concerning changes of important physical properties during relaxation.

An abundance of experimental and theoretical work exists concerning the relaxation of amorphous linear homopolymers and their blends. Less work exists concerning the relaxation of crosslinked polymers and little or none addresses the curve fitting of these data. Epoxy resins are used extensively in the aerospace and electronics industries, increasingly in the form of epoxy–thermoplastic blends. Structural components made from these materials are often used at temperatures which are sufficiently high such that physical ageing can occur. Physical ageing is associated with conformational rearrangement, increased molecular packing and densification which is often accompanied by embrittlement of the polymer[1,5]. The change of properties has serious implications for the durability of structural epoxy resin systems and may lead to premature and catastrophic failure. It is possible that curve fitting of relaxation data may enable the prediction of the time required for serious deterioration of physical properties to occur at a specific temperature.

The purpose of blending polyethersulphone (PES) with epoxy resin is to produce a two-phase system in which the dispersed phase is PES-rich and able to improve the toughness of the epoxy resin significantly without compromising the modulus and glass transition temperature (T_g)[6,7]. In the course of investigating the physical ageing of such systems at Brunel, combinations of epoxy, PES and hardener have been used which do not apparently lead to phase separation. These systems have no commercial use but have not been discarded because they are interesting from a microstructural viewpoint. It is desirable to know something about the way in which the PES has been incorporated into the epoxy by, for example, the formation of chemical bonding between the two components and how this affects the physical ageing behaviour. This information may be useful in understanding the behaviour of phase-separated systems in which there occurs a degree of mixing between the epoxy and the PES. The epoxy and the corresponding blends with PES have been used in a study of the curve fitting of enthalpy relaxation data. This communication gives some details of the results of attempts to curve fit enthalpy data to a simple equation which uses the KWW relaxation function.

Experimental

A difunctional epoxy resin, Epikote 828 (Shell), was prepared in unmodified form and with PES and then cured with 4,4′-diaminodiphenylsulphone (DDS) at a concentration of 36 parts per hundred of resin (phr). The PES was Victrex 5003P, a low molecular weight PES, which was dissolved in dichloromethane solvent prior to mixing with the resin. The PES was blended with the resin at concentrations of 20 and 30 phr. The epoxy resin and DDS were first dissolved at 140°C and the PES–solvent mixture was then added, at which temperature a large proportion of the solvent was removed. Further solvent was removed by degassing in a vacuum oven at 140°C for 1 h. All of the materials were cast into open moulds and cured for 2 h at 180°C and 2 h at 200°C. Specimens were cut from the cured mouldings and scanned at 20°C min^{-1} on a Perkin-Elmer DSC-2 to ensure that the materials were fully cured. Additional checks were performed using i.r. spectroscopy in which the disappearance of the epoxide band at 910 cm^{-1} was monitored. Specimens were cut from the mouldings, equilibrated at 20°C above the calorimetric midpoint T_g and quenched between aluminium plates at 25°C. They were then annealed at 180°C for various times. Specimens (10–12 mg) were scanned on the differential scanning calorimeter and the thermograms of

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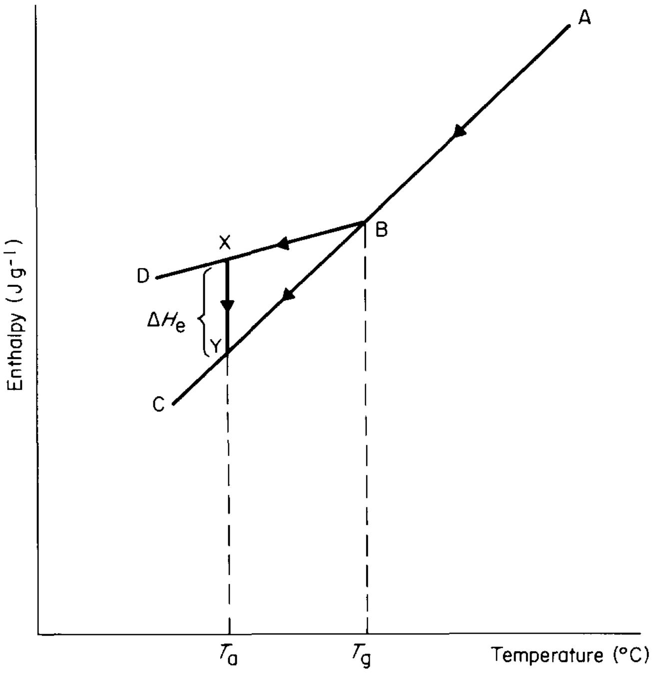

Figure 1 Plot of enthalpy *versus* temperature: path ABC, equilibrium cooling curve; path ABD, typical experimental cooling curve; path XY, approach of enthalpy to equilibrium value

aged and unaged materials were subtracted. The enthalpy relaxation was measured as the area of the peak of the subtracted curves.

Theoretical model

The KWW function is used to approximate a summation of exponential relaxation times[4]:

$$\phi(t) \approx \exp(-t_a/\tau_{WW})^{\beta} = \int_0^{\infty} \rho_{WW}(\tau)\exp(-t_a/\tau)\,d\tau \tag{1}$$

where t_a is the time of annealing, τ_{WW} is the relaxation time for the KWW function, ρ_{WW} is the Williams–Watts distribution function, τ is the exponential relaxation time and $0 < \beta < 1$ is a constant related to the width of the distribution of the relaxation times.

A simple non-linear equation for enthalpy relaxation adapted from an equation for viscoelastic properties[8,9] is:

$$\Delta H(t) = \Delta H_e[1 - \phi(t)] \tag{2}$$

where $\Delta H(t)$ is the enthalpy lost as a function of time and ΔH_e is the enthalpy that must be lost to reach equilibrium (cf. *Figure 1*).

Results and discussion

The dynamic mechanical spectra of the cured epoxy resin and the corresponding blends (not shown) were almost identical and there was no means by which the materials could be distinguished. This suggests that phase separation is not present or that the size of the second phase is too small to be detected. For the purposes of this work, the materials containing PES were considered to be effectively single phase. It is possible for a reaction to occur between the hydroxyl-terminated PES chains and the epoxy and DDS which may allow the PES to be incorporated into the network. The PES may be able to form crosslinks which would be longer and more flexible than the short epoxy–DDS crosslinks. The i.r. spectra of the blends and the neat cured resin (not shown) are almost identical except for evidence that some of the hydroxyl terminations at the ends of the PES chains are still intact. Raghava[6], in a similar investigation using a different epoxy, suggested that i.r. spectroscopy provided minimal evidence for reaction between the epoxy and the PES chain ends. A reaction between the epoxy and PES is expected but 100% reaction is unlikely because the formation of the network imposes diffusional restrictions upon the reactants. The possible formation of an epoxy–DDS–PES copolymer type of structure containing a mixture of short epoxy–DDS and longer (and perhaps more mobile) PES crosslinks would be expected to change the relaxation behaviour of the materials compared with the unmodified epoxy. The structure of the blends may allow them to relax faster than the neat epoxy at the same temperature.

It is possible to use a simple physical model to envisage the effect of the presence of PES chains on the relaxation rate. The unmodified cured epoxy resin can be thought of as a large number of epoxy chains tightly bound together by very short and stiff crosslinks. These links are very effective restraints which prevent the chains from moving very far or very rapidly. The opposite extreme is when all of the crosslinks consist of PES chains. These crosslinks are long and more flexible than the short links and allow the network more freedom to move. It is probable that the length and bulk of the PES chains also results in an increased total free volume due to the necessity for the randomly coiled chains to be self avoiding. The case for the epoxy cured with hardener and PES may be between these two extremes. The structure may consist of a mixture of short and long chain crosslinks. It is possible to imagine the highly crosslinked epoxy as consisting of a total free volume composed of a large number of small holes whilst the imaginary PES crosslinked epoxy contains larger holes. The amount and distribution of free volume affects the rate of the relaxation process[5]. A high level of free volume below T_g leads to a high driving force for relaxation and initially high relaxation rates. The distribution and size of the local free volume will affect the molecular mobility, larger holes giving rise to higher molecular mobility and therefore faster initial relaxation. Therefore, if the two materials described have the same initial levels of total free volume it is expected that the neat epoxy, with its greater constraints on molecular motion, will relax more slowly. Considering the case of the materials in this study, as more PES is added to the epoxy resin, the structure will become more open and an increased relaxation rate is expected.

One way of testing these hypotheses is by curve fitting the data from enthalpy relaxation experiments. A program was written in BASIC to perform the non-linear least squares curve fit. An initial estimate for ΔH_e was used and with the experimental values of $\Delta H(t)$ the relaxation function was calculated. This allowed an estimate of β to be determined for a given ΔH_e. The values of $\Delta H(t)$ calculated using a particular

Table 1 Curve fitted constants

Material	ΔH_e (J g^{-1})	β	τ (min)
828/DDS	3.35	0.26	4699.4
828/DDS/20 phr PES	3.13	0.36	3269.7
828/DDS/30 phr PES	2.52	0.52	760.0

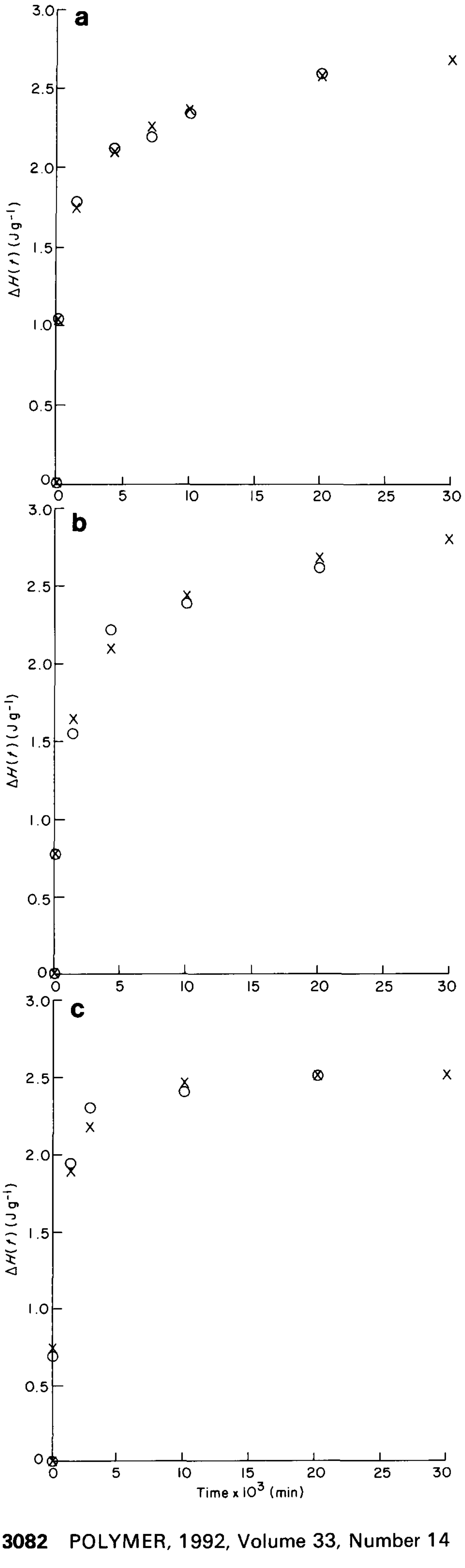

Figure 2 Plot of enthalpy change *versus* time at 180°C: (a) 828/DDS; (b) 828/DDS/20 phr PES; (c) 828/DDS/30 phr PES. ×, Theoretical points; ○, experimental points

combination of ΔH_e and β were compared with the experimental values and the value of ΔH_e adjusted until the error between the calculated and experimental values of $\Delta H(t)$ was minimized. The enthalpy change with time is shown in *Figure 2*. The dependence of relaxation rate on the PES content is reflected in the constants determined by curve fitting shown in *Table 1*. The value of the constant β is seen to increase with PES content which suggests a narrowing of the distribution of relaxation times and a shift towards more exponential behaviour. The corresponding characteristic relaxation times are seen to decrease with PES content. The results in *Table 1* seem to support the hypothesis that the incorporation of PES chains in the structure of the epoxy resin somehow increases the speed of relaxation. The value of ΔH_e is seen to be different for the materials and this represents the enthalpy which must be lost in order to achieve the equilibrium state, appropriate to the annealing temperature (T_a). This constant is also a possible indicator of the difference in the structures of the materials.

Conclusions

This communication has reported the use of the method of curve fitting of enthalpy relaxation data for epoxy resins. The constants determined from the curve fitting can be related to the way in which the materials relax. The method appears sensitive to the effects of changing the amount of PES and therefore the structure of the materials. Extreme care must be exercised when interpreting these results because it is known that the constant β can be sensitive to the changing physical structure[10]. It is also possible that in apparently cured resins the physical ageing process can enable further reaction to occur which may affect the enthalpy data at long times. Further investigations are being conducted into the application of this method to enthalpy, dynamic mechanical and dielectric relaxation data for single phase and phase-separated materials. Whilst reaction between the PES and the epoxy is expected, the extent of the crosslinking is unknown. A more comprehensive investigation into the structure and modelling will be the subject of later publications.

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