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Absorption and glass transition temperature of adhesives exposed to water and toluene

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ABSTRACT

If adhesives are to be used in practical applications, such as for aerospace or marine components, it is essential that their long-term behaviour when exposed to aggressive environments, natural or man-made, should be known. The objective of this paper is to determine the liquid absorption behaviour of epoxy adhesives under complete immersion in two solvents (water and toluene) at two different temperatures (room temperature and 60 °C) and the effect on their glass transition temperature (T_g). The specimens were periodically removed from their environment for weighing and T_g measurement, the latter by using a rapid method which was developed previously by the authors. The rate of weight gain of the specimen (sorption) and the equilibrium level were higher for the higher temperature immersion than for the low temperature. The equilibrium level reached for toluene was higher than that of water. The values of T_g were significantly influenced by the liquid uptake. Finally, heating to a temperature above the T_g of the adhesive, even in a very short time, was found to significantly influence the results of the liquid uptake.

1. Introduction

Environmental exposure can have deleterious effects which seriously compromise the durability of adhesively-bonded structural joints. In practice, moisture ingress into bonded joints is the primary cause of dramatic reductions in the mechanical and thermomechanical properties [1–3]. Factors influencing the moisture absorption can be categorized as internal or external. Internal influences are, for example, the physical and chemical nature of the material. Major external influences are the temperature, the relative humidity, and the ambient pressure. The majority of factors influencing moisture absorption and the mechanical properties of polymers are understood relatively well [4].

The mechanism of diffusion of a low molecular weight solvent into polymers was explained by Fujita [5] and Crank [6]. Fujita [5] showed that the solvent molecules could penetrate the polymer. Crank [6] established various mathematical formulae to describe the various forms of diffusion. Movement of the penetrant solvent molecules into the polymer occurs because of a concentration gradient. It is assumed that, as a result of energy fluctuations within the polymer, holes are being formed and destroyed continuously in the free volume and the diffusion will depend on the concentration of holes to be large enough to receive penetrant molecules.

Any diffusion process which is governed by the concentration gradients present, obeys Fick's laws. Fick's first law states that the flux in the x direction F_x due to a concentration gradient dc/dx in this direction, is given by

$$F_x = -D\frac{dc}{dx} \tag{1}$$

where D is the diffusion coefficient and c is the concentration. For a flat sheet where x is the direction perpendicular to the sheet, Fick's second law can be derived, which is:

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

If the plate has a thickness h and is exposed to equal concentrations on each side (immersed in liquid or with the same relative humidity on each side, Fig. 1), Fick's law has the solution, as given by Crank [6], for a constant diffusion coefficient,

$$\frac{m_t}{m_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{\frac{-D(2n+1)^2\pi^2 t}{h^2}\right\} \tag{3}$$

where m_t is the mass attained at time t, and m_∞ that attained at equilibrium. For diffusion in a thin flat sheet, Crank [6] has shown

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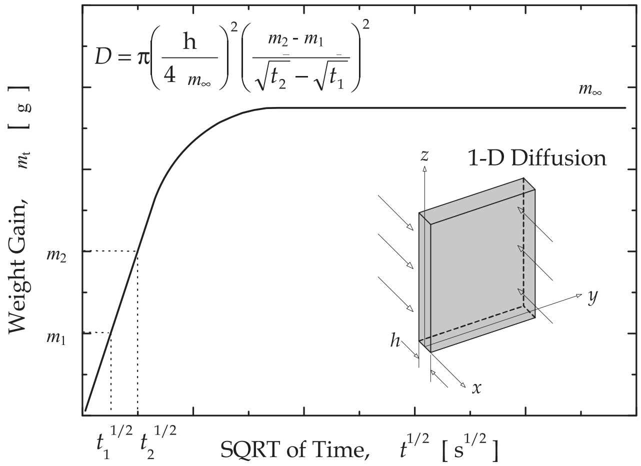

Fig. 1. Theoretical absorption curve and diffusion parameters for simple, one-dimensional Fickian diffusion.

that the above equation can be reduced to

$$D = \left(\frac{M_t}{M_\infty}\right)^2 \times \frac{\pi}{16} \times \frac{h^2}{t} \tag{4}$$

where M_t is the relative mass uptake and M_∞ is the saturation level, both in percentage. By measuring the slope of the M_t/M_∞ vs. $\sqrt{t}$ graph, it is possible to calculate the value of D. But it should be noted that D is also inversely proportional to the saturation concentration [squared]. This is because the driving force at the surface is the concentration gradient at the surface and the infinitesimal surface layer will always be at the saturation value. As the saturation value may well change with time as the polymer experiences thermodynamic changes and (most probably) mechanical stresses, the driving conditions themselves may well change with time.

The diffusion coefficient, D (m^2/s), is temperature dependent [7] and, for ideal systems, follows an Arrhenius relationship, in the form

$$D = D_0 e^{\left(-\frac{E_a}{RT}\right)} \tag{5}$$

where E_a is the activation energy, R is the universal gas constant, and T the absolute temperature. For polymers, Arrhenius plots of D against $1/T$ are often linear but there may be discontinuities in the diffusion coefficient-temperature curves near phase transitions. For example, diffusion rates can increase significantly when the temperature is increased above the glass transition temperature (T_g) [8]. Apart from the chemistry of the polymeric material, diffusion depends on factors such as applied mechanical stress or strain, porosity or voids in the bulk of the polymer mass and the presence of interfaces (e.g. polymeric adhesives bonding two metal parts together) [9]. Diffusion plots are obtained by plotting the mass change (gain), m_t, as a function of the square root of time (Fig. 1). The initial portion of this curve is linear and the diffusion coefficient D is determined from the slope of this linear part, as shown in Fig. 1. While many researchers have calculated values of D using the solution for a constant diffusion coefficient, it is far from likely that this truly represents reality. In practice, $D=D(c)$, i.e. D is a function of the concentration and is not constant. This is most likely due to the solvent causing plasticisation. Crank [6] refers to several theories as to why D may not be constant. These theories are based partly on physical observation and partly on simplifications to enable an algebraic solution to be obtained. The two stage theory [10] and the diffusion–relaxation model are examples [11], while it is likely that there is a whole spectrum of relaxation times. Crank also refers to stress or strain dependence occasioned by differential swelling in different parts of the specimen. Crank says that none of the known models can account satisfactorily for all the known aspects of anomalous diffusion. A synthesising model is still needed to include the combined effects of history, orientation, and stress on the diffusion process within the polymer system and on the surface concentration. We know that a fully saturated specimen may well experience swelling and it is likely to have a reduced T_g. Now this is, of course, the situation at the surface immediately after a specimen is exposed to an aggressive environment where we will have a swollen (and hence in compression) region where the local diffusion coefficient may well be much higher than further inside. The simple solution given by Crank for a constant value of D is therefore at best an approximation of values of D calculated for D vs. $\sqrt{t}$. The only certainties are the initial and final states.

The nature of the epoxide–water molecule interaction has been investigated by many researchers. Apicella et al. [12] proposed three different modes for the water sorption of epoxy systems: bulk dissolution of water in the polymer network, moisture sorption onto the surface of holes that define the excess free volume of the glassy structure, and hydrogen bonding between hydrophilic groups of the polymer and water. Several authors [13–16] have also reported that water exists in epoxides in two distinct forms. One is the free water that fills the micro cavities of the network, and the other is the water bound by strong interactions with polar segments such as epoxy rings, glyceryls or the nitrogen atoms of the amine compound.

Once within an adhesive, there are several possible ways by which water may cause weakening of a joint or of the adhesive. These have been reviewed by Ashcroft and Comyn [3] and include altering the properties of the adhesive in a reversible manner (such as plasticisation), altering the properties of the adhesive in an irreversible manner (such as causing it to crack, craze or hydrolyse), and attacking the adhesive–adherend interface causing swelling stresses. Plasticisation decreases the value of T_g, The introduction of a plasticiser, which is a molecule of lower molecular weight than the adhesive, has the ability to impart a greater free volume per unit volume of material since there is an increase in the proportion of end groups and it has a T_g lower than that of the resin itself. Hydrogen bonding reduces the free volume of polymers and thus increases the T_g [17–19].

While some common methods can be used to measure T_g, they usually take a long time and the corresponding equipment is expensive. A slow test might alter the polymer characteristics by evaporating moisture or by further curing the polymer. From an industrial perspective, it is therefore desirable to have a method to measure T_g rapidly so as to minimize the change of the original state of the specimen. The damping at resonance method described in Zhang et al. [20] is based on the observation that the damping changes as the properties of the polymer vary with the change of temperature. Thus, when the temperature in the specimen is at T_g, the damping will reach a peak. There are several definitions of T_g depending on the parameter measured (rate of change of the modulus, coefficient of thermal expansion, etc.) [21]. All are at or near the same temperature. The damping properties are measured using a feedback circuit which maintains the vibration of a beam at resonance while the temperature changes (see Fig. 2) [20]. The objective of the technique used here was to determine the glass transition temperature of a (thermosetting) polymer. Various options exist for the format of the specimen, but the system chosen is believed to be the best for various reasons. If the beam is coated with a continuous layer of polymer, it is difficult to ensure a uniform temperature distribution, and there may be too much damping to maintain a clear resonance. We therefore chose to use a short (10–20 mm) length of polymer with a relatively stiff constraining layer. The short length helps with the