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Hygrothermal ageing of epoxy based coatings

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Water sorption kinetics, and equilibria at different temperatures, and mechanical tests have been performed on different epoxy based coatings. The resins show different water transport properties and consequently different mechanical properties of the wet system, depending on the temperature and formulation. This can be explained in terms of water plasticization and microcavity formation in the system when exposed to high temperatures.

1. Introduction

Epoxy resins are widely used as protective coatings against corrosion. The excellent chemical resistance coupled with superior adhesion to metals has given these materials an important position in the coating field.

The cured film should be designed to be pinhole free, to adhere tightly to the surface and to possess the best possible resistance to environmental attacks [1]. It has been shown that higher water absorption usually gives more rapid adhesion losses causing severe failure in service, but it seems that adhesion loss takes place before any gross water pickup has occurred [1]. On the basis of the data showing that water penetrates the paint film very quickly, and probably spreads along the boundary layer, it was proposed [2] that adhesion loss is caused by the action of water on the boundary layer, which is probably different in composition from the bulk polymer. Still more problems arise when water soluble substances are present in the substrate. As these go into solution and cross the membrane towards the more dilute side, very high osmotic fluxes can be generated and blistering will amost inevitably result.

In addition to these so called transport properties of the cured films, the effect of the environment on the properties of the coatings must be considered. In fact previous results on water sorption in epoxy resins have shown that both the kinetics and the apparent equilibrium of the sorption phenomena can be strongly influenced by the temperature and humidity history which the samples have undergone prior to the experiment [3–5].

In the case of epoxy composites it has been shown that their elevated mechanical properties are strongly influenced by moisture absorption from high humidity environments. This effect, especially at high temperatures, has been associated with moisture induced plasticization and/or micromechanical damaging [6, 7]. While the plasticization effect is a reversible phenomenon, the microcavitation is not recoverable, unless the material is exposed to temperatures higher than its glass transition temperature [8]. The damaging process, caused by the synergistic effect of sorbed moisture and temperature is particularly evident on the solubility behaviour where an additional weight gain is observed when the samples are exposed to cycling condition of environment and temperature (thermal spikes) [5–8].

All these considerations seem also to be suitable for the damaging of protective paints. In fact in the real application of heat exchangers with coated pipes, a sudden reduction of the flow rate of the cold fluid can raise the temperature by several degrees, inducing irreversible damage in the polymer. For naval coatings, the lifetime of the protective layer can also be strongly influenced either by the daily and the seasonal thermal cycles or by the frequent hygrothermal cycles during service.

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In this work a series of systematic experiments on water sorption in epoxy based coatings have been performed. The loss of mechanical properties and the depression of the glass transition temperature of the materials has been related to the effect of water plasticization of the resin.

2. Theory

For an homogeneous polymer system, the transport of diffusing substances through unit area of a section can be successfully described by Fick's laws:

$$J = -D\frac{\partial c}{\partial x}, \tag{1}$$

and

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

where J is the rate of transfer per unit area of section, c is the concentration of diffusing substance, x the space co-ordinate measured normal to the section and D is the diffusion coefficient. In Equations 1 and 2 the assumption is held that D is a constant and that there is a gradient of concentration only along the x axis.

The solution of Equation 2 for a plane sheet of thickness, l, with constant concentration of diffusant, S_t, gives [9]

$$\frac{S_t}{S_\infty} = 4\left(\frac{Dt}{l^2}\right)^{1/2}\left[\frac{1}{\pi^{1/2}} + 2\sum_{n=0}^{\infty}(-1)^n \,\mathrm{ierfc}\, \frac{nl}{2(Dt^{1/2})}\right] \tag{3}$$

Equation 3 can be easily simplified for short times

$$\frac{S_t}{S_\infty} = 4\left(\frac{Dt}{l^2}\right)^{1/2}\left(\frac{1}{\pi}\right)^{1/2}. \tag{4}$$

So from a plot of S_t/S_∞ against $(t/l^2)^{1/2}$ the value of D can be deduced.

For glassy polymers the apparent solubility in any given sample, S_∞ may be regarded as the sum of two terms, the first one, S_p representing the equilibrium content of water in the compact resin, and the second one, S_2 representing the amount of water which may be present in the microcavities [5]

$$S_\infty = S_p + S_2 \tag{5}$$

S_2 is equal to ρx when ρ is the density of water at that temperature and x the volume fraction of microactivities. In a similar way the two terms may be considered, one history independent and the other history dependent, so one may write:

$$S_\infty(T, \tau, a, \alpha) = S_p(T, a) + S_2(T, \tau, a, \alpha) \tag{6}$$

where T and a are actual temperature and external activity of water, and τ and α are the previous thermal and activity history.

TABLE I Coatings tested and their formulations

Material	Supplied by	Formulation
Vetolite	Veneziani Zonca	Epoxy–Tar
Titania EP	Duco	Epoxy–Bentonite–TiO_2
Araldite GY 250	Ciba Geigy	Epoxy
Araldite 302	Ciba Geigy	Epoxy

3. Experimental procedures

3.1. Materials

Specimens were prepared from the materials reported in Table I. The resins and the curing agent were hand mixed at room temperature in the ratio outlined by the respective technical notes. The mixture was then poured into PMMA moulds, kept in a dry atmosphere at 35° C for 24h. Curing was initiated at 80° C under vacuum for 24h and finally the temperature was brought to 110° C for a curing stage of 3 days.

Samples were subsequently stored in a desiccator containing anhydrous silica-gel, before determining the effect of hygrothermal history on the resin properties.

3.2. Mechanical characterization

3.2.1. Clash–Berg experiments

Mechanical tests were performed by using a Clash–Berg torsional stiffness apparatus.

Specimens of 60mm × 10mm × 3mm were subsequently tested over a broad range of temperatures while the specimen was completely submerged in silicon oil. The angular deflection, α, was measured after application of a torque M_t for 10sec. The values of the shear moduli G(10) were calculated according to the following equation:

$$G(10) = 917 \times \frac{M_t l}{u\alpha ab} \tag{7}$$

where a, b and l are, respectively, the width, the thickness and the length of the specimen and u is a tabulated parameter which depends upon the ratio a/b [10].

3.2.2. *Stress–strain experiments*

Specimens of a dumb-bell shape, with a thickness of 0.6 mm, a minimum width of 5 mm and a distance between the grips of 5 cm, were loaded in tension by an Instron Universal Testing Machine Model 1112, equipped with a temperature controlled chamber for tests on dry materials and with a thermostatically controlled water bath for tests on water saturated samples.

3.3. Thermal analysis

The calorimetric behaviour of all the resins had been investigated using a Perkin-Elmer DSC-1 differential scanning a calorimeter, at a scanning rate of 16 K min^{-1} in a N_2 atmosphere. The temperature scale was calibrated using pure reference compounds.

3.4. Sorption kinetics and equilibria

Gravimetric liquid sorption experiments were performed by weighing 3.0 cm x 3.0 cm x ~ 0.02 cm samples repeatedly on a Mettler analytical balance following repeated immersion in water maintained at constant temperature. The samples were removed from the water, blotted, placed in a weighing bottle, weighed and then replaced in the constant temperature water bath.

Water sorption values are indicated as S, the percentage weight gain from the dry weight, and plotted as a function of $t^{1/2}/l$ where l is the thickness of sample ranging from 0.1 to 0.3 mm. Sorption equilibria were achieved over a period of 1 to 3 months, depending on the temperature of the test.

4. Results and discussion

The shear moduli obtained in torsion experiments for the four series of samples are reported in Fig. 1. In all cases a large decrease in moduli is observed at temperatures corresponding to the T_g of the materials.

The T_g values were also measured by differential scanning calorimetry (DSC) and are reported in Table II together with those obtained from mechanical tests according to the Tobolsky method.

Stress–strain measurements performed on dry and wet (dipped in water at 45° C until asymptotic water uptake was reached) materials revealed important differences in mechanical behaviour among the four series of samples (Table III).

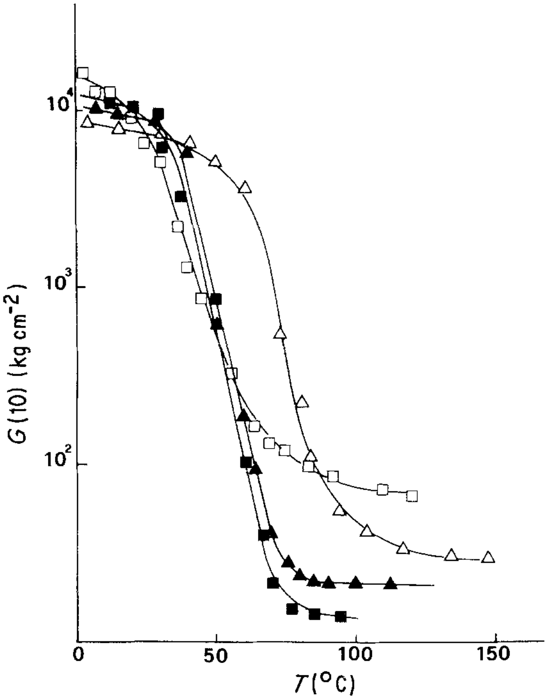

Figure 1 Torsional test results for dry samples: (▲) Araldite 250, (△) Araldite 302, (□) Vetolite, (■) Titania.

In fact, while for Vetolite and Titania the prevalent effect of water is to plasticize the polymer (increasing the elongation at break, ϵ_b), for the two Araldite coatings the water immersion also could remove low molecular weight substances present in the resin as plasticizing agents, making the material more brittle.

Water sorption data at 2, 25 and 45° C, are reported in Figs 2–5. The kinetic behaviour appears to be described adequately by Fickian diffusion, since a linear initial slope is exhibited by the sorption curves in the S against $t^{1/2}/l$ plots. Moreover data obtained on films with varying thickness superimpose on the S–$t^{1/2}/l$ diagram (though the range of thickness investigated is not very wide, 0.1 mm $< l <$ 0.4 mm) and an apparent diffusion coefficient can be extracted from the initial slope by making use of the classical early time approximation:

$$\frac{S_t}{S_\infty} = \frac{4}{\pi^{1/2}}\left(\frac{Dt}{l^2}\right)^{1/2} \tag{8}$$

TABLE II Glass transition temperatures

Coatings	Clash-Berg T_g (°C)	DSC T_g (°C)
Araldite 250	60	68
Araldite 302	72	67
Vetolite	44	50
Titania	53	60

TABLE III Results of stress–strain tests on dry or wet samples

Coatings	σ_b (kg cm^{-2})		ϵ_b (%)		E (10^3 kg cm^{-2})	
	dry	wet	dry	wet	dry	wet
Araldite 250	570	90	5.1	1.3	17	7.5
Araldite 302	550	160	4.5	2.4	17	9.0
Vetolite	230	34	0.8	12.0	45	5.0
Titania	130	13	1.7	20.0	7.3	1.8

where S_∞ is the asymptotic value of S and D is the apparent diffusion coefficient.

While the solubility values at 2 and 25° C are not significantly different, the value at 45° C is certainly higher than the other two. We would therefore expect that a sample brought to equilibrium at 45° C would exhibit water desorption if brought to 25 or 2° C at a later stage.

When this experiment was performed, however, the opposite behaviour was observed as shown in the upper part of Fig. 2. This is in line with previous works [5] where it was shown that the synergistic effect of moisture and temperature can induce irreversible damage in the polymeric network. However a slight difference was found among Vetolite, Titania and Araldite coatings. In fact for Araldite 250 and Araldite 302 the samples had apparently reached equilibrium at 45° C; when brought down to 25° C and then to 2° C slight additional sorption of water occurred (Table IV). Since at 45° C these systems are still in a glassy state (in fact the two glass transition temperatures for Araldite 250 and Araldite 302 equilibrated in water at 45° C are 60° C and 59° C respectively) the ΔS values could be due to irreversible damage produced by synergistic effect of microcrack formation in the polymeric resin [5–8]. The volume fraction of these microcavities can be calculated, assuming a standard state at 2° C in which $S_2 = 0$ and also that their formation rate at 45° C is sufficiently fast, so that while sorption proceeds to apparent equilibrium, the value of S_2 also reaches an equilibrium value, $S_2^{45^\circ\mathrm{C}}$. In Table IV the ΔS values obtained on samples brought first to 45° C and then to 25° C, and samples first equilibrated at 45° C, then at 25° C and finally at 2° C are reported.

Only for Araldite 302 is the value of S_∞ at 25° C higher than S_∞ at 2° C; in all the other cases the water uptake at 2° C is always larger. This behaviour can be explained by analysing the different mechanisms of water sorption in the resin. As already mentioned, the apparent solubility S_∞ may be regarded as to the sum of two terms; S_p representing the amount of water in the resin, and S_2 representing the amount of water in the microvoids. S_p slightly increases with temperature, while S_2 decreases, once the microvoid content is stable. This means that, except for Araldite 302, the amount of microvoids is not too much increased in bringing the samples from 2 to 25° C. Different behaviour is found at $T = 45°$ C, where the fraction of microvoids is much larger than at lower temperature.

A slightly different analysis can be developed for Vetolite and Titania, whose glass transition temperatures, after the equilibrium water content at 45° C was reached, are 27° C and 29° C respectively. This means that the higher values of S_∞ at 45° C are due to absorption of water in a rubbery like system and not in a rigid glassy

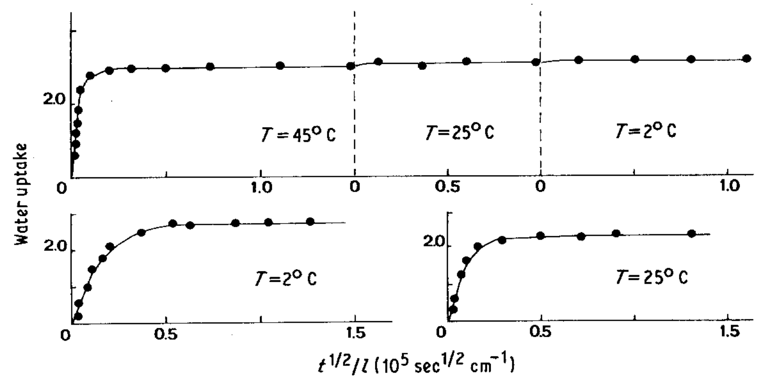

Figure 2 Sorption behaviour of Araldite 250.

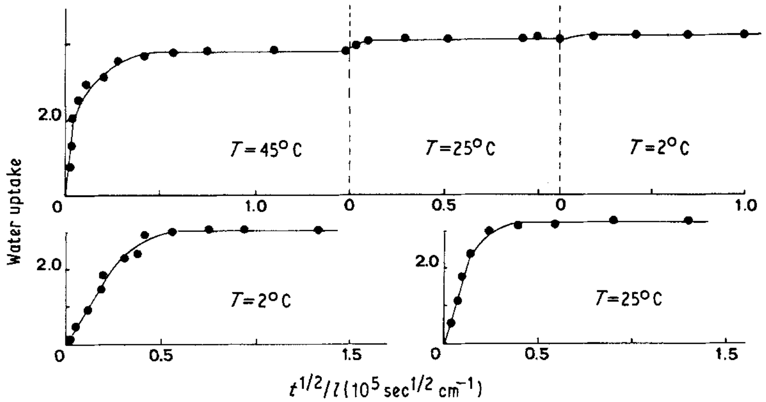

Figure 3 Sorption behaviour of Araldite 302.

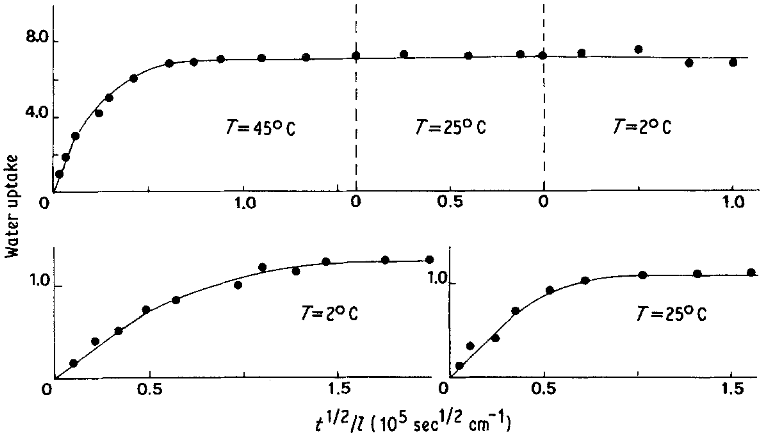

Figure 4 Sorption behaviour of Vetolite.

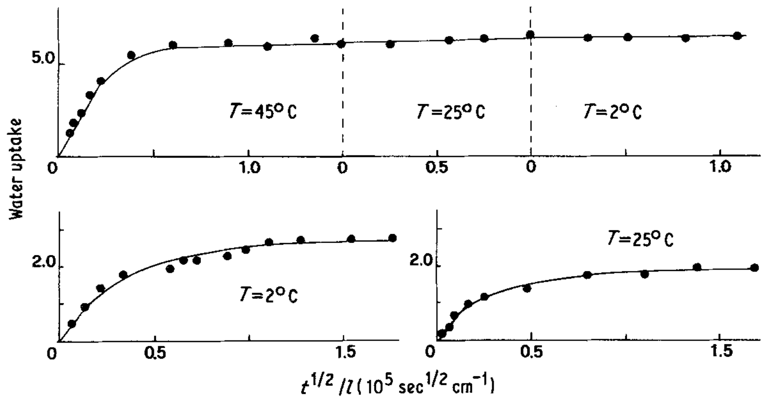

Figure 5 Sorption behaviour of Titania.

TABLE IV Effect of temperature and prior history of the apparent sorption equilibrium

Coatings	$S^{2^\circ\mathrm{C}*}$	$S^{25^\circ\mathrm{C}}$	$S^{45^\circ\mathrm{C}}$	$S^{45\to25^\circ\mathrm{C}}$	ΔS_1	$S^{45\to25\to2^\circ\mathrm{C}}$	ΔS_2	$D^{2^\circ\mathrm{C}\dagger}$	$D^{25^\circ\mathrm{C}}$	$D^{45^\circ\mathrm{C}}$
Araldite 250	2.75	2.35	3.00	3.15	0.8	3.20	0.45	18.0	46.0	180
Araldite 302	3.05	3.25	3.80	4.15	0.9	4.25	1.20	5.7	22.0	120
Vetolite	1.25	1.10	7.10	7.40	6.3	6.40	5.15	1.3	2.8	15.0
Titania	2.70	1.95	6.15	6.45	4.5	6.45	3.75	5.7	15.0	10.0

*S and ΔS in g per 100 g.

†D in 10^{-10} cm^2 sec^{-1}.

material, so the large difference of sorption between 25° C and 45° C is not surprising if the particular formulation of these batches are considered. In fact, Vetolite and Titania are formulated as blends of epoxy with coal tar and bentonite, suspending agents and titanium dioxide, respectively.

The different hydrophyllic behaviour of the continuous polymeric phase and the filler can induce larger variations in terms of chain mobility in the coating. This means that water plasticization can affect transport and mechanical properties of these materials much more than for systems in which only the epoxy component is present.

In conclusion, it has been shown that sorption–desorption experiments can give useful informations on the performance of polymeric coatings. An interesting approach is to correlate environmental ageing of the varnish with the corrosion of the metallic support. Further improvements of our research will be the correlation of adhesion loss, blisters and plasticization induced in the polymeric resin by the sea water at different temperatures.

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