# Influence of relative humidity on the development of internal stresses in epoxy resin based coatings

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Solvent-free epoxy resin based coatings have been applied and left for 24 hours at room temperature for initial setting under dry conditions. The curing process of the coatings was then completed at different relative humidity conditions. Meanwhile internal stress development was monitored as a function of time using the restrained beam deflection technique. Internal stress build up in solvent-free epoxy coating during the post-curing process was found to be highly dependent on the degree of relative humidity (RH) and the type of the curing agent. The development of tensile internal stress during the curing process of the different epoxy coatings took place only under low relative humidity atmospheres (<10–30%, depending on the curing agent), whereas compressive internal stress advanced at higher relative humidity conditions.
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## 1. Introduction

It is well established that internal stresses built up in an organic coating have adverse effects on its durability and service life [1–6]. Internal stresses originate in solvent-free thermoset coatings during the cross-linking process [7–9] that generates a volumetric contraction or shrinkage of the film. In adherent paint films, this shrinkage occurs with some resistance from the adhesion of the film to the substrate. This resistance is a source of internal stress. The extent to which shrinkage develops may also be restricted by molecular factors such as steric hindrances and chain entanglements [9]. The stresses that develop during solidification may change during the lifetime of the coating because of physical or chemical changes that take place as the result of interactions with its environment. These changes in internal stress are "active" energy-elastic stresses similar in kind to those referred to as "residual stresses" in moulded polymers [10]. In this paper, the term "internal stress" is used to describe the total stress of this kind in the coating, and therefore includes contributions that accrue during solidification and those which are caused by subsequent physical or chemical changes.

Volumetric changes induced by absorption and desorption of water as a result of variation in relative humidity (RH) can act as a source of internal stress in organic coatings [11]. Initial absorption of water causes the coating to swell and may cause compressive stress to develop, reversing the sense of the as-prepared tensile stress produced by shrinkage. A number of studies have covered the effect of liquid water and humidity on stress development and its dissipation in organic coatings [8, 12–14]. For example, Negele and Funke [12] studied the changes that take place in the development of internal stress in a number of cured organic coatings exposed to wet conditions. In this work a decrease in the magnitude of internal stress was observed in epoxy-resin based coatings, and this was attributed to molecular relaxation when the glass transition temperature, $T_g$, of the coating was lowered to below the ambient temperature by the plasticizing action of the absorbed water. Negele and Funke [12] also proposed that this allowed the sites of adhesive bonds at the substrate-coating interface to redistribute until an equilibrium condition was established.

Wet/dry cycling was also carried out by Gu Yan and White [13] on two cured marine coatings (vinyl copolymer-based thermoplastic and solvent-borne epoxy-based thermoset). As found also by Negele and Funke [12], an increase in (tensile) internal stress occurred during the desorption stage in both coatings. The effect was larger with the thermoplastic coating than with the thermoset one. The effect of wet/dry cycling was not totally reversible, and a monotonic change in the magnitude of internal stress was superimposed on top of the cyclic changes, leading to an overall increase in the tensile stress levels. Similar measurements were carried out on a bi-layer coating system (thermoset on the top of thermoplastic); the stresses developed in the bi-layer system were generally smaller than those in single layer coatings, and were generally less sensitive to the wet/dry cycling.

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Perera and Van den Eynde [14] studied the effect of wet conditions on the development of internal stress in organic coatings; (polyurethane-, epoxy- and alkyd/melamine-based systems). Their findings were in general agreement with those reported in the papers cited above [8, 12, 13], as water induced compressive internal stress in the coatings. The development of this stress was followed by stress relaxation [14]. Relaxation was also observed in the tensile stresses that arose in the coating during the drying stage. It was concluded that the lower the $T_g$ of the coating, the faster is the decrease of the stress.

In the study carried out by Croll [8] on a solventless epoxy resin coating cured with diethylenetriamine (DETA) variations in the internal stress magnitudes at particular coating thicknesses were observed. This was assigned to two competing processes taking place during the curing process: firstly, film shrinkage due to structural change induced by conversion; and secondly, production of a plasticized layer in the film due to absorption of ambient humidity. This phenomenon is closely related to the work reported here and this topic is discussed further in Section 4.

The work reported here concerns the effect of moisture on internal stress development during the curing of epoxy coatings.

## 2. Experimental
### 2.1. Materials
The epoxy resin and the hardeners used in the experiments reported here along with the mix ratios are shown in Table I. DER 331®, manufactured by DOW Chemical Co., is an undiluted diglycidyl ether of bisphenol A (DGEBA)-based liquid epoxy resin with an epoxy equivalent mass of 182–192 g/mol. Such low molecular mass grades of epoxy resin have become standard because of their versatility in many coating applications.

Five different types of amine curing agents were used in this study in conjunction with the epoxy resin (EP). The curing agents were: 4,4′-diaminodiphenylmethane (H1); diethylenetriamine (H2); cycloaliphatic amine based on isophorone diamine (H3); polyaminoimidazoline based hardener (H4); and polyamidoamine based adduct hardener (H5).

### 2.2. Mixing procedure
The mixing of the epoxy resin (EP) with the curing agents H2 – H5, was carried out on batches of 100 grams under vacuum using a mechanical paddle stirrer. The mix ratios of EP to each hardener are given in Table I.

Each batch was mixed under vacuum for about 3 minutes at moderate speed. Then the mix was allowed to stand for 5 min before application.

As H1 is a solid at room temperature, a different mixing technique was required to obtain an appropriate mixture that was suitable for use as a coating at ambient temperature. Therefore a total batch of 100 g was prepared by melting H1 at 100°C and mixing it with equal parts of EP at this temperature. Then the mixture was added to the remainder of the EP resin at room temperature and mixed under vacuum to get the final mix at a temperature of about 35°C. The mix was then allowed to stand for 5 min before application. It should be noted that in spite the mixed material being at about 35°C at the commencement of application, the coated substrate reached room temperature ($23 \pm 1$°C) within a period of <2 minutes (confirmed using an IR thermometer). That means that the vitrification stage took place at room temperature as in the case of the mixtures based on the liquid curing agents.

### 2.3. Sample preparation
After completing the base-hardener mixing process (2.2), samples were prepared for the restrained substrate beam deflection method [1] by applying the coatings onto completely flat shims (150.0 mm × 23.0 mm × 0.1 mm) that were de-greased using MEK (methyl ethyl ketone) prior to coating. The substrates were kept horizontal on a glass sheet during the coating application, that was carried out using a narrow paint brush. A strip 5 mm at each end of the shims was left uncoated.

As the coatings used throughout this study were neat epoxy systems, free from fillers or rheological modifiers, the coatings were self-smoothing and formed a uniform thickness across the substrate. The thickness of the coatings ranged between 0.7 mm and 0.9 mm. Immediately after the coating application, the samples were clamped onto steel blocks 150.0 mm × 23.0 mm × 10 mm at each end using G-clamps. Details of this test method have been published elsewhere [1]. All samples were then left to have an initial cure at room temperature for 24 hours in an enclosure containing silica gel to ensure that moisture did not affect this part of the curing process.

After the initial cure of all the epoxy resin systems under investigation, the samples were divided into three groups. Each group was then exposed at $23 \pm 1$°C to one of three different relative humidity atmospheres: 0% RH; 52% RH; and 97% RH. The RH control was

TABLE I Details of the materials used

| Ref. Name | Material | Grade | Commercial name | Supplier | Mix ratio (phr)[a] |
|---|---|---|---|---|---|
| EP | Diglycidyl ether bisphenol A | Commercial | DER 331 | Dow chemical | — |
| H1 | 4,4′-Methylenedianiline | Lab | — | Acros organics | 26[b] |
| H2 | Diethylenetriamine | Commercial | — | UC/Dow chemical | 11[b] |
| H3 | Cycloaliphatic polyamine | Commercial | Aradur 42 | Vantico | 22[c] |
| H4 | Polyaminoimidazoline | Commercial | Aradur 140 BD | Vantico | 50[c] |
| H5 | Polyamidoamine | Commercial | Aradur 450 BD | Vantico | 60[c] |

[a]Parts per hundred parts of epoxy resin (EP), by weight.
[b]Stoichiometric ratio.
[c]As recommended by the manufacturer.

obtained by using silica gel (0% RH), saturated aqueous solution of sodium dichromate (52% RH) and saturated aqueous solution of potassium sulphate (97%) respectively [15].

## 2.4. Internal stress measurements
### 2.4.1. Curvature measurement
Restrained samples were released from the steel block only during the curvature measurement process. This is essential as any prolonged duration in the unrestrained state would enable curing and stress relaxation to take place under different conditions [1]. To measure curvature, the samples were clamped lightly in one location so that they were free to bend with the width direction vertical, and held above a piece of white paper. The contour of the curved surface was copied onto the paper and the curvature determined using standard geometric measurements.

### 2.4.2. Internal stress calculation
For a coating with Young's modulus $E_c$, Poisson ratio $\nu_c$ and thickness $a$ on a substrate with Young's modulus $E_s$, Poisson ratio $\nu_s$ and thickness $b$, the relationship between the radius of curvature $R$ and the internal stress in the coating $\sigma_c$ is given by [13]:

$$\sigma_c = \{aE_c/6R(1 - \nu_c)\}\{(1 + 4\alpha\beta + 6\alpha^2\beta + 4\alpha^3\beta$$
$$+ \alpha^4\beta^2)/(1 + \alpha)(1 + \alpha\beta)\} \quad (1)$$

where $\alpha = b/a$ and $\beta = \{E_s/E_c\}\{(1 - \nu_c)/(1 - \nu_s)\}$.

This form of the relationship between the residual stress and the curvature takes account of the true position of the neutral surface, which is displaced in our case from the mid-plane of the substrate as $t_c > t_s$.

For the calculations presented here, $E_c$ and $E_s$ were taken to be 3.4 GPa and 200 GPa respectively while $\nu_c$ and $\nu_s$ where taken to be 0.34 and 0.29 respectively. Internal stress measurements were performed periodically and plotted as a function of time for each epoxy system used throughout this study.

## 3. Results
Figs 1–5 show the development of internal stress in the five different epoxy-based coatings, under different rel-
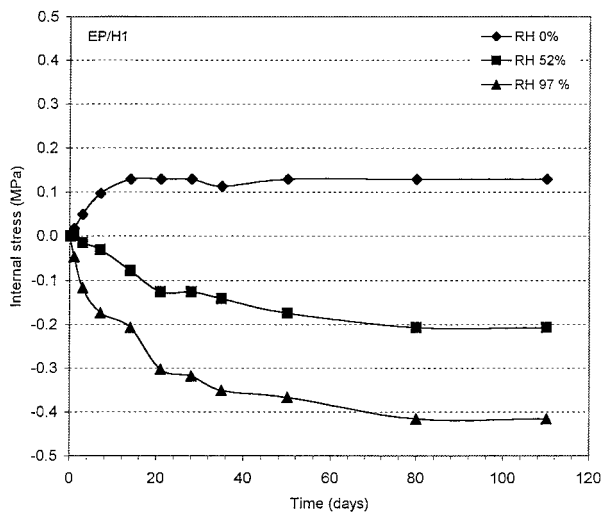


*Figure 1* Internal stress development in EP/H1 coating during the curing process under different RH%; 0%, 52% and 97%.
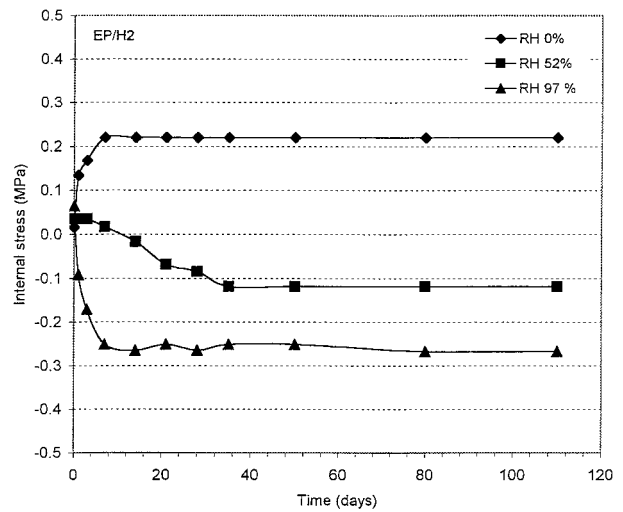


*Figure 2* Internal stress development in EP/H2 coating during the curing process under different RH%; 0%, 52% and 97%.
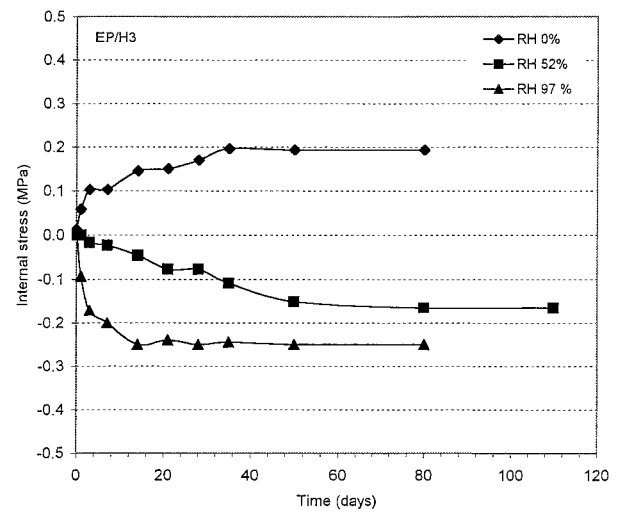


*Figure 3* Internal stress development in EP/H3 coating during the curing process under different RH%; 0%, 52% and 97%.
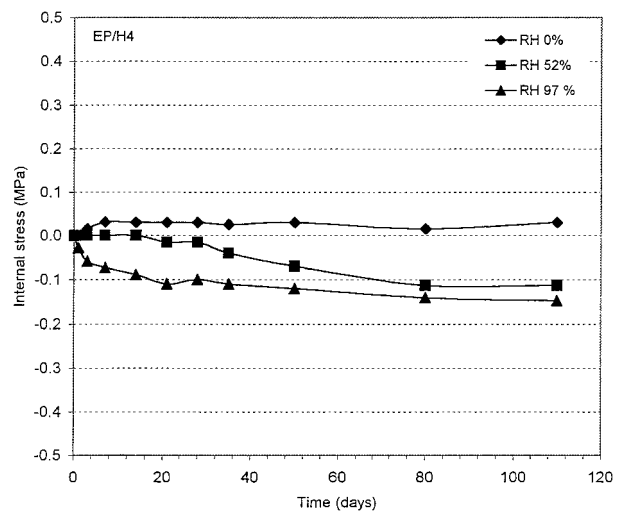


*Figure 4* Internal stress development in EP/H4 coating during the curing process under different RH%; 0%, 52% and 97%.

ative humidity environments, as a function of time. As curing proceeded, all of the epoxy systems developed tensile internal stress under dry conditions. Apart from EP/H2, for which the as-prepared (24 hour dry initial cure) tensile stress was ~0.03 MPa, the as-prepared
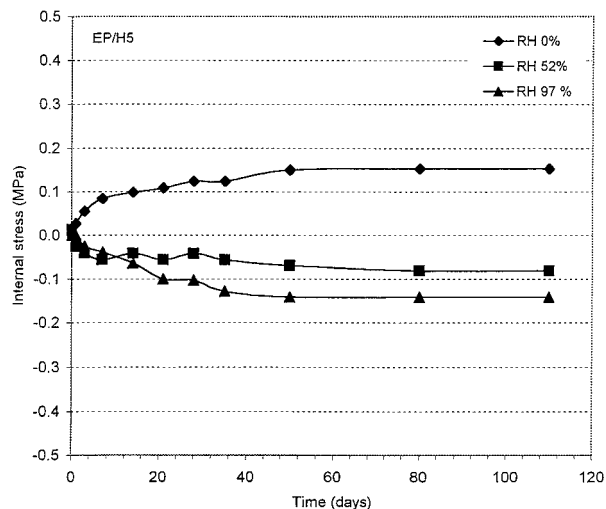
*Figure 5* Internal stress development in EP/H5 coating during the curing process under different RH%; 0%, 52% and 97%.

stresses were below the level of experimental uncertainty. On prolonged curing under the three different conditions applied here, the internal stress magnitudes reached a plateau after approximately 30–60 days. For dry conditions the plateau (tensile) stress values were 0.13 MPa (EP/H1); 0.22 MPa (EP/H2); 0.19 MPa (EP/H3); 0.03 MPa (EP/H4); and 0.15 MPa (EP/H5) respectively.

At 52% RH and 97% RH the internal stress suffered progressive negative incremental change and became compressive after a period of time that varied with composition and humidity. Once the stress reversed to become compressive the magnitude increased with time. The ultimate (plateau) values of internal stress for the coatings tested at 52% RH were −0.21 MPa (EP/H1); −0.12 MPa (EP/H2); −0.17 MPa (EP/H3); −0.11 MPa (EP/H4) and −0.08 MPa (EP/H5). Increasing the RH to 97% led to even greater compressive internal stresses, with plateau values of −0.42 MPa (EP/H1); −0.27 MPa (EP/H2); −0.25 MPa (EP/H3); −0.15 MPa (EP/H4); and −0.14 MPa (EP/H5).

The plateau values of stress in Figs 1–5, are plotted as a function of RH% in Fig. 6. If the smooth monotonic relationships indicated by these plots are truly representa-
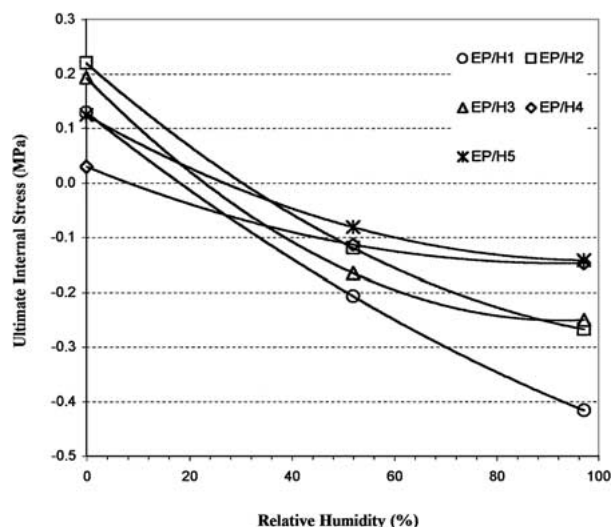
tive of the behaviour then interpolation suggests that compressive stresses would develop in EP/H4 at RH values as low as 10% whereas for EP/H2 and EP/H5 the development of compressive stresses would require a RH value above ∼30%.

## 4. Discussion

The selection of epoxy hardeners used in this study included a wide range of amine curing agents covering the commonly used examples, such as aromatic amine, aliphatic amine, cycloaliphatic amine, polyaminoimidazoline and polyamidoamine.

The initial preparation stage, in which the coatings were kept under dry conditions for 24 hours was adopted for reasons that are more relevant to other parts of a larger project concerning post curing of the epoxy based coatings at elevated temperatures. That part of the work will be reported elsewhere [16]. The current paper focuses only on the effect of RH on the room temperature curing process.

Internal stresses measured in this piece of work are generally lower than those reported in the literature partly because they are based on the restrained beam deflection method instead of the free-to-bend beam deflection method which is more commonly used [10, 16]. It is shown elsewhere [1] that the free to bend beam deflection method gives an overestimate of the stress likely to develop on a substrate that is rigid and resists bending (as used here, and as is encountered in the field when the coating is applied to a massive engineering structure such as steel plate).

From Figs 1–5, it can be observed that the values of ultimate internal stress for EP/H1, EP/H2, EP/H3 and EP/H5 cured under dry conditions were fairly similar whereas in EP/H4 the stress was too small to measure accurately. Since these values are for coating systems cured without any influence of moisture or uneven temperature, they may indicate the relative tendencies of the different epoxy systems towards the build up of curing stresses. In making any such assessment, it must be assumed that good adhesion is developed between the coating and the substrate at an early stage of curing. On the other hand, the rate of stress development under such conditions reflects the rate of cross-linking, and is a combination of both physical and chemical changes.

At 52% and 97% RH, compressive stresses developed during curing in all the epoxy resin based coatings tested. This may be partly due to incomplete curing [16] which kept the structure relatively open, allowing water molecules to penetrate easily into the coating, causing swelling and creating compressive internal stresses. Meanwhile cross-linking will continue to develop but at reduced rates as a result of the hindrance effect and polarity of absorbed water molecules that delay the chemical reaction between cross-linking elements. In that case the ultimate value and the rate of build up internal stress are not only dependent on the generic type of the curing agent, but also highly dependent on the degree of cure at which the coating becomes exposed to moisture, while the driving force for the penetration of moisture into the structure of the epoxy system is strongly influenced by the RH%.



*Figure 6* Effect of relative humidity on the ultimate internal stress built up in epoxy coating systems.

Results presented in Figs 1–5 showed that formulated hardening systems, EP/H4 (polyaminoimidazoline-based) and EP/H5 (polyamidoamine-based) exhibited low response to the effect of water in the development of compressive stresses. This may be attributed to the chemical structure of these two hardeners as well as to the formulation used by the manufacturer during the manufacturing process.

Results presented in the Fig. 2 on the development of internal stress in DETA at 52% RH appear at first sight to be in disagreement with those presented by Croll [8], in which compressive internal stresses were observed at such a relative humidity only at coating thicknesses less than 60 $\mu$m, whereas for greater thicknesses, tensile internal stresses were reported. The difference between the results reported above and those of Croll can be reconciled when it is recognised that the overall testing period used in Croll's investigation [8] was less than 24 hours, with no initial curing period. On the other hand, in addition to the water sensitivity, the DGEBA + DETA epoxy system is known to have tendency to cause blushing, i.e., formation of amine carbonate by reaction with atmospheric carbon dioxide. That will have more effect on the values of internal stress in relatively thin coatings formulated using DETA. A further difference between the current work and that of Croll derives from the different procedures used to measure the internal stress.

The apparently systematic relationship between the ultimate internal stress and RH for each of the coatings shown in Fig. 6 merits comment. The curves drawn on Fig. 6 are quadratics of the form:

$$\sigma = A - B(RH) + C(RH)^2$$

where A, B and C are constants. Although it is hardly surprising to find that a quadratic can be made to fit three data points, it is worth noting that, if it could be shown that this equation truly represents the behaviour, then A would be related to the basic shrinkage properties of the epoxy system, whereas B and C relate to the sensitivity of the epoxy system towards moisture.

## 5. Conclusions
Residual stress measurements have been made on a family of epoxy resin based coatings made with a range of hardeners. Samples have been held in environments with different relative humidity values (0%, 52% and 97% respectively) for long periods (up to 4 months). A special feature of the work has been the use of restrained substrate conditions, so that the results are unaffected by relaxation modification caused when the substrate is allowed to bend.

Tensile stresses developed in the coatings conditioned in a dry atmosphere whereas in 52% RH and 97% RH compressive stresses developed. In each case the stress magnitude levelled off to a plateau after ~30–60 days. The plateau values for each of the resin systems was different and plots of the plateau values versus RH for each of the resin systems seemed to follow a very consistent trend.

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