# Hygrothermal history dependence of equilibrium moisture sorption in epoxy resins

**A. Apicella, L. Nicolais, G. Astarita and E. Drioli**
*Istituto di Principi di Ingegneria Chimica, Universita' degli Studi di Napoli, Piazzale Tecchio,* 80125 *Naples, Italy*
(*Received* 31 *December* 1979; *revised* 2 *June* 1980)

Water uptakes in sorption experiments made on thin sheets of an epoxy resin have been followed by means of a quartz microbalance placed in a temperature and humidity controlled cell. Attention has been given to the humidity history dependence of the apparent water solubilities at constant temperature. The sorption behaviours under the same temperature and humidity conditions have been successively compared for samples with different hygrothermal histories. Additional sorptions have been carried out from liquid water at low temperatures (2 and 20°C). Equilibrium moisture sorptions have been found to be represented in the same temperature and humidity conditions both by linear and upward isotherms, depending upon the humidity history to which the system had been previously subjected. Such humidity history dependence, which is progressively lost as the test temperature is decreased, has been attributed to a microcavitational damage process in the form of localized solvent crazing.

## INTRODUCTION

Fibre reinforced plastics are being utilized increasingly for structural applications where their long-term properties are of primary importance. As a result the problem of the environmental effects on the mechanical performance is attracting attention. 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[1-9]. 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. The damaging process, governed by the synergistic effect of sorbed moisture and temperature, is particularly evident on the solubility behaviour where an additional weight gain is observed[1,3,6] when the samples are exposed to cycling conditions of environment and temperature (thermal spikes).

This additional weight gain is attributed to moisture entrapment during microcracking of the resin, since glass transition temperature changes are not observed[6].

Most of the published work is concerned with the combined effects of moisture and temperature on the sorption of a composite matrix material. While the sorption behaviour is reasonably well described by classical diffusion laws[1,2,6], history dependent equilibrium moisture solubilities are usually found[1,3,6,10]. Sorption behaviour anomalies are particularly evident at elevated temperatures. Although extensive studies have been carried out in the 'real-life' conditions or in particular environments, systematic investigations on temperature and humidity history dependence of moisture sorption in epoxy resins have not been found in the scientific literature.

This work is part of a research program where both sorption equilibria and kinetics of water in epoxy resins have been investigated under different conditions of temperature and humidity. In a previous paper[10] the authors introduced a physical solubility model to describe the temperature history dependence of liquid water sorption in the same epoxy. Equilibrium weight gains were described as being progressively affected by microcavity formation as the temperature was increased. The microcavitational nature of the induced damage has been confirmed[11] by means of an analysis, based on the Dual Mode Sorption Theory, which relates the increase of the apparent solubilities with the observed effective diffusion coefficient depressions. Data of weight gain changes in sorptions of water in thin sheets of an epoxy resin at different temperatures and relative humidities are reported. Equilibrium moisture uptakes, usually reported to be represented by power functions of the relative humidity with exponents ranging from 1 to 2 or higher values[1,2-14], have been obtained and interpreted in the light of the above physical model.

## EXPERIMENTAL

### *Materials*

Specimens were prepared from Epikote 828 (kindly supplied by Shell Italiana, Co) using commercial Triethylene-tetramine (TETA) (Montedison SpA) as curing agent. Distilled water was used in the sorption experiments. Dissolved gases were removed by repeated freeze–thaw cycling, under vacuum, using liquid nitrogen as refrigerant. The epoxy samples were prepared following the same procedures previously described[10].

### *Sorption kinetic experiments*

Moisture sorption kinetics and apparent equilibria in epoxy films of thickness 0.030 cm were determined by means of a quartz spring microbalance[15] served by a standard vacuum system. The quartz springs with a sensitivity of 0.50 mg $mm^{-1}$ were obtained from the Ruska Corporation, Worden Quartz Products Division, Houston, Texas, USA. The sample temperature was maintained constant by circulating thermostated water

0032-3861/81/081064–04$02.00

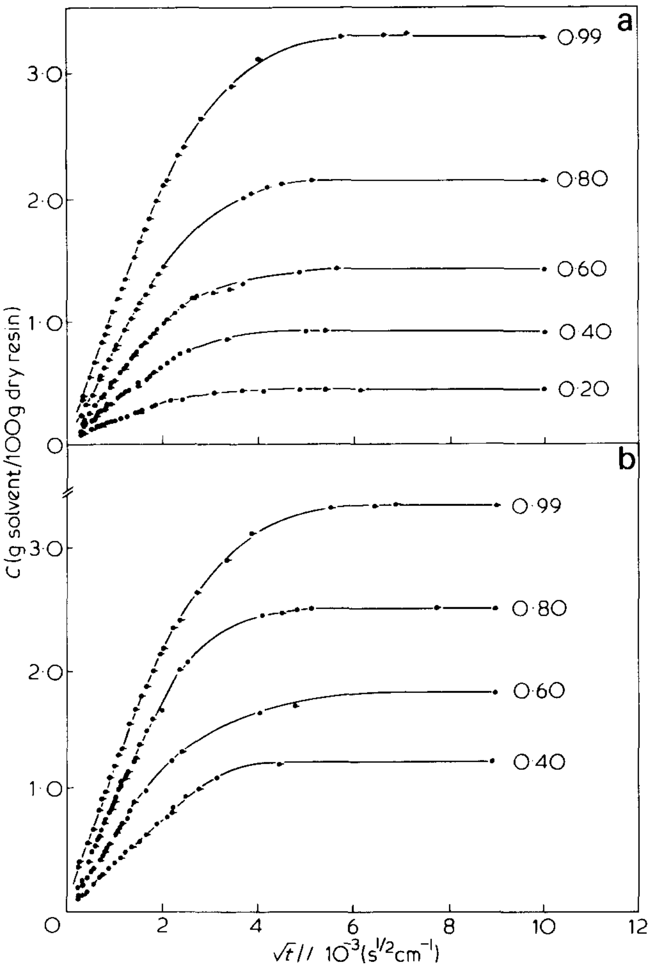

*Figure 1* First (a) and second (b) set of sorptions (●) and desorptions (●—) in experiments performed at different water vapour activities (numbers on the curves). $T$ = 75°C

through a water jacket surrounding the sorption cell. Different activities of the penetrant have been maintained in the system by imposing and controlling different pressures of water vapour by means of a mercury differential manometer.

Gravimetric liquid sorption measurements were performed by weighing $3.0 \times 3.0 \times 0.05$ cm$^3$ samples repeatedly on a Sartorious analytical balance following immersion in water maintained at constant temperature. The samples were removed from the water, blotted, placed in a weighing bottle, weighed and finally replaced in the constant temperature water bath.

Sorption data are indicated as $C$, percentage of weight gain referred to the dry weight, and plotted as a function of $\sqrt{t}/l$, where $l$ is the thickness of the samples ranging from 0.2 to 0.4 mm for vapour sorption and from 0.4 to 0.6 for liquid sorptions. Sorption equilibria were achieved over 2 to 200 days depending upon the test temperature.

## RESULTS AND DISCUSSION

Constant temperature sorptions and desorptions have been carried out on the same sample at progressively higher humidity levels. Once the sample has been equilibrated at the highest humidity level a second set of sorptions and desorptions have been followed. The temperatures studied were 75, 60, 45, 30, 20 and 2°C.

*Figure 1* shows polymer weight gains, expressed as grams of water per 100 grams of dry resin, as functions of the square root of time normalized to the sample thickness[16] ($l$) in experiments performed at 75°C. Numbers on the curves refer to the activity at which the specific test has been run. The activity is defined as the ratio between the water vapour pressure in the sorption cell and the saturated water vapour pressure at the temperature of the experiment.

For activities higher than 0.60, first sorption experimental points (*Figure 1a*) have not been reported since the initial part of the curve does not follow the classical Fickian diffusion predictions[11]. Conversely in *Figure 1b*, sorption and desorption kinetics have been reported for all activities indicated showing that in this case all the data at low times are correlated by straight lines. In *Figure 2*, equilibrium solubilities at 60°C, obtained from the asymptotic values of the sorption curves both for the first and the second set of sorptions, are reported for different values of the external penetrant activity. Open circles refer to the progressive moisture weight gains which have been reached in the first set of sorptions. The isotherm is not linear (upward) showing positive deviations from linearity at higher activities. Once the maximum value of external relative humidity has been experienced by the sample, the equilibrium water uptakes were linear with the activities. The differences in the sorption behaviour, for the same environmental conditions, may be attributed to a progressive damage that is produced in the material equilibrated at increasingly higher moisture contents. Once the maximum equilibrium moisture content has been achieved and the temperature is not increased, no additional damage should be induced in the resin. The polymer–water system then behaves linearly since the internal state of the material does not change during the subsequent experiments. In this case an apparent Henry's law constant might be defined as the slope of the equilibrium linear isotherm. The overall system is then identified by an additional internal state variable which is a function of both the temperature and the moisture content. Once the system is fixed the sorption kinetic becomes a reversible phenomenon. In fact the equilibrium values of the solubility for a third set of sorption

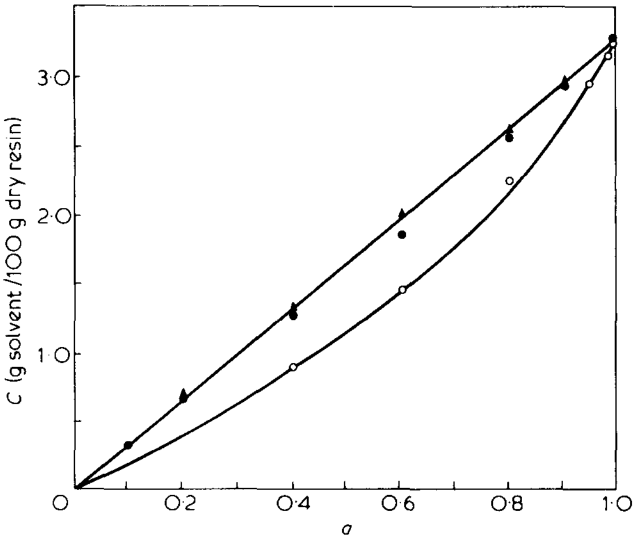

*Figure 2* Equilibrium solubility isotherms at $T$ = 60°C from: first (○); second (●) and third (▲) set of sorptions

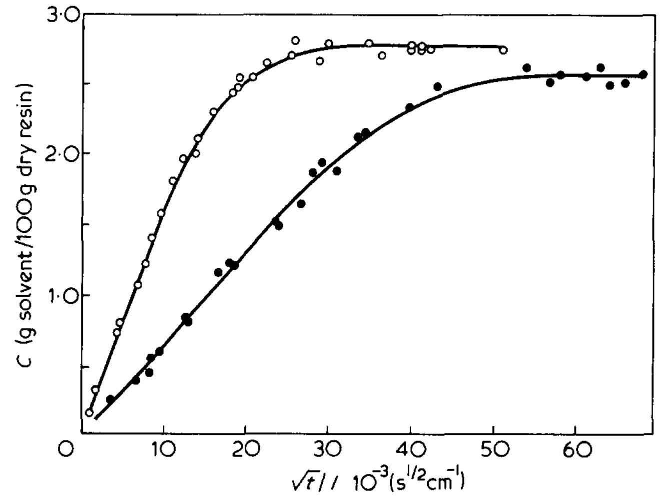

*Figure 3* Weight gains as a function of time in liquid water sorption at 20° (○) and 2°C (●)

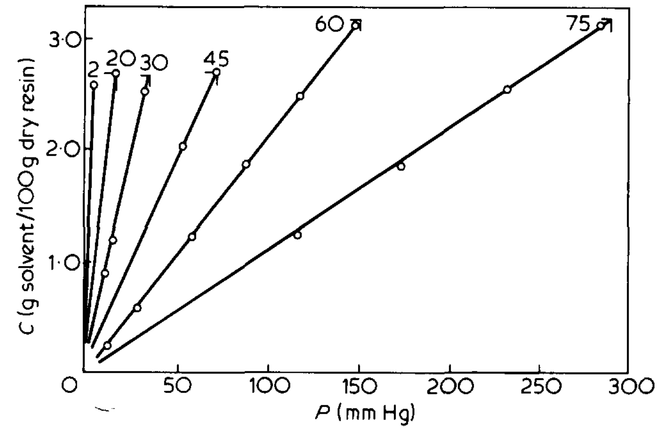

*Figure 4* Equilibrium solubility isotherms as a function of the actual water vapour pressure

experiments, reported in *Figure 2*, show a good agreement with the previous data.

The same procedure has been followed for temperatures both higher (75°C) and lower (45 and 30°C) than the previous one. Upward isotherms relative to the first set of sorption equilibrium solubilities at 75, 45 and 30°C showed an initial, apparently linear part, followed by progressive positive deviations for activities higher than 0.60. The possibility of the existence of an apparently initial linear region is in agreement with a previous observation[11] indicating that at low moisture contents, irrespective of the test temperature, the damage induced in the resin is irrelevant. The Henry's constant obtained on the 'as cast' polymer at low activities from the initial slope of the sorption isotherm should be then referred as relative to an undamaged state. Once the sample has been equilibrated at the highest humidity level, the system behaves linearly for all activities and temperature studies with a higher overall apparent Henry's law constant than in the undamaged state (initial slope of the upward isotherm).

At lower temperatures, 45 and 30°C, the differences between the linear and upward isotherms have been observed to be less pronounced according to the temperature dependence of the damage in the resin–water system[10,11]. Low temperature environments are, in fact, inducing lower damage than a higher temperature environment, even under the same conditions of moisture content, and therefore have pronounced humidity history dependence of the apparent solubilities. Moisture *per se* is not effective in producing any microcavitation in the resin but, as already pointed out in the literature[1,6], the synergistic effect of moisture and temperature is effective in the damaging process.

For temperatures lower than 30°C (in particular 20 and 2°C) sorption from liquid phase, $a = 1.00$, has been followed and the data are reported in *Figure 3*.

In *Figure 4* water solubilities in resins previously equilibrated at high humidity levels as function of actual vapour pressures (in mm of Hg) and for different temperatures, are shown. For experiments made in the liquid phase, saturated water vapour pressures at the temperature of the tests are used as abscissa, while for tests performed in the vapour phase, isotherms break at a pressure equal to the relative saturated water vapour pressures. The overall apparent Henry's law constants $k$, calculated from *Figure 4*, are plotted in the van't Hoff diagram of *Figure 5*. On the same Figure, apparent Henry's law constants for undamaged resin, obtained from the initial slope of the upward isotherms, are also reported. Specimens equilibrated at high humidities and at different temperatures are not expected to show apparent Henry's law constant that can be correlated by straight lines in a van't Hoff diagram since they possess different degrees of bulk damage.

Conversely, a straight line correlates the solubility constants of the resins referred to as 'undamaged' (low temperature and activity tests) and reported in *Figure 5*. The increase in the apparent solubilities and the upward shape of the isotherms may be attributed to irreversible morphological changes occurring in the bulk polymer at increasingly higher humidities and temperatures. However, once the state of the material has been fixed by the hygrothermal history, again a linear relationship

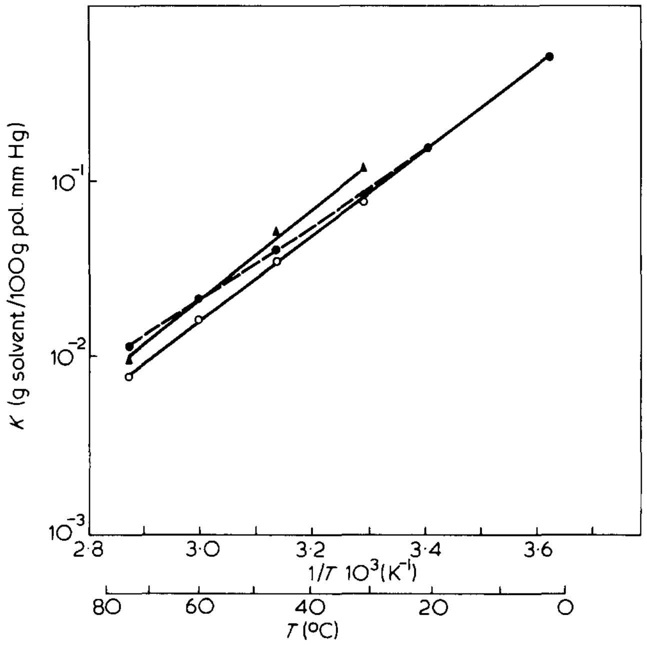

*Figure 5* Apparent Henry's law constant vs. 1/*T* from: initial slope of isotherms (○) (referred to undamaged state); final slope of the isotherms for resins damaged at test temperature (●); slope of the linear isotherms obtained for samples previously exposed at *T* = 60°C and *a* = 0.99 (▲)

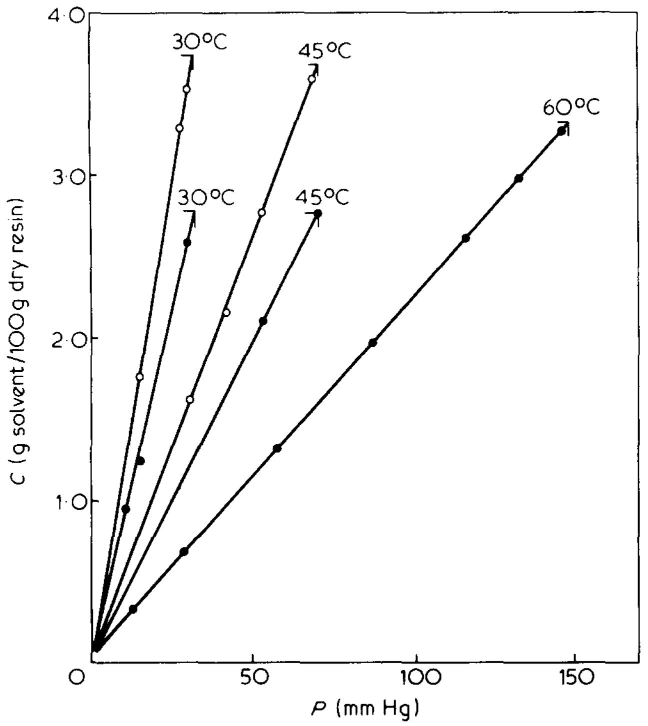

***Figure 6*** Comparison between the linear isotherms at 30 and 45°C obtained for samples equilibrated at the test temperature (●) and previously equilibrated at 60°C and $a$ = 0.99 (○)

should be found. The solubility isotherms for tests performed at 30 and 45°C on samples previously equilibrated at 60°C and at an activity of 0.99, are reported in *Figure 6*. For such system, linear isotherms have been observed and are compared with those obtained for samples equilibrated at the test temperature only, 45 and 30°C, the higher degree of damage is shown by a higher solubility constant. The overall apparent Henry's law constants, obtained from *Figure 6* and at 75°C from a low activity ($a = 0.20$) experiment on a sample previously equilibrated at 60°C and $a = 0.99$, are reported in *Figure 5*. As expected, a straight line, parallel to the one corresponding to the undamaged resin, correlates the higher values of the apparent solubilities found for samples of a fixed damage.

## CONCLUSIONS

A systematic series of water sorption experiments on an epoxy resin both from liquid and vapour phase, at different temperatures, has been performed to investigate the effect of the hygrothermal history on the apparent equilibrium moisture content of such a system. Sorbed moisture induces different degrees of irreversible damage in the resin depending upon the temperature and humidity levels imposed on the samples. The resin may undergo solvent crazing in the presence of sorbed moisture depending on the temperatures and relative humidities to which the samples have been previously exposed. For low temperatures ($T < 20°C$) or for low external penetrant activities ($a < 0.60$) the material seems to be left essentially undamaged by the sorbed moisture. At higher temperatures or activities, sorption is influenced by the previous temperature and humidity histories. Changes of the apparent solubilities are responsible for the upward shape of the isotherms once the damaging process is active. When damage reaches its maximum value as a result of the exposure to more severe environments (higher temperatures or himidities), linear sorption isotherms with higher apparent Henry's law constants are, in fact, observed in any subsequent sorption experiment.

A microcavitational damaging process has been attributed to the presence of network inhomogeneities, i.e. low and high crosslinking density regions[13], which, on sorption, may favour localized crazing by differential swelling stresses. At low environmental relative humidities, which correspond to lower water uptakes, the localized damage in the bulk polymer seems to be irrelevant.

## ACKNOWLEDGEMENTS

This work was sponsored by the United States Air Forces Office of Scientific Research, Contract AFORS–77–3369.

The authors are grateful to Dr. Petropoulos for helpful discussion and constructive comments on this work.

## REFERENCES

1 McKague Jr., E. L., Hakias, J. E. and Reynolds, J. D. *J. Compos. Mater.* 1975, **9**, 2
2 Chi-Hong and Springer, G. S. *J. Compos. Mater.* 1976, **10**, 2
3 Weitsman, Y. *J. Compos. Mater.* 1976, **10**, 193
4 Morgan, R. J. and O'Neal, J. *J. Mater. Sci.* 1977, **12**, 1966
5 Ishai, O. and Arnon, U., ASTM STP 658, (Ed. J. R. Vinson) Am. Soc. for Tests Mat., 1978, p 267
6 Browing, C. E. *Polym. Eng. Sci.* 1978, **18**, 16
7 Loos, A. C. and Springer, G. S. *J. Compos. Mater.* 1979, **13**, 17
8 Keenen, J. D., Seferis, J. C. and Quinlivan, J. F. *J. Appl. Polym. Sci.* 1979, **24**, 2375
9 Ishai, O. and Arnon, U. *J. Test. Eval.* 1977, **5**, N.4, 320
10 Apicella, A., Nicolais, L., Astarita, G. and Drioli, E. *Polymer* 1979, **20**, 9
11 Apicella, A., Nicolais, L., Astarita, G. and Drioli, E. *Polym. Eng. Sci.* 1981, **21**, 19
12 Shen, C. H. and Springer, G. S. *J. Compos. Mater.* 1976, **10**, 36
13 McKague Jr., E. L., Reynolds, J. D. and Halkias, J. E. *J. Eng. Mater. Technol.* 1976, **48**, H,92
14 McKague Jr., E. L., Reynolds, J. D. and Halkias, J. E. *J. Appl. Polym. Sci.* 1978, **22**, 1643
15 Illers, K. J. *Makromol. Chem.* 1969, **127**, 1
16 Crank, J. 'The Mathematics of Diffusion', Oxford Univ. Press, 1975