

LONG TERM SERVICE LIFE OF REINFORCED AND UNREINFORCED EPOXY - VINYL ESTER RESINS EXPOSED TO MOISTURE

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Summary

The Derakane 411 Vinyl Ester and Epoxy resins evaluated in this paper, and many modern polymers in general, have an intrinsic chemical resistance to water. This means that surface corrosion by water in the presence of oxygen, in contrast to most metals, is not a significant issue. On the other hand, water is adsorbed on the resin surface and subsequently diffuses into the resin matrix.

If the equilibrium water solubility weight in the polymer is small, often Fick's First and Second Laws are applied to interpret gravimetric data and to predict the impact of diffusion in an industrial context. However, in this paper it is shown that Fick's Laws need some slight - but rather principal - adjustments for analysis of water uptake data¹ in epoxy resins, like Derakane 411. Reason is that local adsorption of water on specific sites in the polymer, results in additional uptake, which is currently not included in Fick's law. Moreover, we demonstrate that if the matrix contains fibre reinforcements that have a sharp boundary with the resin, instationary multilayer diffusion interpretation must be applied in addition, because the water diffusivity and concentration gradient are discontinuous.

1. Introduction

Currently, thermoset and thermoplastic materials reinforced with fibres or metals are widely applied in all kinds of high performance applications, and their application will grow considerably in the near future. Their low weight, mechanical strength and chemical resistance make them attractive construction materials.

Already since the forties of the twentieth century many researchers have focused on exposure unreinforced and reinforced polymers to hygrothermal conditions. Ultimately, the water mass flux through the material - as applied in containments and membranes - must be predicted correctly and/or the mechanical retention of structures (bridges, body parts for cars and trains) in weathering conditions is of interest.

¹ Data generated by gravimetric sorption experiments such as ASTM D570.

2. Anomalous Water Diffusion?

If a resin based sheet or plane structures is exposed to water, for short times, water weight increases linearly as a function of the square root of time. Subsequently the uptake profile levels off to equilibrium. This is all in line with Fick's first and second laws. However, at longer times, the water uptake continues, and the attained equilibrium appears to be a pseudo equilibrium.

See figure 1 for a representative insight in the water absorption of epoxy coating for 12 years(!)

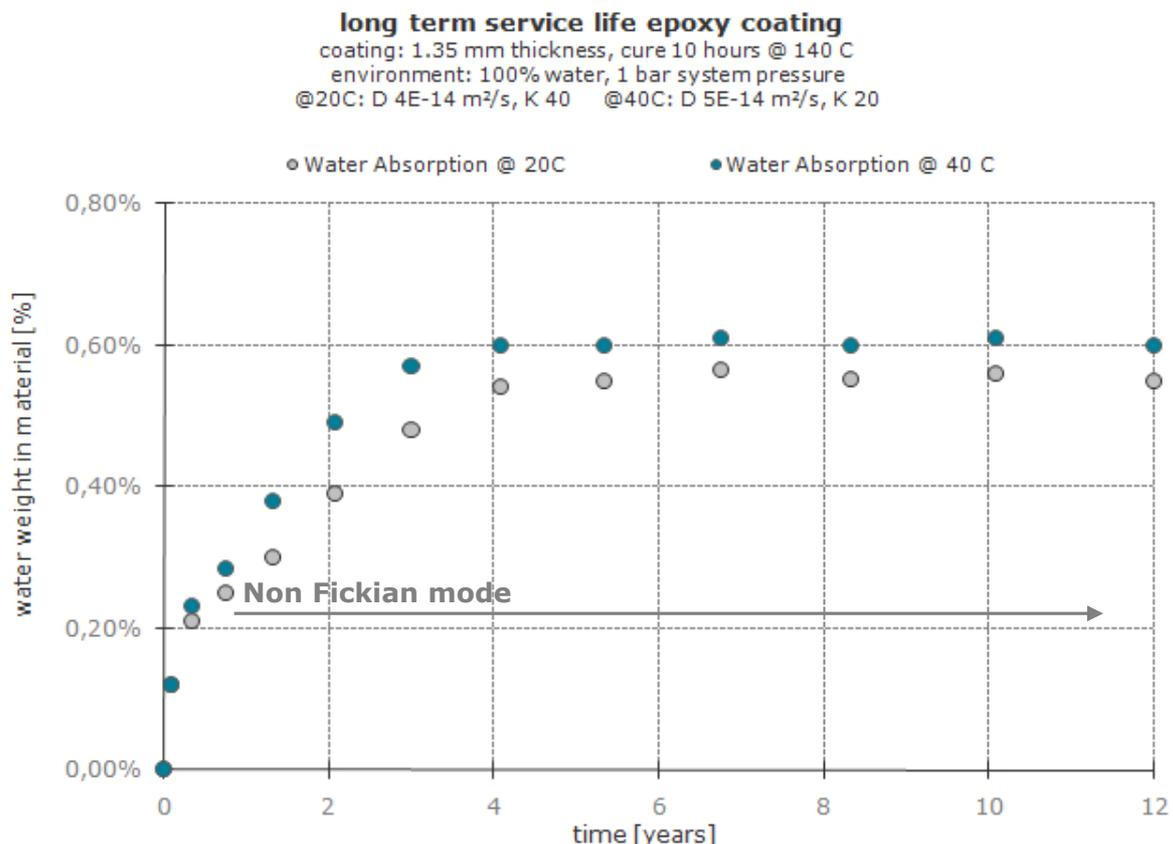


Figure 1: For longer times the Fickian pseudo equilibrium - obtained approximately after 9 months - almost completely disappears. The non Fickian mode - explained more thoroughly below - becomes the prevailing mechanism. Note that D is diffusion coefficient and K is the dual mode equilibrium constant.

The observed anomaly is often related to the physical-chemical state of the resin-fibre interface. This interface is usually facilitated by an additional chemical: sizing. Insufficient adhesion (as a result of insufficient wetting) or chemical degradation of sizing, could lead to water accumulation at the interface and subsequent or simultaneous capillary water uptake. Moreover, if fibre with sizing would be properly shielded by surrounding resin, even osmotic pressure

could drive the formation of a blister, initiating additional dimensional change and causing pathways for additional capillary water uptake.

However, uptake anomalies are also observed for resins and thermoplastic materials *without* fibres. Moreover, the chemical resistance of sizings has been improved to a substantial extent. Hence, fibre wetting and hydrolysis resistance have been fairly optimized and therefore accumulation and degradation by water is not significant *if* fibre and sizings are properly shielded by an appropriate resin or thermoplastic polymer.

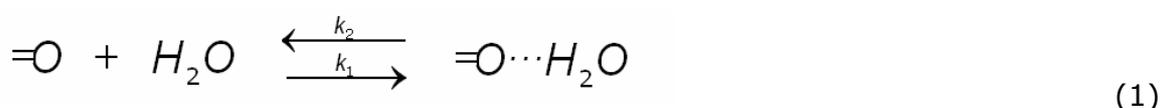
At this point, it is also noteworthy that Interlaminar Shear Strength (ILSS) experiments give some indication of the physical-chemical interaction of sized fibres and resin. However retention of ILSS values in hygrothermal conditions is a relative complex combination of material properties. If, for example the resin matrix - under the load of water - swells to a small extent, the available elastic energy decreases, hence the ILSS decreases. The same holds if the resin matrix is hydrolyzed (for example Polyvinyl Acetate).

So, since many parameters are involved, obviously ILSS results should be handled with caution when used for demonstrating sizings interfacial strength and corrosion resistance in different resin or thermoplastic materials².

Back to water diffusion. What else can cause the anomalous smooth uptake of water for relative long times? Computer simulations - in which water molecules simultaneously to diffusion, are adsorbed on specific sites in the matrix - show very good agreement with uptake data. The intrinsic assumption is that we have a mobile and immobile amount of water, which will be in equilibrium with each other.

In Derakane vinyl ester resins, the double bonded Oxygen group is an appropriate site for local water adsorption. To model this kinetically, it is assumed that at least one water molecule is adsorbed on the specific site and - after some time - is desorbed. The localized sorption in the model thus means one water molecule per site. The total amount of water that is adsorbed and desorbed then depends on the "reaction" rate and availability of sites. It will be shown that a more complex model, in which 2 or 3 molecules are adsorbed on specific locations, is not necessary for the material evaluated. However, for more hydrophilic polymer with a significant free volume, such a model may be useful.

Symbolically the local adsorption is expressed as follows:



² Similar problems occur with related tests, such as peel tests.

3. Influence of Glass Fibre Reinforcement

The presence of glass fibres in the matrix may have a noticeable effect on the diffusion rate. If the fibre reinforcement has a sharp boundary with the resin, and the fibre represent a significant volume (> 10 volume %), such as for example woven roving glass fibres, the water diffusion rate and solubility are discontinuous. Locally in the roving, the diffusion rate and solubility may both decrease with a factor 10 or even more. This is due to tightness of glass fibres and the fact that fibres with appropriate sizings are capable of resisting swelling pressure generated by the permeant³. Hence, local mass flux may decrease with a factor 100. This phenomenon will cause bends in the uptake profile of - for example - a plane sheet.

4. Analysis

Uptake experiments were carried out in compliance with ASTM D570. As stated it is assumed that diffusion is accompanied with reversible bimolecular kinetics between the polar site of the molecular chain and the water. The absorption process is expressed by the following pair of equations [ref. 7]:⁴:

$$\frac{\partial \varepsilon_t'}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial \varepsilon_w'}{\partial x} \right) - \frac{1}{\beta} \frac{\partial \varepsilon_s'}{\partial t} \quad (2)$$

$$\frac{\partial \varepsilon_s'}{\partial t} = k_1 \cdot \varepsilon_w' \cdot (\varepsilon_{s0}' - \varepsilon_s') - k_2 \cdot \varepsilon_s' \quad (3)$$

with:

- ε_t' total volume fraction of water in the polymer or composite;
- ε_w' volume fraction of *unbound* water;
- ε_s' volume fraction of *adsorbed* water;
- ε_{s0}' saturated volume fraction of *adsorbed* water;

³ The dissimilarities of diffusion in plane sheets samples and real FRP equipment (such as pipeline samples) can - to an important extent - be attributed to the degree and orientation of glass fibres.

⁴ For simplicity we use concentration gradients as a driving force for diffusion. For hydrophilic polymers this is usually not correct and then we must use chemical potential gradients (Maxwell - Stefan diffusion equation). Then, the diffusion coefficient is usually not constant, and significantly dependent on the water concentration. Modification of Fick's laws to Maxwell - Stefan diffusivities in a binary system is not difficult and rather straightforward. An example is the uptake of water in Polyamide (PA).

- β porosity of the matrix material (here assumed to be unity for simplicity);
- k_1 rate constant for production of s , units: $[s^{-1}] \times [\text{vol. fraction}^{-1}]$;
- k_2 rate constant for removal of s , units: $[s^{-1}]$.

The phenomenon that adsorption has a noticeable effect on the diffusion process is due to the relative slow rate⁵ of the hydrogen bond driven adsorption component of the solubility. One should realize that the concept of unbound (mobile) and adsorbed water (immobile) is relative and only gets its meaning from temporary trapping by relative strong hydrogen bonding⁶. Moreover, the above set of equations is only valid if the diffusion coefficient is not a - or very little - function of concentration. This is expected to range approximately from Liquid Crystal Polymers (LCP, 0.1 wt% uptake) to hydrophobic Polyimides, and includes polymers like Polyether-Etherketone (PEEK), Polyphenylene Sulphide (PPS) and Polyoxy-Methylene (Acetal Resin).

Below we see the fit with the uptake curve of water in Derakane 411 Vinyl Ester Epoxy resin.

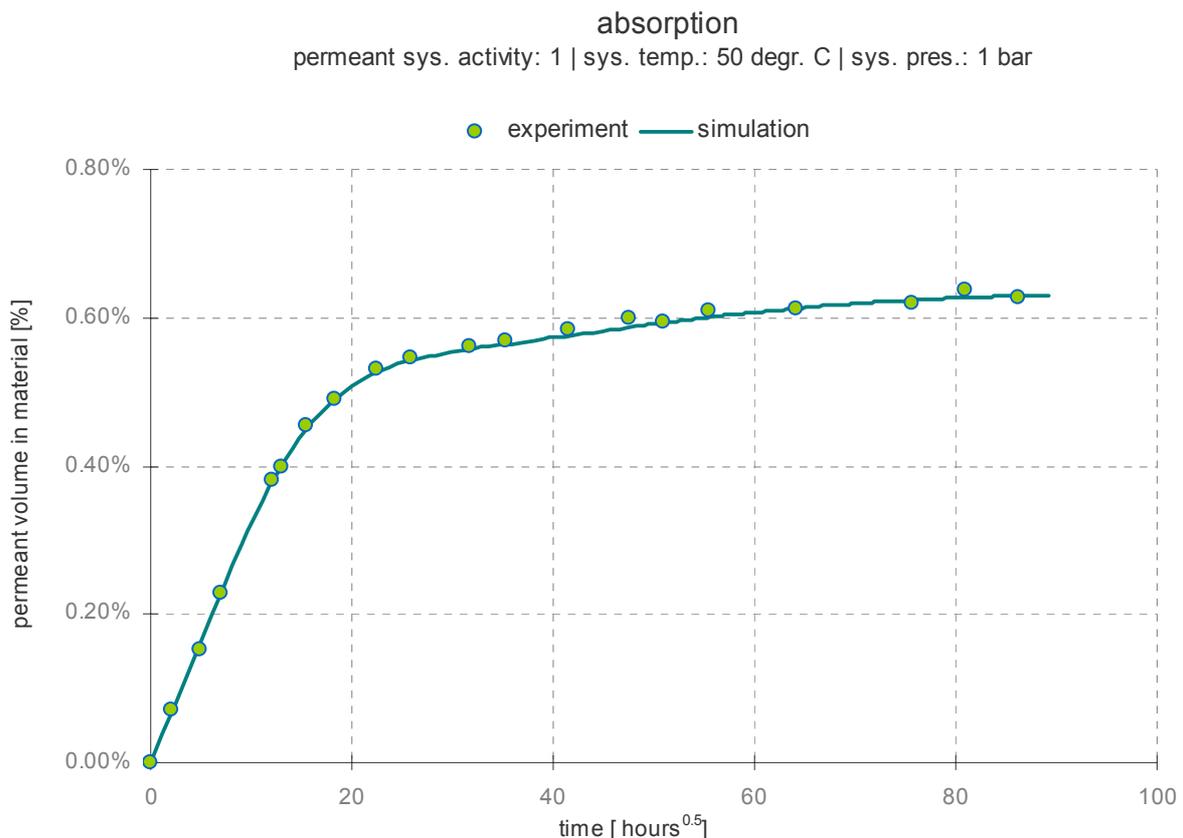


Figure 2: Water absorption in plane sheet (thickness 2.6 mm).

⁵ Read: the adsorption kinetics is of comparable order or slower than the zero concentration diffusion rate.

⁶ In older versions of the dual site theory it is sometimes stated that the immobile phase is due to the presence of micro voids, which is of course utterly nonsense.

The constants of interest are obtained used a IDC-SAC simulation program. They are listed below:

$$\begin{aligned} D &: && 9 \cdot 10^{-13} \text{ m}^2 \text{ s}^{-1}; \\ k_1 &: && 5 \cdot 10^{-5} \text{ s}^{-1} \text{ vol. fraction}^{-1}; \\ k_2 &: && 3 \cdot 10^{-8} \text{ s}^{-1}. \end{aligned}$$

From the reference simulation using Fick's law it becomes clear that the best possible fit for the diffusion coefficient would have been slightly smaller than $9 \cdot 10^{-13} \text{ m}^2 \text{ s}^{-1}$. Thus, the immobilized phase decreases the effective mass transport into the material to some extent. It is generally known that immobilization caused by different phenomena, including localized adsorption, local accumulation at filler particles and also swelling, causes a substantial decrease in overall mass transport. It is obvious that a correct interpretation of the phenomenon is essential for the determination of the diffusion coefficient. Specifically for extrapolation of diffusivities to low chemical concentrations or chemical activities.

It is interesting to assess whether local adsorption of water also takes place in reinforced resin composites. Hence, experiments with glass fibre woven roving plane sheets with an approximate similar thickness were carried out. The sheets were symmetrically laminated with two woven roving mats. The woven roving mats were well protected from the water by a sufficient boundary layer of Derakane resin. The woven roving mats contain appropriate sizings and binders. TGA analysis revealed that the total fibre content was 23 volume percent. The direction of the water diffusion will mainly be perpendicular to the direction of the fibres. Below the uptake curve including the fits of interest are shown.

Since the composite includes reinforcements with a sharp boundary with the surrounding cast resin, multilayer diffusion theory must be used in addition to the diffusion-local adsorption model. The diffusion coefficient in the woven roving section will show a major step downward. Moreover, the solubility is much lower in the woven roving section. It is also expected that the local degree of adsorption in the woven roving areas, is decreased since the fibre structure and the shear with the fibres, opposes the small swelling pressure that accompanies local sorption.

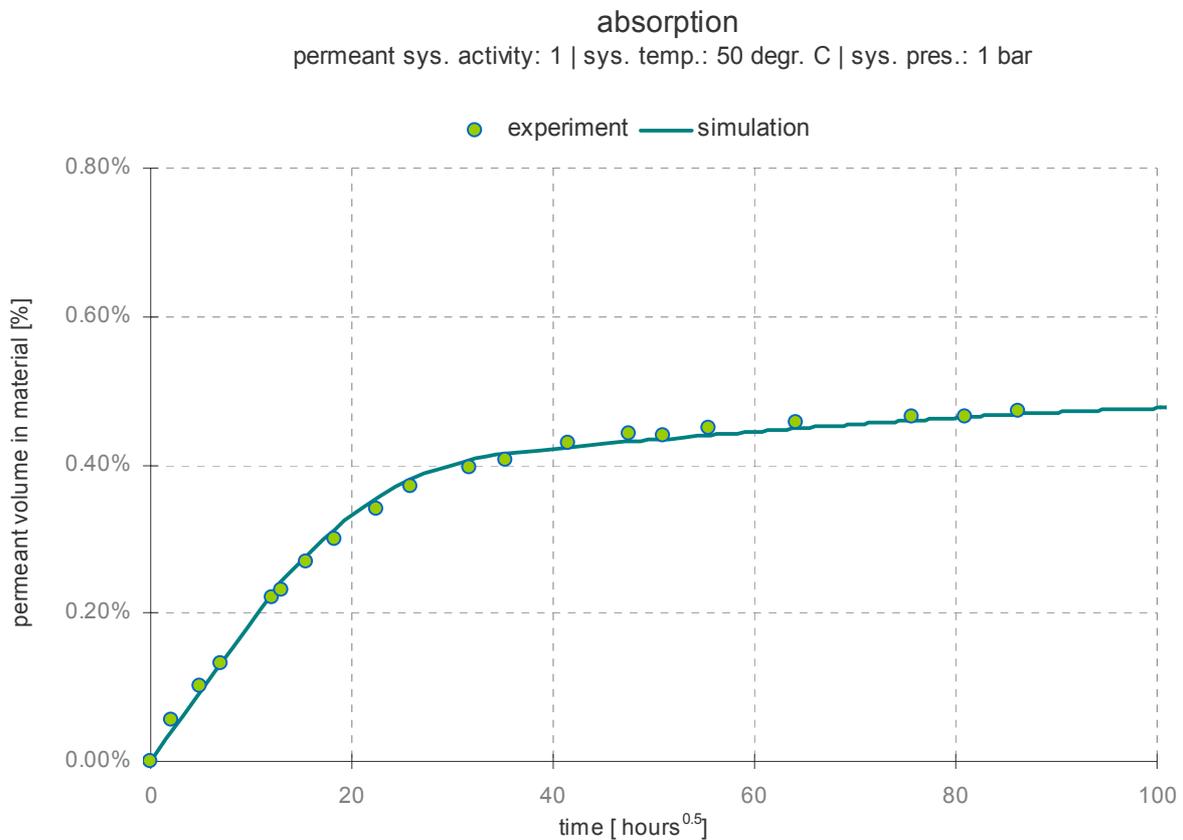


Figure 3: Water absorption in resin with woven roving glass fibres (thickness 2.6 mm).

Key figures for the composite:

$$D : 9 \cdot 10^{-13} \text{ m}^2 \text{ s}^{-1} ;$$

$$D_{\text{woven.roving}} : 9 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1} ;$$

$$k_1 : 3 \cdot 10^{-5} \text{ s}^{-1} \text{ vol. fraction}^{-1} ;$$

$$k_2 : 1 \cdot 10^{-8} \text{ s}^{-1} .$$

From the fits it is obvious that indeed the adsorption rate kinetics decreases due to the presence of glass fibres. The swelling is - for some part - effectively restrained by the reinforcing layers.

5. Sorption Isotherm

In the experiment, samples were exposed to 100% water. In order to predict the total water absorption of the polymer or composite when exposed to lower water activity, a predictive model for the sorption is required. A general model based on the previous considerations is worked out below.

Because a hydrophobic polymer is considered, the unbound water uptake follows Henry's law:

$$\varepsilon'_w \cdot K = \frac{p_w}{p_w^0} \tag{4}$$

with:

- K : Henry constant (based on volume fractions) [-];
- p_w : partial pressure of water in surroundings [Pascal];
- p_w^0 : vapour pressure of water in surroundings [Pascal].

Compliant with the above equations for the fraction of adsorbed water, the adsorbed volume is defined as follows [ref. 7]:

$$\varepsilon'_s = \varepsilon'_{s0} \cdot \frac{\frac{k_1 \cdot \varepsilon'_w}{k_2}}{1 + \frac{k_1 \cdot \varepsilon'_w}{k_2}} \tag{5}$$

The total water solubility then yields:

$$\varepsilon'_t = \varepsilon'_w + \varepsilon'_s \tag{6}$$

For reinforced Derakane 411, the predicted isotherm is depicted below.

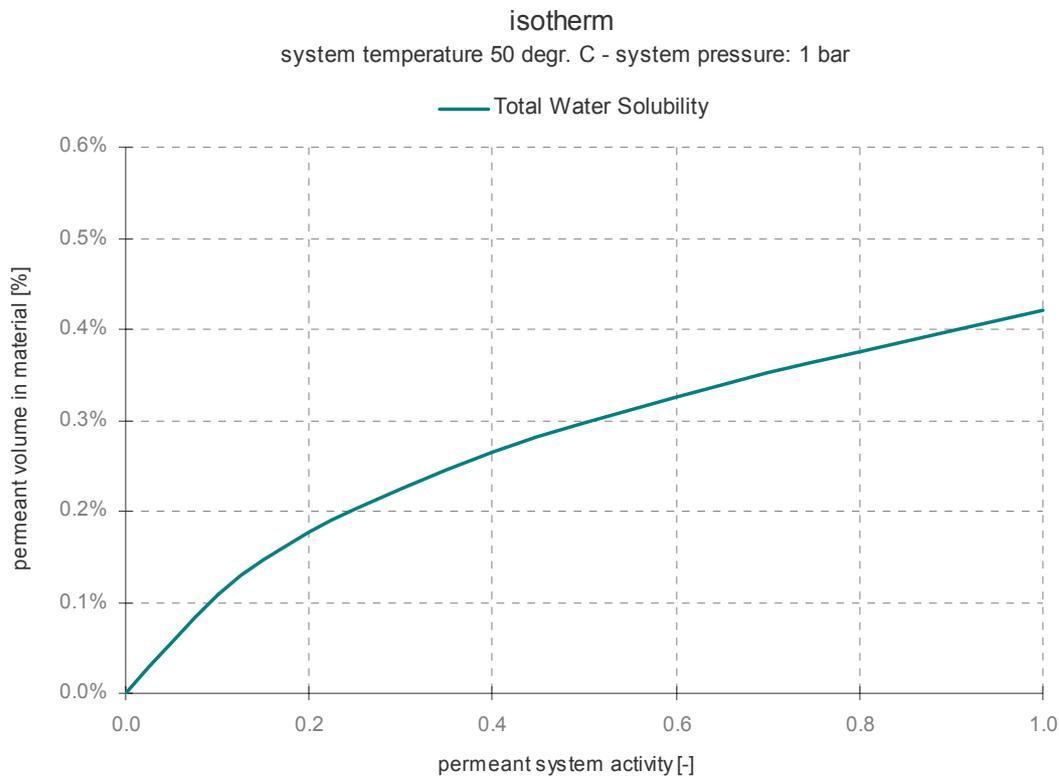


Figure 4: Water isotherm in resin with woven roving glass fibres.

This basic isotherm shows satisfying agreement with literature data on Vinyl Ester resin, Polyester resins, Epoxy and several Polyimides. Slightly modified versions of the above isotherm have proved to be useful for several Polyurethanes and Polymethyl-methacrylate (PMMA).

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