

# Mechanics of Moisture for Polymers: Fundamental Concepts and Model Study

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## Abstract

Reliability issues associated with moisture have become increasingly important as advanced electronic devices demand for new materials, more function integration and further miniaturization. However, the fundamentals of the mechanics of moisture transport and the subsequent failures in polymers have not been investigated extensively. This paper is devoted to some fundamental concepts of moisture absorption, diffusion, and swelling. The mathematical descriptions of moisture phase transition with temperature, and the governing equations for a deforming polymer with moisture effect are presented. The non-Fickian sorption behavior is discussed and a widely-used two-stage theory is introduced. It has been found that water sorption (immersion into liquid water bath) has very different transport mechanism at surface compared to the moisture sorption (moisture in air). The state of moisture within polymers and its interactions with polymer matrix, fillers and additives are discussed. It has been suggested that, in most of cases, the majority of absorbed water molecules neither show significant interaction with other water molecules nor with their environment. Those 'unbound' moisture stays in free-volumes and does not contribute to hygroscopic swelling. Swelling is caused by water molecules bound to the polymer matrix. Although the free volume fraction is usually in the range of 1% to 5%, the pore size is always below nanometers and not detectable by the conventional measurement techniques such as SEM and mercury intrusion. An approximate estimate of free volume fraction using weight gain data is introduced. A vapor pressure model, which allows the whole-field vapor pressure calculations, is presented. Finally the

framework of the governing equations for a deforming polymer with consideration of moisture is presented.

## 2. Fickian and Non-Fickian Kinetics

Fickian transport in polymers is described by

$$\frac{\partial C}{\partial t} = D(\nabla^2 C) \quad (1)$$

This equation is known as the general diffusion law or Fick's second law of diffusion (Fick's law, for short).  $C$  ( $\text{kg}/\text{m}^3$ ) is the penetrant concentration,  $t$  (s) the time, and  $D$  ( $\text{m}^2/\text{s}$ ) is the diffusion coefficient or diffusivity of the moisture in the polymer.  $D$  is the pivotal parameter determining the rate of transport. It may depend strongly on concentration [14, 15].

The temperature dependence of the diffusion constant can be described by the Arrhenius equation as follows

$$D = D_o \exp -\frac{E_d}{kT} \quad (2)$$

where  $D_o$  is a pre-factor,  $E_d$  is the activation energy,  $k = 1.38 \times 10^{-23}$  J/K is the Boltzmann's constant,  $T$  the absolute temperature. In some published papers, the minus sign inside the exponential function was omitted and a negative activation energy was used. It should be noted that the pre-factor and the activation energy constants are different across the glass transition temperature.

Fig.1 is a typical plot for the so-called Fickian absorption kinetics. Characteristic features of such curve are: 1. an initially linear plot of  $M$  (weight gain) as a function of  $t^{1/2}$  (in one-dimensional diffusion), where  $M$  is the mass of moisture; 2. With increasing  $t$ , the absorption curve smoothly levels off to a saturation level  $M_\infty$ . The saturated moisture concentration  $C_{\text{sat}}$  is often used to describe the capacity of moisture absorption at given humidity and temperature conditions as follows

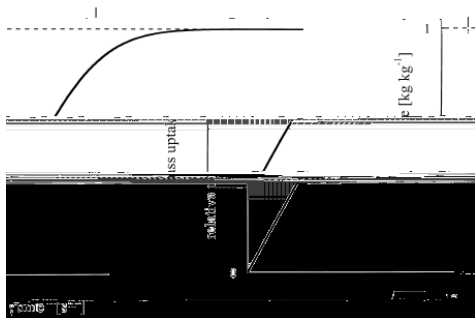


Fig.1. Schematic of a typical Fickian absorption curve. The relative weight gain  $M(t)/M_\infty$  is plotted as a function of the square root of time

phenomenologically independent contributions: a diffusion part  $M_F(t)$  that is governed by Fick's law and a structural part  $M_R(t)$ , resulting from polymer relaxations. The total weight gain at time  $t$  may be expressed as the linear superposition of these contributions, as follows

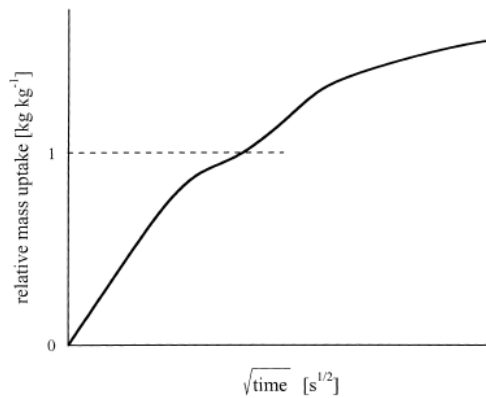


Fig.3. Schematic picture of a typical two-stage absorption curve. The relative weight gain  $M(t)/M_\infty$  is plotted as a function of the square root of time.  $M(t)/M_\infty=1$  for the (fictitious) Fickian saturation level.

$$M(t) = M_F(t) + M_R(t) \quad (5)$$

$M_F(t)$  is given by solutions of the diffusion Eq. (1). It is assumed that more than one independent relaxation process is possible, so  $M_R(t)$  is given by

$$M_\infty(t) = \sum_i M_{\infty,i} (1 - e^{-k_i t}) \quad (6)$$

where  $M_{\infty,i}$  represents the equilibrium absorption due to the  $i$ th relaxation process, and  $k_i$  is the first-order relaxation constant of the  $i$ th relaxation process. Originally, the model has been developed for diffusion in spherical particles, but it has also been applied to diffusion in polymer films, e.g. [18].

Bismaleimide-triazine (BT) resin/glass fiber laminates are commonly used as a substrate core material in microelectronic packaging. Their moisture absorption and diffusion behavior have a significant impact on package reliability. Fig. 4 plots the moisture weight gain for a thickness of 0.6mm at 30°C/60%RH. It clearly shows the two-stage moisture absorption. The material behaves

vapor uptake. More studies are needed to understand the surface diffusion mechanism. Throughout this paper, unless it is stated, the moisture absorption process is generally assumed.

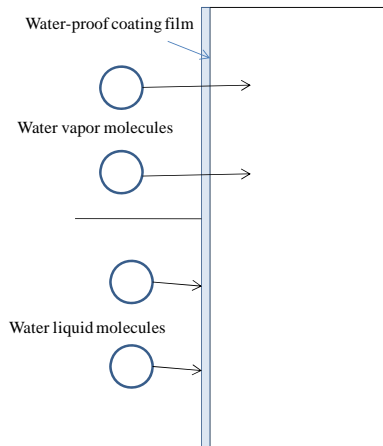


Fig.5. Schematic pict

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ranges from one to nearly four times of the strain induced by the CTE mismatch over a  $\Delta T$  of  $45^\circ\text{C}$  for  $T > T_g$  or over a  $\Delta T = 100^\circ\text{C}$  for  $T < T_g$ . For some underfill materials, the hygroscopic swelling induced strain is comparable to the thermal strain caused by thermal expansion over a temperature range of  $100^\circ\text{C}$  orders of magnitude! The typical values of the hygroscopic swelling range from 0.1% to 0.5%. The volume change of

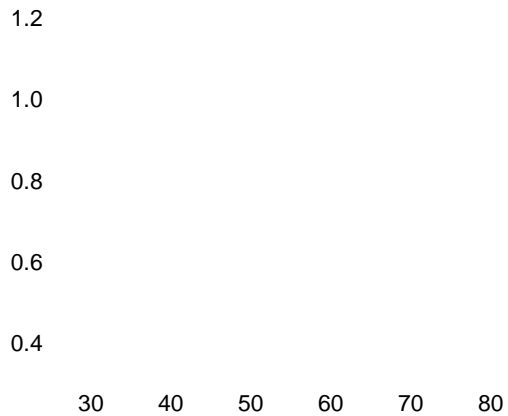
bound estimates of the coefficient of hygroscopic swelling of materials. An integrated finite element analysis methodology, which couples the transient moisture diffusion and the hygroscopic swelling with the temperature change and all nonlinear viscoplastic analysis was reported in ref. [6].

#### **7. Saturated Moisture Concentration and Solubility**

Saturated moisture concentration  $C_{\text{sat}}$ , as defined in the equation (3), is a measure of the moisture absorption capacity under given humidity and temperature conditions. It should be noted that the saturated moisture



Fig. 13 plots the saturated moisture concentration for a low-Tg die-attach film as a function of temperature at 60%RH level. It shows a strong dependency with temperature. This film has a Tg around 35°C. It reveals that in the temperature region above the Tg, the saturated moisture concentration depends strongly on the temperature. As a matter of fact, since the saturated moisture concentration has strong dependency on the free volume fraction based on equation (11), it is suggested that the saturated moisture concentration will increase significantly above the glass transition temperature, as illustrated in Fig. 6.



Therefore the vapor pressure remains as the saturated vapor pressure as follows

$$p(T) = p_g(T), \text{ when } C(T) / f = \rho_g(T)$$

$$\frac{w}{D \cdot C_{sat}} \frac{\partial C_{sat}}{\partial t} \neq 0 \quad (36)$$

when the saturated moisture concentration  $C_{sat}$  becomes dependent on the time  $t$ . Equations (33) and (35) indicate the simple thermal-moisture analogy does not apply when

$$\begin{aligned}
\langle \sigma \rangle &= \frac{1}{V} \int_V \sigma dV = \frac{1}{V} \left[ \int_{V_s} \sigma dV + \int_{V_f} \sigma dV \right] \\
&= \frac{V_s}{V} \langle \sigma_s \rangle^s + \frac{V_f}{V} \left[ \frac{1}{V_f} \langle \sigma_f \rangle^f \right]
\end{aligned} \tag{41}$$

where

$$\langle \sigma_\pi \rangle^\pi = \frac{1}{V_\pi} \int_{V_\pi} \sigma_\pi dV \tag{42}$$

which, presents the average over one-phase. Then we have

$$\langle \sigma \rangle = (1-f) \langle \sigma_s \rangle^s - f \mathbf{m} \langle p \rangle = \sigma' - \mathbf{m} \langle p \rangle \tag{43}$$

This is how we obtained equation (39). For clarity, we do not use the symbol  $\langle \sigma \rangle$ , but one should always keep in mind that the quantities are in average at macroscopic level.

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smaller than the volume occupied by the absorbed moisture, which indicates that the moisture in free volumes does not cause the material's swelling.

The saturated moisture concentration is strongly related to the free volume fraction and it has been found that the saturated moisture concentration has weak temperature dependency over a temperature range below the glass transition temperature. However, the saturated moisture content may increase significantly with temperature when the temperature is above  $T_g$ .

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