Moisture diffusion modeling – A critical review

E.H. Wong [a,*], S.B. Park [b]

[a] Nanyang Technological University, Energy Research Institute, Singapore
[b] State University of New York at Binghamton, Department of Mechanical Engineering, United States

ARTICLE INFO

ABSTRACT

Techniques for enforcing the continuity of solute field in heterogeneous solvent under the conditions of steady temperature-humidity, steady temperature but dynamic humidity, and dynamic temperature are reviewed. The continuity of the wetness technique is justified on the principle of equality of chemical potential. The partial pressure technique is one of the many possible forms of pseudo techniques that can be derived from the wetness technique. The direct concentration technique is fundamentally flaw. The peridynamic technique in its original form is restricted to homogeneous solvent. The saturated concentration of solute in solvents decreases with increasing temperature; the rate of change with temperature differs between solvents and this leads to discontinuity of wetness along the interface of solvents. Continuity of wetness at the interface may be enforced using the intervention technique, the internal source technique, or the explicit finite difference scheme. These three techniques have been mutually validated in a reported study.

© 2016 Published by Elsevier Ltd.

Contents

* Corresponding author.
  E-mail address: ehwong@ntu.edu.sg (E.H. Wong).

1. Introduction

1.1. Moisture-induced damages

The bulk of the microelectronic and optoelectronic components today are made of polymeric materials; these include die attach materials; molding compound; underfill materials; optical adhesives and waveguide; conductive/non-conductive adhesives; the laminated substrates, the redistribution and underfill layers in 2.5D and 3D packaging; and not least, the porous low-k dielectric layers between the layers of integrated circuits in the wafer. Being polymeric, these materials are capable of absorbing moisture, retaining moisture, and transporting moisture.

The physical and chemical interactions of moisture with polymers lead to physical, mechanical and, in many instances, chemical changes of the polymers. The extent of these changes vary among polymers. The most pronounce effects of the absorbed moisture is in "plasticizing" the host polymer [1]. This reduces the intermolecular forces of the host polymer leading to reduction of glass-to-rubber transient temperature and increased intermolecular distances [2]. These changes are accompanied by reduction of strength [3], reduction of elastic modulus [4], increase in loss modulus, and not least, increase in volume [5–8]. Mechanically, the combined effects of reduced glass-transition temperature and reduced elastic modulus leads to reduction in the secant modulus of the host polymers and this leads to redistribution of stresses within the host polymers. Differential volumetric expansion leads to mismatched hygroscopic swelling and stresses [7]. Volumetric expansion of optical polymers leads to increase in optical refractive index [9] that would affect the optical impedance of optical interconnection. With a relatively high dielectric constant of 80, the presence of water in porous low-k dielectric materials could very severely compromise its performance [10,11]. Water would also find residence in physical defects such as a crack or a delaminated site; with rapid elevation of temperature, such as experienced by microelectronic assembly during solder reflow, water in these defects turns rapidly into high-pressure vapour [12–14] that could lead to violent cracking of the containing structure. This has been referred to as "popcorn cracking".

The absorption of moisture in fibre-reinforced polymeric (FRP) composites polymers is also a major concern in the communities of aerospace and wind energy because of the accompanied reduction in the strength and the stiffness of the structures [15,16]. Besides polymeric materials, building materials such as concretes and woods are also highly permeable to moisture rendering them susceptible to spalling [17] and swelling [18], respectively.

Other examples of diffusion in engineering applications include the diffusion of dopants in semiconductors; the mutual diffusion of atoms between metallic films or between bulk metals leading to intermetallic compound/s; the diffusion of atoms in solid solution of metallic elements leading to solid-solution hardening; and the diffusion of hydrogen in steels leading to embrittlement; etc. These diffusions are governed by the same physics and are modelled using the same equations. In light of the general applicability of the reviewed techniques to the diverse scenarios of diffusion, the generic descriptions of "solute" and "solvent" are adopted in this article.

1.2. Introduction to diffusion equations

Like the flow of water under gravitational potential, solute diffuses from high chemical potential, μ (J mol^{-1}), to low chemical potential [19,20]. And like gravitational potential, chemical potential is independent of solvents - it is continuous across the interface of solvents. The fundamental equation of diffusion basing on chemical potential is given by

$$\mathbf{J_m} = -\frac{DC}{RT}\nabla\mu, \tag{1}$$

where $\mathbf{J_m}$ (kg m^{-2} s^{-1}) is the flux of solute, D (m^2 s^{-1}) is the diffusivity of solute in solvent, R is the universal gas constant, and C (kg m^{-3}) is the concentration of solute, which is a function of chemical potential [21]:

$$\mu = \mu^o(C^o) + RT\ln(\gamma C/C^o), \tag{2}$$

wherein $\mu^o(C^o)$ is the chemical potential of the solute at the reference concentration C^o and γ is the activity coefficient. Despite being a fundamental equation, Eq. (1) is severely nonlinear and is not conducive for engineering applications.

In engineering applications, the diffusion of solute in solvent has frequently been modelled using the largely linear Fick's laws [22]:

$$\begin{aligned} \mathbf{J_m} &= -D\nabla C \\ \partial_t C + \nabla.\mathbf{J_m} &= \Theta_m \end{aligned}, \tag{3}$$

where $\partial_t C$ is the partial derivative of C with time. The second equation above is a continuity equation, where Θ_m (kg m^{-3} s^{-1}) is the rate of generation of solute per unit volume of the solvent. Fick drew his intuition from the Fourier's law [23] for heat diffusion:

$$\begin{aligned} \mathbf{J_q} &= -\kappa_T\nabla T \\ \partial_t(c_T T) + \nabla.\mathbf{J_q} &= \Theta_q \end{aligned}, \tag{4}$$

Where $\mathbf{J_q}$ (W m^{-2}) is the heat flux, κ_T (W m^{-1} K^{-1}) is the heat conductivity of the conductor, $c_T = \rho c_v$ (J m^{-3} K^{-1}) is the volumetric specific heat of the conductor, ρ (kg m^{-3}) is the density of the conductor, c_v (J kg^{-1} K^{-1}) is the specific heat of the conductor at constant volume, and Θ_q (W m^{-3}) is the rate of heat generation per unit volume of the conductor. However, unlike temperature, which is independent of conductors, the concentration of solute is dependent on solvents and may become discontinuous across the interface of solvents. Thus, Fick's law is valid only for diffusion in a homogeneous solvent (a solvent that is homogeneous in chemical composition, physical phases, and metallurgical construction) that is having uniform temperature. In a heterogeneous solvent or in a homogeneous solvent having non-uniform temperature distribution, diffusion could proceed against the gradient of concentration.

If we substitute T in Eq. (4) with $c_T T/c_T$ and noting that $U = c_T T$ (J m^{-3}) is the volumetric internal energy of the conductor and assuming c_T to be spatially invariant, then we arrive at

$$\begin{aligned} \mathbf{J_q} &= -\alpha\nabla U \\ \partial_t U + \nabla.\mathbf{J_q} &= \Theta_q \end{aligned}, \tag{5}$$

where $\alpha = \kappa_T/c_T$ (m^2 s^{-1}) is the thermal diffusivity of the conductor. In the light that c_T is a property of conductors, $U = c_T T$ is discontinuous across the interface of two conductors that are at the same temperature. It is clear that Fick's law is indeed analogous to Eq. (5), not Fourier's law.

There have been a number of reported approaches for enforcing the continuity of solute at the interfaces of solvents while retaining the linearity of the flux-gradient equation. These approaches are reviewed in Section 2 for diffusion under steady temperature-humidity environment. The temporal variation of humidity can be treated as boundary condition and this is reviewed in Section 3. The temporal variation of temperature presents a unique challenge to enforcing the continuity of solute at the interfaces; various techniques for addressing this challenge are reviewed in Section 4.

2. Diffusion of solute in heterogeneous solvent under steady temperature-humidity environmental condition

2.1. Partial pressure technique

The use of partial pressure as a field variable for modeling the diffusion of moisture in electronic packaging was first presented by

Galloway & Miles [24] using the expression:

$$p_\phi = C/S. \tag{6}$$

where p_ϕ (Pa) has the unit of pressure and Galloway & Miles referred to S (kg m^{-3} Pa^{-1}) as solubility. Eq. (6) takes after the form of Henry's law [25]:

$$p_s = C_{sat}/H, \tag{7}$$

where p_s is the partial pressure of a solute in vapour form, C_{sat} is the saturated concentration of the solute in a liquid or a solid solvent that is interfacing with the solute vapour, and H is known as the Henry's constant of solubility [26].

Galloway & Miles [24] have reported linearity of $C_{sat}(p_s)$ for molding compound between 30%RH and 85%RH and Jang et al. [27] have reported linearity of $C_{sat}(p_s)$ for electronic packaging polymers between 40%RH and 95%RH. However, a close scrutiny reveals some degrees of non-linearity. The $C_{sat}(p_s)$ relations of solute-solvent at constant temperature is generally referred to as sorption isotherms. There are six classifications of sorption isotherm [28], none is reported to be linear. Eq. (8) presents a rather simple description of sorption isotherm for water in polymers [29]:

$$C_{sat} = a_o + a_1 \log\left(1 - p_s/p_g\right), \tag{8}$$

where p_g is the saturated vapour pressure water at the same temperature as p_s, and a_o and a_1 are fitting constants. The non-linear equation may be expressed as $C_{sat} = H^*(p_s)p_s$, where $H^*(p_s)$ is the gradient of the secant line joining the origin ($p_s = 0$, $C_{sat} = 0$) and the point (p_s, C_{sat}). Rewriting Eq. (6) for non-linear $C(p_\phi)$ gives

$$p_\phi = C/S^*\left(p_\phi\right), \tag{9}$$

where $S^*(p_\phi)$ is the secant line corresponding to $H^*(p_s)$. Substituting Eq. (9) into Eq. (3) yields a rather complex relationship between flux and the pseudo partial pressure:

$$\mathbf{J_m} = -D\nabla\left(S^*\left(p_\phi\right)p_\phi\right). \tag{10}$$

The justification of p_ϕ has been argued on the basics of Henry's law assuming a solid solvent is interspersed with interconnected nanopores that are filled with air-vapour mixture [30]. However, the assumed construction of solid solvents is not supported by evidence. It shall be shown in Section 2.2 that the justification for the partial pressure technique is indeed not Henry's law.

2.2. Wetness technique

Wong et al. [30] postulated that the ratio,

$$w = \frac{C}{C_{sat}}, \tag{11}$$

referred to as "wetness" or "fractional saturation", is continuous across the interface of solvents. Wong [31] subsequently provided the proof for the continuity of wetness, which is summarised below: referring to Eq. (2) and applying the equality of chemical potential at the interface of two solvents, A & B:

$$\mu_A^o + RT \ln\left(\gamma_A C_A/C_A^o\right) = \mu_B^o + RT \ln\left(\gamma_B C_B/C_B^o\right) \tag{12}$$

gives

$$\frac{C_A}{C_B} = \frac{\gamma_B C_A^o}{\gamma_A C_B^o} \exp\left(\frac{\mu_B^o - \mu_A^o}{RT}\right) = K_d. \tag{13}$$

Eq. (13) is indeed Nernst's distribution law [32], where K_d is referred to as distribution coefficient. Substituting C_i with $w_i C_{sat,i}$, then

$$\frac{C_A}{C_B} = \frac{w_A C_{sat,A}}{w_B C_{sat,B}} = K_d. \tag{14}$$

The fact that K_d is independent of concentration implies $w_A = w_B$. In other words, w is continuous at the interface.

Substituting Eq. (11) into Eq. (3) but noting that $\mathbf{J_m}$ is proportional to ∇w, not ∇C or $\nabla(C_{sat}w)$, yields

$$\mathbf{J_m} = -DC_{sat}\nabla w$$
$$\partial_t(C_{sat}w) + \nabla.\mathbf{J_m} = \Theta_m. \tag{15}$$

Eq. (15) is the exact analogue of the heat diffusion equation, Eq. (4). Eq. (15) has an interesting physical interpretation: *The quest for every part of the solvents to reach full saturation, $w = 1$, provides the driving force for diffusion; the rate of diffusion is linearly proportional to the gradient of fractional saturation, ∇w* [31].

If we divide the numerator and the denominator in Eq. (14) by arbitrary constants, say S_A and S_B, respectively, such that $S_A/S_B = C_{sat,A}/C_{sat,B}$, then

$$\frac{C_A/S_A}{C_B/S_B} = \frac{w_A}{w_B} = 1, \tag{16}$$

which suggests that the ratio C/S is continuous at the interface of solvents. The constants S_A and S_B may have any arbitrary unit. If S_A and S_B are assigned the unit kg.m^{-3}.Pa^{-1} then C/S has the unit of pressure. The constants S_A and S_B may have arbitrary magnitudes so long as their ratio S_A/S_B equals to $C_{sat,A}/C_{sat,B}$. If the magnitude of S_A and S_B are chosen to be the Henry's constants, H_A and H_B (note: $H_A/H_B = C_{sat,A}/C_{sat,B}$), then $C/S = p_\phi$ becomes the "partial pressure technique" practiced by many researchers [13,24,33,34]. Indeed, the "partial pressure technique" is equivalent to multiplying w by the environmental vapour pressure of the solute, p_s, yielding $p_\phi = wp_s$, which is continuous simply because w is continuous [31]. The continuity of p_ϕ has nothing to do with Henry's law. As a further illustration, if S_A and S_B are assigned the unit kg·m^{-3}.J^{-1} and S_A and S_B are chosen to have the magnitudes such that $C_{sat,A}/S_A = C_{sat,B}/S_B = U_s$, where U_s is the volumetric internal energy of the environmental solute vapour, then the field variable becomes $C/S = U_\phi$. Since the constants S_A and S_B satisfy the condition $S_A/S_B = C_{sat,A}/C_{sat,B}$, then U_ϕ must be continuous at the interface. We now have a new technique: the "internal energy technique". Alternatively, we may arrive at this "internal energy technique" by simply multiplying w by U_s yielding $U_\phi = wU_s$, which is continuous simply because w is continuous. Thus, theoretically we may have unlimited number of techniques for enforcing continuity at the interface: the "partial pressure technique p_ϕ" when w is multiplied by the constant p_s; the "internal energy technique U_ϕ" when w is multiplied by the constant U_s; the "density technique ρ_ϕ" when w is multiplied by the density of the environmental solute vapour ρ_s; or even the "mass technique m_ϕ" when w is multiplied by an arbitrary constant that has the unit of mass, the "time technique t_ϕ" when w is multiplied by an arbitrary constant that has the unit of time; and so on. Clearly, these pseudo techniques are all redundant to the wetness technique.

2.3. Direct concentration approach

This is a hybrid of the Fick's law and the partial pressure technique. Xie et al. [34] applied Fick's law over a domain that is made up of multiple solvents while enforcing the continuity of pseudo partial pressure

at the interface of the solvents using the constraint equation

$$\frac{C_A}{S_A} = \frac{C_B}{S_B} = p_\phi, \tag{17}$$

At first glance, this approach appears to be exactly equivalent to the partial pressure technique. But the two techniques are indeed very different, which is best explained using an illustration. Fig. 1(a) shows a steady-state flow of solute through solvents A & B with the boundary condition, $C(x=0) = C_{AL}$ and $C(x=2L) = C_{BR}$, wherein it has been assumed that $C_{BR} > C_{AL}$. Fig. 1(b) shows the corresponding partial pressure of solute in the solvents wherein it has been assumed that S_B is significantly larger than S_A such that $p_L = C_{AL}/S_A > p_R = C_{BR}/S_B$. If the flux of solute is linearly proportional to the gradient of the partial pressure, then the equivalent circuit is as shown in Fig. 1(b), wherein $L/(D_i S_i)$ is the resistance due to solvent i. The prevailing flux through the solvents is given by

$$\mathbf{J_{mp}} = \frac{p_L - p_R}{L/(D_A S_A) + L/(D_B S_B)}. \tag{18}$$

The flux flows through solvent A and solvent B at a uniform magnitude from $x = 0$ towards $x = 2L$ as shown in Fig. 1(b). If on the other hand, the flux of solute is linearly proportional to the gradient of concentration as suggested by Fick's law and as assumed by Xie et al. [34], then the equivalent circuit is as shown in Fig. 1(a), wherein L/D_i is the resistance due to solvent i. The net flux of solute through the solvents is given by:

$$\mathbf{J_{mc}} = \frac{C_{AL} - C_{BR}}{L/D_A + L/D_B}. \tag{1}$$

The net flux flows through the solvents from $x = 2L$ towards $x = 0$, in opposite direction to $\mathbf{J_{mp}}$. It is clear that $\mathbf{J_{mc}} \neq \mathbf{J_{mp}}$. Denoting C_{AI} and C_{BI} as the concentrations of solute at the interface in solvent A and B, respectively. The constrain equation, Eq. (17), dictates that $C_{BI} = (S_B/S_A)C_{AI}$. This is illustrated in Fig. 1(a). The flux through solvents A and B are given by

$$\mathbf{J_{mc,A}} = \frac{C_{AL} - C_{AI}}{L/D_A}, \quad \mathbf{J_{mc,B}} = \frac{C_{BI} - C_{BR}}{L/D_B}. \tag{20}$$

The conditions $\mathbf{J_{mc,A}} = \mathbf{J_{mc}}$ and $\mathbf{J_{mc,A}} = \mathbf{J_{mc,B}}$ give, respectively,

$$C_{AI} = \frac{D_A C_{AL} + D_B C_{BR}}{D_A + D_B}$$
$$C_{AI} = \frac{(D_A C_{AL} + D_B C_{BR})S_A}{D_A S_A + D_B S_B}. \tag{21}$$

Unless $S_A = S_B$, the flux of solute is discontinuous at the interface. Fig. 1(a) illustrates both $\mathbf{J_{mc,A}}$ and $\mathbf{J_{mc,B}}$ are flowing away from the interface – a system that provides a net gain in solute. This is clearly against the law of physics. Liu et al. [35] investigated the finite element scheme and showed that the ratio of the flux was given by $J_{mc,A}/J_{mc,B} = S_B/S_A$. The direct concentration approach is fundamentally flaw.

2.4. Peridynamics technique

The theory of peridynamics was first proposed by Silling [36] to facilitate modeling of long-range forces and discontinuities such as cracks in a structure. The interactions of the field are described using integral equation over a non-local domain:

$$\rho \ddot{u} = \int_{\mathfrak{R}} f(\mathbf{x'}, \mathbf{x}, t) dV_{\mathbf{x'}} + b(\mathbf{x}, t), \tag{22}$$

where ρ is the density, u is the displacement, and b is the body force density field; f is a force density function that describes the interaction of the bond between material particle $\mathbf{x}$ and a nearby material particle $\mathbf{x'}$. Being non-local, the theory has the unique ability to model discontinuity in field. The peridynamics theory has been extended to modeling diffusion problem by substituting the equation of motion with evolution equations [37,38] and treating individual bond as conduction pathway. Octerkus et al. [39] has provided the formulation for diffusion of solute as:

$$\partial_t C(\mathbf{x}, t) = \int_{\mathfrak{R}} f_c(\mathbf{x'}, \mathbf{x}, t) dV_{\mathbf{x'}}, \tag{23}$$

where

$$f_c(\mathbf{x'}, \mathbf{x}, t) = \frac{6D}{\pi \delta^4} \frac{C(\mathbf{x'}, t) - C(\mathbf{x}, t)}{|\mathbf{x'} - \mathbf{x}|} \tag{24}$$

and δ is the radius that defines the domain of influence, $\mathfrak{R}$. However, Eqs. (23) and (24) are indeed the peridynamics representation of the Fick's law and are therefore valid for diffusion in a homogeneous solvent. One could quite easily extend the above equations to heterogeneous solvent using the idea of wetness to give

$$\partial_t (C_{sat} w(\mathbf{x}, t)) = \int_{\mathfrak{R}} f_c(\mathbf{x'}, \mathbf{x}, t) dV_{\mathbf{x'}}, \tag{25}$$
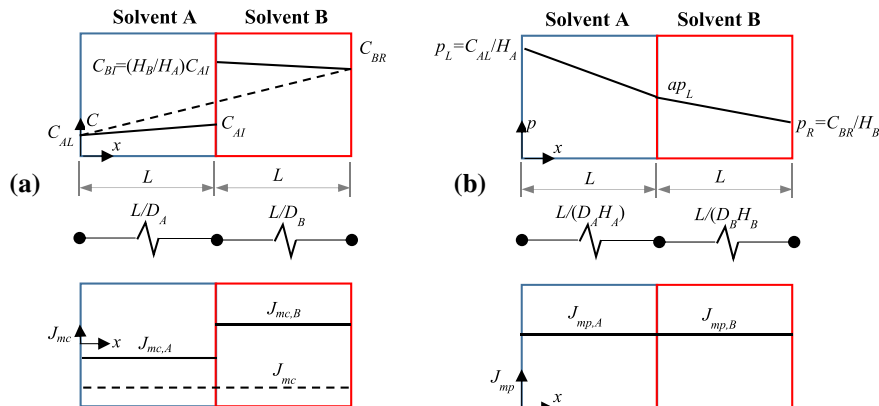

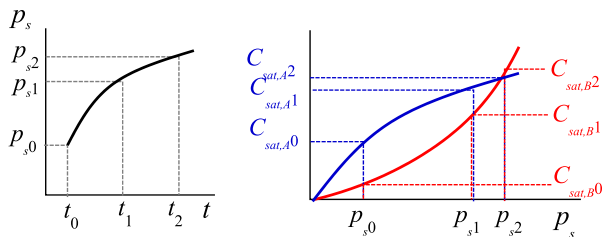Fig. 1. Illustrations of (a) direction concentration approach and (b) partial pressure approach.

where

$$f_c(\mathbf{x'},\mathbf{x},t) = \frac{6DC_{sat}}{\pi\delta^4}\frac{w(\mathbf{x'},t)-w(\mathbf{x},t)}{|\mathbf{x'}\text{-}\mathbf{x}|}. \tag{26}$$

3. Diffusion of solute in heterogeneous solvent under steady temperature but dynamic humidity

In general, the partial vapour pressure of solute is insignificantly small compared to the atmospheric pressure. Under this general circumstance, a change in humidity (hence, the environmental partial vapour pressure of the solute) is "felt" only by the outer surface of the solvents that is exposed to the gaseous solute. It is not "felt" by the interior bulk of the solvents and hence does not alter the bulk properties (D and C_{sat}) of the solvents. Therefore, diffusion under dynamic humidity is a dynamic boundary problem [40].

The problem can be modelled using Eq. (15). The dynamic humidity condition is modelled by dynamically varying the boundary magnitude of w while keeping the bulk properties (D and C_{sat}) of the solvents unchanged. This is illustrated in Fig. 2, which shows diffusion of solute through two adjoining solvents under a dynamic boundary condition, $p_s(t)$. The bulk properties (D and C_{sat}) of the solvents remain unaltered while the partial vapour pressure of the solute varies from $p_s(t_0)$ to $p_s(t_2)$. It is worth noting that one has the freedom to define the magnitude of the bulk property, C_{sat}, for the solvents. Two cases are illustrated in Fig. 2. In one case, the C_{sat} of the solvents was chosen to be equal that at time t_0; that is, $C_{sat,i} = C_{sat,io}$; the boundary conditions are then set to vary from $w = 1$ at $t = t_0$ to $w = C_{sat,i2}/C_{sat,i0}$ at $t = t_2$. In another case, the C_{sat} of the solvents was chosen to be equal that at time t_2, the boundary conditions are then set to vary from $w = C_{sat,i0}/C_{sat,i2}$ at $t = t_0$ to $w = 1$ at $t = t_2$. The above procedure is independent of the linearity of the sorption isotherm and, counter to the claimed by Wong [31], is independent of the proportionality of $C_{sat,A}(p_s)/C_{sat,B}(p_s)$.

Fig. 2. Illustration of boundary conditions under dynamic humidity condition.

4. Diffusion of solute in heterogeneous solvent under dynamic temperature

A change in temperature is "felt" by the interiors of solvents. It alters the bulk properties (D and C_{sat}) of the solvents. The dependence of C_{sat} on temperature presents a unique challenge.

4.1. Temperature dependence of C_{sat}

The rate of change of C_{sat} with respect to temperature may be expressed as

$$\frac{\partial C_{sat}}{\partial T} = \left(\frac{\partial \mu}{\partial T}\right)_n \left(\frac{\partial C_{sat}}{\partial \mu}\right)_T, \tag{27}$$

where n is the molar mass of the solute; the subscripts refer to the conditions that are kept unchanged. The rate of change of chemical potential μ with respect to temperature is given by Maxwell relations [21, 41] as:

$$\left(\frac{\partial \mu}{\partial T}\right)_n = -\bar{s}, \tag{28}$$

where $\bar{s}$ (J mol^{-1} K^{-1}) is the partial molar entropy of the solute in a solution. The rate of change of C_{sat} with respect to chemical potential can be evaluated from Eq. (2) as

$$\left(\frac{\partial C_{sat}}{\partial \mu}\right)_T = \frac{C_{sat}}{RT}. \tag{29}$$

Since $\bar{s}$ is positive, C_{sat} of solute in a solvent decrease with increasing temperature. Diffusion would occur in a homogeneous solvent that is having uniform concentration but having non-uniform distribution of temperature – solute will diffuse from region of high temperature (low C_{sat}, high w) to region of low temperature (high C_{sat}, low w).

4.2. Challenge in modeling

In case of temporally varying temperature, $C_{sat}(T)$ becomes a function of time. The diffusion equations for wetness becomes

$$\begin{aligned}\mathbf{J_m} &= -D(T)C_{sat}(T)\nabla w(C_{sat}(T)) \\ \partial_t[C_{sat}(T)w(C_{sat}(T))] &+ \nabla.\mathbf{J_m} = \Theta_m\end{aligned}. \tag{30}$$

Eq. (30) is unusual in that the field, $w = C/C_{sat}$, varies with time because of two dynamics: (i) diffusion of solute that changes C; and (ii) diffusion of heat that changes C_{sat}. The coupled heat-solute diffusion may proceed as follow: referring to Fig. 3, let δt be the time increment for the temperature in the solvent to increase from T to $T + \Delta T$ through heat diffusion; during this time increment, the solute in a solvent undergoes diffusion and its concentration increase from $C(t,T)$ to $C(t + \delta t, T + \Delta T)$. From the time, $t + \delta t$ to $t + \Delta t$, diffusion of solute occurs at constant temperature, $T + \Delta T$. The coupled heat-solute scheme is computational intensive. Fortunately, the diffusivity of heat in a solid solvent is many orders larger than the diffusivity of solute in the same solid solvent. This allows one to by-pass the modeling of thermal diffusion by assuming δt to be negligibly small such that $C(T + \Delta T) \approx C(T)$.

The dynamic variations of C_{sat} presents a unique challenge when using commercial finite element software, which typically does not have provision for automatic updating of the field $w(C_{sat}(T))$ corresponding to a change in $C_{sat}(T)$. Such updating may have to be performed explicitly by the user. However, updating of w-field may lead to discontinuity of w along the interface, as illustrated in Fig. 4, which shows diffusion of solute through two adjoining solvents that have experienced an instantaneous change in temperature. The capacity for
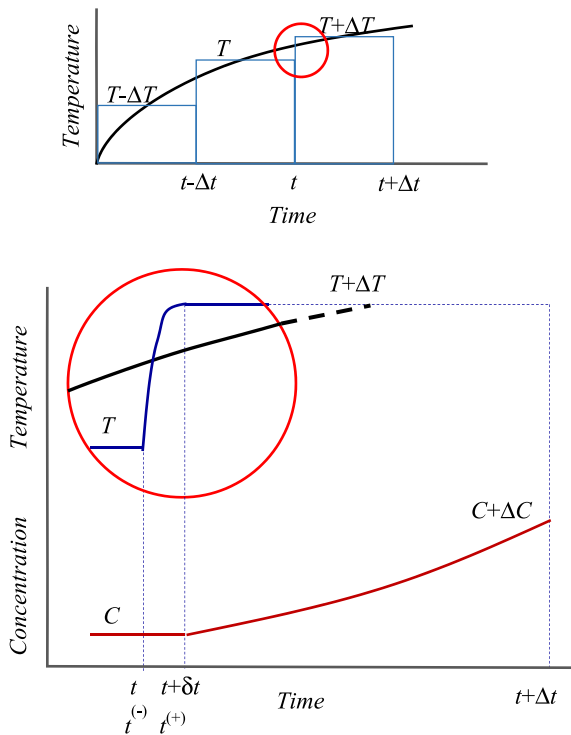
Fig. 3. Illustration of temperature increments as a function of time increments.

solute for the two solvents have become $aC_{sat,A}$ and $bC_{sat,B}$, where a and b are constants. Assuming $a \neq b$, w-discontinuity occurs along the interface.

The need to update $w(C_{sat}(T))$ explicitly and the presence of w-discontinuity were reported by Wong et al. [40,42] and has since attracted the interests of many [27,34,35,43–46]. The solution techniques are reviewed in the following section.

4.3. Special conditions

The modeling of solute diffusion under dynamic temperature condition can be greatly simplified under two special conditions.

4.3.1. C_{sat} independent of temperature

The temperature-dependence of the Henry's solubility constant has frequently been described in the form of van't Hoff equation, which shares a similar form as the Arrhenius equation. Wong & Rajoo [47] characterized the Henry's solubility constant, H, for electronic packaging polymers at 60%RH and at temperatures 30 °C and 85 °C and expressed

Fig. 4. Illustration of w-discontinuity at the interface of solvents due to temperature increment assuming $C(T + \Delta T) = C(T)$.

it in the form:

$$H_{60\%\text{RH}} = H_o \exp\left(\frac{\Delta E_H}{kT}\right). \tag{31}$$

where ΔE_H is the enthalpy of reaction, which for most of the electronic packaging polymers were found to be between 0.44 eV and 0.46 eV. The positive enthalpy of reaction suggests the absorption of moisture by polymers is an endothermic reaction. They also expressed the partial pressure of water vapour at 60%RH at temperatures between 30 °C and 85 °C in the form of Arrhenius equation:

$$p_{60\%\text{RH}} = p_o.\%\text{RH} \exp\left(\frac{-E_p}{kT}\right), \tag{32}$$

and evaluated the activation energy, E_p, to be 0.44 eV. The saturated concentration of moisture in the polymers at 60%RH is given by

$$C_{sat,60\%\text{RH}} = H_{60\%\text{RH}} * p_{60\%\text{RH}} = H_o p_o.\%\text{RH} \exp\left(\frac{\Delta E_H - E_p}{kT}\right). \tag{33}$$

The fact that $\Delta E_H - E_p \approx 0$ suggests that the saturated concentrations of moisture in electronic packaging polymers are insensitive to temperature over the range of temperature investigated. Similar findings on electronic packaging polymers and other polymers have been reported by Jang et al. [27] and others [48–50].

Assuming C_{sat} of solute in all solvents to be independent of temperature within the temperature range of interest, then Eq. (30) is reduced to

$$\mathbf{J_m} = -D(T)C_{sat}\nabla w \\ \partial_t(C_{sat}w) + \nabla.\mathbf{J_m} = \Theta_m. \tag{34}$$

Eq. (34) differs from Eq. (15) only in the temperature dependence of diffusivity.

Jang et al. [27] proposed the "advanced normalization technique":

$$\phi = \frac{C}{M}, \tag{35}$$

where $M = H_o p_o$ assuming $\Delta E_H - E_p = 0$. It is clear from Eq. (33) that M is indeed $C_{sat,100\%\text{RH}}$ or $C_{sat}(p_g)$. Since $M_A/M_B/C_{sat,A}/C_{sat,B}$, the normalized variable $\phi = C/M$ is continuous. But it also satisfies the condition of pseudo technique described in Section 2.2. Indeed, Eq. (35) is equivalent to multiplying w by the constant C_{sat}/M, which is equated to $C_{sat}(p_s)/C_{sat}(p_g) = p_s/p_g = \%\text{RH}$, and yielding $\phi = w.\%\text{RH}$.

4.3.2. $C_{sat,A}/C_{sat,B}$ independent of temperature

When diffusion occurs over a relatively large range of temperature such as during solder reflow, the dependence of C_{sat} on temperature cannot be ignored. However, if C_{sat} of solvents vary nearly proportionately with temperature such that the ratio $C_{sat,A}(T)/C_{sat,B}(T)$ is nearly independent of temperature (this is equivalent to $\Delta E_{H,A} \approx \Delta E_{H,B}$ in Eq. (31) and "a" $\approx$ "b" in Fig. 4), then $w(C_{sat}(T))$ in the solvents varies proportionally such that w-continuity at the interface remains intact. Within solvents A and B, it has been argued that $C(T + \Delta T) \approx C(T)$, which is equivalent to writing $C_{sat}(T + \Delta T)\nabla w(C_{sat}(T + \Delta T)) = C_{sat}(T)\nabla w(C_{sat}(T))$. This implies that $C_{sat}\nabla w$ and hence C_{sat} of solvents A and B may be treated as if they are independent of temperature. The only property that is dependent on temperature is $D(T)$. Thus, diffusion is again governed by Eq. (34).

4.4. General conditions

In general, C_{sat} of solvents varies non-proportionately with temperature such that the ratio $C_{sat,A}(T)/C_{sat,B}(T)$ varies with temperature (this is equivalent to $\Delta E_{H,A} \neq \Delta E_{H,B}$ in Eq. (31) and "a" $\neq$ "b" in Fig. 4).
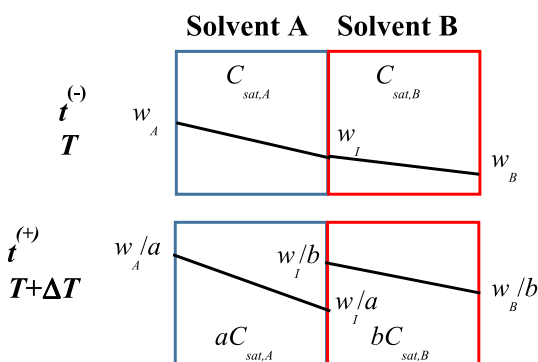
The diffusion of solute is governed by Eq. (30) wherein the w-field needs to be updated explicitly. There have been three reported techniques for updating the w-field: the intervention technique, the internal source technique, and the explicit finite difference scheme.

4.4.1. Intervention technique

The intervention technique was first reported by Wong et al. [40,42] but has received little attention [44,45] partly because of the need for intervention and partly because of the lack of details of its implementation. This technique has been referred to as the "piecewise normalization technique" by Wang et al. [46]. The implementation procedure is summarised below with the aids of Figs. 3 & 4.

- At time t, which is designated as $t^{(-)}$,
  - the solvents are assumed to acquire a uniform temperature T and the volumetric capacity of solvents for solute is $C_{sat}(T)$; from the w-field, $w(t^{(-)})$, the C-field is evaluated as $C(t^{(-)}) = C_{sat}(T).w(t^{(-)})$.

- At time $t + \delta t$ and $\delta t \to 0$, which is designated as $t^{(+)}$,
  - the solvents are assumed to acquire a uniform temperature $T + \Delta T$, and the volumetric capacity of solvents for solute is $C_{sat}(T + \Delta T)$; the C-field is assumed to experienced negligible change over the time increment δt such that $C(t^{(+)}) \approx C(t^{(-)})$;
  - the w-field becomes $w(t^{(+)}) = C(t^{(+)})/C_{sat}(T + \Delta T)$;
    - this has to be updated explicitly with the aid of macro program;
    - w-continuity along the interface is enforced assuming conservation of the concentration of solute along the interface:

$$w\left(t^{(+)}\right) = \frac{C_A(T) + C_B(T)}{C_{sat,A}(T + \Delta T) + C_{sat,B}(T + \Delta T)}. \tag{36}$$

- Between time t and $t + \Delta t$,
  - the diffusivity and volumetric capacity of solvents for solute are $D(T + \Delta T)$ and $C_{sat}(T + \Delta T)$; diffusion of solute takes place according to Eq. (30) but with T substituted with $(T + \Delta T)$.

Because of the linearization of the temperature-time relation (refer to Fig. 3), the quality of the solution shall increase with reducing time increment. It is advisable to perform consecutive runs with reducing time increments to assure the convergence of the solutions.

4.4.2. Internal source technique

The internal source technique was introduced by Wong [32] to eliminate the need for intervention by smearing the update of the w-field over the time increment Δt. Wang et al. [46] gave a more elaborated explanation to the technique. A refined implementation procedure is detailed below (using the terminologies presented in the intervention technique).

- At time $t^{(+)}$,
  - the appropriate C-field in the solvents ought to be $C(t^{(+)}) = C_{sat}(T + \Delta T).w(t^{(+)}) = C_{sat}(T).w(t^{(-)})$; however, if $w(t^{(+)})$ is assumed to be equal to $w(t^{(-)})$, the effective C-field in the solvents is indeed $C_{eff} = C_{sat}(T + \Delta T).w(t^{(-)})$; the "lost" concentration is given by $\Delta C = [C_{sat}(T) - C_{sat}(T + \Delta T)]w(t^{(-)})$.

- Between time t and $t + \Delta t$,

  - the diffusivity and volumetric capacity of solvents for solute are $D(T + \Delta T)$ and $C_{sat}(T + \Delta T)$ and diffusion of solute takes place according to

$$\mathbf{J_m} = -D(T + \Delta T)C_{sat}(T + \Delta T)\nabla w(C_{sat}(T)) \\ \partial_t[C_{sat}(T + \Delta T)w(C_{sat}(T))] + \nabla.\mathbf{J_m} = \theta_m; \tag{37}$$

  - the "lost" concentration, ΔC, is replenished into the solvents as internal source:

$$\theta_m = \frac{\Delta C}{\Delta t}; \tag{38}$$

  - w-continuity is enforced automatically by the condition of flux continuity.

Because of the smearing of the updating of w-field, a smaller time increment than the intervention technique shall be needed. Again, it is advisable to perform consecutive runs with reducing time increments to assure the convergence of the solutions.

4.4.3. Explicit finite difference solution scheme

Yoon et al. [43] established a one-dimensional finite difference solution scheme for Eq. (34). The one-dimensional difference equation, expressed in terms of wetness, takes the form:

$$C_{sat}^t \frac{w_x^{t+\Delta t} - w_x^t}{\Delta t} + w_x^t \dot{C}_{sat}^t - D^t C_{sat}^t \frac{w_{x+\Delta x}^t - 2w_x^t + w_{x-\Delta x}^t}{(\Delta x)^2} = 0, \tag{39}$$

which yields an explicit expression for time-marching of w:

$$w_x^{t+\Delta t} = \frac{D^t \Delta t}{(\Delta x)^2} w_{x+\Delta x}^t + \left(\frac{1 - 2\frac{D^t \Delta t}{(\Delta x)^2} - \dot{C}_{sat}^t}{C_{sat}^t \Delta t}\right) w_x^t + \frac{D^t \Delta t}{(\Delta x)^2} w_{x-\Delta x}^t, \tag{40}$$

wherein the superscript t and the subscript x denote time and spatial dependency. The magnitude of wetness at the interface, w_I, is evaluated using the condition of flux-continuity, $\mathbf{J_{m,AI}} = \mathbf{J_{m,BI}}$, which gives

$$w_I^{t+\Delta t} = \frac{D_A^{t+\Delta t} C_{sat,A}^{t+\Delta t} w_{I+\Delta x}^t + D_B^{t+\Delta t} C_{sat,B}^{t+\Delta t} w_{I-\Delta x}^t}{D_A^{t+\Delta t} C_{sat,A}^{t+\Delta t} + D_B^{t+\Delta t} C_{sat,B}^{t+\Delta t}}. \tag{41}$$

4.4.4. Benchmarking

Wang et al. [46] have recently undertaken an exercise that benchmarked the four solution techniques for modeling diffusion of moisture in heterogeneous solvent under dynamic temperature condition: the "advanced normalization technique" [27], the intervention technique, the internal source technique, and the explicit finite difference scheme.

The test vehicle was made up of two adjoining solvents – solvent A and solvent B – that were experiencing desorption from the two edges of the solvents. One-dimensional diffusion was assumed. Two cases were analysed; the ratio of the saturated concentration of the two solvents, $C_{sat,A}(T)/C_{sat,B}(T)$, was assumed to be constant in one case and non-constant in another case. The comparisons of the concentration evaluated using the four solution techniques for the two cases after
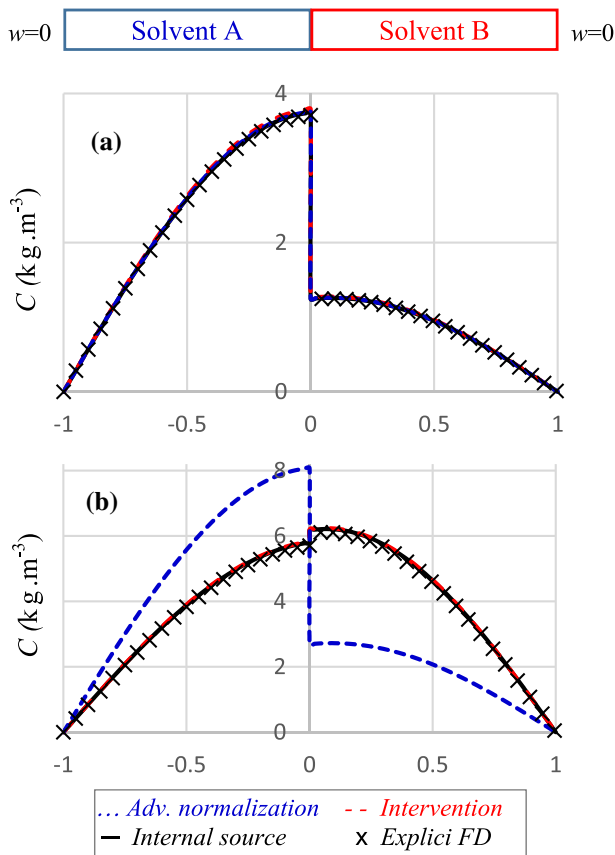
Fig. 5. Reproduction of the benchmarking results by Wang et at. [46] after 80 s of desorption; (a) $C_{sat,A}(T)/C_{sat,A}(B)$ = constant and (b) $C_{sat,A}(T)/C_{sat,A}(B)$ ≠ constant.

intervention technique, the internal source technique, or the explicit finite difference technique.

80 s of desorption are reproduced in Fig. 5. In the case of $C_{sat,A}(T)/C_{sat,B}(T)$ = constant, the four solution techniques have returned similar results. In the case of $C_{sat,A}(T)/C_{sat,B}(T)$ ≠ constant, except for the "advanced normalization technique", the other three solution techniques have returned similar results. The techniques of intervention, internal source, and explicit finite difference have been mutually validated.

5. Summary

Four techniques for enforcing the continuity of solute field at the interface of solvents under the condition of steady temperature-humidity have been reviewed. The wetness technique is found on the principle of equality of chemical potential and is fundamentally sound. The partial pressure technique (p_ϕ) is a pseudo technique, which is simply a multiplication of the wetness, w, by the environmental partial vapour pressure of the solute, p_s; that is, $p_\phi = w.p_s$. There could be unlimited pseudo techniques derived from simply multiplying w by a constant. The direct concentration technique is fundamentally flaw. The peridynamic technique in its original form is equivalent to the Fick's law and is restricted to homogeneous solvent.

Diffusion of solute under the condition of dynamic humidity but steady temperature can be treated rather simply as a dynamic boundary problem using the wetness technique. On the other hand, diffusion of solute under the condition of dynamic temperature is challenging because of the dependence of C_{sat} on temperature that leads to discontinuity of w-field along the interface of solvents. Two special techniques and three general techniques for enforcing this continuity have been reviewed. The special conditions of $C_{sat}(T)$ = constant or $C_{sat,A}(T)/C_{sat,A}(B)$ = constant may be treated using the standard wetness technique but with diffusivity defined as a function of temperature. The general condition of $C_{sat,A}(T)/C_{sat,A}(B)$ ≠ constant may be treated using the

References

[1] H. Levine, L. Slade, Water as a Plasticizer : Physico-Chemical Aspects of Low-Moisture Polymeric Systems, in: F. Franks (Ed.), Water Science Reviews 3: Water Dynamcis, Cambridge University Press, Great Britain 1988, pp. 79–185.
[2] M. Schwartz, The Influence of Environmental Effects, Composite Materials Properties, Nodestructive, Testing and Repair 1996, pp. 117–119.
[3] C. Shen, S. Springer, Effects of moisture and temperature on the tensile strength of composite materials, J. Compos. Mater. 11 (1977) 2–15.
[4] C. Shen, S. Springer, Environmental effects on the elastic moduli of composite materials, J. Compos. Mater. 11 (1977) 250–264.
[5] D. Buckley, M. Berger, D. Poller, The swelling of polymer systems in solvents. I. Method for obtaining complete swelling–time curves, J. Polym. Sci. A 56 (1962) 163–174.
[6] E. Wolff, Polymer Matrix Composites: Moisture Effects and Dimensional Stability, in: S. Lee (Ed.) International Encyclopedia of Composites, vol. 4, VCH, New York 1991, pp. 279–323.
[7] E.H. Wong, R. Rajoo, S.W. Koh, T.B. Lim, The mechanics and impact of hygroscopic swelling of polymeric materials in electronic packaging, J. Electron. Packag. 124 (2002) 122–126.
[8] H. Ardebili, E.H. Wong, M. Pecht, Hygroscopic swelling and sorption characteristics of epoxy molding compounds used in electronic packaging, IEEE Trans. Compon. Packag. Technol. 26 (2003) 206–214.
[9] A. Priyadarshi, S. Lim, M. SG, R. Rajoo, E. Wong, V. Kripesh, E. Namdas, Characterization of optical properties of acrylate based adhesives exposed to different temperature conditions, J. Appl. Polym. Sci. 98 (2005) 950–956.
[10] D. Shamiryan, T. Abell, F. Iacopi, K. Maex, Low-k dielectric materials, Mater. Today 7 (2004) 34–39.
[11] E. Liniger, T. Shaw, S. Cohen, P. Leung, S. Gates, G. Bonilla, ... P. RS, Processing and moisture effects on TDDB for Cu/ULK BEOL structures, Microelectron. Eng. 92 (2012) 130–133.
[12] M. Kitano, A. Nishimura, S. Kawai, Analysis of Package Cracking during Reflow Soldering Process, 26th Int. Reliability Physics Symposium 1988, pp. 90–95.
[13] A. Tay, T. Lin, Moisture diffusion and heat transfer in plastic IC packages, IEEE Trans. CPMT-Part A 19 (1996) 186–193.
[14] E. Wong, S. Koh, K. Lee, K. Lim, T. Lim, Y. Mai, Advances in vapour pressure modeling for electronic packaging, IEEE Trans. Adv. Packag. 29 (2006) 751–759.
[15] W.L. Bradley, T.S. Grant, The effect of the moisture absorption on the interfacial strength of polymeric matrix composites, J. Compos. Mater. 30 (1995) 5537–5542.
[16] M. Li, Temperature and Moisture Effects on Composite Materials for Wind Turbine Blades(MSc Thesis) University of Montana, 2000.
[17] K.D. Hertz, Limits of spalling of fire-exposed concrete, Fire Saf. J. 38 (2003) 103–116.
[18] A.J. Stamm, Shrinking and swelling of wood, Ind. Eng. Chem. 27 (1935) 401–406.
[19] J. Gibbs, The Scientific Papers of J Willard Gibbs, Vol I, Thermodynamics, Dover, New York, 1961.
[20] R. Baierlein, Thermal Physics, Cambridge University Press, 2003.
[21] G. Job, F. Herrmann, Chemical potential—a quantity in search of recognition, Eur. J. Phys. 27 (2006) 353.
[22] A. Fick, On liquid diffusion, Philos. Mag. J. Sci 10 (1855) 31–39.
[23] J. Fourier, Théorie Analytique de La Chaleur, Firmin Didot Père et Fils, Paris, 1822.
[24] J. Galloway, B. Miles, Moisture absorption and desorption predictions for plastic ball grid array packages, IEEE Trans. Compon. Packag. Manuf. Technol. (1997) 274–279.
[25] W. Henry, Experiments on the quantity of gases absorbed by water, at different temperatures, and under different pressures, Phil. Trans. R. Soc. London 93 (1803) 29–274.
[26] J. Carroll, What is Henry's law, Chem. Eng. Prog. 87 (1991) 48–52.
[27] C. Jang, S. Park, B. Han, S. Yoon, Advanced thermal-moisture analogy scheme for anisothermal moisture diffusion problem, J. Electron. Packag. 130 (2008) 011004.
[28] IUPAC, Recommendations for the characterization of porous solids, Pure Appl. Chem. 66 (1994) 1739–1758.
[29] S. Smith, The sorption of water vapor by high polymers, J. Am. Chem. Soc. 69 (1947) 646–651.
[30] E.H. Wong, Y. Teo, T.B. Lim, Moisture Diffusion and Vapour Pressure Modeling for Electronic Packaging, Proc. 48th Electron. Compon. Technol. Conf, IEEE, Seattle 1998, pp. 1372–1378.
[31] E.H. Wong, The fundamentals of thermal-mass diffusion analogy, Microelectron. Reliab. 55 (2015) 588–595.
[32] W. Nernst, Z. Phys. Chem. 8 (1891) 110–139.
[33] T.Y. Tee, Z. Zhong, Integrated vapor pressure, Hygroswelling and thermo-mechanical stress modeling of QFN package during reflow, Microelectron. Reliab. 44 (2004) 105–114.
[34] B. Xie, X. Fan, X. Shi, H. Ding, Direct concentration approach of moisture diffusion and whole-field vapor pressure modeling for reflow process − part I: theory and numerical implementation, J. Electron. Packag. 131 (2009) 031010.
[35] D. Liu, J. Wang, R. Liu, S. Park, An examination on the direct concentration approach to simulating moisture diffusion in a multi-material system, Microelectron. Reliab. 60 (2016) 109–115.
[36] S. Silling, Reformulation of elasticity theory for discontinuities and long-range forces, J. Mech. Phys. Solids 48 (2000) 175–209.
[37] M. Duangpanya, F. Bobaru, A peridynamic formulation for transient heat conduction in bodies with evolving discontinuities, J. Comp. Physics 231 (2012) 2764–2785.

[38] S. Oterkus, E. Madenci, A. Agwai, Peridynamic thermal diffusion, J. Comput. Phys. 265 (2014) 71–96.

[39] S. Oterkus, E. Madenci, E. Oterkus, Y. Hwang, J. Bae, S. Han, Hygro-Thermo-Mechanical Analysis and Failure Prediction in Electronic Packages by Using Peridynamics, 64th Electronic Component Technology Conference 2014, pp. 973–982.

[40] E.H. Wong, S.W. Koh, K.H. Lee, R. Rajoo, Advanced Moisture Diffusion Modeling & Characterisation for Electronic Packaging, 52nd Elect. Compon. Technol. Conf, 2002, pp. 1297–1303.

[41] H. Callen, Thermodynamics, John Wiley and Sons, New York, 1960.

[42] E.H. Wong, S.W. Koh, K.H. Lee, R. Rajoo, Comprehensive treatment of moisture induced failure – recent advances, IEEE Trans. Electron. Packag. Manuf. 25 (2002) 223–230.

[43] S. Yoon, B. Han, Z. Wang, On moisture diffusion modeling using thermal-moisture analogy, J. Electron. Packag. 129 (2007) 421–426.

[44] T. Ikeda, T. Mizutani, N. Miyazaki, Hygro-Mechanical Analysis of LCD Panels, ASME Interpack, ASME, San Francisco 2009, p. 89267.

[45] L. Zhu, D. Monthei, G. Lambird, W. Holgado, Moisture Diffusion Modeling and Application in a 3D RF Module Subject to Moisture Absorption and Desorption Loads, 11th EuroSimE, IEEE, Bordeaux 2010, pp. 1–6, http://dx.doi.org/10.1109/ESIME.2010.5464578.

[46] J. Wang, R. Liu, D. Liu, S. Park, Advancement of moisture diffusion simulation for electronic packaging under dynamic thermal loading, J. Electron. Packag. (2016) (in press).

[47] E.H. Wong, R. Rajoo, Moisture absorption and diffusion characterization of packaging materials—advanced treatment, Microelectron. Reliab. 43 (2003) 2087–2096.

[48] EIAJ test method EDX-4701, 1, Test Method of Resistance to Soldering Heat of Surface Mounting Devices for Integrated Circuits, Electronic Industries Association of Japan, 1990.

[49] C. Shirrell, Advanced composite materials––environmental effects, ASTM STP 658 (1978) 21–42.

[50] C. Soles, F. Chang, B. Bolan, H. Hristov, D. Gidley, A. Yee, Contributions of the nanovoid structure to the moisture absorption properties of epoxy resins, J. Polym. Sci. B Polym. Phys. Ed. 36 (1998) 3035–3048.