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Transport of moisture at epoxy–SiO_2 interfaces investigated by molecular modeling

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ABSTRACT

In this work, the transport of water molecules at the interface of an epoxy molding compound to a SiO_2 (chip surface) is investigated by molecular modelling. Experi-mental results of bulk diffusion of H_2O into a DGGOA/DAIIBA epoxy/hardener system at several temperatures are compared to molecular dynamics results at elevated (artificial) temperatures with respect to activation energies. Molecular modelling allows to trace individual molecules over time. The recorded traces are evaluated in a semi-quantitative way with respect to jump-distances and comparisons are made between bulk diffusion, diffusion at an interface and diffusion at open surfaces of the involved materials. Results show reasonably agreeing activation energies in experiment and simulation and an enhanced transport at open surfaces. A significantly enhanced transport at a perfect interface could not be confirmed in this investigation.

1. Introduction

One of the most prominent failure modes in microelectronics devices is the delamination of epoxy materials (adhesives, moulding compounds). In many cases, the influence of moisture accelerates this process because water not only leads to a swelling in polymers upon absorption, but also weakens the interfacial adhesion between epoxy and substrate surface. It is thus important to understand the physics behind the observed failure modes of packaged electronics.

In the past, the predictive capability of reliability assessment has been successfully enhanced by continuum mechanics simulations (FEM). More recently, cohesive zone modeling is utilized to describe not only stresses and strains, but to allow for delaminating interfaces or fracture of (composite) materials. However, the needed critical parameters still lack a consistent physical interpretation. This is partly due to the fact, that delamination and fracture are essentially molecular phenomena that cannot easily be addressed by continuum methods.

Molecular modeling is a simulation tool of growing interest to the packaging community over the past years [1]. Its advantages lie in the explicit simulation of atomic detail, investigating the phenomena at the molecular level and giving insight to the physical interaction where experimental data is hard to obtain with reasonable effort. In combination with experimental analysis of materials, structure–property correlation helps developing new materials and may even be used as a predictive simulation tool if incorporated in a multi-scale approach [2].

We have presented our method of constructing interface models of crosslinked epoxy networks in previous contributions [3,4], showing first results on the influence of water to thermodynamic work of adhesion. In the following, we would like to present results on the mobility of water molecules in an epoxy moulding compound and at its interface to a chip-surface (SiO_2).

2. Interface delamination

In a previous publication [5], we attempted to split delamination and fracture into contributions of different type which might be investigated separately. In a first approximation, these contributions were:

i. physical interaction: w_{12}
ii. chemical bonds: w_{chem}
iii. mechanical interaction: φ
iv. heat dissipation: Δh

More detailed information on this idea can be found in the publication; however, we would like to point out, that within this scheme, water may influence adhesive strength at the interface on any one of these contributions. Water molecules influence the physical interaction w_{12} as was shown in our work. Chemical bonds of adhesion promoters may be attacked by hydrolysis if water is present. Incomplete wetting of the surface due to roughness may lead to enhanced transport properties as will be shown in this work. Finally plasticization of the epoxy may lead to a

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change in relaxation behavior and thus alter heat dissipation properties. This work therefore joins the sequence of investigations on interface adhesion and delamination by combined experimental and (molecular) simulation methods.

3. Moisture transport

Polymers that are subjected to a moist environment tend to take up water molecules into spaces of free volume between their polymer chains. This process of moisture uptake consists of the adsorption of water molecules (H_2O) from the gaseous phase onto the polymer surface and the transport of H_2O into the polymer matrix. The latter process depletes the surface of H_2O making room for new adsorbent H_2O while the surface concentration establishes an equilibrium between vapor phase as well as with the bulk of the polymer matrix. Equilibrium with the vapor phase is considered to be reached instantaneously compared to the bulk, leading to a constant surface concentration. The concentration gradient towards the inner bulk of the polymer (or more precisely: the gradient of the chemical potential) acts as driving force for Fickian diffusion and was solved by Crank for the described boundary condition and a sheet geometry [6]:

$$\frac{M(t)}{M_\infty} = 1 - \sum \frac{8}{(2n+1)^2\pi^2} \exp\left(-D(2n+1)^2\pi^2 t/d^2\right) \quad (1)$$

In Eq. (1), $M(t)$ and M_∞ denote the mass uptake at time t and at equilibrium, respectively and d is the thickness of a plane sheet with a, $b \gg d$. The coefficient of mutual diffusion D is a measure of the mobility of the water molecules and determines the time necessary to reach a homogeneous concentration within the bulk (equilibrium). Fig. 1 shows a typical measurement of moisture uptake with time along with a fit of the parameters D and M_0 in Eq. (1) to the data.

The mechanism of moisture transport within the epoxy matrix can be considered as a hopping of H_2O molecules in a distribution (with respect to size and position) of sites of free volume within the amorphous polymer matrix. Observing a single molecule or a set of N distinguishable molecules i, the distances $r_i(t)$ from their individual starting points at time t_0 through this random walk adds up to a mean square displacement (MSD):

$$\mathrm{MSD}(t - t_0) = \frac{1}{N}\sum_{i=1}^{N}\left\langle [r_i(t) - r_i(t_0)]^2 \right\rangle \quad (2)$$

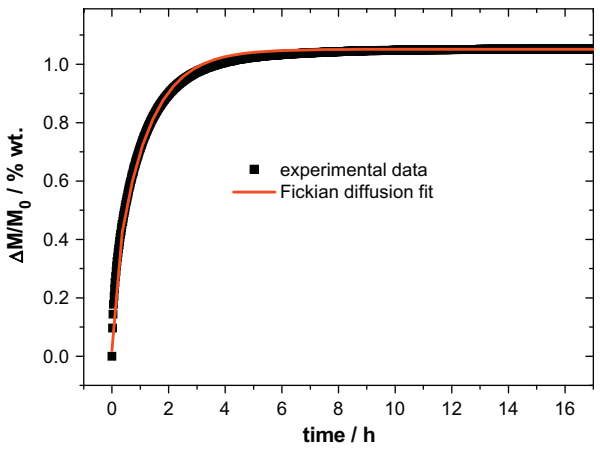

Fig. 1. Typical mass uptake curve of an epoxy resin subjected to humidity conditions (60/60). The red line indicates the fit of Eq. (1) to the data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

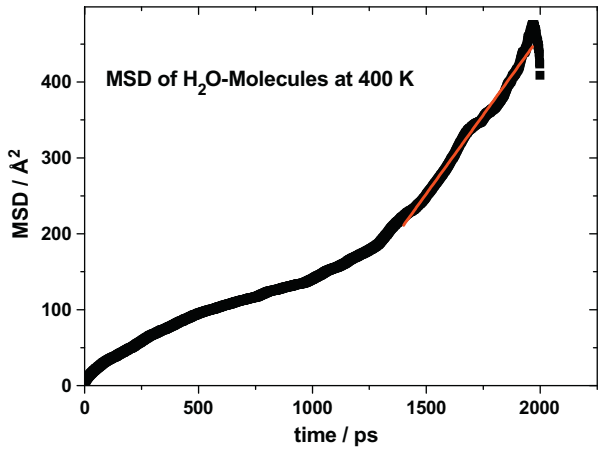

Fig. 2. Typical MSD curve of a set of H_2O molecules in an epoxy matrix at 400 K obtained by molecular modeling. The red line indicates the linear regime (see text). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

This MSD is related to the tracer diffusion coefficient D^* via the Einstein-relation [7] as:

$$D^* = \lim_{t\to\infty}\frac{d}{dt}\frac{\mathrm{MSD}}{6} \approx \frac{\mathrm{MSD}}{6\Delta t} \quad (3)$$

It must be noted that the relation (3) is valid only at large times, in a regime where the MSD progresses linear with time. Fig. 2 shows a typical curve obtained by molecular modeling of a set of N = 8 H_2O molecules in an epoxy matrix at 400 K (127 °C). The regime to fit the data linearly was chosen using the following rules: At small simulation times Eq. (3) is not valid as stated above. A small change in slope (in Fig. 2 at about 1250 ps) indicates a regime where hopping occurs more regularly and hence random walk might be expected. For large times, a smaller number of starting frames is available for MSD-evaluation; scatter from this region is avoided. It must be noted that a set of only N = 8 H_2O molecules provides only poor statistics for a quantitative analysis.

The chosen ensemble is a compromise between the saturation concentration as observed in experiments (8 H_2O molecules per ~2000 matrix atoms) and a reasonable computational effort needed to reach results.

For comparison of the tracer-diffusion coefficient D^* (Eq. (3)) with the mutual diffusion coefficient D (Eq. (1)) the dilute solution limit is assumed as a first approximation where $D \approx D^*$ [8].

4. Experimental diffusion measurement

A trifunctional epoxy resin N,N-Diglycidyl-4-glycidyloxyaniline (DGGOA) and the difunctional substituted Bisphenol A diallylbisphenol A (DAllBA) was chosen as epoxy/hardener system. The imidazole reaction catalyst is not shown in Fig. 3. For a detailed study of the reaction kinetics and preparations see [9].

Castings were prepared in steel sheet moulds ($100 \times 50 \times 1$ mm^3) from degassed mixtures. Curing was done in a convection oven isothermally 2 h at 90 °C until vitrification and then 2 h at 160 °C.

Sorption measurements were done with a Q5000SA sorption analyzer from TA Instruments. Samples of $6 \times 6 \times 0.3$ mm^3 were cut from the cured castings. A three-step isothermal procedure at 40 °C, 50 °C, 60 °C or 70 °C consisting of drying for at least 5 h at 0% relative humidity followed by an absorption at 60% relative humidity for at least 12 h and ended by a desorption at 0% relative humidity for at least 12 h.