

EVALUATION OF TRANSPARENT POLYIMIDE FOR FLEXIBLE SOLAR CELL SUBSTRATES

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Summary

The Polyimides evaluated in this study, 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. Moreover, an important feature of Polyimides is that they are not subject to UV degradation.

On the other hand, Water is adsorbed on the polymer surface and subsequently diffuses into the polymer 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 Polyimide polymers. 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.

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

1. Introduction

Currently, thermoset and thermoplastic materials 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. Nowadays several new Polyimides also have good transparency which will broaden their application from bearings, compressors, valves and piston rings to (transparent) substrate materials for solar cells and organic light emitting diodes.

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.

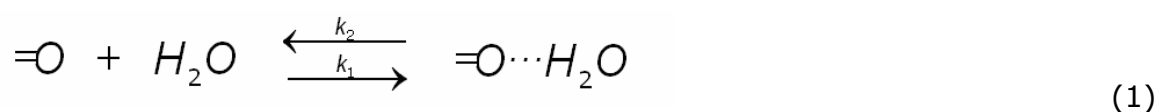
2. Anomalous Water Diffusion

If a Polyimide sheet or plane structure is exposed to Water, for short times, Water weight increases linearly as a function of the square root of time. This is correctly predicted by Fick's law. However, at longer times the levelling off to an expected equilibrium is not smooth, but shows sudden bends and slow continuation of the Water uptake process.

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 Polyimide polymers, 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 strictly 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:



3. Influence of Crystallinity

The presence of crystallinity in the matrix may have a noticeable effect on the diffusion rate. So does the presence of fibre reinforcement. If 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 permeant². Hence, local mass flux may decrease with a factor 100.

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]:³

$$\frac{\partial \varepsilon'_t}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial \varepsilon'_w}{\partial x} \right) - \frac{1}{\beta} \frac{\partial \varepsilon'_s}{\partial t} \quad (2)$$

$$\frac{\partial \varepsilon'_s}{\partial t} = k_1 \cdot \varepsilon'_w \cdot (\varepsilon'_{s0} - \varepsilon'_s) - k_2 \cdot \varepsilon'_s \quad (3)$$

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;

β : *porosity* of the matrix material (here assumed to be unity for simplicity);

² 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.

³ 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).

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 rate⁴ 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 bonding⁵. Moreover, the above set of equations is only valid if the diffusion coefficient is not a - or very little - function of concentration. In case of hydrophilic polymers with a small initial free volume, the diffusivity becomes an exponential function of solubility since the diffusion rate almost immediately follows the plasticization driven by the local solubility. Think of for example Water diffusion in Polyamide.

On basis of the conditions above, we mention a few candidates for the dual mode diffusion phenomenon at 25 degrees Celsius and atmospheric circumstances: Liquid Crystal Polymers (LCP's), Epoxy and Vinyl Ester resins, Polyphenylene Sulphide (PPS), Polyether etherketone (PEEK), and of course several sorts of Polyimide⁶.

Below we see the fit with the uptake curve of Water in an amorphous Polyimide and a partly crystalline Polyimide.

⁴ Read: the adsorption kinetics is of comparable order or slower than the zero concentration diffusion rate.

⁵ 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. On the contrary, the presence of macro voids, for example due to an improper matrix - fibre interface or improper matrix - filler interface, can result in a similar mathematical description as the one shown here.

⁶ It is interesting that the list probably mainly includes nowadays high tech materials, applied in all sorts of new applications, such as in aerospace wings, aircraft noses, etc. However, it is questionable whether the applied accelerated weathering tests are based on the appropriate picture of internal water behaviour.

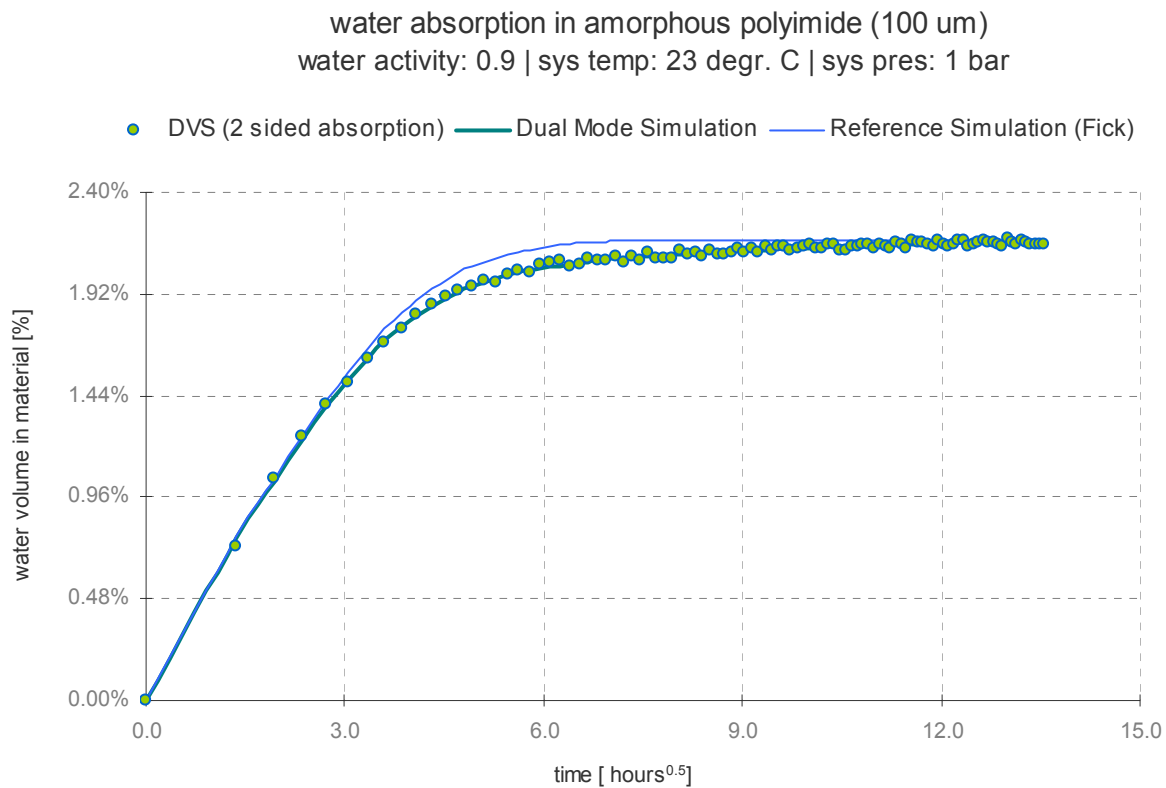


Figure 1: Water absorption in amorphous Polyimide.

The constants of interest were obtained using the IDC-SAC simulation program. They are listed below:

$$D: 3.0 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$$

$$k_1: 3.3 \cdot 10^{-6} \text{ s}^{-1} @ a_w=0.9$$

$$k_2: 6.0 \cdot 10^{-7} \text{ s}^{-1}$$

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 $3.0 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$ ($2.9 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$). 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 in case of extrapolation of diffusivities to low chemical concentrations or chemical activities.

water absorption in partly crystalline polyimide (100 um)
water activity: 0.9 | sys temp: 23 degr. C | sys pres: 1 bar

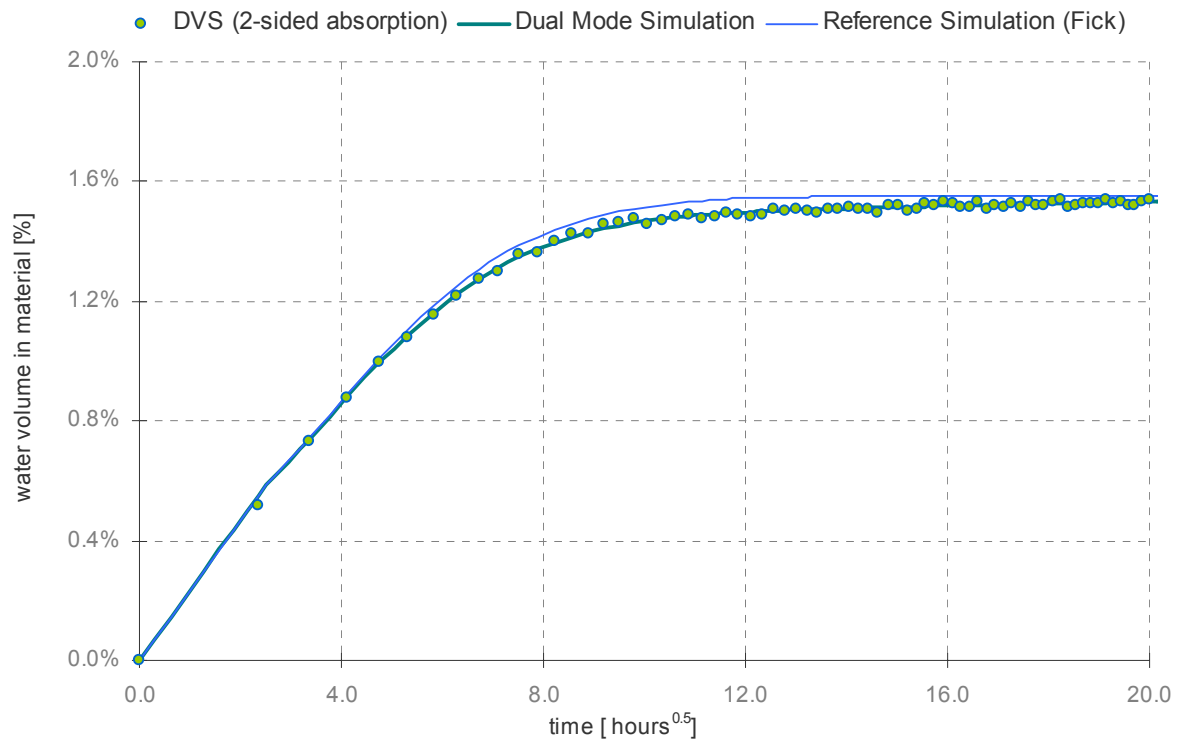


Figure 2: Water absorption in crystalline Polyimide.

Key figures for the composite:

D : $9.9 \cdot 10^{-15} \text{ m}^2 \text{ s}^{-1}$;
 k_1 : $8.8 \cdot 10^{-7} \text{ s}^{-1}$ @ $a_w=0.9$
 k_2 : $2.0 \cdot 10^{-7} \text{ s}^{-1}$.

From the fits it is obvious that indeed the Water diffusion coefficient and adsorption rate kinetics decreases due to the presence of the crystalline fraction. This is as expected.

5. Sorption Isotherm

In the experiment, samples were exposed to various humidities. In order to predict the total Water absorption of the polymer or composite when exposed to other chemical activities (such as very low or pure Water exposure). 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:

$$\varepsilon'_w \cdot K = \frac{p_w}{p_w^0} \quad (4)$$

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]:

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

The total Water solubility then yields:

$$\varepsilon'_t = \varepsilon'_w + \varepsilon'_s \quad (6)$$

For amorphous and partly crystalline Polyimide, the fit of the theoretical isotherms with the DVS experiment is depicted below.

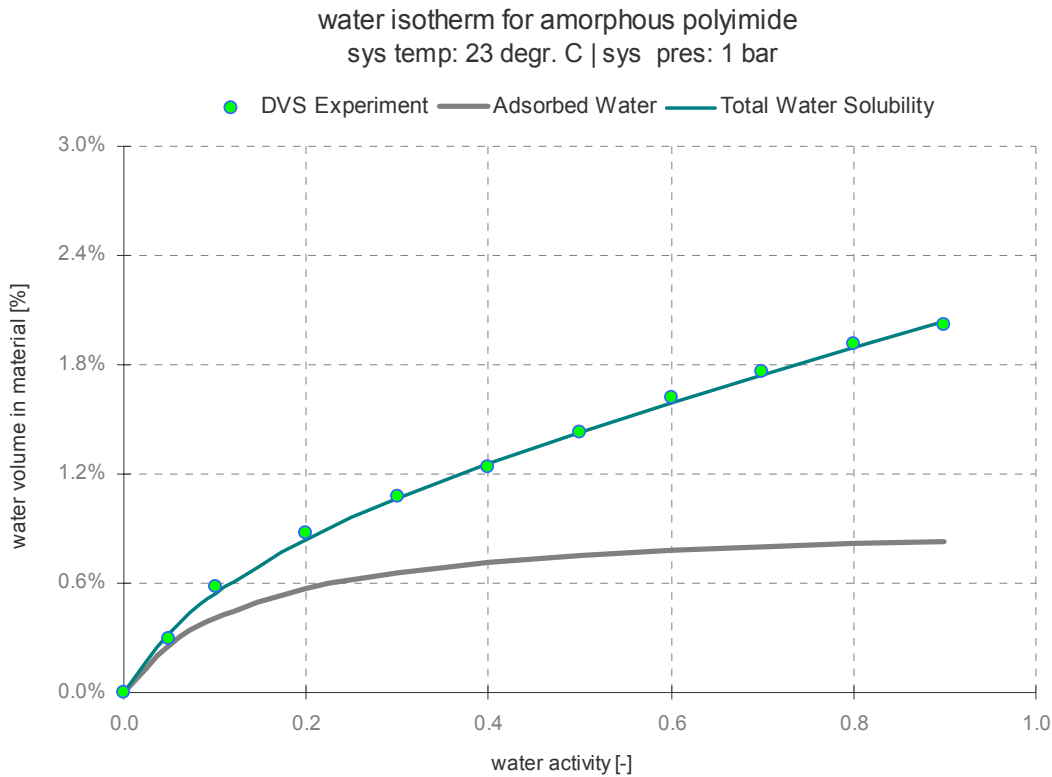


Figure 3: Water isotherm for amorphous Polyimide.

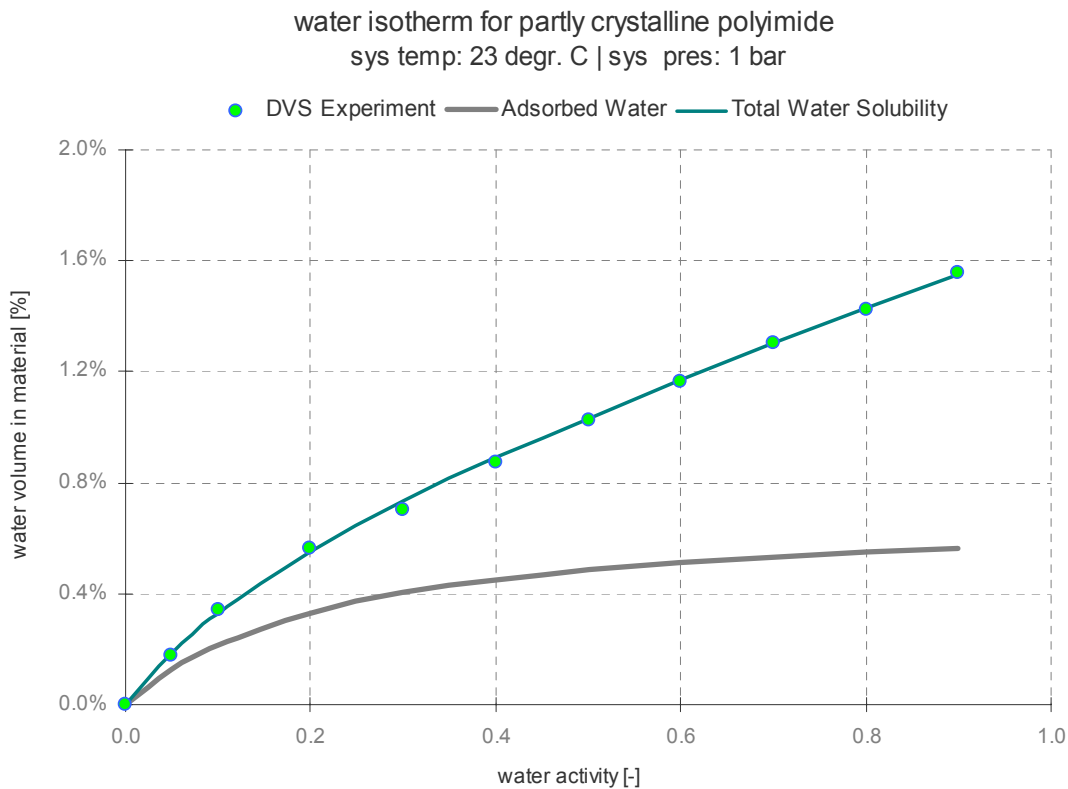


Figure 4: Water isotherm for partly crystalline Polyimide.

Apart from the good fit, this basic isotherm also shows satisfying agreement with literature data on Vinyl Ester resin, Polyester resin and Epoxy resins. Slightly modified versions of the above isotherm have proved to be useful for several Polyurethanes (softening and swelling effects must be included) and Polymethylmethacrylate (PMMA).

6. Industrial Application

If Polyimide is for example used as a transparent substrate material for solar cells, in normal weathering conditions Water (and other species) from the atmosphere will diffuse through the substrate and reach the interface between the substrate and - in this case - Indium Tin Oxide (a transparent electrode). See figure below.

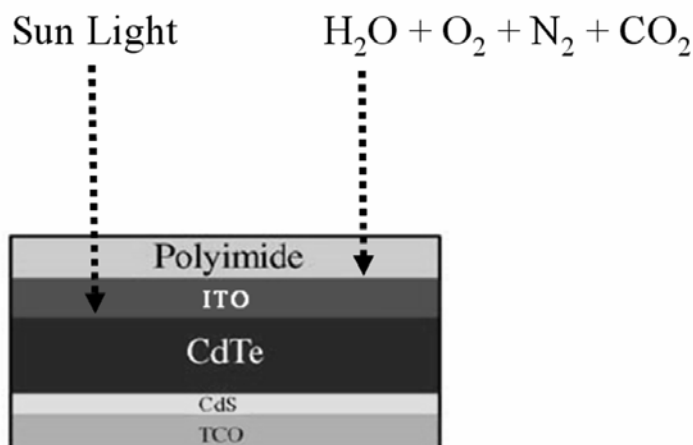


Figure 6: Solar cell and exposure to chemicals and radiation.

For the lifetime - from the viewpoint of chemicals exposure - one diffusion related issue is essential: the swelling of the polymer at the Polyimide - Indium Tin Oxide (ITO) interface. In case of sputtered layers, the interfacial strength between Polyimide and ITO interface is sufficient if the Polyimide does not swell at the interface. Hence, swelling behaviour at the interface is our primary interest.

Besides that dual mode sorption influences the Water penetration time of the Polyimide layer and the mass flux into the layer, the swelling behaviour is also influenced by the dual mode character. Reason is that immobilized Water is "stored" at interaction sites that do not add to dimensional change of the matrix. This is a fundamental difference with Fickian diffusion, where Water volume above the available free volume (very small in Polyimide!) accounts for dimensional change.

For the simulation of the real life weathering conditions we assumed that the solar cell is exposed to for 12 hours at averaged day conditions at 37 degrees Celsius and 0% humidity and subsequently 12 hours at average night conditions at 37 degrees Celsius and 90% humidity. Although this is - with this regard - a very simplistic real-life simulation, the effect of Water absorption and desorption are clarified.

See picture below for the volume of Water present at the Polyimide - ITO interface as a function of the night (red line) and day time (green line) cycle. The Polyimide substrate evaluated is partly crystalline and has a thickness of 50 micrometer.

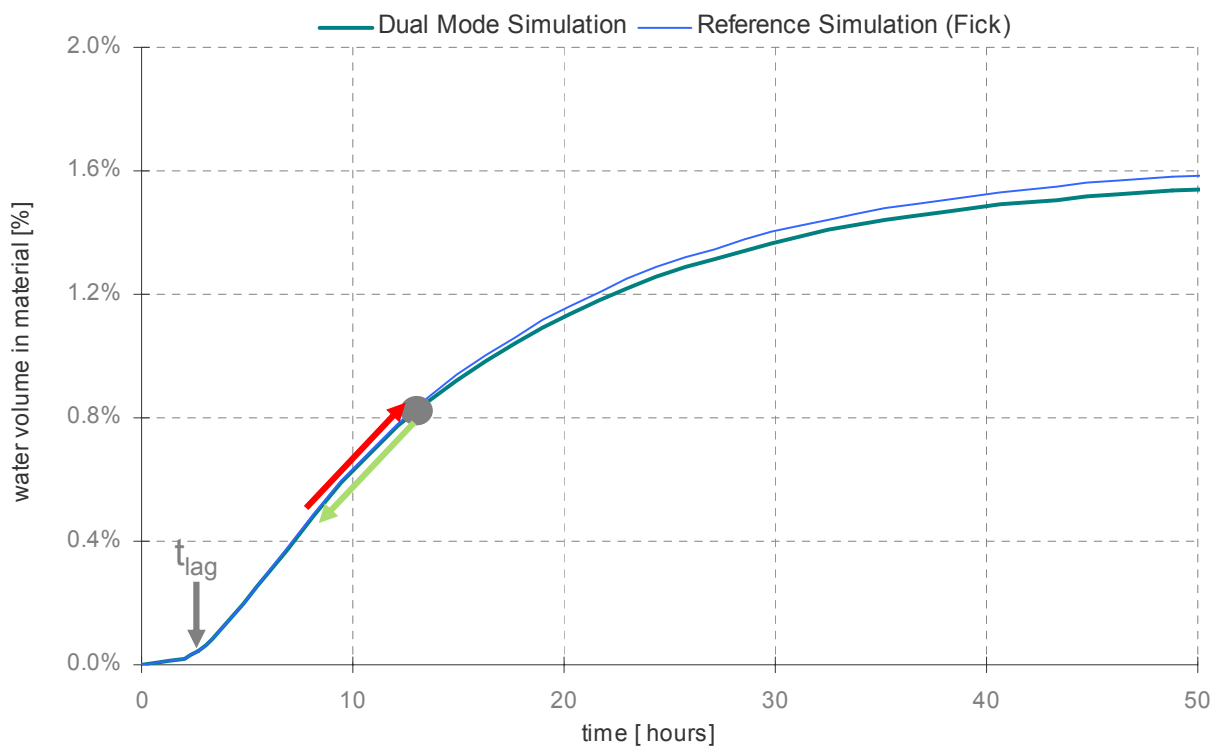


Figure 7: Water volume at the interface during night-day cycle. Dual Mode and Fick simulation.

Here the difference between Fick and Dual Mode are not significant. Now if we determine the swelling behaviour, a total different picture appears. See figure 8.

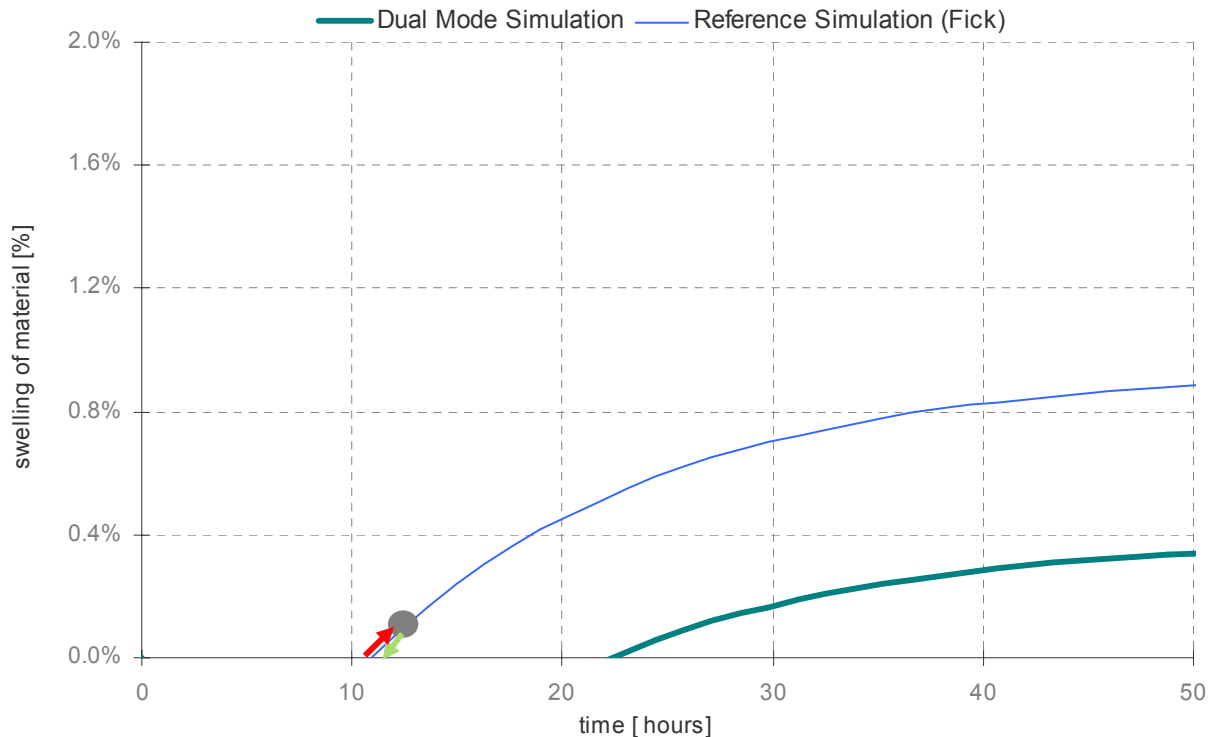


Figure 8: Volumetric change at the interface during night-day cycle. In Dual Mode, the Polyimide does not swell.

7. Conclusion

From this picture it becomes obvious that the Dual Mode character of Water in Polyimide is an essential feature. Whereas the interfacial swelling in case of Fick's law commences at 11 hour exposure, the interfacial swelling in Dual Mode starts at 23 hours exposure. Simulation and experimental analysis of other polymer - metal substrates and multilayer materials like Polyethylene - Aluminum - Polyethylene, reveal that chemical interaction, mechanical interlocking and interfacial swelling are key to a reliable service life. Hence the Polyimide evaluated in this study is a very suitable candidate that has an excellent chemical and physical aging resistance.

References

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- [4] Fukuda, M., Diffusion of moisture in Poly (p-Phenylene Terephthalamide) film: analysis by the adsorption-controlled diffusion equation, *Polymer Engineering & Science*, **36**, 558-567 (1996)