SPE SOCIETY OF PLASTICS ENGINEERS
Plastics Research Online
10.2417/spepro.006846

Accurate characterization of moisture absorption in polymeric materials

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The importance of using the exact solution of the hindered diffusion model is demonstrated on experimental data from a nanoclay/epoxy composite.

Moisture absorption is known to detrimentally affect the mechanical integrity and durability of polymeric materials.[1–3] For example, a moisture content as low as 0.75wt% can lead to substantial reductions in the tensile strength, elastic modulus, and interfacial shear strength of polymer composites.[4] Consequently, it is critically important to accurately characterize moisture absorption in such materials so that their service life behavior (especially for structural load-bearing applications that are designed for long service life) can be predicted.

Although diffusion of a primarily 'Fickian' nature is often observed during initial moisture uptake, numerous polymers exhibit non-Fickian behavior over longer timescales.[5–19] To describe this behavior, several models have previously been proposed.[5–10] Among these models, the Langmuir model—also known as the hindered diffusion model (HDM)—is thought to be particularly effective for describing absorption in polymeric materials[10–19] and is capable of capturing both Fickian and non-Fickian behaviors. The affinity of the polymer for water (associated with specific interactions between water and polymer polar groups) and the diffusivity of water into the polymer (related to polymer interstices, or free volume) both play an important role in the HDM framework. For instance, unbound water molecules are free to diffuse and move through the polymer's interstices. However, molecules that interact with the polymer chains stop diffusing and are considered to be bound. The total moisture concentration in a polymeric material is therefore the sum of the bound and unbound concentrations. Furthermore, the bound moisture is added as a sink term to a conventional Fickian diffusion equation. An additional governing equation links both the bound and unbound moisture concentration. The mass intake can be calculated by integrating the total moisture concentration over the material thickness, and an exact analytical solution for the mass intake is available in the literature.[9, 10]

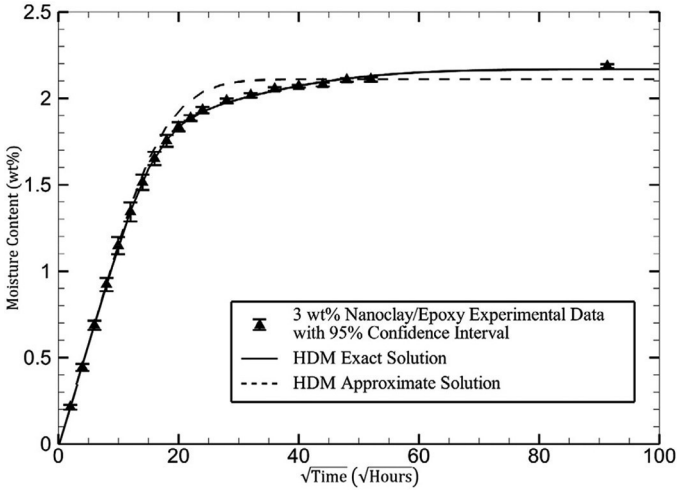

Figure 1. *Comparison between the experimental moisture absorption results for a 3wt% nanoclay/epoxy composite, and the predictions obtained from the exact and approximate solutions of the hindered diffusion model (HDM).*

Despite the prevalence of the HDM in the literature, there is actually little discussion available on exactly how the model should be implemented to recover the set of absorption parameters (i.e., the absorbed moisture content at equilibrium, diffusivity, as well as the rates of unbound molecules becoming bound and vice versa). Indeed, most researchers[10–16] use simple approximations of the model's equations. The exact solutions would yield more accurate characterizations, but these are rarely used because of their perceived complexity. Moreover, the last weight-gain data recorded is generally used as a measure of the absorbed moisture content at equilibrium (M_∞) in absorption experiments. During anomalous absorption behavior, however, moisture absorption decelerates after the initial intake and reaches a pseudo-equilibrium, which is often mistaken for equilibrium. The

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Table 1. *Moisture absorption parameters for the nanoclay/epoxy composite recovered by using the HDM approximate and exact solutions. RMS: Root mean square.*

Recovered parameters	Approximate Solution	Exact Solution
Diffusivity ($\times 10^{-4}$mm^2/hr)	7.61	7.47
Bound→unbound molecules ($\times 10^{-3}$hr^{-1})	7.17	8.43
Unbound→bound molecules ($\times 10^{-3}$hr^{-1})	1.05	1.33
Maximum moisture (wt%)	2.11	2.17
RMS error/data point ($\times 10^{-3}$)	13.66	2.29

absorption then continues at a significantly lower rate and equilibrium is reached at a much higher level. The ad hoc selection of the last data as M_∞, coupled with the approximations made in the simplified version of HDM, can therefore lead to substantial errors in the calculated absorption parameters.

To accurately characterize moisture absorption in polymeric materials, all absorption parameters (including M_∞) need to be determined from experimental data. In our work,[20] we have thus used the HDM in the proper manner to characterize the moisture absorption of an epoxy composite that contained 3wt% nanoclay (I.30E) and that was immersed in water at 25°C. We collected gravimetric data to recover the nanocomposite's absorption parameters, using a search algorithm[20, 21] to simultaneously determine the values of all the absorption parameters for which the error between the experimental data and the model is minimized.

The absorption behavior for our nanoclay/epoxy nanocomposite, as predicted by the recovered model parameters, is illustrated in Figure 1. We show the absorption behaviours predicted by both the approximate and exact solutions of the HDM. We find an excellent agreement between the exact solution and our experimental data. Furthermore, we were able to use the data we collected over a four-month period to accurately predict the moisture uptake of the composite after 11 months. The moisture content that we predict with the approximate HDM solution, however, deviates substantially from the experimental values after the initial linear region has ended.

We also find that the parameter values we obtain from the approximate and exact HDM solutions are considerably different (see Table 1). For instance, there is an 8.6% difference between the maximum moisture intake values we calculate from the approximate and exact solution (2.11 and 2.17%, respectively). These disparities in the calculated absorption parameters indicate that the diffusion kinetics described by the two versions of the model are fairly different (even though the moisture uptake curves in Figure 1 partially overlap in the early part of the absorption process). In addition, the approximate prediction fails to capture the long-term absorption level. Overall, our results indicate that recovering the absorption parameters with the approximate solution yields an almost six-fold increase in the root-mean-square error per data point compared with the exact solution.

In summary, we have conducted a water absorption experiment on a nanoclay/epoxy composite to measure its water-uptake characteristics over time. We have also used both approximate and exact solutions of the popular HDM to predict the water absorption of the polymeric samples. We find that the exact model provides a good match to the experimental data and that it can be used to predict both the short- and long-term absorption of the nanocomposite samples. In addition, our results highlight the importance of using the exact—rather than the approximate—solution of the HDM to characterize moisture absorption in polymeric materials (because the approximate solutions have significantly higher associated errors). Moreover, all absorption parameters (including the equilibrium moisture content) need to be recovered simultaneously from experimental data. In our future work we plan to explore how added inclusions influence the moisture absorption behavior of our polymeric materials.

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