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Moisture absorption and hygrothermal aging in a bismaleimide resin

Li-Rong Bao[a], Albert F. Yee[a,*], Charles Y.-C. Lee[b]

[a]*Macromolecular Science and Engineering Program, The University of Michigan, Ann Arbor, MI 48109-2136, USA*
[b]*Air Force Office of Scientific Research, Arlington, VA 22203, USA*

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Abstract

Moisture diffusion in a BMI resin has been investigated by submerging thin specimens in water. The weight gain of the neat resin deviates significantly from Fick's law in that the uptake continues to slowly increase over an extended time scale. A two-stage diffusion model can successfully fit the experimental data. This model considers the structural relaxation induced by absorbed moisture, which is a good plasticizer of the resin. Desorption and re-absorption experiments indicate that the structural relaxation is irreversible upon desorption of water molecules. Dynamic mechanical analysis results demonstrate the plasticizing and rejuvenating effect of water. © 2001 Published by Elsevier Science Ltd.

Keywords: Water diffusion; Bismaleimide; Non-Fickian diffusion

1. Introduction

Polymer matrix composites are widely used in aerospace applications because of their high strength-to-weight ratios. Carbon fiber composites are especially suitable for aerospace applications due to a number of advantages which are well documented in the literature [1,2]. Advanced composites used in aircraft are often exposed to harsh conditions involving a wide range of temperatures and humidities. Many polymer matrices tend to absorb significant amounts of water when exposed to high humidity. The absorbed moisture has many detrimental effects on the composite performance. Therefore, understanding the molecular mechanisms of moisture diffusion and moisture-induced damages is very important to improving the long-term durability of advanced composites.

The mathematical modeling of the diffusion process is very important to the understanding of diffusion mechanisms. Small molecule diffusion in glassy polymers often displays various deviations from the simple Fickian diffusion [3–5] and different models have been proposed to describe the observed non-Fickian behavior. Some examples are the stress-dependent diffusivity model [3,5], the history-dependent diffusivity model [3,5] and the dual phase diffusion model [5–10]. Besides these models, relaxation has often been associated with the anomalous diffusion behavior of glassy polymers. It is widely agreed that transport in glassy polymers involves both the concentration-gradient-driven Fickian diffusion and the time-dependent relaxation process [3–5,11,12]. Depending on the relative contribution of these two processes, a wide range of behaviors have been observed [3].

The most commonly observed relaxation-controlled transport can be described by the so-called two-stage diffusion. This model was first proposed by Bagley and Long to explain acetone diffusion in cellulose acetate [13]. In their experiments, they observed a rapid initial diffusion step, followed by a slow approach to a final true equilibrium uptake. This two-step uptake leads them to propose that the diffusion process consists of two separate stages. The first stage is controlled by the concentration gradient in the sample and is predominantly Fickian. The second stage is associated with the slow relaxation process of the polymer as the polymer chains slowly rearrange in the presence of penetrant molecules, resulting in additional absorption. When the relaxation process is much slower than diffusion, there is a distinct separation between the two stages. Relaxation is the rate-determining factor in the second stage and the absorbent concentration is virtually uniform throughout the specimen during this stage. Later, Long and Richman described a model which achieved reasonable agreement with the experimental data by considering the surface concentration to have a single exponential dependence on time [14]. Two-stage behavior is not unique to this cellulose acetate system. It has been observed in many

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* Corresponding author. Tel.: +1-734-7644312; fax: +1-734-7634788.
E-mail address: afyee@engin.umich.edu (A.F. Yee).

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other polymer-penetrant systems [11,12,15–18], including moisture absorption in thermoset resins and composites [19–24].

Another anomalous diffusion behavior often observed in glassy polymers is the higher uptake level and diffusivity during the re-absorption experiments [15,18,20–22,24–27]. After the material has been exposed to the absorbent during the first absorption step, the subsequent re-absorption experiments often exhibit higher diffusivity and higher saturation level. This behavior has also been linked to the structural relaxation in polymers [15,18,20,21,24]. According to this model, penetrant molecules can re-arrange the polymer network, causing swelling of the material. After desorption, the network structure is different from the original material because of the 'frozen-in' segmental conformation. This will result in higher uptake in the re-absorption. Many authors have also found that after annealing the desorbed material, the re-absorption behavior became very similar to that of the first absorption [20,21,24]. This confirms the physical rather than chemical nature of absorbent induced structural change.

Various thermosetting matrices have been developed for aerospace applications. Among them, bismaleimides are a leading class of thermosetting polyimides used in high temperature applications. In the current research, we have studied the moisture diffusion properties of a bismaleimide (BMI) resin and its carbon fiber composites. In this paper, we will discuss the water diffusion behavior in the neat resin, with the emphasis on non-Fickian diffusion behavior. We will discuss the diffusion behavior of the composites using this BMI resin in a separate paper.

2. Experimental

2.1. Materials

The BMI used in our research is a commercial three-component BMI resin: Cytec™ 5250-4 RTM. This resin is widely used in aerospace composites because of its superior mechanical and thermal properties. In the following discussion, this resin will be referred to simply as 'BMI'. Two types of carbon fiber fabrics are used in the composites, a uni-weave (unidirectional) and a woven (satin) fabric. The composite panels are manufactured by compression molding. During the compression molding, excess resin called 'flash' is squeezed out of the mold. Flash is ideal in comparison studies between the composite and its matrix resin since it has essentially the same thermal history as the composite. Most of the neat resin samples studied here are from the flash of different composite panels. They are designated as 'fabric type *n*-ply flash', in which fabric type is the type of the carbon fiber fabric, uni-weave or woven, and *n* is the number of plies in the composites. For example, the flash from the 3-ply uni-weave composite is named uni-weave 3-ply flash. As the amount of flash is limited, some neat resin was also molded using the same molding conditions as those used for the composites. These samples display very similar diffusion properties as the flash samples and will be referred to as 'neat resin' in this paper.

2.2. Water absorption

Moisture uptake was determined by soaking thin sections of the material in liquid water and measuring the weight periodically. The thin specimens were obtained by cutting and polishing thicker BMI panels. The resin panels were first cut into thick pieces of 15 mm square. These pieces were then sectioned into thin specimens ($15 \times 15 \times 0.5\ \text{mm}^3$) using a low speed diamond wafering saw. Finally, to achieve uniform thickness within each specimen, the sections were polished using 600 grit sand paper. Prior to absorption experiments, the samples were dried in a vacuum oven at about 70°C until the weight stabilized. The specimens were then immersed in distilled water at different temperatures and the weight change monitored as a function of time. The absorption behavior at four different temperatures, namely, 35, 50, 70 and 90°C, was studied. A Perkin–Elmer AD-4 autobalance was used for the weight measurements.

2.3. Dynamic mechanical analysis

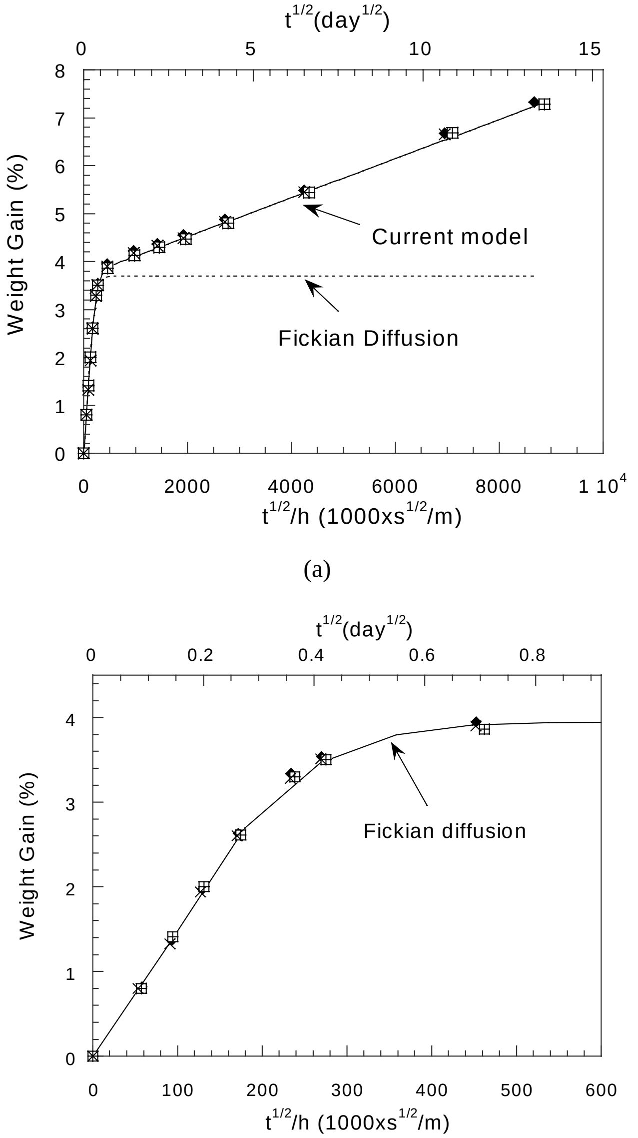
Dynamic mechanical analysis (DMA) was performed using a TA Instrument DMA 2980 operating in the single cantilever mode. Typical specimen dimensions were $25 \times 15 \times 1.3\ \text{mm}^3$. The temperature was scanned from −140 to 330°C using the step mode with 10°C increment. At each temperature, the sample was allowed to equilibrate for 10 min before measurements at 0.1, 1, 10 and 20 Hz.

3. Results

3.1. Moisture uptake

Fig. 1(a) shows the percentage weight gain of the uni-weave 12-ply flash at 70°C as a function of $\sqrt{\text{time}}$/thickness. To demonstrate the short-term weight gain behavior, the initial weight gain curve is also shown in Fig. 1(b). In the plots, different symbols correspond to different specimens tested under the same conditions. As can be seen, the reproducibility of the uptake is excellent among different specimens. All flash and neat resin samples exhibit similar uptake curves. The weight gain data at other temperatures also show similar behavior and are not presented here. As expected, the diffusion rate increases with increasing temperature.

Several features are noted in Fig. 1. First, the moisture uptake of this particular BMI resin is very high (approaching 8% by weight after six months), consistent with the highly polar nature of the BMI resin. Secondly, as shown in Fig. 1(b), the weight gain initially increases linearly with



(a)

(b)

Fig. 1. (a) Weight gain behavior of BMI flash at 70°C. Different symbols are experimental data for different specimens tested under the same conditions. Dotted line is the curve fit from Fickian diffusion model and solid line is the curve fit using our current two-stage model as discussed in the text. (b) Initial uptake behavior of BMI flash. Symbols are experimental data and the solid line is the curve fit using Fickian diffusion model. The initial uptake obeys Fick's law.

respect to $\sqrt{t}$ as predicted by Fick's law. However, no equilibrium uptake level was reached. After the initial fast diffusion, the uptake continues to increase linearly with respect to $\sqrt{t}$ over an extended time scale as seen in Fig. 1(a). Clearly, this behavior cannot be explained by Fickian diffusion (dotted line in Fig. 1(a)).

The continued slow increase in uptake after the initial uptake is consistent with the two-stage diffusion model. Similar to the analysis of Bagley and Long [13], we assume the initial diffusion is controlled by the concentration gradient and thus Fickian. According to Fick's second law, the total weight gain in a sheet of thickness $2h$ is given by [5,28]:

$$M = \int_{-h}^{h} c\,\mathrm{d}x = \left\{ 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp\left[-(2j+1)^2 \pi^2 \left(\frac{Dt}{h^2} \right) \right]}{(2j+1)^2} \right\} \times (M_\infty - M_\mathrm{i}) + M_\mathrm{i} \tag{1}$$

In the above equation, M_i is the initial moisture content of the material at the start of the diffusion experiment; M_∞ is the equilibrium moisture uptake and D is the diffusivity. Eq. (1) is often approximated by the following expression [28]

$$M = \left\{ 1 - \exp\left[-7.3 \left(\frac{Dt}{h^2} \right)^{0.75} \right] \right\} (M_\infty - M_\mathrm{i}) + M_\mathrm{i} \tag{2}$$

During the second stage of diffusion, structural relaxation needs to be considered. Since the BMI resin is deep in the glassy state, the relaxation is much slower than diffusion. In this stage, the concentration profile remains uniform throughout the specimen [13]. In other words, any increment in the saturation concentration will reach equilibrium in the material in a time scale short compared to the structural relaxation time scale. Since the weight gain during the second stage increases linearly with respect to $\sqrt{t}$ as seen in Fig. 1(a), we propose the saturation concentration to be a linear function of $\sqrt{t}$:

$$c_\mathrm{s} = c_0 + k\sqrt{t} \tag{3}$$

then the weight gain is given by

$$M = \int_{-h}^{h} c\,\mathrm{d}x = 2hc_\mathrm{s} = 2hc_0 + 2hk\sqrt{t} = M_0(1 + k'\sqrt{t}) \tag{4}$$

Since the initial diffusion obeys Fick's law, the uptake in the entire experimental time scale can be approximately written as

$$M_t \cong M_{\infty 0}(1 + k\sqrt{t}) \times \left(1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp\left[-(2j+1)^2 \pi^2 \left(\frac{D_x t}{h^2} \right) \right]}{(2j+1)^2} \right) \tag{5}$$

or,

$$M_t \approx M_{\infty 0}(1 + k\sqrt{t})(1 - \exp[-7.3(Dt/h^2)^{0.75}])$$

Curve fit using Eq. (5) is shown in Fig. 1(a) as the solid line. Clearly, a nearly perfect fit was achieved.

In this diffusion model, the structural relaxation is assumed to be much slower than the diffusion process. Therefore, the first and second stages can be treated as diffusion controlled and relaxation controlled, respectively. The assumption is likely valid since BMI resin is deep in the glassy state ($T_g \approx 260°\mathrm{C}$) at the experimental temperature and thus the relaxation process is expected to be very slow.

In the current model, the time dependent saturation concentration is a linear function of $\sqrt{t}$, which seems to contradict the commonly held notion regarding relaxation nature of the second stage. A relaxation-controlled saturation concentration is expected to approach an ultimate equilibrium concentration asymptotically. Yet, no ultimate equilibrium is assumed in the current model, nor is it observed experimentally. This seemingly contradictory fact could be explained by the extremely long relaxation time of the resin deep in the glassy state. When the time scale of the relaxation process is much longer than that of the diffusion experiment, the observed weight gain increase is only at the initial stage of the relaxation with no indication of the final equilibrium uptake.

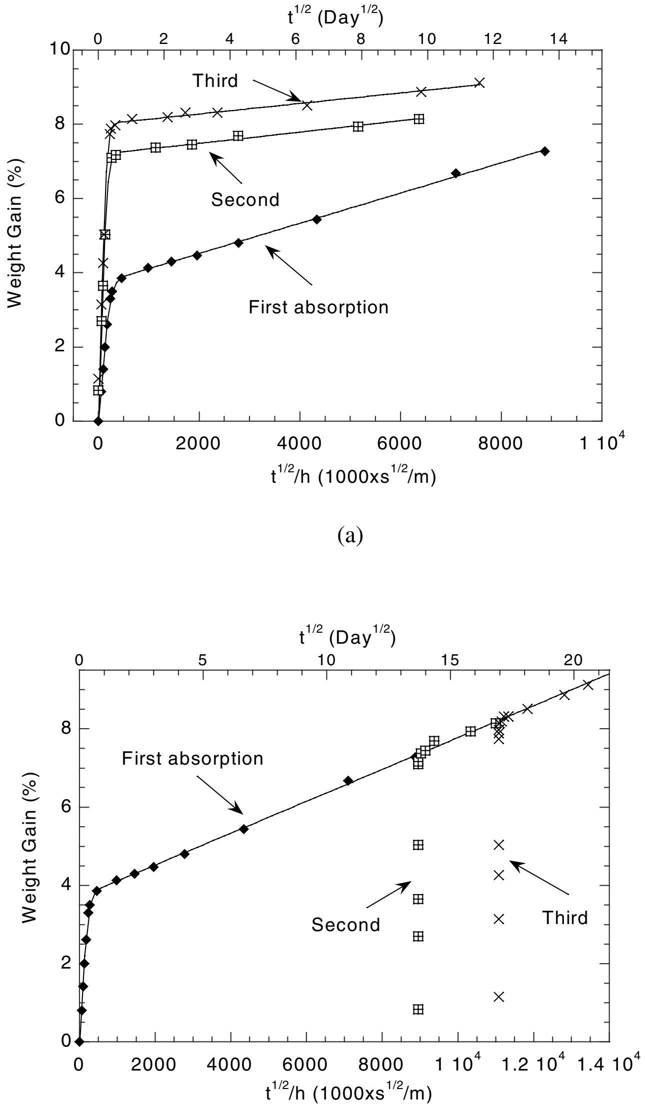
Although the true equilibrium uptake level may be inaccessible under the current experimental conditions, one may be able to accelerate the relaxation process. To this end, the use of thermal spikes is a viable approach. Several authors have observed enhanced moisture uptake when the material is subjected to periodic thermal spikes [29–32]. Since relaxation is much faster at elevated temperatures, the true equilibrium may be reached in a reasonable time scale in a thermal spike experiment. In fact, Xiang and Jones did observe a second uptake plateau when a high enough spike temperature was used [32]. Thermal spike experiments may also be used to simulate certain service conditions.

3.2. Absorption and re-absorption

Desorption and re-absorption experiments were performed to demonstrate the reversibility of the structural change during absorption. After the first absorption experiment, the specimen was dried in a vacuum oven at the temperature of the absorption. The weight of the specimen was monitored until a constant weight was obtained. The same specimen was then used in the second absorption experiment. The same procedure was followed for the third absorption.

Fig. 2 shows one of these experiments at 70°C. Uptake curves of the three absorption steps are shown in Fig. 2(a). Comparing the three absorption measurements, the re-absorption experiments show consistently higher diffusivity and uptake than the first absorption. This implies that the network structural change is irreversible, and the diffusion properties are history-dependent. We have also noticed that a small residual weight gain remained in the material after drying. This may be due to strongly bonded water molecules, which are difficult to remove from the resin.

On the other hand, as seen in Fig. 2(a), the second and third diffusion curves give lower slopes during the second stage of absorption, which seems to suggest that the structural relaxation is slower in the re-absorption steps. However, a close examination of the data indicates that to be not true. The seemingly different slopes are caused by the different time origins selected in the three measurements. In Fig. 2(a), the elapsed absorption time is counted from the start of each absorption step. Since the abscissa is the square root of elapsed time, this changes the slope of the second stage, i.e. k value in Eq. (5). In Fig. 2(b), the same data are plotted in a different way, in which the elapsed time is counted from the start of the first absorption. This time the same slope of the second stage was obtained for all three absorption cycles. Moreover, if first stage diffusion



(a)

(b)

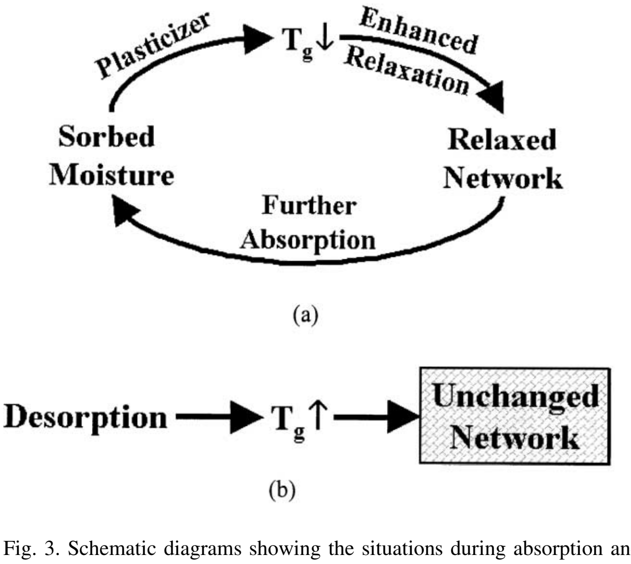
Fig. 2. (a) BMI flash weight gain data of three absorption cycles at 70°C. Symbols are experimental results and the solid lines are curve fit using the current two-stage model. The elapsed time for each cycle was counted from the start of each absorption experiment. (b) The same data as in (a), but the elapsed time was counted from the start of the first absorption step. The solid line is the curve fit of the first absorption. Note that the uptake data during the second stage in the second and third absorption fall onto the same line determined by the first absorption.

is ignored for the time being, the re-absorption steps are obviously the continuation of the first absorption. This observation further confirms that the network structure change is irreversible. The desorption step does not reverse the change in network structure caused by sorbed moisture. The structural relaxation resumes when water molecules are re-introduced into the material. The fact that the same slope is observed in different absorption cycles indicates that the same relaxation mechanism dictates all three diffusion cycles, i.e. the material is in different stages of the same relaxation process.

A direct consequence of the irreversible relaxation is that the absorption behavior is moisture exposure history dependent. This may be of practical importance, since the diffusion behavior may be used to determine the hygrothermal history of a material. If the diffusion parameters of the virgin material, namely, weight gain at the end of the first stage and slope of the second stage, are known, one can determine the 'moisture exposure age' of a sample with unknown history by its moisture absorption behavior.

It is unlikely that the irreversible property change is due to chemical degradations such as hydrolysis and oxidation. No appreciable difference in FT-IR spectra was observed after one absorption–desorption cycle, indicating undetectable levels of chemical reaction during water absorption. In addition, water absorption causes no permanent T_g change, as will be shown in the DMA results in Section 3.3.

The irreversible property change is consistent with the plasticizing effect of water. It is well known that water is a good plasticizer for many polymers. Water has been shown to significantly decrease the T_g of thermosets and their composites, including various epoxies and polyimides [25,33–36]. A decrease in T_g effectively decreases the distance between the resin temperature in the glassy stage and T_g and enhances structural relaxation. As the polymer responds to the swelling stress created by sorbed moisture, the network structure becomes more open and more accessible to additional water, which in turn decreases T_g. As the cycle goes on, the weight gain continues to increase with time, causing the observed deviation from Fickian behavior. On the other hand, when water is desorbed, the plasticizer is removed and T_g increases. Because the relaxation process is suppressed, the network topology cannot relax to the original dry state. In other words, the absorption process is a self-accelerating process while desorption is a self-retarding process. Therefore, the network structure change during water absorption is irreversible. Fig. 3 is a schematic diagram describing the process discussed above. Although the relaxation process is irreversible upon desorption, annealing at elevated temperature after desorption may accelerate relaxation and reverse the moisture induced structural change. Wong et al. [20,21] and Johncock et al. [24] have both shown that annealing the material after one absorption–desorption cycle at temperatures close to the T_g can shift the re-absorption curve back to the original absorption curve.



(a)

(b)

Fig. 3. Schematic diagrams showing the situations during absorption and desorption. (a) During water absorption, the plasticizing effect of water leads to enhanced relaxation and relaxed network structure. (b) During desorption, removing water suppresses the relaxation. The network structure remains unchanged.

3.3. Dynamic mechanical analysis

Dynamic mechanical properties of the material were measured to demonstrate the relaxation property changes during water absorption. Fig. 4 shows the DMA traces of the BMI neat resin before and after one absorption–desorption cycle. For the virgin sample before absorption, three main relaxation peaks were observed. First, the α relaxation at around 270°C is due to the glassy transition. No well-defined peak is observed in this temperature range, because the resin is not fully cured and further curing occurs at above T_g. Secondly, the fairly sharp γ relaxation centered at −100°C is likely to have its origin in localized short-range motions. Finally, a very broad relaxation peak is

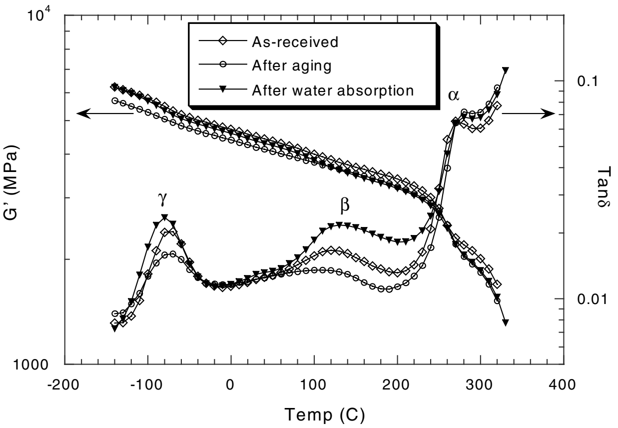


Fig. 4. DMA behavior at 1 Hz for as-received neat resin, after aging in vacuum at 180°C for 24 h and after water absorption–desorption at 70°C. Note that the intensity of the β relaxation peak is reduced after aging and increased after water absorption.

located in the 100–200°C range. This peak is likely due to packing defects in the glassy state, which is sensitive to physical aging. We followed the nomenclature of Yee and Smith [37] and named this peak a β relaxation peak. The fact that this peak is due to structural relaxation is confirmed by aging at 180°C, which considerably decreases the amplitude of this peak as seen in Fig. 4. The ubiquity of β relaxations due to structural relaxation in glasses has been described by Johari.

After the absorption experiment has proceeded for about 2 months, the specimen was dried and DMA was performed again. The glass transition temperature remains almost unchanged, which shows that significant chemical degradation is unlikely. No appreciable difference was observed in FT-IR after one absorption–desorption cycle, also supporting the absence of extensive chemical degradation. However, the relaxation intensity of the β peak increased dramatically after one cycle of sorption/desorption. Comparing the three DMA curves in Fig. 4, we can see that the effect of the moisture absorption is equivalent to the reverse of aging. This is consistent with the notion that water is plasticizing the resin, while aging is akin to anti-plasticization. Absorbed water molecules are apparently able to plasticize the BMI resin and rejuvenate the network. This rejuvenation effect will lead to a more open network structure, faster relaxation, and cause faster diffusion and higher uptake level in the second absorption.

4. Discussion

4.1. Implication of the diffusion model

As we have pointed out in the result part, the structural change during absorption is likely due to network relaxation in the material. If this is indeed true, we should be able to derive the diffusion model based on knowledge of structural relaxation. The following is our first attempt to correlate the two.

It is well known that relaxation in glassy polymers is non-exponential and often nonlinear. The relaxation time is not only a function of temperature but also depends on the structure of the glass and thus time. Isothermal relaxation in a condensed system can be described by the nonlinear stretched exponential decay function with a time-dependent relaxation time [38–40]:

$$\phi(t) = \exp\left[-\left(\int_0^t \frac{\mathrm{d}t'}{\tau(t')} \right)^{\beta} \right] \tag{6}$$

in which $\tau(t)$ is the time-dependent relaxation time and $\beta (0 \leq \beta \leq 1)$ is the fractional exponent or stretching exponent.

In the case of isothermal aging, the relaxation time increases with aging time according to [41,42]:

$$\tau = \tau_0 t^{\mu} \tag{7}$$

Here μ is the relaxation time shift factor defined by Struik and τ_0 is the reference relaxation time. On the other hand, during water absorption, the relaxation time decreases with absorption time because of the rejuvenating effect of water. We follow the similar approach and assume the relaxation time during absorption is given by:

$$\tau = \tau_0 t^{-\nu} \tag{8}$$

Similar to the definition of μ, ν is defined as the moisture relaxation shift factor.

By substituting Eq. (8) into Eq. (6), one gets:

$$\phi(t) = \exp\left\{ -\left[\frac{t^{1+\nu}}{(1+\nu)\tau_0} \right]^{\beta} \right\} = \exp[-(t/\tau')^{\beta'}] \tag{9}$$

in which $\beta' = (1+\nu)\beta$, $\tau' = [(1+\nu)\tau_0]^{1/(1+\nu)}$

Since the moisture uptake during the second stage is controlled by structural relaxation, we can write the saturation concentration as the following function of time

$$c_s = c_0 + (c_{eq} - c_0)[1 - e^{-(t/\tau')^{\beta'}}] \tag{10}$$

When the experimental time scale is much shorter compared to the relaxation time, i.e. $t \ll \tau'$, the above equation can be approximated using the Taylor series expansion, neglecting higher order terms:

$$e^{-(t/\tau')^{\beta'}} \cong 1 - (t/\tau')^{\beta'} \tag{11}$$

$$c_s \cong c_0 + (c_{eq} - c_0)(t/\tau')^{\beta'}$$

During the second stage of diffusion, the moisture concentration is uniform in the material. Therefore, the total weight gain is given by

$$M = 2hc_s = 2hc_0 + 2h(c_{eq} - c_0)(t/\tau')^{\beta'} \quad \text{or,} \tag{12}$$

$$M = M_0 + (M_{eq} - M_0)(t/\tau')^{\beta'} \tag{13}$$

where $M_0 = 2hc_0$, $M_{eq} = 2hc_{eq}$

From this derivation, we can see that when the relaxation time is very long compared to the time scale of the experiment, the observed weight gain will follow a power law relationship during the second stage of diffusion. The power is related to the moisture relaxation shift factor ν and stretching exponent β in the KWW equation. Our data on this BMI system suggests that $(1+\nu)\beta$ for BMI is around 0.5. Since β is usually between 0.2 and 0.3 in the sub-T_g region, ν is close to 1, which is a value found by Struik in many polymers. It will be interesting to measure the relaxation parameters of BMI in water and compare them with the water diffusion properties.

5. Conclusions

We have studied moisture diffusion in a high T_g BMI resin. The neat resin absorbs significant amount of water when exposed to liquid water. Although the initial uptake obeys Fick's law, the weight gain in the later stage deviates from Fickian diffusion, in that the uptake continues to increase over an extended time scale. No equilibrium uptake was observed after nearly a year. A two-stage diffusion model has been proposed and very good agreement with the experimental data has been achieved. In this model, the saturation moisture concentration is assumed to be evolving as a consequence of water induced relaxation. Absorbed water acts as a plasticizer and enhances the relaxation process of the matrix, which causes the observed deviation from Fickian behavior. Desorption and re-absorption experiments demonstrated that the structural relaxation is irreversible upon desorption, consistent with the plasticizing effect of absorbed water. Re-absorption experiments also demonstrate the absorption and re-absorption steps are governed by the same relaxation process. Results of DMA are consistent with our hypothesis that water absorption has a rejuvenation effect on the polymer network. We have also attempted to correlate the mathematical form of this diffusion model to the relaxation process of the polymer.

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