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In situ monitoring of sorption and drying of polymer films and coatings: self-referencing, nearly temperature-independent fluorescence sensors

Christopher J. Ellison[a], Keith E. Miller[a], John M. Torkelson[a,b,*]

[a]Department of Chemical and Biological Engineering, Northwestern University, 3108 Evanston, IL 60208-3120, USA
[b]Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208-3108, USA

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Abstract

Sorption and drying processes were monitored in situ in polymer films by a fluorescence rotor probe, 4-tricyanovinyl-[*N*-(2-hydroxyethyl)-*N*-ethyl]aniline (TC1), a solvatochromatic fluorescence probe, 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DANS), and pyrene. Taking advantage of an intensity ratio to monitor sorption, these fluorescence probes were found to serve as self-referencing sensors of water sorption in polyvinylacetate, with DANS being the most sensitive followed by TC1 and pyrene. Additionally, the shapes of the emission spectra (and thus intensity ratios) for TC1 and DANS were independent of temperature over a range of reasonable expected use temperatures. Covalent attachment of these fluorescence dyes was shown to enable the determination of sorbate levels within particular layers of multilayer films or coatings. Finally, these probes were also shown to provide sensitivity to desorption or drying of both water and organic sorbates.

Keywords: Sensor; Fluorescence; Sorption

1. Introduction

The achievement of non-destructive, in situ monitoring of sorbate levels within polymer films or coatings has been of significant scientific and technological interest for several decades [1–17]. There are many reasons for this interest. The presence of low levels of water within a polymer may yield substantially reduced glass transition temperatures, adhesion, and mechanical properties, enhanced physical and chemical aging of the polymer, enhanced degradation of polymer-reinforcement interfaces within composites, enhanced corrosion at polymer–metal interfaces, and stresses due to differential swelling. A similar impact on polymer properties may be observed via sorption of low levels of organics. While sorption or drying within polymers has traditionally been studied using gravimetric, infrared, and dielectric spectroscopy techniques [15–18], much attention has been focused on capitalizing on the capabilities of fluorescence [1–14] to yield a contactless, non-destructive, in situ monitoring method. In line with these capabilities, there has also been much recent interest in the development of spectroscopic 'noses' [19–23], often employing fluorescence probes or labels within polymer films, which allow for the detection of very low levels and discrimination of toxic organics and explosive agents.

There are several bases on which the fluorescence of probes or labels within polymer films may yield sensitivity to sorbate levels. Some fluorescence chromophores show substantial sensitivity of quantum yield or intensity to local mobility. In particular, increasing levels of sorbate leads to an increase in local mobility and thereby a decrease in fluorescence intensity (via an increase in rate of non-radiative decay from the excited state). A class of fluorescence chromophores known as rotor probes has been found to yield substantial sensitivity to changes in local mobility accompanying polymerization processes [24,25] as well as physical aging and other complex relaxation behavior in polymers [26–29]. Related studies [5,9] have shown that a number of chromophores fitting into the class of rotor probes yield a one-to-one linear relationship between reduction in fluorescence intensity and increasing water sorbate level in polymer films, up to

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* Corresponding author. Tel.: +1-847-491-7449; fax: +1-847-491-3728.
E-mail addresses: ellison3@northwestern.edu (C.J. Ellison), j-torkelson@northwestern.edu (J.M. Torkelson).

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levels of 4–5% sorbate content, as well as quantitative determinations of average Fickian diffusion coefficients for water sorption.

Other fluorescence chromophores possessing a significant intramolecular charge-transfer nature have been shown to yield sensitivity to sorbate levels via local medium polarity or dielectric constant effects, which lead to a shift in the shape and/or location of the fluorescence emission spectrum [4,7,8,11]. Such chromophores, often described as being solvatochromatic, contain electron-donating and electron-accepting moieties and exhibit substantial intramolecular charge separation in their excited state. The fluorescence emission shifts to longer wavelength or lower energy with increasing local medium polarity, because the dipolar excited state is more effectively stabilized by a polar environment [30]. Besides their utility in quantifying sorption or drying in polymer films, these chromophores have also shown utility in other applications that have accompanying changes in local polarity, such as in situ cure monitoring [30–35].

Several other fluorescence-based methods have also been used to follow sorption in polymer films. Fluorescence resonance energy transfer, which has seen significant application in quantifying diffusion coefficients for organic dyes in polymer films [36–40], has recently been employed as means of monitoring water sorption in polymer films [10]. This method yields sensitivity to sorption via a change in spectral shape resulting from differences in the relative levels of fluorescence from energy transfer donor and acceptor chromophores within the polymer upon sorption. Another approach, which has proven effective in yielding indications of trace atmospheric levels of explosive organics used in land mines, is based on the amplified quenching of fluorescence upon sorption of the organic into the polymer [23].

Recently, there has been a growing recognition of the need for such fluorescence-based sensor systems to yield self-referencing measures of the phenomenon or quantity being monitored [35,41–44]. Self-referencing systems eliminate issues related with signal irreproducibility due to the fact that an intensity ratio or other parameter associated with the change in shape or location of the fluorescence spectrum is correlated to the variable being monitored. In contrast to fluorescence intensities, intensity ratios are generally unaffected by excitation source fluctuations or monitoring geometry and thus may be considered inherently self-referencing. Here, we address the use of several self-referencing fluorescence probe systems as sensors for sorption or drying in polymer films and coatings. These include 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DANS), a solvatochromatic fluorescence probe which recently has been shown to yield self-referencing measures of conversion or cure even during non-isothermal polymerizations [35], 4-tricyanovinyl-[*N*-(2-hydroxyethyl)-*N*-ethyl]aniline (TC1), previously investigated via fluorescence intensity measurements as a sorption sensor associated with its rotor-probe characteristics [5], and pyrene. Due to their intramolecular charge-transfer character, both DANS and TC1 dyes undergo sufficiently large shifts in the shapes and locations of their fluorescence spectra to yield highly quantitative measures of sorption via fluorescence intensity ratios. Pyrene has a well-known sensitivity to local polarity of the relative intensities of two of its monomer fluorescence peaks due to the effect of solvent polarity on the vibronic coupling between the first and second excited singlet states [45–49]. It has been commonly applied to the study of micelles [46] and self-assembled monolayers [47] and has also been shown to be useful as a tag to monitor block copolymer formation during processing [50–52]. Here its utility as a self-referencing fluorescence sensor for water sorption within polymer films is characterized for the first time. The relative capabilities of these three fluorescence chromophores to yield self-referencing measures of sorbate levels that are independent of monitoring temperature are also addressed as are the potential advantages of employing such chromophores as fluorescence labels, involving covalent attachment to the polymer, rather than as doped fluorescence probes.

2. Experimental

Poly(vinyl acetate) (PVAc) was used as received from Scientific Polymer Products (nominal $\mathrm{MW} = 260,000$) or Aldrich (secondary standard, nominal $M_n = 52,700$ and $M_w = 124,800$). Poly(methyl methacrylate) (PMMA) was used as received from Scientific Polymer Products (nominal $\mathrm{MW} = 100,000$). Red Devil® Satin 71 polyurethane was used as received from a local distributor. This is a one component, moisture curing polyurethane that consists of approximately 60 wt% prepolymer and 40 wt% xylol.

The fluorescence probe DANS (99 + % purity) was purchased from TCI America and used as received. The fluorescence probe TC1 was synthesized following procedures outlined in Ref. [53]. The arylamino and tetracyanoethylene starting materials were purchased from Aldrich and used as received. Pyrene (99 + % purity) was purchased from Aldrich and used as received.

A random copolymer of methyl methacrylate and TC1-labeled methacrylate was synthesized according to the procedure outlined in Ref. [54]. The copolymer had a TC1 label content of 0.1 mol% as determined by UV/visible absorbance spectroscopy. It was mixed with unlabeled PMMA in a ratio of 1:9 wt:wt of TC1 labeled PMMA to unlabeled PMMA, respectively. This resulted in a final TC1 label content of 0.01 mol% in dry PMMA films.

The PVAc films were prepared from 10 to 15 wt% solutions in methyl ethyl ketone (MEK) or acetone (Fisher, spectroscopic grade) while the PMMA films were prepared from 10 wt% solutions in methyl ethyl ketone (Fisher, spectroscopic grade). All films were solution cast onto glass slides. Probe concentrations were less than 0.2 wt% (based on dry weight of polymer) in polyurethane films and less than 0.08 wt% in PMMA and PVAc films. In all cases, probe concentrations were such that optical densities at the relevant fluorescence excitation wavelength were substantially less than 0.10, ensuring a nearly even excitation of fluorescence probe molecules throughout the film thickness. The solution cast films were first covered with angled petri dishes and dried for several hours at room temperature to produce smooth, uniform surfaces and further dried in a vacuum oven at 60 °C for at least 2 days. These samples were allowed to cool in the vacuum oven at room temperature in the presence of desiccant for at least an hour before use. Polyurethane films were allowed to cure at room temperature under ambient conditions for at least 7 days as suggested by the manufacturer. These samples were then stored in a vacuum oven at room temperature in the presence of desiccant for at least 2 days prior to use.

Multi-layer PVAc/PMMA films were prepared by combining three separate, solution cast films. PVAc was solution cast onto a glass slide while a PMMA film was solution cast onto a second glass slide. The PMMA film was floated from its substrate in a water bath; excess water was wiped from the film that was then placed directly on top of the PVAc film. The resulting bi-layer film was placed in a desiccator for several hours to remove residual water and then placed in a vacuum oven at ~50 °C for 15 min to promote adhesion of the interface. A second PVAc layer was removed from its substrate by floating in a water bath. Excess water was removed from the film, and then this layer was placed on top of the PMMA layer. The resulting tri-layer film was placed in a desiccator overnight and then was placed in a vacuum over at ~50 °C for 15 min with a weight on top of the tri-layer film to ensure that all layers were well adhered. The tri-layer film was stored under vacuum at room temperature and in the presence of desiccant until used.

In cases where gravimetric analysis was employed, films were immersed in the sorbate of interest and carefully weighed on a digital balance after the film had been blotted dry to remove excess sorbate. All fluorescence measurements were taken with a SPEX Flurolog-2 DM1B fluorimeter in the front-face geometry with 1.5 mm excitation and emission slits (bandpass = 2.25 nm). All fluorescence measurements of sorption were taken in situ in a specially designed slide holder that allowed for direct contact of the liquid sorbate with the film of interest. (For further description of the slide holder, see Ref. [5].) Unless otherwise noted, samples containing TC1 were excited at 525 nm, samples containing DANS were excited at 450 nm, and samples containing pyrene were excited at 322 nm. All measurements were conducted at room temperature (nominally 22 °C) unless otherwise noted.

3. Results and discussion

3.1. Fluorescence probes as water sorption sensors in single-layer films

Fig. 1 shows the change in fluorescence emission characteristics for a trace level of TC1 freely doped into PVAc film upon going from a dry state to equilibrium sorption of water (~4.5 wt%) at room temperature. The most striking feature is the greater than 50% reduction in fluorescence intensity due to the uptake of ~4.5 wt% water (based on dry polymer), associated with plasticization effect of water on PVAc leading to both an increase in bulk matrix mobility, as evidenced by a reduction in glass transition temperature [26], and an increase in local mobility sensed by the TC1 probes. Also apparent upon close inspection of Fig. 1 is the fact that there is a modest change in the shape of the fluorescence emission spectrum upon sorption of water, with the wavelength of maximum intensity shifting slightly to the red, a factor that had not been considered in the previous study [5] of the sensitivity of TC1 fluorescence emission to water sorption. This shift in the fluorescence spectrum is consistent with the intramolecular charge-transfer character of the TC1 probe (see inset to Fig. 2 for chemical structure of TC1).

The previous study [5] of the sensitivity of TC1 fluorescence to water sorption established that there was a one-to-one linear relationship of the normalized change in fluorescence intensity to relative mass uptake:

$$(I - I_0)/(I_{eq} - I_0) = M/M_{eq} \quad (1)$$

where $I(M)$ is fluorescence intensity (mass uptake) at sorption time t, $I_{eq}(M_{eq})$ is the fluorescence intensity (mass uptake) at equilibrium sorption, and I_0 is the initial fluorescence intensity of the dry film. Taking advantage of this relationship and the Fickian solution to the problem of sorption with one impenetrable boundary [55], it is possible to use only in situ fluorescence data to determine an average diffusion coefficient, D, for water sorption in the PVAc

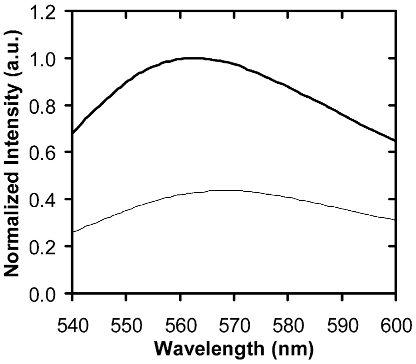

Fig. 1. Emission spectrum of a 50 μm PVAc film doped with 0.0026 wt% TC1 in a sample that is completely dry (thick line) and saturated to equilibrium (~4.5 wt% water, thin line). Intensities have been normalized to the maximum of the dry emission spectrum.

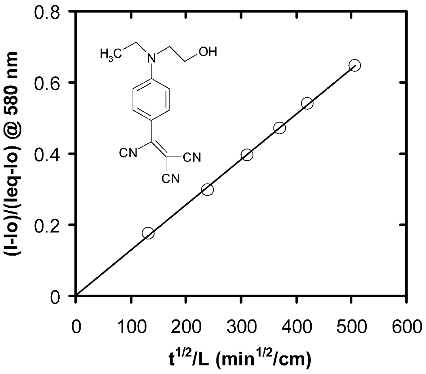

Fig. 2. Determination of the average diffusion coefficient by way of a least squares linear fit of the water sorption data that are less than ~60% of the equilibrium level for a 50 μm PVAc film containing 0.0026 wt% TC1. The inset shows the chemical structure of TC1.

films. For sorption levels less than ~60% of equilibrium sorption, the following equation applies [55]:

$$M/M_{\mathrm{eq}} = 2(D/\pi)^{1/2} t^{1/2}/L \qquad (2)$$

where L is the film thickness. Combining Eqs. (1) and (2), a plot of relative change in fluorescence intensity is predicted to be linear in $t^{1/2}/L$, with a slope that is proportional to $D^{1/2}$. Fig. 2 shows that experimental data (with intensity values taken at a wavelength of 580 nm) are in accordance with the predicted behavior and yield a value of D of 2.5×10^{-8} cm^2/s.

The full series solution to the Fickian diffusion of a sorbate into a film with one impenetrable boundary is required to accurately describe sorption kinetics beyond ~60% of the equilibrium sorption level. This solution is given by [55]:

$$\frac{M}{M_{\mathrm{eq}}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{4L^2} \right) \qquad (3)$$

As indicated in Fig. 3, a comparison of the relative change in fluorescence intensity at 580 nm with the absolute change in the ratio of fluorescence intensities at 580 and 550 nm, I(580 nm)/I(550 nm), shows an excellent correspondence of the two fluorescence parameters with each other and with the full series solution for the Fickian diffusion prediction for relative mass uptake using the average diffusion coefficient determined from Fig. 2. This comparison is important in indicating that for the TC1 probe in PVAc the change in shape of the fluorescence emission spectrum accompanying water sorption may be characterized by an intensity ratio that yields a simple one-to-one correspondence with sorption mass uptake. This means that the TC1 probe can act as a quantitative, self-referencing sensor for water sorption.

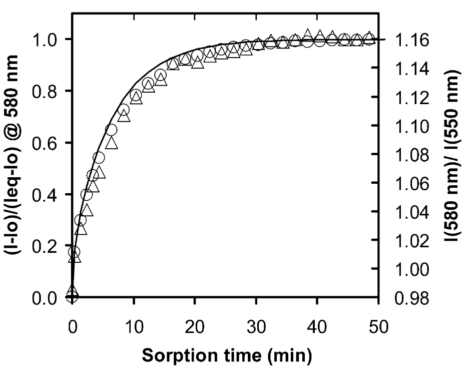

Fig. 3. Sorption progression in a 50 μm PVAc film containing 0.0026 wt% TC1 shown by measuring the relative intensity change at 580 nm (circles) and the intensity ratio, I(580 nm)/I(550 nm) (triangles). Also shown is the Fickian diffusion prediction (solid curve) by including seven terms of the series solution (Eq. (3)).

Similar experiments were undertaken using DANS as the fluorescence probe for quantifying time-dependent water sorption, as illustrated in Fig. 4. As with the TC1 probe, the DANS probe undergoes a major reduction in fluorescence intensity with water sorption. However, as seen in Fig. 4(a), the reduction in fluorescence intensity with sorption is much more wavelength-dependent in the case of DANS than in the case of TC1, an indication of the greater solvatochromatic character of DANS. A comparison of the relative change in fluorescence intensity at one wavelength (560 nm) with an absolute change in a ratio of fluorescence intensities at 610 nm and 560 nm, I(610 nm)/I(560 nm),

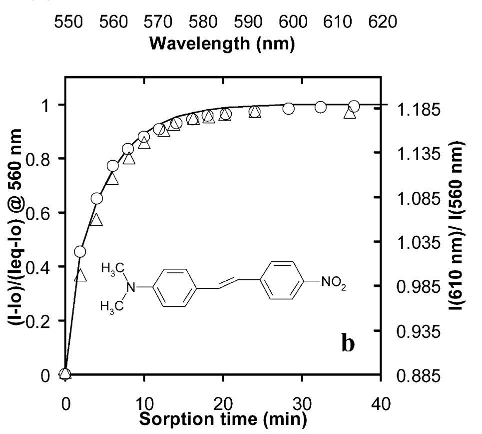

Fig. 4. Water sorption in a 48 μm PVAc film containing 0.02 wt% DANS. (a) Observed shift in fluorescence spectra for the same film as a function of exposure time (from top to bottom 0, 2, 4, 12, 20, 40, 140 min). (b) Sorption progression is shown by measuring the relative intensity change at 560 nm (circles) and the intensity ratio, I(610 nm)/I(560 nm) (triangles). Also shown is the Fickian diffusion prediction (solid curve) by including seven terms of the series solution (Eq. (3)). Inset shows the chemical structure of DANS.

shows an excellent correspondence of the fluorescence parameters with each other and with the full series solution for the Fickian diffusion prediction for relative mass uptake. A value of $D = 3.1 \times 10^{-8}$ cm^2/s determined in a similar manner to that for Fig. 2 is in good agreement with the value of $D = 2.5 \times 10^{-8}$ cm^2/s determined using TC1 to monitor water sorption and with the value of $D = 3.8 \times 10^{-8}$ cm^2/s at 22 °C from Ref. [56]. (It is important to note that the value of D for water sorption in PVAc calculated using DANS fluorescence is within error the same as that calculated using TC1 fluorescence and the same as that of Ref. [56]. The error is likely due to the significant activation energy associated with D, where a 3 °C variation in laboratory/water temperature during or between experiments results in a ~20% change in D [56].)

This comparison illustrates several important points. First, the relative change in fluorescence intensity for the DANS probe in PVAc accompanying water sorption is linear in relative mass uptake, in exactly the same manner as was observed for TC1 and other so-called rotor probes studied in Ref. [5]. This is true in spite of the fact that DANS is considered to be a classic solvatochromatic probe and is not generally described as being a rotor probe, the latter of which has been long understood for decades [5,9,24,26,27] to yield a significant sensitivity of fluorescence intensity to local mobility (which is impacted by water sorption in polymers). Second, because of the fact that DANS has a much greater solvatochromatic character than TC1, the change in fluorescence intensity ratio that is used to characterize the change in spectral shape accompanying water sorption is also greater for the DANS probe. A comparison of Figs. 3 and 4(b) reveals that, on a percentage basis, the change in intensity ratio observed in going from a dry PVAc film to a film at equilibrium water sorption using the DANS probe is nearly twice that obtained using the TC1 probe. Thus, the stronger solvatochromatic nature of the DANS probe results in DANS being a more precise self-referencing sensor for water sorption than TC1.

The effect of water sorption was also studied in PVAc films containing trace levels of pyrene fluorescence probes. The ratio of the fluorescence intensity of the first vibronic band, I(372 nm), to the fluorescence intensity of the third vibronic band, I(383 nm), is known to be highly sensitive to local polarity, with the ratio increasing substantially with increasing polarity [45–49]. The fluorescence emission intensity ratio I(372 nm)/I(383 nm) observed in a dry PVAc film and a PVAc film at equilibrium water sorption level is 1.18 and 1.23, respectively. In contrast to the changes observed with the TC1 and DANS probes, relatively subtle changes are observed in the pyrene spectra. In the case of water sorption in PVAc, this intensity ratio increases less than 5% in going from a dry state to a condition of equilibrium sorption compared to 18% for TC1 (Fig. 3) and 34% for DANS (Fig. 4(b)). Thus, while pyrene can be used as a self-referencing fluorescence sensor for water sorption in PVAc, the level of its sensitivity, as revealed by its change in intensity ratio, is less than one-third that of the TC1 probe and less than one-sixth that of the DANS probe. Thus, the investigations of the TC1, DANS, and pyrene probes described above were successful in revealing the relative abilities of these chromophores to be employed as self-referencing sensors of water sorption in polymer films at 22 °C.

An important issue that has not yet been considered in the research literature is whether fluorescence sensors for quantitative sorption measurement in polymers can yield data that are independent of temperature over a reasonable range of use temperatures. Clearly, if only a relative change in fluorescence intensity at a single wavelength is used to characterize sorption, such data would be a strong function of the temperature at which the data were gathered, because the fluorescence intensities of TC1, DANS, and pyrene probes in dry polymer films are well-known to be significant functions of temperature [28,29,35,57–59]. Fig. 5 compares the temperature dependence of the shapes of the fluorescence spectra for TC1 and DANS in dry PVAc films. Although both TC1 and DANS have temperature-dependent intensities in PVAc, Fig. 5 reveals that their spectral shapes are essentially independent of temperature. Other experiments employing TC1 and DANS in non-polar polymers such as PS (neat PS, no sorbate) also confirm that over similar temperature ranges their fluorescence intensities are temperature dependent as expected while their spectral shapes are temperature independent. Further demonstrating

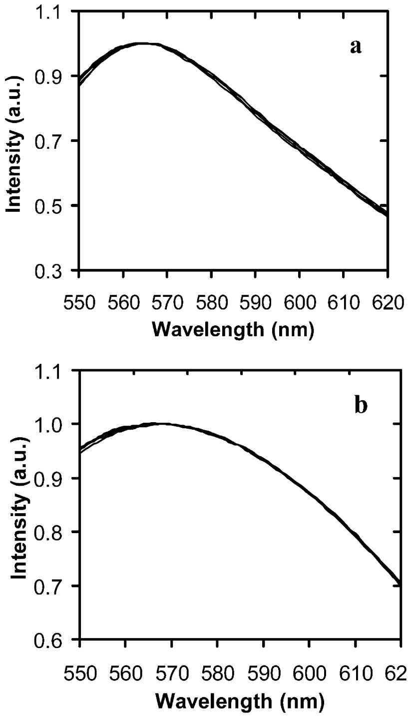

Fig. 5. Emission spectra as a function of temperature for 50 μm PVAc films doped with (a) 0.02 wt% TC1 at 22, 27, 32 and 37 °C (from bottom to top) and (b) 0.02 wt% DANS at 25, 30, 35, 40, 45 and 50 °C (from bottom to top). All spectra were normalized to their maxima.

this fact, Fig. 6 compares the temperature dependence of the shape of the fluorescence spectrum for DANS in a PVAc film that was saturated with water (i.e., contains an equilibrium amount, ~4.5 wt%) at 23 °C. For this experiment, an emission spectrum was taken at 23 °C and then the temperature was increased to 33 °C and a second emission spectrum was taken after several minutes of thermal equilibration. (The film is sufficiently thick, ~500 μm, that significant desorption does not occur during the time required for taking the fluorescence measurements and thermal equilibration.) Fig. 6 shows that the spectral shape of DANS emission in PVAc is essentially independent of temperature even in the presence of water of levels at or near their equilibrium value. This fact reiterates the success of DANS as a self-referencing sensor of water sorption where the intensity ratio (or spectral shape) is not affected significantly by temperature but only by the water content of the sorbate regardless of the kinetics or equilibrium sorption levels.

3.2. Chromophore-labeled polymer as a sorption sensor in single-layer and multi-layer films

The ability to covalently attach fluorescence chromophores to monomers allows for the possibility to produce chromophore-labeled polymers via copolymerization. Such polymers may prove useful in quantitatively monitoring the level of water sorption within a specific layer of a multilayer polymer film or coating without concern for the diffusion of chromophores between polymer layers. Additionally, the covalent attachment of the chromophores to the polymer may prove useful in increasing the fluorescence quantum yield or intensity, due to a reduction in non-radiative decay from the chromophore excited state associated with reduced vibrational mobility accompanying the covalent attachment.

Fig. 7 compares the fluorescence spectra of a TC1-labeled PMMA film with a PMMA film doped with TC1. The two films had identical optical densities of 0.060 at the excitation wavelength of 525 nm, meaning that similar fluorescence intensities should be obtained if the labeled and doped chromophores exhibited identical quantum yields. However, as is evident from Fig. 7, the TC1-labeled PMMA film exhibits much higher fluorescence intensity than the doped film, consistent with the notion that freely doped chromophores should have a greater ability to dissipate their excited state energy through non-radiative means. Additionally, the TC1-labeled film exhibits a fluorescence spectrum that is blue-shifted relative to the doped film. This indicates that the covalent attachment of the TC1 chromophore onto a methacrylate repeat unit yields, on average, a less polar and more rigid environment for the TC1 chromophore than is experienced by TC1 chromophores that are freely doped into the polymer. (Although covalent attachment of DANS to polymer was not attempted here, DANS-labeled-methacrylate-based monomers can be synthesized and copolymerized with other monomers [60]. The authors believe that attachment of DANS to polymer would result in similar levels of sensitivity as seen in DANS doped systems as long as a similar level of intramolecular charge-transfer character is retained. The TC1 labeled methacrylate case discussed here serves as a demonstration that, in general, if labeled monomers/polymers are synthesized appropriately, they allow unique studies that would not otherwise be possible with doped chromophores.)

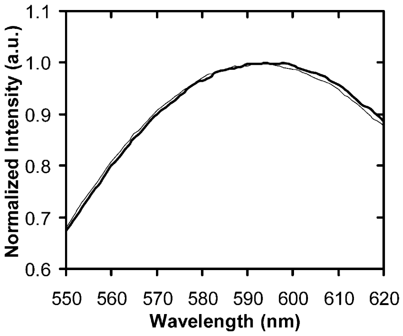

Fig. 6. Emission spectra as a function of temperature for a 500 μm PVAc film doped with 0.02 wt% DANS at 23 °C (light line) and 33 °C (dark line). Prior to taking fluorescence measurements the film was saturated to equilibrium (~4.5 wt% water) at 23 °C. All spectra were normalized to their maxima.

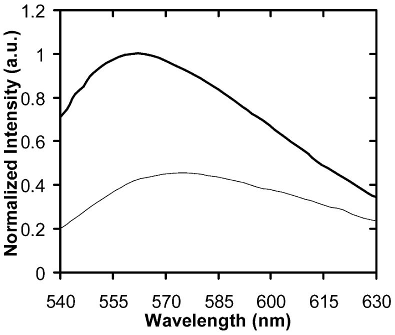

Fig. 7. Fluorescence emission spectra for PMMA doped with TC1 (light line) and a TC1-labeled PMMA (dark line) film. Spectra are normalized with respect to the maximum intensity of the TC1-labeled PMMA film. Both films have absorbances of 0.06 at the excitation wavelength.

Fig. 8 indicates that both TC1-doped and TC1-labeled PMMA films yield excellent agreement between relative intensity change and relative mass uptake during water sorption experiments. Additionally, there is excellent agreement between the experimental data and the expectations for the time dependence of relative change in fluorescence or mass uptake based on Fickian diffusion of the sorbate into the polymer. In the case of the TC1-doped PMMA film, the best-fit Fickian description of the fluorescence and gravimetric data yield an average diffusion coefficient of 8.5×10^{-9} cm^2/s, close to the best-fit value for the average diffusion coefficient of 1.2×10^{-8} cm^2/s obtained with the TC1-labeled PMMA films. Further agreement is observed in the relative change of fluorescence

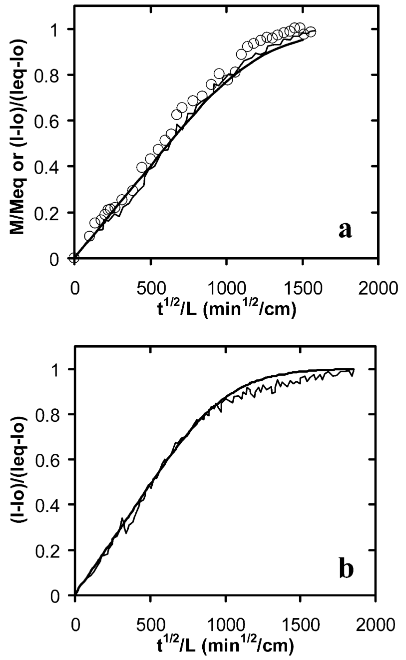

Fig. 8. (a) Relative fluorescence intensity changes (thin solid line) and fractional mass uptake (open circles, measured gravimetrically) during water sorption in a 100 μm-thick PMMA film doped with TC1. The dark smooth line is the best-fit Fickian diffusion prediction to the fluorescence data. (b) Water sorption in a 79 μm TC1-labeled PMMA film. Relative fluorescence intensity changes (thin line) and the best-fit Fickian diffusion prediction (smooth dark line) to the fluorescence data. Emission intensity was measured at 580 nm for both samples.

intensity at 580 nm in the two systems upon going from a dry film to a film at equilibrium water sorption (2 wt%) at room temperature, with a 20% reduction in fluorescence intensity in the labeled system and a 21% reduction in fluorescence intensity in the doped system. These results indicate that there is no deleterious effect to fluorescence sensor capabilities in cases where the TC1 chromophore is covalently attached to the polymer.

Taking advantage of the TC1-labeled PMMA, sorption studies were undertaken in a tri-layer film composed of a PVAc underlayer (100 μm thick), a TC1-labeled PMMA middle layer (80 μm thick), and a PVAc topcoat (100 μm thick). Fig. 9 shows the change in relative fluorescence intensity as a function of the parameter $t^{1/2}/L$, where L was taken as 80 μm, the thickness of the TC1-labeled layer. It is immediately apparent that there is an induction period of ~16 min (~500 min$^{1/2}$/cm in Fig. 9) at early times where the fluorescence intensity is independent of diffusion time. The induction period reflects the time required for water to diffuse through the PVAc topcoat before it penetrates the TC1-labeled PMMA middle layer. Using the Fickian diffusion model, the idealized induction time, t_{ind}, is equal to $L^2/6D$, where L is the layer thickness and D is the average diffusion coefficient [55]. Taking $L = 100$ μm as the thickness of the PVAc topcoat and $D = 3 \times 10^{-8}$ cm^2/s for the average diffusion coefficient of water in the PVAc topcoat, a theoretical value of $t_{\mathrm{ind}} = 9.3$ min is obtained. The underestimation of the theoretical value indicates that either accumulation of water at the interface may occur before penetration into the PMMA layer due to differing average diffusion coefficients of the PMMA and PVAc layers or that a finite amount of water must diffuse into the TC1 labeled PMMA layer before the onset of the sensitivity of TC1 to the presence of the water occurs or both. Nonetheless, water penetration into the TC1 labeled intermediate layer the fluorescence intensity decreases sharply and can be followed easily through changes in relative fluorescence intensity. It should be noted that the value of I_{eq} was approximated from the value expected from a single layer TC1-labeled PMMA layer. The tri-layer film shows a 15% decrease in fluorescence intensity of TC1-labeled PMMA during the time frame of the measurement indicating the PMMA layer is nearly 75% saturated (based on that observed for a similar single layer film). At later times (~110 min equating to ~1300 min$^{1/2}$/cm in Fig. 9), the slope of the relative fluorescence intensity changes, indicating breakthrough of water sorption into the PVAc underlayer.

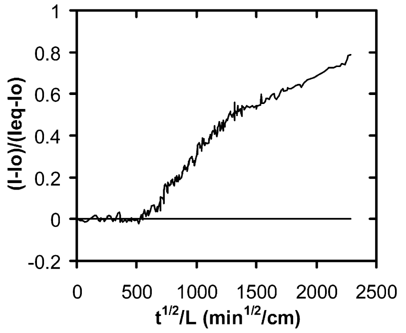

Fig. 9. Relative fluorescence intensity changes during water sorption of a tri-layer coating composed of a 100 μm PVAc topcoat, 80 μm TC1-labeled PMMA intermediate layer and a 100 μm PVAc underlayer.

Water sorption was not followed to equilibrium because the layers eventually began to delaminate from each other at the interfaces. This process is easily detected by a large increase in fluorescence intensity (>50%) when the top PVAc layer no longer adheres and departs from the tri-layer film. This is suggestive of the possibility of using fluorescence techniques to monitor delamination.

3.3. Comparison of the monitoring of sorption and of drying by fluorescence sensors

Fluorescence can provide a quantitative means for monitoring desorption as well as sorption. Shown in Fig. 10 is water sorption and desorption in a polyurethane coating doped with TC1. The shape of the emission spectrum in polyurethane is very similar to that in PVAc, but its peak is slightly blue shifted. The absolute fluorescence intensity decreases by 11.5% upon water sorption to an equilibrium level of 1.0 wt% water based on dry polymer (comparable to that for TC1 in PVAc, ~55% intensity decrease for ~4.5 wt% water uptake). It

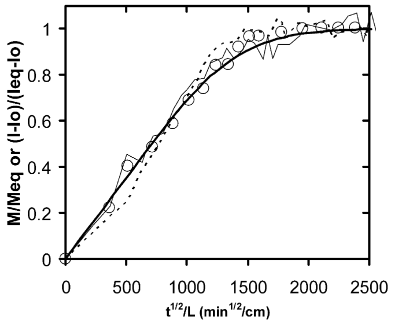

Fig. 10. Relative fluorescence intensity changes at 580 nm during water sorption (thin dashed line) and desorption (thin solid line) with the best fit Fickian model prediction (smooth dark line, fit to the fluorescence sorption data) in a polyurethane coating doped with TC1. Also shown are gravimetrimetric measurements (circles) taken during sorption and desorption.

should be noted that the apparent substantial noise in the polyurethane data results from the fact that the small changes in absolute fluorescence intensity reflect the small amounts of water sorbed for this system. Relative intensity changes were observed to be one-to-one with mass uptake. Diffusion coefficients determined from the best fits of the Fickian model to fluorescence data and gravimetric data are in good agreement with values of 6.5×10^{-9} and 6.1×10^{-9} cm^2/s, respectively, determined in the manner shown in Fig. 2(a). Desorption exhibits nearly exactly the same kinetics as sorption, as expected for these complementary processes.

The fluorescence techniques for monitoring water sorption/desorption described above can be easily applied to appropriate polymer/organic sorbate systems ('appropriate' choices are discussed in Section 3.4). An example is given in Fig. 11, in which fluorescence intensity is used to monitor the drying of MEK from a solution cast PVAc film using TC1. The film was solution cast from an MEK solution containing both PVAc and TC1 such that the drying process that is monitored is the MEK evaporating from the film after it has been cast. Relative fluorescence intensity changes correspond one-to-one with mass loss for this drying process. An increase in fluorescence intensity of 92% corresponded to a loss of mass of 7.0 wt% due to solvent evaporation (the last 7.0 wt% before the film is completely dry). The sensitivity based on absolute intensity of TC1 to MEK in PVAc (13.1% intensity change/wt% MEK desorbed) is comparable to that of the absolute intensity of TC1 to water in PVAc (12.4% intensity change/wt% water sorbed). Future studies focused on more fully understanding the origin of this sensitivity and how it is impacted by the details of both the fluorescence chromophore and the diluent are warranted.

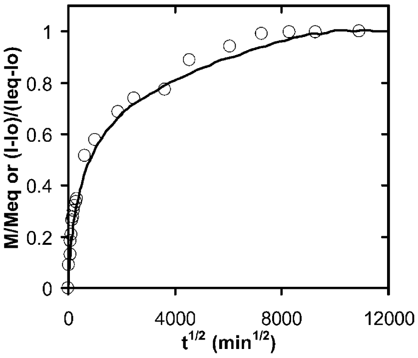

Fig. 11. Relative fluorescence intensity changes (line) and relative solvent mass loss (circles) during drying of MEK from a solution cast PVAc film (22 μm dry thickness) doped with TC1.

It may seem remarkable that changes in fluorescence intensity of TC1 effectively follow the drying process of a polymer film involving desorption of an organic, especially as the kinetics of the processes involved with drying a polymer film are dictated by a complex function of polymer flow, convective heating, evaporation, evaporative cooling and certain mass transfer resistances [61]. Fig. 11 indicates that, at least during the last 5–10 wt% of evaporation, fluorescence can provide a simple means of monitoring these processes non-destructively.

3.4. General guidelines for monitoring sorption and drying via fluorescence probes

Many successes of fluorescence monitoring of sorption and drying kinetics have been described above. However, these cases were for systems with relatively low sorbate content (< 10 wt%). At substantially higher sorbate content, fluorescence monitoring of sorbate levels may prove inappropriate. For example, methanol is sorbed into PMMA to an equilibrium level of 22 wt% at room temperature. The PMMA/methanol system is known to follow Case II diffusion in which solvent penetrates the outermost polymer layer and begins swelling it to the saturation point while simultaneously proceeding to the next layer [62]. As a result, there is a solvent front that advances at constant velocity through the film. This velocity is a function of the relaxation dynamics in the polymer as the solvent swells the film. During sorption experiments using TC1-labeled PMMA, it is observed that the TC1 fluorescence intensity reaches a constant value nearly three times faster than the gravimetric mass uptake reaches saturation. In addition, relative fluorescence intensity changes are not observed to be a one-to-one ratio with mass uptake for this system. Given the nature of rotor probes it is evident that there exists some finite sorbate content at which the average local probe mobility has been increased to a level greater than that which significantly restricts rotations of portions of the fluorescence dye. When this occurs, sensitivity to local sorbate content is reduced, and a simple relationship between mass uptake and fluorescence changes may not exist. In general, the one-to-one relationship of mass uptake with relative fluorescence changes (ratio or intensity) is not trivial and should never be assumed to be universally applicable. Similar limitations may be expected for other non-rotor type fluorescence sensors of sorbate levels, depending on what local property allows for their sensitivity to local sorbate content.

4. Conclusions

Several fluorescence dyes, including TC1, DANS and pyrene, have been examined as self-referencing sensors of water sorption in polymer films that have limited solubility to water. These dyes provide sensitivity to water sorption via fluorescence intensity and intensity ratio. Various levels of sensitivity of dye fluorescence to water content in PVAc were observed. When employing a fluorescence intensity ratio as the fluorescence measurable, DANS proved to be the most sensitive of the three dyes, followed by TC1 and pyrene. The enhanced sensitivity exhibited by DANS compared to TC1 can be attributed to its much greater solvatochromatic character (i.e., greater changes in spectral shape during sorption) compared with TC1. It was found that DANS has nearly temperature-independent spectral shapes (and thus intensity ratios) in dry and 'wet' PVAc over a reasonable range of use temperatures indicating that it can yield a robust, self-referencing measure of sorbate level without regard to temperature. This discovery removes a major obstacle to the practical application of fluorescence sensors as in most cases fluorescence intensity, which is a common measurable in fluorescence sensor studies, is a strong function of temperature while fluorescence spectral shape of solvatochromatic dyes such as DANS is not. As was shown in the case of TC1-labeled PMMA, such dyes may also be adapted successfully to the study of multilayer coatings and films without loss of sensitivity, as long as the fluorescence dye is covalently attached to the polymer of interest. Furthermore, the ability of fluorescence probes to monitor the kinetics of water sorption and drying was demonstrated for a polyurethane film, showing that these complementary processes are amenable to the use of fluorescence techniques. Finally, these probes were shown to be applicable in characterizing levels of organic sorbates such as MEK in polymers, as long as the sorbate level is sufficiently low that the change in the fluorescence measurable remains a significant function of sorbate level.

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