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Polyurethane-acrylate based films as humidity sensors

Paula Bosch, Almudena Fernández, Enrique F. Salvador, Teresa Corrales, Fernando Catalina, Carmen Peinado *

Instituto de Ciencia y Tecnología de Polímeros, Consejo Superior de Investigaciones Científicas, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

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Abstract

Fluorescence spectroscopy, together with a conventional gravimetric method, were employed to study the mechanism and kinetics of water diffusion in UV-cured polyurethane-acrylate based adhesive films doped with organic fluorescent sensors. The diffusion of water through the films followed Fick's law during almost the whole mass sorption curve. Whilst the fluorescence data showed that boundary conditions are more complex and Fickian behaviour is only observed after different periods, depending on the molar volume of the fluorescent probe and the adhesive composition. The influence of hydrophilic monomers is discussed. Good correlation between diffusion coefficients by both methods is obtained in the range where water uptake is diffusion controlled.

The fluorescence of the studied probes or labels in these films shows high sensitivity to humidity, good long-term stability and fast response time. Therefore, it appears that these doped films can be used as efficient humidity sensors.

Keywords: Fluorescence; Polymeric humidity sensors; Water-uptake

1. Introduction

Water sorption is a well-known problem which causes deterioration of the final properties of a polymer material and thus, it is related to its useful lifetime [1–3]. UV-curable adhesives have replaced traditional methods such as soldering and laser bonding for the assembly of optical components. In these applications the sealant must have excellent moisture-resistant adhesive-strength and a small permeability coefficient of water to prevent the incursion of moisture into the casing. Great efforts have been undertaken to follow the effect of moisture in polymers and different techniques have been used with two purposes: (i) determine the content of water and (ii) evaluate the mechanical properties of the material after exposure to humid environments [4,5]. Water content has been traditionally determined gravimetrically and recently, the self-diffusion coefficients of water in different polymeric matrices have been measured by using the pulsegradient spin echo NMR technique [6], near IR [7] and by using dielectric techniques [8]. The environmental relative humidity affects solvatochromic parameters and in this respect, hydrogen bond acidities and $E_T(30)$ values of the UV–vis absorption spectra of polymers containing Reichardt's dye has been proposed for application in sensor technology. In an attempt to develop optical sensors, fluorescent probes have been added to polymers to be used as humidity sensors [9–15].

New materials containing fluorescent probes have been widely spread due to the simplicity of identification method. Moreover, fluorescent probes incorporated to the polymer matrix (as additives or labels) have allowed to studying processes such as blending, swelling, thermal- and UV-curing [16–18], latex film formation [19] and gelation phenomenon [20]. Fluorescence spectroscopy has been recognized as a powerful analytical technique because of its sensitivity, selectivity and non-destructive characteristics. In addition, the advantage of fluorescence sensing of humidity over the above-mentioned methods is the unique ability of this technique to be followed in situ and in real time. These features are essential for most applications in these technologies. The performance of this method depends on the selection of adequate fluorescent probes.

Water acts as a softening agent increasing the space between polymer chains and producing a plasticizing effect. This behaviour favours the mobility of molecules incorporated to the polymer network due to the free volume increase. In the case of mobility-sensitive or rigidochromic fluorescent

* Corresponding author. Tel.: +34 91 562 29 00; fax: +34 91 564 48 53.
E-mail address: cpeinado@ictp.csic.es (C. Peinado).

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probes there are two possible pathways for deactivation of their singlet excited state: (i) non-radiative internal conversion that involves bond rotation and (ii) fluorescence emission. In general, the presence of water increases the mobility in the polymer matrix decreasing fluorescence emission of the probes incorporated to the solid material film.

Here, we have selected nine different fluorescent probes to monitor water uptake of UV-cured acrylic adhesive films by fluorescence sensing (Fig. 1). Miller has previously reported the use of 4-tricyanovinyl-[*N*-(2-hydroxyethyl)-*N*-ethyl]aniline for quantitative monitoring of water uptake in polymeric coatings [12]. Moreover, 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DMANS) has been shown to serve as self-referencing sensor of water sorption in polyvinylacetate [21]. Different fluorescence parameters were evaluated: wavelength shift, intensity (ratio of intensities at two different wavelengths) and width of the band at half-height. We report here the measurement of diffusion coefficients of water in polymer films by a simple method based on fluorescence technique.

2. Experimental

2.1. Materials

The adhesive formulations were provided by Loctite Corporation. Loctite 350 (L350) is a UV-curable acrylic adhesive containing a photoinitiator while Loctite 312 (L312) requires a further addition of an activator for UV-curing. Both adhesive formulations are viscous systems based on a polyurethane methacrylic binder and a mixture of acrylic monomers as reactive diluents. L312 contains 50–55 wt% of the resin and 35 wt% of hydroxypropyl methacrylate, acrylic acid (5–10 wt%), a substituted silane (0.1–1 wt%) and tributylamine (0.1–1 wt%), whereas, L350 contains 35–40 wt% of the resin and 15–20 wt% of hydroxypropyl methacrylate, 15–20 wt% of lauryl methacrylate (LMA), methyl methacrylate (15 wt%) and acrylic acid (5 wt%).

The photoinitiator Irgacure 651, from Ciba Speciality Chemicals, (2,2-dimethoxy-1,2-diphenylethan-1-one, DMPA) and solvents (analytical grade from Merck) were used without further purification.

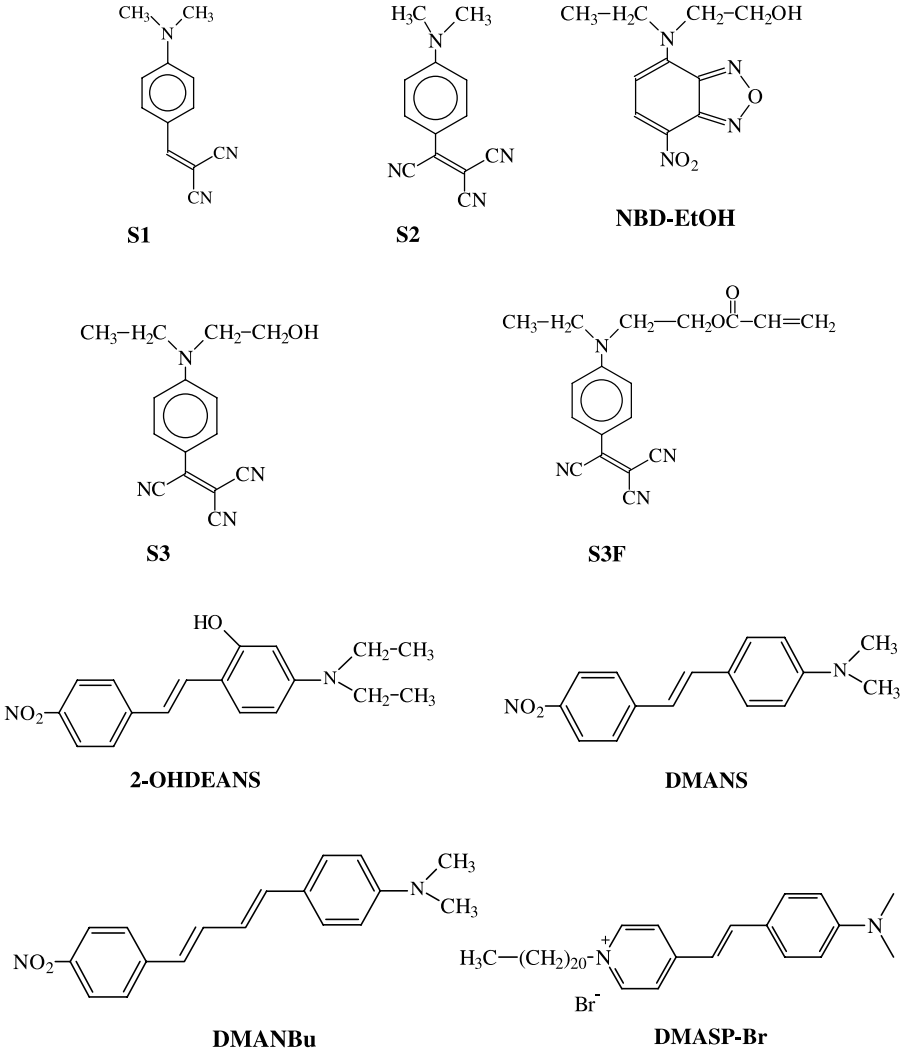

Fig. 1. Structures and abbreviations of studied fluorescence probes.

Fluorescent probes were prepared by the synthesis described previously in the literature. The structure and names of the fluorescent probes is shown in Fig. 1.

2.2. Films preparation

Homogeneous mixtures of adhesive formulation and fluorescent probe (0.03% w/w) were cast onto glass slides covered with polyethylene films using spacers of PTFE (1 mm) . For UV-curing of L312, the commercial photoinitiator DMPA was added to the mixture (1% w/w), whereas L350 contained also DMPA as photoinitiator. Films were cured in a Sun test irradiation system with polychromatic light irradiation under a cut-off filter of 313 nm, allowing to reach limiting conversion. To obtain comparative results the physical state should be the same and pendulum hardness tests were carried out to assure the same degree of cure of all the specimens. Moreover, the dimensions ($3\times1\times0.1$ cm^3) were kept constant for all the specimens. Films were dried at 40 °C until constant weight. A reference fluorescence spectrum was recorded for each sample immediately after curing.

2.3. Water uptake

The water uptake was determined gravimetrically and fluorimetrically during immersion and under different percentages of relative humidity.

2.3.1. Sample swelling

Two methods were employed to monitor water sorption in the cured films: (i) after UV-curing, the samples were immersed in distilled water in quartz cells of 1 cm path length and fluorescence spectra were recorded in situ over the time of measurement. (ii) The samples were placed in a container filled with distilled water and kept at constant temperature (20 °C) in a thermostatically controlled oven. The samples were removed at different times, dried the surface with paper and weighted. They were then replaced in the containers, and this experimental procedure was carried out in less than 3 min. This process was continued until equilibrium swelling was attained (2 days). The measurements of weight were accurate up to 0.0001 g. The samples were then transferred to the oven maintained at 20 °C and a similar process to that above repeated during desorption until the sample weight reached equilibrium.

Water volume was, at least, 4 ml/cm^2 of the total surface of the specimen to avoid the concentration of extracted products by water.

2.3.2. Water vapor up-take

The desired relative humidity of 92% was obtained in the atmosphere of a saturated solution of $10H_2O$ sodium carbonate. Films were placed in closed cells and after reaching a 92% relative humidity, they were weighted at regular intervals and fluorescence was measured. Then, the samples were returned to the cells in less than 3 min.

2.4. Diffusion coefficients

According to Fick's law, the equation for diffusion in one-dimension, when the diffusion coefficient D is constant, is expressed as Eq. (1):

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D(c)\frac{\partial c}{\partial x}\right) = D\frac{\partial^2 c}{\partial x^2} \tag{1}$$

where c is the concentration of diffusing species at time t. For a plane sheet geometry and keeping constant the initial concentration of water, the solution of the Fick equation is given by Eq. (2):

$$\frac{M-M_0}{M_{eq}-M_0} = 1-\sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{4L^2}\right) \tag{2}$$

where L is the thickness of the specimen and $(M-M_0)$ and $(M_{eq}-M_0)$ are the masses of water sorbed or desorbed at times t and ∞, respectively. Eq. (2) is reduced to the well-known Stefan's approximation [22] when $(M-M_0)/(M_{eq}-M_0)$ is small enough (<0.6):

$$\frac{M-M_0}{M_{eq}-M_0} = \frac{2}{L}\left(\frac{Dt}{\pi}\right)^{1/2} \tag{3}$$

The mechanism of transport and water diffusion was studied by analysing the empirical Eq. (4):

$$\log\left[\frac{M-M_0}{M_{eq}-M_0}\right] = \log k + n\log t \tag{4}$$

where k depends on the interactions between the polymer and the solvent and n indicates the type of mechanism of transport [23]. The mechanism of transport follows Fickian's law when the value of n is 0.5, indicating that the diffusion rate of water molecules is slower than that of the polymer segment relaxation processes.

Several authors have found a one-to-one relationship of the normalized change in fluorescence intensity relative to mass up-take [21]. The diffusion coefficient, D, can be calculated by applying the simplified Fick model using the following equation [24]:

$$\frac{M-M_0}{M_{eq}-M_0} = \frac{I-I_0}{I_{eq}-I_0} = \frac{2}{L}\left(\frac{Dt}{\pi}\right)^{1/2} \tag{5}$$

where L is film thickness (divided by 2 if two faces of the sample are accessible to the water penetration), M and I are mass and fluorescence property at a given time, and the subscripts 0 and eq denote measurements at initial time and in equilibrium, respectively.

The experimental data of water content, measured gravimetrically (as $M-M_0/M_{eq}-M_0$), and fluorescence changes, measured as $I-I_0/I_{eq}-I_0$, were plotted versus time and diffusion coefficients were calculated from the slopes.

2.5. General techniques

Gravimetric measurements: the sample mass was recorded by an analytical balance with less than 0.0001 g of error.

UV spectra were recorded by means of a Shimadzu UV-265-FS spectrophotometer.

Fluorescence spectra were recorded on a Perkin–Elmer LS-50B spectrofluorimeter. Excitation wavelengths were selected at the maximum absorption of the fluorescence probe in the cured adhesive. Fluorescence emission measurements have been found to be strongly dependent on the characteristics of the surface of the sample. Special efforts were undertaken for obtaining homogeneous surfaces in samples and specimens with wrinkled surfaces were rejected.

Fluorescence emission spectra were recorded during absorption of water by the adhesive films. Moreover, the intensity of the fluorescence excitation spectra of the probes was followed under the experimental conditions to disregard photodegradation of the fluorescent probe with cumulative exposure to the instrument excitation light. Photodegradation was not observed for any probe.

3. Results and discussion

Water uptake in strips of fluorescent doped polymeric materials have been studied under immersion and in humid atmosphere in order to reproduce the two types of environment in which a polymeric sensor could be useful.

Diffusion of liquids through polymers is a complex process whose quantitative analysis is not trivial and still remains subject to debate [25]. If it is assumed that there are two regions, i.e. less concentrated region near the surface separates itself from the high concentrated region by a boundary, which moves during the swelling (or drying) process. Then the behaviour may be explained by considering a model in which diffusion occurs in two regions separated by a moving interface. However, water absorption is usually discussed in terms of Fickian and swelling mechanism [21,26,27]. Fickian diffusion in polymers is an ideal case of penetrant transport, corresponding to free diffusion of penetrant without interference of polymer chain rearrangement (i.e. structural relaxation). Whether deviations from ideal Fickian behaviour occur depends on the rate of relaxation compared to that of the diffusion. If polymer relaxation is faster than penetrant diffusion, diffusion is followed by instantaneous response of the system, resulting in Fickian behaviour. Discrimination between Fickian or not Fickian behaviour is usually based on the appearance of kinetic absorption curves.

Mass uptake of a polymer film of thickness L is usually obtained as function of time during the transient regimen of liquid sorption at constant solvent activity. Analysis of experimental data is based on solving Fick's second equation according to several methods that have been reviewed by Crank [22].

Although, the doped films are clearly heterogeneous in a microscopic sense, they may be considered homogeneous from a macroscopic point of view in order to study water absorption under different conditions. As a typical example, the mass increase versus time up to equilibrium, during water immersion at 20 °C of a L350 sample, is shown in Fig. 2. The samples absorbed water very rapidly during the first stage (0–18 h) reaching a certain value, the saturation point, where no more water is absorbed and the water content remains constant in the specimens (~2.3 wt%). The swelling behaviour follows the Fickian diffusion model and a coefficient $n=0.55$ was obtained from the plot of $\log(M-M_0/M_{eq}-M_0)$ versus log time (Fig. 3).

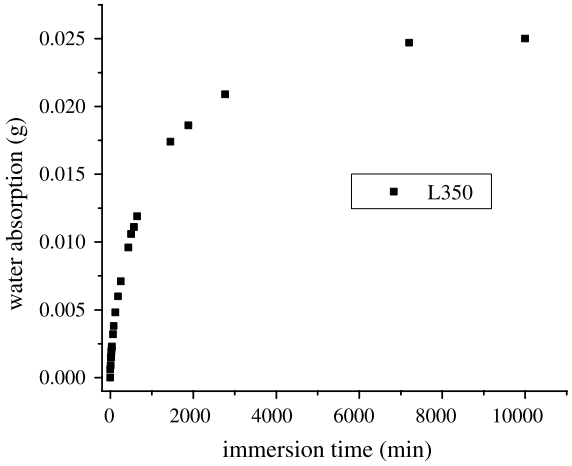

Fig. 2. Plot of mass increase versus time of UV-cured Loctite350 in water immersion at 20 °C. Thickness of film: 1 mm.

Similar behaviour is observed for L312, although a higher diffusion rate and higher amount of water was absorbed than those for L350, as a result of a higher hydrophilicity of the polymer. In this sense, it should be remarked that the composition of both formulations was similar, but L312 contained a higher amount of hydroxypropyl methacrylate (hydrophilic monomer) whether L350 had lauryl methacrylate (hydrophobic monomer). Hodge et al. [28] suggested that polar groups facilitate the water sorption equilibrium, both by the plasticization effects and by the localized binding in itself. Other hypothesis to explain the different behaviour in water

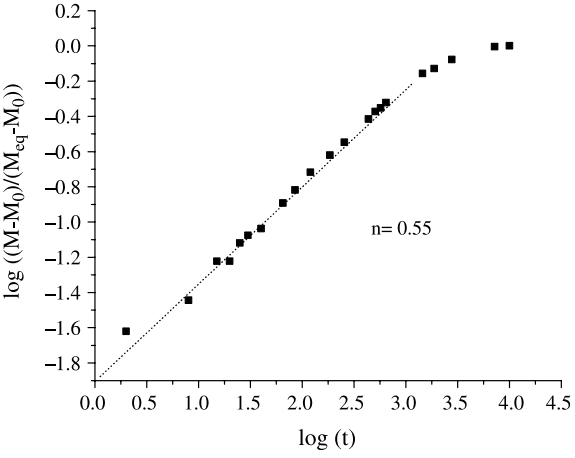

Fig. 3. Fickian model plot. Thickness of L350 film: 1 mm.

sorption of L350 and L312 refers to the free volume, which should not be related to pores. Below the glass transition temperature free volume in polymer is frozen and as far as monomer composition of the adhesive formulation may change the glass transition temperature, it becomes a critical factor. In this regard, the adhesive L312 gives a network with a final degree of conversion lower than that of the L350, involving a higher free volume fraction [29].

The diffusion coefficient is the most important parameter of the Fick's model as it shows the ability of the solvent molecules to penetrate inside the polymer matrix. Diffusion coefficients were calculated from the slope of the linear part of the plot of $(M-M_0)/(M_{eq}-M_0)$ versus $(\text{time})^{1/2}$ and the obtained values are compiled in Table 1.

It has been assumed that the total apparent diffusivity of a thin specimen is the same as the diffusivity through the thickness (single-phase diffusion model), neglecting any edge effect. Actually, this assumption may not be valid. In that case, the determined diffusion coefficients may only be considered as an average value.

The fluorescence emission intensity decreases during water sorption in the UV-cured adhesive films for all the probes studied. Fig. 4(a) and (b) illustrate the changes of the fluorescence spectra of DMANBu due to the swelling of L350 by water and S3 in L312, respectively. As expected, the mobility of fluorescent probes increases in the adhesives swollen by water and thus, the non-radiative processes involving bond rotation are favoured and fluorescence emission diminishes.

The fluorescent probes S2 and S3 were used for monitoring water diffusion in epoxy resins [12], where they act as a good sensors of humidity, although their application in acrylic systems, which absorb less quantity of water, were not reported. Moreover, a novel fluorescent probe S3F having an acrylate moiety was evaluated as humidity sensor. As polymerization takes place, fluorescent probe is covalently linked to the polymer matrix and therefore, the possibility of migration is excluded by using this fluorescent label.

The area or the intensity at the maximum emission wavelength were chosen as fluorescence parameters to follow the process of water uptake in the acrylic adhesive films. The probes show good sensitivity as it is observed in Fig. 5 during the water uptake of L350 and L312. In the first stages of the process, the fluorescence decays rapidly to reach equilibrium where immersion of the samples in water during longer times does not induce any fluorescence changes. However, a different behaviour can be observed depending on the probe and

Table 1
Diffusion coefficient, mass of water absorbed at the equilibrium and fitting parameter n to the Fickian model

Sample	Immersion in water at 20 °C		
	Mass at equil. (%)	n	$D\times10^{12}$ (m^2/s)
L350	2.4	0.55	1.1 ± 0.3
L312	7.2	0.56	4.7 ± 0.2

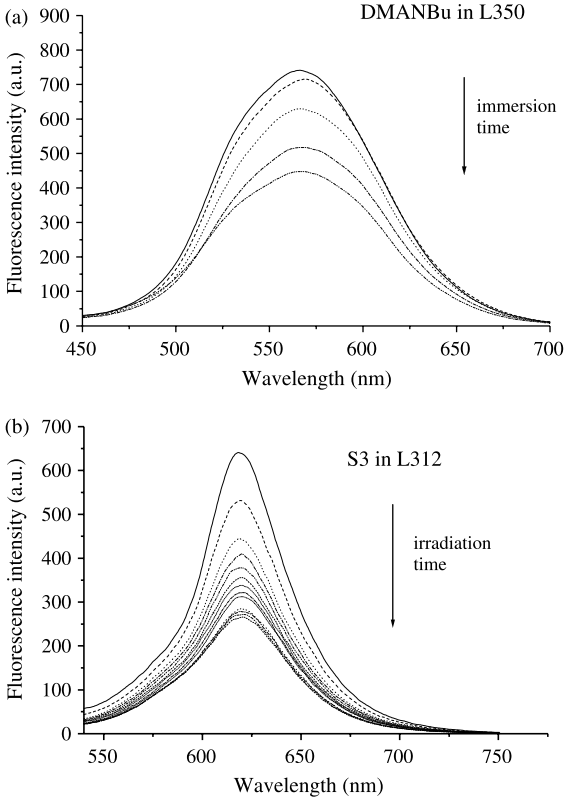

Fig. 4. Fluorescence spectra of DMANBu in Loctite350 (a) and SF3 in L312 (b) during water immersion at 20 °C.

the composition of the acrylate based film. The difference between sensitivities of fluorescence probes may originate from their quenching rate constants and fluorescence life times.

Comparing the different adhesives, fluorescence intensity decreases faster in L312 than in L350 and the change of fluorescence at the equilibrium is lower for the latter. These data are in agreement with gravimetric measurements that show lower absorption rate and lower mass of absorbed water at the equilibrium for L350. The highest sensitivity during water absorption in L350 is shown by DMANS, together with the NBD derivative, and the lowest by the fluorescent label S3F. This fluorescent probe, possessing the same fluorophore than S3, has a reactive acrylate moiety to be anchored to the formed network during the irradiation. In general, lower emission intensity is observed for acrylic monomers containing an electron-donating chromophore than that of the saturated analogue. This phenomenon, termed as fluorescence structural self-quenching effect (SSQE) [30]. However, SSQE was not observed for S3F, due to the ethylene chain spacer between the chromophore and the acrylic double bond, and thus, behaves as an environment-sensitive fluorescent probe. As those fluorescent probes are sensitive to the changes in their microenvironment a different behaviour can be expected depending on their mobility, which is restricted as the polymerization proceeds in the case of S3F. Therefore, the reduced sensitivity of S3F seems to be related to the covalent attachment of the probe to the polymer matrix. Similar results were obtained with

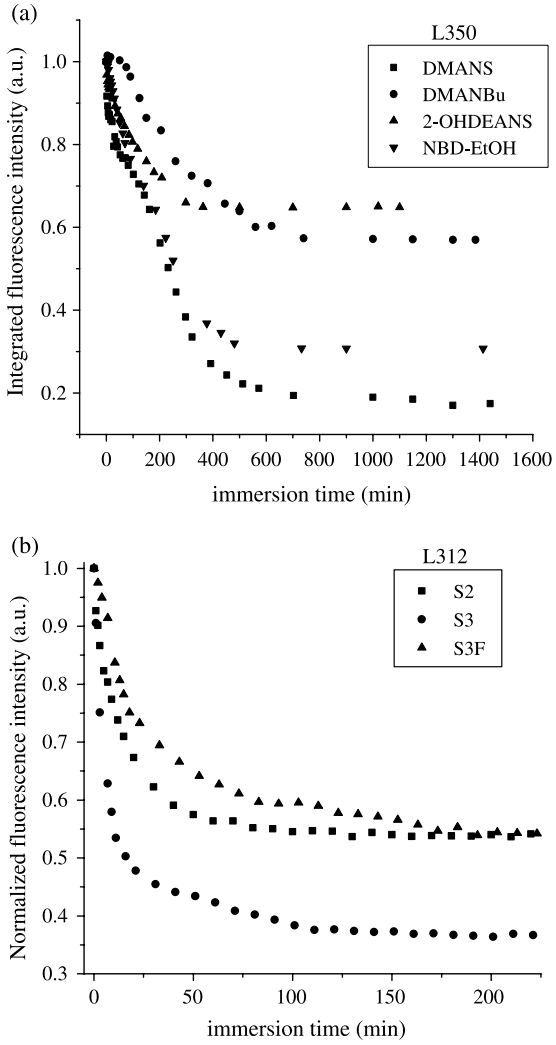

Fig. 5. Fluorescence intensity changes during: (a) the swelling of L350 immersed in water (fluorescent probe: DMANS, DMANBu, DEANS and NBD-EtOH) and (b) swelling of L312 (fluorescent probes: S2, S3 and S3F).

other fluorescent probes monitoring UV-induced polymerization reactions [31].

No fluorescence maximum shifts were detected during water absorption of the adhesives for the fluorescent probes while a slight hypsochromic displacement of 10 nm was observed for the fluorescent label S3F. Again this behaviour is attributed to the attachment of the fluorophore to the polymeric matrix. It has to be pointed out that no fluorescence emission from the water medium has been obtained in any sample, even for long time of immersion. Then, it appears not to be essential anchoring the fluorescent probe to the polymeric matrix, at least under the conditions studied here.

The fluorescence decreases during immersion in water and different behaviour it is observed depending on the volume of the probe (Fig. 5). For instance, DMANBu becomes sensitive only after several minutes and no changes in fluorescence spectra are observed at the first stage of water swelling of the film. This behaviour can be explained by the highest Van der Waals volume of this probe (287 $Å^3$) compared to DMANS (258 $Å^3$) and 2-OHDEANS (266 $Å^3$). Mobility-sensitive probe requires rigidity changes in the polymer matrix to provide a free volume available for bond rotation and a certain degree of plasticization has to be reached before the non-radiative deactivation mechanism is operative for this TICT (Twisted Intramolecular Charge Transfer) fluorescent probe, DMANBu. However, the fluorescence intensity of DMANS and 2-OHDEANS decreases from the begging of the process. The fluorescence intensity of probe DMANS decreases showing two different slopes. The initial one is slower than the gravimetric process indicating different fluorescence contributions depending on the rigidity of the microenvironment of the probe. During the first stage of the water sorption process, the mobility of the fluorescence probes increases at the edges of the sample and until water diffuses to the core of the matrix, inhomogeneous microenvironment due to the concentration gradient is revealed by the fluorescence behaviour. The 2-OHDEANS become sensitive at shorter time than DMANS and this can be explained due to the pre-twisted ground-state structure that favours bond rotation—fluorescence deactivation processes [32].

Photophysical and photochemical behaviour of stilbene and a variety of diarylethylenes in solution have been deeply studied in the past [33–36]. In molecules with a rotatable dimethylanilino group (excellent donor properties), the primary excited-state (Franck–Condon) leads to a fluorescent TICT state by single bond-twist in addition to the stilbene-type 'phantom-singlet' state (P^*) by double bond twisting. Rettig et al. [37] proposed a stepwise relaxation model which involves the TICT and the temperature-activated non-radiative decay via the photochemical funnel with twisted double bond conformation. This latest deactivation pathway may account for the differences observed between the fluorescence response to the water uptake of DMANS and DMANBu, due to the extended double bond conjugation of DMANBu compared to DMANS.

The mechanism of water sorption in the UV-cured adhesives was studied by the analysis of the double logarithmic plot of the fluorescence change versus immersion time (Fig. 6). Although the mass analysis showed good fitting to the Fick's model, the fluorescence changes show a more complex behaviour. In general, fluorescence changes steeply in the very early immersion time and then, fluorescence varies steadily up to the equilibrium state. Two different slopes may come from two different swelling stages, namely early time relaxation and long time Fickian (or moving boundary) behaviours may be the origins of the swelling steps. After the initial stage a good fit to the Fick's law was found for all the probes with the exception of NBD-EtOH. This NBD derivative possess a hydroxyl moiety which may interact with water molecules. However, the fluorescent probe 2-OHDEANS which also has a hydroxyl group in its structure shows a Fickian behaviour during the whole water uptake of the L350 adhesive. The photophysical behaviour of 2-OHDEANS in comparison with DMANS was previously reported [32] and the presence of a hydroxyl group along with a pre-twisted

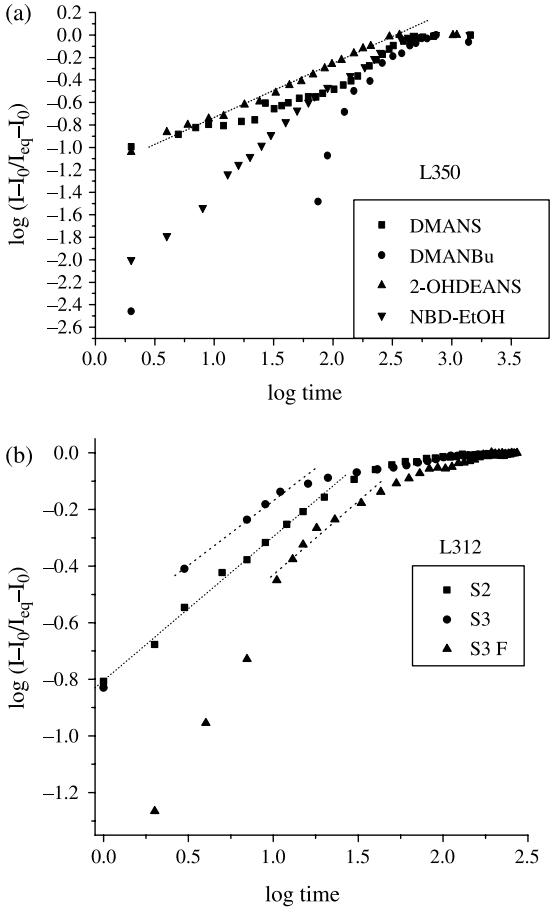

Fig. 6. Plot of the log(Δ*I*) versus log time during: (a) swelling of L350 immersed in water (fluorescent probe: DMANS, DMANBu, DEANS and NBD-EtOH) and (b) swelling of L312 (fluorescent pobes: S2, S3 and S3F). Dotted curves correspond to the fitting to Fick's model.

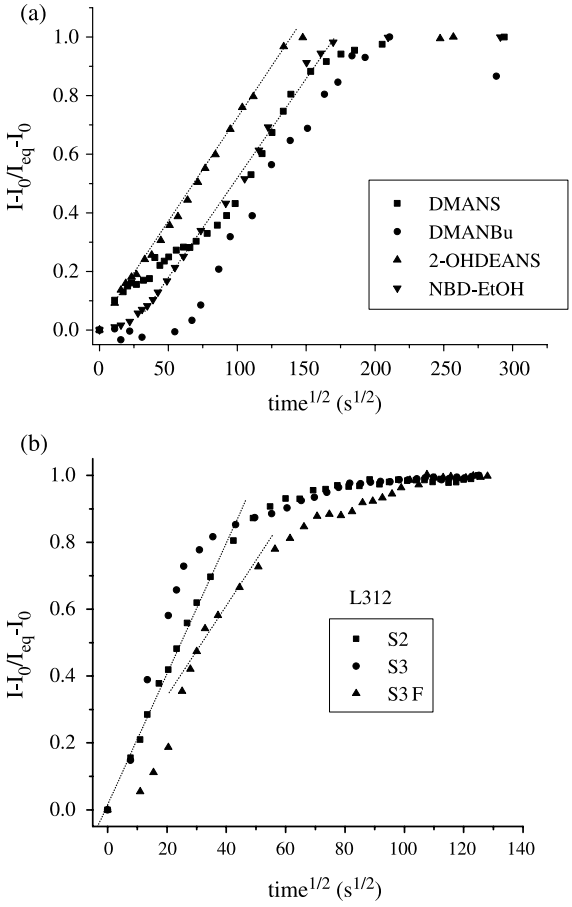

Fig. 7. Plot of $[(I-I_0)/(I_{eq}-I_0)]$ versus square root of time for (a) DMANE, DEASE and DMANBu in L350 and (b) S2, S3 and S3F in L312. Determination of water diffusion coefficient.

geometry of the ground state of this molecule was related to the observed low solvatochromic effect.

According to this mechanism a relationship one-to-one between the mass changes and fluorescence changes was assumed and the diffusion coefficient was determined from the slope of the linear plot of $(I-I_0)/(I_{eq}-I_0)$ versus the square root of the immersion time (Fig. 7).

In Eq. (5), the value of L corresponds to the optical pathlength of the excitation light which gives rise to the fluorescence emission, while for gravimetric measurements L corresponds to the total thickness of the film. The value of L was calculated taking into account that fluorescence cannot be detected for light transmission lower than 5% and the Eq. (6):

$$I_t = 1 - I_a = 1 - I_0(1 - 10^{-Abs}). \quad (6)$$

and the well-known Lambert–Beer law:

$$Abs = \varepsilon c l \quad (7)$$

The concentration of fluorescent probes was 0.05% wt and Table 2 compiles the molecular weight, molar absorption coefficients and optical pathlength for some of the studied fluorescent probes.

Therefore, the fluorescence changes allows to evaluate the transport process through a surface thickness of 140–180 μm, depending on the probe. As described in the experimental part, our specimens are thicker than strictly necessary for following the process through fluorescence measurements. The reason for this is to provide dimensional stability to our specimens, which allows easy handling and processability. This is very important to obtain a sensor device of practical use, but it should not perturb the accurate measurements of the process. In general, we have obtained the same time profile using gravimetric and fluorescence measurements, then making sure that the higher thickness of the sample is not interfering fluorescence monitoring of water uptake.

Another interesting feature is that fluorescence reveals a two phase water absorption mechanism, whereas the measurement

Table 2
Molecular weight, molar absorption coefficients and optical pathlength for some of the studied fluorescent probes

Probe	Pm	ε (l/mol/cm)	L (μm)
S2	222	41,500	139
S3	266	44,000	157
S3F	320	45,500	183

Table 3
Diffusion coefficient and fitting parameter n to the Fickian model, together with the correlation coefficient in the evaluated time range, for water swelling of L350 and L312

Probe	n_{L350}	$D_{L350}\times10^{12}$ (m^2/s)	n_{L312}	$D_{L312}\times10^{12}$ (m^2/s)
S2	0.52 (0.98)	1.2	0.50 (0.997)	5.8
S3	0.53 (0.98)	1.4	0.43 (0.98)	12.0
S3F	0.60 (0.96)	1.7	0.38 (0.98)	8.7
DMANS	0.47 (0.97)	0.7	–	–
DMANBu	0.57 (0.99)	1.5	–	–
2-OHDEANS	0.47 (0.997)	1.0	–	–
NBD-EtOH	0.89 (0.996)	1.2	–	–

of the mass changes only shows a single phase water uptake. The comparison of diffusion coefficients from gravimetric and fluorescence measurements agrees in the immersion time range where both gravimetric and fluorescence changes follow a Fick's model. Table 3 shows the diffusion coefficients of water in L350 and L312 determined by using different fluorescent probes and calculated from the slope of the curve where the water uptake is diffusion controlled.

The value of the average diffusion coefficient determined by using the fluorescent probes are in good agreement within error. The error is likely to be due to the significant activation energy associated with D, where small changes in water temperature during, between, the experiments may result in changes in D. Therefore, all the probes behave as good humidity sensor. However, specific interactions between NBD-EtOH and water prevent its use as humidity sensor and also the covalent attachment of S3F to the polymer matrix reduces its sensitivity.

The solvatochromic shifts of the fluorescence spectra of the studied probes in solution indicate that they behave as polarity sensitive probes. In Table 4 the maxima fluorescence emission wavelengths in cyclohexane and ethyl acetate solutions of these probes are shown together with those in the cured adhesive films. However, no emission wavelength shifts were detected during the water absorption of the cured films, except for S3F. This feature may indicate either that polarity inside the polymer matrix is little affected by the absorption of water or that the migration of the probes inside the polymer matrix is favoured by the swelling of the polymeric network. The last argument agrees well with the observed hypsochromic shift of fluorescent label, SF3, which is covalently attached to the cured adhesive. However, a more detailed analysis shows that

Table 4
Maxima fluorescence emission wavelengths in cyclohexane and ethyl acetate solutions of the probes, together with those in the cured adhesive films

Fluorescent probes	λ_{max} (nm) (in L350)	λ_{max} (nm) (in L312)	λ_{max} (nm) (in cyclo-hexane)	λ_{max} (nm) (in ethyl acetate)
DMANS	588	588	473/500	612
2-OHDEANS	565	584	488/515	615
DMANBu	573	596	495/525	641
S2	608	630	523	568
S3	606	618	523	572
S3F	597	606	522	570

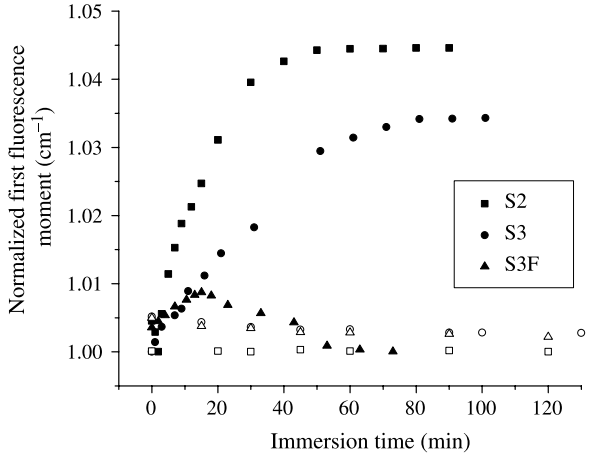

Fig. 8. Changes of the first moment of the fluorescence during water uptake. Open symbols refers to L350 and solid symbols to L312 swelling.

the first moment of fluorescence of S2 and S3 changes during water sorption of L312 but not for L350 (Fig. 8).

The first moment of fluorescence $\langle\nu\rangle$ is defined as the average emission wavenumber and by the Eq. (8):

$$\langle\nu\rangle = \frac{\sum_i \nu_i I(\nu_i)}{\sum_i I(\nu_i)} \tag{8}$$

It can be observed that the first fluorescence moment of S2 and S3 changes more rapidly than mass increase in L312 and does not follow the Fick's law. This behaviour can be related to the higher polarity of the adhesive L312, due to a higher content of hydroxypropyl methacrylate, which may favours H-bonding in the surroundings of the fluorescent probes. Therefore, its excited state must couple more easily with its surroundings and become more stabilized. In the case of S3F, the migration through the matrix is avoided by the covalent attachment to the polymer and no variation of $\langle\nu\rangle$ is observed. The total spectral shift is low as it corresponds to the low amount of absorbed water.

The water uptake of L350 under 92% of relative humidity was monitored by the decrease of fluorescence of S3, S3F and DMASP-Br versus time and diffusion coefficients have been calculated. The results are compared to that by gravimetric measurements in Table 5. The data obtained by both methods, gravimetrically and by fluorescence technique, are in good agreement when the water uptake is monitored under 92% of relative humidity.

As can be seen, the diffusion coefficient calculated by fluorescence under controlled humid atmosphere accurately reproduces those obtained under immersion. This fact makes our sensor films adequate to monitor the water uptake process

Table 5
Diffusion coefficients in L350

Probe	$D\times10^{12}$ (m^2/s) 92%RH, 20 °C
S3	1.2
S3F	1.1
DMASP-Br	1.4
Gravimetric	1.2

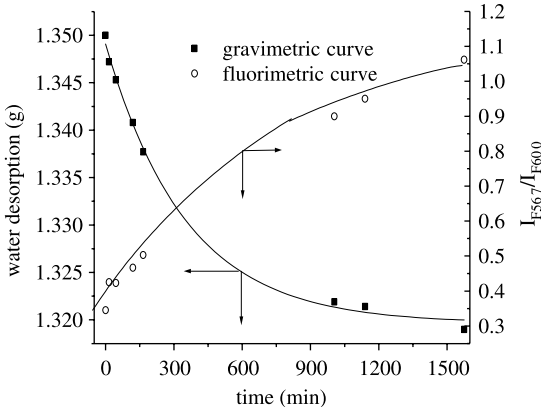

Fig. 9. Water desorption of L350 monitored by gravimetry and by fluorescence (S3F).

under environmental conditions. Moreover, this feature confirms there is no interaction between the water and the cured polyurethane-acrylate based films and the diffusion coefficients are characteristic for the water–polymer system.

Moreover, water desorption was investigated by fluorescence. Fig. 9 shows as expected that the intensity of the fluorescence increases as the mass of the swollen adhesive decreases due to a more rigid microenvironment of the probe. During desorption the same total amount (2.2 wt%) is desorbed which mirrors the total sorption ability of the specimen. Another interesting point derived from this result is that unreacted monomer is not extracted by desorption. During polymerization, unreacted monomer may be trapped into microgels inside the polymer network or inside micropores. The latter is more susceptible to leaching out than the monomer inside microgels. The leachable fraction of unreacted monomer by water is negligible in these adhesives. This feature makes them promising to be applied as or in conjunction with biomaterials as far as the main reason for imcompatibility of polymer materials with biological tissues raises from the presence of unreacted monomer and its ability to migrate to surfaces.

4. Conclusions

We have analysed two polymeric formulations doped with nine fluorescent probes for monitoring water uptake under stationary conditions. Fluorescence allows to follow the process in real time and in situ and the values obtained for the diffusion coefficients agree well with those obtained gravimetrically. In addition, the comparison of fluorimetric measurements and gravimetric method shows that fluorescence reveals a more complex mechanism of water diffusion than that deduced from the macroscopic mass balance. In the first stage of swelling fluorescence intensity decreases steeply and then follows a steady change that obeys the Fick's model. This behaviour is related to the fact that water diffusion in glassy polymers is influenced by plasticization of polymer and by clustering of water molecules. Fluorescence methods are quite effective in the investigation for the microscopic environment around the probe and it was observed that water uptake is governed by Fickian dynamics of diffusion of water molecules into the free volume of the polymer network after an initial period, which depends on the volume of the fluorescent probe and the nature of the adhesive (presence of hydrophilic monomers).

The fluorescent probe incorporated as a label shows less sensitivity to humidity. Given that negligible extraction of the dopants is found under immersion, it is not necessary to incorporate the fluorescent molecules as reactive probes.

Therefore, the addition of fluorescent probes in acrylic adhesives based films offers an advantageous method for in situ monitoring of water uptake during service life.

The good qualities of the developed UV-cured adhesives films doped with fluorescent probes show a potential application for achieving low-cost and high-reliable optical devices for humidity sensors. Moreover, the negligible leached amount of unreacted monomer during desorption shows a potential as adhesives for biomedical applications.

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