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A novel spectroscopic approach to investigate transport processes in polymers: the case of water–epoxy system

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Abstract

A novel experimental approach, based on in situ FTIR spectroscopy in the transmission mode, has been developed to monitor sorption–desorption behaviour of small molecules in polymer films. This technique, along with classical gravimetric analysis, has been used to investigate water vapour transport in an epoxy resin. Aim of the investigation was to elucidate the different types of interaction that water molecules form with the macromolecular network and their change as function of the amount of sorbed water. This analysis has been performed at several water vapour activities (0.08, 0.2, 0.4, 0.6, 0.8) at 24°C by using a FTIR cell specifically designed for the in situ monitoring of water sorption in the epoxy film. Particular attention has been paid to realise a very accurate control of water vapour pressure and temperature in the cell. Water sorption kinetics has been also investigated in the same conditions by using an electronic microbalance. Information gathered from the results of both experimental approaches is potentially useful to clarify the plasticising action of sorbed water. To this aim, the amount of water sorbed by itself, is not a reliable predictor of possible physical effects on the matrix, since the plasticising efficiency of water molecules is expected to change with the level of interaction they establish with the polymeric matrix. FTIR based analysis supplies a very useful experimental tool to discriminate among different types of penetrant–polymer molecular interaction. In fact, several spectroscopically distinguishable 'types' of sorbed water molecules have been detected in the case of the analysed water–epoxy system and their evolution as a function of the penetrant concentration has been followed.

Keywords: Sorption; Water; Epoxy

1. Introduction

The phenomenology of transport of low molecular weight compounds in polymeric materials has raised a great scientific and technological interest over the past 40 years. There are several engineering applications where diffusion behaviour has a major impact: among many others, gas mixtures separation with membranes, drug delivery, barrier structures for food packaging, environmental resistance of polymer based composites and devolatilisation. In this respect, an issue of considerable technological relevance is the durability of epoxy based advanced composites. In fact, these matrices, when exposed to a humid environment, absorb significant amounts of water, which adversely affect most physico-mechanical properties.

In particular, the tetraglycidil-4,4′-diamino-diphenylmethane (TGDDM) cross-linked by 4,4′-diamino-diphenylsulphone (DDS), which is the matrix of choice for advanced aerospace applications, may absorb up to 7% by weight of water [1–3], due to the high concentration of polar groups into the network.

The main documented effects of water on epoxy matrices are, among others:

plasticisation, which occurs by different mechanisms depending on the level of interaction of sorbed water molecules with the matrix;
changes of physical properties, i.e. decrease of mechanical moduli, decrease of yield strength, change of yield/deformation mechanisms;
hygrothermal degradation, i.e. microcracks, ageing, chain scission through hydrolysis, degradation of fibre–matrix interface in composites;
swelling stresses.

If sorbed water molecules in epoxy matrices do establish

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different types of interaction with the matrix (different 'states' of water molecules) a range of different effects on physical properties are expected to be associated to each of them. As a consequence the water uptake alone is not a reliable predictor of possible effects on physical properties of the resin. For this reason several experimental efforts have been put forward to address the issue of the state of water molecules in epoxies. Among the spectroscopic techniques, which have been used for this purpose, the most effective are NMR, dielectric and FTIR spectroscopy. The results obtained by these experimental approaches are still inconclusive and sometimes conflicting [4–14]. However, the apparently contradictory results obtained by these spectroscopic techniques may be partly due to the characteristic time scale of each probing method.

On the basis of these findings several theories have been proposed to interpret water sorption and transport in epoxy resins, but exact molecular details of these phenomena still remain vague. In fact several sorption modes and related states of absorbed water molecules have been envisaged: bulk dissolution, H-bonding interaction between hydrophilic groups of the polymer and water, clustering of water molecules and adsorption onto the surface of free volume microvoids. These sorption modes have been frequently assumed to occur simultaneously.

In a previous paper [14], some of us analysed the desorption behaviour of samples of a cured TGDDM–DDS resin, after saturation with liquid water, using FTIR spectroscopy. As a result of this analysis, performed both in the mid infrared (MIR) and in the near infrared (NIR) ranges, specific assignments have been proposed for the fundamental peaks (MIR) and the peaks resulting from overtone and combination bands of absorbed water molecules (NIR).

Aim of the present contribution is to describe in detail a novel experimental approach to investigate sorption and desorption processes in polymeric films and membranes. It is based on in situ *time resolved* FTIR spectroscopy in the transmission mode. This approach provides not only a mean for monitoring accurately the penetrant sorption kinetics but offers also the possibility of investigating in detail the concurrent development of molecular interactions. In particular, we present the results obtained on water sorption in an epoxy TGDDM–DDS network. Attention has been focused onto the fundamental O–H stretching vibrations, since this is the most sensitive region to H-bonding. Sorption tests have been followed also by gravimetric analysis at several water vapour activities to test the reliability of the spectroscopic method and to gather a better understanding of the absorbance–mass relationship.

2. Background: use of FTIR based techniques for the investigation of mass transport processes

FTIR spectroscopy has been successfully used for the investigation of sorption processes in polymers. This is because it provides not only an accurate determination of the penetrant concentration, thus allowing to obtain reliable mass–time curves, but also because of the rich information at molecular level present in the vibrational spectrum. The latter, in particular, may be used to investigate the molecular interaction between the penetrant and the polymer substrate, which, in many systems, are the key factor that control the transport behaviour. Further advantages of the spectroscopic approach for mass transport studies are the possibility to study multicomponent diffusion and the ability to monitor structural changes occurring in the polymer matrix during penetrant transport.

Significant advancement in this area has been achieved with the development of in situ measurements which dramatically improved the accuracy of the transport kinetics analysis. So far, most of the experimental investigations reported in the literature have been based on FTIR attenuated total reflectance (FTIR-ATR) [15–19]. This technique consists in probing the surface area of the sample in contact with a suitable optical element by an evanescent wave. The application of FTIR-ATR to mass transport studies relies on the spectroscopic observation of penetrant localized within a short (0.5–5 μm) distance from the interface between the polymer film and the optical element (total internal reflection IR crystal). The other side of the film is exposed to proper vapour, gaseous or liquid environment. The key factor to insure the quality of the collected spectrum and hence the accuracy of the quantitative analysis is the efficiency of the contact between the sample and the crystal. This factor is rather difficult to control especially for long term measurements and has often limited the applicability of the technique to short time tests. To optimise the contact often the samples have been prepared by spin coating. This limits the applicability to thermoplastics since thermosets, once cured, are difficult to be removed without damaging the expensive crystal. Furthermore, the use of commercial films is prevented. Recently some authors have proposed the use of pressurizing gas to improve the contact [20,21]; this, however may alter the diffusion behaviour.

A further limitation of this approach is due to the fact that, in ATR, the relationship between absorbance and penetrant concentration is far more complex than in transmission. Manageable mathematical expressions of the mass transport equation in terms of absorbance values have been derived only in the case of low absorbance values and relatively low penetrant concentration, for the case of ideal Fickian and Case II mass transport behaviours.

Finally it is worth noting that in case of films displaying heterogeneous morphology through the thickness ('skin effects' and multilayer structures) interpretation of data can become rather difficult [22].

Most of the aforementioned drawbacks can be avoided by using in situ FTIR spectroscopy in the transmission mode. In this arrangement, a free standing film is placed in a cell which allows careful control of the environment (vapour or gas pressure and temperature).

The interference of the gas–vapour phase has to be eliminated carefully and this is accomplished by using, as background, the spectrum of the cell without the polymer sample, at the test conditions. This procedure imposes an extremely accurate control of the internal atmosphere of the cell, which can be achieved with a proper design of the sorption cell and of the service equipment.

This experimental approach is obviously limited to thin films (generally 5–100 μm) and its extension to liquid penetrants is not straightforward.

3. Materials and methods

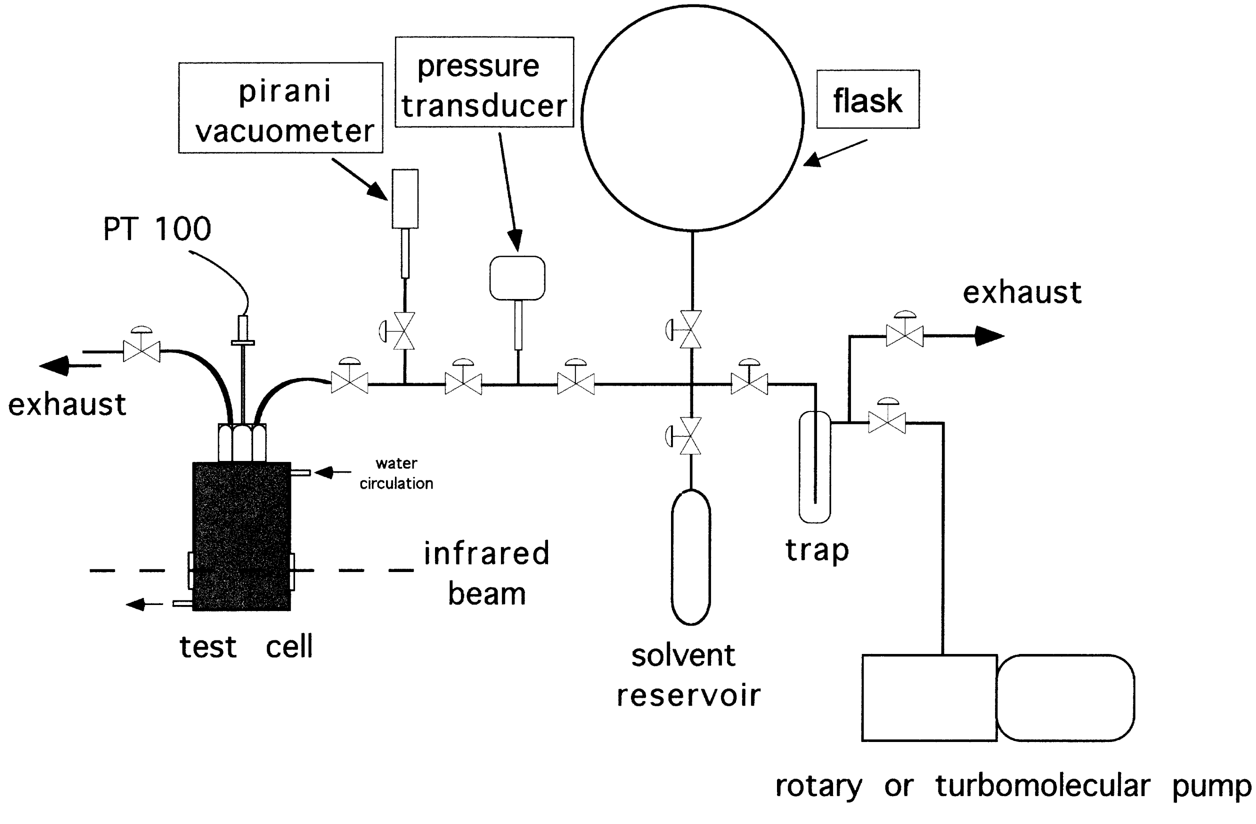
3.1. Materials

The epoxy resin was a commercial grade of tetraglyidyl-4,4′-diamino-diphenylmethane (TGDDM) supplied by Ciba Geigy (Basel, Switzerland), and the curing agent was 4,4′-diamino-diphenylsulphone (DDS) from Aldrich (Milwaukee, WI).

A total of 30 g of DDS were dissolved in 100 g of TGDDM (corresponding to a concentration of 30 phr) at 130°C, degassed under vacuum, and poured in a stainless steel mould. The first step of the curing schedule was conducted at 140°C for 16 h, followed by a post-curing step at 200°C for 4 h.

3.2. Water sorption by in situ FTIR

A vacuum tight FTIR cell has been designed and developed specifically to monitor the FTIR transmission spectrum of the epoxy resin film exposed to a controlled humidity environment (see Scheme 1 for a representation of the apparatus for the in situ FTIR sorption measurement). The cell is made of stainless steel and is equipped with a water jacket for temperature control. KBr windows have been used and sealing between cell and windows is warranted by o-rings. A VCR® fitting enables a leak tight removable closure of the system; the cell is connected through stainless steel 1/8″ tube, welded to the VCR cap to the rest of the apparatus which consists of service lines to pressure transducer and 'Pirani' vacuometer, flask, solvent reservoir and vacuum pump. While the cell is kept at test temperature, the rest of the apparatus remains at 25 ± 0.5°C. Before performing a sorption test, the sample is dried into the cell which is kept at 60°C and, along as the rest of apparatus, under vacuum until complete disappearance of the characteristic water bands. After desiccation, connection to the rest of equipment is closed. The solvent reservoir containing distilled water (degassed through freezing–thawing cycles) is then open to let water vapour enter the apparatus until the desired level of pressure of water vapour is attained. Pressure is monitored by means of a MKS Baratron 121 pressure transducer with a full scale of 100 Torr, a



Scheme 1.

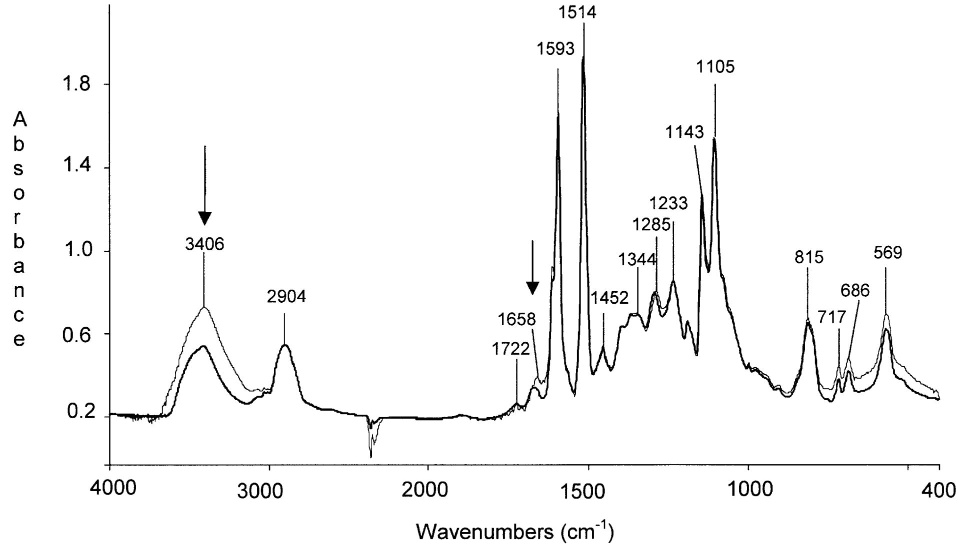


Fig. 1. Transmission FTIR spectra in the 4000–400 cm^{-1} interval for a fully cured TGDDM–DDS in dry state (thick line) and after equilibrium water sorption at a = 0.4 (thin line).

sensitivity of 0.01 Torr and an accuracy of ±0.5% of the reading. After stabilisation of pressure level (the apparatus is pre-loaded at a water vapour pressure level slightly higher then the desired test pressure to take into account the small additive volume of the cell after the opening of the connection), connection to cell is open and IR computerised acquisition (TIME BASE acquisition software package from Perkin Elmer) is simultaneously started. After the attainment of apparent sorption equilibrium, a desorption stage follows: the cell at the fixed water vapour activity is first isolated from the rest of the apparatus, which is then put under vacuum and, when an absolute pressure lower than 0.001 Torr is reached, the connection with cell is open and acquisition started. The desorption is monitored till the attainment of apparent equilibrium.

The instrument used is a Perkin–Elmer System 2000 interferometer equipped with a Germanium/KBr beam splitter and a wide band DTGS detector. Instrumental parameters are as follows: resolution = 4 cm^{-1}, optical path difference (OPD) velocity = 0.2 cm s^{-1}, spectral range 4000–400 cm^{-1}. A single data collection was performed for each spectrum (3551 data points) which, in the selected instrumental conditions, takes 6 s to complete. The signal is acquired as single beam at specific time intervals, which increase as the sorption process gets closer to equilibrium. A typical sorption run lasts about 30 min and acquisition time intervals are 10 s during the first 10 min of the experiment and 60 s afterwards.

Tests were all performed at 24°C and at 5 activity levels of water vapour: 0.08, 0.2, 0.4, 0.6 and 0.8 (ideal behaviour of water vapour is assumed, whence activity is evaluated as the ratio between the pressure of the pure vapour [p] and the water vapour pressure at 24°C [p_o] i.e.: $a = p/p_o$) on samples of thickness equal to 9 ± 0.5 μm.

3.3. Data analysis

The single beam spectra are then processed, to obtain the absorbance spectra, using as background the cell without epoxy sample and filled only with pure water vapour at exactly the same pressure at which sorption test has to be performed. An example of absorption spectra of 'wet' and 'dry' samples is reported in Fig. 1. The only differences between the two spectra are: (i) an increasing intensity of the ν_{OH} band at 3406 cm^{-1} and (ii) the appearance of a shoulder for the TGDDM aromatic ring mode at 1594 cm^{-1}. For a complete description of the entire spectrum see Ref. [23]. The spectra of sorbed water at different times are obtained by eliminating the interference from the polymer substrate using the subtraction spectroscopy technique [24,25], i.e.:

$$A_d = A_s - kA_r \tag{1}$$

where (i) A is the absorbance, (ii) the subscripts d, s and r denote respectively the difference, sample ('wet' specimen) and reference ('dry' specimen) spectra and (iii) k is an adjustable parameter used to compensate for thickness differences between the sample and reference spectra. In our case, since no thickness changes occur upon water sorption, k is consistently equal to unity. The underlying hypothesis for the application of this approach is that the spectrum of the epoxy resin is not affected by the presence of the absorbed water. The frequency region to be analysed in the present contribution is the 3800–2800 cm^{-1} range where the fundamental stretching vibrations of water are located; in Fig. 2 are reported the spectra of sorbed water in the 3800–2800 cm^{-1} range, collected at different sorption times and obtained by the previously discussed procedure, for the case of sorption at a = 0.8.

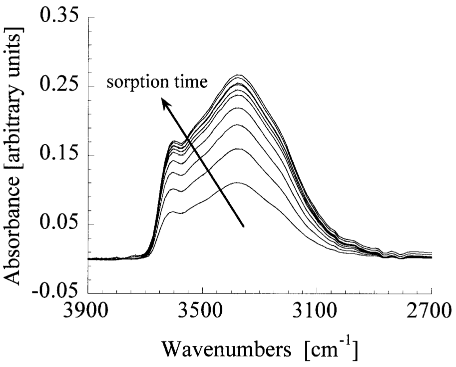


Fig. 2. Subtraction FTIR spectra in the $4000–2500\ \mathrm{cm}^{-1}$ range collected at different sorption times in the case of water vapour sorption test at a = 0.8 in the TGDDM–DDS.

In order to separate the individual peaks in the case of unresolved, multicomponent bands, a curve resolving algorithm was applied, based on the Levenberg–Marquardt method [26]; to reduce the number of adjustable parameters and to insure the uniqueness of the result, the baseline, the band shape and the number of components were fixed. The minimum number of components was evaluated by visual inspection on the basis of abrupt changes of slope of the experimental line-shape. The program was then allowed to calculate, by a non-linear curve fitting of the data, the height, the full width at half height (FWHH) and the position of the individual components.

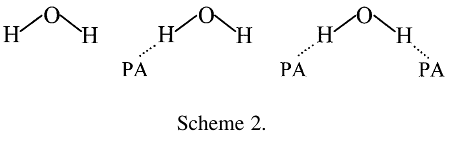
The peak function was a mixed Gauss–Lorentz line shape of the form [27]:

$$f(x) = (1 - L)H\exp\left[-\left(\frac{x - x_0}{w}\right)^2(4\ln 2)\right] + L\frac{H}{4\left(\frac{x - x_0}{w}\right)^2 + 1} \qquad (2)$$

where x_0 = peak position; H = peak height; w = FWHH; L = fraction of Lorentz character.

3.4. Gravimetric analysis

The equipment used to determine weight gain of samples exposed at a controlled relative humidity atmosphere is essentially the same of that described previously, apart from the fact that the measuring cell is substituted by a controlled atmosphere electronic microbalance, CAHN D200, with a sensitivity equal to 0.1 μg. Tests were performed on the same samples used for FTIR analysis in order to avoid the need for thickness correction when comparing sorption data from the two techniques.



Scheme 2.

4. Results and discussion

The subtraction spectrum of the epoxy resin exposed to liquid water in the $3800–2800\ \mathrm{cm}^{-1}$ region has been previously obtained by some of us in the case of thicker samples (about 50 μm) [14]. This spectrum was interpreted on the basis of a simplified association model for water whereby three different water species can be spectroscopically distinguished, according to the reported Scheme 2 (here 'PA' stands for proton acceptor). Spectral interpretation was aided by analysis of the NIR region [14]. Strictly coincident results have been obtained in the present investigation and are reported in Fig. 3, which displays the experimental subtraction spectrum along with its curve-fitting analysis. The peak centred at $3623\ \mathrm{cm}^{-1}$ is related to the asymmetric O–H stretching vibration (ν_3) of unassociated water (i.e. water which does not establish any H-bond, S_0); the broad band at lower frequencies is due to water molecules hydrogen-bonded onto specific sites along the network. This broad band displays a fine structure in the form of discontinuities in the shape, which reflect the occurrence of several types of interactions (S_1, S_2). In particular, referring to the components identified by the curve fitting analysis, the peak at $3555\ \mathrm{cm}^{-1}$ can be associated with S_1 molecules or with weakly interacting S_2 species (sterically hindered interactions and/or weak proton acceptors). Conversely, the two components at 3419 and $3264\ \mathrm{cm}^{-1}$ are associated to S_2 species displaying stronger H-bond interactions. It is difficult to evaluate quantitatively the amount of each type of water molecules, since in this range the molar absorptivity significantly increases with the interaction strength.

It is likely that S_0 and S_1 species are characterised by high mobility and low plasticising efficiency. S_0 molecules

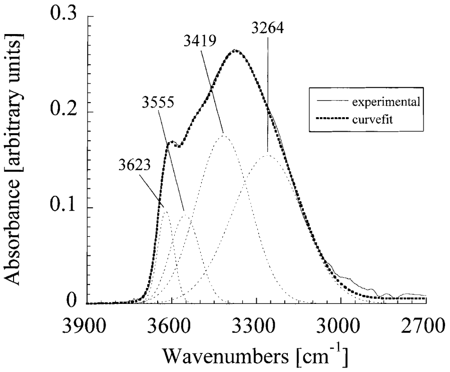


Fig. 3. Curve fitting analysis of the subtraction spectrum corresponding to water absorbed at equilibrium (a = 0.8) in the epoxy resin. The figure displays the four resolved components, the simulated profile and the experimental line shape.

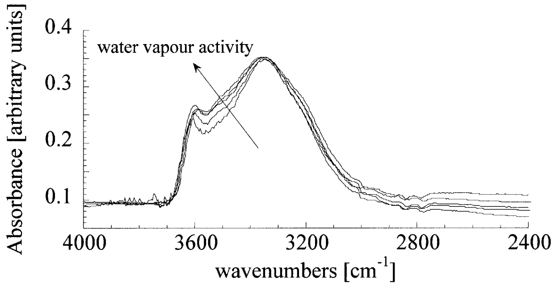


Fig. 4. Subtraction FTIR spectra in the 4000–2800 cm^{-1} range corresponding to water absorbed at equilibrium at different activities in the TGDDM–DDS resin.

should be confined into excess free volume (microvoids) or molecularly dispersed with no H-bonding interactions (bulk dissolution), while S_1 may either interact moderately by H-bonding or may represent self-associated dimers. On the other hand, S_2 molecules are expected to be characterised by a much lower mobility; these species should be firmly bound to specific sites along the polymer network thus exhibiting high plasticising efficiency. Involvement of these species in clusters of more than two water molecules, cannot be entirely ruled out.

The analysis of water spectra in the 3800–2800 cm^{-1} region collected at equilibrium at 5 different activities, reveals a relevant feature: as the activity increases, the component at 3555 cm^{-1} becomes more and more significant. In Fig. 4 the sequence of spectra is reported, after proper rescaling to equalise the heights at maximum. This effect is further evidenced by plotting the results of the curve fitting analysis as a function of water vapour activity (Fig. 5), which show how the relative amount of S_0 and S_2 species decrease with activity, while that of S_1 increases. Although these data cannot be interpreted quantitatively, due to the aforementioned dependence of molar absorptivity on frequency, nevertheless they supply useful qualitative indication on the water/epoxy system. The described findings are consistent with the physical picture of a system where the relative population of interacting water species at equilibrium changes as a function of the external water activity and hence of the total content of absorbed water. In fact, at low activities strong interactions are more likely to develop for enthalpic reasons, while, as the activity increases, strongly interacting sites get closer to saturation and weak interactions play an increasingly significant role.

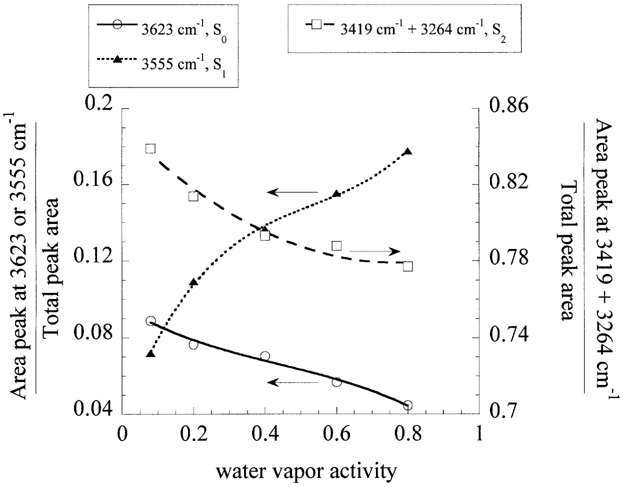


Fig. 5. Relative absorbance area of the different components of the subtraction spectra collected at water vapour sorption equilibrium, reported as a function of water vapour activities. Lines are drawn to guide eye.

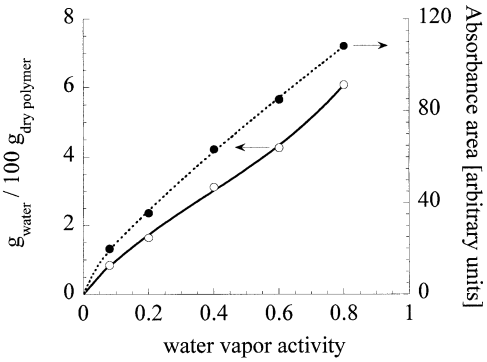


Fig. 6. Sorption isotherms in terms of water sorbed amount and absorbance area of the subtraction spectra as a function of the water vapour activity.

Another important information on resin–water interactions can be gathered by comparing mass and absorbance data collected at sorption equilibrium. In Fig. 6 we report the gravimetric sorption isotherm as measured at 24°C together with the total area of the peak centred at 3408 cm^{-1}. From these data, a plot of absorbance vs water concentration in the resin can be constructed as reported in Fig. 7.

The total absorbance is related to the concentration of the different water species through the following equation [28–30]:

$$\mathscr{A}_{TOT} = l(\epsilon_1 C_1 + \epsilon_2 C_2 + \epsilon_3 C_3 + \epsilon_4 C_4) \tag{3}$$

where $\mathscr{A}_{TOT}$ represents the total area of the band centred at 3408 cm^{-1}, l is the sample thickness, ϵ_i represents the molar absorptivity of the various band components and C_i represents the molar concentration of the different species.

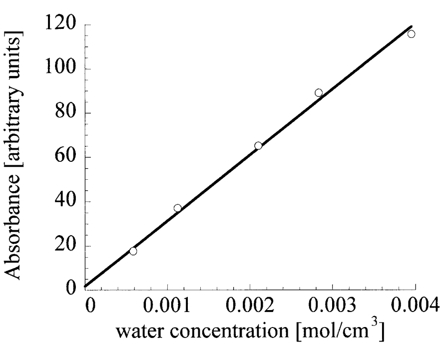


Fig. 7. Absorbance of band at 3408 cm^{-1} as a function of water amount absorbed at equilibrium.

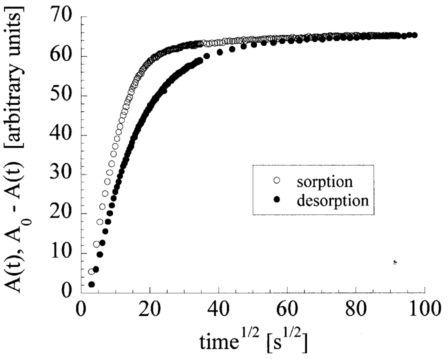


Fig. 8. Sorption and desorption kinetics plots a = 0.4 in terms of absorbance at time $t[A(t)]$ for sorption test and of the difference between absorbance at time 0 $[A_0]$ and absorbance at time t $[A(t)]$ for desorption test.

Subscripts 1, 2, 3 and 4 refer respectively to 3623 cm^{-1} peak (S_0), 3555 cm^{-1} peak (S_1), 3419 cm^{-1} peak (S_2) and 3264 cm^{-1} peak (S_2). Eq. 3 can be rearranged as:

$$\mathscr{A}_{\mathrm{TOT}} = lC_{\mathrm{TOT}}(\epsilon_1 x_1 + \epsilon_2 x_2 + \epsilon_3 x_3 + \epsilon_4 x_4) \qquad (4)$$

where now x_i represent molar fractions.

The observed linearity of the absorbance–concentration plot implies the invariance of the x_i values at equilibrium with total concentration, which is a result apparently conflicting with the spectroscopic findings shown in Fig. 4. It is likely that the increase in x_2 with water activity is not sufficient to bring about an observable deviation from linearity in the absorbance–concentration plot.

The potential of the proposed spectroscopic approach is witnessed by the quality of sorption–desorption curves reported in Fig. 8, which refer to an activity equal to 0.4. Desorption curve lies well below the sorption curve, as expected if the water diffusivity is an increasing function of concentration.

Comparison of gravimetric and spectroscopic kinetics is equally informative (Fig. 9). The two curves are quite close to each other but not exactly superimposable. This effect, which implies a slight deviation from linearity of the dynamic absorbance–concentration curve, could be related to the non-uniform concentration profile within the sample and/or a time dependence of the x_i values. Work is in progress for a deeper understanding of these aspects.

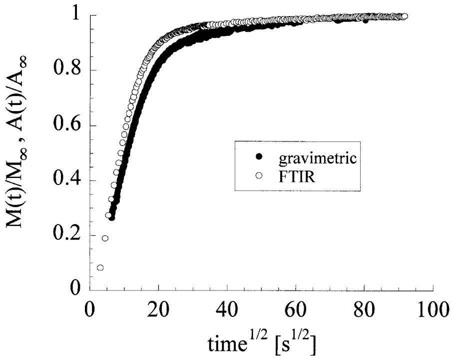


Fig. 9. Gravimetric and FTIR sorption kinetics at a = 0.4 in terms of water mass and absorbance normalised with their respective values at equilibrium $[M_\infty, A_\infty]$.

5. Conclusions

A novel in situ FTIR technique has been presented for the investigation of vapours and gases transport through polymer films. The proposed approach is based on transmission spectroscopy and is able to supply readily interpretable kinetic and equilibrium data. Useful information can be gathered on the evolution of polymer structure, polymer–penetrant and penetrant–penetrant interactions occurring during sorption or desorption. As a model case, water transport through a TGDDM–DDS epoxy resin has been presented. The results confirmed the capability of this spectroscopic technique to effectively collect sorption and desorption kinetic data. Interesting features of the absorbed water spectra have been evidenced, showing the changes with water activity of the water–polymer interactions.

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