

Feature article:

## Time-resolved FTIR/FTNIR spectroscopy: powerful tools to investigate diffusion processes in polymeric films and membranes

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**Abstract:** The application of time-resolved FTIR spectroscopy to investigate diffusion processes in polymers is described. Two thermosetting systems have been studied: a tetrafunctional epoxy resin cured with an aromatic diamine hardener, and a ternary formulation comprising the above components plus a bismaleimide co-monomer. Spectroscopic monitoring of water diffusion, both in the Mid and in the Near IR frequency ranges, yielded accurate and reproducible kinetic curves from which it was possible to evaluate the absolute parameters of diffusion (diffusivity and activation energy). These were found to compare favourably with the values obtained by conventional gravimetric methods. The molecular interactions between the penetrant molecules and the polymer networks were also investigated and it was shown that, in the system containing the bismaleimide component, the fraction of water molecules hydrogen-bonded to the network decreases significantly.

### Introduction

The diffusion of liquids, vapours and gases in polymeric systems is a problem of primary concern both from a fundamental standpoint and for technological applications. In fact, the diffusion behaviour has a major impact in almost any area in which polymeric materials find application. For example, water diffusion is the key factor that controls the performances of materials ranging from inexpensive snack-food packages to costly composite structures for civil and military aircrafts. Diffusion behaviour controls the efficiency of membranes in advanced applications such as gas mixtures separation or the delivery of pharmaceutical compounds in transdermal patches. It is therefore not surprising that investigators in this area are continuously searching for new, more accurate and informative techniques to study this complex and often elusive phenomenon.

In recent years a number of research groups became interested in applying spectroscopy based techniques to diffusion studies. Notable examples of these approaches are the study of polymer self-diffusion by pulsed field gradient NMR [1] and different investigations on the diffusion of gas, vapours and polymers by means of *time-*

*resolved* FTIR spectroscopy [2-9]. In particular, the latter technique provides several appealing features: the very high sampling rate (up to 20 spectra per second) which allows to monitor fast diffusion kinetics, the sensitivity and accuracy of the quantitative analysis, provided that some instrumental requirements are met, the specificity of the spectroscopic technique which allows to investigate multicomponent diffusion. However, of all the advantages that FTIR spectroscopy has to offer in this application, the most relevant is certainly related to the wealth of information at molecular level contained in the vibrational spectrum. If properly interpreted, this information may be used to investigate the polymer-penetrant molecular interactions, which often are the key factor controlling diffusion behaviour, the state of aggregation of penetrant molecules into the polymeric substrate, conformational equilibria of the penetrant and, finally, structural changes that may result in the polymer matrix as a consequence of penetrant sorption or desorption [7,8,10].

So far most of the studies reported in the literature have been based on FTIR-attenuated total reflection (FTIR-ATR). This technique consists in probing the surface area of the sample in contact with a suitable optical element by an evanescent wave. Thus, the concentration of penetrant localized within a short (0.5 - 5  $\mu\text{m}$ ) distance from the interface between the film sample and the crystal is monitored, while the other side of the film is exposed to the proper vapour or liquid environment. Although this approach has been applied with considerable success [2-6] there are a number of limitations, mainly related to the film-crystal contact, which is to be optimised to insure the quality and reproducibility of the spectrum, and the complexity of the absorbance-concentration relationship in ATR. Most of these drawbacks can be avoided if data collection is performed in the transmission mode. In this case, a free standing film is placed in an environmental chamber which allows careful control of the temperature and vapour or gas pressure. The interference of the gas phase surrounding the sample is eliminated by collecting a background spectrum of the empty cell at the test conditions. This imposes an extremely accurate control of the pressure (typically  $\pm 0.01$  Torr) which is achieved by a proper design of the diffusion cell and of the service equipment [7].

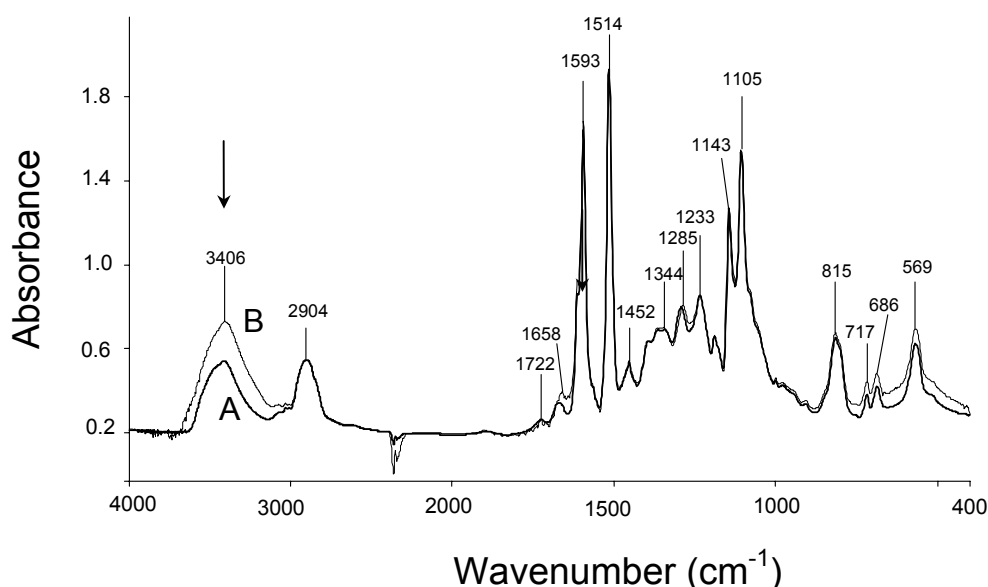
In the present contribution we describe the diffusion of water, as investigated by FTIR spectroscopy, in systems based on a tetrafunctional epoxy resin. The tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) cured with the aromatic diamine 4,4'-diaminodiphenyl sulfone (DDS) is the epoxy formulation generally used as matrix for the production of high performance carbon-fibre composites used in the aerospace industry. The widespread success of this material is due to its excellent properties in terms of rigidity,  $T_g$ , thermal and thermal-oxidative stability, and solvent resistance. It has, however, a serious drawback related to the absorption of large amounts of water (from 4 to 7 wt.-%), which brings about a general deterioration of mechanical properties [8,11,12]. The absorbed water acts as a very efficient plasticizer, reducing the  $T_g$  of the resin by about 20°C for every 1% of absorbed water [8,12,13]. A recently emerged approach to overcome this limitation consists in the formulation of Interpenetrated Polymer Networks (IPNs) in which the co-monomer has low or no tendency to absorb moisture. In particular, systems comprising TGDDM, DDS and 4,4'-bismaleimidodiphenylmethane (BMI) have attracted considerable attention both in the patent [14] and scientific literature [15-17]. In the present study, sorption and desorption characteristics of the neat TGDDM/DDS resin and of a ternary system comprising TGDDM, DDS and BMI are compared. To gather a deeper understanding of the molecular basis of the diffusion properties of these systems, the molecular interactions which are established between the water molecules and the polymer

network are analysed on the basis of the vibrational spectroscopy results obtained both in the mid- and near-infrared frequency ranges.

## Results and discussion

### MIR spectroscopy (4000 - 400 $\text{cm}^{-1}$ )

The transmission FTIR spectra in the MIR range (4000 - 400  $\text{cm}^{-1}$ ) of a fully cured TGDDM/DDS resin in the dry state and after equilibration in a water vapour atmosphere (activity  $a = 0.4$ ) are reported in Fig. 1, traces A and B, respectively. The main features emerging in the spectrum of the “wet” sample are (a) an intensity enhancement of the broad  $\nu_{\text{OH}}$  band centred at 3410  $\text{cm}^{-1}$  and (b) the appearance of a shoulder in the aromatic ring mode of TGDDM at 1593  $\text{cm}^{-1}$ . These are due, respectively, to the stretching and bending modes of absorbed water [18].

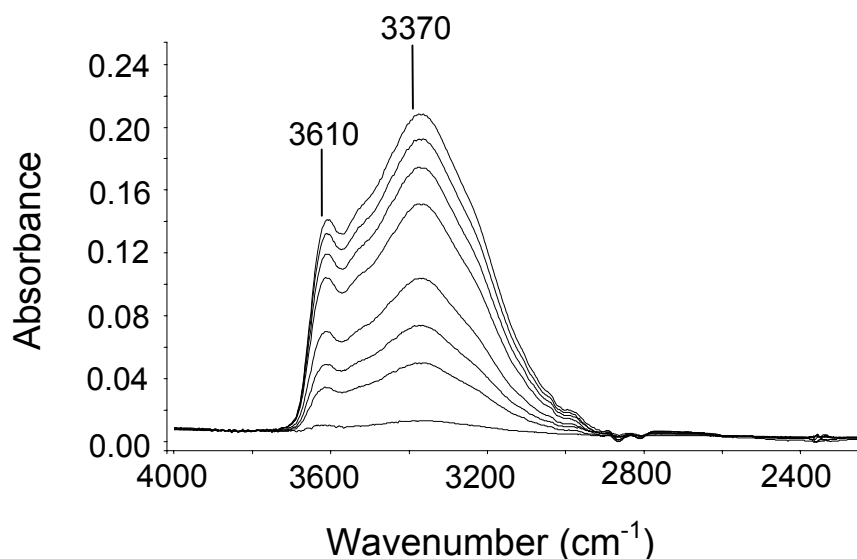


**Fig. 1.** Transmission FTIR spectra in the 4000 - 400  $\text{cm}^{-1}$  interval for a fully cured TGDDM/DDS resin in dry state (A, thick line) and after equilibrium water sorption at  $a = 0.4$  (B, thin line)

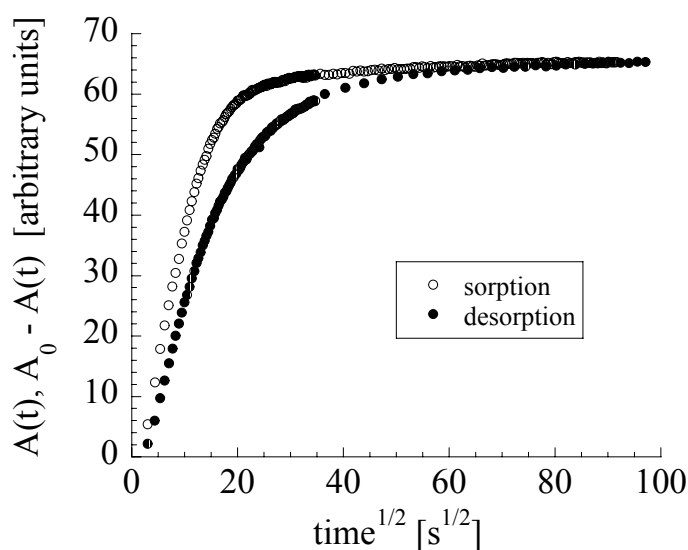
In order to isolate the spectrum of water in the  $\nu_{\text{OH}}$  region, it is necessary to eliminate the interference of the epoxy resin which absorbs strongly in this interval, due to the presence of a conspicuous concentration of hydroxyl groups (see Fig. 1A). This is accomplished by use of spectral subtraction analysis whereby the spectrum of the dry resin is subtracted from that of the water containing sample [18]. The results of such an analysis, relative to different sorption times, and, therefore, to different concentrations of water in the sample, are reported in Fig. 2.

Fig. 2 evidences that the subtraction spectra are very reproducible and are characterized by a relatively narrow peak at 3610  $\text{cm}^{-1}$ , partly superimposed on a much broader absorption centred at about 3370  $\text{cm}^{-1}$ . The high frequency peak can be confidently assigned to unassociated (“free”) water molecules, while the broad band at lower frequency is due to water molecules involved in specific molecular interactions of the hydrogen-bonding type with the polymeric network [19]. A closer inspection of

the  $3370\text{ cm}^{-1}$  band reveals a fine structure in the form of distinct discontinuities in the line shape. Up to four different components have been identified and suitably resolved by curve fitting analysis [7,18]. These features clearly indicate that water molecules establish different types of molecular interactions with the network, i.e., they interact with different proton accepting sites located within the network.



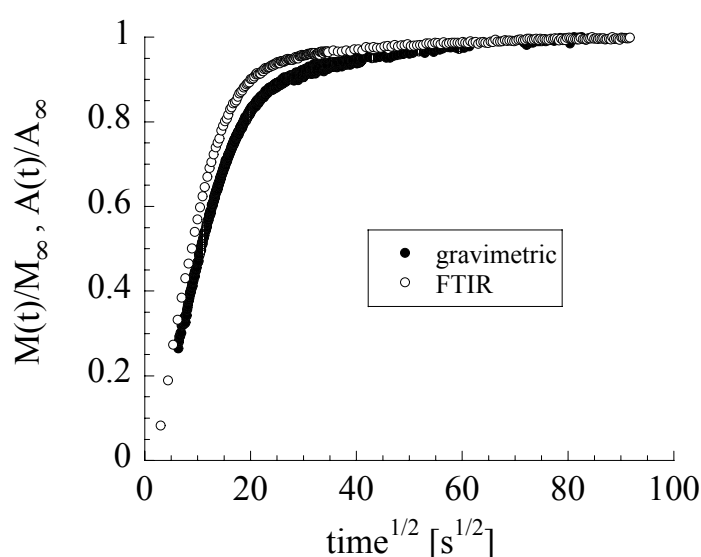
**Fig. 2.** Subtraction FTIR spectra in the  $4000 - 2400\text{ cm}^{-1}$  range collected at different times for the sorption of water in TGDDM/DDS at  $a = 0.4$



**Fig. 3.** Sorption and desorption curves for water vapour activity equal to 0.4. The sorption curve is reported in terms of absorbance at time  $t$ ,  $[A(t)]$ , while the desorption curve is reported as  $A(0) - A(t)$

The integrated intensity of the  $\nu_{\text{OH}}$  band of water (integration limits  $3735 - 2890\text{ cm}^{-1}$ ) provides a sensitive measure of the amount of penetrant concentration in the sample, thus allowing to monitor accurately sorption-desorption kinetics. An example of such

a kind of curves, relative to a water vapour activity of 0.4, is reported in Fig. 3. It is found that the desorption curve lies well below the sorption curve and this behaviour is indicative of water diffusivity being an increasing function of concentration. Accordingly, a pronounced linear region is observed in the  $A(t)$  vs.  $t^{1/2}$  curve relative to sorption, from which it is possible to evaluate the diffusion coefficient. As it is generally observed in these cases, the linear region is considerably shorter for the desorption curve. Equally relevant is the comparison between the sorption kinetics evaluated spectroscopically and that monitored gravimetrically by a Cahn electronic microbalance (see Fig. 4). It is noted that the two curves are close but not exactly superimposable. This effect has been tentatively ascribed to the non-uniform concentration profile within the sample and/or a time dependence of the relative populations of interacting and non-interacting water species in the sample [7].



**Fig. 4.** Comparison between gravimetric and spectroscopic sorption kinetics at  $a = 0.4$ . Water mass and absorbance are normalized with respect to their equilibrium values

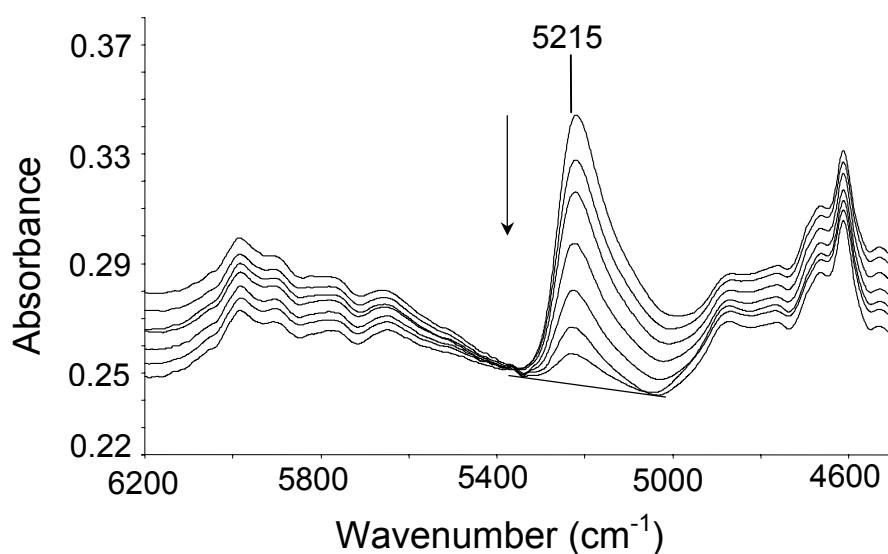
#### *NIR spectroscopy (12 500 to 4 000 $\text{cm}^{-1}$ )*

Near Infrared spectroscopy (NIR, from 10 000 to 4 000  $\text{cm}^{-1}$ ) has important advantages over MIR for investigating extensively hydrogen-bonded systems. These advantages are mainly related to the enhanced resolution of the various components in the  $\nu_{\text{OH}}$  range, coupled with the comparable magnitude of the molar absorbances for bonded and non-bonded species [18,19]. In the case of water diffusion studies, a further advantage is brought about by the much higher spectroscopic contrast of water in the NIR range with respect to MIR. In particular, a characteristic water peak occurs at around 5215  $\text{cm}^{-1}$  due to the combination of the asymmetric stretching ( $\nu_{\text{as}}$ ) and the in-plane deformation ( $\delta$ ) modes. In the systems under investigation this peak is fully resolved, free from interference by the polymeric substrate spectrum and sufficiently intense to be considered as a good candidate for the quantitative determination of the water concentration in the sample.

The transmission FT-NIR spectra in the wavenumber interval 6200 - 4600  $\text{cm}^{-1}$ , collected at increasing times during a desorption experiment carried out on the

TGDDM/DDS resin at 22°C, are shown in Fig. 5. These reveal the gradual decrease in intensity of the water peak, due to the depletion of penetrant molecules from the sample.

It is noted that, in this series of diffusion measurements, we monitored the isothermal desorption of a sample preliminary equilibrated in liquid water at room temperature. This mode was chosen in order to eliminate the spectroscopic interference of liquid water.



**Fig. 5.** FT-NIR transmission spectra collected at different times in the frequency range 6200 - 4600  $\text{cm}^{-1}$  during the desorption experiment carried out at 22°C. The baseline used for evaluating the peak area is also indicated

According to the Lambert-Beer law and for the invariance of the film thickness, we may write:

$$\frac{A_0 - A_t}{A_0 - A_\infty} = \frac{C_0 - C_t}{C_0 - C_\infty} = \frac{M_t}{M_\infty} \quad (1)$$

where the subscripts 0,  $t$  and  $\infty$  refer to absorbance ( $A$ ) or concentration of water in the sample ( $C$ ), at times 0,  $t$  and at equilibrium, respectively. In the same equation,  $M$  is the mass of desorbed water. Thus, absorbance data as a function of time allow direct evaluation of the diffusion parameters. The desorption curves at the various investigated temperatures for the TGDDM/DDS resin are reported in the form of Fick diagrams (i.e., as  $M_t/M_\infty$  vs.  $t^{1/2}$ /thickness) in Fig. 6. All curves display a pronounced linear region extending up to ordinate values around 0.8, and provide a reliable way of determining the system's diffusivities, which are collectively reported in Tab. 1.

The same sort of measurements have been performed on a modified epoxy formulation which contains 4,4'-bismaleimidodiphenylmethane (BMI) as a co-reactive monomer. Owing to the negligible tendency of BMI to absorb moisture, this system exhibits a lower equilibrium water uptake with respect to the unmodified epoxy resin (4.13 wt.-% for the TGDDM/DDS/BMI system and 6.57 wt.-% for the TGDDM/DDS resin). The Fick diagrams at different temperatures for the ternary TGDDM/DDS/BMI system are shown in Fig. 7, and the diffusivities evaluated therefrom are collectively reported in Tab. 1.

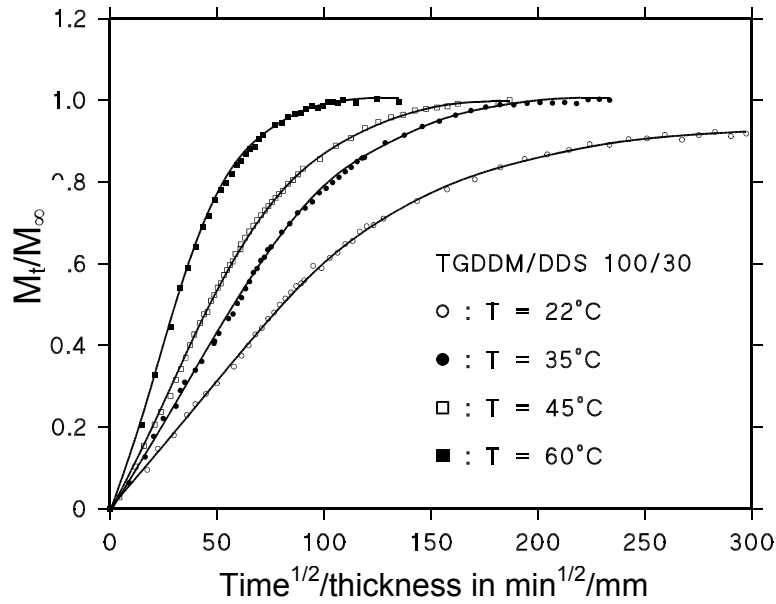


Fig. 6. Fick diagrams for the desorption measurements carried out at temperatures as indicated, on the resin TGDDM/DDS 100/30 (w/w)

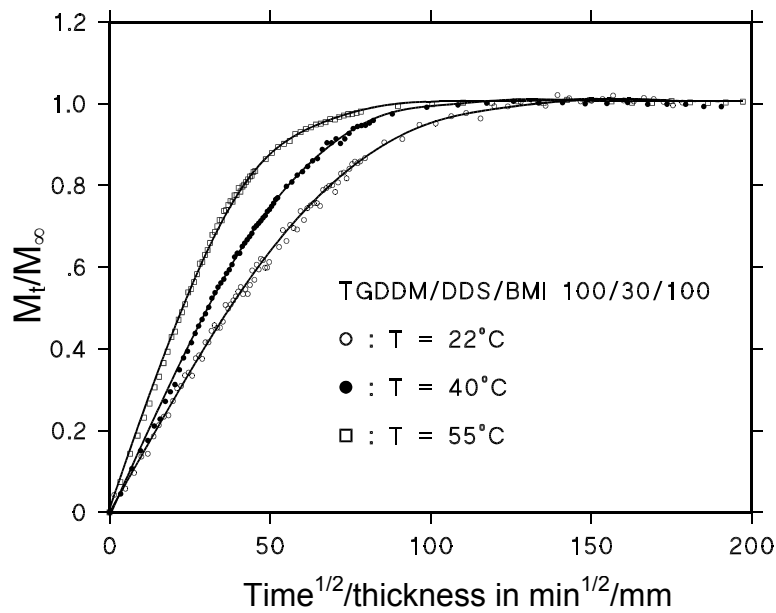


Fig. 7. Fick diagrams for the desorption measurements carried out at temperatures as indicated, on the resin TGDDM/DDS/BMI 100/30/100 (w/w/w)

Comparison of the data in Tab. 1 reveals that the diffusion process in the ternary system is considerably faster than in the unmodified resin. As the temperature increases, the desorption from the ternary mixture remains faster but the difference gets smaller and smaller. While at 22°C the diffusivity ratio between the ternary and the control system is 3.2, it reduces to 1.6 at 60°C.

**Tab. 1.** Diffusion coefficients from FT-NIR desorption measurements (data reported in Fig. 6 and Fig. 7) for the various network systems investigated

Composition (weight ratio)			Temperature in °C	$D \times 10^9$ in $\text{cm}^2 \cdot \text{s}^{-1}$
TGDDM	DDS	BMI		
100 <sup>a)</sup>	30	-	22	$1.5 \pm 0.10$ <sup>c)</sup>
100	30	-	36	$3.1 \pm 0.15$
100	30	-	45	$4.5 \pm 0.20$
100	30	-	60	$9.9 \pm 0.15$
100 <sup>b)</sup>	30	100	22	$4.9 \pm 0.20$
100	30	100	39	$8.3 \pm 0.15$
100	30	100	54	$13.9 \pm 0.25$
100	30	100	60	$15.7 \pm 0.20$

a) Equilibrium water uptake (in liquid water at 22°C): 6.57 wt.-%.

b) Equilibrium water uptake (in liquid water at 22°C): 4.13 wt.-%.

c) 95% Confidence interval.

The diffusion of a penetrant into a polymeric network is a thermally activated process, and, as such, its temperature dependence can be expressed by an Arrhenius-type relationship [20-22], i.e.,

$$D = D_0 e^{-\frac{E_a}{RT}} \quad (2)$$

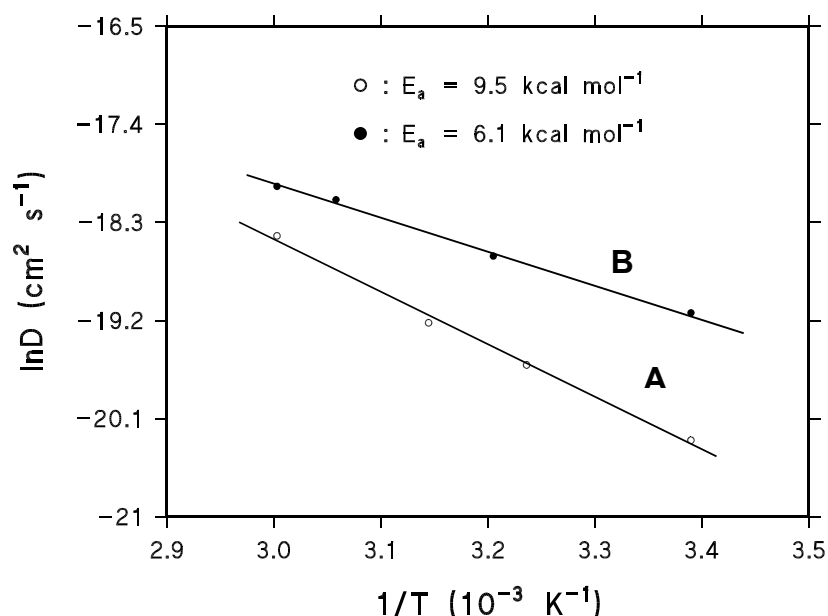
where  $D_0$  is the pre-exponential factor,  $E_a$  is the activation energy of the diffusion process and  $R$  is the gas constant. The plots of  $\ln D$  vs.  $1/T$  for the pure epoxy resin and the BMI containing formulation are shown in Fig. 8, curves A and B, respectively. Both are highly linear, with correlation coefficients,  $r^2$ , equal to 0.995 and 0.997, respectively. For the epoxy resin the values of  $E_a$  and  $D_0$ , calculated from the slope and intercept of the relative straight line, are  $9.5 \text{ kcal} \cdot \text{mol}^{-1}$  and  $1.8 \times 10^{-2} \text{ cm}^2 \cdot \text{s}^{-1}$ , respectively.

These values compare favourably with those reported in the literature for analogous systems obtained by gravimetric sorption measurements at different temperatures. This is particularly true for  $E_a$ , whose value has been reported by different investigators to lie in the range between  $11.8$  and  $8.1 \text{ kcal} \cdot \text{mol}^{-1}$  [11,23]. For the BMI containing system,  $E_a$  is equal to  $6.1 \text{ kcal} \cdot \text{mol}^{-1}$ , i.e., about 1.5 times lower than that of the control material, while the pre-exponential factor remains essentially unchanged ( $1.6 \times 10^{-2} \text{ cm}^2 \cdot \text{s}^{-1}$ ).

The higher diffusion rate in the ternary mixture and the lower activation energy may result from several factors. For instance, it has been demonstrated in previous contributions [15-17] that the ternary system displays a complex IPN-type structure which is more defective and less tightly cross-linked than that of the unmodified epoxy network. This topological effect may contribute to enhance water diffusivity and lower activation energy for diffusion. A further contribution is certainly related to



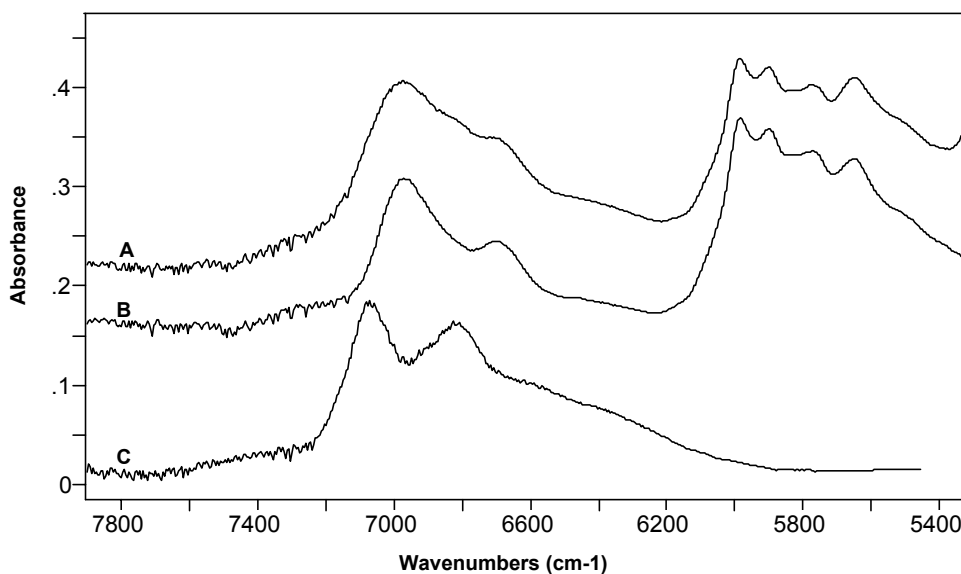
molecular interactions between the penetrant molecules and the polymeric substrate. These provide trapping sites which slow down the movements of the diffusing water within the network. Thus, reducing the concentration of these sites (amino-alcohol groups of the TGDDM/DDS network) by dilution with an inert monomer (BMI) improves the penetrant mobility.



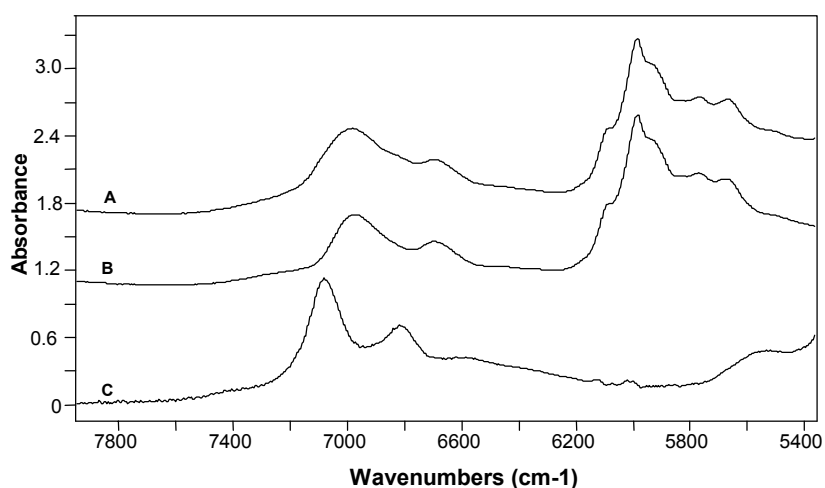
**Fig. 8.** Arrhenius plots of the diffusion coefficients for the resin TGDDM/DDS 100/30 (w/w) (○) and the resin TGDDM/DDS/BMI 100/30/100 (w/w/w) (●)

Another region of the NIR spectrum that contains relevant information is the one between 7800 and 6000  $\text{cm}^{-1}$ , where overtones and combinations of the two stretching fundamentals ( $\nu_{\text{as}} + \nu_{\text{s}}$ ) of water occur. As in the MIR interval, also in this wavenumber range the TGDDM containing networks display an intense and complex  $\nu_{\text{OH}}$  band due to self-associated hydroxyl groups of the epoxy resin, which obscure the water spectrum. In fact, sorption of water into the network causes a general increase of the total absorbance area, particularly at around 6800 and 6400  $\text{cm}^{-1}$  (compare spectra A and B of Fig. 9 and spectra A and B of Fig. 10).

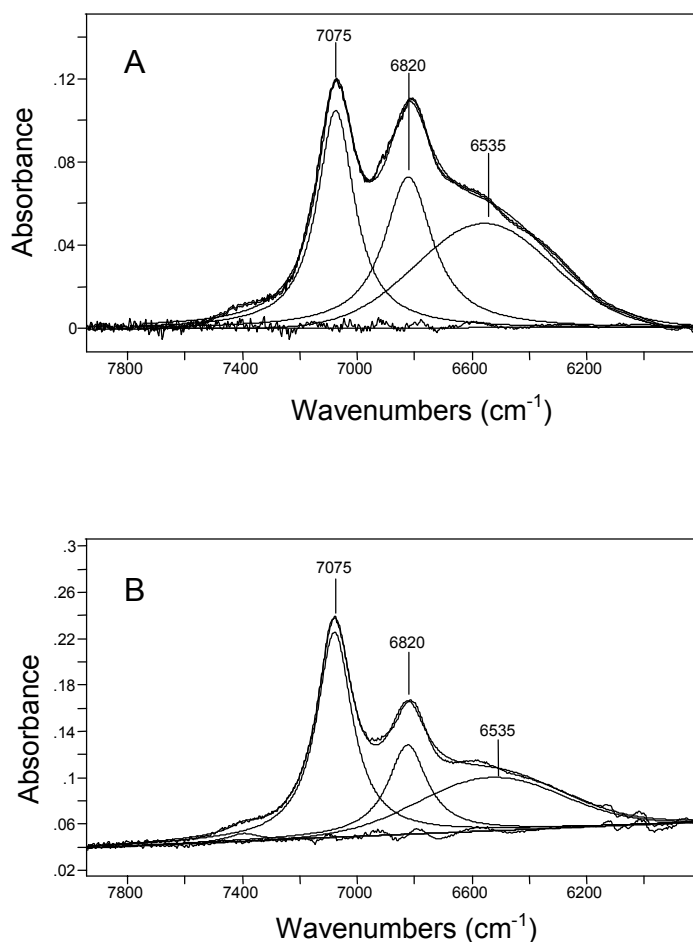
Again, subtraction spectroscopy was employed to eliminate the interference of the network spectrum and to isolate the spectrum of sorbed water [18]. The difference spectra reported in Fig. 9 and Fig. 10, traces C, evidence a three component profile consisting of two sharp, fully resolved peaks centred at 7075 and 6820  $\text{cm}^{-1}$ , partly superimposed onto a broader band at lower wavenumbers (around 6535  $\text{cm}^{-1}$ ). It is noted that in the two difference spectra the peak positions remain the same, while the relative intensities of the three components change. In Fig. 11A and 11B is reported the curve fitting analysis of the spectral profiles of Fig. 9C and Fig. 10C, performed according to the method described in detail in refs. [7] and [18].



**Fig. 9.** Transmission FT-NIR spectra in the range 7800 - 5400  $\text{cm}^{-1}$  for the resin TGDDM/DDS. Trace A: Sample containing 6.2 wt.-% absorbed water. Trace B: Dry sample. Trace C: Difference spectrum A minus B. The absorbance scale refers to spectra A and B. To facilitate the comparison, spectra A and B have been arbitrarily shifted along the ordinate axis, and the absorbance scale of spectrum C has been amplified by a factor of 4



**Fig. 10.** Transmission FT-NIR spectra in the range 7800 - 5400  $\text{cm}^{-1}$  for the resin TGDDM/DDS/BMI. Trace A: Sample containing 4.6 wt.-% absorbed water. Trace B: Dry sample. Trace C: Difference spectrum A minus B. The absorbance scale refers to spectra A and B. To facilitate the comparison, spectra A and B have been arbitrarily shifted along the ordinate axis, and the absorbance scale of spectrum C has been amplified by a factor of 4



**Fig. 11.** Curve fitting analysis in the 7800 - 5800  $\text{cm}^{-1}$  range, relative to: (A) the spectrum of water absorbed in the resin TGDDM/DDS (6.2 wt.-%); (B) the spectrum of water absorbed in the resin TGDDM/DDS/BMI (4.6 wt.-%)

On the basis of model compounds studies [18,19] it was possible to propose likely assignments for the three peaks resulting from the curve fitting analysis. In particular, the component at 7075  $\text{cm}^{-1}$  has been attributed to a combination of the  $\nu_{as}$  and  $\nu_s$  modes of non-hydrogen bonded ("free") water molecules. The peak at 6820  $\text{cm}^{-1}$  arises from the combination of  $\nu_{nb}$  and  $\nu_b$  fundamentals in self-associated water molecules forming a single hydrogen bonding interaction (water dimers). Finally, the broad component centred at 6535  $\text{cm}^{-1}$  is due to a ( $\nu_{as} + \nu_s$ ) combination of water molecules whose hydrogens are both involved in strong hydrogen bonding interactions with proton accepting groups located on the polymeric network. The half-band width of this component (three times larger than the 7075  $\text{cm}^{-1}$  peak and four times larger than the peak at 6820  $\text{cm}^{-1}$ ) is related to the occurrence of different interactions (i.e., with different proton accepting groups) which produce a comparatively large distribution of hydrogen-bonding strengths. Thus, the two high frequency peaks correspond to water molecules characterized by a high molecular mobility, since they do not interact with the polymeric network. It is reasonable to presume that these species are confined into excess free volume elements (microvoids) of an appropriate size not to have any effect on physical properties related to molecular

relaxations. Conversely, the water molecules giving rise to the low frequency band are molecularly dispersed within the network and are responsible for the plasticization and other detrimental effects caused to the material. In this respect, it is worth noting that a quantitative estimation of the population of bound water which can be achieved from the present spectral data would give a direct estimation of the plasticization effect. This approach would have definitive advantages over thermal techniques (DSC, dynamic-mechanical analysis) which rely on measurements of  $T_g$  depression, in so far as for these tests a certain amount of water will desorb while the sample is heated in the course of the experiment.

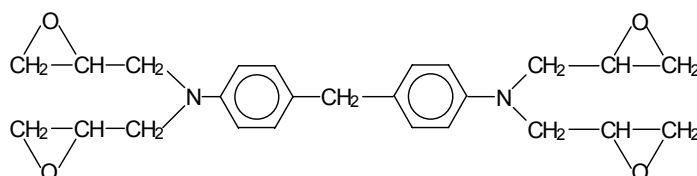
Comparison of Fig. 10 and Fig. 11 clearly indicates that in the TGDDM/DDS/BMI system the relative amount of bound water decreases significantly with respect to the unmodified epoxy resin, owing to the presence of the inert BMI network within the IPN-like structure. Thus, the presence of BMI has two beneficial effects: it reduces the total amount of absorbed water as well as the fraction of water molecularly bound to the network.

## Experimental part

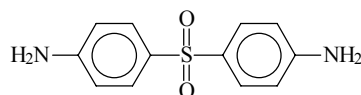
### Materials

The tetraglycidyl-4,4'-diamino-diphenylmethane (TGDDM) resin was supplied by Ciba-Geigy (Basel, Switzerland). This resin has an epoxy equivalent weight (EEW) of  $124.1 \text{ g}\cdot\text{eq}^{-1}$ , which is 15% lower than the calculated stoichiometric value, due to partial hydrolysis of the oxirane rings prior to curing. The resin hardener was 4,4'-diaminodiphenylsulfone (DDS), supplied by Aldrich (Milwaukee, WI). The bismaleimide resin component was *N,N'*-bismaleimide-4,4'-diphenylmethane (BMI) also from Aldrich. All reagents were used without further purification. The structure of these components is shown below.

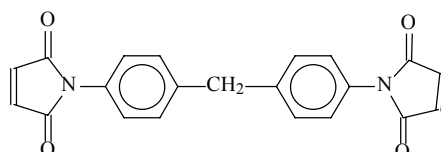
a) TGDDM: Tetraglycidyl-4,4'-diaminodiphenylmethane



b) DDS: 4,4'-Diaminodiphenylsulfone



c) BMI: *N,N'*-Bismaleimide-4,4'-diphenylmethane



TGDDM and DDS were mixed at 120°C in a weight ratio 100 : 30 (corresponding to a mole ratio of 1 : 0.5) with vigorous mechanical stirring to obtain a homogeneous (visually transparent) solution. The mixture was then degassed for 15 min in vacuum and poured into a stainless-steel mould. Curing was conducted at 140°C for 16 h, followed by a post-curing step at 200°C for 4 h. The ternary formulation was prepared by adding to the TGDDM/DDS solution 100 parts by weight of BMI powder. Mixing was continued at 100°C until complete dissolution of the BMI powder. Curing and post-curing were done as above.

### Techniques

The *time-resolved* FTIR measurements were made on thin films placed in a suitably constructed diffusion cell, which allows careful control of internal pressure ( $\pm 0.01$  Torr) and temperature ( $\pm 0.2^\circ\text{C}$ ). The cell was placed in a Perkin-Elmer System 2000 interferometer equipped with a Germanium/KBr beam splitter and a wide band DTGS detector. Instrumental parameters were as follows: resolution =  $4\text{ cm}^{-1}$ , optical path difference (OPD) velocity =  $0.2\text{ cm/s}$ , spectral range  $4000 - 400\text{ cm}^{-1}$  (MIR) or  $8000 - 4000\text{ cm}^{-1}$  (NIR). A single data collection was performed for each spectrum (3551 data points) which, for the selected instrumental conditions, took 6 s to complete. The signal was acquired as single beam at specific time intervals which increased as the sorption process approached equilibrium. A typical sorption run lasted about 30 min and acquisition time intervals were 10 s during the first 10 min of the experiment and 60 s afterwards.

In the NIR frequency range an isothermal desorption mode was used, so that spectroscopic interference due to liquid water could be eliminated. Samples of 0.15 - 0.25 mm thickness were previously equilibrated with respect to the amount of absorbed water by immersion in a deionized water bath, thermostatically controlled at  $22(\pm 0.2)^\circ\text{C}$ . To obtain meaningful and reproducible results, the NIR measurements in the  $\nu_{\text{O-H}}$  region were carried out on samples 3.5 - 4.0 mm thick, owing to the reduced absorbance of the O-H stretching modes in comparison to the water band used for monitoring its concentration ( $5215\text{ cm}^{-1}$ ). For these samples, 300 spectra were signal-averaged for each measurement.

### Conclusions

An experimental approach to investigate the diffusion of gases and vapours through polymeric films is presented. It is based on *time-resolved* FTIR measurements in the transmission mode and it is able to provide accurate and reproducible kinetic data. This method has been applied to two epoxy based systems, namely a binary TGDDM/DDS formulation and a ternary system in which the TGDDM/DDS resin is modified by the addition of a bismaleimide co-reactive monomer (BMI). Spectra were collected both in the MIR and NIR frequency range. In both regions the absolute diffusion parameters (i.e., diffusivity,  $D$ , and activation energy for diffusion,  $E_a$ ) evaluated spectroscopically compare well with those determined by conventional gravimetric methods. An additional feature of the NIR frequency range is the possibility of getting qualitative and quantitative information on the molecular interactions of the hydrogen-bonding type established between absorbed water and specific sites within the polymeric network. The spectroscopic analysis revealed the presence of non-interacting water and hydrogen-bonded water which is primarily responsible for the plasticization of the material. It has been demonstrated that the presence of BMI

in the ternary system not only reduces the overall amount of water absorbed at equilibrium but also reduces the fraction of water molecularly bound to the network.

**Acknowledgement:** Thanks are due to Mr. G. Orefice for helping in the realization of the environmental chamber for FTIR diffusion studies and for technical assistance in the spectroscopic measurements.

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