

FTIR–ATR Studies of the Structure and Dynamics of Water Molecules in Polymeric Matrixes. A Comparison of PET and PVC

Christopher Sammon,[†] Carine Mura,[†] Jack Yarwood,^{*,†} Neil Everall,[‡] Ron Swart,[#] and David Hodge[#]

Sheffield Hallam University, Materials Research Institute, City Campus, Sheffield S1 1WB, UK,
Wilton Materials Research Centre, PO Box 90, Wilton, Middlesbrough, TS6 8JE, UK, and
Zeneca Specialities, PO Box 42, Hexagon House, Blackley, Manchester M9 3DA, UK

Received: November 11, 1997; In Final Form: February 10, 1998

We report a systematic FTIR study of the perturbation of water “sorbed” into the polymers PET and PVC as a function of crystallinity (PET) or plasticizer content (PVC). Band shapes of the composite $\nu(\text{OH})$ band of H_2O obtained by the ATR technique have been fitted to individual components, corresponding to those recently found for pure water itself. A detailed quantitative analysis of the frequency shifts and relative intensities has led to conclusion that these component bands show direct evidence for the breaking of the water network in the polymer matrix and that this process depends on the polymer chemical and/or physical properties. Evidence is also found for interactions of water with the polymer at the lower end of the hydrogen bond interaction scale. The component band relative intensities (compared with those of pure water) have been used to compute an intensity enhancement parameter, P , which is a measure of the perturbation of a particular water distribution due to dissolution in the polymer matrix. For PET, P varies systematically with density, reflecting the ability of water to penetrate the polymer microstructure. For PVC the plasticizer content (and hence T_g) has a considerable influence on the sorption (and swelling) process and on the equilibrium content and state of water. Thus, ATR–FTIR has been used for the first time to demonstrate, via intensity enhancement, the extent of electronic perturbation at a polymer/water interface.

1. Introduction

It has been known for a long time^{1–5} that polymer surface bound water is (i) different from bulk water, for example, in its restricted motion,^{6–14} and (ii) important for the behavior of such surfaces in the context of such phenomena as protein dynamics,^{5,16} food preservation,^{17,18} and polymer mechanical relaxation.^{17,19}

Professor John Finney²⁰ has summarized and emphasized the situation vis-à-vis the need to approach the characterization of such perturbed water. To quote, “we need a better understanding of the effect of hydration on structural and dynamic properties in order to control industrially relevant processes.” One exciting approach to fulfilling this need is to start with characterizing the properties of this “special”/bound water. Indeed, much work has been published in this area already using spectroscopic techniques, such as NMR,^{12,22,23} FTIR and Raman,^{24,35} neutron scattering,^{10,11,14} and light scattering.^{9,21} The main problem tends to be our ability to distinguish bound water from bulk water, and various techniques have been devised to circumvent this problem. These include the use of selective probes,^{12,23} spectral contrast,^{10,11,14,32} and spectral subtraction.^{24,26}

The ATR–FTIR technique³⁶ has considerable potential in this area for several reasons. As Marechal has pointed out,²⁴ the spectra obtained are free from saturation artifacts, a major problem when studying water by infrared spectroscopy. The sampling depth^{36,37} is dependent on controllable parameters³⁶ and is of the order of 0.5 to 2.0 μm . The spectra can be collected in real time^{38–41} on the scale of the diffusion

processes^{38–44} at a polymer interface in contact with a liquid reservoir (Figure 1). The technique described here to study the perturbation of water in a polymer matrix makes good use of these attributes (along with the subtraction technique mentioned above). There are, however, some essential experimental requirements which must be fulfilled. High quality reproducible data require good optical contact with the ATR crystal, and polymer films must be spread, cast, or spun onto the crystal from a suitable solvent. For most polymers this is not a serious problem (see section 2).

There have been a number of papers published recently on the perturbation of water molecules close to an organic interface using vibrational spectroscopy. These include the study of microemulsions^{45–48} and polymers.^{24–29,31–35} The water bands studied have included those due to the $\nu(\text{OH})$; $\nu(\text{OD})$ and $b(\text{OH})$; $b(\text{OD})$ modes. Changes of frequency, intensity, and shape have been interpreted in terms of bound and free water (up to three different water species in some systems),^{47–49} water clustering,^{28,31–33} water orientation,³⁰ and water networking.^{28,29} The structure of water in polymer solutions^{45,49} has been reviewed.^{29b}

It has been questioned^{45,49} whether a well defined hydration number can be deduced from spectroscopic measurements and, even further whether distinctly different electronically perturbed states of water can be detected. Or whether, as is thought in some quarters, the change in properties in nonbulk water molecules in these systems is more likely to be gradual depending on the precise distance from the organic interface. These arguments are reminiscent of those around the same issues for liquid water itself which ensued in the 1960s and 1970s⁵⁰ vis-à-vis mixture and continuum models. Nevertheless, there

[†] Sheffield Hallam University.

[‡] Wilton Materials Research Centre.

[#] Zeneca Specialities.

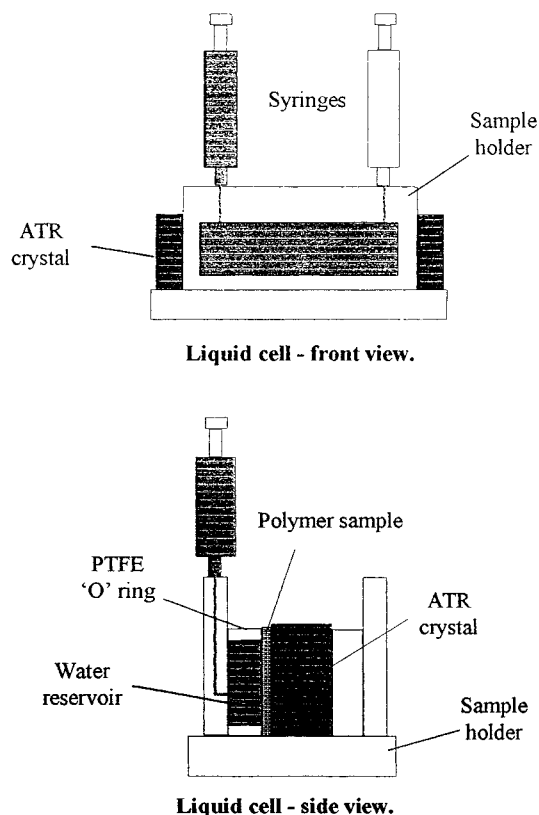
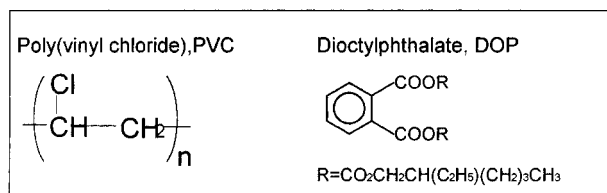


Figure 1. ATR cell in which perturbation measurements were made.

(a) PVC/20% DOP



(b) PET (all trans crystalline conformation)

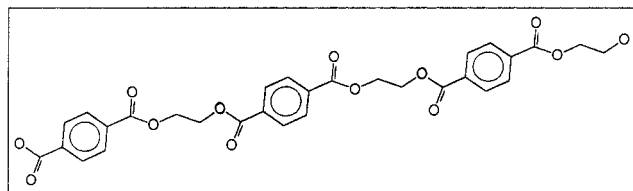


Figure 2. Structures of the polymers studied.

has recently arisen new literature on liquid water (based around new and much more extensive data),^{52–57} in which the liquid water (a pseudo-polymeric material) is treated as though it were composed of a mixture of “defect”, and “nondefect” water molecules with interchange between them as a function of temperature (with broken hydrogen bonds only being relevant at high temperature and pressures). It follows that the band shapes observed for water in polymer matrixes (Figures 3, 4, and 5) can, at least in principle, be treated in the same way. This paper explores that possibility for water sorbed into the polymeric materials PET and PVC shown in Figure 2.

The O–H stretching vibrational modes of liquid water lead to a very complicated vibrational spectrum, complicated by both intermolecular and intramolecular O–H oscillator coupling. This coupling occurs between the $\nu_s(\text{OH})$ and $\nu_{as}(\text{OH})$ (which would be present in the gas phase of H_2O with no intermolecular

interactions) and between the O–H oscillators on *different* molecules (which would need to be compared with totally decoupled O–H or O–D bands of HOD in the gas phase where isotopic substitution leads to the decoupling process). These coupling processes promote delocalization in the liquid at room temperature in such a way that distinct and isolated O–H vibrational modes are no longer meaningful. The liquid is also subject to structural disorder on a picosecond time scale, by the breaking of intermolecular hydrogen bonds (but this “disorder” will be long-lived on the vibrational time scale). This picture of liquid water has been established largely by comparison of Raman and infrared spectra with that of ice 1h and with that of the vapor phase. It would tend to dictate against the interpretation of the Raman and infrared spectra of isosbestic points^{52,56,57} in terms of a simple two-state model consisting of hydrogen bonded and non-hydrogen bonded water molecules. Nevertheless, this is the interpretation that has been made in the spirit of the ‘mixture’ model, first introduced⁵¹ many years ago. However, the continuum model is still also valid in the sense that each of the contributing profiles which have been deconvolved from infrared and Raman spectra, usually has a distinct shape and substantial width. This width (Table 1) is, of course, consistent with a wide range of hydrogen-bonding distances and intermolecular bond angles within each of the major water types.

Although the Raman spectra of liquid water⁵² has been studied in some detail, quantitative infrared spectra of the stretching modes of liquid water have been examined with less rigor, mainly because of the very high inherent band intensity which demands the use of the now commonly available ATR technique (as used in this paper). The most recent work on liquid water has also been found to be consistent with the two-state model mentioned above. However, in this case, Marechal and co-workers^{24,55} have implied, from the temperature dependence of the infrared spectrum of water, that the two-state model is associated with two different types of hydrogen-bonded water. Type I water, whose component intensity increases with increasing temperature, is considered to be loosely bound water but hydrogen bonded molecules, which have rapid diffusional rotational along the Z-axis. Type II water molecules, whose intensity component decreases with temperature, are clearly more strongly hydrogen bonded water molecules which show only vibrational motion about the Z-axis. According to the analysis of Marechal et al.,⁵⁵ the two component spectra have extremely similar bandwidths and it therefore seems unlikely that the reorientational dynamics dominate the band shape. However, Marechal has not considered the effects of vibrational relaxation on the band shape.

2. Experimental Section

All measurements were carried in a liquid - holding ATR cell (Graseby - Specac Plc) at ambient temperature, $25 \pm 2^\circ\text{C}$ (see Figure 1). The data were taken as a function of time in connection with water diffusion measurements.

Polymer thin films (Figure 2) were prepared by casting from a solvent (DMF for PVC and *o*-chlorophenol for PET) to give a uniform thickness of 15–25 μm . They were subsequently annealed at 60°C in an oven for at least 2 h to remove solvent.

All the materials were Analar grade from Aldrich or were obtained from the sponsoring companies. Diethyl phthalate (DOP) plasticizer was purchased from Aldrich. PET copolymer materials were provided by ICI. All the materials were used without further purification.

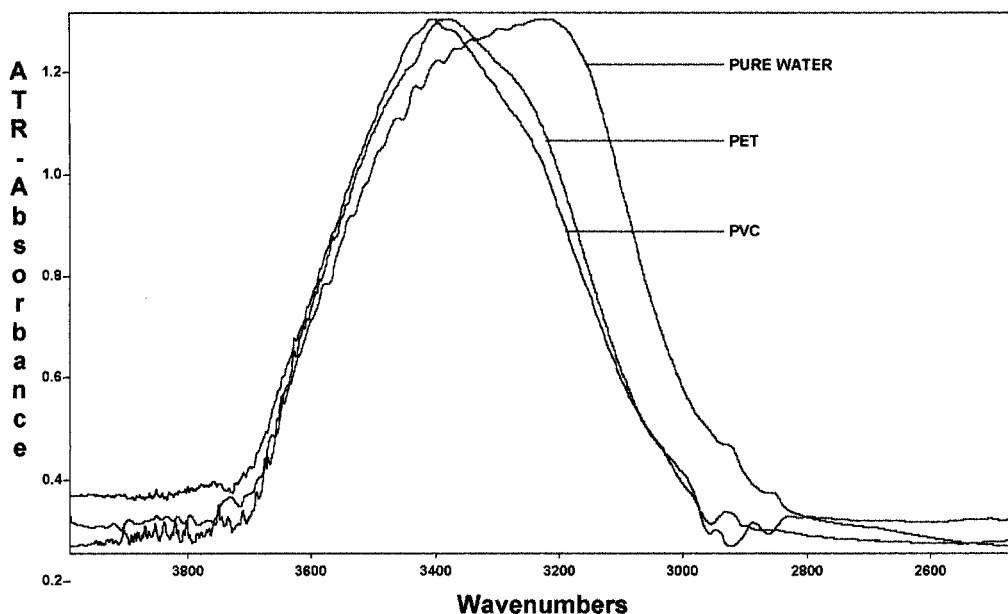


Figure 3. Infrared spectra of water in PET (0.48 abs units) and PVC (0.69) compared with pure water (0.99) spectrum.

TABLE 1: Summary of Band Positions and Frequency Shifts for Water in PET and PVC Compared with Values in Pure Water (25 °C)

	water		water/PET		water/PVC		shift/cm ⁻¹	
	$\nu_{\max}/\text{cm}^{-1}$	$\Delta\nu^{1/2}/\text{cm}^{-1}$	$\nu_{\max}/\text{cm}^{-1}$	$\Delta\nu^{1/2}/\text{cm}^{-1}$	-10	+15	PET	PVC
band 1	3606	97	3609 (3598–3609)	87	-33	-33	+11	+26
band 2	3510	159	3508 (3518–3508)	147	-35	-27	-10	+15
band 3	3386	228	3385 (3418–3385)	201	3387 (3420–3387)	242	-33	-33
band 4	3192	290	3233 (3268–3233)	269	3233 (3260–3233)	165	-35	-27

The concentrations of water in the polymer at equilibrium, typically after several days, were obtained by direct weighing.

3. Results and Discussion

(i) **General Observations.** Infrared spectra obtained using the attenuated total reflection technique (ATR) for water diffusing into the two polymers as a function of time are shown in Figures 4A and 4B (respectively) for PET and PVC. Comparison with pure water is made in Figure 3. From these spectra it is obvious that (a) the shape of the water spectrum in the 3000 to 3600 cm^{-1} region varies as a function of time and is quite different from that of the pure water obtained under the same conditions in the same cell (Figure 3); (b) the whole profile, presumably containing both symmetric and antisymmetric stretching modes of water, is dramatically shifted to low frequency compared with the profile of pure water; and (c) the general features of shifting of the $\nu(\text{OH})$ band profile are similar although not identical for PET and PVC (Table 1).

Thus the general features observed when water is absorbed into these two polymeric films are similar for both materials. In particular, (1) the spectra show relatively weakly hydrogen bonded (and/or rotationally hindered molecules) with a band in the 3600- cm^{-1} region, as indeed is found for pure water,²⁴ and (2) there are usually three (but possibly four) other bands which correspond to water molecules engaged in different degrees of hydrogen bonding, either with themselves or with the polymer surface.

Although the details of the electronic perturbation of the water molecule will obviously depend on the nature of the polymer

chemistry, it has been generally found,^{26–35} for a wide range of polymers, that water dissolved in a organic medium (either an organic solvent or polymer matrix) is, on average, more weakly hydrogen bonded than that of water molecules in the pure water network. This is probably due to a combination of different phenomena, including the breaking of the water network to produce smaller clusters and the (weaker) hydrogen bonding of water molecules to the polymer chemical groups. This would then obviously be expected to lead to a shift of the hydrogen bonding $\nu(\text{OH})$ profile to higher frequencies (Figures 3 and 4). As the amount of water (as measured by the ATR intensity) increases, the water molecule “clusters” tend to increase in size again and the average frequencies of the component bands (Figures 5 and 6) move back toward lower frequencies. However, they never reach the values that have been obtained for pure water (Table 1).

(ii) **Band Fitting.** More detailed analysis of the spectra has been achieved by fitting the overall band profile in the way shown in Figures 5 and 6. The similar process for pure water is shown in Figure 7. Band decomposition was achieved using the curve fitting routine provided in the Grams-32 software package. The strategy adopted was to use fixed band shape ratios (50% Gaussian/50% Lorentzian) with all other parameters allowed to vary upon iteration. The statistical parameters defined in the software manual were used as a guide to “best fit”. The χ^2 values could be reduced, as expected, by allowing the band shape to vary also (with five additional parameters!), but the chemical conclusions were not significantly altered.

Details of the component band parameters are shown in

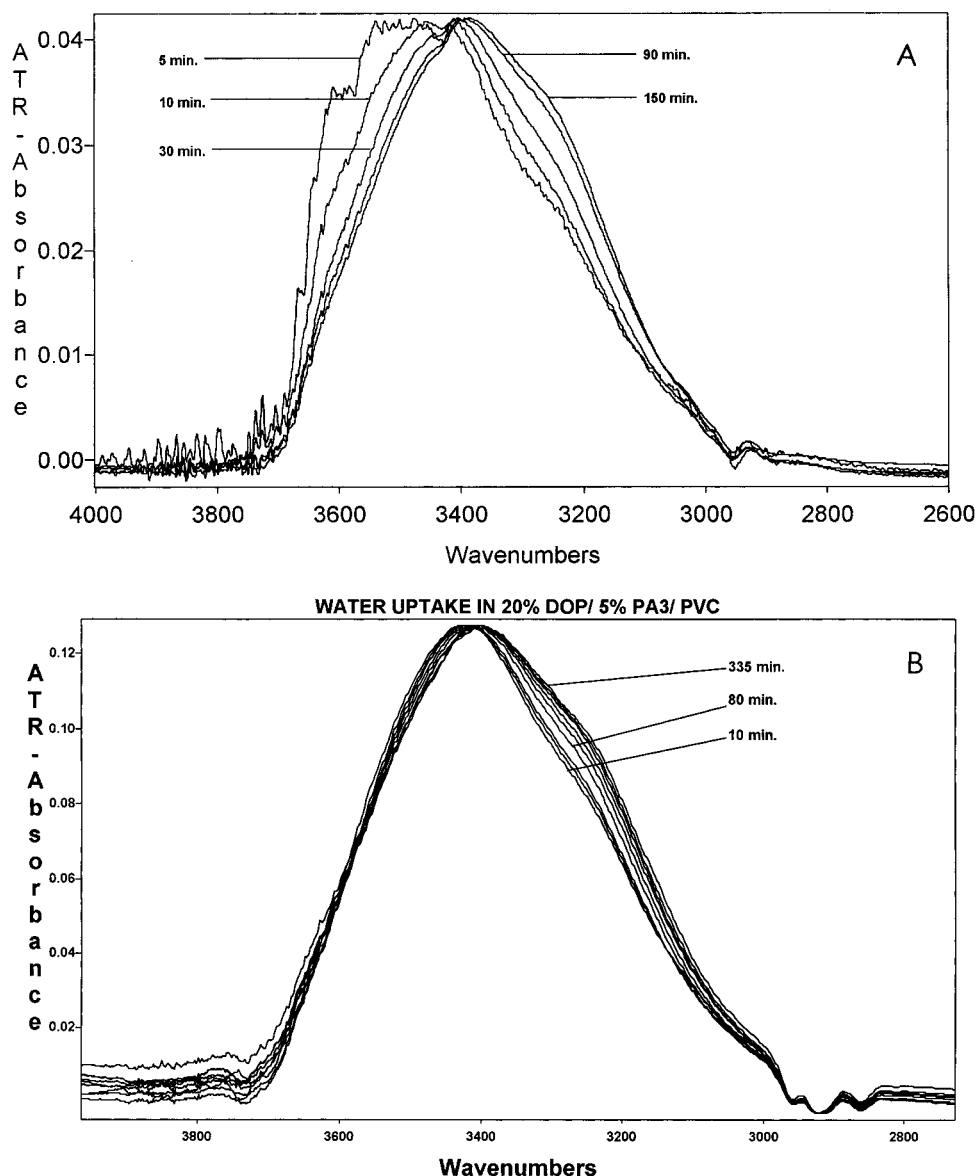


Figure 4. Infrared spectra of water in (A) PET and (B) PVC as a function of time.

Tables 2 and 3 and the following conclusions can be reached from these data.

1. Most of the component bands (Figures 8 and 9) increase in intensity with time in the way expected since the polymer is in contact with the water reservoir in real time throughout the experiment. However, there are large discrepancies between the intensities of the component bands for water in the polymer and water molecules in the pure water. This emphasizes that, in infrared spectroscopy, there are likely to be large changes of extinction coefficient when water molecules engage in or are released from their hydrogen bonding environment (see section 3iii).

2. Most of the component bands also show a general shift to high frequency when water dissolves in the polymer (in accordance with the overall band profile shift), but there are some notable exceptions. These may be deduced from Figures 10 and 11. In particular, the two highest frequency bands of water in PVC and one of the high-frequency bands in PET show a shift to *high* frequency, as the amount of water in the polymer increases. This implies that, when water first dissolves in the polymer, these two water environments are different from those in the liquid water. This provides support for assertions in the literature^{26–35,59} about the “significant” degree of water hydration

of the polymer. Furthermore, it would appear that these interactions result in water environments displaying stronger hydrogen bonding (presumably between water and the polymer) compared with the corresponding interactions in liquid water. In all cases, as the amount of water in the polymer increases, the component bands shift to lower frequency, reflecting the movement back toward the water environment to be found in liquid water, but always less strongly hydrogen bonded than in the full water network. This implies that at low concentrations of water the network is broken to such an extent that the water molecules are arranged in smaller clusters within the polymer microstructure, but that these clusters increase in size (as expected) as the amount of water reaches saturation.

More light may be thrown on the question of the state of water in PVC by the examination of the water molecule spectrum as a function of time both for adsorption and desorption. These results are shown in Figure 12. Figure 12A shows the change of the OH band structure as water is removed from the PVC film. The spectra were obtained by ratioing against the spectrum of the dry film. In other words, the spectra show the state of water which is still in the polymer. As may be seen from the variation of overall band profile, as a function of time, there is a distinct shift to low frequency as water is

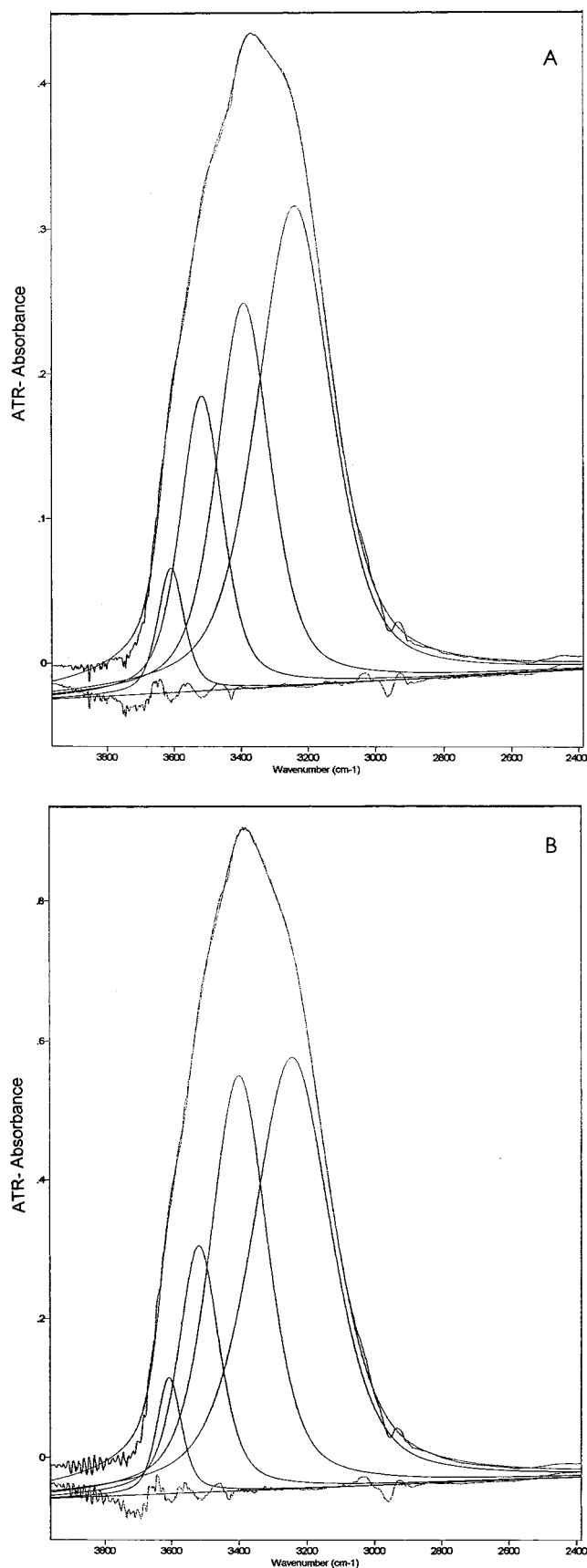


Figure 5. Band fitting results for water in PET at equilibrium. (A) highest crystallinity (25%), (B) lowest crystallinity (4%).

gradually removed by the desorption process (in a stream of nitrogen). This means that water in the polymer at longer time is, on average, more strongly hydrogen bonded. It therefore

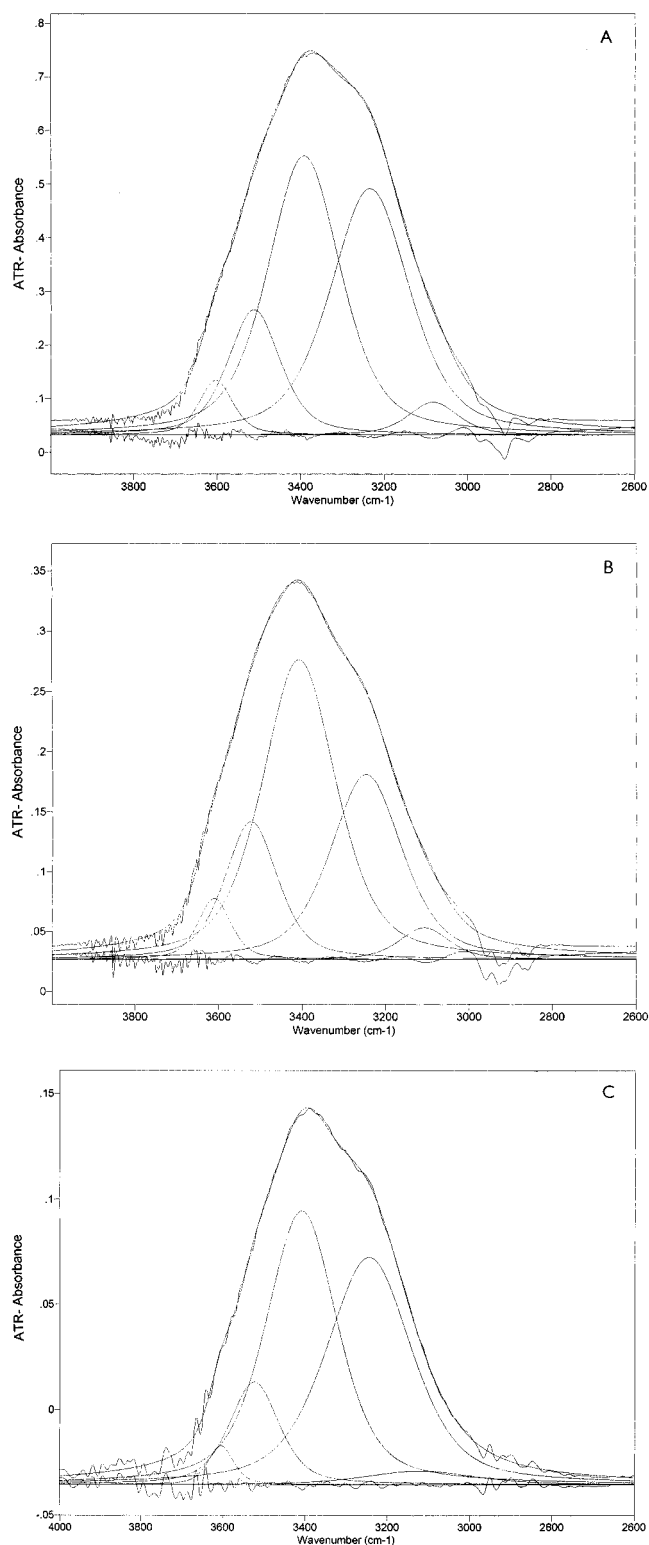


Figure 6. Band fitting results for water in PVC at equilibrium. (A) pure PVC, (B) PVC/DOP (20%), (C) PVC/DOP (30%).

follows that the water molecules removed first are the more weakly hydrogen bonded molecules (as expected). This is confirmed by examination of the same data, but now where the wet film spectrum is ratioed against the film containing the equilibrium (saturation) concentration of water. In Figure 12B the absorbance data are therefore negative because such spectra show the difference between the water spectrum at equilibrium and that at any particular point in the desorption. In effect, this procedure gives an indirect measure of the water which

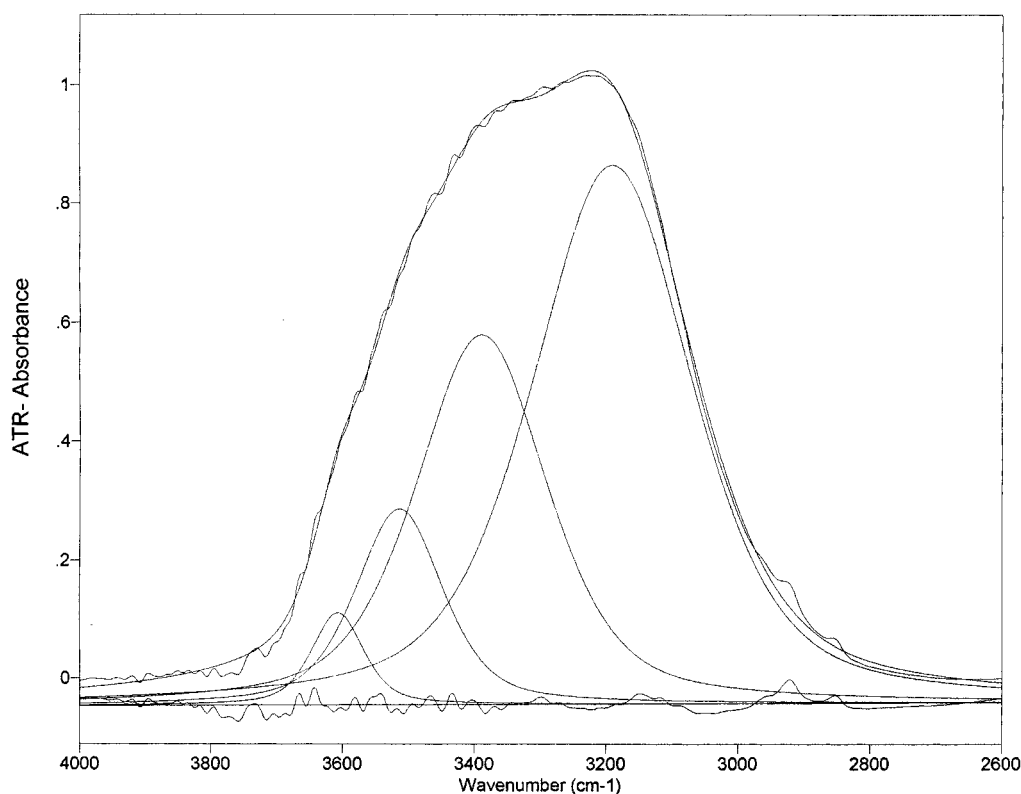


Figure 7. Band fitting results for pure water at 25 °C.

TABLE 2: Band Parameters for Water in PET as a Function of Crystallinity (Density) Including *P* Factor of Eq 3

position/ cm ⁻¹	area/ cm ⁻¹	width/ cm ⁻¹	rel %	$\epsilon \times 10^{-7}/$ cm mol ⁻¹	factor
Ratio (0:1)—4.9% Crystalline Sample—0.95% Water					
3606	18.8	88	4.2	81.1	43.0
3517	63.5	142	14.3	65.8	34.9
3399	151.2	201	34.1	32.0	17.0
3243	210.0	276	47.4	29.8	15.8
Ratio (1:3)—8.4% Crystalline Sample—0.89% Water					
3606	17.6	87	4.2	81.0	43.0
3516	61.8	144	14.9	68.3	36.3
3399	136.9	198	32.9	34.2	18.1
3244	199.0	276	47.0	30.2	16.0
Ratio (1:2)—11.2% Crystalline Sample—0.84% Water					
3607	16.5	88	4.3	80.5	42.8
3516	58.3	144	15.1	68.3	36.3
3398	126.4	198	32.6	30.3	16.1
3244	185.8	274	48.0	29.8	15.8
Ratio (1:1)—18.2% Crystalline Sample—0.75% Water					
3607	14.6	90	4.4	79.6	42.3
3517	51.5	145	15.5	67.6	35.9
3397	105.6	196	31.9	28.3	15.0
3243	159.2	271	48.1	28.6	15.2
Ratio (1:0)—25.0% Crystalline Sample—0.60% Water					
3608	10.3	93	4.7	70.3	37.3
3517	38.4	149	17.6	62.9	33.5
3391	62.8	189	28.7	21.1	11.2
3241	107.1	261	48.0	24.1	12.8
Pure Water/20 °C					
3613	12.7	77	1.8	1.883	
3526	52.8	140	7.5	1.883	
3395	258.4	216	36.4	1.883	
3224	385.3	263	54.3	1.883	

has been removed. The profile peaks at 3400 cm⁻¹ with only a shoulder in the 3200 cm⁻¹ region. It therefore follows that the water which has “left” the polymer is relatively weakly

TABLE 3: Band Parameters for Water in PVC as a Function of Addition of a Plasticizer (DOP) Including the *P* Factor of Eq 3

	position/ cm ⁻¹	width/ cm ⁻¹	area/ cm ⁻¹	rel %	ϵ/cm mol ⁻¹	factor
PVC (0.95% water)	3603	94	12	3.78	2.83e8 ^a	15
	3512	151	43	13.56	3.07e8	16
	3390	215	143	45.11	4.37e8	23
	3231	218	119	37.54	1.73e8	9
20% DOP/PVC (0.35% water)	3607	97	7	5.26	4.38e8	23
	3515	154	25	18.80	4.77e8	25
	3403	203	60	45.11	4.96e8	26
	3245	209	41	30.83	1.63e8	9
30% DOP/PVC (0.28% water)	3600	81	2.5	3.14	2.04e8	11
	3517	132	9	11.32	2.09e8	11
	3409	193	31	39	3.19e8	17
	3248	251	37	46.54	1.82e8	10
water	3606	95	20	3.43		
	3512	153	68	11.66		
	3390	220	160	27.44		
	3196	296	335	57.46		

^a Read as 2.83×10^8 .

hydrogen bonded compared with that which remains in the film. This demonstrates very nicely the ability to examine the state of water during sorption and desorption processes by using such spectra in innovative ways.

(iii) Intensity Changes. For an ATR experiment the absorbance of a particular band at wavenumber ν is given^{36,58} by:

$$\text{Abs} = \log(I_0/I_\nu) = \epsilon_\nu c d_e \quad (1)$$

where ϵ is the extinction coefficient (a molecular quantity), and c and d_e are the concentration and effective path length, respectively. For ATR d_e is obtained from well-known equations⁵⁸ (assuming $l \gg dp$, the semi-infinite thickness limit) and the number of reflections, N . The corresponding integrated band intensity (obtained approximately from the measured band area)

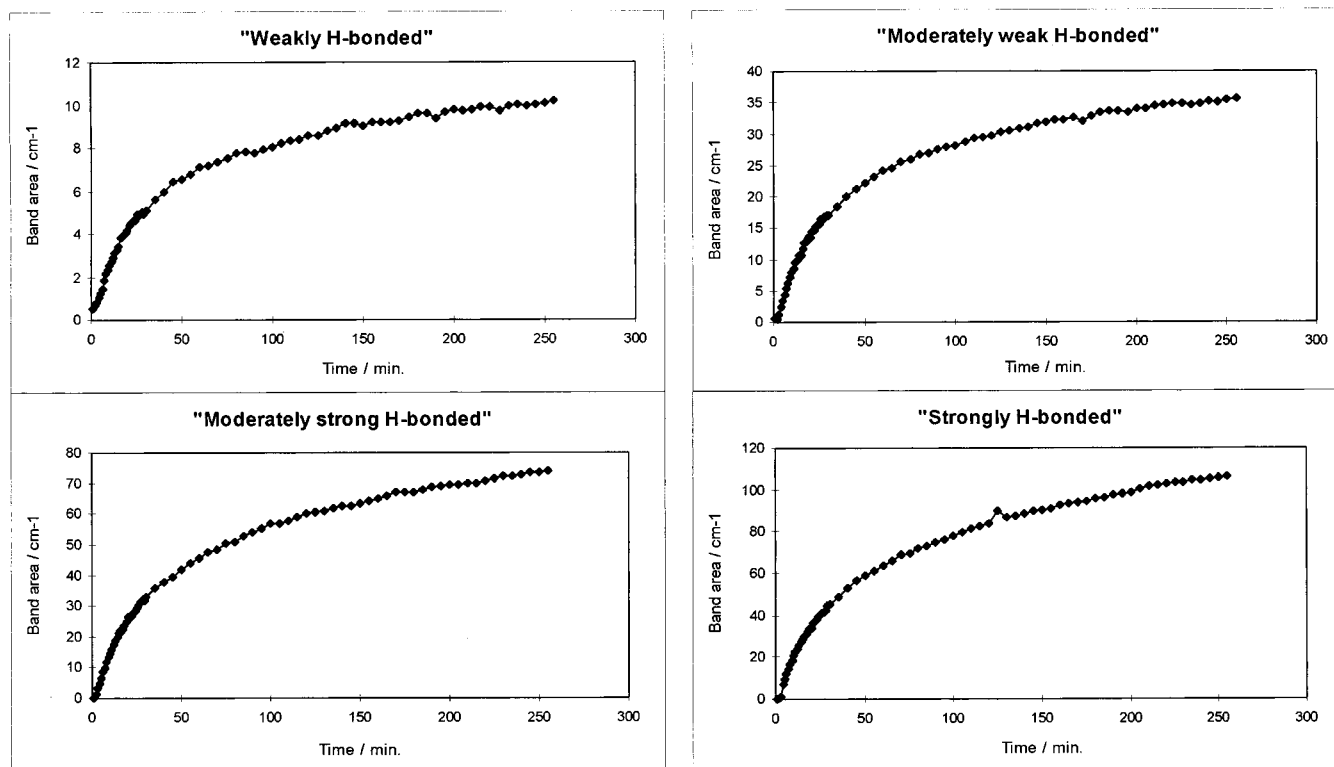


Figure 8. Changes of intensity with time for the four bands of water in PET.

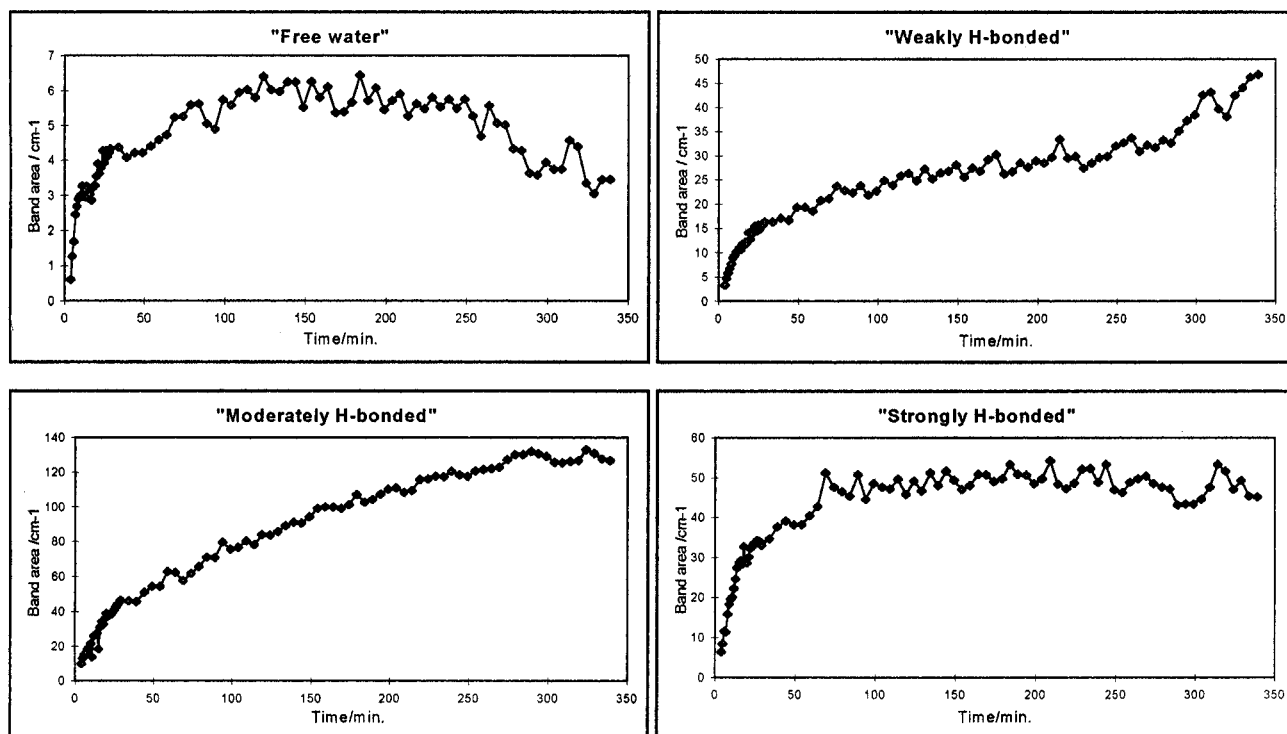


Figure 9. Changes of intensity with time for the four bands of water in PVC.

is:

$$B = \int \epsilon_\nu d\nu = \text{area}/cd_e \quad (2)$$

For pure water the values of ϵ and B_w are well known^{24,45,50} and depend critically on the ("perturbed") molecular environment. Comparison of B values for component bands of water in the polymer film with those for pure water will therefore give a

measure of that perturbation. Following, Maeda et al.,²⁹ we write:

$$P = B_p/B_w \quad (3)$$

Where P represents some measure of the oscillator perturbation due to sorption in the polymer. All that is needed to calculate P is the concentration of water in the polymer of equilibrium

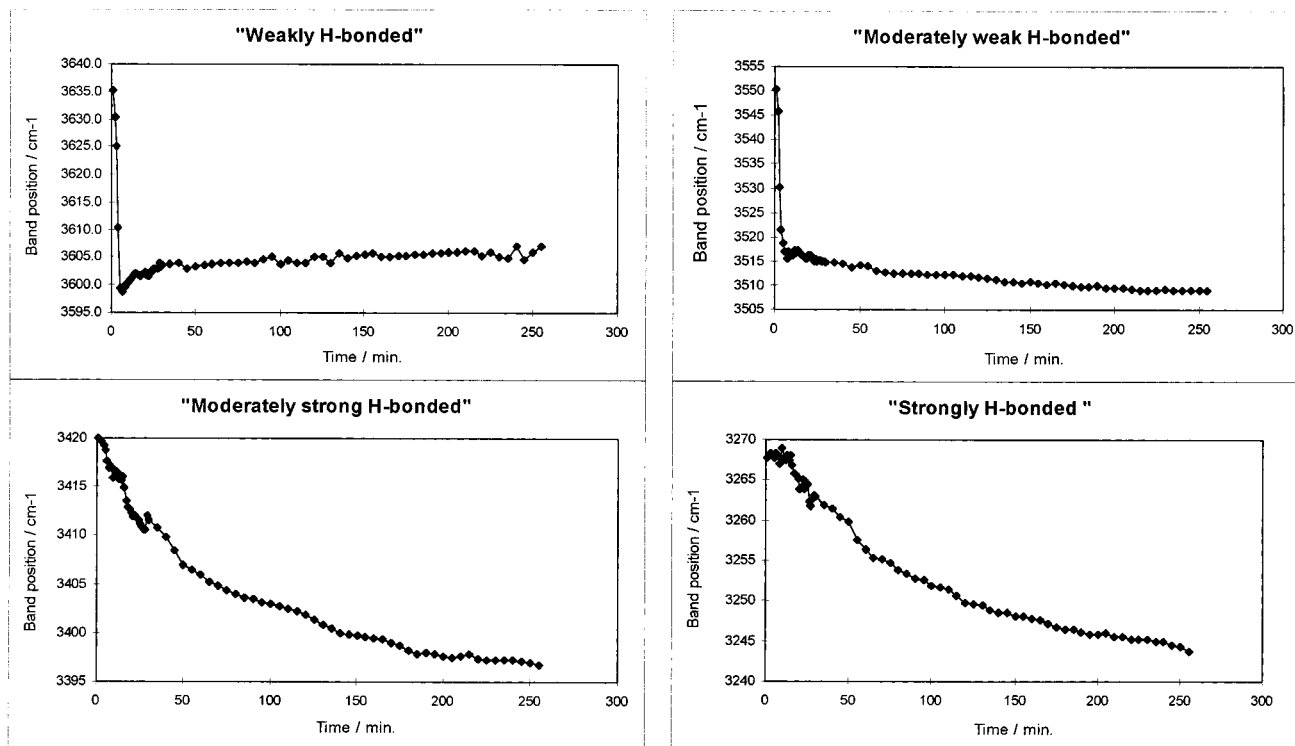


Figure 10. Changes of frequency with time for the four bands of water in PET.

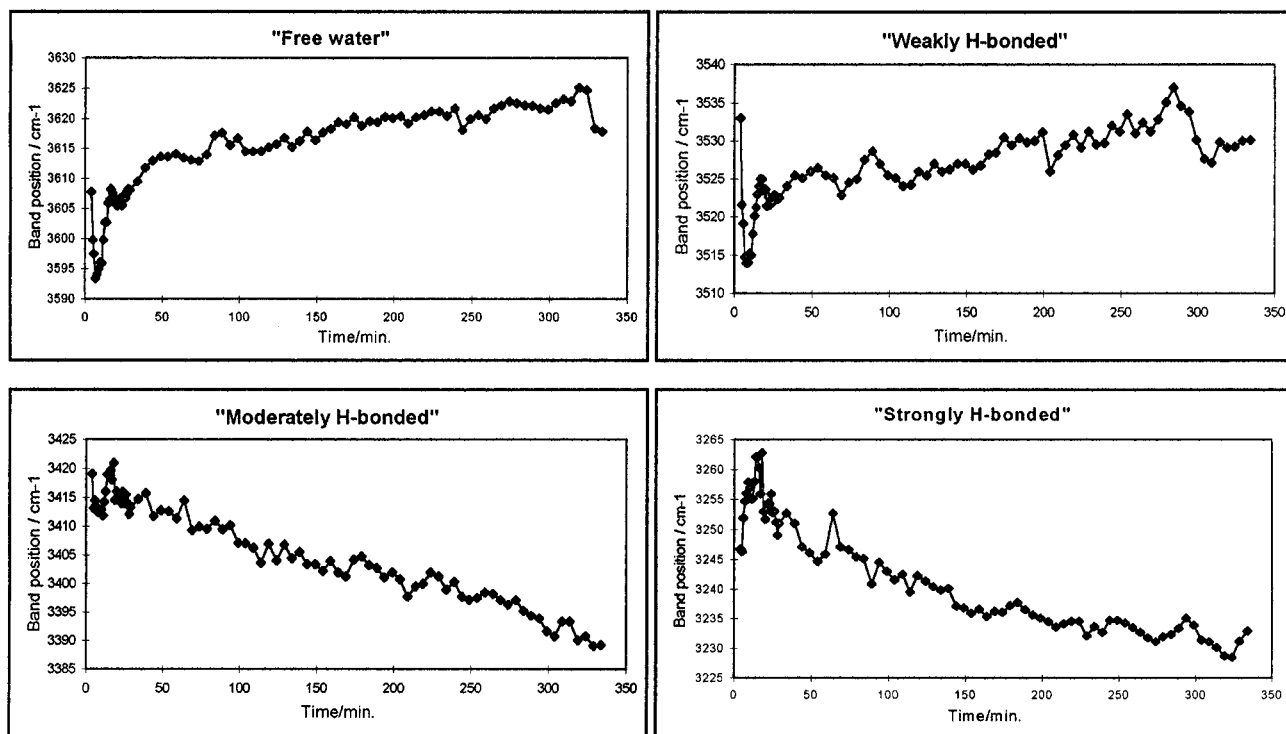


Figure 11. Changes of frequency with time for the four bands of water in PVC.

(obtained gravimetrically) along with the measured intensity of water in the polymer (B_p) and in pure water (B_w). P may then be related to the physical and chemical properties of the polymer; for example, in our case the crystallinity (or density) in the case of PET and plasticizer content (or T_g) in the case of PVC. The important assumptions inherent in this process should be noted, i.e., (a) our spectra contain only intensity from water in the polymeric matrix (as the spectral shape would indicate), (b) a homogeneous distribution of water molecules occurs

among the sites, (c) changes of B are due only to network "perturbation" and/or interaction with polymer, and (d) there is a one to one correspondence of the component bands of pure water with those of water in the polymer.

Note also that only band area *ratios*, obtained under identical conditions, have been used. No attempt has been made to compute absolute infrared intensities. Only minor baseline corrections have been applied to our spectra. The relative "path lengths", d_e , of the water and "water in polymer" (assumed to

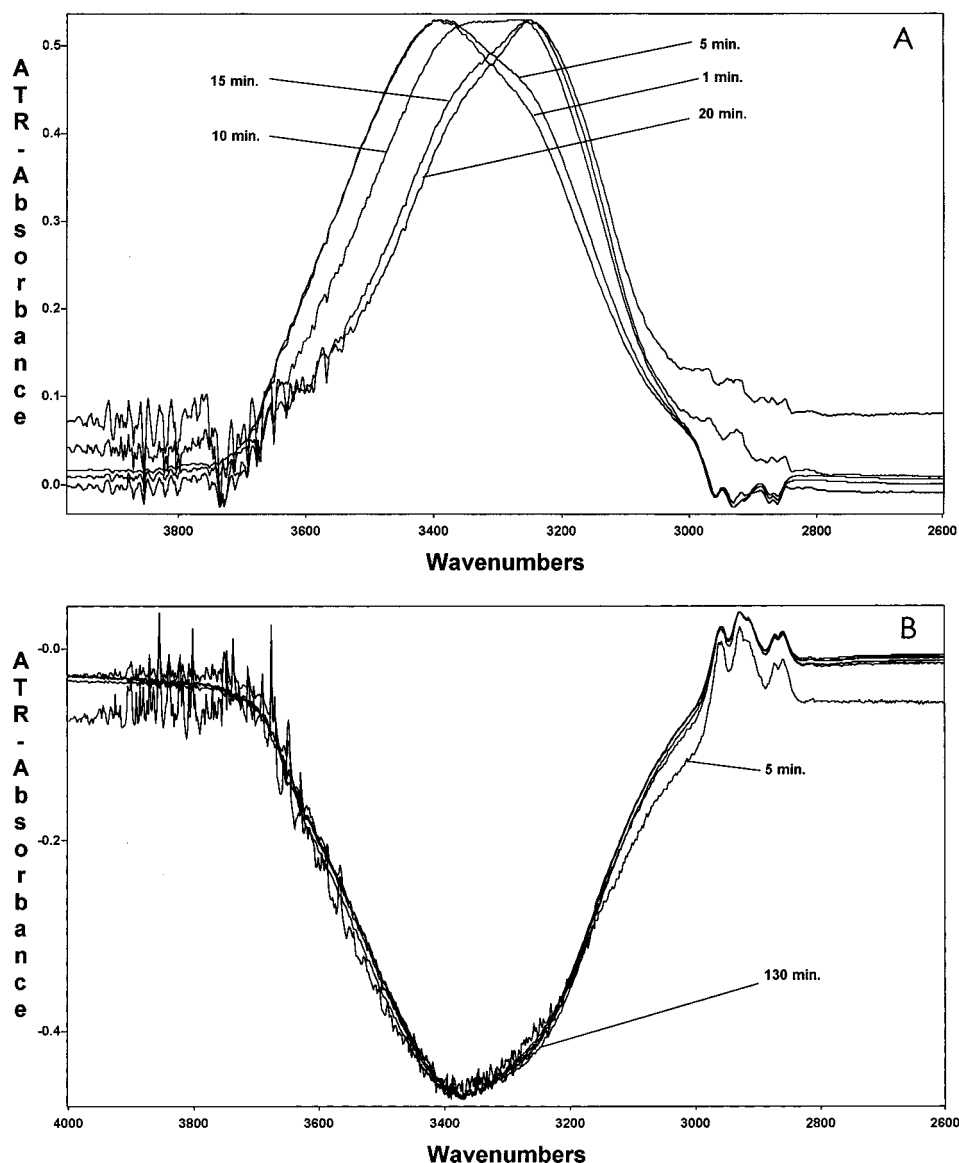


Figure 12. Water bands in PVC for desorption: (A) ratio against dry film, (B) ratio against water saturated film.

have $n = 1.5$ in the presence of $<1\%$ of water) were used to measure the ratios of B values from the measured component band areas as follows:

$$P = \frac{B_p}{B_w} = \left(\frac{C_w}{C_p} \right) \left(\frac{d_w}{d_p} \right) \frac{\text{area}^p}{\text{area}^w} \quad (4)$$

The values of P are given in Tables 2 and 3 for the two polymers. As may be seen, the following types of behavior may be described.

(i) For both polymers the water band at lowest frequency ($\sim 3190 \text{ cm}^{-1}$ in pure water) is relatively less important for sorbed water. This, of course, reflects the breaking of the strongly hydrogen bonded water network and the greater importance of more weakly bound water species at frequencies near $3380\text{--}3530 \text{ cm}^{-1}$.

(ii) P factors of the order of 10–50 are generally obtained. These result from a severe intensity or transition moment ($\partial\mu/\partial q$) enhancement when water is ‘sorbed’ into these polymers. This could be due to a “breaking” of the tetrahedral (network) symmetry in pure water and is supported by rather low P values for lower frequency (more strongly interacting) bands. The

phenomenon has not been reported before as far as we know, and will be followed up in future work.

(iii) The P values vary systematically for the three lowest frequency bands of water in PET (these changes can be seen from Figure 5). Generally, P decreases with the crystallinity level. This could reflect the decreasing amount of water taken up by the (more dense) crystalline PET films.

(iv) For PVC the P values are dramatically affected by whether DOP is added as a plasticizer. With 20 or 30% DOP the polymer maybe above its T_g at 25°C so the behavior toward water (including swelling) is expected to change. The water content of pure PVC is considerably higher than that of the plasticized material (Table 3). This could be due to swelling of the latter. Nevertheless, the proportion of “free” water (at 3618 cm^{-1}) in plasticized PVC is lower than that for pure PVC, and interaction of the H_2O with the DOP ester group is strongly implied.

The well-known difficulties of uniquely fitting IR band profiles must lead to caution against over interpretation of our data. Nevertheless, we believe that sufficient high quality systematic work on water^{52–57} has been published to give us considerable confidence about the number of bands present and

their changes in frequency and relative intensity as the water molecule environment changes. For example, in fitting our data for the pure water profile, we get very similar frequencies and relative intensities to those obtained by Christy et al.⁵⁶ by a more sophisticated least squares spectral resolution. They do not, however, agree with those of Sutander and Frances.³³

Thus, we have demonstrated how quantitative IR intensities may be used to monitor the state of water in saturated polymer films. Since such data are sensitive to differences in chemical and physical properties of the polymeric material this technique promises to be useful for the study of polymer microstructure as well as providing valuable information about the uptake and retention of "solvent".

References and Notes

- (1) Falk, M.; Poole, A. G.; Goymour, C. G.; Wyss, H. R. *Can J. Chem.* **1970**, *48*, 607, 1536.
- (2) Blinska, B.; Wilczek, T. *Stud. Biophys.* **1976**, *55*, 81.
- (3) Ikada, Y. *Seminar on Polymers and Water*; The Society of Polymer Science: Japan, 1980.
- (4) Quinn, F. X.; Kampff, E.; Smyth, G.; McBrierty, V. J. *Macromolecules* **1988**, *21*, 3191.
- (5) Pethig, R. *Annu. Rev. Phys. Chem.* **1992**, *43*, 177.
- (6) Bellissent-Funel, M.-C.; Teixeira, J.; Bradley, K. F.; Crespi, H. L.; Chen, S. H. *J. Phys. (Paris)* **1992**, *2*, 955; *Physica B* **1992**, *180/181*, 740.
- (7) Doster, W.; Bachleitner, A.; Dunau, R.; Hiebl, M.; Lüscher, E. *Biophys. J.* **1986**, *50*, 213.
- (8) Teixeira, J.; Stanley, H. E. *J. Chem. Phys.* **1980**, *73*, 3404.
- (9) Tao, N. J. In *Water and Biological Macromolecules*; Westhof, E., Ed.; MacMillan Press Ltd.: London, 1993; Chapter 9, pp 266–292.
- (10) Settles, M.; Doster, W. *Faraday Discuss.* **1996**, *103*, 269.
- (11) Bryant, R. G. *Annu. Rev. Biophys. Biomol. Struct.* **1996**, *25*, 29.
- (12) Otting, G.; Liepinsh, E.; Wuthrich, K. *J. Am. Chem. Soc.* **1991**, *113*, 4363; *Science* **1991**, *254*, 974;
- (13) McBrierty, V. J.; Coey, J. M. D.; Boyle, N. G. *Chem. Phys. Lett.* **1982**, *86*, 16.
- (14) Giordano, R.; Teixeira, J.; Wanderlingh, U. *J. Mol. Struct.* **1993**, *296*, 271; *Physica B* **1995**, *213*, 769.
- (15) Goodfellow, J. M.; Knaggs, M.; Williams, M. A.; Thornton, J. M. *Faraday Discuss.* **1996**, *103*, 339 and references therein.
- (16) Kauzmann, W. *Adv. Protein. Chem.* **1959**, *14*, 1.
- (17) Sartor, G.; Johari, G. P. *J. Phys. Chem.* **1996**, *100*, 10450.
- (18) Belton, P. S. The Physical State of Water in Foods. In *Food Freezing, Today and Tomorrow*; Bold, W. B., Ed.; Springer-Verlag: Berlin, 1991.
- (19) McBrierty, V. J.; Keely, C. M.; Coyle, F. M.; Huan, X.; Vij, J. K. *Faraday Discuss.* **1996**, *103*, 255; *J. Mol. Struct.* **1995**, *355*, 33.
- (20) Finney, J. L. *Faraday Discuss.* **1996**, *103*, 1 and references therein.
- (21) Tao, N. J.; Lindsay, S. M.; Rupprecht, A. *Biopolymers* **1989**, *28*, 1019.
- (22) Ernst, J. A.; Chubb, R. T.; Zhou, H. X.; Groggenhorn, A. M.; Clore, G. M.; *Science* **1995**, *267*, 1813.
- (23) Denisov, V. P.; Halle, B. *Faraday Discuss.* **1996**, *103*, 227 and references therein.
- (24) Marechal, Y.; Chamel, A. *J. Phys. Chem.* **1996**, *100*, 8551; *Faraday Discussions.* **1996**, *103*, 349.
- (25) Nguyen, Q. T.; Byrd, E., and Lin, C. J. *Adhes. Sci. Technol.* **1991**, *5*, 697. Nguyen, Q. T.; Favre, E.; Ping, Z. H.; Neel, J. J. *Membr. Sci.* **1996**, *113*, 137.
- (26) Falk, M. *Can J. Chem.* **1980**, *58*, 1495. Quezado, S.; Kwak, J. C. T.; Falk, M. *Can. J. Chem.* **1984**, *62*, 958.
- (27) Luck, W. A. P.; Schiöberg, G. D.; Sieman, U. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 136.
- (28) Scherer, J. R.; Bailey, G. F.; Kird, S.; Young, R.; Malladi, D. P.; Bolton, B. *J. Phys. Chem.* **1985**, *89*, 312. Scherer, J. R.; Go, M. K.; Kint, S. *J. Phys. Chem.* **1974**, *78*, 1304.
- (29) Maeda, Y.; Tsukida, N.; Kitano, H.; Terada, T.; Yamanaka, J. (a) *J. Phys. Chem.* **1993**, *97*, 3619, 13903; (b) *Spectrochim. Acta* **1995**, *51*, 2433; (c) *Macromol. Chem. Phys.* **1996**, *197*, 1681.
- (30) Bashir, Z.; Church, S. P.; Waldron, D. *Polymer* **1995**, *35*, 967.
- (31) Murphy, D.; Depinho, M. N. *J. Membr. Sci.* **1995**, *106*, 245.
- (32) Van Alsten, J. G.; Coburn, J. C. *Macromolecules* **1994**, *27*, 3476.
- (33) Sutander, P.; Ahn, D. J.; Franses, E. I. *Macromolecules* **1994**, *27*, 7316; *Thin Solid Films* **1995**, *263*, 134.
- (34) Kusanagi, H.; Yukawa, S. *Polymer* **1994**, *35*, 5637.
- (35) Crupi, V.; Jannelli, M. P.; Magazu, S.; Maisano, G.; Majolino, D.; Migliardo, P.; Ponterio, R. *J. Mol. Struct.* **1996**, *381*, 207.
- (36) Mirabella, F. M. *Appl. Spectrosc. Rev.* **1985**, *21*, 45.
- (37) Pereira, M. R.; Yarwood, J. J. *Polym. Sci., Part B Polym. Phys.* **1994**, *32*, 1881.
- (38) Van Alsten, J. G. *Trends Polym. Sci.* **1995**, *3*, 272.
- (39) Jabbari, E.; Peppas, N. A. *J. Mater. Sci.* **1994**, *29*, 3969; *Macromolecules* **1995**, *28*, 6229.
- (40) Schlotter, N.; Furlan, P. V. *Polymer* **1992**, *33*, 3332.
- (41) Fieldson, G. T.; Barbari, T. A. *Polymer* **1993**, *34*, 1146.
- (42) Pereira M. R. and Yarwood, J. J. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 2737.
- (43) Hajatdoost, S.; Yarwood, J. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1613.
- (44) Balik, C. M.; Xu, J. R. *J. Appl. Polym. Sci.* **1994**, *52*, 975; *Appl. Spectrosc.* **1988**, *42*, 1543.
- (45) Christopher, D. J.; Hills, B. P.; Belton, P. S.; Yarwood, J. J. *Colloid Interface Sci.* **1992**, *152*, 465.
- (46) Gonzalez-Blanco, C.; Rodriguez, L. J.; Velazquez, M. M. *Langmuir* **1997**, *13*, 1938.
- (47) D'Apprano, A.; Lizzio, A.; Turco Liveri, V.; Aliotta, F.; Vasi, C.; Bardez, E.; Donato, D. I.; Larrey, B.; Migliardo, P. *Prog. Colloid Polym. Sci.* **1992**, *89*, 258; *J. Phys. Chem.* **1988**, *92*, 4436.
- (48) Ononi, G.; Santucci, A. *J. Phys. Chem.* **1993**, *97*, 5430.
- (49) Moran, P. D.; Bowmaker, G. A.; Cooney, R. P.; Bartlett, J.; Woofrey, J. L. *Langmuir* **1995**, *11*, 738.
- (50) Falk, M. *Chem. Phys.: Aqueous Gas Solutions* [Proc. Symp.]; Electrochemical Society: Princeton, NJ, 1975, and references therein.
- (51) Walrafen, G. E., In *Water, A Comprehensive Treatise*; Plenum, New York, 1972; Franks, F., Ed.; pp 208–9.
- (52) Walrafen, G. E.; Fischer, M. R.; Hakmatadi, M. S.; Yang, W. H. *J. Chem. Phys.* **1986**, *85*, 6964, 6970; *J. Phys. Chem.* **1988**, *92*, 2433.
- (53) D'Arrigo, G.; Mansano, G.; Mallamace, F.; Migliardo, P.; Wanderlingh, F. *J. Chem. Phys.* **1981**, *75*, 4264.
- (54) Ratcliffe, C. I.; Irish, D. E. *J. Phys. Chem.* **1982**, *86*, 4897.
- (55) Marechal, Y. *J. Phys. Chem.* **1993**, *97*, 2846; *J. Mol. Struct.* **1994**, *322*, 105; *J. Chem. Phys.* **1991**, *95*, 5565; *J. Phys. II* **1993**, *3*, 557.
- (56) (a) Libnau, F. O.; Christy, A. A.; Kvalheim, O. M. *Appl. Spectrosc.* **1995**, *49*, 1431. (b) Libnau, F. O.; Kvalheim, O. M.; Christy, A. A.; Toft, J. *Vib. Spectrosc.* **1994**, *7*, 243.
- (57) Hare, D. E.; Sorensen, C. M. *J. Chem. Phys.* **1990**, *93*, 25, 6954; **1992**, *96*, 13.
- (58) *Internal Reflection Spectroscopy*; Mirabella, F. M., Ed.; Marcel-Dekker: New York, 1993.
- (59) Mitsuhiro, F.; Hiromichi, K.; Noriko, Y.; Osamu, K.; Toshihiko, O. *Polymer* **1990**, *31*, 295.