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ORIGINAL CONTRIBUTION

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Fourier transform infrared study of poly (2-hydroxyethyl methacrylate) PHEMA

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Abstract Fourier transform infrared spectra in the wave number range 450–4500 cm^{-1} of poly (2-hydroxyethyl methacrylate) PHEMA have been studied as functions of water content in the range 38–2.6 wt% and of temperature in the range 300–373 K. The results show changes in the intensities of the stretching frequencies of the carbonyl band, H–O–H bending vibration and O–H stretching vibration with a change in water content and temperature. The results confirm two types of water in the hydrogel polymer system, tightly bound water and loosely bound water. At low concentrations, water is mainly hydrogen-bonded to the polymer and is described as tightly bound water. However, at water concentrations greater than 18% by weight, part of the water exists in a different form and behaves as loosely bound water. For concentrations over 30%, there is some evidence that excess water behaves more loosely bound somewhat like bulk water. Infrared spectroscopic results supplement those obtained by means of NMR by Smyth et al. and by dielectric spectroscopy. Our results also show that some of the water continues to be hydrogen bonded to the polymer until at least a temperature of 373 K when the bulk water should have evaporated. FTIR is found to yield greater site-specific insight into the local behaviour of water in hydrated PHEMA.

Key words Poly(2-hydroxyethyl methacrylate) – hydrogel – Fourier transform infrared spectroscopy – water in polymers

Introduction

Poly (2-hydroxyethyl methacrylate) (PHEMA) and PHEMA-based materials have proved to be of great importance for biomedical applications since their discovery in 1960 [1]. Biocompatibility is due in part to the ability of PHEMA to absorb sizeable amounts of water into the hydrogel network. Hydrogen bonding between the hydrophilic groups of PHEMA and the water molecules is a major contributor. During the past 10 years numerous investigations on the interactions of water with the polymer matrix have been carried out. Following an investigation, using several experimental techniques, Jhon and Andrade [2] proposed a three-state model for water in the hydrogel comprising (a) *bound water*, which is strongly associated with the hydrophilic segments of the hydrogel, (b) *interfacial water*, which is less strongly associated due to hydrophobic interactions, lying between the segments of the hydrogel, and (c) bulk-like water. The study, by Lee et al. [3], on the swelling properties of the hydrogel found that there is no bulk water in PHEMA at water contents below 31 wt% (relative to the dry polymer). NMR spectroscopy of the PHEMA hydrogel by McBrierty and his

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coworkers [4, 5] showed that (a) bulk-like water exists in the hydrogel system at concentrations in excess of 35 wt% and (b) below 20 wt% concentration, water is mostly strongly bound. Dielectric spectroscopy of the PHEMA hydrogel carried out by Xu et al. [6], and by Pathmanathan and Johari [7] showed the effect of bound water on the relaxation of terminal hydroxy groups in the PHEMA polymer side chain which supplemented information obtained from dynamic mechanical thermal analysis (DMTA) and NMR. It clearly demonstrated the existence of bound as well as bulk water at higher concentrations in PHEMA hydrogel.

In this paper, we report on Fourier transform spectroscopy of PHEMA with different water concentrations with a view to obtain more site-specific information about the hydrogen bonding of water and its binding sites. FTIR offers a comprehensive, site-specific fingerprint. The specificity and magnitude of the type of hydrogen bonding strongly influence both the chain conformation as well as its packing. Because of the importance of hydrogen bonding in PHEMA-based hydrogel materials, the absorption bands may reveal whether water is strongly or loosely bound to the polymer. From a study of the carbonyl group stretching vibrations (C=O) and the hydroxyl group (OH) stretching vibrations using IR spectroscopy, in particular, the existence of hydrogen bonding in various polymers [8–18], including some derivatives of methacrylate such as poly (methyl methacrylate) (PMMA), poly (ethyl methacrylate) (PEMA), has been demonstrated. Although IR spectra for dry and wet (with D_2O content) PHEMA were studied by Ratner and Miller [19] some 20 years ago, investigations of PHEMA with different amounts of water using IR spectroscopy has received scant attention since that time. The results of numerous investigations on the effect of the hydrogen bonding on the vibrational bands of C=O and O–H groups in various polymers have addressed, in the main, the influence of hydrogen bonding on the miscibility and the mechanical properties of polymer systems.

Our dielectric study of PHEMA [6] and its hydrated systems provided detailed information about the molecular dynamics of the system. The three relaxation process in dry PHEMA were readily detected: the α relaxation (motion of main chains), β relaxation (motion of the ester side-chains and local motion of the main chains), and γ relaxation (relaxation of the terminal OH groups in the ester chains of PHEMA). The relaxation behaviour of the host polymer was found to be strongly influenced by the presence of water. The effects of water on the polymer [6] system may be summarised as follows:

(a) A fourth relaxation process was identified with the low-temperature phase transition of the super-quenched water changing into a form of ice. This was found in the hydrated systems with water contents > 24 wt% commensurate with the presence of loosely bound water. The process is seen when water content greater than the tightly bound threshold concentration is exceeded.

(b) Low-temperature relaxations in the hydrated polymer arise from a complex interplay of hydrophilic moieties on the polymer chain and absorbed water which, in turn, undergoes a glass transition at 136 K. This relaxation process is assigned to the reorientation of the terminal polar group which is directly hydrogen bonded to the water molecules.

(c) The β relaxation process was found to be particularly sensitive to the various forms of water in the host polymer system, implying that hydrogen bonding exists between the carbonyl groups in the ester side chains and the water molecules.

(d) All molecular relaxation processes are plasticized by mobile water (both loosely bound and bulk water) in the hydrated polymer system.

Experimental section

Sample preparation

As in the dielectric study [6], the PHEMA sample was synthesised using free-radical solution-polymerisation by exposure to UV radiation in the presence of a cross linking agent. Figure 1 shows the chemical structure of PHEMA connected with a cross linking agent. The sample was immersed in distilled water for at least 7 days to ensure a water saturated PHEMA hydrogel. The equilibrium water content W is measured as follows:

$$W = \frac{\text{weight of water in gel}}{\text{weight of dry PHEMA}} \times 100\% \,. \qquad (1)$$

To prepare a dry PHEMA sample, the water-released film is sandwiched between two pieces of plastic sheet under moderate pressure and left in vaccum oven at 333 K for 8 days. We assumed that the concentration of water was equal to zero for the dry sample. The concentration of water in the sample at different stages has been determined by Eq. (1). We found that the concentration of water varied in the range 36.4–1.6 wt%. However, the TGA analysis [6] and our own data discussed below show that ~ 2.6 wt% of water exist in PHEMA even at a temperature of 373 K. Taking this into account the values of water concentrations are corrected to the range 38–4.2 wt%. IR absorbance measurements were made on a very thin hydrated film of 45 μm thickness. In order to

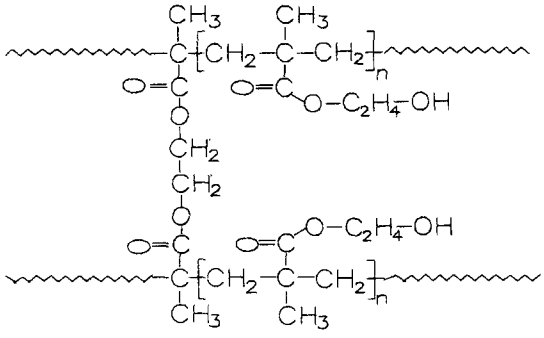


Fig. 1 Chemical structure of PHEMA with a cross-linking agent (ethylene glycol dimethacrylate, EGDMA, 0.34%)

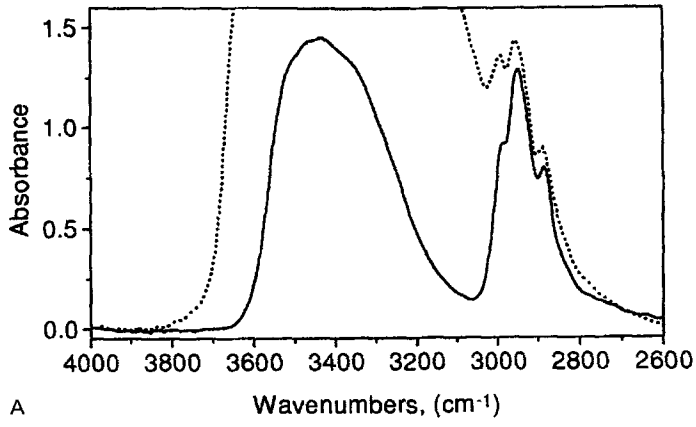
remove the effects of bulk water on the surface of the film, the wet film was first gently wiped using tissue paper. It was then sandwiched between the Si windows of an IR absorbance cell.

IR spectroscopy

A Bio Rad FTS-60A Fourier transform spectrometer with a nitrogen-cooled MCT (mercury cadmium telluride) detector was used for IR measurements. A total of 64 scans were accumulated to generate an absorbance spectrum with a resolution of 2 cm^{-1} in the wave number range 450–4500 cm^{-1}. When studying the influence of the water content, the IR measuring system was kept at a constant temperature of 300 K. IR spectra were recorded as a function of time and, accordingly, the specimen was weighed after each experimental observation. After that IR spectra were recorded for the same sample for temperatures in the range 313–373 K. A temperature controller (Oxford Instruments ITC4) provided temperature stability to within 0.1 K. Background spectra of the Si windows at different temperatures were subtracted from the measured sample spectra and a base line correction was applied. Samples were sufficiently thin so that the transmittance in the spectral range of interest could be measured to a sufficiently high degree of accuracy (except for the three spectra for water contents: 38; 34 and 30 wt% in the range 2800–3600 cm^{-1}).

Spectral fitting procedure

The analysis of the vibrational bands in the hydroxyl (~3400 cm^{-1}) and the carbonyl (~1720 cm^{-1}) stretching regions involved deconvoluting the band under consideration using a standard *Bandfit* program for which the line profile is a weighted sum of Gaussian and Lorentzian



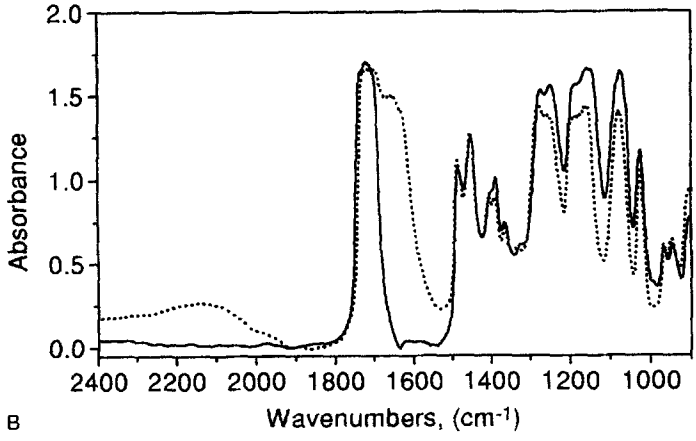


Fig. 2 FTIR spectra of dry and hydrated PHEMA: **A** curves: 1 – water content 38 wt%, 2 – of this sample with water content at ~ 2.6 wt% and $T = 373$ K in the range 4000–2600 cm^{-1}; **B** Continuation of the spectra down to 900 cm^{-1} curves: solid line – at water content 38 wt%, dashed line – at water content ~ 2.6 wt%

functions. It is specified by four parameters:

$$A(\omega) = A_0\left\{\delta_0 \exp\{-\ln[2(\omega - \omega_0/\alpha_0)^2]\} + \left[\frac{1-\delta_0}{1+(\omega-\omega_0/\alpha_0)^2}\right]\right\}, \quad (2)$$

where ω_0 is the line centre, α_0 is the line half-width, A_0 is the line height and δ_0 is a Gaussian fraction.

Results and discussion

Infrared spectra of the hydrogel and the dry PHEMA in the wave number range 900–4000 cm^{-1} are shown in Figs. 2A, B. The progressive depletion of water content in the hydrogel as a function of time is shown in Fig. 3. The water

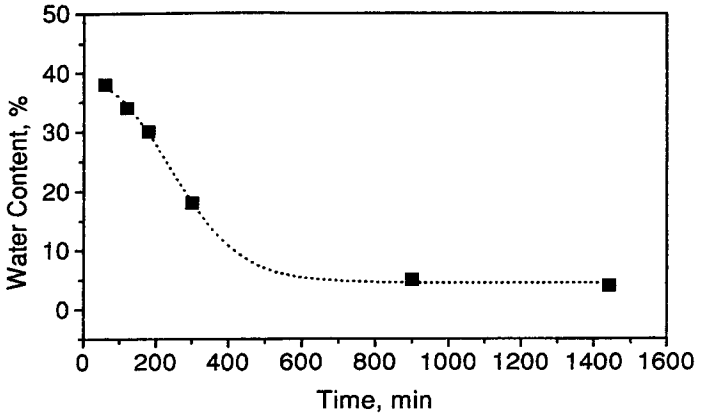


Fig. 3 Time dependence of water content in PHEMA due to the natural evaporation at 300 K

Table 1 Spectral band assignment

Frequency [cm^{-1}]	Possible assignments
3380	ν(O–H), stretching vibration in wet PHEMA
3490	ν(O–H), stretching vibration in dry PHEMA
2986	Antisymmetric and symmetric stretching vibrations: $\nu(CH_3)$, $\nu(CH_2)$, ν(CH)
2950	
2886	
2130	δ(H–O–H) + α (only for wet PHEMA)
1710–1733	ν(C=O), free C=O
1692–1715	ν(C=O), bonded C=O
1483	$\delta(CH_2)$
1367	CH_2 twist and rock
1079	ν(C–O–C)
750	γ(–C–O–)
700	α

Various symbols stand for: ν – stretching, δ – in-plane bending, γ – out-of-plane bending, α – librations.

content decreases most noticeably during the first few hours, after which the water content reaches an equilibrated, long-term, value. Thermogravimetric analysis (TGA) [6] has shown that a small amount of water (bound water) remains in the polymer matrix even at a temperature of 373 K. The effect of water on the host PHEMA can be determined by comparing the spectra of the hydrogel with that of the dry sample. There are four absorption bands whose frequencies and intensities are affected by water.

Band 1 ($\sim 3550\ cm^{-1}$) is a wide and an intense band centred at $3550\ cm^{-1}$ (Fig. 2A). The band is broadened, shifted to lower frequencies and the absorption is significantly increased when the sample contains water. This band is assigned to the OH stretching vibrations [20–22].

Band 2 ($\sim 1720\ cm^{-1}$) in the region $1650–1800\ cm^{-1}$ for the dry sample (Fig. 2B) was shown by many investigators [8–17] to correspond to the stretching vibrations of carbonyl (C=O) groups.

Band 3 ($\sim 2130\ cm^{-1}$) is found to be relatively weak and can be observed in wet samples (Fig. 2B) only. This band is tentatively assigned to a combination band of the H–O–H bending vibrations ($\sim 1650\ cm^{-1}$) and the librations ($\sim 700\ cm^{-1}$) of bulk water molecules [21] which exist in the polymer matrix.

Band 4 ($\sim 700\ cm^{-1}$) occurs only in wet samples. This band with a reduced intensity reflects the librations of molecules of bulk-like water [21].

Before discussing the details of the spectral changes of these bands as a function of water content and temperature, it is noted in passing that bands occurring between 2600 and $3050\ cm^{-1}$ are associated with the symmetric and antisymmetric C–H stretching vibrations of CH_2 and CH_3 groups. Assignments of some important bands are shown in Table 1.

Carbonyl C=O stretching band

The bands corresponding to the carbonyl stretching region ($1540–1820\ cm^{-1}$) for different water contents are shown in Fig. 4. For the dry sample (curves, 5, 6) we find a wide band with a frequency maximum centred at approximately $1720\ cm^{-1}$. This band is comparable to the C=O band found in various polymers with carbonyl groups [8–17]. However, with an increase in the water content, the band becomes more complex since another band with a frequency maximum of $1650\ cm^{-1}$ develops on the low-frequency side. The intensity of the latter band increases with increase in water content and approaches the same maximum value as the C=O peak at 38 wt% of water. This band, centred at $\sim 1650\ cm^{-1}$, is assigned to the bending vibrations H–O–H loosely bound water molecules [20, 21]. Water in the polymer system is known not to behave similar to bulk or free water. The excess water exceeding a threshold of approximately 30% becomes more loosely bound water.

Spectral fitting procedure

In order to obtain information about the individual bands, namely, C=O stretching, H–O–H bending, and the effect of hydrogen bonding on these bands, we need to deconvolute the complex band shown in Figs. 4a, b. For certain water contents, the peak at $\sim 1720\ cm^{-1}$ (Fig. 4a) appears to be flat and for large water content the absorbance varies relatively a little with variation in the water content. We believe that the flatness in the curve around the peak maximum could be due to a combination of two factors rather than to an over absorbance. These factors are (i) two

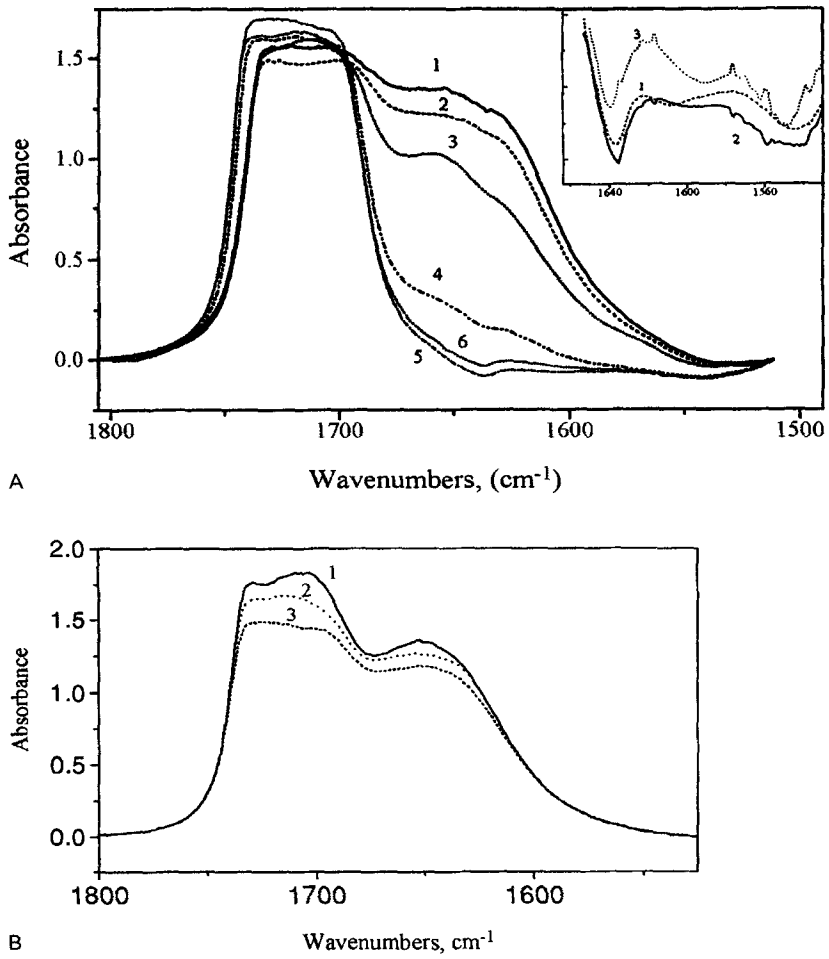


Fig. 4 FTIR spectra of PHEMA in carbonyl stretching frequency range for different water content (in wt%): A 1 – 38, 2 – 34, 3 – 30, 4 – 18, 5 – 5, 6 – 4.2. Insert, curves: 1 – 5, 2 – 4.2 ($T = 300$ K), 3 – ~ 2.6 ($T = 373$ K); B different sample with the water content (wt%): 1 – 46, 2 –41, 3 –37

peaks of equal intensity lie close to each other (ii) scattering of light from the empty pores. Measurements on a different set of sample given in Fig. 4b show that for 46 wt% of water content, flatness as observed for 37 wt% is not repeated. This is presumably due to the fact that some empty pores for 37 wt% get filled when the water content is increased to 46 wt%.

The fitting procedure is first detailed for the dry PHEMA and is then extended to the case of the hydrogel. Literature frequencies data for the components are used in this exercise. The band centred at 1720 cm^{-1} for dry PHEMA (Fig. 4a) is more complex than for a carbonyl group (C=O) stretching vibrational band observed in this region for the non-hydrogen bonded (without self-association) polymer (see, for example, IR spectra for PMMA obtained in [23]). The reason is that the C=O bond is hydrogen bonded within the PHEMA polymer itself. To a first approximation, the following fitting parameters are used: 1700 and 1733 cm^{-1} as frequency maxima for hydrogen bonded and non-hydrogen-bonded C=O stretching vibrations, respectively. This assumption is supported not only by the band shape but also by the IR study of non-associative derivatives of methacrylate like PEMA [14, 16, 17] and PMMA [23]. The frequency maximum for the "free" C=O band is approximately 1730–1733 cm^{-1} for such a system [17, 23]. Finally, C=O band is deconvoluted into three bands with frequency maxima centred at 1734, 1716 and 1699 cm^{-1} (see Tables 2 and 3 and Figs. 5a, b). The assignments for these three bands agree with the literature assignments for the other polymer systems with hydrogen-bonded C=O groups. The dependencies of the integrated intensities and the frequency maxima on the water content, obtained from the fitting procedure, are shown in Figs. 5a, b.

The band with the frequency maximum in the region 1731–1735 cm^{-1} is usually assigned to the "free" (non-hydrogen bonded) carbonyl stretching vibrations of various (polyurethanes [9, 11–13], methacrylates [14, 16, 17] and phenoxy [8] polymers). The broad band centred at ~1695–1700 cm^{-1} is usually assigned to the hydrogen-bonded carbonyl group [11–14, 16, 17]. The band at 1713 cm^{-1} can have several alternative explanations. One

Table 2 Fitting parameters for the C=O stretching vibration band

Water content (wt%)[a]		O–H–O [1] ν (cm^{-1})		O–H–O [2] ν (cm^{-1})		C=O (H-bonded) ν_1 (cm^{-1})		ν_2 (cm^{-1})		C=O ("free") ν (cm^{-1})	
	range	1622–1628		1653–1662		1692–1699		1710–1716		1729–1734	
	average[b]	1625		1657		1696		1713		1732	
		$W_{1/2}$	A	$W_{1/2}$	A	$W_{1/2}$	A	$W_{1/2}$	A	$W_{1/2}$	A
38		30	64.5	22	53.4	24	85.5	12	12.3	14	38
34		30	57	22	49.3	24	84	14	13	14	38
30		30	47	18	37	20	76	13	15	13.6	37.4
18		26	13	16	8	14	53	10	22	13	42
5		9.0	6.0	—	—	13	43	11.6	26.4	13.5	49
4.2		9.0	5.0	—	—	13.6	46	10.5	26	13.5	47.4
T [K]											
313		9.0	5.0	—	—	13.3	48	10	26.4	13	48.5
333		9.0	5.0	—	—	14	54	10	22	13	48
353		9.0	5.0	—	—	13.2	48	10	22	13.7	51
373		9.0	5.0	—	—	13.7	49	10	24	13.1	49.4

[a] Measurements were made at room temperature.
[b] In this row an average value for the frequency maximum is presented for the convenience of further discussions.
Note: $W_{1/2}$ is the half-width, A is the integrated intensity and ν is the frequency maximum of the band.
Note: The parameter δ_0 of Gaussian fraction varied from 45 to 100% for different bands.
Note: [1] Frequencies of the tightly bound water. [2] Frequencies of the loosely bound water.

Table 3 Frequency maxima obtained from the fitting procedure for the C=O band

Water content (wt%) at T = 300 K	Frequency maximum, cm^{-1}		
	C=O (H-bonded)		C=O "free"
	Frequency 1	Frequency 2	
38	1692	1710	1729
34	1694	1712	1730
30	1697	1714	1731
18	1698	1716	1733
5	1699	1716	1734
4.2	1699	1716	1734
Temperature [K]			
313	1699	1717	1734
333	1699	1717	1734
353	1700	1717	1734
373	1700	1717	1734

such possibility involves a unique geometry of hydrogen bonding [13]. Other investigators [11–13] have also observed a carbonyl band at frequencies between those of the free and the hydrogen-bonded C=O bands. They have attributed this band to the irregularly H-bonded carbonyl bonds interlaced in the highly ordered structures. The band at 1713 cm^{-1} could thus be assigned to H-bonding with a specific geometry. As seen from Fig. 5a and Table 2 the intensity of the 1696 cm^{-1} carbonyl hydrogen bonded band decreases with decrease in the water content (as some of C=O bonds become less affected by hydrogen bonding) and the intensity of the band at 1713 cm^{-1} simultaneously increases with the decrease in water content. We find that this is at the cost of the number of hydrogen bonds with a specific configuration increasing with decrease in the water content. At the same time the intensity of the C=O unbonded band changes a little during water evaporation and temperature increase. The most important change in all the curves occurs in the 15–20 wt% water concentration region where more loosely bound water begins to appear.

Wet sample, H–O–H bending vibrations

When the water content in the polymer is increased, an additional band with the frequency of 1657 cm^{-1} is generated from the low-frequency side to the band centred at 1720 cm^{-1}. Because the intensity of this additional band depends strongly on the water content, and guided by literature data, it is assigned to the bending vibrations (H–O–H) of water molecules. Its peak position for pure water is found to be close to 1650 cm^{-1} with a half-width of approximately 30 cm^{-1} [21]. Ratner and Miller [19] have shown that this band in the IR spectra of PHEMA/D_2O systems is absent; the bending vibration of the D–O–D group lies in the 1150–1250 cm^{-1} region [20–22]. Nilsson et al. [24] have shown that for the gel and the liquid crystalline phases of the monooleoylglycerol + water system (with water contents of 17 and 25 wt%), an additional band is observed with the frequency maximum close to 1652 cm^{-1} in the region of the

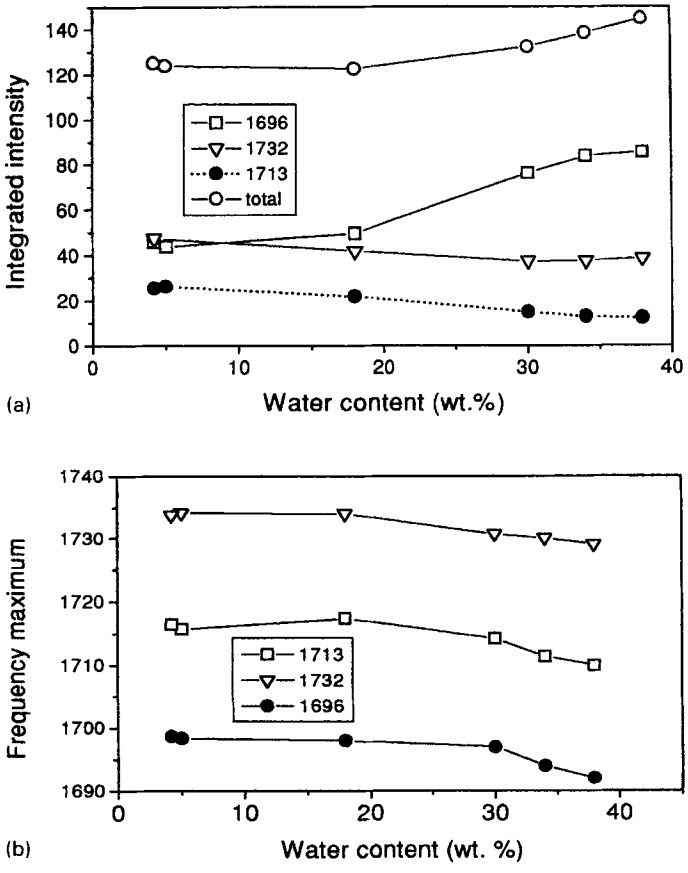


Fig. 5 Dependence on water content of (a) the integrated intensities and (b) frequencies maxima for the carbonyl stretching frequency bands. In Fig. 5a, total implies the total integrated intensity of the band in the region 1780–1540 cm^{-1}

carbonyl stretching vibration. This band for both the aforementioned concentrations possesses a symmetrical contour and does not exhibit any peculiarities at a frequency of around 1635 cm^{-1} as was found for wet PHEMA samples.

Figure 4A reveals an interesting feature in the range of ~1635 cm^{-1}. The band at 1650 cm^{-1} for the bending vibrations of water molecules, as mentioned above, should have a half-width of up to about 30 cm^{-1} [21]. A significant increase in the half-width along with other features observed in Fig. 4A imply that at least two bands in the region 1540–1670 cm^{-1} co-exist. The fitting procedure shows that if the fitting uses only one band in the above region, the results obtained are poor. The band in the 1540–1670 cm^{-1} region is therefore deconvoluted into two bands, with frequency maxima centred at 1657 and at 1625 cm^{-1}. Both these frequencies are average values since the frequency maxima lie in the 1653–1662 cm^{-1} region for the first band and in the 1622–1628 cm^{-1} region for the second band depending on the water content.

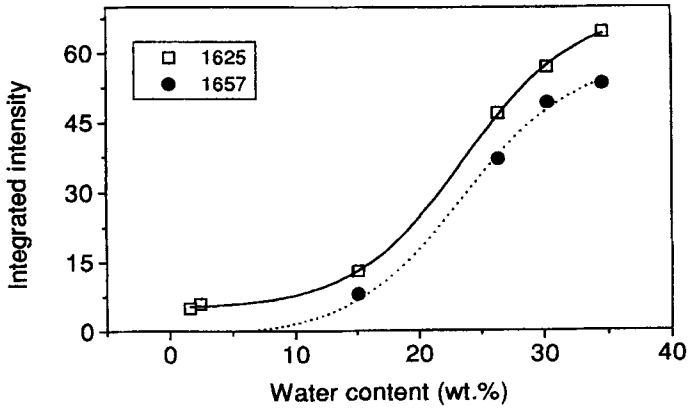


Fig. 6 Dependence on water content of the integrated intensity of H–O–H bending vibrations for tightly bound (□) and loosely bound (●) water

The inset in Fig. 4A shows additional spectra in the region 1600–1650 cm^{-1} for water contents of 5 wt% and 4.2 wt% at 300 K and 2.6 wt% at 373 K. Note that a small band centred close to 1622 cm^{-1} persists at temperatures up to 373 K when all the water present in the polymer matrix should have evaporated. This is explained as follows: there exist a large number of vacant spaces in PHEMA which contain at least two types of water molecules (or hydroxyl groups of water). Some of the water molecules are connected to each other by hydrogen bonding in the same manner as in pure water and the spectra show the H–O–H bending vibration to be at ~1657 cm^{-1}. Another type of water molecule (bound water) forms hydrogen bonds with the polymer, that is, these water molecules are physically bonded to the polymer. Because the water molecules are more strongly bonded to the polymer than to one another, the frequency maximum of the bending vibrations decreases. Figure 6 shows the dependence of the integrated intensity for the two bands, at 1625 and 1657 cm^{-1} on the water content. The band for the bound water is seen at 1625 cm^{-1}. The integrated intensity of both bands decreases with decrease in water content. For water contents below 18 wt%, the integrated intensity of the 1625 cm^{-1} band saturates to a constant value and remains constant during sample heating up to 373 K. This means that water molecules which are hydrogen-bonded to the polymer (tightly bound water) continue to be bonded to the polymer even at a temperature of 373 K, which means that the strength of H-bonding for the molecules is higher than for bulk molecules of water. Note from Fig. 6, that the slope of the two curves changes dramatically above 18 wt%, implying that loosely bound water in the system appears around this percentage. The integrated intensity for the tightly bound water (1625 cm^{-1}) is finite below 18 wt%, whereas for the loosely bound water it is relatively small. Further note that

the integrated intensity of the loosely bound water saturates somewhat about 30 wt% with its frequency decreasing. This possibly implies that the excess water appears to be different and presumably behaves close to bulk-like water above this concentration. These conclusions are in qualitative agreement with the previous investigations of hydrated PHEMA using other techniques [5, 6].

Temperature behaviour of the C=O band

Measurements show that the frequency maxima and the integrated intensities of the "free" C=O band at 1733 cm^{-1} and of the hydrogen-bonded C=O band (at 1695 cm^{-1}) are esentially independent of temperature, within experimental and fitting-procedure limitations. Furthermore, no significant changes in the relative intensities of these two bands with increase in temperature up to 373 K have been observed; however the integrated intensity of another type of hydrogen-bonded C=O band at 1713 cm^{-1} decreases with increase in temperature or reduction in water content. The peak positions of the "free" C=O band and hydrogen-bonded C=O bands change by 5–7 cm^{-1} with increase in water content at room temperature (see Fig. 5b), but do not change with temperature in the interval 313–373 K (Table 3). The temperature dependence is similar to that found for other polymers [11, 12, 25]. These results allow us to conclude that the intermolecular interactions for the C=O bond, not unexpectedly, are different when water is present in the polymer.

The O–H stretching vibration (3800–2800 cm^{-1})

The region of the spectrum where O–H stretching frequencies occur (3800–2800 cm^{-1}) shows significant spectral changes in this region with changes in water content and temperature (Figs. 2A and 7).

The OH streching region is difficult to use for quantitative analysis because of the two kinds of O–H stretching vibrations that exist in this region: O–H stretching vibrations of the "free" and H-bonded pure water (frequency maxima should be at, approximately, 3250, 3420 and 3490 cm^{-1}) and O–H stretching vibrations of "free" and H-bonded hydroxyl group of PHEMA. As shown for pure hydroxyl-containing polymers such as poly(vinylphenol) (PVPh) [10, 15] and phenoxy [8, 18], there exist two bands in this region. The first band with a frequency maximum lying between 3550 and 3570 cm^{-1} reflects the "free" O–H stretching vibration. The second, very broad, band centred at 3360–3400 cm^{-1} is due to the wide variety of hydrogen bonding between hydroxyl groups.

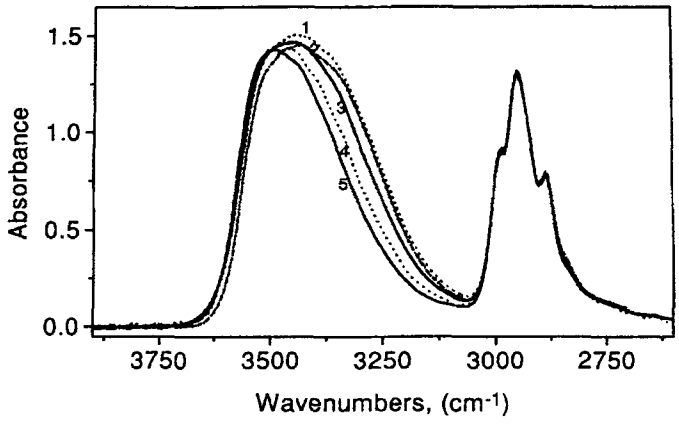


Fig. 7 FTIR spectra of PHEMA in the hydroxyl stretching frequency range for different temperatures: 1 – 300 K, 2 – 313 K, 3 – 333 K, 4 – 353 K, 5 – 373 K

In IR measurements for the O–H stretching region the transmittance is negligibly small for higher water contents, as revealed in curve 1 of Fig. 2A. Hence, the fitting procedure has been confined to the spectra for water contents lower than 30 wt%. It is observed that the intensity of the wide band at 3420 cm^{-1} (the main peak maximum of the OH group for pure water) decreases and the frequency-maximum shifts to somewhat higher frequencies with decrease in the water content from 18–4.2 wt%. As seen from Fig. 7 this band continues to shift to higher frequencies and its half-width decreases with increase in temperature up to 373 K. Since the frequency of the hydroxyl band in pure water is 3420 cm^{-1}, the shape of the band suggests that the tightly bound water is still present in the polymer at 373 K. TGA measurement [6] have shown that this polymer at 373 K contains as much as ~2.6 wt% of water.

The frequency of non-hydrogen-bonded hydroxyl groups depends on the type of polymer. For phenoxy and PVPh, the frequencies are 3570 and 3525 cm^{-1} respectively, [8, 10, 15, 18]. The frequency of the band decreases when the hydroxyl groups are hydrogen-bonded. However it is also found that the frequency difference between the "free" and hydrogen-bonded hydroxyl stretching vibrations is approximately 175 cm^{-1} in both polymers [10]. The decomposition of the band, based on data of limited extent and constrained by the accuracy of the fitting procedure, leads to two maxima at the frequencies of ~3540 and 3350 cm^{-1}. These bands can be assigned to the free and hydrogen-bonded hydroxyl groups, respectively.

Effect of temperature

Spectra in Fig. 7 show that the intensity of the band for the hydrogen-bonded hydroxyl group (low-frequency part

of the spectra) decreases with increasing temperature, whereas the intensity of the band for the "free" hydroxyl group in the polymer is slightly dependent on temperature. This shows that the number of hydroxyl groups that are hydrogen-bonded to water decreases with increasing temperature. The dependence of intensity for the free and H-bonded stretching vibrations on temperature is similar to the observation made for N–H stretching vibrations of amorphous polyamide [27]. It is also found that the frequency of the hydrogen-bonded hydroxyl group increases with increase in temperature. This observation is in line with that made for self-associated polymers [8]. However to make a detailed conclusion about the temperature behaviour of PHEMA, the temperature range of measurements needs to be extended.

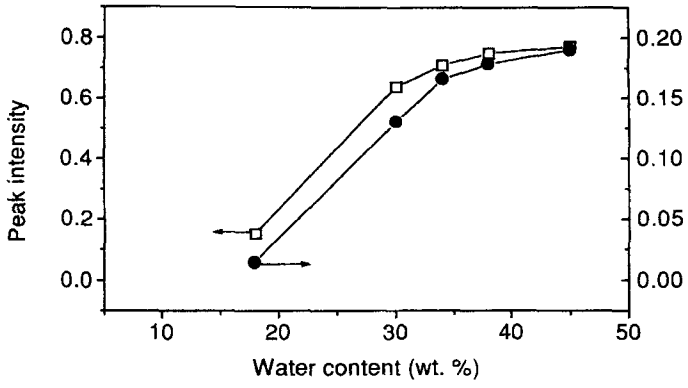


Fig. 9 Peak intensity of bands at 2130 cm^{-1} (●), and 1657 cm^{-1} (□) versus water content

Composite band at 2130 cm^{-1}

Figure 8 shows the IR spectra of the hydrogel PHEMA for different water contents in the spectral range 2500–1900 cm^{-1}. The dependence of the peak intensity of this band, with a frequency maximum at 2130 cm^{-1}, on water content, is shown in Fig. 9. The observed behaviour is similar to the band for bending vibrations of water at 1657 cm^{-1} (also shown in Fig. 9), nevertheless the band at 2130 cm^{-1} is much weaker than at 1657 cm^{-1} and is of measurable intensity only for a minimum of 30 wt%. It is known from the literature [21] that pure water shows a band at 2130 cm^{-1} which is a combination band of the bending vibrations at 1650 cm^{-1} and librations at 700 cm^{-1} (shown in Fig. 10). In the literature, assignment of this band as an "associated water band" [24], for bulk water has been made by some authors. It is interesting to note from Fig. 9 that peak intensities level off beyond

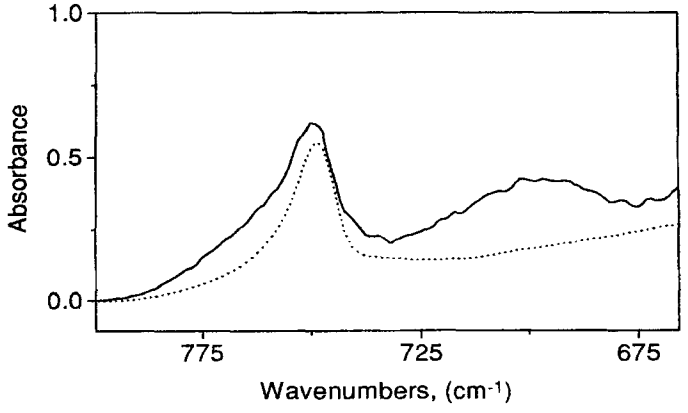
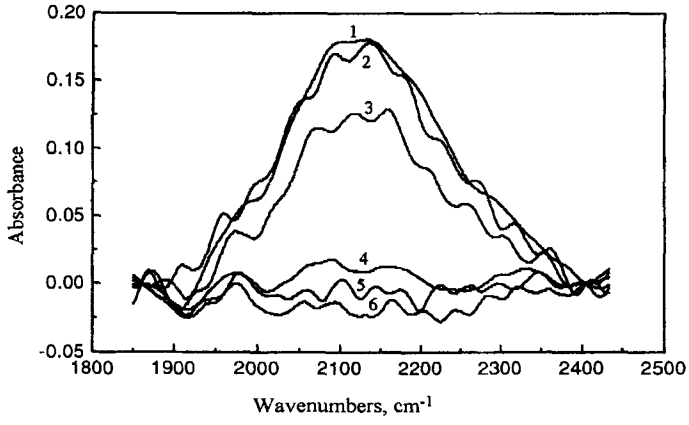


Fig. 10 FTIR spectra of PHEMA in the water libration region as a function of water content (in wt%): curves, full line – 30, dotted line – 18

Fig. 8 FTIR spectra of the 2130 cm^{-1} band for different water contents (water contents as in Fig. 4)



30 wt%, which reinforces the earlier findings that the excess water behaves more like loosely bound water.

The proposed assignment for the 2130 cm^{-1} band is also supported by the results for lipid/water systems [24] in gel and crystalline phases where a weak band in the spectral region of 2000–2600 cm^{-1} has been observed and assigned to vibrations of associated water (as to the combination band of H–O–H bending and the libration mode). It follows that the existence of this band as well as the librational band at 700 cm^{-1} shown in Fig. 10 in the spectrum is a definitive indication of the presence of loosely bound and possibly bulk water in the polymer.

Conclusions

FTIR measurements in the range 450–4500 cm^{-1} for hydrated and dry PHEMA provide site-specific information

about the behaviour of water and its influence on the properties of the polymer system. Three absorption bands whose intensity and position are strongly affected by water, have been analysed: hydroxyl (OH) streching vibration band (with a frequency maximum at $\sim 3550\,cm^{-1}$), carbonyl (C=O) stretching vibration band (frequency maximum at $\sim 1720\,cm^{-1}$) and the composite band involving H–O–H bending vibration and librations of water molecules with a frequency maximum at $2130\,cm^{-1}$. The fitting procedures and frequencies of these bands for non-hydrogen bonded systems from the literature have been used to obtain information about spectral characteristics of the "free" and hydrogen-bonded bands.

The characteristic behaviour of bound water has been elucidated. Loosely bound water exists in systems with water contents greater than 18 wt%, whereas tightly bound water exists for water concentrations below it. Some evidence does exist that more loosely bound water appears above a concentration of 30 wt%. The results also show that there are no sharp boundaries between the thresholds of various forms of water. The amount of tightly bound water decreases with time at a fixed temperature, however a small percentage of bound water (~ 2.6 wt%) remains tightly bound to the polymer up to a temperature of 373 K. These conclusions are in good agreement with those previously reached using other techniques such as NMR, thermogravimetric analysis and dielectric spectroscopy [4–6]. More definitive site-specific analysis must await an FTIR examination of PHEMA/D_2O systems.

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