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Interactions in poly(ethylene oxide)–hydroxypropyl methylcellulose blends

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Abstract

Blends of poly(ethylene oxide) and hydroxypropyl methylcellulose in the form of free films are examined for evidence of specific polymer:polymer interactions. Such interactions might affect the drug release behaviour of compressed matrices incorporating these polymers. The effect of HPMC on the crystallisation of PEO during casting is investigated using differential scanning calorimetry (DSC) and wide-angle X-ray diffraction. Fourier transform infra-red (FT-IR) and Raman spectroscopies are used to examine the possibility of a complex between the two polymers. Thermodynamic interaction parameters are calculated for films cast from water and *N,N*-dimethylacetamide (DMAc) using the Flory–Huggins theory of mixing. The interaction parameter calculated is negative, indicating a miscible blend, and a hydrogen bonding interaction is detected. This hydrogen bonding is less likely to occur in films cast from water than in films cast from DMAc perhaps because residual water can shield the interaction sites.

Finally, a transition involving a sharp reduction in heat capacity at high temperatures is reported. This transition is characterised using DSC and FT-IR and Raman spectroscopies, and is interpreted as a further complexing of the polymers. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene oxide; Hydroxypropyl methylcellulose; Blends

1. Introduction

Hydrophilic polymers are used extensively to formulate matrix tablets for controlled drug delivery. The combination of hydroxypropyl methylcellulose (HPMC) and poly(ethylene oxide) (PEO), two non-ionic polymers, has been shown to give a novel matrix tablet system that allows modification of the rate of drug release compared with pure HPMC. For example, the HPMC/PEO system can be used to increase the release rate at later times [1]. A possible mechanism by which drug release is modified is via a direct polymer:polymer interaction. Studies by Kondo et al. have established that the primary hydroxyl group on cellulose and methylcelluloses can form a hydrogen bond to the ether oxygen in PEO [2,3]. This opens up the possibility of a similar interaction between PEO and the hydroxyl groups on hydroxypropyl methylcellulose. This study aims to find the nature and extent of any interactions between these polymers, and is a natural extension of the work of Kondo et al. and Nishio et al. [2–4].

Films have been studied because any polymer:polymer interaction which occurs in compressed matrix tablets will be exaggerated in a more intimately mixed system. Two different solvents have been used for film casting: DMAc in order to allow a direct comparison with previous studies on similar systems; and water because drug release occurs via penetration of aqueous fluid ingress into the system.

Films are studied, both in the 'as cast' state, in which significant amounts of bound and unbound solvent may be present, and, for interaction parameter analysis, after annealing at elevated temperature. Such annealing might be expected to remove some residual solvent. The possible effects of residual solvent on the nature of the polymer:polymer interactions are discussed.

2. Experimental

2.1. Materials

HPMC K4M Premium grade was purchased from Dow. The nominal molecular weight of this grade is 88,000 and the degrees of substitution for CH_3 and $CH_2CHOHCH_3$ are 4.12 and 19.24%, respectively. PEO with a nominal

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molecular weight of 200,000 was purchased from Union Carbide Corporation. HPLC-grade *N*,*N*-dimethylacetamide (DMAc) and HPLC-grade water were both supplied by Aldrich Chemical Co. Distilled water was supplied by the Department of Materials Science and Metallurgy. All materials were used without further purification.

2.2. Preparation of samples

Separate solutions of 0.8 wt% HPMC and 1.3 wt% PEO were prepared. Aqueous solutions were made by heating two thirds of the water to approximately 85°C, stirring on a magnetic hot plate stirrer, adding the polymer powder to the vortex in a steady stream, then adding the remaining water at room temperature. These solutions were then left to cool, and stirred for 3 days before mixing in the relevant quantities and stirring for a further 3 days. DMAc solutions were made in a similar manner without heating the liquid prior to adding the polymer. The relative amounts (w/w) of the two polymers in the final solutions were 100/0, 67/33, 50/50, 34/66 and 0/100 (HPMC/PEO). Samples will be referred to in terms of their PEO content in per cent. After mixing, the solutions were poured into Petri-dishes and dried at 50°C in air for 3 days followed by 3 days at 50°C under vacuum. Samples were then stored in vacuum desiccators.

2.3. Measurements

Differential scanning calorimetry was carried out on a Perkin Elmer DSC-7 in a nitrogen atmosphere. The instrument was calibrated with an indium standard. The thermal behaviour of the samples was examined by applying controlled heating and cooling regimes. Melting temperature was taken as the peak of the melting endotherm. The error in each measurement was estimated to be ±0.5°C. Where measurements were repeated the error given is the standard deviation divided by the number of measurements minus one.

Wide-angle X-ray diffraction patterns were obtained using a Philips Diffractometer. Samples were placed on a silicon substrate to carry out the scans, and each sample was measured in duplicate to ensure reproducibility. CuKα radiation was produced by a Philips X-Ray generator.

Raman Spectra were recorded using a 780 nm diode laser on a Renishaw Ramascope 1000. Spectra were measured in two or three places on each sample and representative data are shown. Infra-red spectra were recorded using attenuated total reflectance on a Perkin Elmer Infrared Fourier Transform Spectrometer.

3. Results and discussion

3.1. Characterisation of as-cast films

In this section, the behaviour of as-cast films is considered. These films are likely to have small but significant quantities of residual solvent which may be bound to the polymer. Since bound solvent could reduce the extent of specific polymer:polymer interactions by occupying interaction sites, the nature of the solvent used in casting may have an effect on the final properties of the film.

The films were examined under a polarised, transmitted light microscope and similar structural features were observed in films cast from DMAc and water. Pure PEO has a spherulitic morphology with spherulites measuring approximately 0.05 mm in diameter in water-cast, and 0.5 mm in DMAc-cast films. This difference reflects a difference in the balance of spherulite nucleation and growth rates in films cast from the two solvents, which could be due to different levels of impurities or different solvent evaporation rates. All the films cast from blends have a much finer scale structure with very small (non-spherulitic) crystalline domains measuring less than 0.01 mm across and no evidence of gross phase separation in the amorphous phase. It is possible that there was a degree of phase separation in the solutions, which could have lead to some residual phase separation in the amorphous phase of the as-cast films, although none is detectable by the techniques used in this study.

3.1.1. Melt behaviour

DSC traces of HPMC/PEO blends heated to 90°C at 10°C min^{-1} reveal that the PEO melt temperature decreased with increasing HPMC content, as illustrated in Fig. 1. The error bars represent the standard deviation divided by the number of repeats minus one. The decrease was similar for blends obtained from DMAc and water, but films cast from DMAc gave lower melting points across the complete composition range. This lower melting temperature in DMAc-cast films could indicate increased miscibility in the amorphous regions of these blends compared with the water-cast blends, although since the effect is also seen (albeit to a lesser extent) in the pure PEO film, this cannot account for the full difference. It would appear that even in pure PEO, more stable crystals result from casting from water, possibly due to differences in solvent evaporation rates or different levels of impurities in each solvent.

The quantity of PEO melting, as indicated by the melting enthalpy, also decreased with increasing HPMC content, again with DMAc giving lower values across the complete composition range, although the values for pure PEO in this case are very similar. Films cast from both solvents give non-zero intercepts on the %PEO axis of the plot of melting enthalpy vs. %PEO in Fig. 1, indicating that PEO is unable to crystallise below a certain concentration in HPMC. The intercept for blends cast from DMAc is at a higher PEO concentration than for blends cast from water.

The melting enthalpy data indicate that HPMC hinders the crystallisation of PEO in binary blends cast from either solution. This effect is more pronounced for blends cast from DMAc than from water.

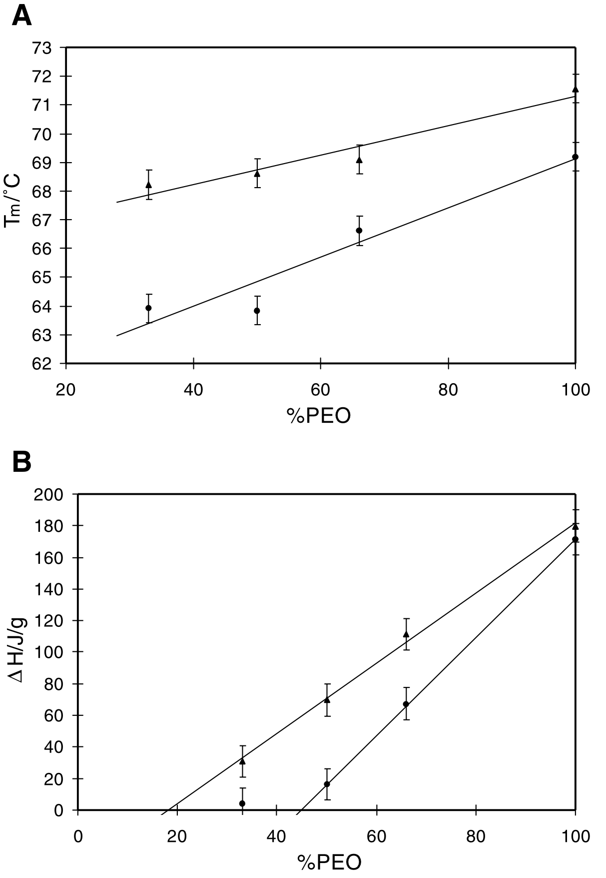

Fig. 1. (A) Peak melting temperature vs. PEO content and (B) melting enthalpy vs. PEO content for as-cast films cast from water (▲) and DMAc (●).

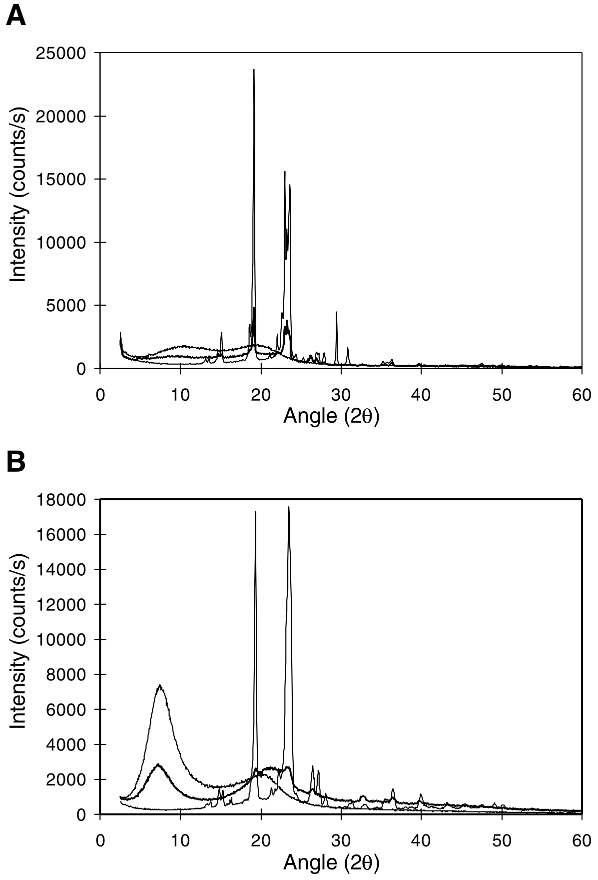

Fig. 2. Examples of the X-ray diffractometer scans used to calculate degrees of crystallinity: (A) water-cast; (B) DMAc-cast. Thin line = 0%PEO; thick line = 50%PEO; medium line = 100%PEO.

3.1.2. Crystallinity

Measurement of crystallinity was carried out by calculating the areas under wide-angle X-ray diffractometer scans. The results were compared with crystallinities calculated from DSC. Examples of the X-ray data used to calculate crystallinity are shown in Fig. 2. The formula used to calculate crystallinity was:

$$\text{crystalline fraction} = \frac{\text{total area} - \text{area of amorphous halo}}{\text{total area}} \tag{1}$$

This calculation assumes that the scatter from each molecule is the same. Melting enthalpies (ΔH), measured using first heat DSC data, were converted into crystallinities by dividing ΔH by the melting enthalpy of 100% crystalline PEO (197 J g^{-1}) [5].

The dependence on solvent suggests that water prevents, to some degree, the interactions between PEO and HPMC. In the absence of water, the polymers interact more strongly and PEO is less able to crystallise during casting. This effect may be due to water interacting with the two polymers, preventing them from interacting with each other, be this on a molecular level, or by a greater degree of phase separation in the casting solution. Alternatively, this effect could be due to differences in impurity levels affecting nucleation rates, or a difference in solvent evaporation rates; with DMAc evaporating more quickly than water, there may be insufficient time for PEO to crystallise as fully as it could with a more slowly evaporating solvent.

Fig. 3 shows the crystallinities of the HPMC/PEO blends calculated from WAXS and DSC data. The crystallinity decreases linearly with decreasing PEO content for films cast from both DMAc and water. This relationship is expected because the content of crystallisable polymer is decreasing linearly. Both plots show non-zero intercepts on the %PEO axes indicating that PEO does not crystallise above a certain HPMC content; the effect is more pronounced for films cast from DMAc, the intercept occurring at about 40%PEO compared to 20%PEO for films cast from water. The DSC and WAXS data are in good agreement and demonstrate the differences between the films cast from water and from DMAc, that is, the PEO in the blend is more able to crystallise when the film is cast from water.

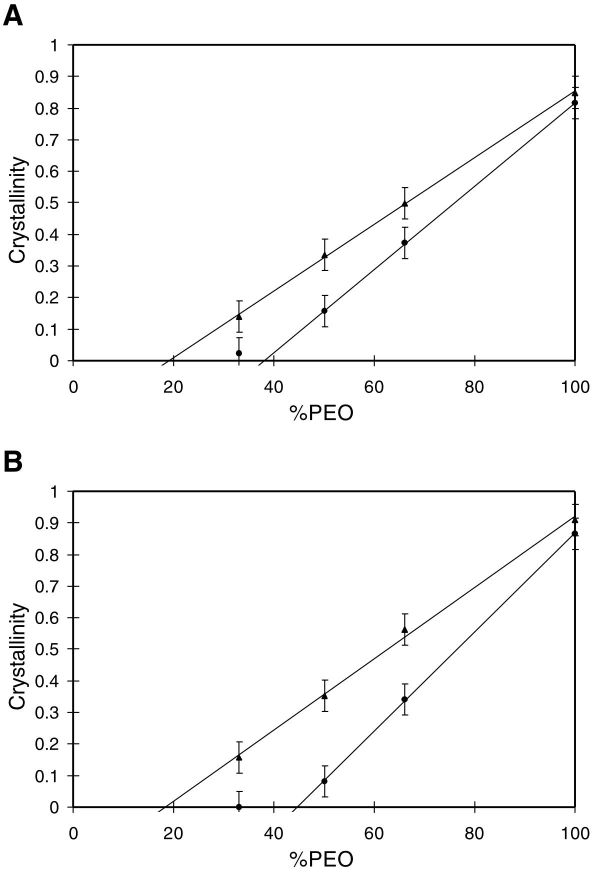

Fig. 3. Crystallinity vs. PEO content measured by (A) wide-angle X-ray diffraction and (B) DSC for as-cast films cast from water (▲) and DMAc (●).

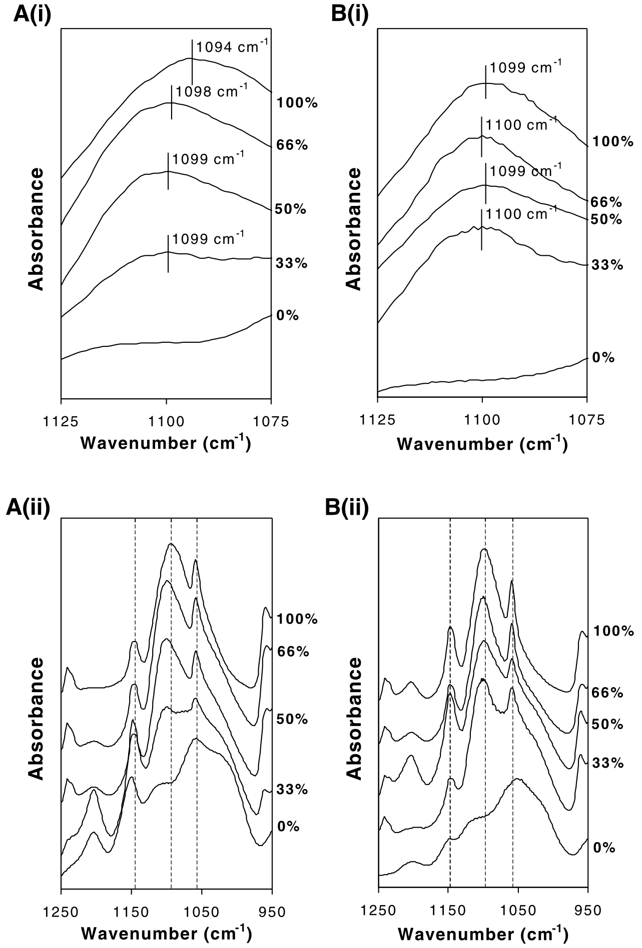

Fig. 4. IR spectra of PEO from films cast from (A) water and (B) DMAc, showing (i) the range 1075–1125 cm^{-3} and (ii) the range 950–1250 cm^{-3}. The percentages refer to the amount of PEO in each blend. The relevant proportion of the pure HPMC spectrum has been subtracted from the blend spectra to obtain these traces.

3.1.3. Vibrational spectroscopy

Fourier transform infra-red (FT-IR) and Raman spectroscopy of as-cast films were carried out in order to detect any peak shifts that could be attributed to weak interactions between the two polymers, such as hydrogen bonding or complexation.

The IR peak of interest is the C–O–C asymmetric stretch at 1100 cm^{-1} [6]. This peak in the PEO spectrum has been shown to shift due to hydrogen bonding to methylcellulose [2,3]. The spectra obtained for blends are shown in Fig. 4. There were no detectable peak shifts for water-cast films, but there was a 5 cm^{-1} shift to higher wavenumber for blends cast from DMAc compared with pure PEO cast from DMAc. This strongly supports the idea that a hydrogen bond can form between PEO and HPMC. The absence of a peak shift in the water-cast films may be because water bonds to the interaction sites, thus preventing the interaction with HPMC and allowing PEO to crystallise more readily. In addition, there could be a greater degree of microphase separation in the amorphous regions of blends cast from water compared with those cast from DMAc, which would also prevent the polymers from interacting.

The region of the Raman spectra of particular interest is 100–600 cm^{-1}. This region contains peaks attributed to PEO backbone vibrations (e.g. C–C–O, C–O–C bends and C–C, C–O internal rotations) [7]. Once again, if a hydrogen bond is formed to the ether oxygen in PEO then these vibrations will be affected. There are no significant peaks in the HPMC spectra.

Fig. 5 shows Raman spectra from as-cast films. The measured spectra for the blends are compared with theoretical spectra for mechanical mixtures of the two polymers. Theoretical spectra were calculated by adding the appropriate fractions (in terms of mass) of the PEO and HPMC spectra. In general, the measured spectra show less intense peaks across the range of wavenumbers indicating that the PEO backbone is being prevented from vibrating. This effect is more pronounced for the DMAc-cast films. This shows that there is a strong possibility that hydrogen bonds have been formed between the hydroxyl groups of HPMC and ether oxygens of PEO, and that water prevents this interaction to some extent.

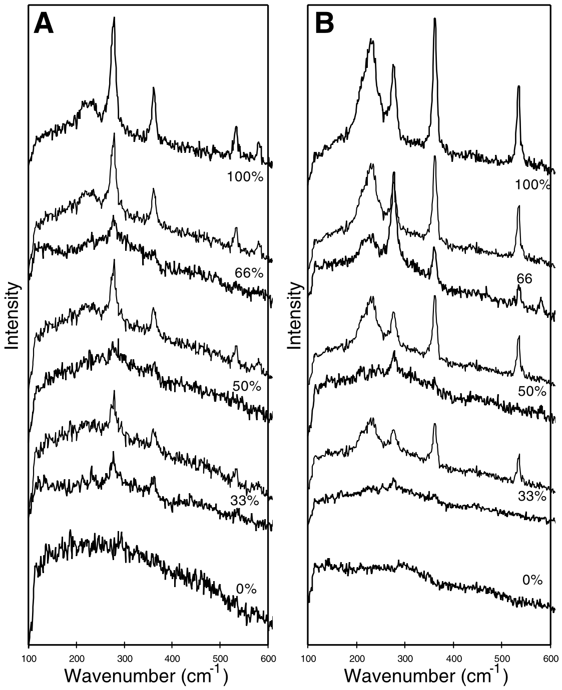

Fig. 5. Raman spectra from films cast from (A) water and (B) DMAc; the upper of each pair (thinner line) is calculated from the measured spectra for pure HPMC and pure PEO and the lower of each pair is the measured spectrum for that blend.

It is clear that the solvent used to cast films is important in determining the degree of interaction between the two polymers in the as-cast state. Water has been seen to prevent the interaction to some extent, possibly because it can bond to the interaction sites on PEO and HPMC. All the evidence presented here strongly suggests that the two polymers can hydrogen bond to each other in a similar way to PEO and 2,3-di-*O*-methylcellulose [2,3], but that the interaction is less likely to occur in films cast from water.

3.2. Flory–Huggins analysis of annealed films

An attempt to quantify the interaction between the PEO and HPMC cast from DMAc and from water was made using the method reported by Kondo et al. [3]. Samples were heated in the DSC to 90°C at 10°C min^{-1} and held for 10 min before quenching at 200°C min^{-1} to the isothermal crystallisation temperature, T_{ic}. The samples were monitored and held at this temperature for at least 10 min after complete crystallisation. The samples were then cooled to 20°C at 10°C min^{-1}, held for 2 min then heated to 90°C at 10°C min^{-1} to measure the subsequent melting temperature, T_{m}.

The thermal profile applied by the DSC first subjects the as-cast film to an annealing treatment at an elevated temperature, to allow full interaction of the polymers in the amorphous phase before controlled crystallisation. Since the annealing temperature of 90°C is considerably higher than the casting temperature of 50°C, it is likely that further residual solvent is driven from the films in this stage. However, it is still possible that some solvent remains bound to the polymer molecules. One might, therefore still expect there to be differences in the behaviour of films originally cast from the different solvents, if the quality of the residual solvent has an effect.

It is important to note here that samples were annealed at a temperature below the T_{g} of HPMC. Ideally, the blends would be annealed at a temperature above the glass transition temperatures of both constituents to allow the amorphous phase to interact fully. However, thermal degradation occurs if the blends are heated above the glass transition temperature of HPMC, invalidating the results. Kondo et al. [3] also encounter this problem, and adopt a similar solution. By following their method, and annealing at 90°C, we enable our results to be directly compared with theirs on PEO blends with cellulose and methylcellulose. Furthermore, we observed an unpredictable transition in the blends studied here at around 130°C, which is discussed later. Annealing at 90°C has the additional advantage of avoiding the complication of this transition occurring in some samples but not others.

The concept of melting point depression to measure the interaction parameter is used because the blends consist of a crystalline and an amorphous polymer. However, morphological effects must also be considered because the degree of perfection and size of polymer crystallites, as well as any interaction between the polymers, affect the melting point of isothermally crystallised polymers. A true Flory–Huggins interaction parameter may only be calculated if morphology is independent of PEO concentration, that is, melting point depression is solely a result of polymer:polymer interactions.

3.2.1. Hoffman–Weeks plots

If morphology is independent of PEO concentration, then the stability parameter, ϕ, which is a function of crystal thickness, will also be independent of PEO concentration. In order to find out the stability, and the equilibrium melting temperature of the PEO crystals in the blends, the observed melting temperatures, T_{m}, of isothermally crystallised PEO were plotted against T_{ic}, the isothermal crystallisation temperature for each blend composition. These plots are known as *Hoffman–Weeks* [8] plots and are shown in Fig. 6. The lines are lines of best fit calculated by the least squares method. Although there is some scatter in the data there is a general increase in T_{m} with T_{ic}. Each data set was fitted to the following equation to estimate a value for stability parameter, ϕ (ϕ being equal to the gradient of the line):

$$T_{\mathrm{m}}^{\mathrm{eq}} - T_{\mathrm{m}} = \phi(T_{\mathrm{m}}^{\mathrm{eq}} - T_{\mathrm{ic}}) \quad 0 \leq \phi \leq 1 \tag{2}$$

$T_{\mathrm{m}}^{\mathrm{eq}}$ is the equilibrium melting point and ϕ, the stability parameter which depends on the crystal thickness. The

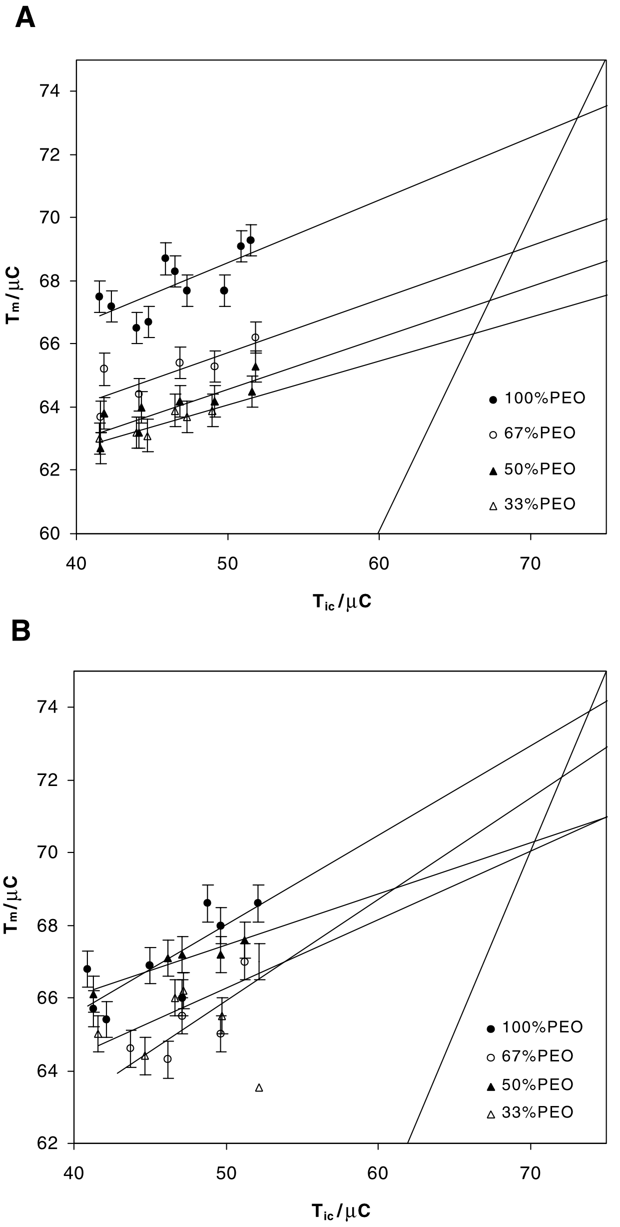

Fig. 6. Hoffman–Weeks plots for (A) DMAc-cast and (B) water-cast films. The broken line is $T_m = T_{ic}$.

Table 1
Stability parameter, ϕ, of PEO crystals

Blend (HPMC/PEO)	DMAc-cast	Water-cast
0/100	0.20 ± 0.07	0.24 ± 0.07
34/66	0.17 ± 0.06	0.3 ± 0.1
50/50	0.16 ± 0.04	0.14 ± 0.03
67/33	0.14 ± 0.03	0.18 ± 0.08

error in ϕ was calculated using the standard method for the error in the gradient of a straight line [9].

The values obtained for ϕ are summarised in Table 1. A stability parameter of 1 implies $T_m = T_{ic}$, and hence describes unstable crystals. A stability parameter of zero implies $T_m^{eq} = T_m$, and hence stable crystals at equilibrium. The values are all significantly greater than zero, indicating that all crystals are fairly unstable.

There is considerable scatter in the data, giving high values of uncertainty in the values of ϕ. However, within the experimental error, the values of ϕ are not dependent on composition for either set of films. Hence, it is assumed that morphological effects have been eliminated in this experiment, and that it is valid to go on to calculate a Flory–Huggins interaction parameter.

The equilibrium melting temperatures, T_m^0, at this heating rate were found by calculating the intersection of the measured T_m vs. T_{ic} lines with the line $T_m = T_{ic}$. The results of these calculations are plotted in Fig. 7. The measured equilibrium melting point decreases with increasing HPMC concentration. The high uncertainty inherent in the data means that the extrapolated lines cross in some cases, which should not occur. This uncertainty is carried through the calculation to allow an assessment of the reliability of the final result. The errors were calculated using the standard method for the error in the gradient and intercept of a straight line [9].

3.2.2. Melting point depression

Flory–Huggins interaction parameters [10] for PEO and HPMC may be estimated using melting point depression, assuming that the depression is due solely to thermodynamic effects (which has been established to be a reasonable assumption within the error of the experiment). The melting point depression is calculated by subtracting the blend equilibrium melting point from the equilibrium melting point of 100%PEO. The uncertainties are given by standard error combination and are high because of the scatter in the melting point data. The values obtained are shown in Table 2.

The conventional formulation for the thermodynamic depression of melting point caused by a diluent is as follows [11]:

$$1/T_m - 1/T_m^0 = -R(V_{2u}/\Delta H_{2u})[\ln v_2/V_2 + (1/V_2 - 1/V_1)v_1 + Bv_1^2/RT_m] \quad (3)$$

where T_m^0 is the equilibrium melting point of PEO and T_m is the observed equilibrium melting point of the blended PEO. Subscripts 1 and 2 refer to HPMC and PEO, respectively, v being the volume fraction of polymer and V being the molar volume of the polymer. V_{2u} is the molar volume of the repeating units of PEO and ΔH_{2u} is the enthalpy of per mole of repeating units of PEO. B is the interaction energy density and R is the gas constant.

V_1 and V_2 are large and hence the entropy term of Eq. (3) may be neglected [11]. The equation can hence be

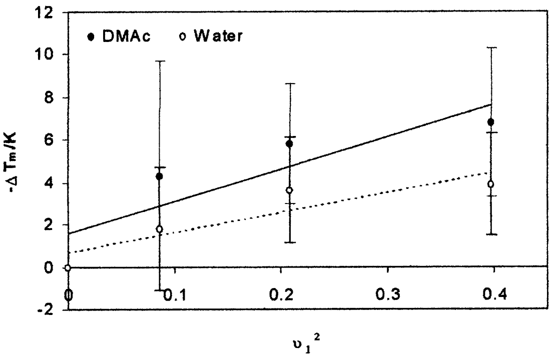

Fig. 7. Plots of the melting point depression, ΔT_m, vs. the square of volume fraction of HPMC, v_1^2, for films cast from water (○) and DMAc (●).

rearranged to the following form, allowing the evaluation of the enthalpic contribution to the melting point depression:

$$\Delta T_m = T_m^0 - T_m = -T_m^0(V_{2u}/\Delta H_{2u})Bv_1^2 \quad (4)$$

where ΔT_m is the melting point depression of the PEO component.

A Flory–Huggins interaction parameter, χ_{12}, may be defined to describe the enthalpy of mixing. It is related to the parameter B [10]:

$$B = RT_m(\chi_{12}/V_{1u}) \quad (5)$$

where V_{1u} is the molar volume of repeating units of HPMC.

Experimental measurements of the melting point depression, ΔT_m, are plotted against the square of the volume fraction of HPMC, v_1^2, in Fig. 7. The volume fraction was calculated using 1.3 g cm^{-1} as an approximate value of the density of HPMC [2] and 1.09 g cm^{-1} as the density of the PEO melt (at 75°C) [12]. The slopes of these plots are equal to $R(V_{2u}/\Delta H_{2u})/B$, thus enabling the calculation of B and hence χ_{12}. Other quantities used in this calculation are: heat of fusion per unit volume ($\Delta H_{2u}/V_{2u}$) of PEO = 240 J cm^{-3} [5], $V_{1u} = 151.86$ cm^3 mol^{-1}. V_{1u} was calculated from the molar mass of HPMC, 197.42 g mol^{-1} and its density.

The lines were drawn by the least-squares fitting method assuming a linear relationship between ΔT_m and v_1^2, and including the point at zero. The non-zero intercept may be attributed to the entropic contribution to the melting point depression, which was assumed to be negligible in the derivation above. Both sets of data yield positive slopes and the values of χ_{12} obtained from them are shown in Table 3.

Table 2
Equilibrium melting points obtained from the Hoffman–Weeks plots in Fig. 6, and the resulting values of melting point depression, calculated by subtracting the blend equilibrium melting point from the equilibrium melting point of 100% PEO

Composition	DMAC-cast		Water-cast	
	T_m^{eq}	ΔT_m	T_m^{eq}	ΔT_m
100% PEO	73 ± 2	0	74 ± 3	0
66% PEO	69 ± 2	−4 ± 3	72 ± 5	−2 ± 5
50% PEO	67 ± 1	−6 ± 2	70 ± 1	−4 ± 3
33% PEO	66 ± 1	−7 ± 2	70 ± 2	−4 ± 3

Table 3
Values of the interaction parameter, χ_{12}, for binary blends with components compatible in the melt

Parameter	DMAc-cast	Water-cast
χ_{12} (at 348 K)	−0.6 ± 0.2	−0.4 ± 0.1

The errors quoted in Table 3 indicate that although water-cast films give a lower interaction parameter than DMAc-cast films, this may be the result of experimental error, and the interaction parameters may, in fact, be the same. If the interaction parameter for the HPMC/PEO blend cast from water is indeed lower than that for the blend cast from DMAc, it may be concluded that the heat treatment at 90°C is not sufficient to remove all residual solvent and that although the polymers are miscible when cast from either solvent, the presence of bound water renders them less so.

The interaction parameter calculated for PEO/HPMC cast from DMAc at 75°C is −0.6 ± 0.2, which may be compared with reported values of −0.51 for PEO/2,3-di-*O*-methylcellulose [3] and −0.67 for PEO/cellulose [4]. A lower value for PEO/HPMC would be expected if the interaction is partly due to hydrogen bonding to hydroxyl groups at the C6 positions on HPMC because some of these OH groups have been substituted in HPMC. As no errors are quoted for the values obtained by Kondo et al. [3] or Nishio et al. [4] no further comparison can be made. We must conclude that the interaction parameters are similar for PEO/2,3-di-*O*-MC and PEO/HPMC cast from DMAc.

3.3. Overview of the polymer:polymer interactions

The results for as cast films have shown that HPMC hinders crystallisation of PEO during solvent evaporation. This effect is greater in DMAc- than water-cast films. Spectroscopy indicates the presence of hydrogen bonds between the two polymers in the DMAc-cast films which do not form in the presence of water, either because water molecules block the interaction sites on both polymers or because there is a greater degree of phase separation in the aqueous solution, which is retained when on drying. The increased hindrance of crystallisation in DMAc cast films is likely to be because of this increased H bonding between the polymers. It is also possible that different solvent evaporation rates or differences in impurity levels when casting from the different solvents play an additional secondary role in controlling the degree of crystallisation in blends cast from different solvents.

The interaction parameter obtained for HPMC/PEO cast from DMAc indicates a similar miscibility in this blend to that in the 2,3-di-*O*-methylcellulose/PEO blend studied by

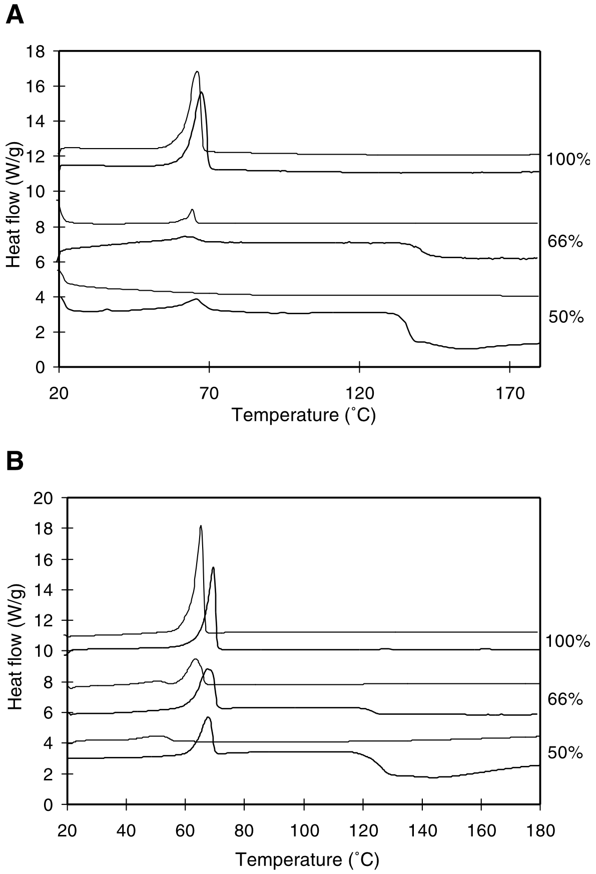

Fig. 8. DSC scans showing the step transition in films cast from (A) DMAc and (B) water. The upper curve of each pair (thinner line) is the second heat after isothermal crystallisation at 50°C. Percentages refer to the amount of PEO in each blend.

Kondo et al. For the blend cast from water it is not possible to determine whether the heat treatment applied has been sufficient to eliminate the effect of the solvent, but it is possible that the polymers are slightly less miscible in this case, suggesting that some bound water remains allowing water to interfere with the interactions between these two polymers.

3.4. Transition at elevated temperature in as cast films

In this section, the high temperature behaviour of as-cast films is considered.

On heating as-cast films in the DSC to 180°C at 10°C min^{-1} a step-shaped transition was sometimes observed. This transition was indicated by a sharp reduction in heat capacity, the opposite of what would be observed for a glass transition. The step never occurred in either pure PEO or pure HPMC cast from either solvent, so it is interpreted as a further polymer:polymer interaction. The height of the step was a maximum for blends containing 50% PEO for films cast from both DMAc and water (Fig. 8). In addition, the temperature of the step was independent of film composition or solvent to within experimental error.

After the first heat, samples were quenched to 50°C at 200°C min^{-1} and allowed at least 30 min to crystallise (the crystallisation was observed during the scan and the sample was left at 50°C for at least 10 min after the crystallisation exotherm was complete). Once crystallisation was complete, the samples were cooled to 20°C then reheated to 180°C at 10°C min^{-1} and the enthalpic behaviour measured. In films originally cast from DMAc, the melting endotherm in the second heat was very small, if it was there at all, showing that very little PEO crystallised after undergoing the step transition. The melt in the second heat was also at a slightly lower temperature in the blends compared with pure PEO, indicating less stable crystals. Samples that did not undergo the step transition showed similar melting behaviour on the first and second heats. This behaviour supports the hypothesis that the transition reflects some additional interaction because the step transition reduces further the crystallisability of PEO.

In films cast from water, two different kinds of crystallisation and melting behaviour have been observed on reheating after the sample had been through the step transition, depending on the film composition. At 66% PEO, most PEO crystallised at the quench temperature, but a smaller amount crystallised only when the sample was cooled below this temperature. The PEO that crystallised at the lower temperature also melts at a lower temperature and was observed as a smaller endotherm. However, for PEO concentrations of 50% or lower, no crystallisation occurred at the quench temperature, the PEO crystallised only during cooling below this temperature, resulting in a small, low temperature endotherm during reheating. These observations may be linked with the size of the step, the height being larger for the 50% PEO samples. One possible explanation is that there is excess PEO in the 66% PEO films, and only some of it engaged in the interaction indicated by the step, leaving that which did not interact able to crystallise at the quench temperature. In film samples containing 50% PEO or less, all of the PEO in the films engaged in the interaction and none was able to crystallise at the quench temperature.

The differences between water- and DMAc-cast films is clear here: it appears that in DMAc-cast films most of the PEO interacts during the step and is prevented from crystallising; however, in water-cast films, a large proportion of the PEO does not interact and melts at a similar temperature to pure PEO. Samples that did not undergo the step transition showed similar PEO melting behaviour on the first and second heats, as shown in Fig. 9.

The drop in heat flow corresponds to a reduction in heat capacity, i.e. a reduction in chain mobility. This could be a consequence of a further complexing of some kind, possibly hydrogen bonding of some PEO ether oxygens to a less stereochemically available hydroxyl group on the HPMC, heat being necessary to mobilise the HPMC sufficiently for the hydrogen bond to be formed. If this is the case, the start of the step may reflect some critical stage in the glass

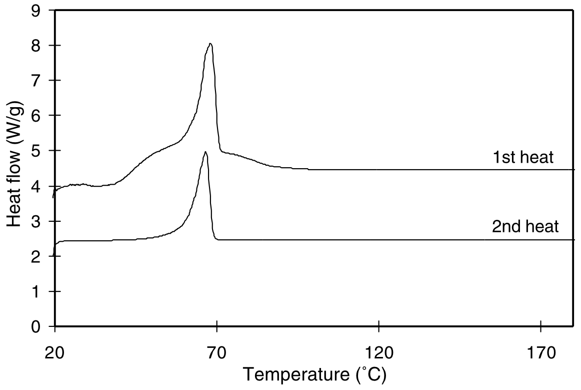

Fig. 9. DSC scans from a 66% PEO film that contained enough water to show the evaporation exotherm.

transition of HPMC. The T_g of HPMC has been measured to occur between 150 and 180°C [13] using DSC at a heating rate of 10°C min^{-1}. This temperature range is slightly above the temperature at which the transition is observed, but low molecular weights of PEO are known to plasticise HPMC [14,15] and chain mobility increased significantly below T_g. On cooling below the step transition temperature the polymer complex is fixed in the glassy state and PEO is unable to crystallise.

The step did not occur in samples that showed a water evaporation endotherm (broad peak underneath the PEO melt), and did not always occur in seemingly dry samples. It is interesting to note that although the Flory–Huggins interaction parameter is not significantly affected by the presence of water during casting, the higher temperature interaction is less likely to occur in films cast from water. One possible explanation might be that despite the high temperature of the interaction, sufficient water remains bound to the specific hydroxyl groups involved in this interaction to prevent it occurring. This bound water would not be detected during a DSC heat, so may be present even in samples that appear dry.

HPMC/PEO blends were investigated to identify the changes occurring due to this step transition using hot stage polarised light microscopy, attenuated total reflectance FT-IR spectroscopy and Raman spectroscopy. The microscopy did not show any changes at the temperature of the transition. The spectroscopic techniques, however, showed significant differences between samples that had been heated through step transition temperature. In the Raman spectra, shown in Fig. 10, peak intensity is significantly reduced for samples that had undergone the step transition compared with those that had not. This indicates that the transition imposes a further reduction in chain mobility to that occurring simply by blending the two polymers during the process of film casting. FTIR spectra (Fig. 10) show a significant difference in the region of the C–O–C asymmetric stretch. The films that have undergone the step transition show a broader C–O–C peak compared with films that have not. This broadening results in a peak shift to lower wavenumber. The change in the C–O–C peak in FT-IR, suggest that hydrogen bonding is the underlying mechanism in the interaction.

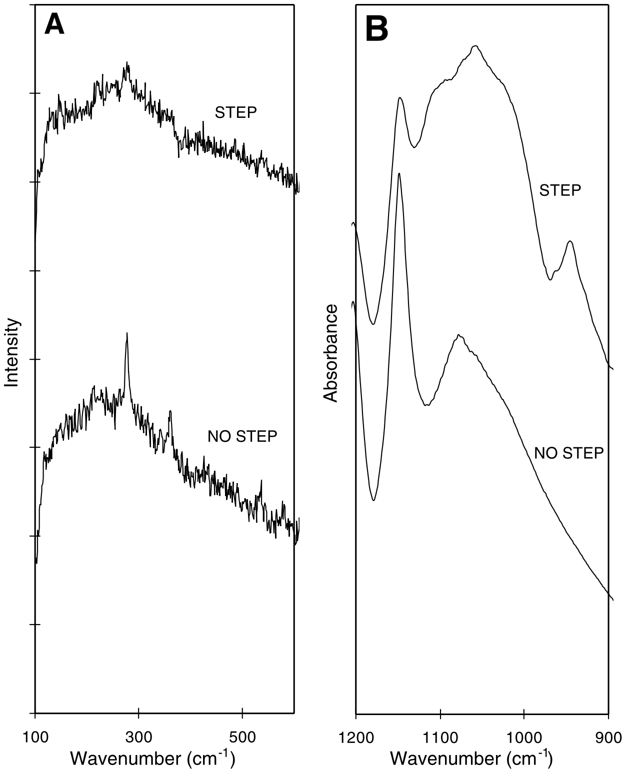

Fig. 10. (A) Raman spectra and (B) FT-IR spectra from 66% PEO, heated films cast from water.

Whether or not this step occurs in a given set of films has proved to be unpredictable for both DMAc- and water-cast films, suggesting that the films are sensitive to environmental factors that are difficult to control during the experiments, for example, the humidity of the rooms in which casting and transfer between ovens, desiccators and experimental apparatus. However, the step transition has been highly reproducible in samples taken from specific films that have displayed the transition.

4. Conclusions

Blends of poly(ethylene oxide) and hydroxypropyl methylcellulose in the form of free films have been examined for evidence of specific polymer:polymer interactions. HPMC has been found to hinder the crystallisation of PEO during casting, and to reduce the stability (i.e. melting temperature) of PEO crystals. FT-IR and Raman spectroscopies have revealed a hydrogen bond between the two polymers in DMAc-cast films that does not occur in water-cast samples, perhaps because bound water occupies the sites for bonding.

The Flory–Huggins interaction parameters for the HPMC:PEO blend has been calculated to be -0.6 ± 0.2

for a DMAc-cast blend and -0.4 ± 0.1 for a water-cast blend, indicating that the polymers are miscible, and possibly slightly more so when cast from DMAc solution. Any difference is likely to be due to the heat treatment applied being insufficient to eliminate all of the bound solvent, and indicates that the polymers are less miscible when cast from aqueous solution than from DMAc solution. Again, this could be because bound water occupies potential polymer:polymer interaction sites. The overall conclusion is that this is a miscible polymer blend, and behaves similarly to other PEO–cellulosic blends.

Finally, the transition involving a sharp reduction in heat capacity at high temperatures has been associated with a further complexing between the two polymers, possibly involving hydrogen bonding to a less stereochemically available hydroxyl group on the HPMC.

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