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# Interactions and partitioning of diluents/plasticizers in hydroxypropyl methylcellulose and polyvinyl alcohol homopolymers and blends. Part III: Polyethylene glycol 400

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*Abstract*: The interactions and partitioning of polyethylene glycol 400 (PEG400) in hydroxypropyl methylcellulose (HPMC), polyvinyl alcohol (PVA) and their blends have been investigated by means of torsional braid analysis (TBA). PEG400 was shown to be a better plasticizer for HPMC than PVA, in agreement with solubility parameter predictions. Incorporation of PEG400 in blends of PVA and HPMC did not alter the incompatibility between the two homopolymers and plasticized both phases. The PEG400 content in the two phases was calculated by fitting Kelley–Bueche and quadratic expressions to the experimental data, enabling determination of the PEG400 partition coefficient. The data showed a selective partitioning of PEG400 in the HPMC phase for plasticizer contents less than 20% w/w. At higher concentrations, PEG400 continued to partition selectively into the HPMC phase for blends with 60 and 80% PVA but started partitioning in the PVA phase for blends with 20 and 40% PVA.

*Key words*: Aqueous – polyvinyl alcohol – hydroxypropyl methylcellulose – interactions – plasticizer – partitioning – solubility – polyethylene glycol

## Introduction

Despite the extensive literature on the plasticization of polymers, little is known about the partitioning of plasticizers in the different phases of heterogeneous polymer blends [1]. This is the third part in a series of papers [2, 3] dealing with this issue. Earlier publications have reported data on the partitioning of diethylene glycol (DEG) [2] and glycerol [3] in blends of hydroxypropyl methylcellulose (HPMC) and polyvinyl alcohol (PVA); the two homopolymers have been shown to be totally incompatible [4]. In both systems, the plasticizer/diluent did not alter the incompatibility of the two polymers and their total segregation into two almost pure phases in the blend over all the composition range. In the case of glycerol, a better plasticizer for PVA [5], it was shown that the plasticizer partitioned selectively into the PVA phase. DEG, a good plasticizer for both polymers [5], also partitioned selectively into the PVA phase with the exception of the 50:50 PVA:HPMC system where it was randomly mixed. In both systems the plasticizer selectivity decreased with increasing concentration in agreement with the presence of compatibility limits [5, 7]. The behaviour was successfully rationalised in terms of the relative strength of interactions between polymer and diluent/plasticizer with the help of the Hansen solubility parameters [5]. We now consider the final case of a plasticizer which would interact preferentially with HPMC compared to PVA.

## Experimental

### *Materials*

Hydroxypropyl methylcellulose (HPMC Pharmacoat 606) was supplied by Shin Etsu Chemical Co., Japan, and had molecular weight $\bar{M}_n$ of 60 100 g mol$^{-1}$ and polydispersity of 2.2. Poly(vinyl alcohol) (PVA Poval 205) was obtained from Kurraray Co., Japan, with $\bar{M}_n$ of 73 900 g mol$^{-1}$ and polydispersity of 1.7. The PVA grade used was 88% hydrolysed and had a viscosity of 4.5–5.4 mPas in 4% aqueous solutions at 20 °C. PEG400 was monodisperse ($\bar{M}_w/\bar{M}_n \leq 1.06$) with molecular weight $\bar{M}_n$ of 410 g mol$^{-1}$ and was supplied by BDH. The molecular weights were determined by gel permeation chromatography (GPC) with tetrahydrofuran as the carrier solvent and polystyrene standards. In the case of PEG400, the column was calibrated with monodisperse polyethylene oxide standards and the carrier solvent was dimethyl formamide. All materials were used as received.

### *Techniques*

The dynamic mechanical spectra of homopolymers and blends were recorded by means of a torsional braid analyser (TBA) at ca. 1 Hz from − 30° to 150 °C and at a heating rate of 1 °C min$^{-1}$. The TBA instrument used has been described in detail elsewhere [6]. The polymer system under investigation was supported on glass braids consisting of two glass yarns twisted to produce 2.5 turns per inch and heat cleaned at 500 °C for 1 h. Sample preparation involved soaking of the heat-cleaned glass braids in 10% w/v aqueous solutions for at least 3 h, followed by oven air drying at room temperature and vacuum drying at 50 °C to constant weight. The data are presented in terms of the logarithmic decrement and relative rigidity as a function of temperature. The *Tg* values quoted correspond to the temperature of the maximum logarithmic decrement.

## Results and discussion

### *Plasticization of homopolymers*

As the effect of PEG400 on HPMC and PVA has already been discussed [5], earlier observations in terms of *Tg* variation with increasing PEG400 concentration, are summarised in Fig. 1. Both *Tg* and relative rigidity decreased with increasing PEG400 content consistent with plasticization of both homopolymers. A shoulder was observed in the logarithmic decrement curve at around 50° to 60 °C for systems with high PEG400 content ( ≥ 30% w/w). A much broader shoulder extending over ca. 60 °C ( − 10 °C to 50 °C) was recorded for PEG400-PVA systems with in excess of 20 w/w plasticizer. The presence of these shoulders indicates the presence of incompatibility in both systems at high PEG400 contents and is consistent with observations with a range of plasticizers/diluents in cellulose ethers and esters and PVA [7, 8].

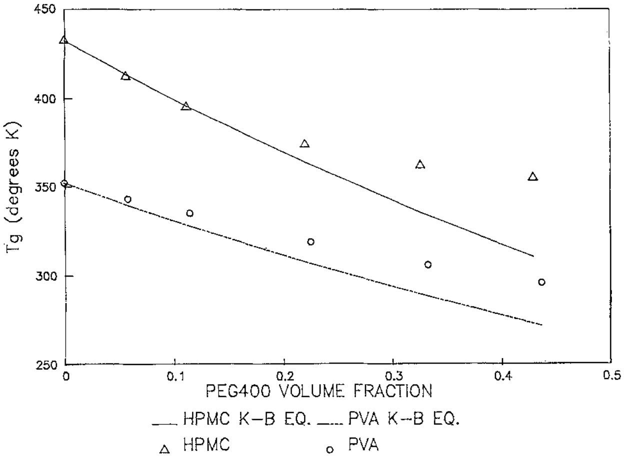

Fig. 1. Effect of PEG400 concentration on the *Tg* of HPMC (△) and PVA (○) homopolymers. The lines represent the predictions from the Kelley–Bueche (Eq. (1))

### *Plasticization of blends*

Addition of PEG400 in blends of PVA/HPMC did not affect the incompatibility of the two polymers and their almost total segregation into two phases (Figs. 2–6). In general, the dynamic mechanical spectra of the plasticized blends showed typical two-phase behaviour with two $\alpha$ relaxations in the logarithmic decrement and relative rigidity curves (Fig. 3) at temperatures corresponding to the *Tg*'s of the two homopolymers. In the case of 40:60 w/w PVA/HPMC blend with 40% w/w PEG400, only one *Tg* was recorded in the logarithmic decrement curve with a corresponding broad transition in the relative rigidity. This is likely to be due to the significant shift of

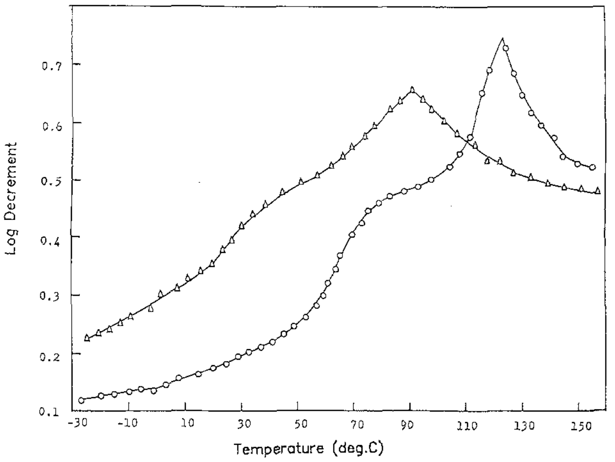

Fig. 2a. Dynamic mechanical spectra for 20:80 w/w PVA:HPMC blends with 10% (○) and 30% (△) w/w PEG400

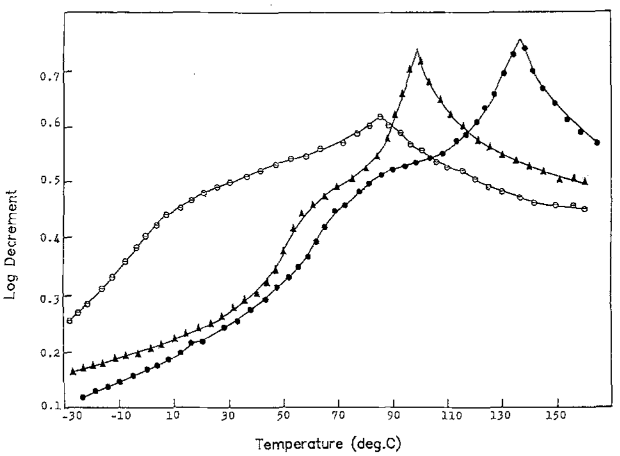

Fig. 2b. Dynamic mechanical spectra for 20:80 w/w PVA:HPMC blends with 5% (●), 20% (▲) and 40% (⊖) w/w PEG400

the $Tg$ of HPMC towards that of PVA, rather than the presence of a homogeneous system. The $Tg$ of the two phases followed the expected behaviour, decreasing with increasing PEG400 concentration (Figs. 7 and 8). The shoulder in the logarithmic decrement curve at temperatures below the $Tg$ of the PVA-rich phase was also observed for the PVA/HPMC blends, particularly those with high PVA ($\geq 60\%$ w/w) content.

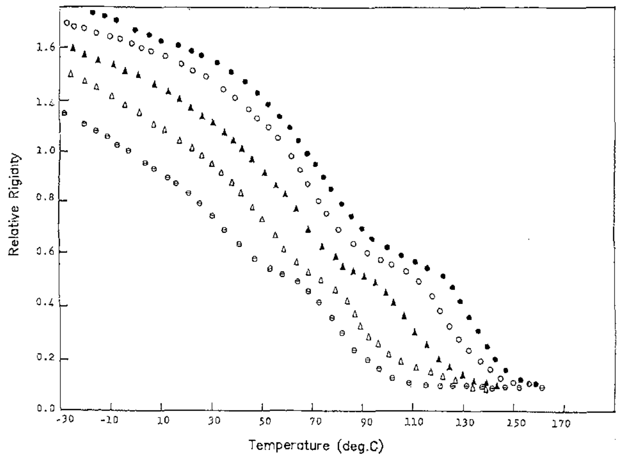

Fig. 3. Typical relative rigidity curves for the systems of Figs. 2a and 2b

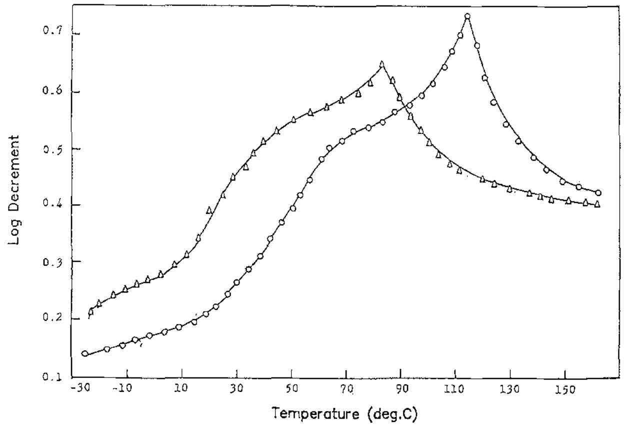

Fig. 4a. Dynamic mechanical spectra for 40:60 w/w PVA:HPMC blends with 10% (○) and 30% (△) w/w PEG400

### *Kelley–Bueche prediction and polymer-plasticizer compatibility*

The glass transition temperature of the plasticized polymers ($Tg$) can be predicted from the glass transition temperatures of polymer ($Tg2$) and plasticizer ($Tg1$) using an expression derived by Kelley and Bueche [9]:

$$Tg = \frac{\alpha_1 \Phi_1 Tg1 + \alpha_2 \Phi_2 Tg2}{\alpha_1 \Phi_1 + \alpha_2 \Phi_2}, \tag{1}$$

where $\alpha$ is the thermal expansion coefficient and $\Phi$ is the volume fraction; subscripts 1 and 2

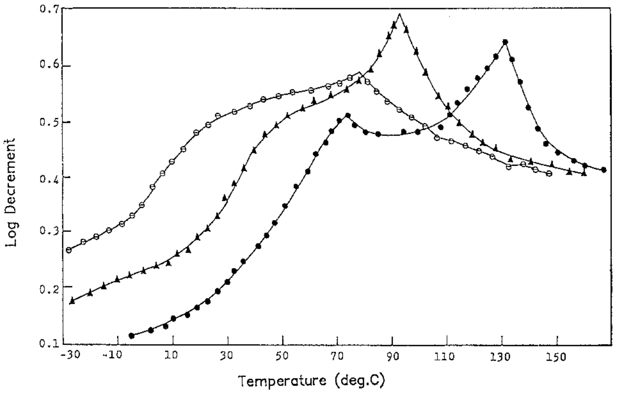

Fig. 4b. Dynamic mechanical spectra for 40:60 w/w PVA:HPMC blends with 5% (●), 20% (▲) and 40% (⊖) w/w PEG400

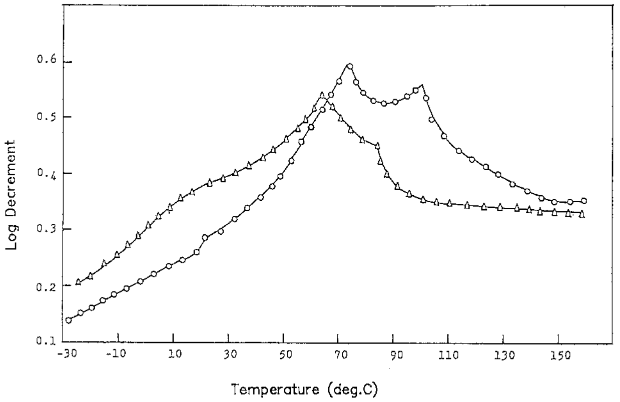

Fig. 5a. Dynamic mechanical spectra for 60:40 w/w PVA:HPMC blends with 10% (○) and 30% (△) w/w PEG400

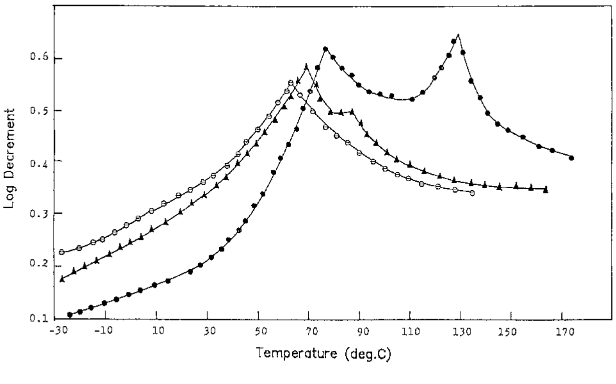

Fig. 5b. Dynamic mechanical spectra for 60:40 w/w PVA:HPMC blends with 5% (●), 20% (▲) and 40% (⊖) w/w PEG400

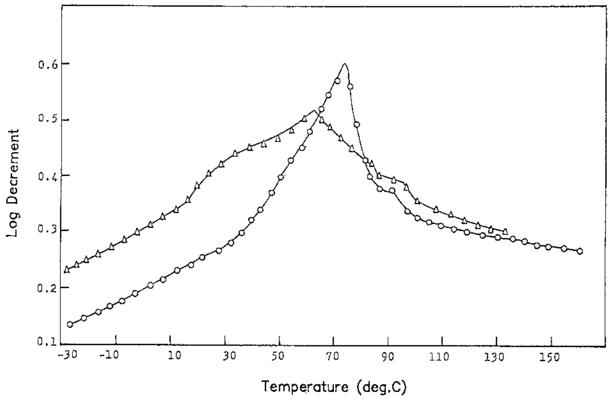

Fig. 6a. Dynamic mechanical spectra for 80:20 w/w PVA:HPMC blends with 10% (○) and 30% (△) w/w PEG400

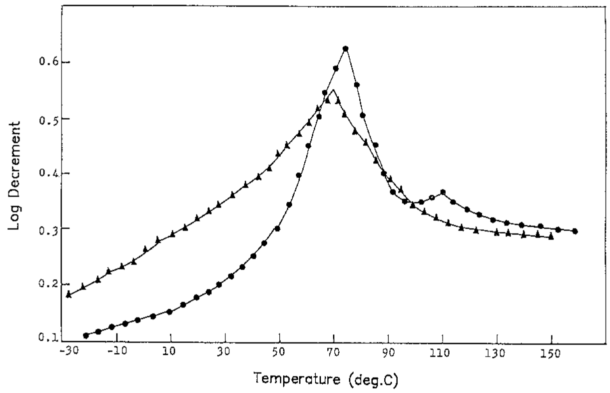

Fig. 6b. Dynamic mechanical spectra for 80:20 w/w PVA:HPMC blends with 5% (●) and 20% (▲) w/w PEG400

correspond to PEG400 and polymer, respectively. Table 1 summarises the values of all the parameters used in our calculations [10].

The experimental behaviour of HPMC deviated from the predicted $Tg$ values at PEG400 contents exceeding ca. 15% (Fig. 1). This is consistent with earlier observations with cellulose ethers and esters and phthalates and glycols [7, 8]. It is, however, worth noting that a satisfactory data fit was obatained up to that limit. No significant improvement in the data fit was obtained by adjusting the value of $Tg1$. In the case of PVA, the fit of the Kelley–Bueche predictions was poor, indicating reduced platicizing efficiency and interactions of PEG400 with this polymer. An improved

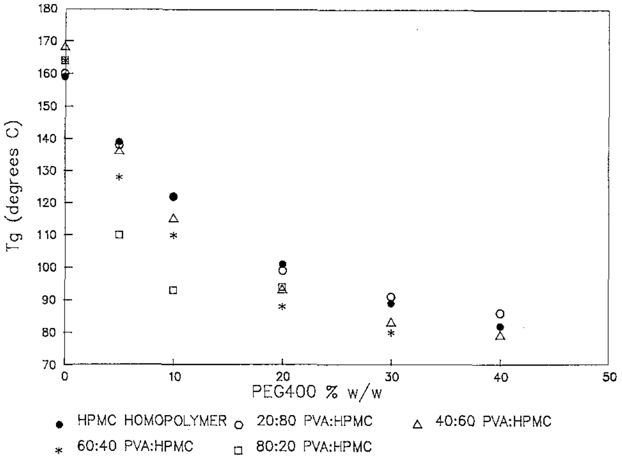

Fig. 7. Variation of the *Tg* of the HPMC-rich phases with increasing PEG400 bulk concentration. HPMC homopolymer (●); (○) 20:80 PVA:HPMC; (△) 40:60; (*) 60:40; (□) 80:20

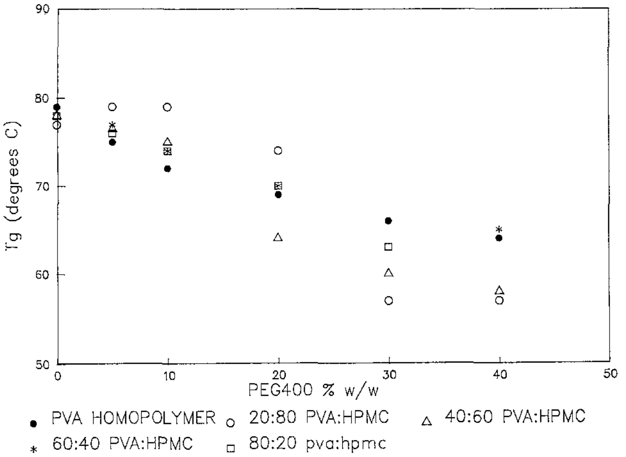

Fig. 8. Variation of the *Tg* of the PVA-rich phases with increasing PEG400 bulk concentration. PVA homopolymer (●); (○) 20:80 PVA:HPMC; (△) 40:60; (*) 60:40; (□) 80:20

data fit was obtained by adjusting the *Tg* of PEG400 to an apparent value of 320 °K.

The efficiency of the plasticizer with the two polymer systems was evaluated by the approach proposed earlier [3] and based on the plasticizer efficiency parameter, *E*, defined by the following equation:

$$\Delta Tg = E\alpha_1 \Phi_1 (Tg1 - Tg2) \,. \tag{2}$$

Table 1. Parameters used for the Kelley–Bueche calculations

| Component | $\alpha \times 10^4$ (°K$^{-1}$) | *Tg* (°K) | $d_{20}$ (g cm$^{-3}$) |
|---|---|---|---|
| HPMC | 4.8 | 432 | 1.26 |
| PVA | 4.8 | 352 | 1.30 |
| PEG400 | 7.3 | 204 | 1.12 |

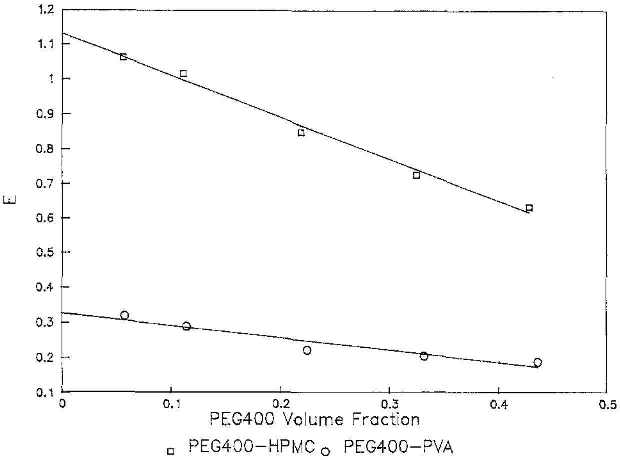

Fig. 9. Variation of plasticizer efficiency parameter *E* with PEG400 concentration for PEG400-HPMC (□) and PEG400-PVA (○)

It is clear from Fig. 9 that PEG400 is a more efficient plasticizer for HPMC than PVA, in agreement with the prediction based on the solubility parameters (Table 2). The affinity of PEG400 for the two polymers can be expressed in terms of the Flory–Huggins interaction parameter, $\chi$, using the following equation [11–13]:

$$\chi = \frac{V(\delta_2 - \delta_1)^2}{RT} \,, \tag{3}$$

where $V$ is the molar volume of the polymer segment, $T$ is the absolute temperature and $R$ the gas constant. Values of $\chi$ of 1.133 and 0.02 were calculated from Eq. (3) for PVA and HPMC respectively, confirming the increased affinity of PEG400 for the latter polymer. Inspection of Table 2 reveals that the relative matching of the propensity for polar and hydrogen bonding interactions between HPMC and PEG400 are responsible for the increased affinity.

Table 2. Solubility parameters of PVA, HPMC and PEG400

| | MPa$^{1/2}$ | | | |
|---|---|---|---|---|
| Component | $\delta_t$ | $\delta_d$ | $\delta_p$ | $\delta_h$ |
| PVA | 32.7 | 16.4 | 14.7 | 24.2 |
| HPMC | 22.8 | 14.4 | 5.8 | 16.7 |
| PEG400 | 21.3 | 16.5 | 3.5 | 13.0 |

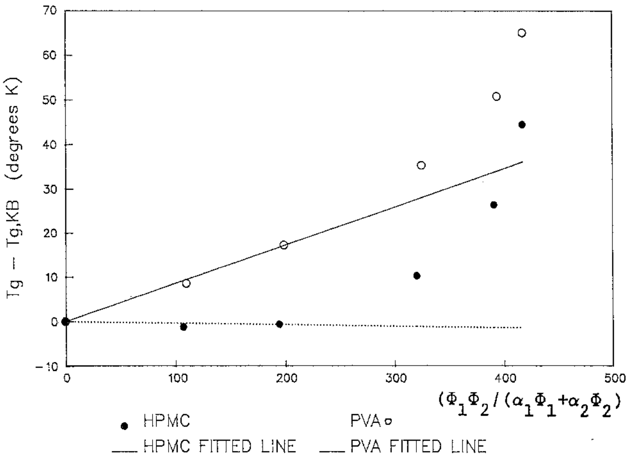

Fig. 10. Plot of $(Tg\text{–}Tg^{\mathrm{KB}})$ as a function of $\Phi_1\Phi_2/(\alpha_1\Phi_1 + \alpha_2\Phi_2)$ according to Eq. (7). (●) PEG400/HPMC; (○) PEG400/PVA; (– – –) PEG400/HPMC fitted line; (——) PEG400/PVA fitted line

Rearrangement of Eq. (1) to take into account fractional free volume non-linear additivity contributions [14] yields a modified Kelley–Bueche equation:

$$Tg = \frac{\alpha_1\Phi_1 Tg1 + \alpha_2\Phi_2 Tg2}{\alpha_1\Phi_1 + \alpha_2\Phi_2} - K_\Phi \frac{\Phi_1\Phi_2}{\alpha_1\Phi_1 + \alpha_2\Phi_2} . \tag{3}$$

The interaction parameter $K_\Phi$ encompasses all polymer-plasticizer interactions resulting in free volume changes in the blend above the linear additivity. The first term of the right-hand side expression of Eq. (7) corresponds to the original Kelley–Bueche prediction, $Tg^{\mathrm{KB}}$ (cf. Eq. (1)). A plot of $(Tg - Tg^{\mathrm{KB}})$ against $\Phi_1\Phi_2/(\alpha_1\Phi_1 + \alpha_2\Phi_2)$ should be a straight line with $-K_\Phi$ as the slope. In the case of HPMC (Fig. 4), the predicted values were lower than the experimental ones, the deviation increasing rapidly at concentrations in excess of 10% w/w. The initial slope gave a value of 0.005 for $K_\Phi$ for this system. In the case of PVA (Fig. 4), the predicted values were consistently lower than the experimental ones, giving rise to a $K_\Phi$ of $-0.085$. The data corroborate an earlier proposition that the deviation of the plots of Fig. 9 from the linear behaviour reflects dependence of the interaction parameter $K_\Phi$ on the plasticizer concentration. This would be consistent with changes in the compatibility between polymer and plasticizer with increasing plasticizer concentration, which has been shown to affect the plasticizing efficiency [15]. In agreement with the data from the systems with glycerol and DEG, the absolute value of $K_\Phi$ was smaller for the polymer-plasticizer pair with the higher affinity. This would suggest that increased polymer-plasticizer interactions facilitate a more efficient creation of free volume.

### *PEG400 partition into the two bend phases*

The volume fraction of plasticizer, $\Phi_1$, responsible for the drop of the original glass transition temperature of the polymer, $Tg2$, to a value of $Tg$, is given by:

$$\Phi_1 = \frac{\alpha_2(Tg2 - Tg)}{\alpha_2(Tg2 - Tg) + \alpha_1(Tg2 - Tg1)} . \tag{8}$$

The value of the $Tg1$ used was the apparent one calculated by fitting Eq. (1) to the experimental data in the case of PVA. In the case of HPMC, the fit of Eq. (1) was poor at PEG concentration greater than 10% w/w irrespective of the $Tg1$ value used. For this reason, we fitted the experimental data to a quadratic equation by means of linear least squares:

$$Tg(K) = 411.775\,\Phi_1^2 - 351.023\,\Phi_1 + 430.950 . \tag{9}$$

The experimental values of the glass transition of the PVA- and HPMC-rich phases ($T_g$) were used in Eqs. (8) and (9). The analysis is simplified by the strong incompatibility of the PVA/HPMC [4] and, hence, the negligible variation in the $Tg$

Table 3. Partition coefficients, *L*, of PEG400 inHPMC and PVA phases with PEG400 weight fraction and PVA/HPMC blend composition

| *L* | PVA weight fraction | | | |
|---|---|---|---|---|
| PEG400 weight fraction | 0.20 | 0.40 | 0.60 | 0.80 |
| 0.05 | ∞ | 2.08 | 1.29 | 1.23 |
| 0.10 | ∞ | 2.25 | 1.07 | 1.33 |
| 0.20 | 3.38 | 0.77 | 1.42 | 1.57 |
| 0.30 | 0.51 | 0.89 | — | — |
| Theoretical | 4.13 | 1.55 | 0.69 | 0.26 |

of the two phases due to polymer-polymer interactions. The volume fraction of the plasticizer in the two phases corresponds to the amount of PEG400 mixed on a molecular level with the polymers. We define partition coefficient, *L*, as the ratio of the volume fraction of PEG400 in the HPMC phase, $\Phi_1^{\mathrm{HPMC\ PHASE}}$, over that in the PVA phase, $\Phi_1^{\mathrm{PVA\ PHASE}}$.

$$L = \frac{\Phi_1^{\mathrm{HPMC\ PHASE}}}{\Phi_1^{\mathrm{PVA\ PHASE}}} \qquad (10)$$

Values of the calculated partition coefficients and the theoretical values are summarised in Table 3. The theoretical *L* values are those of the partition coefficients determined from the blend composition and assuming no selectivity. These were calculated from the ratio of the volume fraction of the two polymers in the blends for the varying blend composition. The partition of PEG400 in the two phase HPMC/PVA system was not random. Blends with 60% and 80% w/w PVA showed a highly selective partitioning of PEG400 into the HPMC-rich inclusions over all the PEG400 concentration range (5 to 40% w/w). The same behaviour was observed for blends with 20% and 40% w/w PVA, but only for the low PEG400 concentration range from 5% to 10% w/w, with selective partitioning of PEG into the HPMC-rich matrix rather than the PVA-rich inclusions. As the plasticizer content exceeded 10% w/w, PEG400 started partitioning increasingly and selectively into the PVA-rich phase (Table 2).

## Conclusions

TBA analysis showed that PEG400 is a more efficient plasticizer for HPMC than PVA, in agreement with the Hansen solubility parameter prediction. Treatment of the experimental *Tg* data with a modified Kelley–Bueche expression yielded values for the interaction parameters $K_\Phi$ for the two systems. The negligible value for $K_\Phi$ of PEG400/HPMC confirmed the presence of interactions between the polymer and PEG400 which facilitated a comparatively more efficient creation of free volume. The incompatibility between PVA and HPMC did not alter with addition of PEG400 over all the blend composition range. The partition coefficients, *L*, for the two systems at varying PEG400 concentrations were calculated from the experimental *Tg* data of the two homopolymers and their blends. PEG400 partitioned selectively into the HPMC-rich phase of the blends for low plasticizer concentrations ($\leq$ 10% w/w). At higher concentrations ($>$ 10% w/w) the trend persisted for the blends with the PVA as the matrix (60 and 80% PVA). On phase inversion, PEG400 partitioned increasingly and selectively into the PVA-rich phase.

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