Colloid & Polymer Science Colloid Polym Sci 272:48–56 (1994)

Interactions and partitioning of diluents/plasticizers in hydroxypropyl methylcellulose and polyvinyl alcohol homopolymers and blends. Part II: Glycerol

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Abstract: The interactions and partitioning of glycerol in polyvinyl alcohol (PVA), hydroxypropyl methylcellulose (HPMC) and their blends has been studied by means of torsional braid analysis (TBA). Glycerol was shown to be a more efficient plasticizer for PVA than HPMC in agreement with solubility parameter prediction. Kelley–Bueche-type equations were fitted to the experimental *Tg* data and initial slopes yielded an interaction parameter, K_{Φ}, between glycerol and the two polymers. Incorporation of glycerol in PVA/HPMC blends did not alter the incompatibility of the two polymers and plasticized both phases. The compositions of the two plasticized phases were calculated from Kelley–Bueche expressions fitted to the experimental data, enabling determination of the glycerol partition coefficients into the two phases. In blends with 20–60% PVA, glycerol partitioned selectively into the PVA-rich phase whereas in the system with 80% PVA, glycerol partitioned selectively into the HPMC-rich inclusions.

Key words: Aqueous – polyvinyl alcohol – hydroxypropyl methylcellulose – interactions – plasticizer – partitioning – solubility – glycerol

Introduction

Hydroxyprolyl methylcellulose (HPMC) and polyvinyl alcohol (PVA) are water soluble polymers used for tablet coating [1, 2]. Plasticizers are often added to depress the *Tg* and the modulus of the polymers eliminating the development of internal stresses which are responsible for coating cracking and bridging of the intagliations [1]. We have already reported on the plasticization of a range of cellulose ethers and esters by phthalates and polyethylene glycols [3, 4, 5]. The capability of the different plasticizers to depress the *Tg* and modulus of these polymers was closely linked to their compatibility with the polymer. Phase separaton of the plasticizer in the polymer matrix occurred above a critical plasticizer concentration. The compatibility limit and the plasticizing efficiency of phthalates and glycols were rationalised in terms of the interactions between plasticizer and polymer including hydrogen bonding and polar interactions.

This paper deals with the plasticization and interactions of glycerol with HPMC and PVA homopolymers and their blends. Blends of PVA and HPMC have been shown to be incompatible due to significant discrepancies in the polar and hydrogen bonding characteristics of the two polymers [6]. Addition of glycerol into these heterogeneous systems can give rise to partitioning of glycerol into one or both phases depending on its interactions with the two polymers. It has been reported that diethylene glycol, an efficient plasticizer for both PVA and HPMC, partitioned preferentially to the PVA-rich phase with the exception of the system with 50:50 w/w

PVA/HPMC which showed no selective partitioning [5]. In contrast to the diethylene glycol, glycerol is a better plasticizer for PVA than for HPMC.

Experimental

Materials

Poly(vinyl alcohol), PVA POVAL 205, was supplied by Kuraray Co., Japan, with $\bar{M}n$ of 73.9 kg mol^{-1} and polydispersity of 1.7. It was 88% hydrolysed with a viscosity of 3.4 mPas in 4% aqueous solutions at 20 °C. Hydroxypropyl methylcellulose, HPMC Pharmacoat 606, was supplied by Shin Etsu Chemical Co., Japan, with molecular weight of 60.1 kg mol^{-1} and polydispersity of 2.2. Both polymers were used as received. Reported molecular weights were determined by size exclusion chromatograpy (GPC) with tetrahydrofuran as the carrier solvent and polystyrene standards calibration. Distilled water was used as solvent. Dissolution of PVA required slight heating at 60 °C and stirring. Glycerol was supplied by BDH and was used without any further purification.

Methods

The dynamic mechanical behaviour of homopolymers and blends was studied by means of a torsional braid analyser (TBA). TBA is a sensitive torsional pendulum with the polymer supported on a glass braid. The instrument monitors the response of the composite specimen to a small sinusoidal stress (ca. 1 Hz) as a function of temperature. The instrument has been described in detail in an earlier report [7]. Glass braids consisted of two glass yarns doubled to produce about 2.5 turns per inch were impregnated with polymer by immersion in 10% w/v aqueous polymer solutions for at least 2 h. Excess polymer solution was removed before air oven drying at room temperature followed by vacuum drying at 50 °C overnight. Samples were stored over dried silica gel unitl tested. The data are reported in terms of the logarithmic decrement and the relative rigidity as a function of temperature [7]. The *Tg* values quoted correspond to the temperature of the maximum logarithmic decrement.

Results and discussion

Plasticization of homopolymers

We have already reported the effect of glycerol on the dynamic mechanical spectra of HPMC and PVA [8]. Figure 1 summarizes the variation of the *Tg* for both systems. The *Tg* and the modulus of both polymers decreased with increasing glycerol concentration. At higher glycerol contents (30 and 40% w/w) a plateau at around 40° to 80 °C appeared for the HPMC systems, attributed to the melting of glycerol-rich phases separating out (*Tm* = 20 °C). A similar plateau appeared at ca. 0 °C for PVA but only at 40% glycerol.

Plasticization of blends

Incorporation of glycerol in the PVA/HPMC blends did not affect the compatibility of the two components. The dynamic mechanical spectra showed a typical two-phase behaviour with two α relaxations observed in the logarithmic decrement and relative rigidity curves (Figs. 2–6). Samples with low PVA weight fractions (0.2 to 0.4) showed a broad *Tg* or shoulder instead of a well defined peak for the PVA-rich phase. The two-phase nature of these mixtures is, however, corroborated by two clear inflections in the relative rigidity of these samples (Fig. 3). The *Tg* of the two phases followed the expected behaviour, decreasing with increasing glycerol concentration (Figs. 7 and 8). It is interesting to note that, in the case of

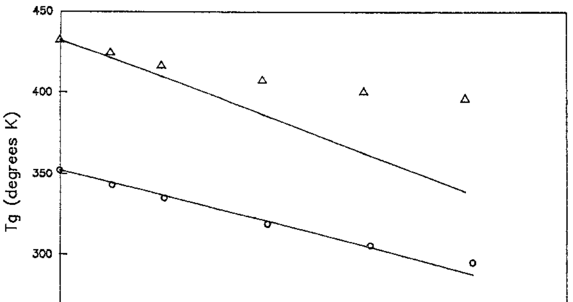

Fig. 1. Effect of glycerol concentration on the *Tg* of HPMC (Δ) and PVA (○) homopolymers. The continuous lines represent the predictions from the Kelley–Bueche (Eq. (1))

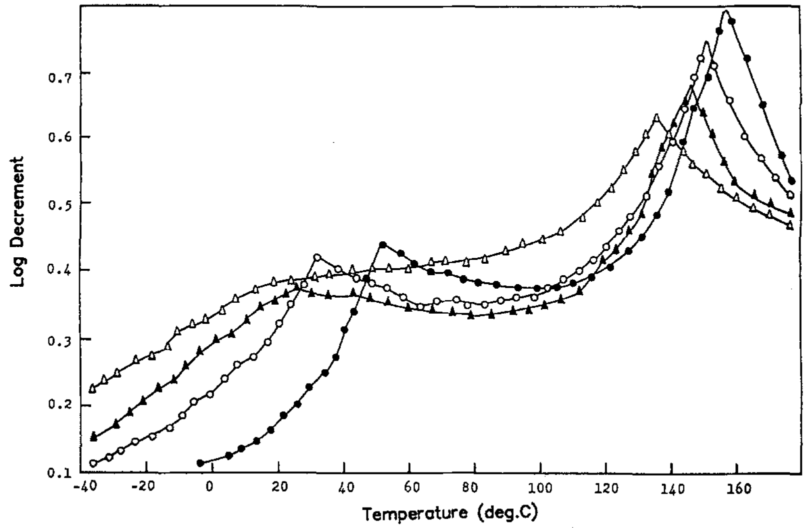

Fig. 2. Dynamic mechanical spectra for 20:80 w/w PVA:HPMC blends with 5% (●), 10% (○), 20% (▲) and 30% (△) w/w glycerol

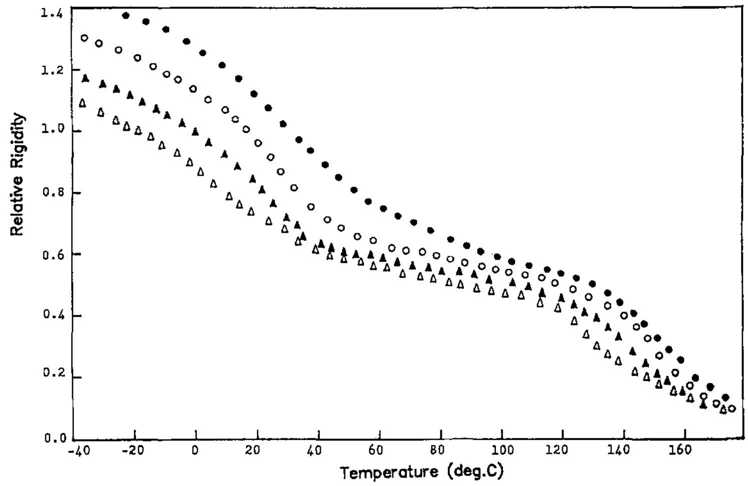

Fig. 3. Typical relative rigidity curves for the systems of Fig. 2

the HPMC-rich phase, the *Tg* of the plasticized phase was consistently greater than that of the corresponding homopolymer (Fig. 7). That was not the case for the plasticized PVA-rich phases as seen in Fig. 8.

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 the polymer (*Tg*2) and plasticizer (*Tg*1) using the Kelley-Bueche equation [9]:

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

where α is the thermal expansion coefficient and Φ is the volume fraction. Subscripts 1 and 2 correspond to glycerol and polymer respectively. Table 1 summarizes all the parameters used in our calculations [10].

The experimental behaviour of HPMC deviated from the predicted *Tg* values at glycerol contents exceeding ca. 15% (Fig. 7). This is consistent with earlier observations with a range of cellulose ethers and esters and a series of plasticizers [3, 4]. An improved data fit was obtained

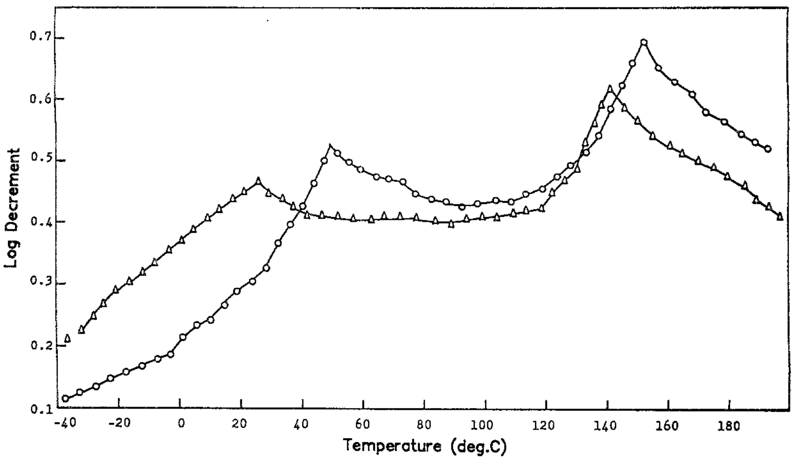

Fig. 4a. Dynamic mechanical spectra for 40:60 w/w PVA:HPMC blends with 10% (○) and 30% (△) w/w glycerol

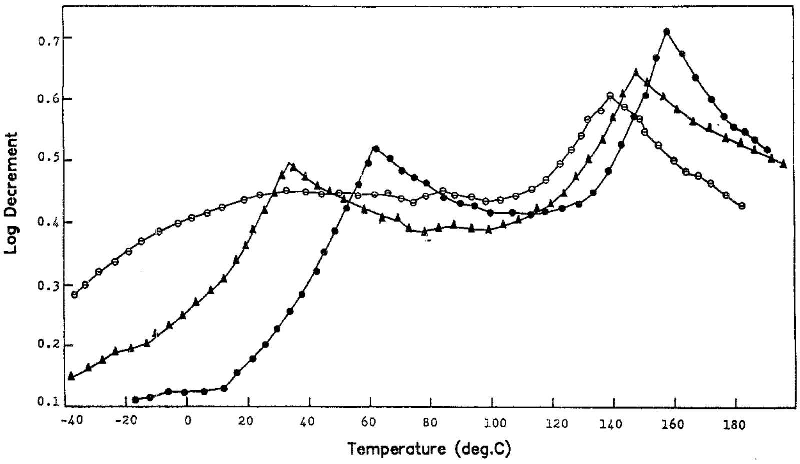

Fig. 4b. Dynamic mechanical spectra for 40:60 w/w PVA:HPMC blends with 5% (●), 20% (▲) and 40% (∅) w/w glycerol

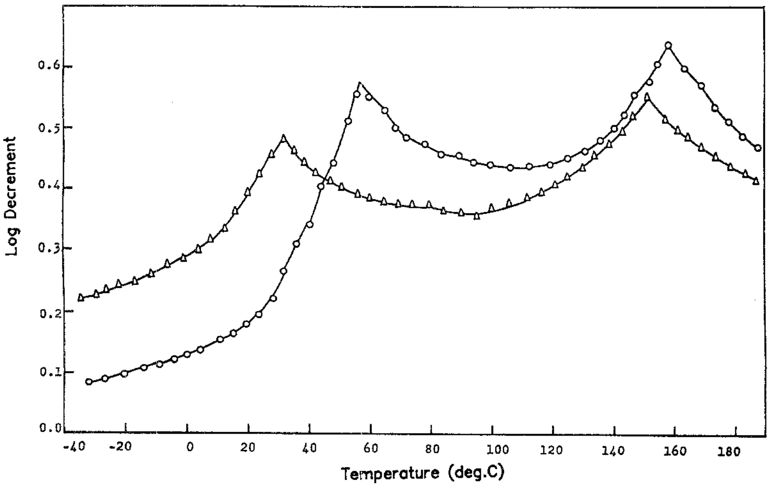

Fig. 5a. Dynamic mechanical spectra for 60:40 w/w PVA:HPMC blends with 10% (○) and 30% (△) w/w glycerol

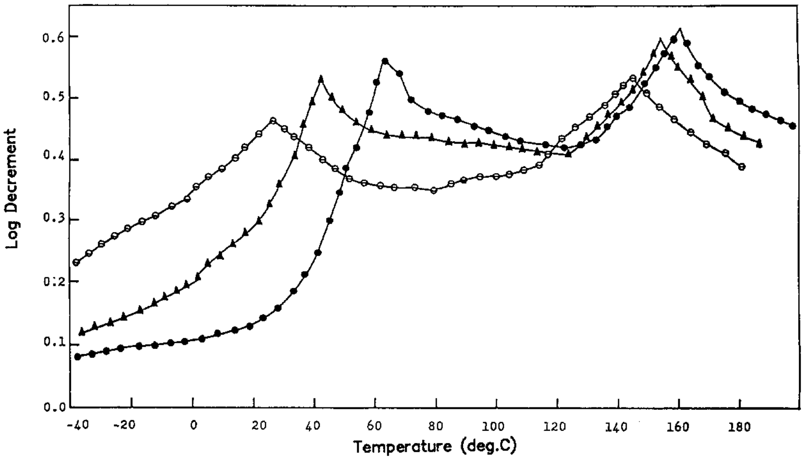

Fig. 5b. Dynamic mechanical spectra for 60:40 w/w PVA:HPMC blends with 5% (●), 20% (▲) and 40% (∅) w/w glycerol

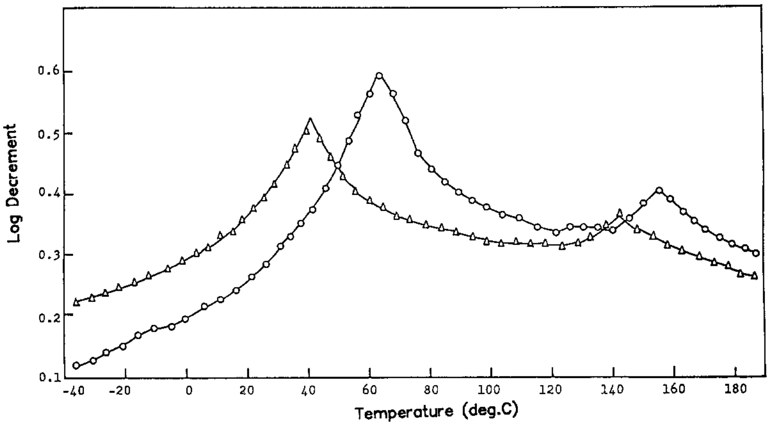

Fig. 6a. Dynamic mechanical spectra for 80:20 w/w PVA:HPMC blends with 10% (○) and 30% (△) w/w glycerol

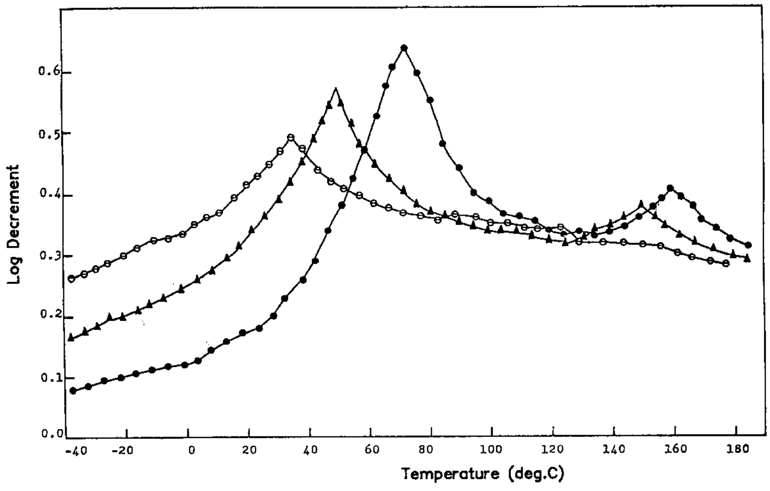

Fig. 6b. Dynamic mechanical spectra for 80:20 w/w PVA:HPMC blends with 5% (●), 20% (▲) and 40% (∅) w/w glycerol

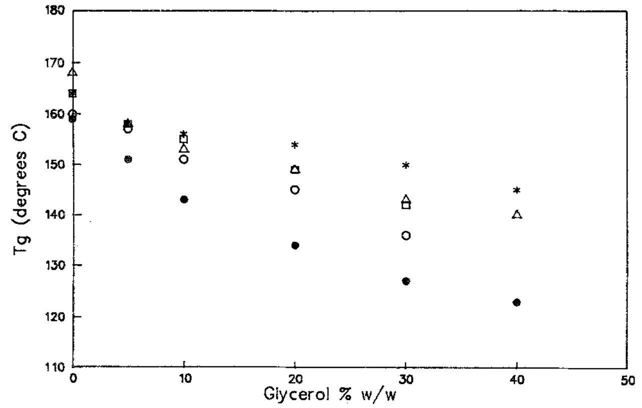

Fig. 7. Variation of the *Tg* of the HPMC-rich phases with increasing glycerol bulk concentration. HPMC homopolymer (●); (○) 20:80 PVA:HPMC; (△) 40:60; ( ) 60:40; (□) 80:20

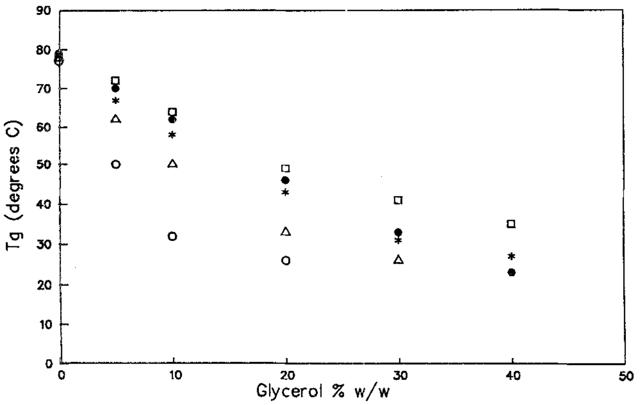

Fig. 8. Variation of the *Tg* of the PVA-rich phases with increasing glycerol bulk concentration. PVA homopolymer (●); (○) 20:80 PVA:HPMC; (△) 40:80; (*) 60:40; (□) 80:20

Table 1. Parameters used for the Kelley–Bueche calculations

Component	$\alpha \times 10^4$ (cm^{-1})	Tg(°K)	d_{20}(g cm^{-3})
HPMC	4.8	432	1.26
PVA	4.8	352	1.30
Glycerol	4.4	188	1.261

by adjusting the *Tg* of the glycerol from its experimental value of 188 °K to an apparent value of 300 °K. In the case of PVA, the fit of the Kelley–Bueche predictions was satisfactory up to high glycerol concentration ($\leq$ 30% w/w) (Fig. 1). This is consistent with an increased plasticizing efficiency of glycerol with this polymer and is perhaps an indication of its greater affinity and compatibility for PVA. Again, a more satisfactory fit was obtained by adjusting the *Tg* of glycerol to an apparent value of 210 °K.

The plasticizing effectiveness of glycerol, PE, with PVA and HPMC is conventionally calculated from the extent of depression of the polymer from its original value, Tg^0, to a value of *Tg* divided by the volume fraction of plasticizer responsible for this depression, Φ_1 [11]:

$$\mathrm{PE} = \frac{Tg^0 - Tg}{\Phi_1}\,. \tag{2}$$

We believe that this approach does not take into account the discrepancy in the properties of the polymer-plasticizer pair such as *Tg* and α. A more accurate picture can be obtained from the deviation of the actual *Tg* from the expected one. By rearranging Eq. (1), we obtain

$$\Delta Tg = Tg - Tg2 = \alpha_1 \Phi_1 (Tg1 - Tg2)\,. \tag{3}$$

This value would represent the *Tg* depression of the polymer by a fully efficient plasticizer. Deviations from this value would represent a reduction in the plasticizing efficiency. This can be accounted for by introducing a plasticizer efficiency parameter, *E*, in the above equation 3:

$$\Delta Tg = E \alpha_1 \Phi_1 (Tg1 - Tg2)\,. \tag{4}$$

The theoretical maximum of *E* is 1. Figure 9 shows the variation of parameter *E* with increasing glycerol concentration for glycerol-PVA and glycerol-HPMC systems. It is clear that glycerol is a more efficient plasticizer for PVA than HPMC. This is consistent with the prediction based on the solubility parameters (Table 2). The affinity of glycerol for the two polymers can be expressed in terms of the Flory–Huggins interaction parameter, χ, using the following equation [12, 13, 16]:

$$\chi = \frac{V(\delta_2 - \delta_1)^2}{RT}\,, \tag{5}$$

where *V* is the molar volume of the polymer segment, *T* is absolute temperature and *R* the gas constant. Values of χ of 0.5 and 1.6 were calculated from Eq. (5) for PVA and HPMC respectively, confirming the increased affinity of glycerol for the former polymer. Inspection of Table 2

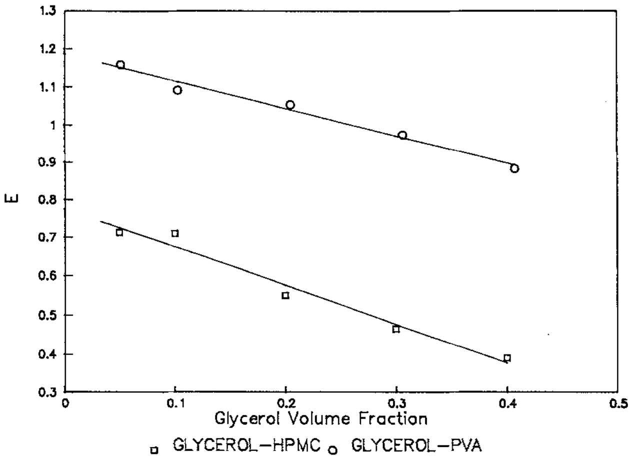

Fig. 9. Variation of parameter E with glycerol concentration for glycerol-HPMC (□) and glycerol-PVA (○)

Table 2. Solubility parameters of PVA, HPMC and glycerol

	MPa$^{1/2}$			
Component	δ_t	δ_d	δ_p	δ_h
PVA	32.7	16.4	14.7	24.2
HPMC	22.8	14.4	5.8	16.7
Glycerol	29.1	17.1	11.8	28.6

reveals that the relative matching of the propensity for polar and hydrogen bonding interactions between PVA and glycerol are responsible for the increased affinity.

Braun and Kovacs [15] have argued that the deviations of the experimental data from Eq. (1) arise from the basic assumption of the Kelley–Bueche approach of the additivity of the fractional free volume of the two components of the system, f_1 and f_2. They suggested that the total free volume (f) includes a non-linear term:

$$f = \Phi_1 f_1 + \Phi_2 f_2 + K_\Phi \Phi_1 \Phi_2 \,. \tag{6}$$

The constant K_Φ was defined as an interaction parameter encompassing all polymer-plasticizer interactions resulting in free volume changes in the blend above the linear additivity. Rearranging Eq. (1) to take into account these contributions, we obtain a modified Kelley-Bueche equation:

$$Tg = \frac{\alpha_1 \Phi_1 Tg1 + \alpha_2 \Phi_2 Tg2}{\alpha_1 \Phi_1 + \alpha_2 \Phi_2} - K_\Phi \frac{\Phi_1 \Phi_2}{\alpha_1 \Phi_1 + \alpha_2 \Phi_2} \,. \tag{7}$$

The first term of the right-hand side expression of Eq. (7) corresponds to the original Kelley–Bueche prediction, Tg^{KB} (cf. Eq. (1)). A plot of $(Tg - Tg^{KB})$ against $\Phi_1\Phi_2/(\alpha_1\Phi_1 + \alpha_2\Phi_2)$ should be a straight line with $-K_\Phi$ as the slope. Figure 10 shows the relevant plots for glycerol-HPMC and glycerol-PVA systems. In the case of HPMC, the predicted values were lower than the experimental ones, the deviation increasing rapidly at glycerol concentrations in excess of 10% w/w. The initial slope was calculated to be 0.035 with a correlation coefficient of $R^2 = 0.999$. In the case of PVA the predicted values were slightly lower or equal to the predicted ones, giving rise to a very small and negative slope of 0.008 with a correlation coefficient of $R^2 = 0.848$. We have argued in an earlier publication that the deviation of the plots of Fig. 9 from the linear behaviour reflects dependence of the interaction parameter K_Φ on the glycerol 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 [16]. It is interesting to note that increased free volume was calculated for the glycerol-PVA compared to the glycerol-HPMC. Again this is consistent with earlier findings for the systems diethylene glycol-PVA and diethylene

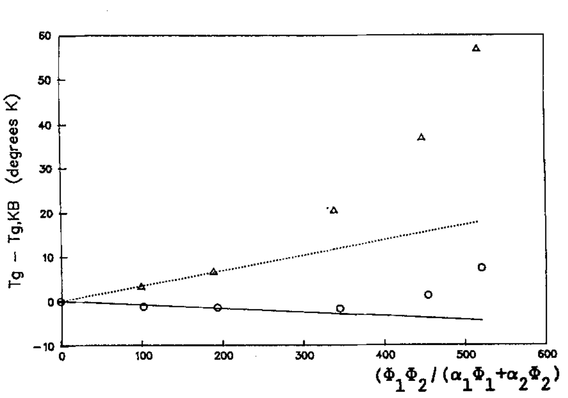

Fig. 10. Plot of $(Tg - Tg^{KB})$ as a function of $(\Phi_1\Phi_2/(\alpha_1\Phi_1 + \alpha_2\Phi_2))$ according to Eq. (7). (△) glycerol/HPMC; (○) glycerol/PVA; (···) glycerol/HPMC fitted line; (——) glycerol/PVA fitted line

glycol-HPMC which were attributed to the crystallinity of the PVA-rich phases compared to the amorphous nature of the HPMC ones [5].

Glycerol partition into the two blend phases

The volume fraction of plasticizer, Φ_1, responsible for the drop of the original glass transition temperature of the polymer, $Tg2$, to a value of Tg, can be calculated by rearranging the Kelley–Bueche expression (Eq. (1)):

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

The value of the $Tg1$ used was the apparent one calculated from fitting Eq. (1) to the experimental data; the experimental values were used for the glass transition of the PVA- and HPMC-rich phases (Tg). The analysis is simplified by the fact that the blend has been shown to be totally incompatible [6] and, therefore, no significant variation in the Tg of the two phases would be expected from polymer-polymer interactions. The volume fraction of the plasticizer in the two phases would correspond to the amount of glycerol mixed on a molecular level with the polymer. We can now define a partition coefficient, L, as the ratio of the volume fraction of glycerol in the HPMC phase, $\Phi_1^{\mathrm{HPMC\,PHASE}}$, over that in the PVA phase, $\Phi_1^{\mathrm{PVA\,PHASE}}$.

$$\mathrm{L} = \frac{\Phi_1^{\mathrm{HPMC\,PHASE}}}{\Phi_1^{\mathrm{PVA\,PHASE}}}\,. \tag{9}$$

Values of the calculated partition coefficients and the theoretical values are summarized in Table 3. The theoretical L values correspond to the value of the partition coefficient determined from the blend composition and assuming no selectivity. They were calculated from the ratio of the volume fraction of the two polymers in the blends with varying blend composition. The partition of glycerol in the two phase HPMC/PVA system was not random. Blends with 20% to 60% PVA showed selective partition of glycerol into the PVA-rich phase in agreement with its increased affinity for PVA. The extent of this selectivity appeared to decrease with increasing PVA content in the blend. In the system with PVA as the matrix the trend was reversed with glycerol partitioning selectively into the HPMC-rich dispersed phases. The causes of this behaviour cannot be ascertained at present, although we could speculate that it is related to the crystalline nature of PVA and glycerol. Increasing glycerol content in the blends appeared to have an effect on its partitioning behaviour, with the partition coefficient moving in all cases towards its theoretical value. This is consistent with the presence of a compatibility limit in the PVA-glycerol system.

Table 3. Partition coefficients, L, of glycerol in HPMC and PVA phases with glycerol weight fraction and PVA/HPMC blend composition

L	PVA weight fraction			
Glycerol weight fraction	0.20	0.40	0.60	0.80
0.05	0.12	0.63	0.52	1.03
0.10	0.22	0.54	0.40	0.66
0.20	0.32	0.43	0.31	0.54
0.3		0.49	0.31	0.62
Theoretical	4.13	1.55	0.69	0.26

Conclusion

The dynamic mechanical spectra suggest that glycerol is a better plasticizer for PVA than HPMC in terms of its capability to reduce their Tg and relative rigidity. A modified Kelley–Bueche equation led to calculation of an interaction parameter, K_Φ for the two systems, encompassing polymer-plasticizer interactions responsible for deviation of the total system free volume from linear additivity. In the case of HPMC, a negative K_Φ confirmed the presence of such interactions. A very small positive value was calculated for the glycerol-PVA system in agreement with results on similar systems and apparently inconsistent with the prediction form the solubility paramters. The crystallinity of the PVA phases leading to reduced free volume can perhaps resolve this apparent contradiction.

Incorporation of glycerol in PVA/HPMC blends did not alter the total segregation of the two polymers in two almost pure phases. Glycerol was shown to partition selectively into the PVA-rich phases in blends with 20% to 60% w/w PVA. The opposite was the case for the 80:20 w/w PVA/HPMC blend. The preferential partitioning of glycerol into one phase of the blend did not change with increasing glycerol concentration, although its extent decreased.

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Received January 14, 1993;
accepted February 2, 1993

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