Intermolecular hydrogen bonding in cellulose/poly(ethylene oxide) blends: thermodynamic examination using 2,3-di-*O*- and 6-*O*-methylcelluloses as cellulose model compounds

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This paper discusses the miscibility of cellulose/poly(ethylene oxide) (PEO) blend systems from the view point of the relationship between hydrogen bond formation and regiochemistry of hydroxyl groups in cellulose. Thermodynamic examination of the systems using 2,3-di-*O*- and 6-*O*-methylcelluloses (23MC and 6MC) as cellulose model compounds was carried out by differential scanning calorimetry. The values of two parameters, interaction energy density characteristic, B, and interaction parameter, χ_{12}, assessed by the thermodynamic analyses indicated evidence of polymer–polymer interaction in 23MC/PEO blends and lack of interaction between 6MC and PEO in their blends. Optical microscopic observation of the blend systems revealed the same phenomena. Results of the two investigations support our proposal of a regiochemical effect of hydroxyl groups in cellulose analysed by Fourier transform i.r. spectroscopy; that is, primary hydroxyl groups at the C6 position of the glucose unit of cellulose interact predominantly with ether oxygen in PEO, while secondary hydroxyls at the C2 and C3 positions are not engaged in hydrogen bonding. However, in pure cellulose/PEO blend each negative magnitude of the values was much larger than the sum of the values of each parameter for the 23MC/PEO and 6MC/PEO blends, indicating the presence of secondary polymer–polymer interaction.

(Keywords: blends; hydrogen bonding; thermal analysis)

INTRODUCTION

Cellulosic blends with synthetic polymers, such as polyacrylonitrile[1–3], poly(vinyl alcohol) (PVA)[4–6], poly(ε-caprolactone)[7,8], poly(ethylene oxide) (PEO)[9,10], poly(ethylene terephthalate)[11,12], poly(4-vinylpyridine)[13] and polyvinylpyrrolidone[14], have been studied extensively as biodegradable polymer blends. In these studies, the miscibility of the blends was examined by Fourier transform infra-red (*FT*i.r.) spectroscopy[1,8,11,12], differential scanning calorimetry (d.s.c.)[4,5,9,10], optical microscopy[3], wide-angle X-ray diffraction[1], dynamic mechanical measurements[1,2,4,7] and solid-state ^{13}C nuclear magnetic resonance (n.m.r.)[13–15]. The polymer–polymer interaction for the miscibility is thought to be due mainly to hydrogen bonding between three hydroxyl groups in the anhydroglucose unit of cellulose and the functional groups of the synthetic polymers. However, since each of the three hydroxyl groups in the repeating unit of the cellulose is quite different in terms of regiochemistry and polarity, the hydrogen bond formation is not easily clarified. Moreover, this difference is considered to be an important factor influencing the physical properties including solubility, crystallinity, reactivity, gelation and liquid crystallinity. Nevertheless, the difference in hydrogen bond formation depending on the regiochemistry has not been reported in relation to miscibility in cellulose blends.

Nishio *et al.* examined polymer–polymer interaction of the cellulose/PEO blend by d.s.c. in order to elucidate the miscibility[9] and the diluent effect of the cellulose component[10]. They investigated polymer–polymer interaction by observing the phase transition of the crystallized PEO component, but did not include the specific regiochemistry of hydroxyl groups in cellulose. Recently, we reported the formation of hydrogen bonds in cellulose/PEO and cellulose/PVA blends with *FT*i.r. in the light of the differences in regiochemistry and polarity of the OH groups in cellulose molecules[16]. The work was carried out using cellulose model compounds with regioselectively methyl-blocked hydroxyl groups (OH), 2,3-di-

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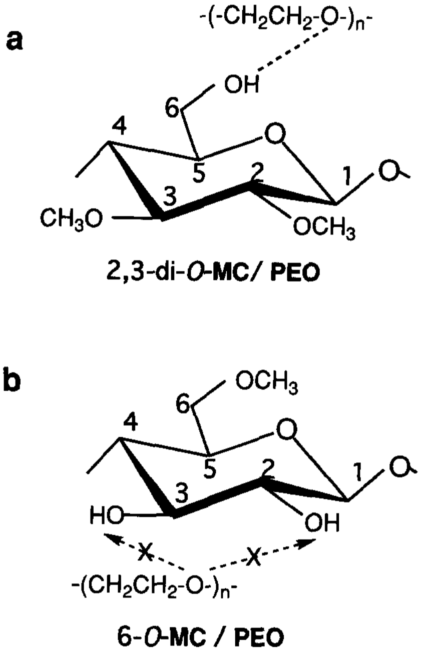

Figure 1 Proposed hydrogen bonding schemes for the 2,3-di-*O*-methylcellulose (a) and 6-*O*-methylcellulose (b) blended with PEO

O-methylcellulose (23MC)[17] and 6-*O*-methylcellulose (6MC)[18] (*Figure 1*). From the *FT*i.r. study of the MC/PEO blend samples, it was revealed that the hydrogen bond between the primary OH group at the C6 position of anhydroglucose unit and the ether oxygen in the PEO skeleton is more favourable than other hydrogen bonds formed in secondary OH groups at the C2 and C3 positions, as shown in *Figure 1*. In the present report we verify the regiochemical effect proposed in our previous paper[16], and elucidate the hydrogen bond formation in pure cellulose/PEO blends using d.s.c. and optical microscopy.

EXPERIMENTAL

Materials

Two cellulose model samples, 23MC and 6MC (*Figure 1*), were prepared by the methods reported previously[17,18]. Each polymer had a uniform structure and the weight average molecular weight of both samples was determined to be approximately 2×10^4 on the basis of their g.p.c. elution curves calibrated with polystyrene standards. Pure cellulose was a bleached sulfite pulp with a degree of polymerization of 935. PEO was a Carbowax poly(ethylene glycol) sample with a nominal molecular weight of 2×10^4, purchased from Fisher Scientific. *N,N*-dimethylacetamide (DMAc; h.p.l.c. grade, from Aldrich Chemical Co., Inc.) was used without further purification.

Sample preparation

DMAc was used as the common solvent for all samples except pure cellulose. Each homopolymer component was dissolved separately in DMAc; the concentration was 0.8 wt% for the MC samples and 2 wt% for PEO. All solutions were filtered and stored in a closed container.

The two solutions of the MC and PEO were mixed at room temperature in the appropriate proportions. The relative compositions of the two polymers in the mixed solutions were 80/20, 65/35, 50/50 and 30/70 (MC/PEO) by weight. After stirring for more than 3 days, blend films were prepared by casting from the mixed solution as follows: 1 g of each blended solution was poured into a flat-bottomed tray and then heated to 50°C in air for 3 days. The solvent was evaporated to yield an as-cast film. The film was further dried for 2 days under high vacuum at 50°C to completely remove residual DMAc, and stored in a desiccator. Pure cellulose film was prepared by casting of LiCl–DMAc cellulose solution[4], followed by subsequent washing and drying. The blended films were found to be predominantly amorphous when checked by wide-angle X-ray diffraction[16].

The densities of the three highly amorphous cellulosic homopolymer films, pure cellulose, 23MC and 6MC, were measured by pycnometry in a medium of *p*-xylene and carbon tetrachloride. The characterization data of the cellulosic homopolymer sample films are listed in *Table 1*.

Measurements

D.s.c. was performed on ~4.2 mg sample of PEO component in the blends by means of a Perkin–Elmer DSC-7 in a nitrogen atmosphere. The instrument was calibrated with an indium standard. The thermal properties of the samples were examined in the following way: the thermograms of the MC/PEO blended samples were obtained in the first heating, the second heating, and cooling scans at a rate of $10°\mathrm{C\,min^{-1}}$. The first heating scan was carried out in the temperature range of 20–95°C. After rapid cooling ($\sim 200°\mathrm{C\,min^{-1}}$), the second heating scan was made to obtain the melting point, T_m, in the same temperature range. This procedure was carried out for characterizing the samples melt-crystallized in the d.s.c. pan. The cooling scan was performed after the sample was kept at the terminal temperature in the second heating process for 5 min in the d.s.c. pan to select the range of the isothermal crystallization temperature for the following d.s.c. experiment in each blend sample. The T_m of each sample was determined from the maximum of the melting peak.

Determination of the equilibrium melting point, T_m^{eq}, was performed by d.s.c. measurement as follows: film specimens weighing 5–17 mg each were heated to 95°C in aluminium sample pans and maintained at this temperature for 7 min to eliminate PEO crystalline residues. The samples were quenched to the selected isothermal crystallization temperature, T_{ic}, held at T_{ic} for 1 h to allow complete crystallization and then cooled to 20°C. For each sample, the melting point, T'_m, was measured in the heating process. From the T'_m plots *versus* T_{ic} (Hoffman–Weeks plots), T_m^{ef} was obtained.

Optical micrographs were obtained with an Olympus optical polarizer.

RESULTS AND DISCUSSION

Hoffman–Weeks plot

As described in the Introduction, we recently clarified by *FT*i.r.[16] that while primary hydroxyl (OH) groups at the C6 position of 23MC are engaged in hydrogen bonding with ether oxygen of PEO, the secondary OH groups at the C2 and C3 positions of 6MC do not form a hydrogen bond with PEO (*Figure 1*). A thermodynamic approach by d.s.c. is an alternative method to verify the above result. Since PEO crystallizes and the 23MC and 6MC become amorphous in the blended films, as in the

Table 1 Characterization data for the three cellulosic homopolymer amorphous film samples

Sample	Molecular weight	Density ($g\,cm^{-3}$)
Cellulose	1.2×10^5	1.50
2,3-di-*O*-MC	4.0×10^4	1.30
6-*O*-MC	3.5×10^4	1.30

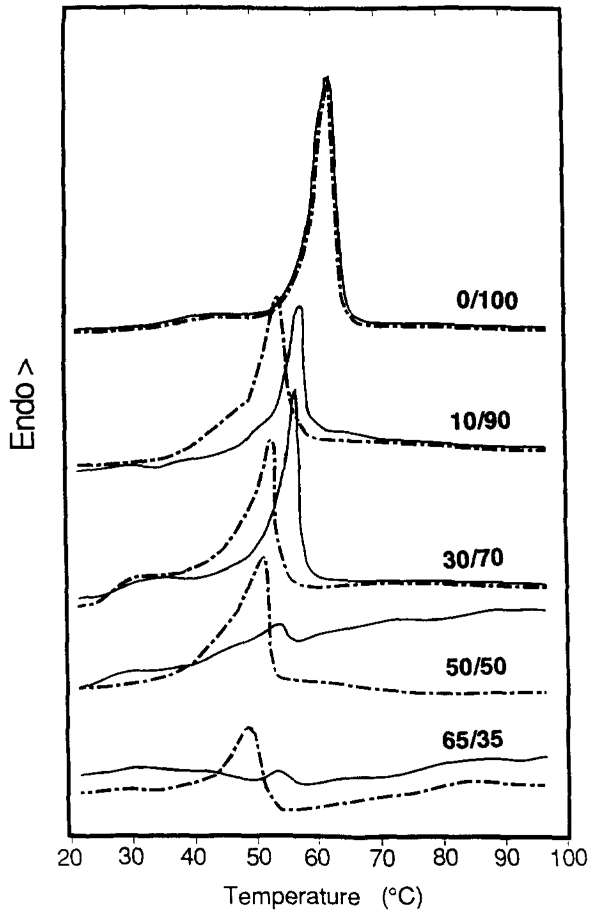

Figure 2 D.s.c. melting thermograms in the second heating cycle for a series of 23MC/PEO (— · — ·) and 6MC/PEO (——) blends

case of pure cellulose/PEO, the concept of analysis by melting point depression for 23MC/PEO and 6MC/PEO films is a potentially useful scheme for quantifying the thermodynamic behaviour of the systems[4,9,19–23]. In fact, melting point depression in the second heating scans is evident in our calorimetric study of both 23MC/PEO and 6MC/PEO systems (*Figure 2*), as reported in pure cellulose/PEO blends[9]. However, there are some issues, such as morphological effects that must be considered. The effects are known to be mainly due to the degree of perfection and the finite size of crystals[24]. *Figures 3* and *4* show Hoffman–Weeks plots[24] of the observed melting points (T'_m) *versus* the isothermal crystallization temperature (T_{ic}) for the 23MC/PEO and 6MC/PEO blend samples, respectively, at various compositions. A linear relationship is observed between T_{ic} and T'_m. If it is assumed that the PEO crystals are perfect and of finite size and that no recrystallization takes place during the melting run, the experimental data in *Figures 3* and *4* can be fitted by the following equation for isothermal crystallization[19,24]:

$$T_m^{eq} - T'_m = \phi(T_m^{eq} - T_{ic}) \qquad 0 \leqslant \phi \leqslant 1 \qquad (1)$$

where T_m^{eq} is the equilibrium melting point and ϕ is the stability parameter which depends on the crystal thickness. T_m^{eq} for the PEO blended with MC can be obtained by extrapolation with a least-square fit of the data by equation (1) to the intersection with $T'_m = T_{ic}$. The parameter ϕ was determined from the slope of each straight line. In equation (1), where ϕ assumes a value between 0 and 1, $\phi = 0$ implies $T_m^{eq} = T'_m$ for all T_{ic}, whereas $\phi = 1$ implies $T'_m = T_{ic}$. This means that the crystals are most stable at $\phi = 0$ and unstable at $\phi = 1$. The values for ϕ are summarized in *Table 2*. The values of ϕ for each 6MC/PEO sample are less than 0.2 and are independent of the composition, suggesting that the crystals should be fairly stable. The melting point depression of the 6MC/PEO system does not appear to be due to morphological effects. On the other hand, the values of ϕ for the 23MC/PEO samples depend on the

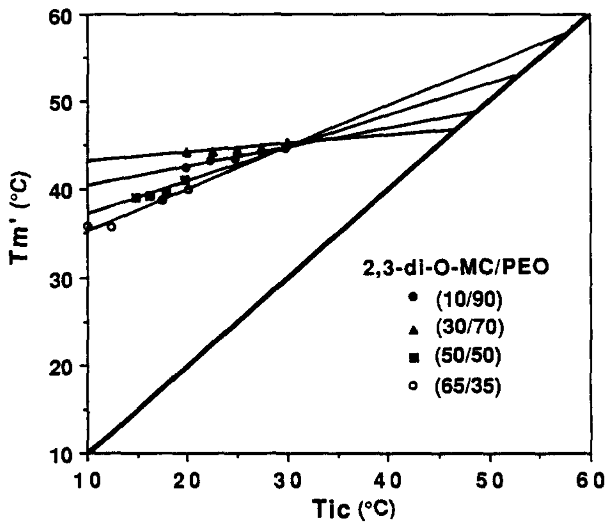

Figure 3 Hoffman–Weeks plot of the melting temperature, T'_m, of PEO crystals in the 23MC/PEO blend *versus* the isothermal crystallization temperature, T_{ic}

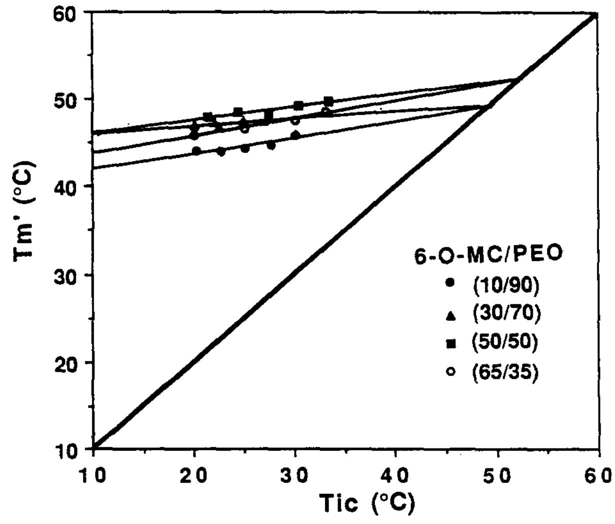

Figure 4 Hoffman–Weeks plot of the melting temperature, T'_m, of PEO crystals in the 6MC/PEO blend *versus* the isothermal crystallization temperature, T_{ic}

Table 2 Stability parameter, ϕ, of PEO crystal

Blend composition (MC/PEO)	23MC/PEO	6MC/PEO
0/100	0.066	0.066
10/90	0.218	0.200
30/70	0.089	0.101
50/50	0.369	0.165
65/35	0.476	0.210

composition: for the 50/50 and 65/35 blends in particular ϕ shows high values, indicating that the PEO crystals should be considerably unstable. This seems to be a morphological effect caused by the hydrogen bonding interaction between the two polymers as shown in *Figure 1*, while in the 6MC/PEO system the hydrogen bonding interaction was not perceived by *FT*i.r. If the melting point depression of the 23MC/PEO system is not due mainly to morphological effects, ϕ should be a constant and the straight lines in *Figure 4* should have similar slopes[19]. Thus, it is shown that the morphological effects in this 23MC/PEO system cannot be sufficiently removed by Hoffman–Weeks plots to obtain the real equilibrium melting points. Small-angle X-ray scattering (SAXS) is a tool to measure lamellar thickness by the long period. By this measurement the morphological contributions to the melting point depression can also be estimated using the Gibbs–Thomson relationship[25,26]. Unfortunately, the scattering maxima of the PEO in the blends could not be observed in the SAXS profile because of the low crystallinity.

The samples used for the Hoffman–Weeks plots were observed by polarized optical microscopy. The micrographs are shown in *Figure 5*. Some melt-crystallized samples showed spherulites of PEO. The 6MC/PEO blends containing more than 35 wt% PEO showed spherulites and the 80/20 sample gave a dark and uniformly isotropic image between crossed polars. On the other hand, the 23MC/PEO samples showed spherulites at compositions of 10/90 and 30/70. The samples containing less than 50 wt% PEO did not show PEO spherulites but had a rod-like texture. This suggests that the morphology is affected by the change of polymer–polymer interaction between 23MC and PEO. This change corresponds to the stability parameter of 23MC/PEO shown in *Table 2*.

Two different PEO homopolymer films prepared by casting or coagulation were also observed by polarized optical microscopy. It was clear that cast and melt-crystallized pure PEO gave a spherulitic texture while the pure PEO film coagulated from DMAc solution showed a rod-like texture which may be due to polymer–solvent interaction. Compared with this result, the change of morphology in the 23MC/PEO system mentioned above may be attributed to the fact that the 23MC can play the role of solvent for the dilution. In addition, the fluctuation of stability parameter ϕ for the 23MC/PEO system (*Table 2*) can be caused by the morphological change.

Melting point depression

Melting point depression can be explained by two effects, morphological effects and thermodynamic effects[19]. Since the amorphous 6MC and 23MC homopolymers may show diluent effects in our blend systems, we assume thermodynamic effects in mixing of crystalline polymer and amorphous polymer[4,5,9,19–23] in order to explain the melting point depression of the systems. The thermodynamic mixing of the two polymers was studied by Scott[27] using the Flory–Huggins approximation[28]. The conventional formulation for the thermodynamic depression of the melting point caused by a diluent is as follows:

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

where T_m^0 is the melting point of PEO and T_m is the observed melting point of the blended PEO. In this equation, subscripts 1 and 2 refer to the cellulosics and PEO, respectively: v_1 and v_2 refer to volume fractions while V_1 and V_2 refer to molar volumes. V_{2u} is the molar volume of the repeating units of 2, ΔH_{2u} is the enthalpy of fusion per mole of the repeating units of 2, and v_1^2 is the square of the volume fraction of non-crystallizable component 1. B is the interaction energy density characteristic and R is the gas constant.

When V_1 and V_2 are of the order of 10^4–10^6, the entropy term of equation (2) can be neglected entirely[20]. In the present case, V_1 and V_2 are calculated to be 3.1×10^4 for 23MC, 2.7×10^4 for 6MC, and 1.8×10^4 for PEO, on the basis of data in *Table 1* and literature data[29]. Then equation (2) can be rearranged to the following form, which can evaluate the enthalpic contribution to the

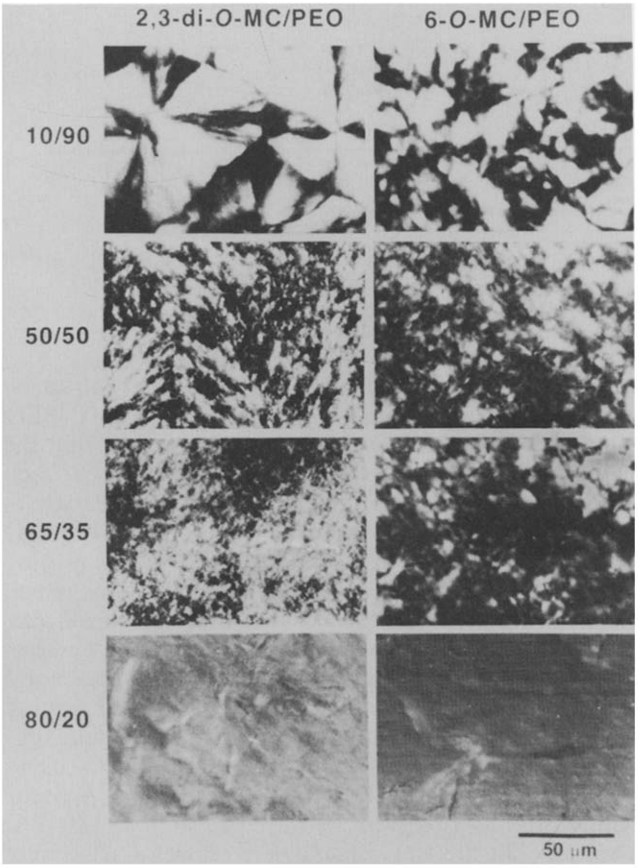

Figure 5 Polarized optical micrographs of a series of 23MC/PEO and 6MC/PEO blends with the same thermal history as the d.s.c. samples

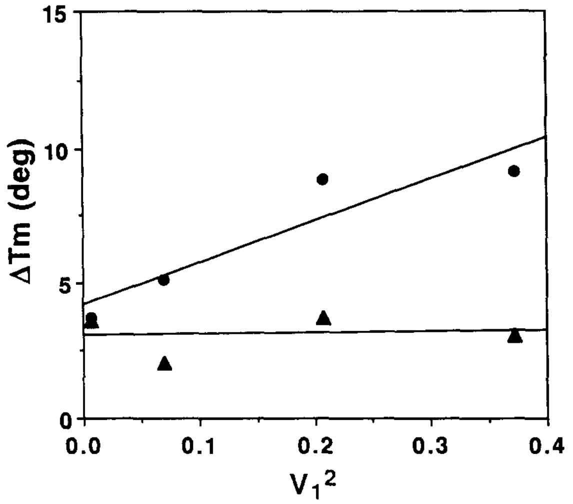

Figure 6 Plot of the melting point depression, ΔT_m, *versus* the square of volume fraction of the cellulosics, v_1^2, for 23MC/PEO (●) and 6MC/PEO (▲)

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

	Cellulose/PEO[9]	23MC/PEO	6MC/PEO
B (J cm^{-3})	−18.0	−10.0	−0.30
χ_{12} (at 348 K)	−0.67	−0.51	−0.014

melting point depression:

$$\Delta T_m = T_m^0 - T_m = -T_m^0(V_{2u}/\Delta H_{2u})Bv_1^2 \quad (3)$$

where ΔT_m is the melting point depression of PEO component.

Equation (2) employs a Flory–Huggins interaction parameter, χ_{12}, to describe the enthalpy of mixing, which is related to the parameter *B*:

$$B = RT(\chi_{12}/V_{1u}) \quad (4)$$

In *Figure 6* the experimental data of the melting point depression, ΔT_m, of each system are plotted *versus* v_1^2. The solid line was drawn by the least-square fitting method assuming a linear relationship between ΔT_m and v_1^2. The volume fraction was calculated using the density data of the cellulosics in *Table 1* and 1.09 g cm^{-3} as the density of PEO melt (at 75°C)[29]. Both straight lines yielded positive intercepts. The presence of the intercepts might be the result of a residual entropic effect[19–22] which may be due to the molecular weight of PEO[23]. From the slopes of the two ΔT_m and v_1^2 plots, we can assess values of parameters *B* and χ_{12} from equations (3) and (4), in combination with the other necessary quantities as follows: the heat of fusion per unit volume ($\Delta H_{2u}/V_{2u}$) of PEO[30] is 208 J cm^{-3}; V_{1u} = 146.15 cm^3 mol^{-1} for 23MC and 135.38 cm^3 mol^{-1} for 6MC. The V_{1u} values are calculated from the molar masses (190 for 23MC and 176 for 6MC) and densities (*Table 1*) for each cellulosic. The slopes of the two straight lines were 16.19° and 0.45° for 23MC/PEO and 6MC/PEO, respectively.

From these calculations, the thermodynamic interaction parameters were evaluated as shown in *Table 3*. The fairly large negative values for the *B* and χ_{12} parameters of the 23MC/PEO blend strongly suggest that the two polymers interact thermodynamically in the mixture. In the 6MC/PEO blend, the negative magnitude of the parameters is quite small, suggesting that the present system is immiscible. These results agree quite well with our previous results by *FT*i.r.[16]: the interaction indicated by the thermodynamic method coincides with our proposal for hydrogen bond formation in the MC/PEO blend as shown in *Figure 1*. This means that through the thermodynamic approach of the blends using cellulose model materials, the presence of the hydrogen bond between hydroxyls at the C6 position of cellulose and ether oxygens of PEO skeleton in the MC/PEO is verified. It could also be considered that the formation of hydrogen bonds only at the C6 position is due to the effect of the position of the substituents on the conformation of the cellulose chain. In the crystalline solid state, cellulose adopts a two-fold screw conformation stabilized by O(3)O(5) hydrogen bond; on the other hand, tri-*O*-methylcellulose shows a flexibility in conformation between a two-fold screw and a three-fold screw, depending on the conditions of crystallization[31,32]. In the case of mixed structures such as those studied here, one could very well have a drastic conformational change of the cellulosic chain in going from 23MC to 6MC. However, in the present experiments we observed interference in the crystallization of the PEO component by the amorphous MC. Therefore, the conformational change of the two MCs in the crystalline solid state could not greatly influence the association with PEO.

Polymer–polymer interaction in pure cellulose/PEO blend

In the above section, we considered the depression of the melting point, ΔT_m, by the thermodynamic effects of mixing. In this approximation, ΔT_m can be divided into additive parts stemming from entropic and enthalpic contributions:

$$\Delta T_m = (\Delta T_m)_S + (\Delta T_m)_H \quad (5)$$

where $(\Delta T_m)_S$ is the melting point depression caused by the entropic effects and $(\Delta T_m)_H$ is the melting point depression caused by the enthalpic contribution. In equation (4), it is assumed that $(\Delta T_m)_S$ should be omitted. Thus, in the calculation using equation (4) we were obliged to estimate ΔT_m of our blend systems by assuming that it is completely due to the enthalpic contribution, in spite of the presence of the morphological effects. As a result, the obtained values of parameters *B* and χ_{12} for the 23MC/PEO and 6MC/PEO blends (*Table 3*) should be larger than the real ones due to the enthalpic contribution alone.

Nishio *et al.*[9] evaluated the parameters *B* and χ_{12} in a cellulose/PEO system using the equilibrium melting point to remove the morphological contribution; the values are shown in *Table 3*. We cannot simply compare those values, but the negative magnitude of both values for the cellulose/PEO systems are much larger than the sum of each value for the other two MC/PEO systems, although the corresponding values for the two systems are assessed to be larger than the real values, as mentioned above. This indicates that the polymer–polymer interaction in cellulose/PEO cannot be explained only by the hydrogen bond as shown in *Figure 1*. In other words, secondary interaction can be formed in the blend with cellulose.

Here we observed by polarized optical microscopy the melt-crystallized pure cellulose/PEO at various compositions

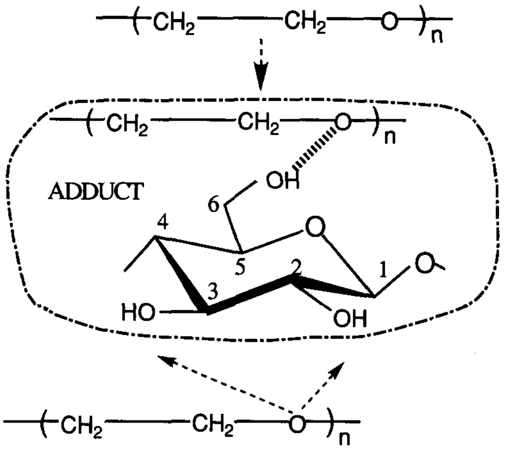

Figure 7 Schematic mechanism for the formation of polymer–polymer interactions in cellulose/PEO blends

with the same thermal history as the MC/PEO samples. In the micrographs, neither spherulite nor rod-like texture was observed even in the 10/90 cellulose/PEO sample. Instead, the cellulose/PEO samples showed a uniformly isotropic image through all compositions. The phenomenon is different from that in the two MC/PEO systems mentioned in the previous section. This also suggests the presence of additional polymer–polymer interaction in the cellulose/PEO blend.

From these results, the mechanism shown in *Figure 7* can be proposed for the development of the interaction in the cellulose/PEO blend. Since hydrogen bonding between the C6 position hydroxyls and skeletal oxygen of PEO is more favourable, at first the two polymers are trapped to form a large adduct, which is a complex between cellulose and PEO, by the hydrogen bond, and the mobility of the molecules is restricted. Then another PEO molecule interacts with the adduct either by hydrogen bonding between the remaining free hydroxyls in cellulose and oxygen in PEO, or by van der Waals bonding between PEO molecules.

CONCLUSION

To characterize the polymer–polymer interaction in cellulose/PEO blends, calorimetric studies were carried out on cast films of 23MC/PEO and 6MC/PEO blends. The two systems employed as a model system for the cellulose/PEO blend showed depression in the melting point of PEO crystalline parts with an increase in the amount of the cellulosic component. To explain this phenomenon, approximation for thermodynamic mixing of two polymers, the crystalline and amorphous polymers, was applied to the obtained data, since both cellulose components were in the amorphous state in the blends. The analysis yielded values for the interaction parameter, χ_{12}, of -0.51 and -0.014 for 23MC/PEO and 6MC/PEO, respectively, at 75°C. Comparison of the magnitude of the two χ_{12} parameters in each system suggested that 23MC interacted with PEO and 6MC was immiscible with PEO. This is in good agreement with the result of *FT*i.r. analyses in our previous paper[16]. Thus, the interaction shown by the thermodynamic studies can be considered as hydrogen bonding between hydroxyls at the C6 position of cellulose and oxygens of the PEO skeleton. Although morphological and entropic contributions are not sufficiently removed to obtain the real equilibrium melting temperatures used for the values of B and χ_{12}, the sum of the values for the two MC/PEO systems was much smaller than the magnitude of the parameter for cellulose/PEO. This indicates the presence of secondary polymer–polymer interaction in the pure cellulose/PEO blend.

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