Bulk and surface characterization of cellulose/poly(vinyl alcohol) blends by Fourier-transform infra-red spectroscopy

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The miscibility and surface selectivity of cellulose/poly(vinyl alcohol) (PVA) blends were investigated by Fourier-transform infra-red (*FT*i.r.) and attenuated total reflection (*FT*i.r.-a.t.r.) spectroscopy. The blends were prepared in film form by casting mixed polymer solutions in a common solvent (dimethylsulphoxide–tetraethylammonium chloride) onto a glass plate and successively coagulating the solutions with ethanol. The dried films were optically clear irrespective of blend composition. The transmission *FT*i.r. measurements revealed that the crystallinity of each polymer component decreased with increasing content of the blending partner. These findings strongly suggest a certain level of miscibility of cellulose and PVA. The compositions of the film surfaces on the glass (substrate) side and the ethanol (coagulant) side were also examined by *FT*i.r.-a.t.r. via two methods: (1) a method using the ratio of the integrated area of an absorption peak centred at 897 $\mathrm{cm^{-1}}$ (cellulose) to that of a peak centred at 918 $\mathrm{cm^{-1}}$ (PVA); and (2) a least-squares curve-fitting method in the range 850 to 1200 $\mathrm{cm^{-1}}$. The results obtained by both these methods lead to the conclusion that the concentration of PVA was higher than that of cellulose at the glass-side surface, whereas no selectivity was detected at the ethanol-side surface.

(Keywords: characterization; cellulose; poly(vinyl alcohol); blends; Fourier-transform infra-red spectroscopy)

INTRODUCTION

The number of studies on blends of cellulose with cellulose derivatives or synthetic polymers is increasing[1-5], because of an increase in the number of common solvents[6] for cellulose and synthetic polymers discovered for blending and because of demands for improvement in the properties of cellulose by blending. Jolan *et al.*[1] worked on blends of cellulose with cellulose triacetate and poly(acrylonitrile), and found a certain level of miscibility for both series of cellulose blends. The mechanical properties were optimized at a composition containing 90 wt% cellulose[1]. Field *et al.*[2,3] used infra-red spectroscopy, differential scanning calorimetry (d.s.c.) and an X-ray measurement to investigate blends of cellulose and poly(ethylene terephthalate). Recently Nishio *et al.*[4,5] studied cellulose and poly(vinyl alcohol) (PVA) blends prepared by a solution–coagulation method utilizing a common solvent, *N,N*-dimethylacetamide– lithium chloride. From d.s.c., dynamic mechanical and wide-angle X-ray measurements, they found that cellulose was partially miscible with PVA.

In the present paper we report the result of bulk and surface characterization of cellulose/PVA blends prepared from solutions in another common solvent, a mixture of dimethylsulphoxide and tetraethylammonium chloride (DMSO-TEAC). The DMSO-TEAC mixture was reported to be a suitable solvent for cellulose fibre spinning by Kamata *et al.*[7]. Blending of cellulose with PVA was motivated here to improve the mechanical properties of cellulose fibres by a mixed spinning method.

Needless to say, Fourier-transform infra-red (*FT*i.r.) spectroscopy is one of the most powerful techniques to investigate multicomponent systems because it provides information on the blend composition as well as on the polymer–polymer interaction. Anton *et al.* have applied a linear least-squares regression method to the analysis of infra-red spectra of multicomponent mixtures of xylene isomers[8,9] and a polystyrene/poly(phenylene oxide) blend[9] in order to estimate quantitatively the composition of the individual components. Haaland *et al.*[10] examined several linear regression curve-fitting techniques. Garcia[11] employed a digital subtraction technique to clarify the presence of intermolecular interactions between polystyrene and poly(vinyl methyl ether) blends in a miscible state. Among many techniques in *FT*i.r. spectroscopy, attenuated total reflection (*FT*i.r.-a.t.r.) spectroscopy is particularly useful for surface investigations. Iwamoto *et al.*[12,13] proposed a method of quantitative analysis of surfaces and thin layers by *FT*i.r.-a.t.r. This method is called the *FT*i.r.-a.t.r. subtraction method. As they stated, a quantitative analysis with *FT*i.r.-a.t.r. requires high reproducibility of an *FT*i.r.-a.t.r. spectrum and a well defined reference band. They attained these requirements by designing a special *FT*i.r.-a.t.r. attachment and by use of a Ge crystal as an internal reflection element (IRE). In our case, both curve-resolving and curve-fitting methods were employed. These methods allowed us to use the area of the individual absorption bands and/or a wide range of the absorption spectrum, since they minimized errors encountered in a series of *FT*i.r.-a.t.r. measurements. In this paper, we apply these

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methods to bulk and surface characterization of blends of cellulose with PVA.

EXPERIMENTAL

Sample

A mixture of dimethylsulphoxide (DMSO) and tetraethylammonium chloride (TEAC) (3/1 w/w) was used as the common solvent for cellulose (CE) and poly(vinyl alcohol) (PVA). The cellulose solution obtained with this mixed solvent, DMSO-TEAC, found by Kamata *et al.*[7] as a suitable solvent for cellulose, was colourless, odourless, non-volatile and transparent, and the degree of polymerization was not noticeably decreased or degraded as stated in the literature[7]. PVA was also dissolved in DMSO-TEAC without phase separation or sedimentation. Since the details of the procedure of dissolution of cellulose in DMSO-TEAC are described in the literature[7], we only briefly summarize the procedure. Cellulose from wood pulp (Alaska Pulp Co. Ltd.), having degree of polymerization of 850, was immersed in DMSO, then milled by a kneader and dissolved by adding TEAC at elevated temperature (~90°C). The final ratio of the composition of TEAC to DMSO was ~1/3. Thus a 5 wt% cellulose solution was obtained. The degree of polymerization (*DP*) of cellulose in the solution was measured to be ~700. The decrease in *DP* was attributed mainly to the milling process. Further degradation of cellulose in the solution was not detected by viscometry. Commercially available poly(vinyl alcohol) (PVA) having $DP = 1800$ was resaponified. The final degree of saponification was 99.98 mol%. This resaponified PVA was dissolved in DMSO-TEAC, and a 5 wt% PVA solution was prepared. These PVA and CE solutions were mixed together with a mechanical stirrer at ~40°C, in the desired ratio of $\mathrm{CE/PVA} = x/(100-x)$ by weight. The mixed solutions were clear irrespective of composition in the temperature range examined, 20–100°C. These solutions were cast onto a glass plate and coagulated in film form in a bath filled with ethanol at room temperature. The films were washed with excess ethanol, then peeled off from the glass plate and dried. Each film was kept between two pieces of filter paper and was further dried and stored in a vacuum oven at 60°C until used. CE and PVA homopolymer films were also obtained in the same manner. Films having overall compositions of CE/PVA = 0/100, 30/70, 50/50, 70/30, 90/10 and 100/0 were thus prepared. The film thickness was in the range of 10–20 μm for i.r. transmission measurements and 50–100 μm for *FT*i.r.-a.t.r. measurements.

*FT*i.r. *measurements*

Infra-red spectrograms were obtained with a Firis 100 *FT*i.r. spectrometer (Fuji Electric Co. Ltd). For *FT*i.r.-a.t.r. measurements, ZnSe was used as an IRE. Reflection measurements by using a specular reflectance accessory were also conducted for evaluating the polymer–glass interaction. The angle of incidence was chosen to be 30°. The numbers of scans were 64, 512 and 128, respectively, for the transmission *FT*i.r., *FT*i.r.-a.t.r. and reflection measurements. The spectra obtained were analysed on an NEC personal computer, PC9801VX, with a curve-resolving program developed in our laboratory. The details of the curve-resolving method were described elsewhere[14]. Decomposed spectra were used for quantitative analyses of blend compositions.

RESULTS AND DISCUSSION

Bulk characterization

Figure 1 shows absorbance survey spectra for (a) cellulose, (b) PVA and (c) CE/PVA (50/50). Absorption bands around 3000 cm^{-1} labelled ν(CH) and $\nu(\mathrm{CH_2})$ are due to CH and $\mathrm{CH_2}$ stretching vibrations, respectively. The CH wagging band, δ(CH), of cellulose and the C–C–C stretching band, ν(C–C–C), of PVA are related to the crystalline bands of cellulose and PVA, respectively. These assignments were carried out based on the literature[15,16]. *Figure 1c* shows the observed spectrum of a 50/50 blend of cellulose and PVA, together with the reproduced one obtained by assuming the additivity of pure components. The observed and reproduced spectra are roughly superimposed on each other. The significant deviations at ν(OH) and δ(CH) and in the region below 1000 cm^{-1} are attributed to some structural change occurring due to mixing, e.g. change in the degree of crystallization by mixing.

The methylene stretching band is usually used as a reference band in order to estimate the degree of crystallinity of both cellulose and PVA[17]. In the case of cellulose/PVA blends, however, both cellulose and PVA have absorption bands around this region. Therefore these bands could not be used as reference bands without resolving them into individual absorption bands. We decomposed the i.r. spectra around the $\mathrm{CH_2}$ and CH

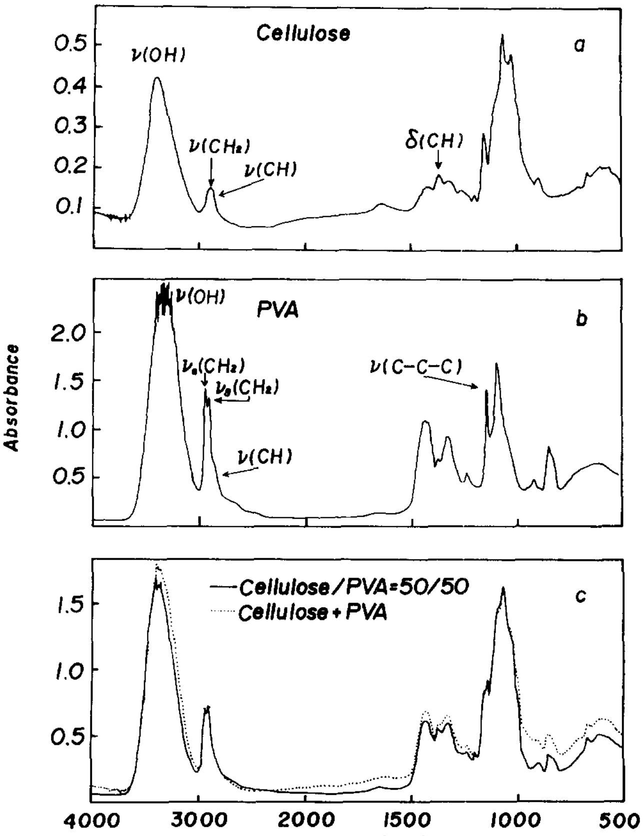

Figure 1 Absorbance survey spectra for (a) cellulose, (b) PVA and (c) CE/PVA (50/50) blend films

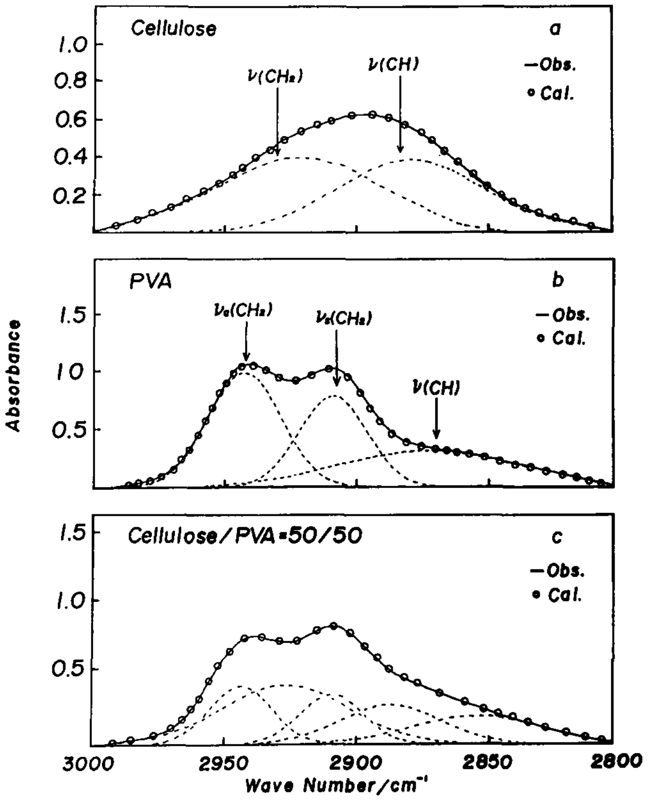

Figure 2 Observed absorbance spectra (full curves) of (a) cellulose, (b) PVA and (c) CE/PVA (50/50) blend films in the CH_2 and CH stretching region. The broken curves indicate the curve-resolved individual spectra and open circles the recomposed spectra using the individual spectra

stretching bands into two and three individual absorption bands, respectively, for pure cellulose and PVA films. *Figure 2* shows the result of the curve-resolving procedure. The full curve, broken curves and open circles denote respectively the observed spectrum, the individual contributions and the reproduced total spectrum based on these individual contributions. Here we assumed the symmetry of the individual absorption bands, and so the individual bands can be expressed as a linear combination of Lorentzian and Gaussian functions. As shown in *Figure 2a* the spectrum for a cellulose film was decomposed into the methylene stretching band, $\nu(CH_2)$, and the CH stretching band, ν(CH). The PVA absorption spectrum, shown in *Figure 2b*, was resolved into the antisymmetric $\nu_a(CH_2)$ and symmetric $\nu_s(CH_2)$ stretching bands of CH_2 groups, and the CH stretching band, ν(CH). *Figure 2c* shows the absorption spectrum for a CE/PVA (50/50) blend. This spectrum was decomposed into five individual contributions based on the knowledge of the cases of the homopolymers, i.e. *Figures 2a* and *2b*. As shown in *Figure 2c*, the observed full curve and the reproduced total spectrum (open circles) are in good agreement.

All of these five absorption bands were examined as a candidate for the reference bands to estimate the crystallinity of cellulose and PVA. If the additivity of the absorbance is preserved in this absorption region (in other words, there is no interaction between different individual absorption bands), the fraction of PVA is given by:

$$\omega_{PVA} = k_{PVA}A_{PVA}/(k_{PVA}A_{PVA} + k_{CE}A_{CE}) \qquad (1)$$

where k_i and A_i (i = PVA or CE) denote the coefficients related to the absorptivity and the absorbance of component i respectively. By rewriting equation (1), one gets:

$$\omega_{PVA}^{-1} = 1 + \frac{k_{CE}A_{CE}}{k_{PVA}A_{PVA}} \qquad (2)$$

Therefore a linear relationship between ω_{PVA}^{-1} and A_{CE}/A_{PVA} is expected. Possible combinations of the two cellulose bands ($\nu(CH_2)$, ν(CH)) and three PVA bands ($\nu_a(CH_2)$, $\nu_s(CH_2)$, ν(CH)), shown in *Figure 2*, were examined to find a pair suitable for adoption as A_{CE} and A_{PVA}. Among the six combinations, the pair $A_{CE}(2887)$ and $A_{PVA}(2908)$ satisfied the requirement with the least deviation from equation (2), as shown in *Figure 3*, where x of $A_i(x)$ denotes the wavenumber at the absorption peak maximum. The full line crosses the ordinate at $\omega_{PVA}^{-1} = 1$ and the correlation coefficient is 0.9865.

In order to clarify the miscibility of the CE/PVA blends, the indices of crystallinity were evaluated as follows. Since the CH bending absorption band at 1369 cm^{-1}, δ(CH), and the C–C–C stretching absorption band at 1143 cm^{-1}, ν(C–C–C), are known to be crystalline absorption bands, for cellulose and PVA respectively, we defined the following ratios with respect to the corresponding internal reference as the indices of crystallinity:

$$I_{CE} = A_{1369}/A_{2887} \qquad (3)$$

$$I_{PVA} = A_{1143}/A_{2908} \qquad (4)$$

These indices indicate the relative contributions of the crystalline phases of cellulose and PVA to the pure or blend films. However, it has to be noted here that neither I_{CE} nor I_{PVA} means the absolute degree of crystallinity, because of lack of information on the absorptivity for A_{1143}, A_{1369}, A_{2887} and A_{2908}. *Figure 4* shows the variations of I_{CE} and I_{PVA} for as-coagulated (open symbols) and annealed (at 150°C for 120 s) (filled symbols) blend films, as a function of the weight per cent of PVA component in the samples. It is clear from this figure that the indices of crystallinity of both components decrease by blending. This observation indicates a certain level of miscibility between cellulose and PVA, because a mixed polymer chain suppresses crystallization. The observed tendency is consistent with the result of d.s.c. measurements reported by Nishio *et al.*[4,5]. Since the crystalline structures for both cellulose and PVA do not depend on PVA composition[4,5], i.e. there is no definitive evidence of a so-called mixed-crystal structure, it is concluded that PVA and cellulose are miscible in the

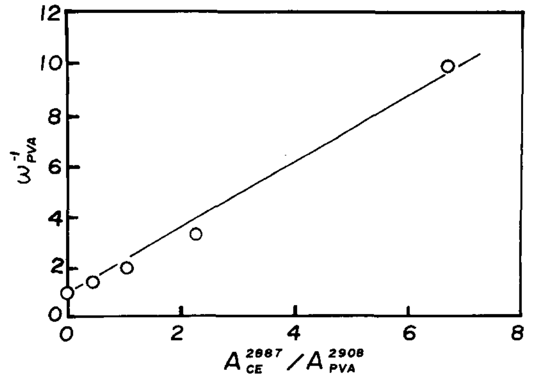

Figure 3 Reciprocal fraction of PVA component as a function of the ratio $A_{CE}^{2887}/A_{PVA}^{2908}$

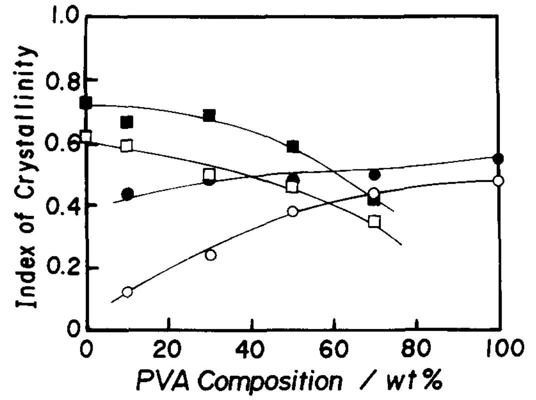

Figure 4 PVA composition dependence of the indices of crystallinity for as-coagulated PVA (○) and cellulose (□) and annealed PVA (●) and cellulose (■)

amorphous region. Nishio *et al.*[4] reported that there was a great degree of miscibility at the molecular level in blends containing more than 60 wt% cellulose based on their results on viscoelastic and thermal measurements. In *Figure 4*, however, the indices of crystallinity are smoothly varying with blend composition, and this may allow us to expect the presence of relatively good miscibility at any composition. When the blend films were annealed at 150°C for 120 s, the indices of crystallinity increased appreciably. In addition, the indices of crystallinity became less dependent on the composition. This may result from phase separation induced by crystallization.

Surface characterization

Since wettability of materials greatly depends on the surface composition, it is of importance to examine the surface composition for polymer blends. Here we employed the *FT*i.r.-a.t.r. technique.

Figure 5 shows the *FT*i.r.-a.t.r. absorption spectra in a relatively high wavenumber region (2600–3800 cm^{-1}) for (a) cellulose, (b) PVA and (c) 50/50 blend film, measured for the ethanol-side (full curve) and glass-side (dotted curve) surfaces. As can be seen from the figure, the absorption spectra for the ethanol-side and glass-side surfaces are more or less identical for both pure cellulose and PVA, whereas those of the blend film are significantly different. In the case of the blend film, the PVA concentration seems to be enriched at the glass-side surface, since the double peak around 2900 cm^{-1} characteristic of PVA is higher in the spectrum obtained for the glass side than that for the ethanol side. A similar phenomenon was observed in the lower wavenumber region, as shown in *Figure 6*.

Figure 6 shows the results of *FT*i.r.-a.t.r. measurements in the range 850–1200 cm^{-1} at the glass-side surface and at the ethanol-side surface for (a) cellulose, (b) PVA and (c) a CE/PVA (50/50) blend. As can be seen, only the spectrum for the CE/PVA (50/50) blend shows a significant difference in surface character. Absorption spectra in this wavenumber region are composed of various types of C–O stretching bands (around 1000 cm^{-1}) and a CH bending or stretching band (around 900 cm^{-1}). Since cellulose (*Figure 6a*) and PVA (*Figure 6b*) have very distinctive absorption bands in this region, surface selectivity undoubtedly takes place in the blend (*Figure 6c*). In the case of the C–O stretching region, curve resolving can hardly be performed, since too many peaks are present close to each other. Contrary to this, the absorption peaks at 897 and 918 cm^{-1}, characteristic of cellulose and PVA respectively, seem to be easily separated from each other. We assigned the absorption band with a peak maximum at 897 cm^{-1} to be the antisymmetric out-of-plane stretching–breathing of cellulose, and that at 918 cm^{-1} to be the CH_2 rocking, $\gamma(CH_2)$, of PVA. These peaks were examined in the same manner as in the case of methylene stretching bands, and, as a result, it was found that these absorption bands could be used as reference bands for analyses of the surface composition of CE/PVA blends. In order to estimate the surface selectivity, we first define the ratios R_{CE} and R_{PVA} as follows:

$$R_{CE}=A_{CE}(897)/A^{\circ}_{CE}(897) \tag{5}$$

$$R_{PVA}=A_{PVA}(918)/A^{\circ}_{PVA}(918) \tag{6}$$

where $A(x)$ and $A^{\circ}(x)$ are the areas of an absorption band centred at x (cm^{-1}) evaluated for blends and homopolymer films, respectively. Therefore, the following ratio is a convenient measure of the surface selectivity:

$$R_{CE}/R_{PVA}=[A_{CE}(897)/A_{PVA}(918)][A^{\circ}_{PVA}(918)/A^{\circ}_{CE}(897)] \tag{7}$$

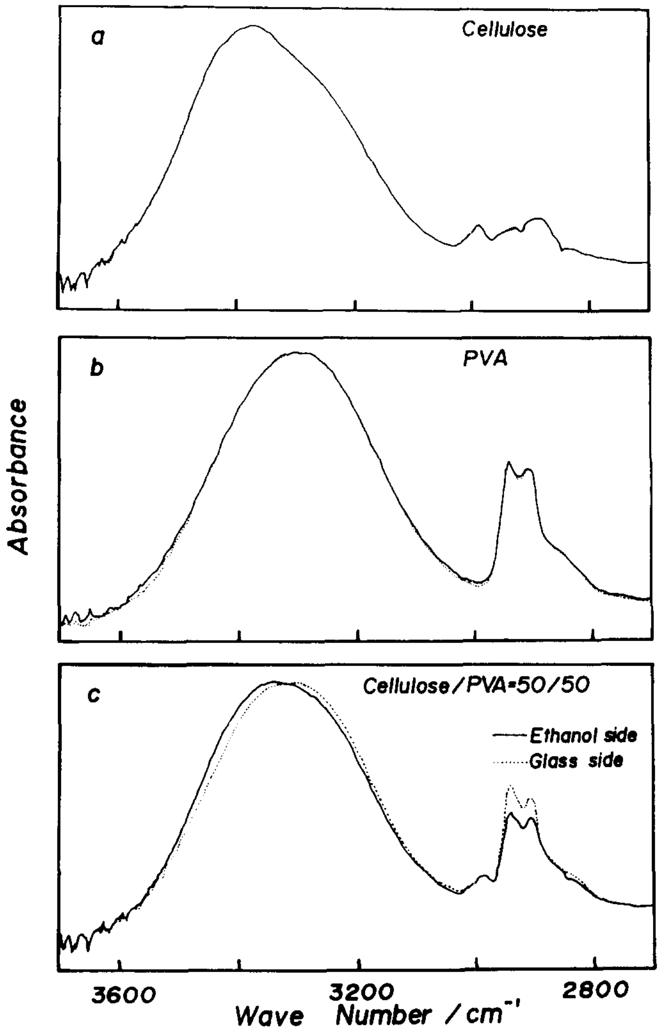

Figure 5 *FT*i.r.-a.t.r. absorbance spectra of (a) cellulose, (b) PVA and (c) CE/PVA (50/50) samples in the CH_2 and CH stretching region. The full and dotted curves show the spectra obtained for the ethanol-side (coagulant-faced) surface and glass-side (substrate-faced) surface, respectively

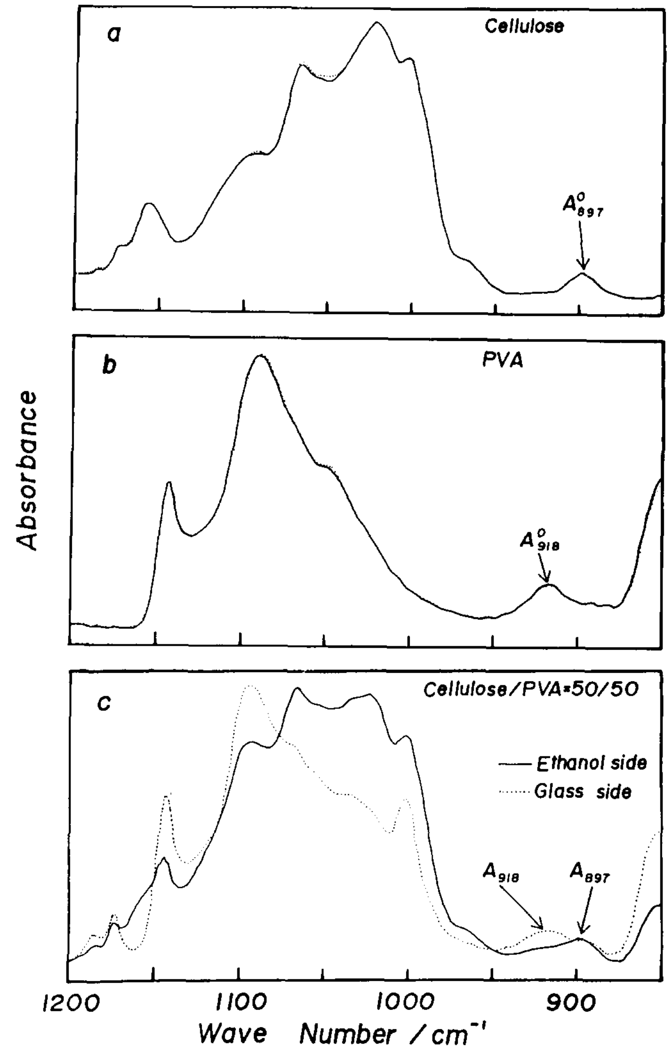

Figure 6 *FT*i.r.-a.t.r. spectra of (a) cellulose, (b) PVA and (c) CE/PVA (50/50) samples in the absorption range 1200-850 cm^{-1}. The full and dotted curves show the spectra obtained for the ethanol-side (coagulant-faced) surface and glass-side (substrate-faced) surface, respectively

It should be noted at this point that one has to worry about the reproducibility of the *FT*i.r.-a.t.r. measurements. The *FT*i.r.-a.t.r. absorbance depends upon the area of the sample attached to the IRE and how the sample is fitted on the IRE. The ratio of $A_{CE}(897)/A_{PVA}(918)$ for CE/PVA blends can be determined uniquely since these uncertainties related to the attachment of the sample and IRE can be cancelled out by taking the ratio. In the case of determination of A°_{PVA} and A°_{CE}, however, both A°_{PVA} and A°_{CE} have to be measured separately on the individual pure components, which might introduce uncertainties into the evaluation of these absorbances. We tried to minimize these errors by using samples having the same area and by applying roughly the same pressure to contact the sample on the IRE throughout the *FT*i.r.-a.t.r. measurements. The fraction of PVA at the surface was thus estimated based on the following equation:

$$f_{PVA} = R_{PVA}/(R_{CE} + R_{PVA}) \tag{8}$$

The absorption peaks at 897 and 918 cm^{-1} are relatively small, which may lead to some errors in the evaluation of the surface selectivity. Therefore we also tried to employ an alternative method, i.e. a least-squares curve-fitting method on a relatively wide range of the spectrum. The least-squares curve-fitting technique was thus applied to estimate the composition at the surface. Since an absorption spectrum for pure components can be easily obtained in the case of an investigation on blends, the least-squares curve-fitting technique is quite fruitful. The observed *FT*i.r.-a.t.r. spectrum for a blend film, $S_{obs}(x)$, was fitted with the linear combination of the spectra of the pure components, $S_{calc}(x)$:

$$S_{calc}(x) = (1 - f_{PVA})S^{\circ}_{CE}(x) + f_{PVA}S^{\circ}_{PVA}(x) \tag{9}$$

where f_{PVA} is again the fraction of PVA component at the surface. In equation (9), $S^{\circ}_{i}(x)$ is the *FT*i.r.-a.t.r. absorbance spectrum for pure component i. The wavenumber range for the curve fitting, however, has to be chosen where no significant specific interaction between the components is discernible. Otherwise a specific interaction causes a non-trivial shift on the spectrum, which may result in a fatal error in the regression analysis. In the case of cellulose and PVA blends, we found that the distinctive absorption region around 1000 cm^{-1} was quite suitable for this purpose, since the absorption bands in this range are broad enough to avoid significant errors in the curve-fitting procedure. The least-squares curve fitting was conducted by comparing the observed spectrum, $S_{obs}(x)$, with the calculated one, $S_{calc}(x)$. The range of curve fitting was chosen to be 850–1200 cm^{-1}.

Figure 7 shows a typical result of the curve fitting (upper) at the ethanol side and the deviation $S_{obs}(x) - S_{calc}(x)$ (lower) for a CE/PVA = 50/50 blend sample. The observed spectrum was well reproduced by choosing the surface PVA fraction f_{PVA} to be 0.458.

Figure 8 summarizes the results of the surface analyses. In this figure, the f_{PVA} values determined by the least-squares curve-fitting method (circles) and by using equation (8) (squares) are plotted against total PVA content in bulk films. Filled symbols indicate data at the ethanol side, whereas open symbols represent data at the glass side. The broken diagonal line indicates the case

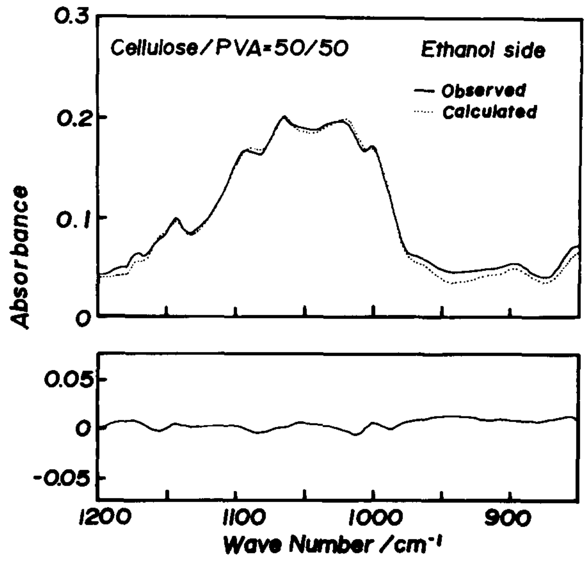

Figure 7 A typical example of the result of curve fitting for the ethanol side of a CE/PVA = 50/50 blend. The full and dotted curves in the upper figure denote the observed and calculated spectra, respectively. The lower figure shows the result of subtraction of the observed and calculated spectra

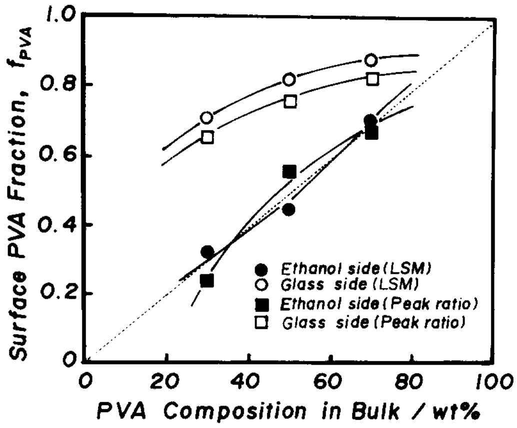

Figure 8 Bulk composition dependence of the surface PVA fraction f_{PVA} estimated by the least-squares regression method (circles) and by the ratio of absorbance areas of $A_{\mathrm{CE}}(897)$ and $A_{\mathrm{PVA}}(918)$ (squares). The filled and open symbols represent the ethanol-side surface and glass-side surface, respectively

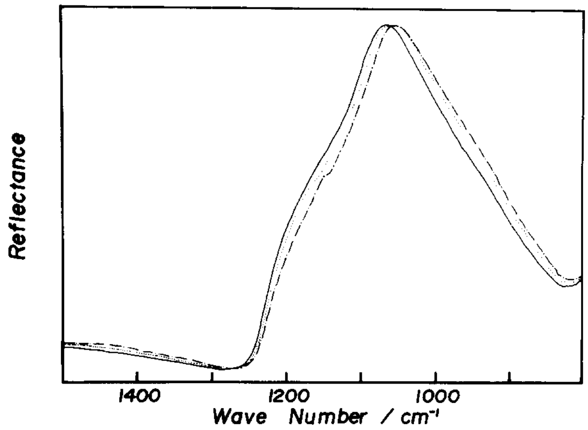

Figure 9 Reflection spectra of: —, glass; —·—, PVA-coated glass; ......, cellulose-coated glass. The thickness of the coated film was ~0.5 μm. The spectra were taken with a specular reflectance accessory

where the surface composition is the same as the bulk composition. It is clear from the figure that the PVA concentration at the glass-side surface is significantly higher than that in the bulk, whereas there is no selectivity on the coagulant-faced surface (ethanol side). Since hydrogen bonds play a dominant role in the glass–polymer interaction, a miscibility prediction based on the solubility parameter cannot be applied to such a case at the glass side. A naive discussion in terms of the solubility parameters of PVA, cellulose and ethanol seems to be inadequate even in the case of the ethanol side. The solubility parameters are $\delta_{\mathrm{PVA}} = 12.6\,\mathrm{cal\,cm^{-3}}$, $\delta_{\mathrm{CE}} = 15.4\,\mathrm{cal\,cm^{-3}}$ and $\delta_{\mathrm{Et}} = 12.7\,\mathrm{cal\,cm^{-3}}$ for PVA, cellulose and ethanol[6]. Although δ_{Et} is very close to δ_{PVA}, ethanol is a poor solvent for PVA. Therefore no selectivity at the ethanol side is caused because ethanol is a poor solvent for both cellulose and PVA.

Figure 9 shows reflectance spectra of a glass plate, PVA-coated glass plate and cellulose-coated glass plate. The thicknesses of the coating cellulose and PVA films were designed to be ~0.5 μm, roughly half the penetrating depth of the a.t.r. measurement in this particular case and roughly an optimum thickness for investigation of the interaction between the glass and either cellulose or PVA film. This was attained by casting a dilute solution of PVA or cellulose having a carefully adjusted concentration. As can be seen from *Figure 9*, the Si–O stretching band of glass with a peak maximum at around $1070\,\mathrm{cm^{-1}}$ shifts to lower wavenumber by $13\,\mathrm{cm^{-1}}$ in the case of the PVA-coated glass. On the other hand, a shift of $8\,\mathrm{cm^{-1}}$ was observed for the cellulose-coated glass.

Therefore we conclude here that the PVA concentration is higher at the glass-side surface of CE/PVA films because PVA has a higher affinity for glass than does cellulose. It should be noted here that a thin layer of pure PVA may exist on the top of the glass-side surface instead of a PVA-enriched blend surface, since *FT*i.r.-a.t.r. provides an average composition over a distance of the order of a micrometre from the surface. Verification will be carried out using X-ray photoelectron spectroscopy (x.p.s.) in the near future.

Surface selectivity in blends might be easily generated not only by substrate but also by coagulants, which will be applied for production of films and/or fibres having a concentration gradient along the thickness and/or radial direction.

CONCLUSIONS

The bulk and surface characterization of CE/PVA blend films prepared from solutions in DMSO-TEAC was carried out. The blend films were optically clear at any composition. Transmission *FT*i.r. measurements revealed that the indices of crystallinity of cellulose and PVA decrease with increasing concentration of PVA and cellulose, respectively, in the blends. These findings suggest strongly the miscibility of amorphous cellulose and PVA chains. By annealing the blend films, the indices increased and became less dependent upon the composition. This may be explained via phase separation induced by crystallization.

The surface selectivity on the glass and ethanol sides was examined via two methods, utilizing (1) the ratio of the area of an absorption peak centred at $897\,\mathrm{cm^{-1}}$ (cellulose) to that of a peak centred at $918\,\mathrm{cm^{-1}}$ (PVA) and (2) least-squares curve fitting. Results obtained by both methods indicated that PVA concentration at the glass-side surface was higher than that in the bulk, whereas no selectivity was detected at the ethanol-side surface. The higher affinity between PVA and glass rather than between cellulose and glass was verified by an appreciable shift in peak position of the Si–O stretching band for the PVA-coated glass.

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