

Cellulosic blends with poly(acrylonitrile): characterization of hydrogen bonds using regioselectively methylated cellulose derivatives

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Hydrogen bonds in cellulosic blends with poly(acrylonitrile) (PAN) were characterized in terms of hydroxyl regiochemistry in the celluloses using Fourier transform infra-red (FTi.r.) spectroscopy. Regioselectively substituted *O*-methylcelluloses (MC), 2,3-di-*O*-methylcellulose (23MC) and 6-*O*-methylcellulose (6MC), were used as cellulosic model components. Wide-angle X-ray diffraction studies of the cast films of blends having more than 50 wt% cellulosic content showed them to be highly amorphous, indicating the presence of a certain interaction between the celluloses and PAN. FTi.r. analysis revealed that the hydrogen bonds in cast films washed with solvents were only engaged between the primary hydroxyl groups (OH) at the C-6 position of cellulose and the nitrile group (CN) of the PAN molecule, while there was no evidence for polymer–polymer interactions in the secondary hydroxyl groups at the C-2 and C-3 positions in celluloses or in the ether oxygens such as ring oxygen (O-5) and glucosidic linkage oxygen. In contrast, the remaining DMAC after film cast seems to have an additional interaction to connect the two polymer components, which makes the blends more miscible. Quantitative analysis was also carried out to ascertain the amounts of OH at the C-6 position engaged in the intermolecular hydrogen bonds. © 1998 Elsevier Science Ltd. All rights reserved

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INTRODUCTION

Much attention has been concentrated in both the academic and industrial research fields on polymeric blends, the studies of which are of importance^{1,2} in significantly improving the properties of blend components. Cellulosic blends with a number of synthetic polymers^{3–16} have been studied extensively as biodegradable polymer blends. The miscibility of these blends was examined by Fourier transform infra-red (FTi.r.) spectroscopy^{3,10,13,14}, optical microscopy⁴, wide-angle X-ray diffraction (WAXD)³, differential scanning calorimetry (d.s.c.)^{5–7}, dynamic mechanical measurement^{3,5,6} and solid state ¹³C-nuclear magnetic resonance (n.m.r.)^{15–17}. Nishio *et al.*⁵ examined polymer–polymer interactions in pure cellulose/polyacrylonitrile (PAN) blend systems using d.s.c. and a dynamic mechanical technique in order to elucidate the miscibility of the blends. They reported high miscibility at the molecular level in the amorphous regions of the blends having compositions with more than 50 wt% of cellulose content. However, they did not refer to the details of interchain hydrogen bonds between the two polymers, especially from the viewpoint of the regiochemistry of OH groups in a cellulose repeating unit.

Recently, Kondo and Gray^{18–20} developed methods to prepare *O*-alkylcellulose derivatives with a controlled distribution of substituents. Of these derivatives, 2,3-di-*O*-methylcellulose (23MC)¹⁹, which has the primary OH

groups at the C-6 position, can form inter- and intramolecular hydrogen bonds, whereas 6-*O*-methylcellulose (6MC)²⁰ can only form intramolecular hydrogen bonds^{21–23}. Thus, these two regioselectively methylated cellulose derivatives should be useful in correlating hydrogen bonding formation with physical properties. More recently, using FTi.r., d.s.c., and polarized optical microscopy, Kondo *et al.* also reported on the miscibility of cellulose/PEO²⁴ and cellulose/PVA^{25,26} blend systems from the viewpoint of the correlation between hydrogen bonding formation and the regiochemistry of OH groups in cellulose.

In the present paper, continuing the above studies^{24–26}, we have attempted to clarify the formation of interchain hydrogen bonds in cellulosic/PAN blend systems using FTi.r. spectroscopy. In particular, we have focused upon the following two aspects: (1) the characterization of the regiochemical effects in hydrogen bonding formation in 23MC and 6MC as model cellulose compounds, and (2) to quantitatively determine the amount of OH groups engaged in interchain hydrogen bonds. These approaches have allowed us to draw a number of conclusions concerning the hydrogen bonds in cellulosic/PAN blend systems.

EXPERIMENTAL

Materials

The cellulosic materials 23MC and 6MC were prepared by the methods described in previous papers^{18–20}. Each polymer was found to have a uniform structure, that is, every structural unit was regioselectively substituted. The weight-average molecular weights of both samples were

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approximately 2×10^4 on the basis of their SEC (size exclusion chromatography) elution curves calibrated with polystyrene standards. Poly(acrylonitrile) (PAN) with a nominal molecular weight of 2.5×10^4 , purchased from Polyscience, Inc., was washed with chloroform and successively with methanol before use. H.p.l.c.-grade *N,N*-dimethylacetamide (DMAc; Aldrich Chemical Co., Inc.) was used as a solvent without further purification.

Film preparation

DMAc was used as the common solvent for all samples. Solution concentrations were 0.8 wt% for MC samples and 2.0 wt% for PAN samples. All solutions were filtered and stored in a closed container under nitrogen atmosphere.

The polymer solutions thus separately prepared at 50°C were mixed in the desired proportions at room temperature. The relative compositions of the two polymers in the mixed solution were 100/0, 85/15, 70/30, 60/40, 50/50, 40/60, 30/70, 15/85, and 0/100 (cellulosics/PAN) by weight. After stirring for more than 3 days at 50°C, blend films were prepared by casting from the mixed solution. One gram of each blended solution was poured into a flat bottomed polypropylene tray (Nalge Co.) and heated to 50°C for 1 week under reduced pressure. The DMAc solvent was evaporated to yield an 'as-cast' film. It was further dried for another 1 week under high vacuum at 50°C, and successively washed with acetone for 23MC/PAN and water for 6MC/PAN, respectively, to completely remove the residual DMAc from the blend films. The washed films were dried. Both films, 'as-cast' and washed, were then used for measurements by Wide Angle X-ray Diffraction (WAXD) and FTi.r. spectroscopy. All the films prepared in this study were sufficiently thin ($\sim 10 \mu\text{m}$) to comply with the Beer-Lambert law²⁷.

Measurements

WAXD patterns of the film samples were recorded by computer using $\text{CuK}\alpha$ radiation (50 kV and 120 mA) produced by a JEOL JDX-8200 X-ray generator. FTi.r. spectra were obtained using a Perkin-Elmer SPECTRUM 2000 FTIR spectrophotometer. Samples for the FTi.r. measurements were prepared using the film-casting method and DMAc solutions mentioned above or by KBr disk technique. The wavenumber region investigated ranged from 4000 to 400 cm^{-1} ; a total of 64 scans with a 0.5 cm^{-1} resolution were signal averaged and stored. The artificial i.r.

spectra were made by addition of the two homopolymer spectra depending on their compositions. The real and the artificial spectra were obtained and processed with the software package PE GRAMS 2000.

Curve fitting for the i.r. peak deconvolution²³ was performed by GRAMS/32 'CurveFit' analysis using the Perkin Elmer System 2000. The value and the true shape of the peak involved in the hydroxyl absorption bands for 23MC and 6MC was set to be flexible from two to four and Lorentzian, respectively. The resolution was set to be 4 cm^{-1} . The other conditions were flexible and the calculations were repeated until a best-fit was obtained which exhibited more than 0.99 for the R^2 of the fitting.

RESULTS AND DISCUSSION

The WAXD patterns of the 6MC/PAN and 23MC/PAN blend systems (Figure 1A and Figure 1B, respectively) were obtained to examine the morphological contribution of each component for the two blend systems. The diffraction maximum of the PAN homopolymer represented by 0/100 shows a peak at $2\theta = 17.2^\circ$ due to the (100) plane of a hexagonal unit²⁸. The diffraction peak due to the PAN crystal in both blend systems disappeared gradually with increase of MC content, and finally became very diffused. Blends with compositions having more than 50 wt% of both cellulosics exhibited highly diffuse reflection patterns, indicating them to be predominantly amorphous. In the blends having composition ranges with more than 50 wt% of cellulosics, the MC/PAN blend films became highly amorphous for both blend systems, and therefore the morphological contribution of each homopolymer can be considered negligible when interpreting the following FTi.r. results. This coincides with the change of T_g according to composition for pure cellulose/PAN blend films examined by d.s.c.⁵. This suggests that a certain interaction may occur between the cellulosics and PAN.

FTi.r. spectroscopy characterization of MC/PAN blends using 'as-cast' films

6MC/PAN blend. Figure 2A shows the i.r. absorption bands due to OH groups for all 6MC/PAN blend samples. The intensity of the OH absorption bands increased with increasing cellulosic content; however, the peak maxima (3469 cm^{-1}) did not shift at all. The i.r. absorption band of the nitrile group (CN) which appeared at 2244 cm^{-1}

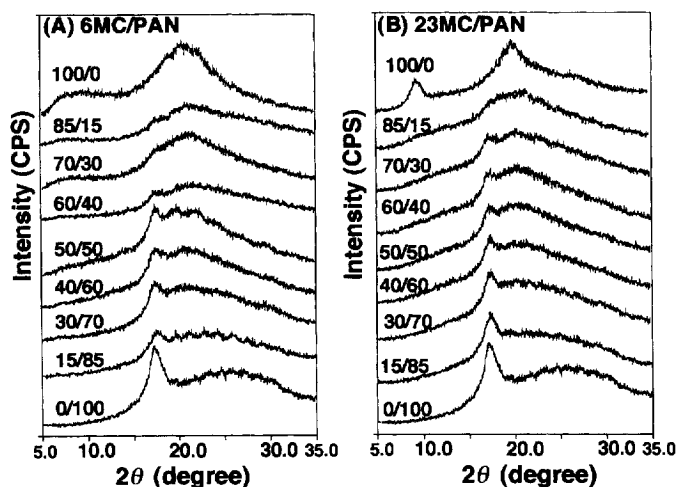


Figure 1 Wide-angle X-ray diffraction (WAXD) patterns of (A) 6MC/PAN and (B) 23MC/PAN blend systems

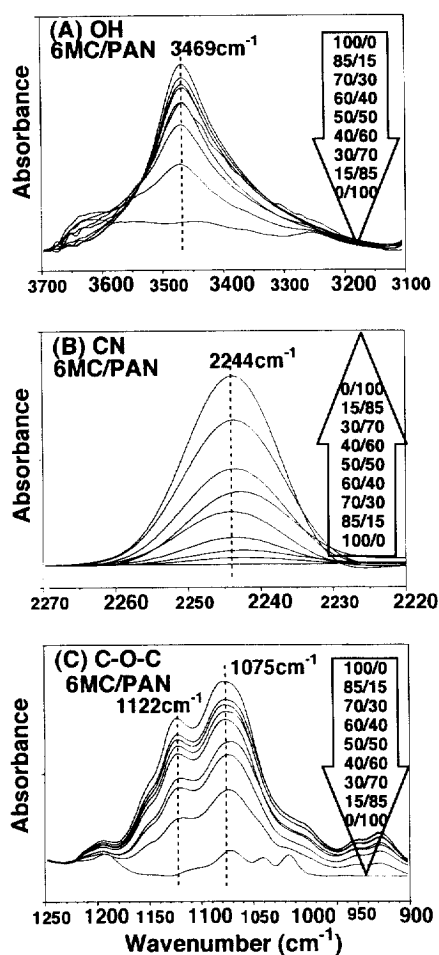


Figure 2 FTIR spectra of 6MC/PAN blends in the region of (A) OH, (B) CN, and (C) C–O–C stretching vibration

also did not shift from the position of the PAN homopolymer (Figure 2B). The C–O–C frequencies in the blends shown in Figure 2C also exhibited no change in position or peak shape. Since the OH and C–O–C absorption bands were due to 6MC, and the CN band was due only to PAN, Figure 2 demonstrates an absence of hydrogen bonds between 6MC and PAN. This is not supported by X-ray results. One reason is that 6MC may have effects as a diluent resulting in the blends showing microphase separation.

23MC/PAN blend. Three characteristic i.r. band regions due to C–O–C, CN, and OH stretching vibration for 23MC/PAN blend films are shown in Figure 3A–C, respectively. The i.r. peak maxima due to the ring oxygen (O-5), the glucosidic linkage oxygen, or the methyl ether oxygen (OCH₃) did not change in position or shape in all composition ranges of the blends (Figure 3A). Thus, all of the ether oxygens in 23MC did not form significant hydrogen bonds. Figure 3B shows the CN absorption bands for each 23MC/PAN blend sample, together with the artificial bands (broken line). In fact, the CN bands did not fit the above artificial CN bands and the peak maxima of the real CN bands shifted slightly to lower wavenumbers by a maximum of 3 cm⁻¹ from the position of the PAN homopolymer. Since the i.r. spectra were obtained with a resolution of 0.5 cm⁻¹, the difference of 3 cm⁻¹ can be considered as a significant change, indicating that the CN group in the PAN molecular chain may be participating in hydrogen bonding engagement. In Figure 3c, the real spectra of OH absorption bands due to 23MC are also compared with the artificial bands. These artificial bands were synthesized mathematically by addition of two spectra for components at the composition ratio of two homopolymers (23MC and PAN). When there is no significant interaction in the blend, the artificial band should coincide with the real band. The peak maxima of the blend samples shifted to lower wavenumbers by more than 10 cm⁻¹ from those of the artificial spectra which have the same OH absorption band position as the 23MC homopolymer. Because 23MC has only a primary OH group at the C-6 position of the anhydroglucose unit and yet the PAN has no OH absorption band, this shift can be due to the hydrogen bonds formed at the cellulosic OH groups at the C-6 position. In addition, remarkable differences in peak shape between the real and the artificial spectra were observed in the i.r. region due to OH stretching vibration. This suggests that a rearrangement of hydrogen bonding may occur as the blend compositions change.

Mechanism for hydrogen bonding

As described above, the i.r. bands due to the OH at C-2 and C-3 positions (Figure 2A), due to CN (Figure 2B), and due to ether oxygens (Figure 2C) including the ring oxygen (O-5) and the glucosidic linkage oxygen did not shift over the whole composition range of 6MC/PAN blends. On the other hand, the OH absorption bands for the C-6 position in the 23MC/PAN blends shown in Figure 3c changed in peak maxima and peak shape. The CN stretching absorption bands in the blends also had a significant shift in their peak

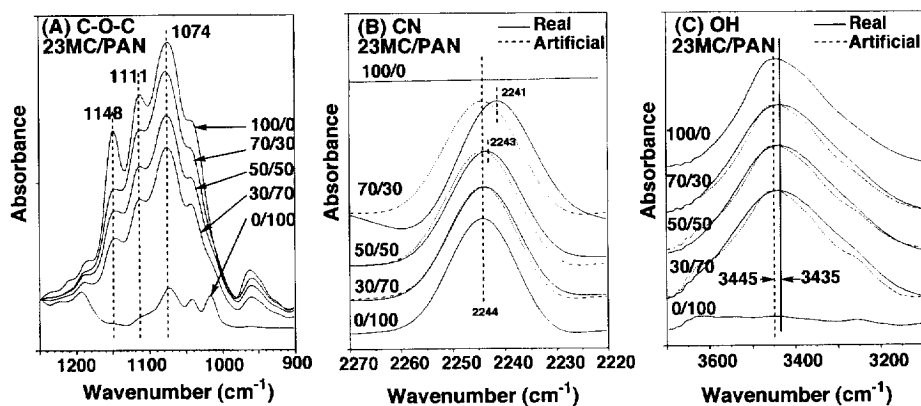


Figure 3 FTIR spectra of 23MC/PAN blends in the region of (A) C–O–C, (B) CN, and (C) OH stretching vibration

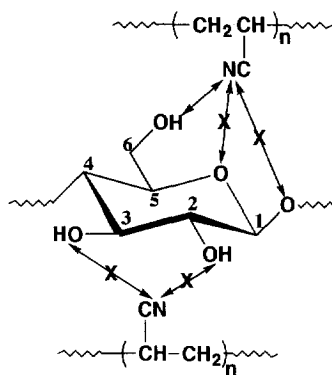


Figure 4 Proposed hydrogen bonding between cellulose and PAN

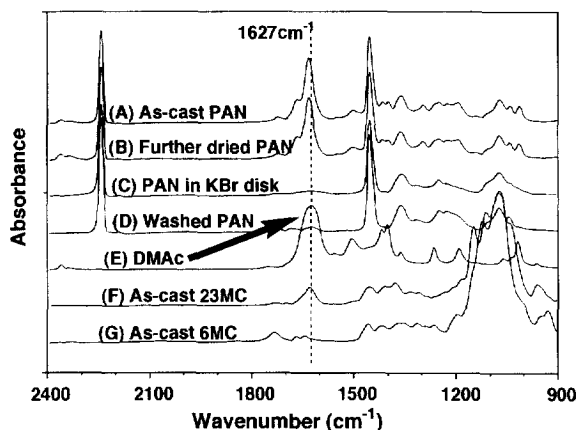


Figure 5 FTIR spectra of PAN homopolymer prepared by (A) 'as-cast' film at 50°C for 3 days, (B) 'as-cast' film at 100°C for 3 days or more, (C) KBr pellet, (D) 'as-cast' film washed with water, together with spectra of (E) DMAc, (F) 'as-cast' film of 23MC, and (G) 6MC

maxima. These results indicate that the interaction between OH at the C-6 position of cellulose and CN of PAN may exist as interchain hydrogen bonds in a pure cellulose/PAN blend system as illustrated in Figure 4.

However, we have to consider the existence of residual DMAc after solvent removal when using our casting method, as strong interactions between PAN and DMAc occurred as shown in Figure 5. The i.r. spectrum for an 'as-cast' film of PAN homopolymer had a characteristic absorption band at 1635 cm⁻¹ with a strong intensity (Figure 5A). This band was not removed by our film-casting conditions or even by severe conditions such as 100°C drying under high vacuum for 3 days or more as shown in trace B. However, the band was not observed in the spectrum for powdered PAN in a KBr disk (trace C) and, moreover, it had completely disappeared from the spectrum of the film washed with water (trace D). Thus, the i.r. band was demonstrated to be not a characteristic one for PAN, but for DMAc used as a solvent as shown in trace E. These results indicate that a certain amount of DMAc may be entrapped or interact with PAN molecules in the blend films. Conversely, the intensity of this band was very small in the i.r. spectra of cast films from 23MC and 6MC homopolymers (traces F and G, respectively), indicating that the interaction between PAN and DMAc can be stronger than that between cellulose and DMAc. Therefore, to avoid the 'solvent effect' in the formation of hydrogen bonds in the blends, all the film samples were again prepared as 'as-cast' film followed by washing with proper solvents and drying.

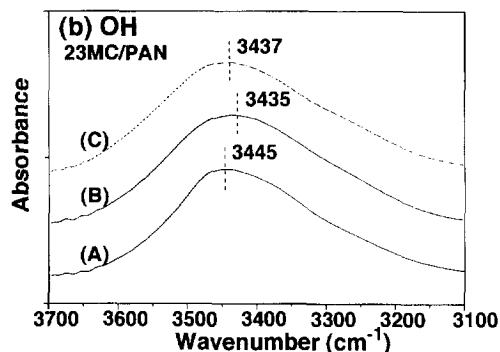
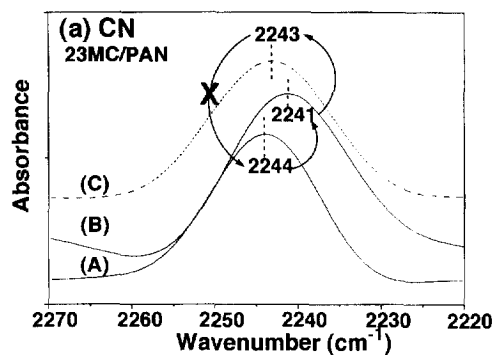


Figure 6 FTIR bands due to (a) CN and (b) OH stretching vibration: trace A in both (a) and (b) is of 'as-cast' film of PAN and 23MC homopolymer, respectively. In both (a) and (b), trace B is of 'as-cast film' and trace C is of solvent washed film of the 23MC/PAN (70/30) blend

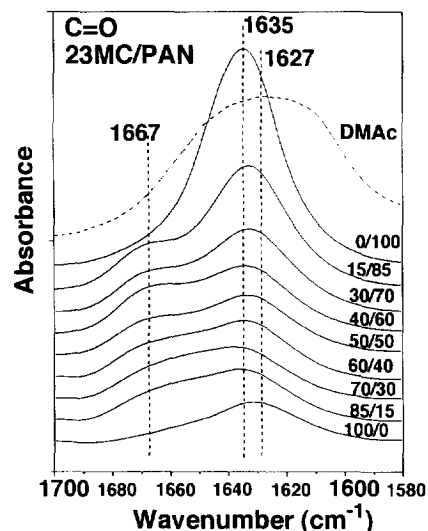


Figure 7 FTIR spectra of the carbonyl stretching vibration region of the 23MC/PAN blend systems

All 6MC/PAN blend films were washed with water and 23MC/PAN blends with acetone to completely remove the residual DMAc. The i.r. spectra for 6MC/PAN blends did not exhibit any change after washing with water but the i.r. spectra for 23MC/PAN blend films washed with acetone differed from those obtained before washing. Figure 6a shows that trace b due to the CN stretching vibration for the 'as-cast' film of the 23MC/PAN blend (70/30 w/w) was changed to trace c by washing with acetone. However, trace c did not completely return to the original position of the PAN homopolymer (trace A). The bands due to OH stretching vibration for the same film show a similar

behaviour to the CN bands (Figure 6a). This indicates the presence of a direct interaction between the CN groups of PAN and the OH groups of 23MC at the C-6 position as the interaction did not completely disappear upon the removal of DMAc. There is another possibility for the interaction among the three components PAN, DMAc, and 23MC. All of the 23MC/PAN blend films prior to washing were again examined by FTIR spectroscopy to examine the existence of specific interactions between the three components (23MC/DMAc/PAN).

Figure 7 shows a characteristic i.r. band for the carbonyl group in DMAc. The peak maxima and the shape as well as the intensity at 1627 cm^{-1} changed to 1635 cm^{-1} after blending with 23MC and PAN. In addition, a new band appeared at 1667 cm^{-1} . The two bands at 1635 and 1667 cm^{-1} were not due to PAN and 23MC homopolymers. This may be explained in the following way: firstly, PAN can easily interact with DMAc to give i.r. bands at 1635 cm^{-1} and, secondly, the interacted carbonyl groups start to form engagements with 23MC to yield the i.r. band at 1667 cm^{-1} . The decrease in i.r. intensity of the DMAc (carbonyl) group may be due to increase in 23MC content, as the interaction between DMAc and 23MC is less favourable than the interaction between DMAc and PAN. The newly formed interaction can be between the three components 23MC, DMAc, and PAN. The mixed absorption bands of the carbonyl groups (1635 and 1667 cm^{-1} at the peak maxima) due to the interaction of DMAc in the 23MC/PAN blend was deconvoluted into two peaks by the curve fitting method (mixed Gaussian and Lorentzian modes) to investigate the quantitative contribution of each interaction. The ratio of relative peak area for interacted carbonyl groups calculated from the peak area of total carbonyl groups are plotted as a function of 23MC content in Figure 8. This figure indicates that the interacted carbonyl ratio reached an equilibrium value of approximately 25% of the total carbonyl amount with increasing 23MC content.

The OH absorption bands of the 23MC/PAN blend were also deconvoluted into three components by using the above curve fitting method²³ to identify the difference between the real and the artificial spectra as shown in Figure 3C. Figure 9 shows a typical OH absorption band with 70/30 (w/w) blend composition and the three deconvoluted peak components. These components in the region of OH absorption for cellulose are well defined as free OH²³, intra- and intermolecular hydrogen bonded OH^{21,23,25} for

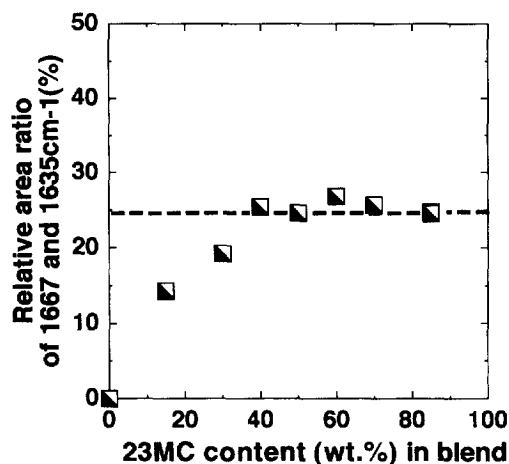


Figure 8 A plot of relative area ratio of the two carbonyl bands at 1667 and 1635 cm^{-1} versus 23MC content in 23MC/PAN blends

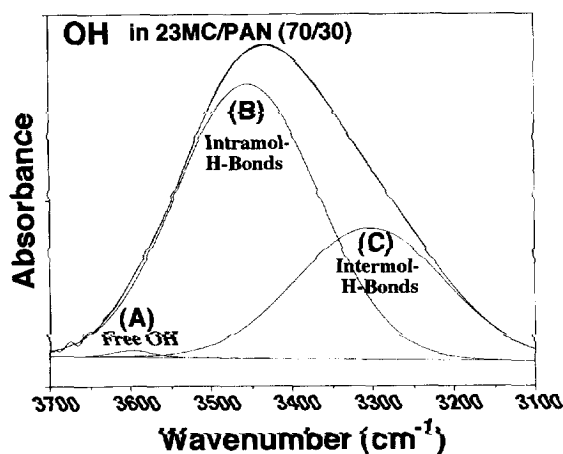


Figure 9 OH i.r. absorption band of 23MC/PAN (70/30) blend and the three deconvoluted peak components (A), (B) and (C)

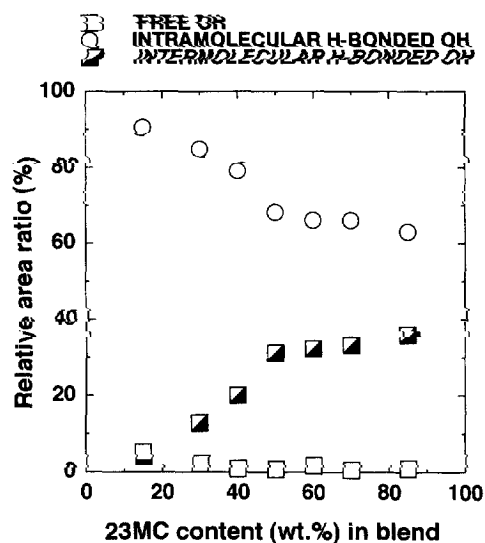


Figure 10 A plot of the relative area ratio of deconvoluted three hydroxyl components versus 23MC contents in 23MC/PAN blends.

bands A, B, and C in Figure 9, respectively. The relative area ratio of the three different OH components are plotted versus 23MC content for all blend compositions (Figure 10). The amounts of free OH were less than 2% of the total OH groups. The relative ratio of OH component due to the intermolecular hydrogen bonds (3300 cm^{-1}) gradually increased until 23MC content reached 50 wt% and then saturated. In contrast, the OH component attributed to the intramolecular hydrogen bonds (3460 cm^{-1}) showed opposite behaviour to that of the intermolecular hydrogen bonds with increasing 23MC content. This indicates that OH groups at the C-6 position changed from intramolecular hydrogen-bonded OH to intermolecular by the rearrangement of the hydrogen bonding between 23MC and other molecules. It is also indicated that the amount of OH groups engaged in the intermolecular hydrogen bonds is about 30%. The good agreement between the behaviour of carbonyl and hydroxyl groups in the 23MC/PAN blend indicates that the carbonyl groups in DMAc engaged in hydrogen bonds with CN groups of PAN simultaneously interacted to some extent with cellulosic OH groups at the C-6 position.

Considering the case of pure cellulose/PAN blends prepared by coagulation with methanol, the amount of

residual DMAc seems to be much less than the present cases. Therefore, in a pure cellulose/PAN blend system, the direct interaction between OH at the C-6 position and CN may contribute to the change of thermomechanical properties reported in a previous paper⁵, though the interaction was found to be weak by our FTi.r. analyses. In other words, interestingly, in the cellulosic blends, the strength of hydrogen bonds between molecules may not have much influence on the properties as long as they exist. To evaluate the strength of hydrogen bonds, d.s.c. analysis is one of the best approaches. Unfortunately, this approach was impossible because the melting point of PAN was much higher than the degradation point of our methylcellulose samples.

CONCLUSIONS

The formation of hydrogen bonds in terms of the hydroxyl regiochemistry of cellulose was characterized by i.r. analyses of the blend films of PAN and regioselectively substituted 23MC or 6MC as cellulose model compounds. Two kinds of samples, 'as-cast' films and cast films after washing, were subjected to the FTi.r. analyses. In all samples, the secondary OH groups due to the C-2 and C-3 positions of the cellulosic did not form hydrogen bonds with either the carbonyl or nitrile groups. Ether oxygens such as ring oxygen (O-5) and glucosidic linkage oxygen in the cellulosic did not participate in the hydrogen bonding formation with other molecules. The i.r. analyses of 'as-cast' films indicated direct evidence of hydrogen bonding formation between OH at the C-6 position and CN groups. Further i.r. investigations revealed that the carbonyl groups in DMAc formed hydrogen bonds not only with primary OH groups at the C-6 position of the cellulosic but also with CN groups of the PAN molecular chain. In addition, the i.r. band shifts of the 23MC/PAN/DMAc blend system were slightly greater than those of 23MC/PAN system. This result indicates that the DMAc component gives an additional interaction in the blend system with three components, 23MC/DMAc/PAN, indicating hydrogen bonds engaged between OH at the C-6 position and the CN with DMAc as the intermediate. The quantitative i.r. results suggested that about 30% of primary OH groups at the C-6 position interacted with other molecules by intermolecular hydrogen bonds.

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