Blends of cellulose with polyacrylonitrile prepared from *N,N*-dimethylacetamide–lithium chloride solutions

Yoshiyuki Nishio*, Saroj K. Roy and R. St John Manley†
Pulp and Paper Research Institute of Canada, and Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2A7
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Blend films of cellulose with polyacrylonitrile were obtained over the whole composition range from solutions in *N,N*-dimethylacetamide–lithium chloride by coagulation in a non-solvent. Visual inspection and optical microscopic observation gave no indication of phase separation in any of the blends. Detailed characterization of the state of miscibility was carried out by wide-angle X-ray diffraction, differential scanning calorimetry and dynamic mechanical measurements. The wide-angle X-ray diffraction patterns of the blends were composed of the diffraction rings from the individual polymer crystals, but qualitative estimates showed that the degree of crystallinity was low, especially in the cellulose component. From an estimation of the glass transition temperature by differential scanning calorimetry and dynamic mechanical techniques, it was found that the blends exhibited considerable miscibility at the molecular level in the amorphous regions above 50 wt% cellulose content. A possible explanation of the results is presented through consideration of a specific interaction between the hydroxyl groups of cellulose and the nitrile groups of polyacrylonitrile.

(Keywords: cellulose; polyacrylonitrile; blends; dimethylacetamide/lithium chloride; miscibility; characterization)

INTRODUCTION

Much attention has been focused on polymer blends during the past decade in both academic and industrial research fields. It is anticipated that such materials will show new, desirable physical and/or physicochemical properties not to be expected in conventional homopolymers. Compatibility and phase-separation behaviour, morphological characteristics, mechanical properties, permeability and adsorption, etc., have been extensively investigated in many systems of multicomponent polymers[1,2]. Somewhat surprisingly, however, there have been few detailed studies dealing with polymer blends where one component is unmodified cellulose, except for mechanical blends in the form of fibres. This is probably due to certain disadvantages inherent in the preparation of cellulose blends with synthetic polymers; e.g. cellulose cannot be melted and no convenient organic solvent for the polymer was known until quite recently. In the past few years a variety of new solvents for the dissolution of cellulose have been described[3–6] and thereafter as a matter of course the study of cellulose blends has also become a subject of increasing interest[7–10].

This paper is concerned with the miscibility characterization of cellulose with polyacrylonitrile (PAN) in blend films regenerated from mixed polymer solutions in *N,N*-dimethylacetamide (DMAc)–lithium chloride (LiCl). Similar attempts to obtain cellulose/PAN blends have previously been made using different solvent systems, e.g. *N,N*-dimethylformamide (DMF)–nitrogen dioxide (NO_2)[7] and dimethylsulphoxide (DMSO)–paraformaldehyde (PF)[8], where transparency, tensile mechanical properties, etc., of the blends were described, but there was little detailed examination of the miscibility of the two polymers. The solvent DMAc–LiCl used in the present work is known as a so-called 'true solvent' of cellulose in which no appreciable degradation of the molecules takes place, and thus could also be of importance in future practical applications[11–15]. In the present investigation, we found that cellulose/PAN blend films can be easily obtained over the entire composition range by use of DMAc–LiCl, and from measurements of differential scanning calorimetry (d.s.c.) and dynamic mechanical relaxation we found that there is high miscibility at the molecular level in the amorphous regions of the blends above 50 wt% cellulose content. This result is discussed by considering the possibility of a specific chemical interaction between the two polymers.

EXPERIMENTAL

Sample preparation

A wood pulp with a degree of polymerization (*DP*) of 935 was used as the cellulose sample. The other polymer, polyacrylonitrile (PAN), was purchased from Polyscience Inc.; the nominal molecular weight was 150 000. Reagent-grade *N,N*-dimethylacetamide (DMAc) (Aldrich Chem. Co. Inc.) was stored for more than 1 week over potassium hydroxide before use. Lithium chloride (LiCl) (Aldrich Chem. Co. Inc.) was dried for 24 h at ~80°C in a vacuum oven and stored in a desiccator until used.

DMAc–LiCl used as a common solvent for both

*On leave from Faculty of Engineering, Fukui University, Bunkyo 3-9-1, Fukui 910, Japan
†To whom correspondence should be addressed

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polymers was prepared at a salt concentration of 4 wt% by stirring a mixture of weighed amounts of DMAc and LiCl at about 50°C. The cellulose sample treated by a solvent exchange technique[15] successively with water, methanol and DMAc was added to the DMAc–LiCl solution at room temperature so as to give an actual cellulose concentration of 1.5 wt%. The cellulose fibres dissolved gradually in the solvent under continuous stirring over a few days. After stirring for 1 week, the viscous cellulose solution was filtered through a coarse fritted-glass funnel under full mechanical pump vacuum. A 1.5 wt% PAN solution in DMAc–LiCl was also prepared in a similar manner as above.

The polymer solutions thus separately prepared were mixed in appropriate ratios at room temperature. The mixed solutions were stirred for at least 2 days and then poured into a rectangular glass tray with a flat bottom. By gently applying a proper amount of ethanol as coagulant onto the spread solution, the cellulose/PAN blends were precipitated instantaneously in a gel form. The gel films were steeped for about 4 h in ethanol which was exchanged for fresh aliquots several times. The samples were finally washed successively with methanol, water and ethanol. This seemed to be a more effective treatment for thoroughly extracting DMAc and LiCl, compared with a rinse with ethanol only. The washed samples were allowed to dry slowly on a Teflon plate at room temperature. The solid films finally obtained were further dried at ~55°C overnight under high vacuum and stored in a desiccator until used. Cellulose and PAN homopolymer films were also obtained by the same coagulation method as mentioned above. In what follows, the composition of the cellulose/PAN blends will be denoted by the ratio of weight contents of the components.

Sample characterization

Wide-angle X-ray diffraction (WAXD) patterns were recorded in a flat-plate camera using nickel-filtered Cu K_α radiation from a Philips generator operated at 40 kV and 20 mA. Differential scanning calorimetry (d.s.c.) was made on 10–20 mg samples with a Perkin–Elmer DSC-2C. The scans were run at a heating rate of 20°C min^{-1} from 40°C up to 220°C in an atmosphere of nitrogen. The result of the first run is not described here because the thermograms were often disturbed due to the presence of trace amounts of DMAc and/or water. The result of the second run, which was done after rapid cooling following the first heating, is usually reported. Dynamic mechanical measurements were carried out with a Rheovibron model DDV-II viscoelastometer (Toyo Baldwin Co. Ltd) at 11 Hz usually in the temperature range −40 to 210°C, the temperature being raised at a rate of about 1°C min^{-1}. Prior to the measurement, for removal of the last traces of solvents and relaxation of possible stresses, the sample was sandwiched between a glass plate and a cardboard strip and heated in an oven at about 150°C for 10 min.

RESULTS AND DISCUSSION

Solutions of cellulose/PAN blends were optically clear at the polymer concentration (1.5 wt%) studied here, and neither precipitation of the polymers nor separation into bilayers took place to the naked eye over the whole range of the composition (90/10–10/90) even after 2 months. Solid blends prepared from the solutions by regeneration in a coagulant were also transparent. From observations under an optical microscope, there appeared to be no indication of phase separation at any higher level above micrometre size.

The WAXD patterns of the blend films showed no anomalous diffraction rings distinct from those coming from the individual crystalline structure of each polymer. The cellulose component gave diffuse diffraction rings at angular positions corresponding to the cellulose II modification, as illustrated for an 85/15 blend in *Figure 1*. A broad ring ($2\theta = 20°$) resulting from the (1 0 $\bar{1}$) and (0 0 2) reflections of cellulose II is observable just outside the main PAN ring ($2\theta = 17°$), and another diffuse ring located at $2\theta = 34°$ can be assigned as arising from the (0 4 0) planes of cellulose II. It is generally known that celluloses precipitated in non-aqueous media with avoidance of stress are predominantly amorphous[16]. The low crystallinity of the cellulose component seems to be due not only to the mild precipitation conditions but also in part to the presence of the other polymer component PAN. Actually, the X-ray reflection intensities of cellulose were drastically reduced with increasing PAN content and in a 30/70 blend no appreciable diffraction maximum of the cellulose crystals could be observed. On the other hand, a ring at $2\theta = 17°$ coming from the (1 0 0) and (0 1 0) planes of the pseudo-hexagonal PAN lattice[17,18] could be perceived in the blends whose cellulose/PAN composition ranged from 10/90 to 90/10. PAN is commonly assumed to be a semicrystalline polymer which exhibits only a regularly repeating chain-to-chain lateral ordering and has no definite longitudinal repeat spacing in the crystalline phase[17–19]. Accordingly, it may be presumed that the present system is a poorly crystalline blend containing a small amount of crystalline material dispersed in a more abundant amorphous phase. In what follows, the miscibility in the amorphous regions of the blends is discussed in some detail on the basis of the results of measurements of the glass transition temperature T_g using d.s.c. and dynamic mechanical techniques.

The d.s.c. thermograms of selected cellulose/PAN

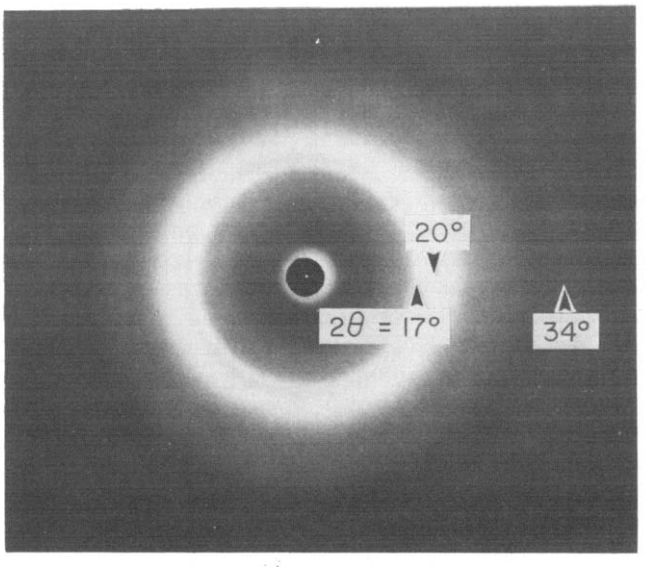


Figure 1 Wide-angle X-ray diffraction pattern of a cellulose/PAN (85/15) blend prepared from solution in DMAc–LiCl

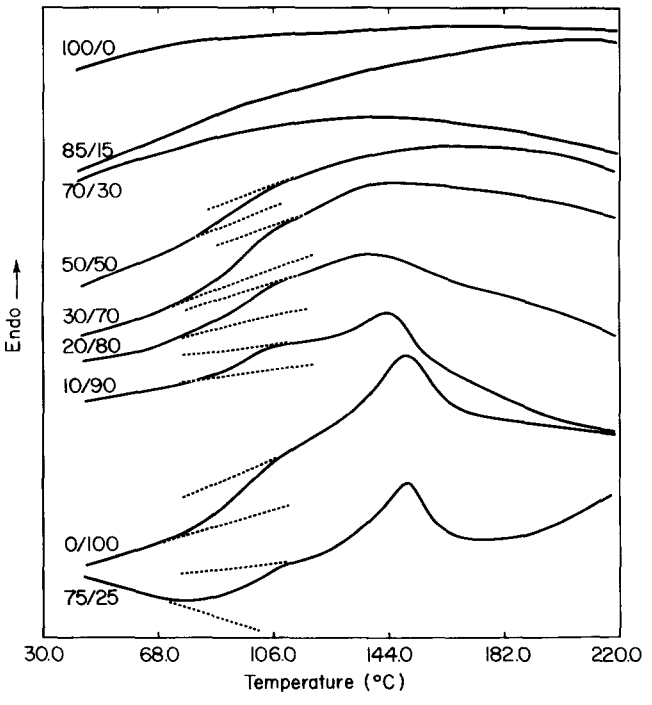


Figure 2 Differential scanning calorimetric thermograms of cellulose/PAN blends (100/0–0/100) obtained from solutions in DMAc–LiCl and a mechanical blend (75/25) of fine powders of both polymers. The numbers denote the weight percentage of each component

samples are shown in *Figure 2* where, for comparison, a thermogram of a blend obtained by mechanical mixing of both polymers as a fine powder is also given. In the d.s.c. curve of the PAN homopolymer film, there is an apparent change in slope in the temperature range 77–104°C and an endothermic peak around 150°C. The former change corresponds to a discontinuity in heat flow (which is related to specific heat), caused by passing through the glass transition of PAN on heating. The glass transition temperature T_g of PAN was estimated here to be 89°C from the midpoint of the discontinuity of specific heat. This T_g value lies between 85°C reported by Bohn *et al.*[17] and 104°C reported by Krigbaum *et al.*[20] in their dilatometric studies. On the other hand, it should be noted that the appearance of the broad peak at 147°C is not due to the normal melting of PAN crystals. Usually, PAN bulk polymers undergo a thermal reaction above ~250°C before the melting temperature T_m is reached[20–23]. Krigbaum *et al.* have given 317°C for the T_m value from the determination of melting point depression by a dilatometric technique using polar solvents as a diluent[20]. In the case where the PAN original powder was used in our d.s.c. experiment, no endothermic peak was observed up to 220°C in the first scan, while the glass transition was apparent over the range of about 80–110°C. In the second scan, however, we obtained almost the same d.s.c. thermogram as shown for the PAN film in *Figure 2*. Therefore, the endothermic peak visible at about 150°C can be attributed to disappearance of some kind of ordering of PAN, i.e. the melting of 'imperfect' PAN crystals developed as a result of the d.s.c. first heating up to 220°C followed by rapid cooling to 40°C.

As cellulose is blended with PAN up to 50 wt%, the glass transition of PAN tends to lose its prominence with an accompanying slight elevation in the T_g value. In addition, as soon as a small amount of cellulose is blended, the endothermic peak of imperfect PAN crystals becomes broader and its maximum position shifts to the lower temperature region. The peak is already diffuse in a 30/70 blend and then disappears above this cellulose content. The observed melting point depression and peak broadening indicate that the ordered association of PAN molecules is restrained by the presence of cellulose. This suggests that the miscibility of the two components increases with an increase in cellulose content.

Above 50 wt% cellulose in the blend composition, not only the endothermic peak but also the glass transition is no longer detectable in the temperature range of the d.s.c. scan. In contrast with this, mechanical blends of both polymers exhibited the PAN glass transition as well as the melting of the imperfect crystals in the d.s.c. thermograms (second run), as demonstrated for a sample with 70/25 composition in *Figure 2*. As is generally known, it is difficult to estimate precisely the T_g value of unmodified cellulose. According to the literature[24–27], the cellulose T_g is described to be in the region 200–250°C in dielectric, n.m.r. and other studies, in spite of the occurrence of significant chemical decomposition in the temperature region. In our d.s.c. study, the cellulose sample was beginning to decompose above ~240°C with no evidence of clear discontinuity in specific heat due to the glass transition.

Judging from the d.s.c. results, the present blend system does not show thermodynamic miscibility in the composition range 0/100–50/50 of cellulose/PAN. Above 50 wt% cellulose content, however, it is possible that there may be a high level of miscibility in the blends, notwithstanding the fact that no new distinguishable glass transition could be observed in the d.s.c. thermograms.

As far as detection of T_g is concerned, dynamic mechanical testing may be more sensitive than calorimetric measurements in many cases of blend studies[28]. Accordingly, acting on the possibility of finding the glass transition of the blends with more than 50 wt% cellulose, we next measured the dynamic mechanical relaxation. The results are given in *Figures 3* and *4*.

Figures 3a and *3b* show the temperature dependence of the mechanical loss tangent (tan δ), and the dynamic storage modulus (E') and loss modulus (E''), respectively, for samples containing 100–50 wt% PAN. The dynamic mechanical properties of PAN homopolymers have previously been investigated by other workers[29–32]. Okajima *et al.* have studied solution-spun PAN filaments in detail and discussed the existence and origin of three relaxations, α_x (140–160°C), α_a (85–110°C) and β (40–70°C)[32]. In the present work, a PAN film obtained by the same procedure as applied for preparation of the blends exhibited a peak of tan δ with the maximum at 106°C and a slight shoulder in the range 140–170°C, as shown by the full curve in *Figure 3a*. The major tan δ peak can thus be designated as the α_a relaxation reflecting the glass transition of PAN. In the corresponding temperature region, a large decrease in E' and a peak in E'' also occur as seen in *Figure 3b*; here, the temperature at which E'' exhibits a maximum is somewhat lower than that of the tan δ maximum. The slight shoulder visible around 155°C on the PAN tan δ curve probably corresponds to the α_x transition defined by Okajima *et al.* They showed that the transition became prominent when PAN filaments were steamed at temperatures above 108°C and suggested that a less ordered crystalline phase generated by such a heat

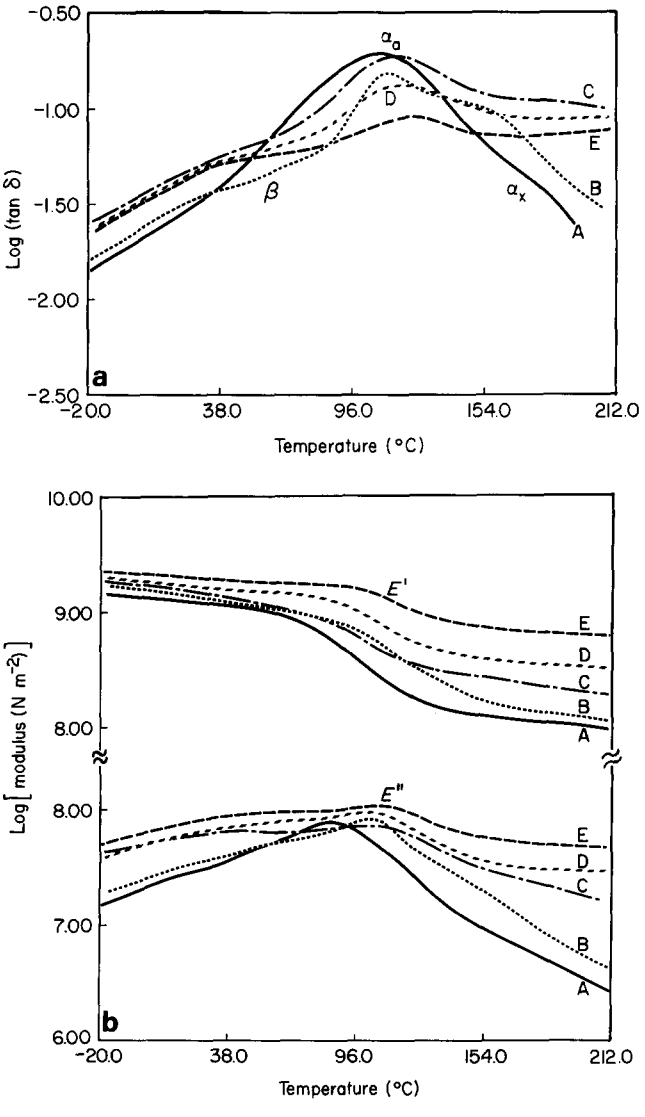


Figure 3 Temperature dependence of (a) the mechanical loss tangent (tan δ) and (b) the dynamic storage modulus (E') and loss modulus (E'') measured at 11 Hz for a series of samples containing 100–50 wt % PAN. Cellulose/PAN: A, 0/100; B, 0/100 (the preparation conditions differ from those of the other blends—see text); C, 20/80; D, 30/70; E, 50/50

treatment contributed to the appearance of the α_x relaxation. In *Figure 3*, a result obtained using another PAN sample is also given for comparison. This sample was allowed to dry overnight at ~100°C immediately after the coagulation followed by washing. On the tan δ curve of this PAN sample the α_x relaxation is clearer than that in the PAN sample described above. As previously discussed, it appears that in the d.s.c. study a small amount of imperfect PAN crystals is generated during the first heating cycle of the experiment. Presumably the α_x transition is due to molecular motion accompanying the disappearance of such an ill-defined crystalline phase induced by wet heating above 100°C or by heat treatment at higher temperatures.

In the present mechanical relaxation study it is of great interest to ascertain whether the PAN α_a peak shifts significantly by blending cellulose with PAN. As can be seen from *Figure 3*, when blending 20 or 30 wt % cellulose with PAN, the peaks of tan δ and E'', and the marked E' decrease, occur at slightly higher temperatures in comparison with the case for pure PAN samples; however, each main relaxation is still considered to be essentially the glass transition of the PAN amorphous phase separated from the cellulose phase. The extent of the shift in T_g becomes somewhat more perceptible at a composition of 50/50. This behaviour is consistent with the observed tendencies in the d.s.c. results.

When the cellulose content reached more than 50 wt %, a dramatic change took place with respect to the position of the main relaxation. In *Figure 4* the temperature dependences of tan δ, E' and E'' are shown for a series of samples with cellulose content above 50 wt % in the same logarithmic scale as in *Figure 3*. Here the glass transition, thought to originate from the molecular relaxation in the PAN amorphous phase, is no longer discernible. As the cellulose content increases from 70 wt % up to 90 wt %, the temperature shift of the principle transition becomes more and more pronounced, in spite of the broadening of the tan δ and E'' peaks and the decrease in magnitude of the E' drop. The main transition temperature, which varies sensitively depending on the composition, apparently corresponds to the T_g of the 'amorphous mixture' of cellulose and PAN which was not detected in the d.s.c. measurements for the blends containing more than 50 wt % cellulose.

The T_g value of the cellulose/PAN blends estimated from the tan δ and E'' plots are summarized in *Table 1*,

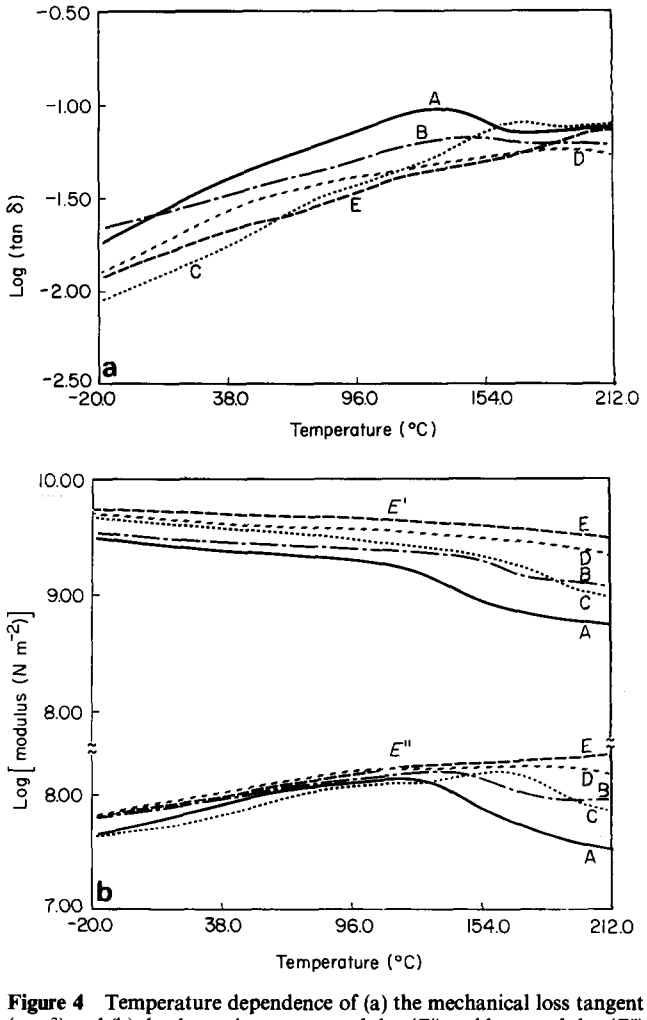


Figure 4 Temperature dependence of (a) the mechanical loss tangent (tan δ) and (b) the dynamic storage modulus (E') and loss modulus (E'') measured at 11 Hz for a series of samples with the cellulose content above 50 wt %. Cellulose/PAN: A, 70/30; B, 80/20; C, 85/15; D, 90/10; E, 100/0

Table 1 Glass transition temperatures of cellulose/PAN blends

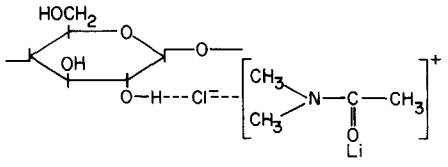
Cellulose/PAN (weight ratio)	Glass transition temperature (°C)		
		Dynamic mechanical	
	D.s.c.[a]	tan δ	E''
0/100	89	106 (111)[b]	87 (103)[b]
10/90	93	–	–
20/80	93	115	103
30/70	94	115	104
50/50	97	121	109
70/30	nd[c]	131	125
80/20	nd	148	146
85/15	nd	170	166
90/10	nd	194	192
100/0	nd	nd	nd

[a] From the midpoint of the discontinuity of specific heat
[b] For a sample dried at ~100°C immediately after coagulation followed by washing
[c] Not detected

where the data obtained from the d.s.c. study are also compiled. The T_g of cellulose itself could not be detected even by the dynamic mechanical measurements in the temperature range −40 to 220°C. As shown in *Figure 4a*, the tan δ value of cellulose increased almost monotonically with increasing temperature, except for two faint shoulders over the ranges 0–50°C and 80–150°C. The E' decreased continuously without any significant drop as the temperature was raised (see *Figure 4b*). A plot of the T_g values listed in *Table 1* against cellulose content (*Figure 5*) enabled us to predict the cellulose T_g to be approximately 240–260°C from the extrapolation to the 100% cellulose content. Interestingly, a T_g value of 250°C estimated from a torsional braid analysis of a regenerated cellulose[26] is just in the predicted temperature range.

In the ideal case for determination of polymer miscibility by utilization of T_g, if a polymer blend exhibits a single glass transition between the T_g values of both components and if the sharpness of the transition is similar to that of each component, then the system can readily be regarded as a highly miscible polymer blend[2]. In the present study, however, one component is cellulose, which hardly shows a clear glass transition until appreciable thermal degradation begins to occur. Taking into account the apparent suppression of the cellulose T_g, it seems reasonable to conclude from the evidence shown above that the present system exhibits a considerable miscibility at the molecular level in the amorphous regions above 50 wt% cellulose content.

For an understanding of the above miscibility behaviour, it is instructive to consider the possibility of a specific chemical interaction, e.g. proton transfer, between cellulose and PAN molecules. Cellulose molecules contain three hydroxyl groups in the anhydroglucose units and this is extremely favourable for such a specific interaction. Although the mechanism of dissolution of cellulose in DMAc–LiCl has not yet been completely established, it has been suggested[6,12,14,15] that the polymer is able to dissolve by forming some kind of complex with the solvent system. According to McCormick *et al.*[6,15], the hydroxyl protons on the anhydroglucose units hydrogen-bond to the chloride anion (Cl^-) which is in turn associated with a macrocation $Li[DMAc]^+$, as shown below:



In the case where there exists another polymer containing proton-accepting groups in the cellulose solution, the hydroxyl protons bound to the solvent complex could be separated from the anhydroglucose unit with an accompanying Cl^- as a counterion and transferred to the acceptor group. The other polymer, PAN, used here contains a –CN side group having a large dipole moment. As is commonly accepted for this polymer, strong intermolecular attractions are liable to occur due to dipole–dipole association between pairs of nitrile

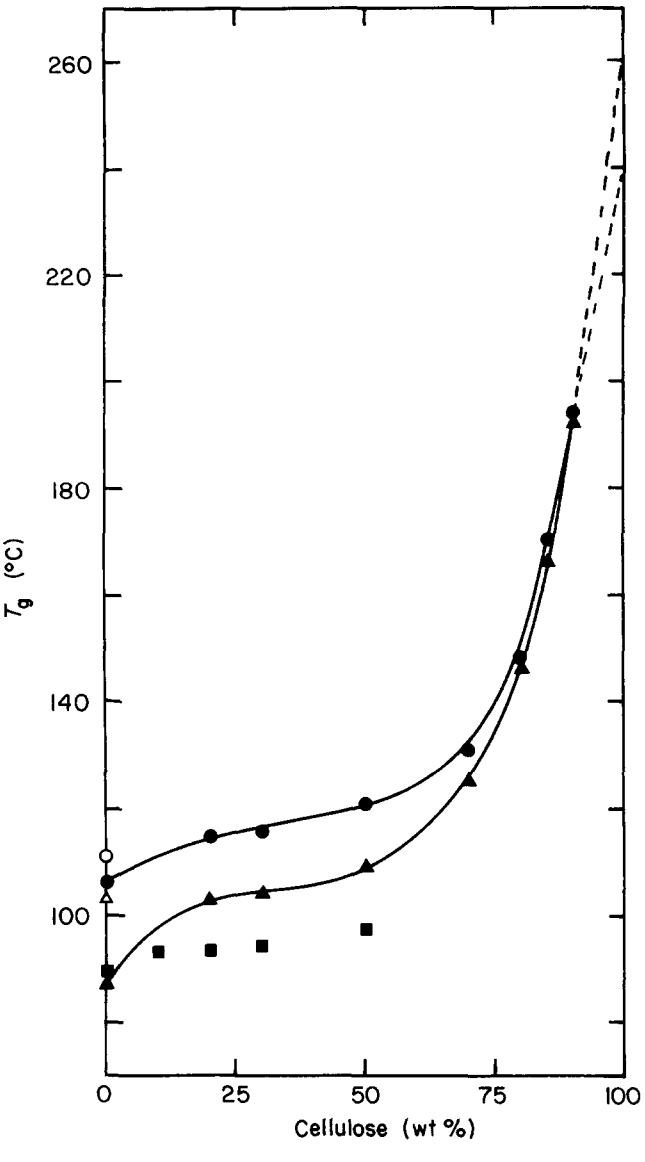
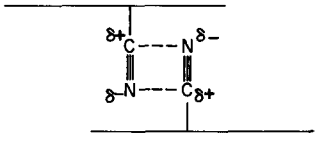
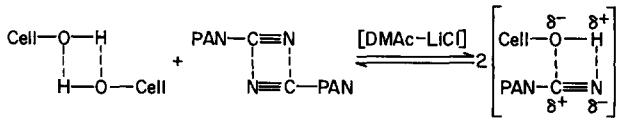


Figure 5 Plot of glass transition temperature against cellulose content in the blends. Filled circles correspond to data from tan δ measurements, solid triangles are data from E'' measurements, and squares are data from d.s.c. measurements. The open circle and open triangle correspond to the data in parentheses in *Table 1*. Extrapolation of the data to 100% cellulose content indicates that the T_g of cellulose lies in the range 240–260°C

groups[2,3], whose dipoles are oppositely oriented as shown below:



This dipole–dipole interaction is responsible for the poor solubility of PAN in most common solvents. Thus, this polymer dissolves only in polar aprotic solvents such as DMF, DMSO, DMAc, etc. In the present study, we noted qualitatively that the dissolution of PAN in DMAc–LiCl was completed more rapidly compared with the case where only DMAc was used. This suggests that the addition of LiCl to DMAc contributes to further weakening of the dipole–dipole interactions between nitrile groups. At higher proportions of the PAN component in the starting blend solution, there is probably still a tendency for dipole–dipole attractions between PAN molecules, without the action of a large amount of –CN groups as a proton acceptor. As the concentration ratio of cellulose to PAN increases, however, the proton-accepting capacity of the nitrile groups in PAN would manifest itself so strongly that the state of miscibility is markedly enhanced in the blend solution. It may then be assumed that the following equilibrium is attained by the strong interaction between cellulose and PAN with the aid of DMAc–LiCl:



It is also reasonable to suppose that such a good state of miscibility in solution can be carried over to a considerable extent into the solid produced by rapid coagulation of the blend solution.

The importance of specific interactions defined by the proton donor–acceptor concept is now well recognized for understanding the attainment of miscibility in many polymer blend systems[1,2]. At present, we have no direct evidence for the above-mentioned specific interaction for this system. For the precise quantification, further study will be required together with the complete elucidation of the dissolution mechanism of cellulose in the DMAc–LiCl solvent. From a practical standpoint, the intimate cellulose/PAN blends discussed here are expected to show desirable properties that cannot be realized in mechanical blends.

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