

Studies of Polymer-Cellulose Blends Prepared from Solution

AMIR H. JOLAN and ROBERT E. PRUD'HOMME,* *Département de Chimie, Université Laval, Québec 10, PQ, Canada G1K 7P4*

Synopsis

The conditions under which cellulose-cellulose triacetate (CTA) and cellulose-poly(acrylonitrile) (PAN) blends can be prepared from solution, are described in this paper. These two systems form transparent films when the blend contains less than 50% PAN or 60% CTA. Young's modulus, tensile strength, and elongation at rupture were measured for these blends. These values usually are between those of the corresponding homopolymers, except for the blend containing 10% polymer (PAN or CTA) which has a tensile strength value larger than that of cellulose. This result seems to indicate a certain level of compatibility for this blend. However, x-ray measurements indicate the presence of two crystal structures for these systems, suggesting that compatibility does not exist at the molecular level, in the crystalline fraction of the samples.

INTRODUCTION

Several synthetic polymer blends have been studied in the recent years and some of them are demonstrating unexpected physical and/or mechanical properties. These blends must present a certain level of compatibility as demonstrated experimentally by one or several of the following criteria¹: transparency of the films, a single glass transition temperature, a mixed crystal structure.

Very few attempts have been made to prepare blends where one of the two components would be cellulose. This could have been difficult several years ago when no convenient solvent was available to dissolve the cellulose. But in recent years, solvents have been reported that have two remarkable properties: they do not degrade induly the cellulose and they can be used to dissolve as well a certain number of synthetic polymers and cellulose derivatives.

It has been shown that cellulose can be dissolved by a solution of nitrogen dioxide in a very polar and aprotic solvent like dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO).²⁻⁴ The cellulose is found within the solution in the form of a nitrite ester;⁴ it can easily be regenerated by contact with a protic solvent like alcohol and water. Several synthetic polymers or cellulose derivatives can be added to the solution, which remains clear, and films can be regenerated from these solutions.^{4,5}

The cellulose can also be dissolved in an aqueous solution of a cyclic amine oxide, probably forming a cellulose-cyclic amine oxide complex.⁶ The cellulose can then be regenerated into films or fibers. Several synthetic polymers can be dissolved in the same solvent and solid blends formed by regeneration^{6,7} or solvent evaporation.⁷

Finally, it has been reported that cellulose and some synthetic polymers and cellulose derivatives can be dissolved in a polar and aprotic solvent containing a certain amount of sulfur dioxide and of an amine.⁸

* To whom all correspondance should be sent.

We have then used the NO_2 -DMF solvent to prepare cellulose-polymer solutions containing different proportions of polymer. Films were regenerated from these solutions. The mechanical properties and the x-ray structure of these blends were determined. Only the NO_2 -DMF solvent was used in this work since it is rapidly prepared and it gives a quick dissolution. The cyclic amine oxide solvent was not used since its preparation is rather slow (it requires several hours according to Refs. 6 and 7), and the SO_2 -amine-DMF solvent was rejected since it does not rapidly dissolve the cellulose contrary to what is claimed in reference 8.

DISSOLUTION AND DEGRADATION OF THE CELLULOSE

A cellulose fluff was used in this work. This fluff was prepared from Whatman filter paper No. 42, which was suspended in water, torn into shreds in a mixer, and solvent exchanged in ethanol and benzene. The fluff was finally obtained by evaporation of the benzene.

The preparation of cellulose solutions was made as follows: a 2% cellulose fluff suspension was prepared in DMF or DMSO and kept at 5°C . To this solution, liquid NO_2 also kept at 5°C in a refrigerated buret, was added while vigorously stirring. The dissolution was completed within 5 min giving a transparent green solution. It has been found experimentally that seven moles of NO_2 are required per mole of anhydroglucose unit of cellulose. Below this value, the dissolution is incomplete. Increasing concentrations of NO_2 have been reported to produce a larger amount of degradation of the cellulose.⁹ Higher concentrations of cellulose were possible, but at 3% concentration, the solution became very viscous and the regeneration of cellulose films did not succeed. These results are in agreement with the findings of several groups of workers.²⁻⁵

It has been reported before that degradation of cellulose takes place in the NO_2 -DMF solvent.^{3,9-11} We have found that if the cellulose solution is kept at room temperature, it degrades rapidly and film formation is impossible after about 12 hr. However, if the solution is maintained between 0° and 5°C , it has been reported that a degree of polymerization (DP) larger than 600 can be preserved.^{4,10}

In order to more precisely check this point, viscosity measurements were made on cellulose samples recovered from the solution kept at 5°C . After the dissolution, solution aliquots were taken at different times and poured in a nonsolvent (usually ethanol) with vigorous stirring. The precipitated cellulose was dried and viscosity measurements were made in cupriethylenediamine ("Ecusta Cellulose Solvent" from Allied Chemicals) in an Ubbelohde viscometer. From the value of the intrinsic viscosity of the cellulose $[\eta]$, its degree of polymerization DP, and its molecular weight MW, were calculated according to

$$[\eta] = 5.88 \times 10^{-3} \text{ DP} \quad (1)$$

Results thus obtained are presented in Table I. It is seen that the DP of cellulose decreases during several hours, but that after one day it reaches a constant value which is maintained for several weeks. This value of DP is similar to that of commercial cellophane films. Cellulose solutions kept at 5°C , between 1 and 23 days, were then used to prepare films.

The films were made by regeneration in a nonsolvent on a glass plate. The

TABLE I
Measurements of the Intrinsic Viscosity of Cellulose Kept at 5°C for Various Times in
DMF-NO₂ Solvent

Time kept in solution	$[\eta]$ (dl/g)	DP	MW (g/mole)
Initial cellulose	6.60	1120	181,000
20 min	5.80	985	159,000
50 min	5.60	950	154,000
120 min	5.40	920	148,000
1 day	4.70	800	129,000
2 days	4.68	796	128,000
4 days	4.50	765	124,000
10 days	4.40	750	121,000
13 days	4.70	800	129,000
23 days	4.50	765	124,000

plate was first washed with ethanol or methanol. The solution was poured on the plate and washed with nonsolvent. A second glass plate was put on top of the preparation to make a film of uniform thickness. After 30 min, the top plate was removed, the preparation washed with the nonsolvent and the sample placed in an oven at 50°C for drying. Dryness was checked by heating a fraction of the film on a Mettler hot stage and observing on a microscope for the evaporation of solvent. Dry films were used for further measurements.

CELLULOSE-POLYMER SOLUTIONS

Several synthetic polymer and cellulose derivatives are reported to be soluble in DMF or DMSO.^{4,6} As shown in Table II, cellulose acetate and triacetate, poly(vinyl acetate), poly(methyl methacrylate), poly(acrylonitrile), and carboxy-methyl-cellulose form transparent 1% concentration solutions in DMF or DMSO. They also form a transparent and stable 1% concentration solution when mixed with cellulose in NO₂-DMF. However, only cellulose acetate and triacetate, polyvinyl acetate and polyacrylonitrile form transparent films when the cellulose-polymer solution is regenerated. The transparency of the films is a necessary requirement in order to have interesting mechanical or physical

TABLE II
Preparation of Cellulose-Polymer 50%-50% Solutions and Films

Polymer	Solubility of a 1% solution in DMF or DMSO	Cellulose-polymer 50%-50% solution (1% concentration)	Blend
Cellulose acetate	Completely soluble	Transparent solution; no phase separation	Transparent film
Cellulose triacetate			
Poly(vinyl acetate)			
Poly(methyl methacrylate)			
Poly(acrylonitrile)			
Carboxy-methyl-cellulose			Turbid film
Nylon 6,6	Insoluble	—	—

properties of the blend. It indicates a certain compatibility between the phases of the mixture.¹ However, as we will see in more details later, this is not an absolute criterion for compatibility. Even if nontransparency of the film can be taken as a sure indication of incompatibility, transparency does not indicate complete compatibility.

On the basis of Table II, we have chosen for further studies two of these polymers: polyacrylonitrile (PAN) and cellulose triacetate (CTA). Films were regenerated from the polymer-cellulose solution in the same manner as indicated for cellulose. PAN and CTA films were prepared by solvent evaporation.

However, it was not possible to prepare with these polymers, cellulose-polymer solutions for all polymer compositions. As indicated in Table III, transparent solutions can be made only with 60% or less CTA in the mixture. Furthermore, these solutions are not in a thermodynamic equilibrium state since they precipitate after a certain time. This time period is however long enough to permit one to prepare films from these solutions. These blends seem to be stable since they keep their transparency even after one year.

For the cellulose-PAN solutions, the situation is similar to that presented in Table III, except that precipitation already occurs for a solution containing 60% PAN.

MECHANICAL PROPERTIES

Tensile mechanical properties of the blends were measured with an INSTRON tensile machine, Model 1130, at room temperature, and at about 20% humidity. The rate of elongation was 0.83%/min in all cases. All samples were 7 mm wide and about 9 cm long (about 6 cm between the grips). The thickness of all samples was measured with a micrometer. All experimental data reported are an average of at least six measurements, and in most cases of nine or ten measurements.

Stress-strain curves obtained for some cellulose-CTA blends are presented

TABLE III
Preparation of Cellulose-CTA Solutions and Films

% CTA in cellulose-CTA solution (2% concentration) (%)	Remarks on the solution	Solvent used	Nonsolvent used	Blend
0	Transparent, stable	DMF or DMSO	Ethanol or methanol	Transparent
10				
20				
30	Transparent; precipitation after 2.5 hr	DMSO	Ethanol	
40				
50				
60				
70	Instantaneous precipitation	DMF or DMSO	—	—
80				
90				
100	Transparent; stable	—	Solvent evaporation	Transparent

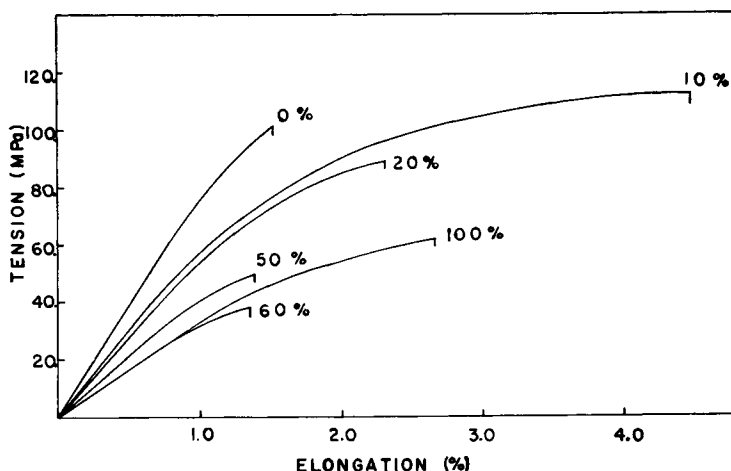


Fig. 1. Stress-strain curves for the cellulose-CTA blends.

in Figure 1. It is seen that most curves are included between those for cellulose and CTA indicating intermediate values of Young's modulus, of tensile strength and of elongation at rupture. The only notable exception is the curve for the blend containing 10% CTA which we shall discuss later on.

Individual values of Young's modulus, tensile strength and elongation at rupture for all the cellulose-CTA blends investigated are presented in Table IV. All modulus values are found between those of cellulose and CTA. The tensile strength and elongation at rupture values for the blend containing 10% CTA are higher than those for the cellulose while they are smaller than those for CTA for the blends containing 40%–60% of CTA.

It is not clear from these results whether the components of the blends are compatible or not. If compatibility exists, one could expect values of tensile strength equal or larger than those computed using the laws of mixture since it has been shown that compatible blends of poly(2,6 dimethyl-1, 4 phenylene oxide) (PPO) with random copolymers of styrene and 4-chlorostyrene, present a maximum in the plot of tensile strength vs. volume fraction of PPO, while incompatible blends present a minimum in such a plot.¹³ Values of Young's modulus reported in Table IV are lower than those calculated from the law of mixture. The tensile strength of the blend containing 10% CTA is higher than

TABLE IV
Mechanical Properties of the Cellulose-CTA Blends

% CTA in the blend	Young's modulus (GPa)	Tensile strength (MPa)	Elonga- tion at rupture (%)
0	7.87	102	1.43
10	6.10	112	4.22
20	5.59	90.8	2.32
30	5.13	83.2	2.25
40	3.73	43.1	1.51
50	4.37	49.7	1.39
60	3.29	38.1	1.33
100	3.29	61.8	2.66

those of the two homopolymers and the tensile strength of the blend containing 20% polymer is about equal to the value expected from the law of mixture. Other tensile strength values are lower than those calculated. These results seem to indicate the possibility of having a certain level of compatibility in the range of composition containing between 0% and 20% CTA.

Similar results are presented in Table V for the cellulose-PAN system. All reported values of Young's modulus are between those of the two homopolymers. The tensile strength of the blend containing 10% PAN is higher than that for the cellulose; those for the blends containing 30%–50% PAN are smaller than that for PAN. The stress-strain curves for this system are similar to those for the cellulose-CTA system, presenting no yield point in any case.

All modulus and tensile strength values, except that for the blend containing 10% PAN, are lower than those predicted from the laws of mixture. This seems to indicate no compatibility for the components of this system except in the region where the blend contains between 0% and 10% PAN.

X-RAY MEASUREMENTS

Mechanical properties measurements only give an indirect indication upon the compatibility of blend components. Direct evidences can be gained by observing the crystal structure of the blend, especially in a case as the present one, where the two components are partially crystalline.

Our x-ray measurements were made using a Philips generator equipped with a vertical goniometer and a special sample holder permitting one to make transmission studies. A Cu $K\alpha$ target was used.

X-Ray results are presented in Figure 2 for the cellulose-CTA blends. The cellulose pattern is that of cellulose II, characterized by large peak maxima at $2\theta = 13^\circ$ (101), 19° ($10\bar{1}$), 21° (002), and 33° (040).¹⁴ The CTA pattern is that of CTA II with large peak maxima at 9° , 10.5° , 13° , 17.5° , 18.5° , 22° , and 23° .¹⁵ The blends present composite x-ray patterns where the peaks characteristic of both CTA and cellulose can be seen. For example, the cellulose peak at 21° is seen for all blends. The cellulose peak at 33° is also present in all blends. However, it is clearly observed that the intensity of this latter peak decreases drastically in the blends indicating that the crystallinity of the cellulose component is seriously reduced, as soon as a small amount of CTA is present. There is no indication in these curves of the presence of a mixed crystal structure for the blend.

TABLE V
Mechanical Properties of the Cellulose-PAN Blends

% PAN in the blend	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at rupture (%)
0	7.87	102	1.43
10	6.54	125	3.64
20	4.53	79.0	1.94
30	5.35	72.4	1.60
40	4.16	61.3	1.60
50	3.59	43.7	1.26
100	3.38	74.5	3.82

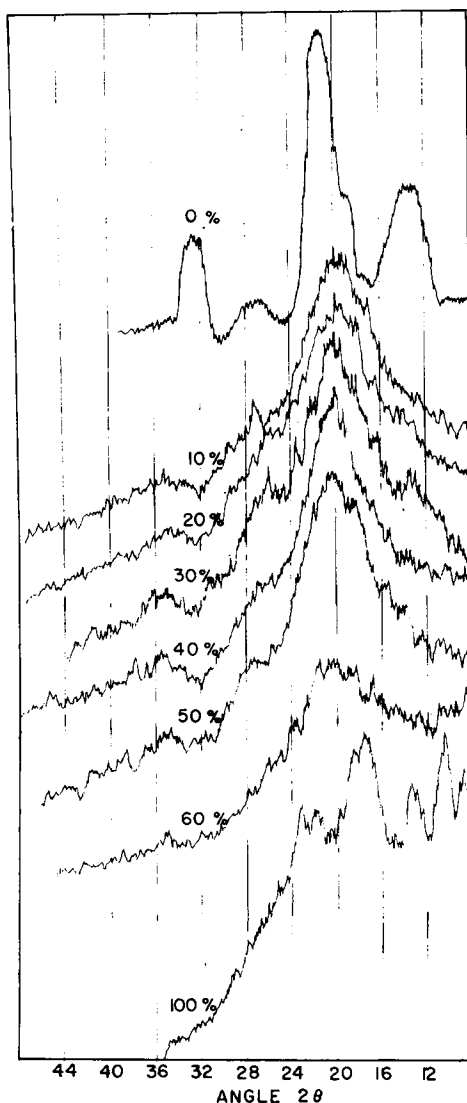


Fig. 2. X-Ray scattering curves for the cellulose-CTA blends.

In Figure 3, x-ray curves for the cellulose-PAN system are presented. The PAN curve is characterized by a large peak at 17° .¹⁶ This peak can be seen in all blends, even in the one containing only 10% PAN. Similarly, the cellulose 21° and 33° peaks are detected for all blends although the crystallinity of the cellulose is greatly reduced when PAN is present in the film. No indication of a mixed crystal structure can be seen in these curves.

The above x-ray results clearly indicate that at the molecular level, there is no compatibility between the two phases of the blend in the crystalline fraction of the sample. Compatibility would result in the formation of a mixed crystal structure giving rise to an x-ray curve having no direct relation with those of the two separate components of the blend. But this does not rule out the possibility of having a certain form of compatibility in the amorphous fraction of the blends which is far more important than the crystalline one.

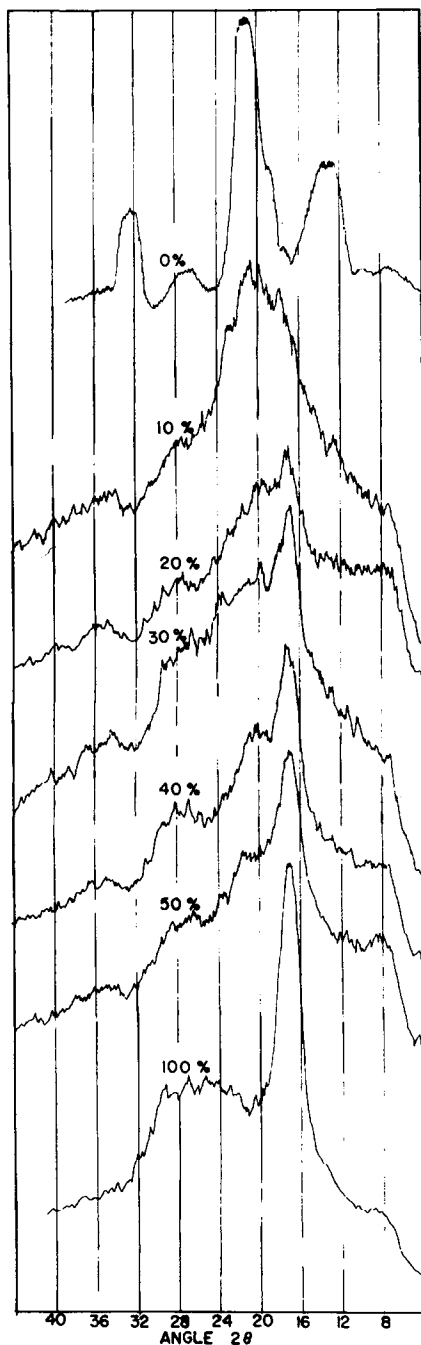


Fig. 3. X-Ray scattering curves for the cellulose-PAN blends.

DISCUSSION AND CONCLUSION

It is thus possible to prepare cellulose-CTA and cellulose-PAN blends that present a certain level of compatibility since the films prepared from these blends are highly transparent. But it must be clear that transparency is not a criterion for total compatibility. It is rather an indication of the nonsegregation of the

phases at the micron size level. Phase separation at this level would necessarily lead to light scattering and high turbidity of the films.¹⁷

On the other hand, x-ray measurements give direct evidences of the presence or absence of compatibility at the molecular level. In the present case, it is clear that the compatibility does not exist in the crystalline units but, as we said before, this does not exclude completely the possibility of having compatibility at the molecular level in the amorphous regions of the sample.

Since we have shown that compatibility exists in these blends at the micron size level but that it probably does not exist at the molecular level, the following question arises: At what point does phase separation occur in these systems? The mechanical properties can only give indirect indications about this problem. But looking at Tables IV and V, we are tempted to say that for blends containing more than 20% polymer the compatibility is not extended at the submicron level while for those containing 10% PAN or CTA, or 20% CTA, the compatibility probably exists at the submicron level since in the former case the tensile strength values are lower than those expected from the law of mixture while for the latter case, they are higher than those predicted from the law of mixture. It seems reasonable to observe different levels of compatibility for blends containing different polymer compositions.¹ When the polymer fraction is low, the polymer molecules can be relatively well dispersed in the cellulose matrix while when it is high, polymer domains will be formed inside the cellulose matrix. In this latter case, if the polymer-cellulose interaction is not strong, large defect zones can thus be formed and can decrease drastically the mechanical properties of the blend.

Moreover, it is interesting to observe that the compatibility range in the cellulose-CTA blend is larger than that in the cellulose-PAN blend. This is reasonable since the structural form of CTA is quite similar to that of cellulose and this may favor a better dispersion of the CTA in the matrix, or/and a better cellulose-polymer interaction than with PAN.

One can note that the whole discussion about compatibility has been made without reference to the solubility parameters of the components of the blends. Even if the solubility parameter has been often used as a criterion for compatibility, it is now recognized that it has very little value especially when dealing with solid components which are partially crystalline and hydrogen bonded.¹

This work was supported by grants from the National Research Council of Canada and the Ministère de l'éducation de la province de Québec (FCAC). This study is included in the research program of the Groupe de recherche sur les macromolécules (GRM) of Laval University.

References

1. S. Krause, *J. Macromol. Sci., Rev. Macromol. Chem., C*, **7**, 251 (1972).
2. L.-P. Clermont, Canadian Patent No. 899, 559, May 9, 1972.
3. L.-P. Clermont, and F. Bender, *J. Polym. Sci., Part A-1*, **10**, 1669 (1972).
4. R. G. Schweiger, *Tappi*, **57**, 86 (1974).
5. British Patent No. 1, 198, 236, July 8, 1970.
6. British Patent No. 1, 144, 048, March 5, 1969.
7. British Patent No. 1, 144, 759, March 12, 1969.
8. British Patent No. 1, 197, 322, July, 1970.
9. M. Pasteka and D. Mislovicova, *Cell. Chem. Technol.*, **8**, 107 (1974).
10. D. Mislovicova, and M. Pasteka, *Cell. Chem. Technol.*, **8**, 481 (1974).
11. M. Pasteka and D. Mislovicova, *Cell. Chem. Technol.*, **9**, 325 (1975).

12. S. Newman, L. Loeb, and C. M. Conrad, *J. Polym. Sci.*, **10**, 463 (1953).
13. J. R. Fried, F. E. Karasz, and W. J. Macknight, *Bull. Am. Phys. Soc.*, **22**, 312 (1977).
14. O. Ellefsen and N. Norman, *J. Polym. Sci.*, **58**, 769 (1962).
15. B. S. Sprague, J. L. Riley, and H. D. Noether, *Text. Res. J.*, **28**, 275 (1958).
16. R. B. Beevers, E. F. T. White, and L. Brown, *Trans. Faraday Soc.*, **56**, 1535 (1960).
17. R. S. Stein and R. E. Prud'homme, *Polym. Lett.*, **9**, 595 (1971).

Received March 29, 1977

Revised June 1, 1977