Partial Miscibility of Cellulose–Polyacrylonitrile Blends

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Synopsis

Cellulose-polyacrylonitrile (PAN) blends have been prepared by the regeneration of 2% concentration solutions in dimethylformamide–NO_2 solvent. The blends are transparent when containing between 0 and 50% by weight of PAN. Dynamic mechanical measurements indicate a shift in glass transition temperature T_g of PAN for the blends, suggesting partial miscibility between cellulose and PAN. Experimental density values larger than those predicted theoretically are also in agreement with this conclusion.

INTRODUCTION

The degree of miscibility (compatibility) of a blend is generally determined by using one or several of the following criteria: the transparency of the films, the observation of a single T_g, the glass transition temperature, the observation of a decrease in T_m, the melting temperature, and an increase in the blend density.[1] Other methods such as light scattering, NMR, or gas permeation studies are less often used.

But none of the above-mentioned methods can be considered as absolute:

(1) The transparency of a blend sample can be due (i) to true miscibility between the blend components or (ii) to a phase separation forming domains having dimensions smaller than the wavelengths of visible light; (iii) it can be an indication that both components have the same refractive indices[2] or (iv) it can be due to the formation of two layers while the solvent is evaporating for films prepared in this manner.[3]

(2) The observation of a single T_g for a sample is a clear indication of blend miscibility.[1] But examples are known where so-called compatible blends give a broadening of the two calorimetric transition widths[4,5] or where partial miscibility induces a displacement of the T_g of the individual blend components.[5–7]

(3) For crystalline–amorphous blends, the observation of the depression of T_m is also a very strong indication of blend miscibility. This observation is often coupled with a rapid decrease of the degree of crystallinity with blend composition.[8] But several miscible blends do not have a crystalline component.

(4) Usually, the density ρ of immiscible blends is given by[9,10]

$$\rho^{-1} = w_1\rho_1^{-1} + w_2\rho_2^{-1} \tag{1}$$

where ρ_1 and ρ_2 are the densities, and w_1 and w_2 are the weight fractions of the components 1 and 2 of the blend. Miscible blends may have densities larger than those predicted by eq. (1).[10–15] But an increase in density for an immiscible blend

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has also been observed.[15]   It thus seems that an increase in density as compared to the prediction of eq. (1) is a strong, but not an absolute proof of blend miscibility.   On the other hand, it has been suggested that an increase in the deviation from eq. (1) means an increase in miscibility[10–14] leading eventually to a maximum in the density–composition curve in the cases where total miscibility is present.[5,15]

In view of the facts reported above, it is clear that it is necessary to combine several methods in order to be able to decide upon the partial or complete miscibility of blend components.   We have followed this approach for cellulose-polyacrylonitrile blends, and the result of this investigation is reported in this paper.

CELLULOSE–POLYACRYLONITRILE BLENDS

Cellulose–polyacrylonitrile blends can be prepared by the regeneration of 2% concentration solutions in dimethylformamide (DMF) or dimethylsulfoxide (DMSO).   The polyacrylonitrile (PAN) is directly soluble in the DMF or the DMSO, but the cellulose has to be solubilized by the addition of NO_2, which transforms the cellulose into a cellulose nitrite ester.   However, the regeneration of the solution retransforms the nitrite ester into pure cellulose.   The molecular weight of the cellulose used is 127,000.   The PAN was obtained commercially from Aldrich Chemicals (No. 18,131-5).   The regeneration was made in ethanol or methanol.   Cellulose–PAN transparent blends could only be prepared for a PAN weight percent between 0% and 50%.   Details about film preparation can be found elsewhere.[17,18]

The miscibility criteria mentioned in the preceeding section of this paper have been applied to the cellulose–PAN blends and are reported in the following paragraphs:

Transparency

All prepared blends in the composition range between 0% and 50% by weight of PAN are transparent.   The refractive index of cellophane films[19] being 1.542 and that of polyacrylonitrile[20] being 1.518, the transparency cannot be due to the matching of the refractive indices of the blend components.   The transparency of cellulose–PAN films can then only be due to true compatibility or to the formation of domains having dimensions smaller than the wavelength of visible light; it cannot be due to the formation of two layers since the films were not prepared by solvent evaporation.

Observation of T_g

The dynamic mechanical spectra of the different blends have been measured on a Rheovibron DDV-II apparatus (Toyo Baldwin Co.) at a frequency of 110 Hz, as a function of temperature.   Even if we proceeded under nitrogen atmosphere, decomposition of the cellulose occurred from 150°C.   This latter temperature constitutes an upper limit above which we cannot trust our results, and consequently they will not be reported here.   The loss tangent tan δ and the loss modulus E'' curves obtained for cellulose, PAN, and two cellulose–PAN blends

are reported in Figure 1. In agreement with previous publications, the tan δ curve of cellulose increases slowly in this temperature range without any indication of a transition.[21] The T_g of cellulose is reported at 230°C in the literature.[20,21] The T_g of PAN is found from the E'' curve of Figure 1 at 92°C, in agreement with the literature values.[20]

The E'' and tan δ curves for the blend containing 12.5% PAN are monotonous. The small peaks seen in those curves are certainly not significant. The E'' curve for the blend containing 30% PAN has a well-defined peak at 115°C which seems to indicate a shift in T_g for this blend and thence a partial degree of miscibility.

However, one has to be cautious in interpreting these curves since the shift observed in the E'' curve of the 30% PAN blend could eventually be explained as resulting from an additive effect from the two components. In order to investigate this possibility, we have used the model approach previously described by Locke and Paul[22]: mechanical models are used to compute the loss modulus of the blend from the loss modulus values of the pure components. If the experimental shift is predicted from these calculations, it is certainly not due to the miscibility of the blend components since the models assume discrete noninteracting phases. If the experimental shift is not predicted by the calculations, it can be due to partial miscibility or to the inadequacy of the model. However, several models can be used to reduce the latter possibility.

In the present paper, we have used the three models proposed by Locke and Paul,[22] namely, the parallel, the series, and the dispersion model, described respectively by the following equations:

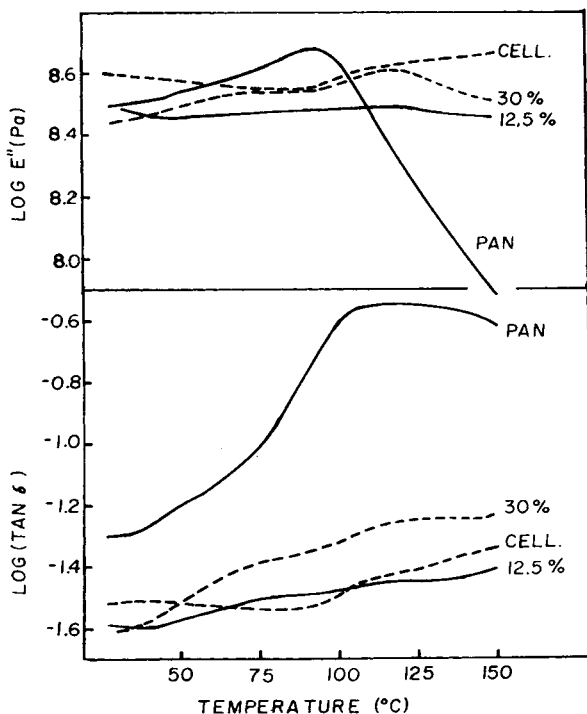$$E^* = E_1^* + v(E_2^* - E_1^*) \tag{2}$$

Fig. 1. Loss tangent tan δ and loss modulus E'' values obtained as a function of temperature for cellulose, PAN, and cellulose–PAN blends containing 12.5% and 30% PAN.

TABLE I
Experimental and Calculated Values of E^*, E'', and tan δ for blend containing 30 wt-% PAN[a]

Temp., °C	E^*_{exp}, GPa	E^*_{PA}, GPa	E^*_{DIS}, GPa	E''_{exp}, MPa	E''_{PA}, MPa	E''_{DIS}, MPa	tan δ_{exp}	tan δ_{PA}	tan δ_{DIS}
30	10.5	9.68	9.44	275	333	333	0.025	0.034	0.035
40	10.0	9.26	9.02	288	328	328	0.026	0.035	0.036
50	9.77	8.79	8.56	309	322	322	0.030	0.037	0.038
60	9.55	8.40	8.16	331	323	322	0.036	0.038	0.039
70	9.13	8.16	7.84	346	332	330	0.039	0.041	0.042
80	8.71	7.89	7.47	346	345	341	0.042	0.044	0.046
90	8.32	7.55	6.96	346	361	354	0.044	0.048	0.051
100	7.94	6.92	6.18	363	351	347	0.047	0.051	0.056
110	7.59	6.09	5.30	398	313	313	0.052	0.052	0.059
120	7.08	5.79	4.94	407	281	277	0.056	0.048	0.056
130	6.61	5.81	4.89	380	275	263	0.057	0.047	0.054
140	6.17	5.62	4.69	346	273	252	0.057	0.048	0.054
150	5.89	5.61	4.65	323	280	251	0.058	0.046	0.054

[a] The calculations are based on eqs. (2) (PA model) and (4) (DIS model).

TABLE II
Experimental and Theoretical Density Values of Blends at 23°C

PAN, wt-%	Exp. density, g/cc	Density, eq. (1), g/cc
0	1.508	—
5	1.487	1.488
10	1.473	1.468
12.5	1.475	1.459
20	1.438	1.432
30	1.416	1.397
40	1.383	1.366
50	1.370	1.331
100	1.192	—

$$E^* = \left[\frac{1}{E_1^*} + v \left(\frac{1}{E_2^*} - \frac{1}{E_1^*} \right) \right]^{-1} \tag{3}$$

and

$$E^* = E_1^* \left[\frac{3E_1^* + 2E_2^* - 3(E_1^* - E_2^*)v}{3E_1^* + 2E_2^* + 2(E_1^* - E_2^*)v} \right] \tag{4}$$

where E^*, E_1^*, and E_2^* are the complex moduli of the blend, of the cellulose, and of the PAN, respectively, and v is the PAN volume fraction. Calculations were made using these equations for the blend containing 30 wt-% PAN and for the temperature range covered in Figure 1 and the results for the parallel and the dispersion models are presented in Table I. The values obtained for the series models are totally unacceptable.

It is seen from Table I that the calculated values of E^* are significantly lower than those obtained experimentally, but the parallel model seems to give a somewhat better agreement. The experimental E'' curve present a maximum at 120°C while the calculated ones show a maximum at 90°C. Similarly, the experimental tan δ curve presents a maximum at about 140°C while the calculated ones show a maximum at 110°C. These results show that the shift toward higher temperatures observed for the blend is not a simple dispersion peak in two immissible polymers. It can be related to a partial miscibility between the two components of the blend.

Crystal Structure

In previous publications[17,18] we have shown that the PAN–cellulose blend x-ray intensity curves still contain the peaks characteristic of the cellulose crystal structure and of the PAN crystal structure. It is then clear that a mixed crystal structure is not formed in these blends and, consequently, that the crystalline phase of the blend is not miscible. It was also observed that the incorporation of a small amount of PAN in cellulose films decreases drastically the degree of crystallinity of the sample. The degree of crystallinity of the blends is certainly smaller than 10%.[17,18]

On the other hand, it is known that totally miscible blends like polycaprolactone (PCL) and poly(vinyl chloride) (PVC) do not present a mixed crystal structure.[23,24] The crystal structure of the PCL is unperturbed by the presence of PVC. It is then necessary to postulate the presence of a miscible amorphous

structure in these blends.   Similar results are found for other miscible blends.[5,24-27]

This behavior suggests that the amorphous phase of cellulose–PAN blends can be miscible, even if its crystalline phase is not.   The low degree of crystallinity of cellulose–PAN blends will favor such a behavior.

Observations of the T_m of the samples could not be made since cellulose decomposes before reaching T_m and since PAN undergoes a thermal crosslinking reaction before T_m.[28]

Density

The densities of cellulose–PAN blends are given in Table II.   These values were obtained in a density gradient column kept at 23°C and calibrated with drops of CsCl aqueous solutions.   These densities are compared with the values calculated from eq. (1).   It is seen that the densities of the blends are larger than those obtained from eq. (1), suggesting a partial miscibility of the blends.   The increase in density is of the order of 1% and it is larger for the blends containing 20% or more PAN.   This result is most likely due to an overestimation of the ρ_1 value used in eq. (1).   In this calculation, ρ_1 was taken equal to 1.508 g/cc, the value obtained experimentally for cellulose films.   But it has been shown previously[17,18] that the crystallinity of the cellulose in the blends is drastically reduced.   A value smaller than 1.508 g/cc should be used in the calculation.

CONCLUSIONS

Several measurements must be combined in order to demonstrate the partial miscibility of polymer blends.   In the present study, the transparency of the films, the observed shift of their T_g, which cannot be explained by a dispersion effect, and the increase in density strongly suggest a partial miscibility for the cellulose–PAN blends prepared from a DMF–NO_2 solution.   On the other hand, the x-ray measurements clearly indicate that the partial miscibility must occur in the amorphous fraction of the sample since a mixed crystal structure does not appear for the blend samples.

Cates and White reported several years ago the preparation of PAN–cellulose fibers.[29]   The components of these fibers were immiscible since the fibers were opaque and had densities in agreement with the prediction of eq. (1) (for undrawn fibers).   X-ray diagrams did not show any mixed crystal structure.   However, the fibers were prepared from the hydrolysis of PAN–cellulose acetate fibers.   Consequently, the observed degree of immiscibility reflects the immiscibility between PAN and cellulose acetate, whereas in our work the preparation of the films is made by regeneration of PAN–cellulose nitrite solutions and must reflect more directly the real degree of miscibility between PAN and cellulose.

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