Properties of Polyacrylonitrile–Cellulose Blends

INTRODUCTION

In a first report, we had shown that it is possible to prepare cellulose–polyacrylonitrile (PAN) blends which contain up to 50% PAN and whose films are transparent.[1] These films were realized from dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) solutions. Cellulose could be solubilized in these solvents by the addition of NO_2. Some of these films had a tensile strength slightly larger than that of cellulose.

More recently we have shown that the components of these blends were partially miscible since an increase in glass transition temperature T_g of PAN was observed in the blends by dynamic mechanical measurements.[2] The high tensile strength values of such blends must be related to the partial miscibility between the blend components as proposed in the literature,[3] since immiscibility would result in a drastic decrease of tensile strength with blend composition.[3,4]

In order to improve the mechanical properties of cellulose–PAN blends, one can synthetize graft celluloses in which the graft segment is PAN and prepare a three-component blend. As a matter of fact, this method has been used in the literature in several instances for other blends, and significant improvements in tensile strength have resulted.[5–10] It is then the purpose of the present note to report upon the mechanical properties of cellulose–PAN blends, of graft celluloses, of graft cellulose–PAN blends, and of graft cellulose–cellulose blends, all samples being prepared in the same experimental conditions.

EXPERIMENTAL

The graft cellulose was prepared by introducing 10 g pulp (a fluff prepared from Whatman filter paper No. 42) at 30% consistency into a flask purged with nitrogen. The monomer acrylonitrile was then added. The amount of monomer varied depending upon the graft level desired. After 5 min of contact time, a solution of 0.40 g ceric ammonium nitrate dissolved in 140 g HNO_3 (1%) was added. The flask was continuously flushed by nitrogen. After standing at room temperature for 3 hr with occasional stirring, the graft cellulose was filtered, washed, and dried.[11]

PAN homopolymer is certainly formed at the same time as the graft cellulose. Extraction of this homopolymer has been made by leaving the graft cellulose in DMF at 50°C during 24 hr. It was found that about 20% of the added PAN could be removed by this procedure for samples having graft levels lower than 60%. The difference is more important at larger graft levels, but these samples are not reported in the present note. All graft samples used herein are unextracted ones, and the reported graft levels include both PAN homopolymer and grafted PAN.

The films were prepared by dissolving separately PAN, cellulose, and/or graft cellulose in DMF or DMSO, and by adding NO_2 to the cellulose and to the graft cellulose mixtures at 5°C. Clear solutions which can be mixed together were then obtained. The final solution remained clear. It was regenerated in methanol or ethanol on a glass plate.[1,2]

Density measurements were conducted by the flotation method in carbon tetrachloride–ethyl acetate mixtures at 25°C. Mechanical properties were measured on an Instron tensile tester Model 1130 at room temperature, and at 20% relative humidity. The rate of elongation was 0.83%/min in all cases. All samples were 7 mm wide and about 9 cm long. All experimental data reported are an average of at least six measurements and in most cases of nine or ten measurements.

RESULTS

The results obtained are summarized in Table I. First of all, tensile strength, Young's modulus, and elongation at rupture values of cellulose–PAN blends have been measured. The films used in these measurements have been prepared from 1.5% concentration solutions instead of the 2% concentration used in the previous work, and this procedure gives rise to values which are slightly different from those obtained previously, particularly for samples having high cellulose contents.[1] However, the same trends are observed: decreasing values of Young's modulus with PAN compo-

TABLE I
Mechanical Properties[a]

Sample	PAN, wt. %	Tensile strength, MPa	Elongation at rupture, %	Young's modulus, GPa	Density from eq. (1), g/cm³	Density, g/cm³
Cellulose	0	83	2.5	6.0	—	1.481
Blend	10	91	3.5	5.4	1.443	1.444
Blend	20	73	3.2	4.5	1.406	1.414
Blend	30	76	3.1	4.4	1.372	1.379
Blend	40	65	2.7	4.3	1.339	1.318
Blend	50	70	2.9	4.3	1.308	1.284
Blend	60	73	2.6	4.6	1.278	1.257
Blend	70	83	2.9	4.8	1.249	1.242
Blend	80	79	3.2	4.0	1.222	1.215
Blend	90	77	4.2	3.8	1.196	1.195
PAN	100	75	3.3	3.4	—	1.141
Cellulose	0	83	2.5	6.0	—	1.481
Graft cellulose	7	80	2.3	5.1	—	—
Graft cellulose	14	93	3.1	5.9	1.429	1.449
Graft cellulose A	22	77	2.8	5.0	1.398	1.415
Graft cellulose	29	55	2.6	3.7	1.376	1.389
Graft cellulose	34	36	1.4	3.3	1.358	1.371
Cellulose	0	83	2.5	6.0	—	1.481
A + cellulose	7	92	3.3	5.5	1.455	1.456
A + cellulose	16	81	3.2	5.5	1.422	1.439
A	22	77	3.2	5.0	1.398	1.415
A + PAN	32	79	2.6	4.8	1.365	1.361
A + PAN	46	77	2.4	5.2	1.321	1.334
A + PAN	61	67	2.5	4.5	1.274	1.285
A + PAN	77	69	3.5	3.9	1.231	1.209
PAN	100	75	3.3	3.4	—	1.171

[a] Measurements made at a relative humidity of 20%.

sition and a maximum in tensile strength at about 10% PAN. The data presented in other parts of the table have been obtained in the same experimental conditions such that comparison is possible. Blends containing more than 50% PAN have also been prepared. These films could not be made from 2% solutions, but they are obtainable by the actual procedure.

For the cellulose–PAN blends, most values of tensile strength are between 70 and 80 GPa, which is comparable to the values of cellulose and of PAN. Young's modulus values are decreasing regularly from cellulose to PAN. Both series of data can be interpreted as being due to a system which is partially miscible because otherwise much lower results should be obtained.[3-8]

The second series of results concerns graft celluloses where graft levels, expressed herein in PAN wt-%, are lower than 34%. At higher graft levels transparent films could not be prepared. For graft levels of 7%, 14%, and 22%, the results are quite similar to those of cellulose–PAN blends, including the maximum in tensile strength at 14% PAN. No significant improvement can be detected. A quite similar result has been reported previously in the literature.[12] For samples having graft levels of 29% and 34%, a significant decrease in tensile strength and in Young's modulus is seen which has to be associated to a partial degradation of the cellulose during the grafting reaction.

At the bottom of Table I results are presented for blends of sample A (graft cellulose containing 22% PAN) with cellulose (compositions of 7% and 16% in PAN) and with PAN (compositions of 32%, 46%, 61%, and 77%). The results of this series of samples are quite similar to those obtained for regular cellulose–PAN blends, with a regular decrease in Young's modulus with composition and a maximum in tensile strength at 7% PAN. Other values of tensile strength are similar to that of PAN. The small differences observed are not significant.

Density values for the three series of samples are also reported in Table I. The density d of an immiscible blend is usually given by[13,14]

$$d^{-1} = w_1 d_1^{-1} + w_2 d_2^{-1} \tag{1}$$

where d_1 and d_2 are the densities and w_1 and w_2 are the weight fractions of the components 1 and 2 of the blend. The densities of the cellulose–PAN blends are in most cases slightly lower than those predicted by eq. (1), contrary to the results obtained previously.[2] The densities of the graft samples are larger than the predicted ones. This result is expected since the cellulose and PAN molecules are chemically linked together in the graft sample, and consequently they are forced to pack closely. Finally, the densities of the graft cellulose–polymer samples are slightly larger than the predicted ones, but the increase is smaller than that observed for the graft polymers.

X-Ray diffraction traces of several of these samples have also been recorded. They all indicate a regular PAN or cellulose crystal structure with no tendency to the formation of a mixed crystal structure. But the degree of crystallinity of the cellulose in any of these blends decreases as compared to that found in pure cellulose.[1] Consequently, the density of 1.481 g/cm^3 used in eq. (1) is overestimated. This overestimation is probably partially responsible for the fact that calculated densities for cellulose–PAN blends are larger than those obtained experimentally.

CONCLUSIONS

The densities reported in this note for three different series of sample suggest a small increase in miscibility between cellulose and PAN in this order: cellulose–PAN blend < graft cellulose–polymer blend < graft cellulose. But the mechanical properties recorded are almost the same for the three series of samples. We note particularly a maximum in tensile strength at low PAN content and otherwise values of tensile strength and Young's modulus that are intermediate between those of the two parent homopolymers. The mechanical properties values suggest that the three systems are partially miscible as shown before. But the small increase in miscibility suggested by the density measurements is not seen in comparing the mechanical properties of cellulose–PAN blends, of graft celluloses, and of graft cellulose–polymer blends. This result indicates that the increase in miscibility is very small or that the mechanical properties measured are only slightly influenced by a change in degree of miscibility. These results finally indicate that even if in several instances the use of a graft copolymer may lead to improved mechanical properties of a blend,[5–10] the improvement may be in other instances quite insignificant.[5,15]

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