Cellulose–polyacrylonitrile blends: 2. Effect of graft copolymer on the phase properties in dimethylacetamide/LiCl

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The effect of a graft copolymer based on cellulose (CE) and polyacrylonitrile (PAN) on the compatibility of the two homopolymers in solution was analysed. Samples of copolymers containing different proportions of CE and PAN were synthesized. In order to reduce the degradation of the cellulose chain we tested different synthetic routes. After extraction of PAN homopolymer, the reaction products were composed of pure CE and copolymer; the percentage of PAN with respect to the total weight varied between 13 and 32.2%. A significant increase in compatibility was obtained by using graft copolymers in mixtures with the homopolymers, as evident from both ternary phase diagrams and morphology of solution-cast films. Moreover, solutions containing the graft copolymer showed a liquid crystalline phase at high concentration.

(Keywords: cellulose; polyacrylonitrile; graft copolymer)

INTRODUCTION

In a recent paper[1] the phase diagram of ternary blends based on cellulose (CE), polyacrylonitrile (PAN) and dimethylacetamide (DMAc) + LiCl, has been determined. The system changes from a homogeneous to an isotropic biphasic solution and finally to a mixture containing two phases, one anisotropic (CE) and the other isotropic (CE/PAN), with increase in the overall polymer concentration. According to these results, a complete demixing in the solid state has been predicted. A few literature data confirm these findings: films showing biphasic morphologies have been obtained by casting[2,3]. Moreover, matrix–fibril type fibres have been produced by wet spinning of CE/PAN blends in dimethylsulfoxide (DMSO)[4]; adhesion between the PAN matrix and CE fibrils is quite poor and has been explained on the basis of low chemical compatibility between the components.

In order to introduce a suitable amount of flexible chains into the nematic phase, the synthesis of rigid or semirigid polymers containing flexible side chains has been considered. In fact, according to the theoretical predictions of Ballauff[5], segregation of flexible chains from the nematic liquid crystal is hampered owing to their chemical links with the rigid core, and the ordering process is practically unaffected by the presence of side chains. When synthesis of CE copolymers with flexible side chains is performed, some problems arise. The process does not generally involve all the CE chains. Moreover, flexible homopolymer is formed, so that the product reaction contains neat CE, copolymer and flexible homopolymer. The homopolymer is easily extracted by using a selective solvent, while the residue is a blend of CE and copolymer. Of course, this hampers the study of the molecular properties of the pure copolymer and only general information about the behaviour of its blends can be obtained.

In this paper we present some phase diagrams of CE/copolymer/PAN/diluent and preliminary results about the texture of solution-cast films.

EXPERIMENTAL

Cellulose

Regenerated cellulose (CEa) produced by Lenzing AG (Austria), was used for all the grafting experiments, after a double extraction at reflux with methylene chloride and water.

Degraded cellulose samples (CEb and CEc) were used for the study of the phase behaviour with PAN. These

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samples were obtained after treatment of sample CEa with iron sulfate in H_2O_2 (CEb) or with ceric ammonium nitrate (CEc), using the same conditions to produce graft copolymers (see below). The degree of polymerization (DP) of CE, determined by viscosity measurements in cupriethylenediamine at 25°C[6], is reported in *Table 1*.

^{13}C n.m.r. spectra of the samples dissolved in DMAc + 7% LiCl, were recorded at 25°C using a Bruker AC-300 spectrometer operating at 75 MHz. The ^{13}C signals were assigned by correlative techniques and the δ values were referred to tetramethylsilane as internal standard.

Polyacrylonitrile

The PAN sample (DP = 1925)[1] was used both for the ternary diagrams with CE at different DP and in mixtures with copolymers, in order to increase the PAN content of the grafted samples.

Grafted PAN was characterized after oxidation of cellulosic chains with periodate, followed by complete degradation with alkali[7]. PAN was collected, washed with water and methanol, dried, dissolved in dimethylformamide (DMF) and precipitated with methanol/water, 2:1 (v/v) mixture. The molecular weight was determined from the intrinsic viscosity in DMAc at 20°C[8].

Cellulose–polyacrylonitrile graft copolymers

Preparation of copolymers was performed in heterogeneous conditions[9] and took place in two main steps. The first was the activation of CE, i.e. formation of initiation centres along the chain, where the side chain of PAN would grow. CE was treated with 0.1 M ceric ammonium nitrate in 0.01 N HNO_3 (30 min at room temperature) or, alternatively, with 0.08 M iron sulfate in 0.001 N H_2SO_4 (30 min at room temperature followed by heating at 60°C). The second step involved the addition of a known amount of acrylonitrile monomer under nitrogen atmosphere. The copolymerization proceeded for 24 and 2 h, for Ce^{IV} and Fe^{II}–H_2O_2 initiation, respectively.

Products were washed, dried and treated with DMF at 90°C to extract PAN homopolymer. A selective solvent was not found to extract CE homopolymer; therefore the grafted product (CEPAN) is a mixture of the copolymer with CE homopolymer.

Table 1 Characteristics of the cellulose samples

Sample	Viscosity (dl g^{-1})^a	DP
CEa	1.66	250
CEb	1.13	170
CEc	0.67	100

[a] Obtained in 0.5 M cupriethylenediamine at 25°C

Reagents and solvents

All the reagents were analytical grade. DMAc (Fluka–Buchs) was distilled and stored over Riedel-type 4 Å molecular sieves. Lithium chloride (Riedel-de Haen, RG) was vacuum dried for 24 h at 200°C. Acrylonitrile (AN) (Merck) and cerium ammonium nitrate (Merck) were used without further purification.

Phase diagram

Stock solutions of CE and CEPAN in DMAc + 7% LiCl were prepared by McCormick's method, reported previously[1]. Ternary mixtures were obtained by mixing stock solutions of CE or CEPAN with PAN samples and stirring slowly at room temperature for a few weeks. The boundary between the homogeneous and the heterogeneous phase was determined by optical analysis of solutions of increasing overall polymer concentration, at a constant ratio between the polymeric components. Optical microscopy and centrifugation experiments were performed in order to determine the number of phases in equilibrium. The boundary position was also determined by progressive dilution of the biphasic samples until a homogeneous phase was observed.

The concentration at which the anisotropic phase appeared, C'_p, was determined for samples CEa and CEb, and CEPAN samples 1 and 2, according to the method described previously[10]. Concentrations, C_p, are usually given as grams of polymer per 100 g of solution or, in some cases, as polymer volume fraction. The latter were calculated from the corresponding C_p by using the partial specific volumes (v_s) of CE and PAN and the specific volume of the solvent (V_1). These quantities were determined pycnometrically at 25°C and found to be $v_{sCE} = 0.64\ ml\ g^{-1}$, $v_{sPAN} = 0.907\ ml\ g^{-1}$ and V_1 DMAc + 7% LiCl = 1.003 ml g^{-1} (ref. 1). Determination of C'_p and the optical analyses of films were performed with a Reichert Polyvar Pol polarizing microscope.

Film preparation

CEPAN and CE/PAN mixture solid films were cast from homogeneous isotropic solutions in DMAc + 7% LiCl, at $C_p = 6\%$. These solutions were poured onto a flat glass plate, spread with a blade to obtain films of about 30 μm thickness, then left for 30 min under inert atmosphere at room temperature and coagulated in a non-solvent. The films were washed with water to remove LiCl, dried and analysed with a polarizing microscope.

RESULTS AND DISCUSSION

Graft copolymerizations onto cellulose were carried out in heterogeneous reaction systems. In these conditions the reaction proceeds mainly in the amorphous regions of CE and simultaneously produces graft copolymer and PAN homopolymer. In this reaction, degradation of CE could not be ignored. In order to simulate the degradation

Table 2 Characteristics of grafted products

Sample	Initiator	AN/CE (mol/mmol)	PAN/(PAN + CE) (w/w, %)	DP, CE	DP, PAN	CE/PAN (mol/mol)
CEPAN 1	Fe/H_2O_2	3.26	13	170	830	10.7
CEPAN 2	Fe/H_2O_2	4.35	22.2	170	1320	8.9
CEPAN 3	Ce^{IV}	2.45	32.2	100	760	5.2

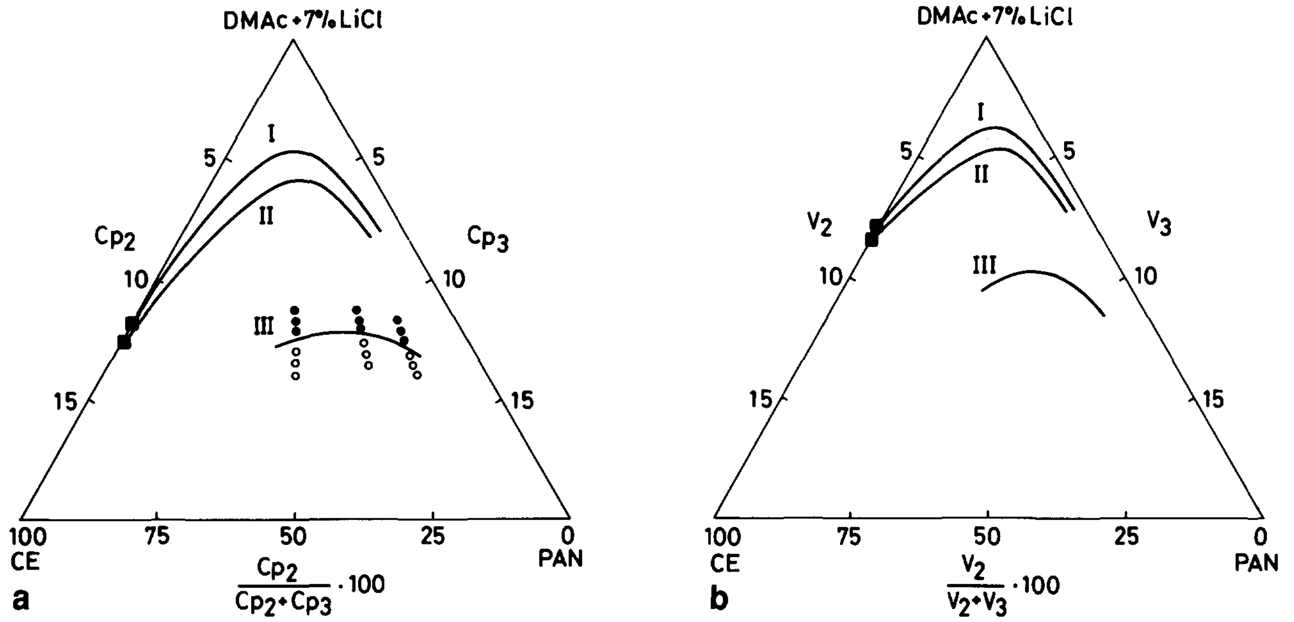

Figure 1 Ternary phase diagrams for the system CE/PAN/DMAc+7% LiCl; composition is expressed as polymer weight per cent (a) and as polymer volume fraction (b). Curves I, II and III refer to the boundary between the two phases for different molecular weight cellulose samples. I, DP=250; II, DP=170; III, DP=100. Experimental points for homogeneous (●) and biphasic (○) solutions are reported only for curve III; ■, concentration at which an anisotropic phase appears

of CE during the grafting initiation step, oxidation tests were performed on CEa (DP=250), using the same conditions of the grafting reactions. Samples of degraded cellulose (CEb and CEc, with DP=170 and 100, respectively) were obtained in this way. ^{13}C n.m.r. spectra did not show the formation of C=O groups, nor C_2–C_3 cleavage of the anhydroglucose units.

Table 2 reports the main characteristics of the copolymerization products. This type of blend, composed of unreacted CE with the graft copolymer, is generally roughly characterized in the literature and used as obtained to produce fibres and films[11–13]. However, while a knowledge of the conditions that bring about particular final morphologies is useful for general applications, we consider that it is even more important to characterize the macromolecular properties of the product in order to better understand the compatibilizing properties of the copolymer and to extend its exploitation. In this respect it would be useful to study the number and length of grafts by changing the polymerization conditions.

If only one PAN molecule is grafted onto a CE molecule, the molar ratio between unreacted CE and grafted polymer, calculated from the data of *Table 2* (column 7) is 9.7, 7.9 and 4.2 for CEPAN 1, 2 and 3, respectively.

On the whole, our products contain a high percentage of degraded but ungrafted CE, and copolymer with long chains of the flexible component. The DP of CE has been assumed to be equal to the DP of the cellulose samples CEb and CEc, obtained as described in the Experimental part. This is important, not only for the investigation of the miscibility of CE/copolymer/PAN in solution, but also for the final properties of these blends. For example, we recall that the mechanical properties of CE fibres improve as the molecular weight increases[14,15]. From this point of view it would therefore be convenient to accomplish the grafting process starting from CE with higher molecular weight. Before discussing the influence of grafted polymer on miscibility, the effect of the DP of CE on miscibility with PAN must be elucidated.

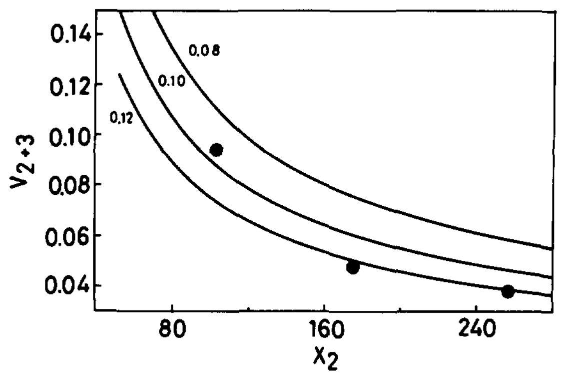

Figure 2 Polymer volume fraction at the plait point (V_{2+3}), *versus* the degree of polymerization (X_2). Theoretical curves have been calculated according to equation (1) (see text) for different χ_{23} values, as indicated on the curves. The reference volume, V_r, has been taken as 100 ml mol^{-1}

Figure 1a illustrates the demixing curves of the system diluent/CE/PAN (components 1, 2, 3) for the three CE samples. By converting weight fraction to volume fraction, *Figure 1b* is obtained. An increase in miscibility with decreasing DP of CE is observed, in agreement with the Flory–Huggins theory[16]. This behaviour is valid whether or not the solvent–polymer interaction parameters, χ_{12} and χ_{13}, are identical.

When $\chi_{12}=\chi_{13}=0$, theory allows a simple calculation of the overall volume fraction of polymer, V_{2+3}, corresponding to the maximum of each demixing curve (plait point)[17]:

$$V_{2+3}=\frac{1}{2}\left[\left(\frac{1}{X_2}\right)^{1/2}+\left(\frac{1}{X_3}\right)^{1/2}\right]^2\frac{1}{\chi_{23}} \qquad (1)$$

where X_2 and X_3 = DP of polymers 2 and 3, respectively, in terms of a reference volume V_r, and χ_{23} = the Flory–Huggins interaction parameter. If X_3 is constant (as we deal with only one sample of PAN) it is possible to plot V_{2+3} *versus* X_2 for different χ_{23} values. *Figure 2*

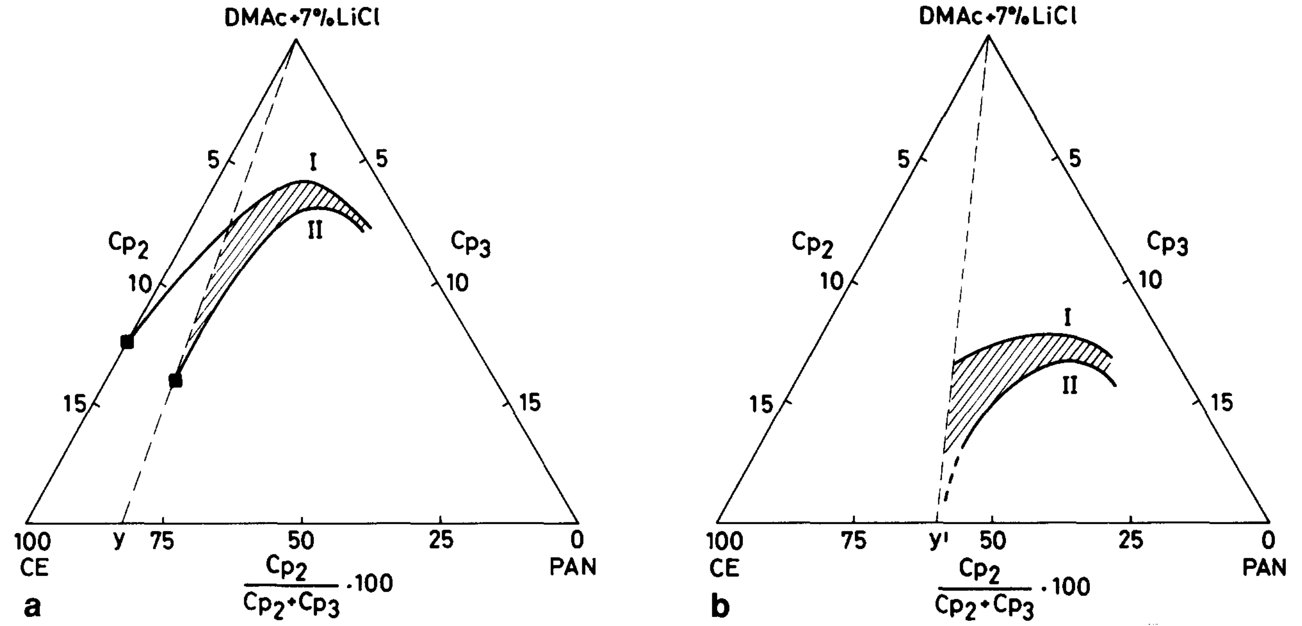

Figure 3 Ternary phase diagrams for the system CEPAN/PAN/DMAc+7% LiCl for different CE samples: (a) DP=170; (b) DP=100. The base axis gives the composition in terms of CE and PAN, irrespective of whether or not PAN is grafted to CE. ■, Concentration at which an anisotropic phase appears. The hatched area indicates the increase of miscibility from pure homopolymer mixture (curve I) to homopolymer with graft copolymer mixture (curve II)

shows a few of these curves. The experimental V_{2+3} values are also reported, and they follow the trend of the curves. However, we must remember that for our system $\chi_{12} \neq \chi_{13} \neq 0$[1] and therefore the agreement must be considered as merely indicative.

Figures 3a and *b* show the phase diagrams of CEPAN 2 and 3 (*Table 2*) with PAN homopolymer. The base axis gives the overall composition in terms of CE and PAN, irrespective of whether or not PAN is grafted to CE. PAN homopolymer is present only for compositions on the right of points y and y', and its percentage corresponds to the difference between the total PAN and 22.2 or 32.2, respectively. The position of the demixing curves indicates an increase of miscibility with respect to the corresponding curves relative to the pure homopolymers.

For CEPAN 1 and 2, no demixing was observed up to an overall concentration of 13.5 or 14%, respectively, at which a liquid crystalline phase appears, while for the homopolymer blends, with the same ratio of CE/PAN, demixing already appears at an overall concentration of about 6–8%. This result suggests the possibility of forming a lyotropic phase containing the copolymer, in agreement with the Ballauff theory which predicted that rigid chains containing flexible side chains can form a mesophase[5]. The critical concentration for the appearance of a mesophase increases with the content of the flexible component. *Figure 4* shows the theoretical trend of C'_p *versus* flexible polymer concentration. The experimental points are also reported and are in good agreement with the theoretical prediction, taking into account that the curve refers to an athermal system and that samples 1 and 2 do not correspond to pure copolymers. Further investigations are necessary to clarify this point.

The physical mechanical properties of blends in the solid state depend mainly on the level of compatibility, in the equilibrium condition, between the components. It has been observed that, starting from CE/PAN mixtures, both homogeneous and heterogeneous films can be obtained[2,3,18–21]. Taking into account the incompatibility in the solid state[1], homogeneous films can be obtained only if a high rate of coagulation or evaporation is used and the homogeneous molecular organization in dilute solution is frozen in the solid state. *Figure 5* shows the morphology of films composed of CE/PAN mixture containing 22.2% PAN. The phase separation appears more evident if DMAc/water is used as coagulant (*Figure 5a*) instead of water (*Figure 5b*). The effect can be explained in terms of an improvement of the demixing promoted by a lower coagulation rate.

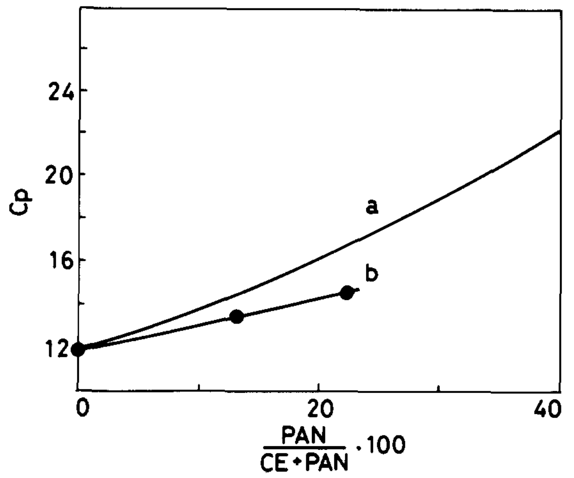

Figure 4 Critical concentration for the appearance of the nematic phase *versus* graft copolymer percentage: a, theoretical curve (ref. 5); b, experimental data

Films obtained from CEPAN 2 (which contains 22.2% PAN) using the same coagulation conditions show a homogeneous texture. These results are evidence of a higher compatibility between PAN and CE in the CEPAN samples where the PAN chains are chemically linked to the CE chains. These homogeneous solutions, both in isotropic and in more concentrated liquid crystalline phases, could be used to obtain fibres and films with remarkable properties. Spinning CEPAN samples from the liquid crystalline phase to obtain high

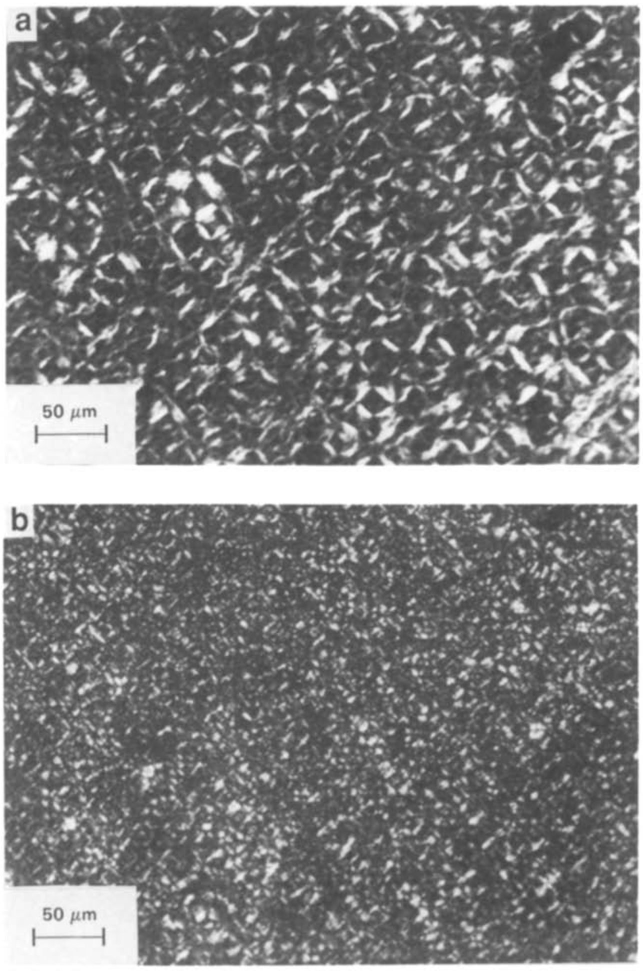

Figure 5 Optical micrographs of morphologies developed in solution-cast films of CE/PAN mixture in DMAc+7% LiCl at $C_p=6\%$, prepared by coagulating in DMAc/water (85:15) (a) or water (b)

modulus cellulosic fibres with increased resistance to microorganisms, due to the grafting of PAN, is under investigation in our laboratories.

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