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Optically anisotropic polymer blends: hydroxypropylcellulose/polyvinylpyrrolidone

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Abstract

In this paper, solid blends of HPC/PVP obtained by polymerization in situ of NVP are analyzed. These blends retain the initial organization of HPC in NVP in terms of liquid crystalline structure and banded texture. It is also demonstrated that the banded texture may be stabilized with respect to thermal cycles by crosslinking the samples. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hydroxypropylcellulose; Polyvinylpyrrolidone; Blend

1. Introduction

Polymerization of vinylic monomers containing a suitable amount of a mesogenic polymer has been used recently to prepare solid blends which retain the liquid crystalline organization of the mesogen. In order to get this result, two conditions must be satisfied: firstly, it is necessary that the mesogenic polymer concentration is sufficiently high to give liquid crystals, secondly, the polymerization 'in situ' of the vinylic monomer must occur at a significantly faster rate than any phase separation. In this case, it is also possible to freeze specific structures of the system, as banded texture, which otherwise would decay with time.

The mesogenic component of these solutions is often a cellulose derivative, like hydroxypropylcellulose (HPC) [1–3], cellulose diacetate [4], (cyanoethyl)propylcellulose [1], cellulose carbanalilate [5], etc. due to their solubility in various solvents. The latter are unsatured monomers, like acrylic acid [4], methacrylic acid [1], 2-hydroxyethylmethacrylate [2], *N*,*N*-dimethylacrylamide [6], acrylonitrile [2], etc.

In majority of the cases, solutions submitted to the monomer polymerization contain about 50–60% (w/w) of the mesogenic polymer as the liquid-crystalline phase is considered to be well organized and stable at these concentrations. Consequently, the solid blends so obtained show the anisotropic organization previously existing. However, aging the solid samples for a long time at temperature above T_g results in phase separation of the flexible component, as observed in Ref. [3]. This phenomenon is mainly determined by the fact that the anisotropic phase does not accept the presence of flexible chains (except at low molecular weight) in equilibrium condition (entropic contribute) [7]. Moreover, a second reason may be due to the compatibility level at the amorphous state between the components, which may contribute to the demixing process (enthalpic contribute).

In this paper, we will show the behaviors of hydroxypropylcellulose/polyvinylpyrrolidone (HPC/PVP) blends obtained from concentrate solutions of HPC in the monomer NVP and we will also suggest how to retain the anisotropic organization. An interesting aspect is that the two polymers are compatible in the amorphous phase.

2. Experimental

2.1. Materials

An HPC sample, supplied by Hercules Inc., was used after purification (water dissolution and centrifugation to eliminate solid particles) for all the experiments. Its molecular weight was 10^5, the molar degree of substitution MS = 4.2 ± 0.2 determined in our laboratory by NMR technique. MS is defined as the total number of molecules of propylene oxide that have combined with the original cellulose per anhydroglucose unit. The MS value is greater than 3, the maximum degree of substitution DS due to the occurrence of oligo (1,2-alkylenoxy) side chain.

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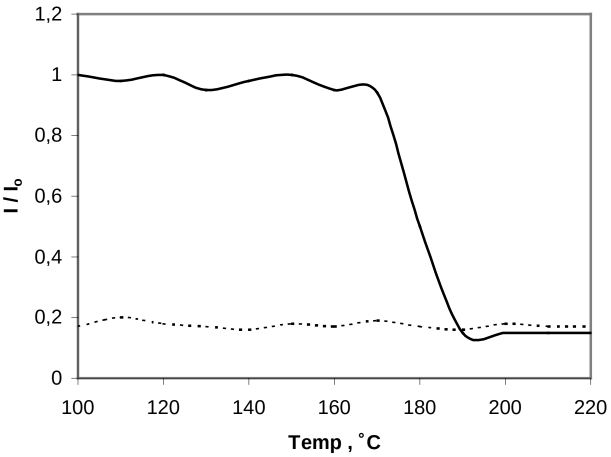

Fig. 1. Relative light transmission I/I_0 under crossed polarized light against temperature for HPC/PVP blend 60/40 w/w. Full line heating cycle; dashed line cooling cycle.

Vinylpyrrolydone monomer (NVP) was supplied by Fluka Chemical and used after the elimination of the stabilizer, by vacuum distillation under nitrogen flow. PVP, molecular weight 360 000, was supplied by Fluka Chemical.

Hydroxycyclohexilphenylchetone (Aldrich) and ethyleneglycol-dimethacrylate (Fluka Chemika) (photoinitiator of NVP polymerization and PVP crosslinker, respectively) were used as received.

Blends HPC/PVP were obtained by mixing solutions of the neat polymers in ethanol and evaporating the solvent.

2.2. Methods

An optical microscope Polyvar Pol, equipped with a Mettler FP82 hot stage, was used to determine the presence of liquid crystals by observing each sample under polarized light between crossed nicols. A photometer connected to a computer capable to measure the light intensity variation during thermal cycle was used to determine the phase transition temperature of the samples. Band structure, following the relaxation of anisotropic samples after application of a linear shear, was also observed as well as the transition from anisotropic to isotropic phase at T_{NI}.

T_g of the neat polymers and of their blends and T_{NI} of the anisotropic samples were determined by using a Perkin–Elmer DSC7 apparatus.

The molecular weight of photopolymerizated PVP was obtained by size exclusion chromatography (Waters Millipore). The universal calibration curve was obtained by using polyethylene glycol standard (Fluka).

3. Results and discussion

Solutions of HPC in NVP were prepared by using the following method: a mother solution of HPC at low concentration ($c_p \cong 10\%$) was obtained at room temperature simply by mixing the components. Then, some aliquots of that mixture were concentrated eliminating a part of the monomer by evaporation in air stream. Check of the weight trend with time allowed the obtainment of seven samples having HPC concentration c_p between $\cong 30$ and 80% (w/w). No limit of HPC solubility was observed.

Below $c_p \cong 40\%$, the samples, observed at the polarizing microscope, were isotropic, at $c_p \cong 40\%$, a light anisotropy started to appear, and at $c_p > 40\%$, the anisotropy became progressively stronger. On this base, $c_p = 40\%$ was assumed as the lower limit concentration at which the liquid crystalline phase is stable. This value may be transformed in terms of volume fraction v'_p, by using $\rho_{HPC} = 1.17$ g/ml and $\rho_{NVP} = 1.040$ g/ml and assuming a simple additivity rule. The result $v'_p = 0.37$ agrees with literature data for HPC in various solvents: in particular, v'_p ranges from 0.28 in acetic acid to 0.42 in dimethylsulfoxide [4]. This range may be considered excessively wide if we take into account that v'_p should depend only on the axial ratio of the mesogenic polymer [8], that is the length over diameter ratio for rigid polymers or the same ratio referred to the Kuhn segment for semiflexible chains [9,10].

Moreover, concerning the polymer–solvent interaction, as expressed from χ_{ps} parameter, no influence on v'_p is expected, except for $\chi_{ps} > 0.05$ [8]. There are three reasons which may be considered to explain the observed range of v'_p values: (a) the HPC chain rigidity could depend on MS or, MS being equal, on the hydroxypropyl groups distribution along the chain. In this case, it would be meaningless to associate a specific v'_p to any HPC sample, (b) the chain rigidity could depend on specific interactions with the solvent, and (c) even for a given MS, v'_p may depend on the molecular weight as observed for other semiflexible polymers [11].

Coming back to our system, a final observation concerns the capacity to give banded texture when an anisotropic sample relaxes after linear shear: this fact represents a further confirmation of its mesogenicity and it was observed in all our anisotropic samples.

A sample having composition HPC/NVP = 60/40 was prepared according to the method described in Section 2, upon the addition of 2% of photoinitiator (with respect to NVP). A thin layer was radiated with $\lambda = 368$ nm for 1 h, after storing one day in a dark room at low T. Conversion of NVP in PVP was $\cong 98\%$. The remaining NVP was eliminated by putting the sample under vacuum at low T for 2 h. In an aliquot of the sample, PVP homopolymer was extracted by selective solvent and M_w of 300 000 was determined by HPLC analysis.

The liquid crystalline organization was retained after the polymerization process as well as the banded texture, when present in the original sample.

The transition temperature from anisotropic to isotropic phase (T_{NI}) of the HPC/PVP blends was determined by DSC. $T_{NI} \cong 200$°C was found by using a heating rate of 20°C/min.

Fig. 1 shows the change in birefringe with temperature,

Table 1
Glass transition temperature of HPC/PVP blends

HPC/PVP (w/w)	T_g (°C)
100/0	40
80/20	88
60/40	150
20/80	177
0/100	180

measured by monitoring the change in relative transmission of the polarized light I/I_0. I_0 is the transmission light at room temperature and I the transmission light at a given temperature. On heating, the birefringe disappeared at about 190°C, and on cooling, the birefringe did not reappear.

To better understand the reasons of the phenomenon, blends of HPC and preformed PVP were prepared as previously described. Five mixtures with a content HPC/PVP from 0/100 to 100/0 (where 100 means the neat polymer) were analyzed by optical microscopy and thermal analysis. Only the samples 80/20 and 100/0 were birefringent under crossed nicols and DSC analysis confirm the existence of melting peak $T_{NI} = 203°C$.

Table 1 shows T_g values at different HPC/PVP ratios. T_g increases from the value 40°C, characteristic of HPC, to 180°C, characteristic of PVP. Deviation from linearity is positive.

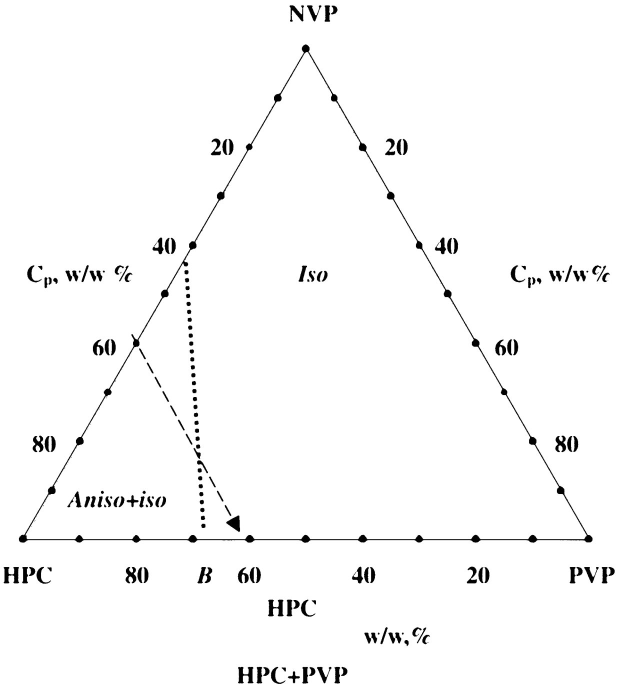

Fig. 2. Hypothetical phase diagram for system made of solvent, rigid and flexible polymer. The dotted line is the border between biphasic and monophasic area. The dashed line gives the conversion of a HPC/NVP 60/40 liquid crystalline solution to a HPC/PVP 60/40 isotropic solid blend.

From these data, two main conclusions can be drawn:

> HPC and PVP are compatible in the isotropic amorphous phase as demonstrated by the presence of a unique value of T_g at a given composition.
> The anisotropic phase is made of HPC as the melting temperature T_{NI} is 203°C in all cases.

On this basis, it is evident that PVP does not take part in the liquid crystalline organization, notwithstanding the compatibility between HPC and PVP.

From a theoretical point of view, Flory [7] demonstrated that mixtures of rigid nematogenic (1) and flexible (2) polymers dissolved in a common solvent (3) demix at $v_{1+2} > v'_p$. A biphasic system, containing one anisotropic phase made of the rigid component and solvent (1 + 3) and one isotropic phase made of the flexible polymer plus solvent and a certain amount of the rigid one (1 + 2 + 3), is formed. The demixing between rigid and flexible chains increases by increasing the overall polymer concentration, becoming total as the solvent is reduced to 0.

Anisotropic solutions at low overall polymer concentrations, containing little amounts of flexible chains, are expected to form only when the molecular weight of the components is low.

These conclusions were demonstrated to be valid also for semi-rigid polymers [12].

The phase behaviors described were explained on entropic base, assuming a complete athermicity of the system.

Recently, Inomata et al. [13] extended the original Flory's treatment to mixtures with strong unfavorable interactions between the polymers highlighting the enthalpic contribute to the phase equilibrium. A first consequence is that in the presence of a solvent, at low v_{1+2}, triphasic equilibria may occur, as experimentally observed [14,15]. When the solvent is absent, a complete demixing with the formation of a liquid crystalline phase containing the rigid component and an isotropic phase containing the flexible one is predicted.

The case of strongly favorable interactions was not examined. However, it could be reasonable to presume in this situation the existence of equilibrium at the solid state between a liquid crystal and an isotropic phase, containing the flexible as well as some amount of the rigid chains. This could be the case of HPC/PVP blends as the two polymers are compatible.

Fig. 2 shows the hypothetical phase diagram NVP–HPC–PVP; c'_p for the binary mixtures HPC–NVP is about 40%: from this point, a curve (dotted line) goes to B point on the base that is the axis concerning the solid HPC–PVP blends. The solid mixture having an HPC content between 100% and B are formed by a liquid crystalline phase made of neat HPC and an isotropic phase having B composition. At lower HPC content, only an isotropic phase is present due to the strong favorable interaction HPC–PVP. This hypothesis in

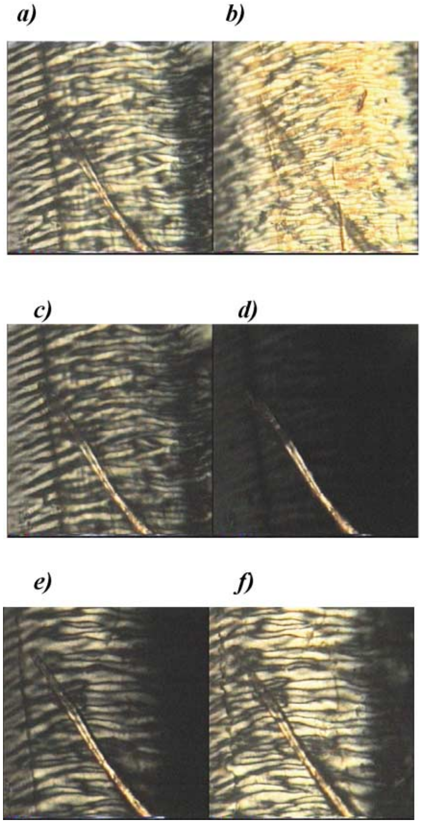

Fig. 3. Band texture of HPC/PVP blend obtained by polymerization in situ of NVP in the presence of a crosslinker. The sample was heated from 25 to 210°C and subsequently cooled to room temperature: (a) 25°C; (b) 100°C; (c) 150°C; (d) 210°C; (e) 100°C; (f) 25°C.

our opinion is reasonable and could explain our results. In fact, the mixture HPC/VP 60/40 retains the liquid crystal organization after polymerization, but the sample becomes isotropic when it is cooled after heating at $T > T_{\mathrm{NI}}$ (see dashed line in Fig. 2).

The problem of stabilizing the band texture in HPC/PVP blends with PVP obtained by NVP polymerizated in situ was solved by crosslinking the binary blends.

The sample selected for this experiment was the solution HPC/NVP 60/40: 5% (w/w) of the crosslinker with respect to NVP was added before the radicalic initiator. After homogenization, UV light irradiation, a thin layer of the crosslinked sample was tested by swelling in water. No loss of polymer was observed and the film recovers its initial aspect after drying in air.

When a shear was applied before NVP polymerization, the banded texture (Fig. 3a) is freezed inside the film: it is stable by heating at least at 140°C and subsequently tends to completely disappear about at T_{NI}. The texture is recovered by cooling as visible in Fig. 3e and f. The cycle heating–cooling may be repeated many times with the same result. A similar result was obtained by Wojciechowski et al. [3] regarding the phase separation of the flexible polymer at $T > T_{\mathrm{g}}$ and the permanence of banded texture of a few systems of cellulose derivatives–acrylic acid when a network is formed.

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