# POLYIMIDE EMBEDDING IN LYOTROPIC POLYMER MATRIX FOR SURFACE-RELATED APPLICATIONS: RHEOLOGICAL AND MICROSCOPY INVESTIGATIONS

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A partially aliphatic polyimide was embedded in different proportions in a matrix of hydroxypropyl cellulose in lyotropic phase through shear casting method. The interactions in the system and its compatibility were analyzed from rheological tests. Morphological features were investigated with polarized light microscopy revealing an ordered mosaic texture composed of anisotropic domains. Their uniformity and size depend on the system composition. Atomic force microscopy was used for a deeper examination of the surface morphology revealing an ordering tendency induced by the lyotropic matrix. The resulted data are important in designing polymer systems with tunable surface morphology as required in electronics or bio-technologies.
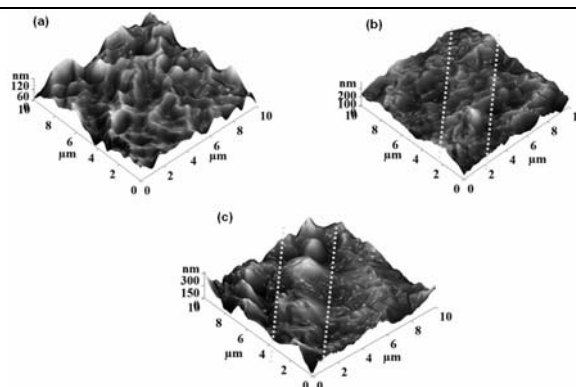
INTRODUCTION

In the past decades, surface-related applications have gained an increased attention in various industries leading to the development of the strategies used to pattern polymers.[1] The interest in controlling the polymer topography at different length scales has its origin in the diversity of synthetic and biological polymers, and the ability to create novel materials with multiple functions.[2] Polymer patterns typically have high fidelity, owing to the suppressed lateral diffusion of macromolecules. The production of such structured surfaces is required in biotechnologies concerning guided cell growth[3,4] and in fabrication of semiconductor, plastic microelectronics, and display devices.[5] For these practical purposes there is also needed to have a material with specific features, such as high chemical resistance, good film-forming ability, and stability at elevated temperatures. These demands are entirely fulfilled by a particular class of high-performance polymers, namely polyimides (PIs).[6,7] Adaptation of their surface properties is made through various techniques in order to induce a certain degree of anisotropy that is helpful for instance in ordering molecules or cells cast on the polymer support.[8,9] However, the classical rubbing and UV irradiation

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methods have some disadvantages including generation of static electricity, undesired photochemical reactions and of exceeding material.

The self-aligning nature of polymer liquid crystals was proved to be suitable for molding purposes.[10] Upon applying a shear deformation to a lyotropic solution one achieves high degree of molecular orientation. Particularly, concentrated solutions of cellulose derivatives in organic solvents subjected to shearing present specific textures, which due to the longer relaxation time can be maintained until solidification. In this category one can include hydroxypropyl cellulose (HPC), which in crystalline state is characterized by a unique helicoidal supramolecular structure in which the alignment of cellulose molecules occurs at a small angle in one layer to another. In the presence of a strong shear field HPC solutions change their cholesteric texture into a banded one.[11,12] In our previous work[10] it was shown that this structural order can be induced in polyimide precursors which can interact with the lyotropic matrix through hydrogen bonding. The pattern size depends on the system composition and also on the structure of dianhydride moieties.[13]

This study is focused on the preparation and characterization of polyimide/HPC blends from the point of view of their interactions, compatibility and surface morphology. The novelty of this work consists in the fact that a new polyimide with many ether bridges is introduced in the HPC matrix.

According to the morphology data, this system has a greater surface tendency of ordering.

RESULTS AND DISCUSSION

The microstructure and interactions occurring among the polyimide embedded in the liquid crystal mesophases were extracted from rheological studies. First the lyotropic matrix, consisting in HPC solutions in DMAc, was subjected to shear experiments. Onogi and Asada[14] hypothesized the universal existence of three shear flow regimes to describe the viscosity of polymer liquid crystals: a shear thinning regime at low shear rates (Region I), a Newtonian plateau at intermediate shear rates (Region II), and another shear thinning regime at high shear rates (Region III). However, it is hard to evidence experimentally all three domains. According to Fig. 1, one can notice that the viscosity-shear rate dependence exhibits only Region III, proposed by Onogi and Asada.[14] The Newtonian plateau that should be found at low shear rates, as a consequence of "dispersed polydomain" structure, is not evidenced in our experiment. The dependence of viscosity (taken at shear rates close to zero) on HPC concentration in DMAc is displayed in the small plot of Fig. 1. From this inset one can observe a maximum at/or near the critical concentration in the 20–60 wt.-% concentration. This point delimitates the anisotropic phase formation.
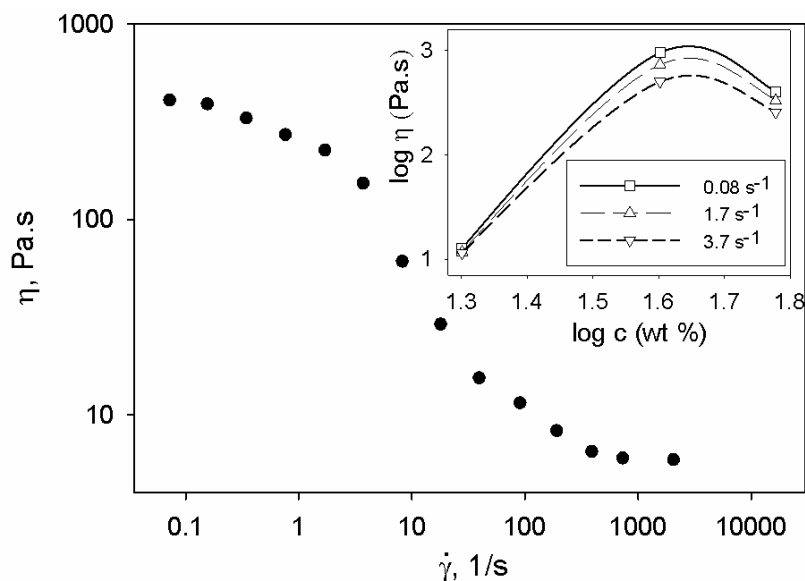

Fig. 1 – Shear viscosity dependence on shear rate for 60 wt% HPC in DMAc. The small plot shows
the dependence of shear viscosity on concentration (20, 40 and 60 wt%) at different shear rates.
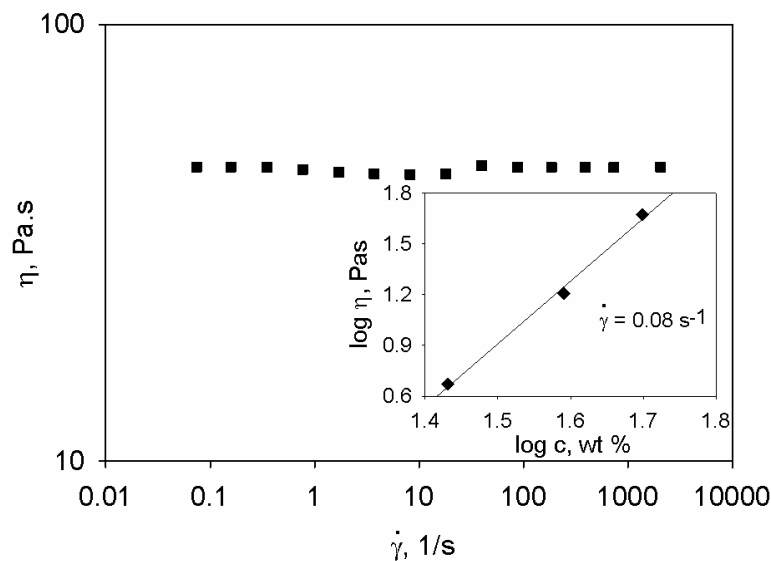
Fig. 2 – Shear viscosity dependence on shear rate for 50 wt% polyimide solution in DMAc. The small plot shows the dependence of shear viscosity on concentration (30, 40 and 50 wt%) at 0.08 s^{-1} shear rate.

As the concentration is increased, the isotropic solutions show a monotonic increase in shear viscosity. Viscosity is enhanced until a maximum value, when the isotropic to anisotropic transition is approached. The ordering of macromolecules in the HPC/DMAc system is associated with a viscosity lower than that of the isotropic solutions. In this context, below a certain critical shear rate, the isotropic solutions are Newtonian. The viscosity maximum can be correlated with the anisotropic phase appearance only when the shear rate is low (close to zero).[11] Therefore, at a constant shear rate of 0.76 s^{-1}, the critical concentration of about 46 wt% appears to be the concentration at which a distinct change in the rheological properties occurs indicating that after this point the HPC solutions in DMAc are in liquid crystalline phase. Upon formation of the anisotropic phase, viscosity starts to decrease.

On the other hand, the rheological experiments performed on the polyimide solutions in DMAc show that no modifications of viscosity during shearing take place. The constant viscosity region over the entire shear rate domain is typical for Newtonian samples, as noticed in Fig. 2. At the working polyimide concentration of 50 wt%, which is placed in concentrated domain, the dependence of viscosity on concentration at a shear rate of 0.08 s^{-1} is following a power law $\eta \propto c^x$. The exponent x is about 3.8 (see the inset from Fig. 2). This dependence coincides with the theoretical prediction for concentrated polymer solutions in which entanglements between the macromolecules appear.[15]

The flow behavior of the PI/HPC blends is presented in Fig. 3. Introduction of a higher percent of HPC reduces the Newtonian regime. Given the fact that the values of the blend viscosity for all compositions are placed between the two individual components one can conclude that their mixture is compatible. From the analysis of the flow curves of the individual components it can be considered that the constant viscosity domain is rather characteristic to PI solution than to HPC one. An important rheological parameter that reflects the interactions from the blend system is the activation energy of the flow process, E_a. The latter can be determined from the dependence of shear rate viscosity (at a shear rate close to zero) on the temperature. This variation follows the Arrhenius relation:

$$\eta_0 = A \cdot \exp(E_a / RT) \qquad (1)$$

where η_0 is the zero shear viscosity ($\eta_0 = \lim_{\dot{\gamma} \to 0} (\eta)$), A is the pre-exponential factor, T is the absolute temperature and R is the universal gas constant.

Linearization of relation (1) allows determination of the E_a from the slope of the straight line of $\ln \eta_0$ versus 1000/T (inset from Fig. 3), which is equal to $E_a/1000\ R$.
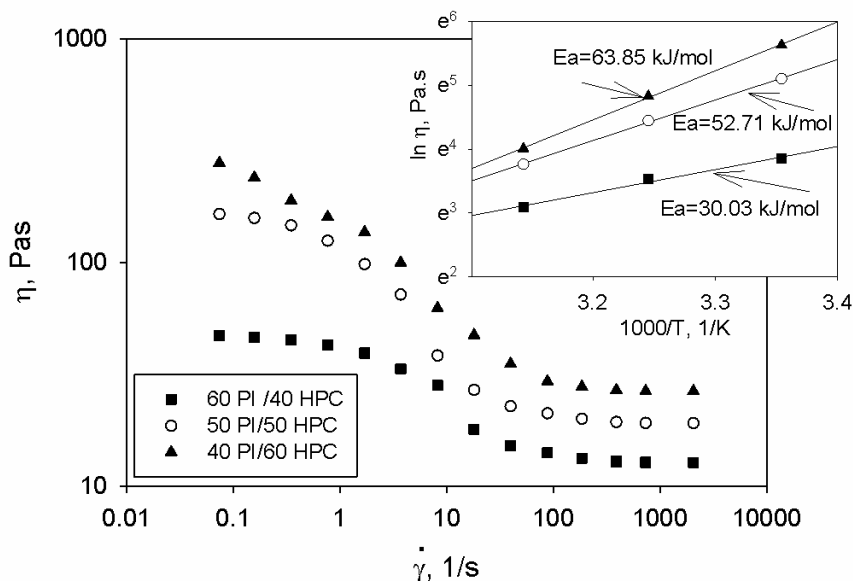
Fig. 3 – Shear viscosity dependence on shear rate for PI/HPC in DMAc.
The small plot shows the dependence of shear viscosity on reciprocal temperature at 0.08 s^{-1} shear rate.

For the evaluation of E_a the viscosity was chosen at a shear rate close to zero (0.08 s^{-1}). A lower energy barrier for the movement of polyimide segments in the solvent implies low values of E_a. In the case of polymer solutions under analysis here, this barrier can be related to the interaction between the counterparts of the system. The small graph from Fig. 3 displays the plot of ln η *versus* reciprocal temperature for investigated PI/HPC solutions. It can be observed that the studied solutions follow the Arrhenius expression and that the resulting flow activation energy is influenced by the chemical structures. The HPC polymer interacts with DMAc solvent through hydrogen bonding, whereas the recurring anhydroglucose units reduce the flexibility of the HPC chains, resulting higher value for flow

activation energy, namely 57.81 kJ/mol.[16] Blending of the liquid crystal polymer with the polyimide leads to a decrease of the E_a values from 63.85 kJ/mol for 40 PI/60 HPC, to 52.71 kJ/mol for 50 PI/50 HPC and finally to 30.03 kJ/mol for 60 PI/40 HPC.

The morphology of the PI/HPC blends was examined through polarized light microscopy (PLM), as shown in Fig. 4. It is widely known that the HPC lyotropic solutions in DMAc exhibit a specific banded texture when they begin to relax after shear cessation. In this case, the polarizing microscopy image of HPC reveals alternating bright and dark lines perpendicular to the shear direction.[11] On the other hand, owing to its isotropic nature, the polyimide gives a dark image when is placed under crossed polarizers.
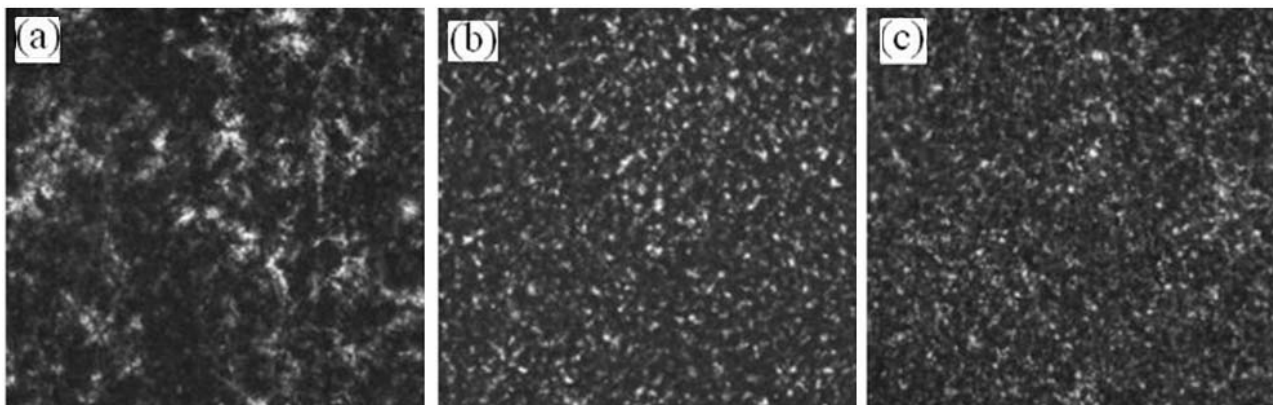

Fig. 4 – PLM images of PI/HPC films obtained between crossed polarizers at room temperature for different weight ratios of the components: (a) 60 PI/40 HPC, (b) 50 PI/50 HPC, and (c) 40 PI/60 HPC.
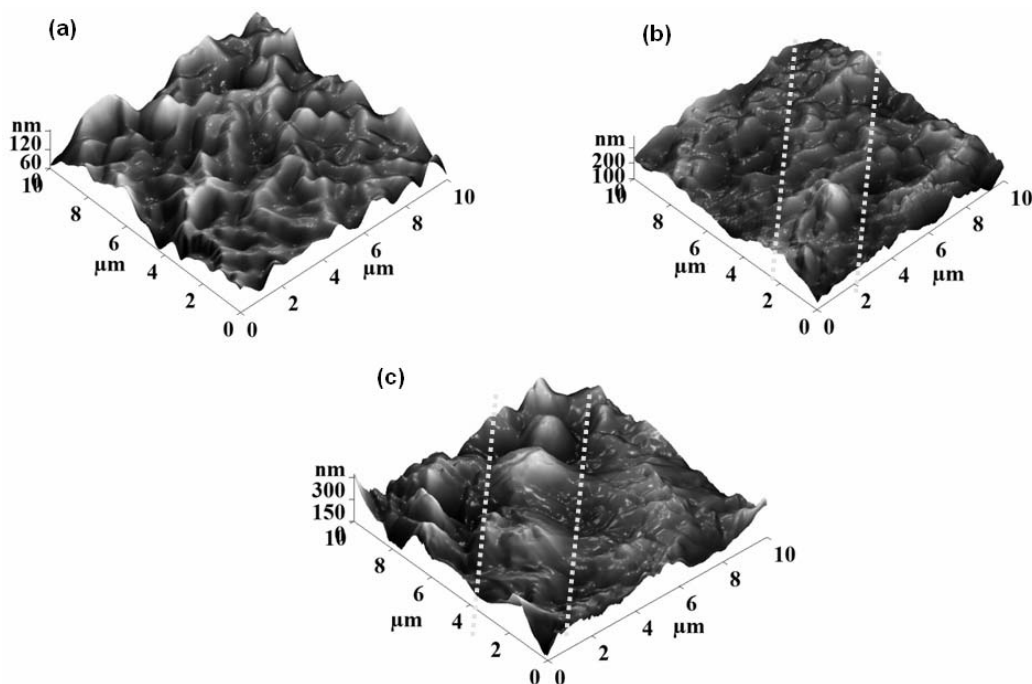
Fig. 5 – AFM images of PI/HPC films obtained at room temperature for different weight ratios of the components:
(a) 60 PI/40 HPC, (b) 50 PI/50 HPC and (c) 40 PI/60 HPC.

The banded pattern is modified by the presence of the isotropic PI component. The PI/HPC samples subjected to shearing lead to morphology composed of white birefringent domains surrounded by dark zones corresponding to the isotropic imide polymer. Fig. 4 shows that the birefringent domains are almost uniform and present for all blending percents, while their size depends on the system composition. At the mixing ratios of 40 PI/60 HPC and 50 PI/50 HPC one can observe a mosaic-like morphology. This is no longer remarked for 60 PI/40 HPC, where the white regions are randomly distributed and their sizes are irregular. In addition the dimension of the lyotropic domains is smaller as the HPC content increases and they are more regularly distributed in the system.

Further investigations on the induced pattern in the epiclon-based polyimide using lyotropic liquid crystal template are possible through AFM imaging (Fig. 5).

Previous studies of HPC films indicate that, after shear cessation, a primary set of "large" bands appears perpendicularly to shear direction, while orthogonal deformation to bulk orientation leads to a secondary periodic structure containing "small" bands formed parallel to the second deformation direction.[10] By mixing HPC with the polyimide, the surface pattern is modified. The shear-induced anisotropy is strongly affected by the inevitable relaxation of the chains, when the external field is removed. By introducing polyimide into the ordered HPC matrix, relaxation will take place collectively, due to the fact that the highly concentrated and aligned polymers cannot individually relax and, therefore, the inner stress generates a periodical contraction in the HPC matrix and different packing modes are noticed. When the isotropic PI component prevails, on the scanning area of $10 \times 10\ \mu m^2$ one can observe a small tendency of surface structuring, but not yet ordered in the form of bands (Fig. 5 (a)). In this case the formations have maximum heights of about 120 nm. Further increase of liquid crystal content increases the probability of occurrence of band-like ordered structural formations, with heights of 200 nm, surrounded by previously observed organization (Fig. 5 (b)). Instead, the bands of 300 nm in height are better shaped/defined at the composition of 40 PI/60 HPC system, as highlighted in Fig. 5 (c), due to the predominance action of the anisotropic component.

The inherent long-range ordering tendencies of the used matrix and, specifically, of its pattern-forming properties, open new perspectives to achieve ordered polymer microstructures. Pure and applied research concerning the shear generated morphology of isotropic/anisotropic polymer blends will gain higher importance in realization of display devices. Moreover, considering the

biocompatible character of the liquid crystal matrix and of the used dianhydride monomer,[17] implicitly of the corresponding polyimide,[3] one can conclude that these surfaces with ordering tendency are adequate for developing cell culture substrates with tuned surface morphology.

EXPERIMENTAL

Materials. High purity chemicals: 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride (EPICLON, Merck, 98 % purity), 1,4-bis(p-aminophenoxy)benzene (*p*-BAB, Sigma-Aldrich), N,Ndimethy-lacetamide (DMAc, Sigma-Aldrich 99.5 %, anhydrous), 1-methyl-2-pyrrolidinone (Sigma-Aldrich, anhydrous, 99.5 %), hydroxypropyl cellulose (HPC) (LF, KlucelTM) were used as received.

Polymer synthesis. The polymer containing alicyclic units was prepared by polycondensation reaction of the EPICLON with the aromatic diamine *p*-BAB. The polyimide precursor, namely the poly(amic acid) (PAA), was further transformed by thermal treatment into the corresponding PI. The details of reaction steps were reported in other works.[18,19]

Blends and films preparation. The polymer powder (PI and HPC) was weighed and placed into a flask with known weight. HPC was then mixed with an appropriate amount of DMAc to obtain a 60 wt% concentration, while the concentration of polyimide solutions in DMAc was 50 wt%. These two main solutions were blended in different proportions in order to obtain: 40/60, 50/50 and 60/40 PI/HPC mixing ratios. The resulting system was deposited onto a glass substrate. Films were cast and sheared simultaneously at room temperature (Scheme 1).

Characterization. Shear viscosity tests were made on a Bohlin rheometer with a measuring system having cone-plate geometry. The cone has a diameter of 4 cm and an angle of 4 degrees. Shear rate was ranged from 0.07 to 2000 s^{-1} and for activation energy determination the temperature was varied from 25 to 45°C.

Polarized light microscopy (PLM) investigations were performed with an Olympus BH-2 polarized light microscope under cross polarizers.

Atomic force microscopy (AFM) measurements were performed on a SPM SOLVER Pro-M platform (NT-MDT, Russia) at room temperature in semi-contact mode, using a commercially available cantilever NSG 10 (NT-MDT, Russia) with a probe tip radius of 10 nm.

CONCLUSIONS

The paper deals with preparation of composite system by embedding in different proportions a polyimide in a liquid crystal polymer matrix. The obtained system was rheologically analyzed highlighting that at the concentration of 60 wt% HPC in DMAc the solution is in lyotropic phase exhibiting a shear thinning behavior, while for 50 wt% polyimide in DMAc the sample presents Newtonian domain. The flow activation energy increases with HPC content in the samples, indicating a higher barrier for flow that is useful in maintaining the morphology resulted after removing the shear deformation. PLM images show a mosaic-like texture more uniformly distributed when the anisotropic phase prevails. AFM studies indicate that enhancement of liquid crystal content increases the probability of occurrence of band-like ordered structural formations. These biocompatible surfaces with ordering tendency are suitable for bio-applications, particularly for cell culture purposes.
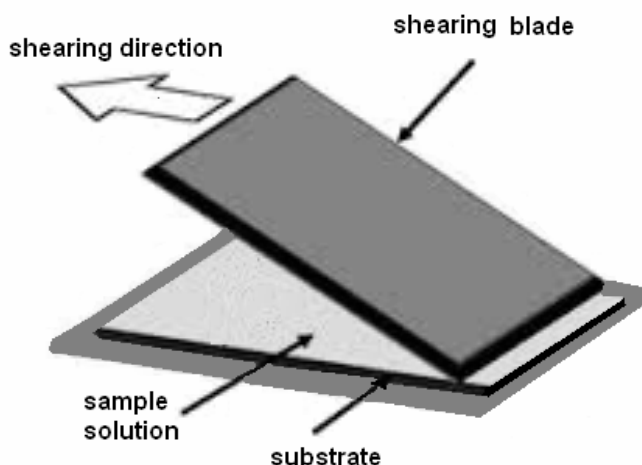
Scheme 1 – Schematic representation of shearing process of the PI/HPC samples.

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