

Structural reorganization in films of cellulose derivatives in the presence of colloidal particles

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Received 19 March 2004; received in revised form 30 June 2004; accepted 12 July 2004

Abstract

Water-cast films of two ethers of cellulose, hydroxypropylcellulose (HPC) and hydroxyethylcellulose (HEC), with dispersed silica particles, were deposited on flat substrates. X-ray specular reflectivity was used to characterize the structure of these solid ca. 1000 Å thick films as a function of the added colloidal fraction. It was shown that the structural changes resulting from increasing amounts of incorporated silica particles pass through distinctively different routes in the case of HPC- and HEC-based films. However, the structures in the two cases are similar at sufficiently high colloidal fraction.

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Keywords: X-ray reflectivity; Cellulose derivatives; Silica particles

1. Introduction

In recent years, macromolecular structures and phase transformations at interfaces and in thin polymer films have been objects of extensive theoretical and experimental studies [1]. Such interest is due to observed conformational changes and ordering effects, which are relevant to a variety of potential applications in biology, medicine and industry. One of the challenging tasks in this research field is the study of hybrid polymer–inorganic systems, in particular, complex three-dimensional structures of colloidal dispersions of small particles in polymeric films and associated topological defects (such systems generate non-trivial topological constraints and singularities that affect the physical properties of the ‘host’ polymeric systems and can be used for desired and tunable adjusting of micro- or nanoheterogeneous materials). Although mechanical, viscoelastic, thermal and optic macroscopic properties of such complicated and structured multicomponent systems are studied now intensively, their structural organization is still poorly understood on the microscopic level [2–10]. And

reasons of that is non-trivial interplay of different contributions in creating of final structural picture: the basic structure of the polymer, colloid–polymer and colloid–colloid interactions, geometrical parameters of colloidal particles and polymer chains, the colloid fraction to polymer matrix ratio, etc. Recently, a strong effect of silica nanoparticles on the large-scale spherulitic morphology of hard domains of segmented polyurethanes was studied by atomic force microscopy and ultra small-angle X-ray scattering [11]. It has been shown that addition of silica suppresses fibril formation in spherulites due to disruption of short-scale domain structure, attributed to segment phase separation in unfilled polyurethanes.

In our study we have chosen two hydroxyalkyl ethers of cellulose: hydroxypropylcellulose (HPC) and hydroxyethylcellulose (HEC), as ‘host’ polymers. Presence of highly ordered thin film architectures of cellulose derivatives and the ability to modify, regenerate, and reshape cellulose and polysaccharide derivatives with unique chemical, physical, and physiological properties have kept interest in these polymers high over the past decade [12]. Cellulose and its derivatives, being chiral, tend to have cholesteric supramolecular ordering in solutions [12,13]. The cellulose chains are stiffened by van der Waals forces and by inter- and intramolecular hydrogen bonding and form microfibrils.

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HPC is one of the most common lyotropic water-soluble ether of native cellulose and its concentrated aqueous solutions display optical properties typical of cholesteric liquid crystals [14,15]. Moreover, in our previous work, evidence of preferential alignment of the liquid crystalline (LC) domains in thin HPC films at the substrate surface was obtained [16]. At the same time, there is a notable lack of investigations describing the physical properties and morphology of highly-concentrated HEC solutions and films. It is known that solutions of HEC can be described by entanglements of the polymer chains, however the formation of a certain ordered structures of spherulitic type in the 65–70% aqueous solutions has been reported [17,18].

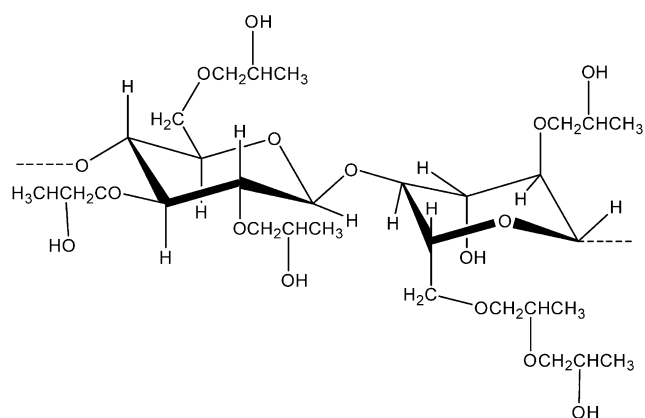
When colloidal particles are added to a LC matrix, their presence may alter the orientational distribution and the textural organization. The rheology and flow-induced microstructure of suspensions of particles (smallest diameter is 280 Å) in LC solutions of HPC at a concentration of 55 wt% has been studied by a combination of rheological and X-ray scattering techniques [4]. X-ray scattering data indicate that the addition of 10% silica particles reduces the overall orientation order. But there is still a lack of information regarding structural arrangements in solid polymeric films containing nanoparticles of size comparable to the molecular scale. In this communication, we use specular X-ray reflectivity (XRR) measurements to study the effect of small inorganic particles on the molecular ordering in the complex HPC- and HEC-colloidal silica films along the substrate normal.

2. Experimental

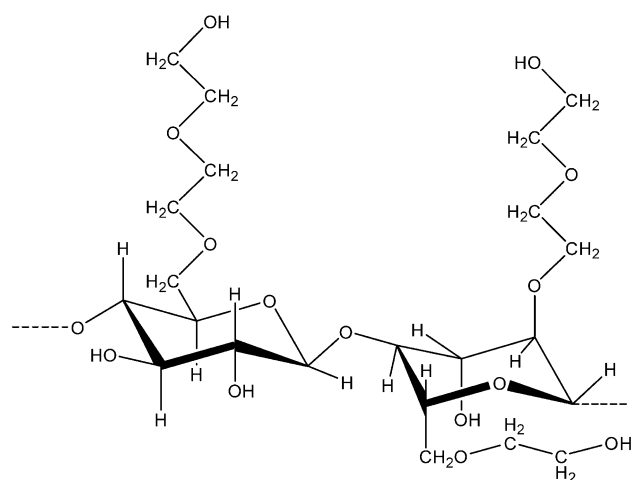
HPC (Klucel EF) was obtained from Hercules Inc. Nominal value for M_w is reported in the product literature as 80,000 [19]. Molar substitution (MS, the average number of moles of hydroxypropyl substituent per mole of anhydroglucose residue) is 3.8 according to the manufacturer. HEC of M_v , ca. 90,000 was purchased from Aldrich Chemical Co. This sample has an MS of 2.5 (5 ethylene oxide groups/2 anhydroglucose units). The chemical structures of HPC and HEC molecules are shown in Fig. 1. Powdered samples were dried under vacuum at 70 °C for 6 h before use. Aqueous solutions of Nyacol[®] 215 colloidal silica (SiO_2 , 15 wt%, pH=11) with an average particle size of about 40 Å were purchased from Eka Chemicals Inc.

Aqueous solutions with polymer concentration of 1 wt% were prepared. Deionized, distilled water (18 MΩ cm) was used for preparing solutions. The solutions were continuously stirred until homogenization at room temperature. Complex solutions of HPC or HEC and colloidal particles were prepared by mixing and subsequent stirring 70 ml of 1 wt% polymer solution with different amount (0.25–8.0 ml) of aqueous colloidal solution.

The substrates (3"×1"×0.1"), silicon (100) with a native oxide layer of ~15 Å thickness and a surface roughness $\sigma \sim 3$ Å (by XRR), were purchased from Umicore



Hydroxypropylcellulose (HPC)



Hydroxyethylcellulose (HEC)

Fig. 1. Schematic representation of the chemical structures of HPC and HEC molecules.

USA Inc., Semiconductor Processing Division. They were cleaned in a strong oxidizer, a mixture of 70% sulfuric acid and 30% hydrogen peroxide (70:30 v/v), for 1 h at 90 °C, rinsed with copious amounts of distilled water and stored in water before use. Prior to preparing the films, the wafers were removed from the water and blown dry under a stream of nitrogen. We spread thin films by dipping the substrates in the polymer or polymer + colloid solutions, withdrawing them at constant speed of 1.5 mm/s to get uniform film thickness, and subsequent air-drying in horizontal position at room temperature. Solution concentration and withdrawal speed affect the film thickness. The parameters used for film deposition gave typical film thicknesses of about 1000 Å.

XRR studies were performed at beam line X23B of the National Synchrotron Light Source using a four-circle Huber diffractometer in the specular reflection mode (i.e. incident angle θ is equal to exit angle). The reflected intensity was measured as a function of the momentum

transfer component $q_z = (4\pi/\lambda) \sin \theta$, perpendicular to the reflecting surface. X-rays of energy $E = 10.0$ keV ($\lambda = 1.24$ Å) was used for all measurements. The beam size was 0.4 mm vertically and 1.5 mm horizontally. The samples were kept under slight overpressure of helium during the measurements to reduce the background scattering from the ambient gas and radiation damage. The experiments were performed at room temperature. The off-specular background was measured and subtracted from the specular counts.

3. Results and discussion

Specular reflectivity of X-rays or neutrons gives structural information about thin solid or liquid films in the direction perpendicular to the film/substrate interface. The methodology and comprehensive XRR analysis of HPC films of different thicknesses were reported in our recent work [16]. For thin films of thickness 200–5000 Å, a preferential orientation of LC domains with a planar orientation parallel to the substrate was located in the film-substrate interface region. The typical reflectivity pattern for HPC film contains a prominent peak at about $q_m = 0.60$ Å⁻¹ (Fig. 2) due to the formation of the anisotropic LC phase. Spacing and crystallite size are $\bar{a} = 2\pi/q_m = 10.3 - 10.5$ Å and $L = \lambda/(\beta \cos \theta) = 50$ Å, where β is the full width at a half-maximum intensity of the Bragg peak observed at a mean exit angle of θ , q_m is the position of the Bragg peak. With increasing amount of silica particles

dispersed in anisotropic thin solid films of HPC (~ 1000 Å), the LC peak diminishes (see vertical arrow in Fig. 2) and a peak at $q_z = 0.07$ Å⁻¹ appears. This peak is attributed to the periodic spacing between colloidal particles and corresponds to a distance of about 90–100 Å. This means that at least one microfibril of domain size 40–50 Å exists between the silica particles. The fixed position of colloidal interference maximum and the increase in its intensity with increased particle fraction mean that there is compensation of negative particle charge enhancing the formation of silica clusters. This is due to adsorption of HPC on silica particles, a polymer-induced depletion attraction of these particles and pH change during dissolution of Nyacol[®] 215 in a large volume of neutral HPC solution. The pH effect is of minor consequence to this aggregation as was shown by our studies (not shown in this paper) of complex HPC and HEC films based on polymer solutions with pH = 11. A large part of these aggregates are accumulated at the substrate surface during film deposition procedure and are locked there after evaporation of water [16]. XRR data show that the added colloidal particles, which concentrate in the film-substrate region, destroy the preferential crystallite alignment in that area (end of the vertical arrow in Fig. 2). With further increase of colloidal fraction, an interference peak in this angular region appears. Showing a larger \bar{a} (12.4–13.5 Å) and smaller crystallite size (28–29 Å) than for conventional HPC films. The obtained structural parameters are in good agreement with the X-ray diffraction data for a dry fiber of HPC. The diffraction pattern of HPC indicates that the polymer crystallizes as fibers of hexagonally-packed rods with an average center-to-center distance of 12.8 Å [15]. X-ray diffraction measurements also show that the diameter of the HPC microfibril is about 30 Å [14].

Let us consider the complex polymer/colloid films based on another hydroxyalkyl ether of cellulose, HEC. HEC has a reduced tendency to form LC phase in aqueous systems than HPC [20]. This is confirmed by the XRR pattern of HEC film, which has no pronounced LC peak as in the case of HPC films (Fig. 3, top data). Incorporation of silica particles to the HEC films leads to appearance of a highly oriented state, which is indicated by pronounced interference maximum in the reflectivity curves (Fig. 3). Spacing and correlation length for the complex HEC films with addition of 4 ml of colloidal solution are $\bar{a} = 12.6 - 12.8$ Å and $L = 30 - 37$ Å. These are close to parameters obtained for the complex HPC films. That means that final structural states of HPC and HEC films with added of colloidal mesophases are quite similar.

The differences in structural behaviors of pure HPC and HEC films of similar molecular weight (without silica colloid) must be related to different substituents (side groups) of these cellulose derivatives and their conformational changes (steric effects) at high polymer concentrations during formation of the films. It is apparent that the tendency towards lyotropic mesomorphism in polymeric systems is mainly determined by the degree of

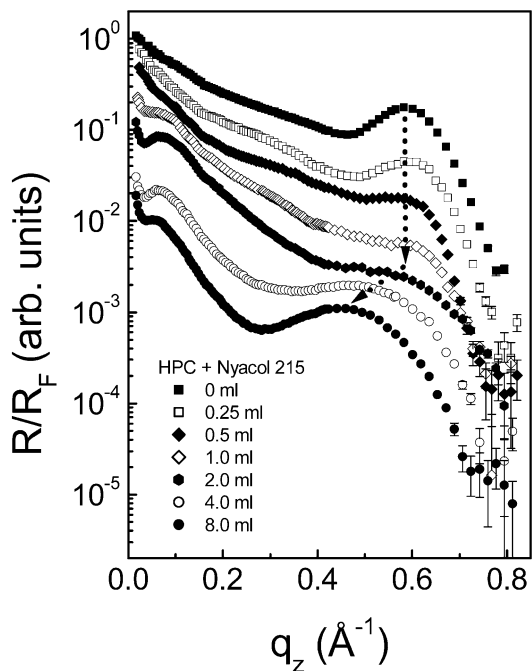


Fig. 2. Normalized specular X-ray reflectivity pattern for HPC films (thickness of about 1000 Å) with different amount of Nyacol[®] 215 colloidal silica, which was added to 70 ml of original HPC solution. The arrow follows the highest peak positions of the LC peaks.

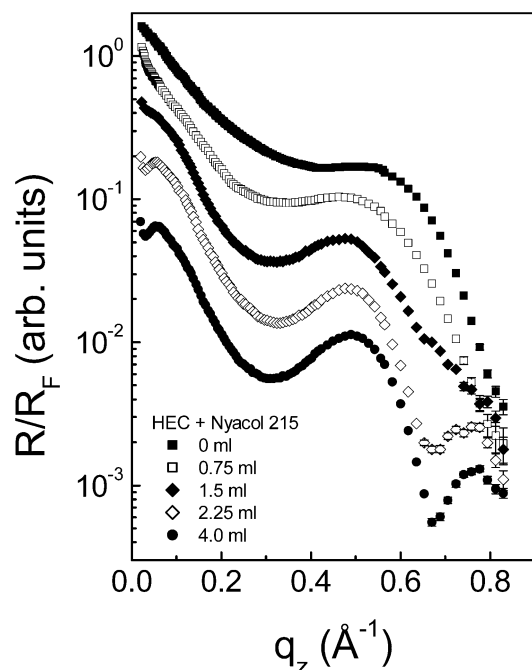


Fig. 3. Normalized specular X-ray reflectivity pattern for HEC films (thickness of about 1000 Å) with different amount of Nyacol[®] 215 colloidal silica, which was added to 70 ml of original HEC solution.

anisodiametry of macromolecules. The flexibility of the skeleton chain of cellulose derivatives is mostly determined by the secondary cyclization of the macromolecular structure by intramolecular hydrogen bonds rather than by steric hindrance due to the size of substituting groups [13]. Formation of intra- as well as intermolecular hydrogen bonds leads to the appearance of rigid extended mesogenic fragments and increased anisodiametry. The hydroxylpropyl groups are rather hydrophobic, which lowers the affinity of HPC for water and gives a sufficient condition for ordered phase formation. In comparison, HEC is much less hydrophobic and its solutions contain entanglements of the polymer chains, which become locked into an unoriented concentrated gel.

Incorporation of agglomerates of nanocolloidal particles into HPC or HEC films leads to structured alignment of the polymer chains in a polymer/colloid matrix with similar structural parameters. Such structural reorganization can be a result of two effects. First, 'geometrical' changes in the conditions of supermolecular alignment of polymer chains (HPC or HEC) are observed. In the case of complex films, not only does the substrate surface become rough because of accumulation of silica aggregates at the substrate, but also rough interfaces between polymer and silica clusters in bulk of the film are formed. Such a 'rough' state of interfaces attenuates the confinement effect¹. Increasing interface

¹ A preferable direction is still present during formation of the films on the substrate as is indicated by the presence of specular interference peak in the reflectivity pattern.

roughness produces 'bulk' conditions for molecular arrangement during film formation, and is one of the reasons for the similarity of structural parameters obtained for HPC in bulk and in complex HPC- and HEC-colloidal silica films. The second factor that influences the behaviors of cellulose derivatives (and the resulting structural state of the films) is the competing interactions in polymeric materials and between the polymer chains and silica clusters. The similar structural picture for the complex HPC (with addition of 8 ml of silica) and HEC (4 ml) attests that the polymer-colloid interactions (the ether-silanol hydrogen bonding [21]) are predominant and abolish the diversity of these polymers (due to different hydrogen bonding and the dispersion interactions of the substituents). For some films of HEC with higher content of silica, an additional reflectivity peak around $q_z = 0.76 \text{ \AA}^{-1}$ was observed (Fig. 3). This peak corresponds to spacing $\bar{a} = 8.3 \text{ \AA}$, which is close to a diameter of the molecule and can be related to a structured alignment of isolated (non-fibrillar) chains of this polymer. Two factors may be responsible for such behavior: the relative scale-dependent increase of surface smoothness of silica agglomerates with more colloid, and the 'locking' of some polymer chains in such a conformation during non-controlled solvent evaporation and film formation (kinetic factors must also be important at very high polymer concentrations). The HEC-colloidal silica films prepared from solutions with pH=11 show similar structural parameters and trends in XRR patterns as the conventional ones. Slightly different parameters of LC phase were obtained for pH=11 based films of HPC, however there is not a principal difference in the picture of structural changes in those films and the conventional ones as colloidal fraction increases. A clearer understanding of all processes that occur during formation of such complex systems needs further multidisciplinary studies.

4. Conclusions

Complex solid films of cellulose derivatives (HPC and HEC) with colloidal silica deposited on smooth surface have been studied by specular XRR. The structural rearrangement of polymer chains in the presence of dispersed colloidal particles was tracked as a function of the added silica fraction. In the case of HPC, the molecular-scale morphology proceeds from a preferential alignment of the LC domains of HPC in the film-substrate region parallel to the substrate surface, through destroying this alignment by incorporation of colloidal particles, to recovered structured alignment of the polymer chains in a polymer/colloid matrix. Addition of silica particles to the HEC films leads from the entangled polymer chain state to the appearance of a highly oriented state with structural parameters similar to HPC/colloid films. In both cases in the final states, molecules of HPC and HEC form an

ordered liquid-crystalline microfibril phase with structural parameters typical of hexagonally packed rods. Such experimental behavior of cellulose derivatives-based films can be explained as a competing interplay of liquid crystallinity-producing interactions (including excluded volume interactions resulting from a presence of colloidal particles) and polymer/silica clusters interactions in the confined conditions of thin films.

Acknowledgements

This work was supported by the US National Science Foundation under grant no. DMR-0305494. XRR measurements were performed at beam line X23B of the National Synchrotron Light Source, which is supported by the US Department of Energy.

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