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Mesomorphic organisation of (2-hydroxypropyl)cellulose under the influence of silica networks

P. WOJCIECHOWSKI[1], T. HALAMUS[1*], U. PIETSCH[2]

[1]Department of Molecular Physics, Technical University of Łódź, ul. Żeromskiego 116, 90-924 Łódź, Poland

[2] Physics, Siegen University, Fachbereich 7, Walter-Flex-Str. 3, D-57068 Siegen, Germany

Mesomorphic behaviour of (2-hydroxypropyl)cellulose (HPC) within organic–inorganic hybrid materials was investigated. Hybrid materials HPC/silica were prepared by means of the sol-gel process, with hydrolysis and condensation of (tetraethoxy)silane taking place in the mesomorphic environment of HPC. Solid films of HPC/silica were investigated using the Raman spectroscopy, differential scanning calorimetry, thermo-optical analysis, and small angle X-ray scattering. Additionally, swelling by water was tested. The analysis of the results leads to the following conclusions: (i) silica has a strong stabilisation effect on the mesomorphic organisation of HPC: the glass transition temperature and isotropisation temperature of HPC are shifted to higher values; (ii) X-ray measurements reveal a nano-scale organisation of the HPC/silica hybrids with *d*-spacing equal to 65Å; a long-range organisation within HPC/silica hybrids seems to be related to a surface induced ordering; (iii) curing of HPC/silica hybrids affects the swelling behaviour.

Key words: *(2-hydroxypropyl)cellulose; phase transition; hybrid composite; sol-gel*

1. Introduction

In the past 20 years, research on the mesomorphic behaviour of cellulose derivatives has been focused on cholesteric liquid-crystalline phases after discovery of cholesteric phases of (2-hydroxypropyl)cellulose (HPC) in concentrated aqueous solutions by Werbowyj and Gray [1]. HPC forms thermotropic as well as lyotropic liquid crystalline phases in many solvents. The investigations were not limited to the cellulose derivatives alone but studies of the molecular structure of composites based on the cellulose derivatives with hydrophilic polymers have also been carried out. They have shown an effect of the hydrophilic polymers on the phase transitions of the mesomorphic cellulose derivatives [2–5]. Hybrid composite systems of the cellulose

[*]Corresponding author, e-mail: halamus@p.lodz.pl

derivatives with an inorganic component were also investigated, albeit to much smaller extent [6, 7]. Organic-inorganic hybrids of polysaccharides occur in nature: in the rice plant, for example, amorphous silica is supplied, transferred, and precipitated in the polysaccharide matrix. Generally, an inorganic phase in biocomposites is regularly and highly organised in a polymer matrix. These sophisticated biomineralization processes are difficult to be repeated and carried out in artificial systems [8].

A hybrid material based on HPC and silica was obtained ca. 10 years ago by Yano [6], who investigated the influence of silica network on the molecular motion of HPC analysing the dynamic viscoelasticity. The tanδ curve of HPC shows a high, sharp peak at 110 ºC (α_1 relaxation) and two smaller peaks at 25 ºC (α_2 relaxation) and at –45 ºC (β relaxation). The α_1 peak of the micro-hybrids broadens and its height decreases as the silica content increases. Mechanical properties of the HPC/silica hybrids are improved in comparison with HPC: for example the ultimate strength of HPC is 5 MPa, whereas the strength of the hybrid composites is up to 18 MPa. Microphase-separation processes in the HPC/silica hybrids were recently investigated by Thomas and Antonietti [7]. Their studies revealed that the suprastructure of HPC in the HPC/silica system is essentially preserved. The HPC/silica hybrids resemble the microporous silicate glasses impregnated by low molar mass liquid crystals [9]. Investigations of the condensed matter in porous matrices have revealed various novel properties and effects not observed in the same substances when studied as bulky samples. In this paper, we analyse an influence of the silica network on the mesomorphic organisation and properties of HPC. We performed the Raman spectroscopy (RS), differential scanning calorimetry (DSC), X-ray, thermo-optical analysis (TOA), as well as swelling experiments.

2. Experimental

Sample preparation. (2-Hydroxypropyl)cellulose (HPC) (M_W = 100 000) and (tetraethoxy)silan (98%) (TEOS) were supplied by the Aldrich Chemical Company and used without further purification. Hybrid materials of HPC/silica were prepared according to the sol-gel process: appropriate amounts of HPC (e.g., 2.0 g) were mixed in the flask with 1.2 g TEOS, 1.0 g aqueous hydrochloric acid (pH = 1) and 15.8 g ethyl alcohol. Calculated values of silica content were estimated from the initial amount of TEOS assuming that TEOS was completely converted to silica, and all volatile liquids have evaporated. All the samples were homogenised by stirring for 4 h and stored for 48 h. The viscous liquid was then poured out on a Teflon plate. The mesophase organisation of HPC occurred during the solvent evaporation. The HPC/silica films (thickness 0.5 mm) were then dried during 8 h in the temperature of 80 °C under vacuum. Reference HPC films were obtained by casting from ethanol solution.

The HPC/silica round samples with the diameter of 1.5×10^{-2} m, and the thickness of 3×10^{-4} m were investigated in terms of their swelling abilities in water at pH = 5.5 by a weighing method with an accuracy of 1×10^{-4} g. The water uptake (h) is expressed as the ratio of the mass of water in a sample to the mass of the dry sample.

Material characterisation. Differential scanning calorimetry (DSC) measurements were carried out by using a DuPont Instruments 910DSC, employing the heating rate of 10 ºC/min. The thermo-optical analysis (TOA) was carried out using a Mettler Toledo FP-84 hot stage and a polarised microscope. The TOA analysis consists in measuring the relative intensity of light, I_T/I_0, transmitted through a sample placed under a microscope between crossed polarisers as a function of linearly increasing temperature (I_T and I_0 are the intensity of the transmitted light at temperature T and at the room temperature, respectively). The heating rate in our experiments amounted to 2 ºC/min. The Raman investigations were performed using a dispersive spectrometer Jobin–Yvon T64000 equipped with a confocal microscope. The Raman spectra were obtained at 293 K using the argon ion laser (λ = 514 nm). The X-ray diffraction patterns of HPC/silica hybrids were measured in the Institute of Physics, University of Potsdam.

3. Results and discussion

3.1. Raman scattering

The analysis of silica in the HPC/silica hybrids was performed using Raman spectroscopy. The reference sample (100% SiO_2) was obtained by the sol-gel process of TEOS similar to the HPC/silica hybrids. Figure 1 shows Raman spectra of silica, pure HPC and of the HPC/silica hybrids containing 25 wt. %, 50 wt. % and 80 wt. % of silica.

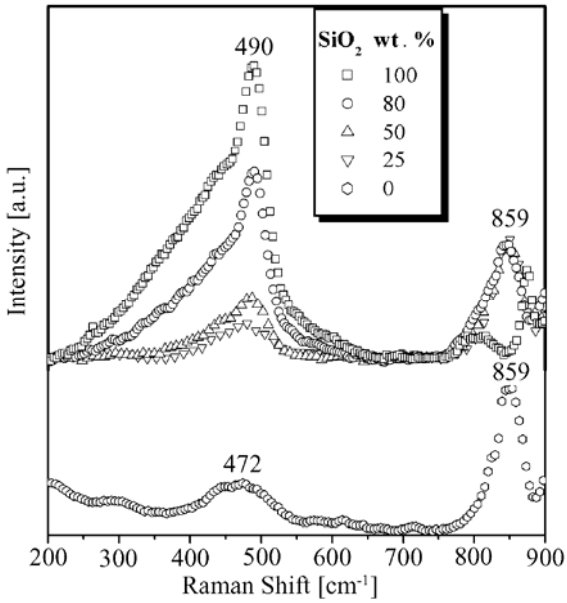

Fig. 1. Raman spectra of silica in the HPC/silica hybrids (upwards), Raman scattering of HPC (bottom)

The main Raman scattering of silica is detected in the frequency range of 250–650 cm^{-1} with maximum at 489 cm^{-1} [10]. The Raman spectrum of pure HPC in this range shows two bands at 472 cm^{-1} and at 859 cm^{-1}. The spectra for the hybrid composites are normalised with respect to the 859 cm^{-1} band of HPC. The silica scattering band observed around 489 cm^{-1} is also detected in the hybrids systems, however with a lower intensity, due to a lower concentration of silica network in the HPC/silica hybrids. The width as well as position of the 489 cm^{-1} line are characteristic of the three-dimension inorganic network of silica [10].

3.2. DSC and X-ray scattering measurements of HPC/silica systems

The complex morphological order of HPC in films cast from solvent was described by Samuels [11] and by Rials and Glasser [12]. Thermal and dynamic mechanical analysis (DMTA) of HPC shows that the material consists of three distinct phases in the bulk: a crystalline phase, an amorphous phase and a phase exhibit-

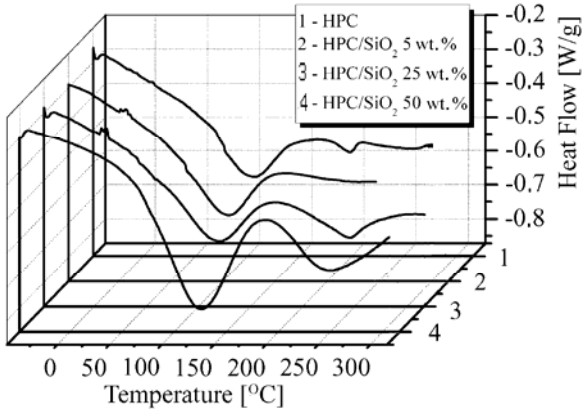

Fig. 2. DSC heating curves for HPC and HPC/silica hybrids (first scan)

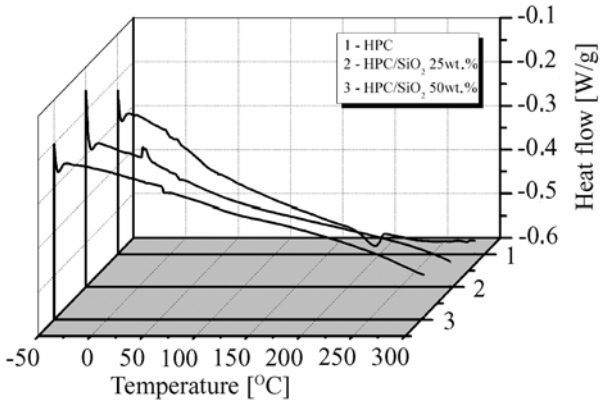

Fig. 3. DSC heating curves for HPC and HPC/silica hybrids (second scan)

ing an intermediate level of order (intermediate phase). The contribution of the intermediate phase is strongly enhanced in HPC films cast from solvents in which HPC forms a lyotropic liquid crystalline phase.

Figures 2 and 3 show the first and second scans of DSC thermograms of HPC and HPC/silica films. The glass transition of HPC, expected at ca. 10 ºC, is not visible in the first scan because it is overlapped by a very broad endothermic effect, connected with the presence of the intermediate phase of HPC. It should be mentioned that HPC is a hydrophilic polymer containing about 2 wt. % of water when stored in air in normal conditions. The broad endothermic peak around 100 ºC observed during the first DSC scan is related to the presence of water in the intermediate phase of HPC. The enthalpy of this transition is equal to ΔH = 40 J/g.

The thermogram of HPC during the second scan reveals the glass transition at 10 ºC, because the endothermic transition of intermediate phase dominating during the first heating is strongly suppressed and moved to a slightly lower temperature. The endothermic peak detected at 200 ºC in the first as well as in the second scan (the transition enthalpy ΔH = 2.8 J/g) corresponds to the transition of HPC from the thermotropic phase to the isotropic phase, appearing in HPC at high temperatures [2]. The results of the investigations of phase transitions in HPC by means of DSC are consistent with the results presented in the literature derived from mechanical methods [12].

Figure 2 shows the first scans of DSC thermograms not only for HPC but also for the hybrid systems of the HPC/silica with different contents of silica. The values of ΔH and the transition temperatures are listed in Table 1. It can be seen that the phase transition of the intermediate phase of HPC is shifted to higher temperatures (from 108 ºC to 124 ºC) and the transition enthalpy increases from ΔH = 29 J/g in the sample containing 5% of silica to ΔH = 134 J/g at 50 wt. % of the silica content.

Table 1. Transition temperatures (T_{100} , T_{200}), corresponding enthalpies (ΔH) and glass transition temperatures (T_g) for HPC and HPC/silica hybrids

Sample	Scan I				Scan II
	T_{100} [°C]	ΔH_{100} [J/g]	T_{200} [°C]	ΔH_{200} [J/g]	T_g [°C]
HPC	104	40	200	2,8	10
HPC/SiO_2 5 wt. %	108	29	227	3,7	–
HPC/SiO_2 25 wt. %	118	41	246	26,6	38
HPC/SiO_2 50 wt. %	124	134	247	46,4	53

The results presented above strongly suggest that silica or its intermediate compounds affect the thermal behaviour of HPC. The hydrolysis of TEOS and, in particular, condensation of the silanol (SiOH) groups takes place in the lyotropic liquid crystalline phase of HPC. Hence products of the hydrolysis of TEOS can interact with HPC macromolecules by hydrogen bonds enhancing the stability of the intermediate phase of HPC. At the same time the isotropisation transition of the thermotropic phase

appearing at 200 ºC in HPC, disappears in the composite HPC/silica. Instead, an endothermic effect shows up at a higher temperature (Table 1). This transition implies processes occurring inside silica associated with the condensation of free silanol groups. Hence, the second stage of solidification of the HPC/silica hybrid occurs probably in the temperature range 200–240 ºC. This process has a major influence on the thermal stability of the HPC/silica hybrids.

Figure 3 shows second DSC scans in the investigated systems. At low temperatures, the thermograms show a glass transition at about 10 ºC for HPC, and at 38 ºC and 53 ºC for HPC/silica containing 25 wt. % and 50 wt. % of silica, respectively (Table 1). No other thermal transitions can be detected in the hybrid HPC/silica systems. In particular, the effect associated with the isotropisation, observed at 200 ºC in HPC, disappears in the hybrids.

An increase of the glass transition temperature with increasing silica contents suggests a cross-linking of HPC or/and an orientation ordering of HPC in the silica micropores. It is known that the polymer characteristics and structure may substantially change in silica microporous glasses [9]. The thermal stability of polymers in micropores is higher than that of the respective bulk polymers. The effect can be explained using the concepts of surface-induced ordering effects. In order to confirm this assumption, small angle diffraction X-ray patterns (SAXD) of HPC/silica hybrids were investigated.

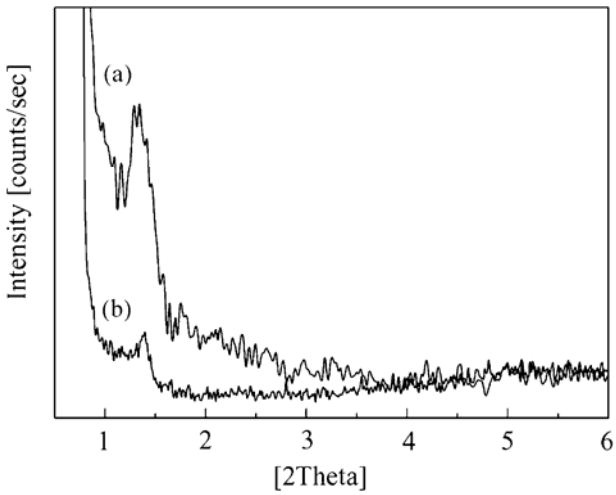

Fig. 4. X-ray diffraction patterns of HPC/silica hybrids:
a) 25 wt. % of silica, b) 50 wt. % of silica

Figure 4 shows small-angle X-ray (SAXD) diffraction patterns for two HPC/silica hybrids with different concentrations of silica. SAXD peak position was found insensitive to the weight ratio of HPC to silica: the SAXD patterns of the investigated samples show the diffraction at $2\theta = 1.37^{o}$ for both concentrations of silica with the *d*-spacing of 6.5 nm. The diffraction intensities are, however, different: the SAXD

peak of the HPC/silica composite is higher when the amount of HPC in the silica environment is larger. Taking into account that the SAXD patterns of pure HPC or pure silica do not contain any diffraction peak at this 2θ range [13], the X-ray investigations indicate that the SAXD pattern at $2\theta = 1.37^{o}$ is associated with HPC macromolecules incorporated in silica pores. A possible explanation may be the orientation ordering of HPC macromolecules near the inner pore surface. The surface of a silica pore wall contains a large number of SiOH groups that can form hydrogen bonds with HPC.

A similar effect of orientation ordered regions has been observed in the investigations of the light transmission through porous glass plates, containing in the pores poly(alkyl methacrylates) with a long side group [9]. It should be mentioned that the tendency for self-organisation of HPC, forming lyotropic and thermotropic liquid crystalline phases, is much stronger than in the case of the non-mesogenic poly(alkyl methacrylates).

3.3. Thermo-optical analysis of the HPC/silica hybrids

As was mentioned in Section 2, the thermo-optical analysis consists in measuring transmission of polarised light as a function of temperature. Figure 5 shows thermo-optical (TOA) characteristics of HPC and HPC/silica hybrids in the temperature range 20–250 °C. The HPC/silica hybrids form birefringent films, transparent for the visible light at silica concentrations up to 60 wt. %. Samples with higher concentrations of silica are opaque and fragile.

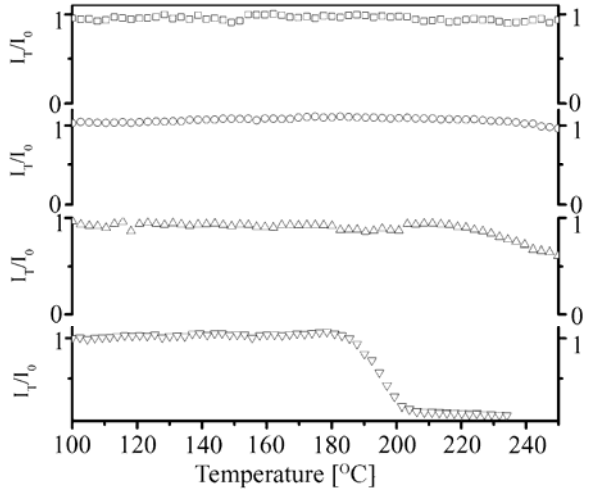

Fig. 5. Thermo-optical characteristics for: HPC (▽) and HPC/silica hybrids:
Δ – 5 wt. %, ○ – 25wt. %, □ – 50 wt. % of silica

Films of pure HPC show a drop of transmission in the temperature range 190–200 °C, due to the transition to the isotropic phase, as was confirmed by DSC.

All the investigated HPC/silica hybrids show birefringence and a high transmission of the polarised light above the isotropisation temperature of pure HPC. The content of the silica as low as 5 wt. % was found to stabilise very effectively the birefringence of the HPC/silica hybrids: the polarised light transmission at 250 °C is equal to 50% of its initial value. For the HPC/silica hybrids containing 25 wt. % or 50 wt. % of silica the transmission of polarised is constant up to 250 °C.

The results of the TOA measurements are consistent with the DSC experiments for the HPC/silica hybrids. Both methods demonstrate that silica in the hybrids hinders the isotropisation process of HPC. On the other hand, the results of dynamic mechanical investigations [6] as well as recently published structural investigations [7] reveal that the suprastructure of HPC in the HPC/silica system is essentially preserved. The ordered state of the HPC/silica system detected above of the isotropisation temperature of HPC is probably associated with the surface effect typical of two-component heterogeneous media.

3.4. Swelling of HPC/silica hybrids

The main objective of our research was the swelling behaviour of the HPC/silica hybrids in water as well as the status of water after the swelling. The HPC/silica hybrids in water immersion are able to form birefringent gels of the organic-inorganic network with water filling the interstitial spaces of the network.

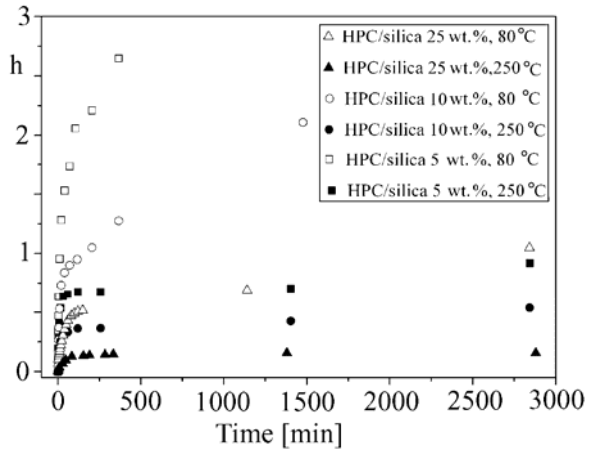

Fig. 6. Water uptake of HPC/silica hybrids vs. time:
open symbols – sample I, closed symbols – sample II

Figure 6 shows a temporal dependence of the water uptake (*h*) of HPC/silica hybrids in the immersion of water for two kinds of samples. Samples I were cured at 80 ºC during 8 h in vacuum and samples II were additionally cured during 10 minutes at 230 ºC. DSC of the HPC/silica hybrids suggested an additional curing effect of

silica at 240 ºC (see Fig. 2). The results presented in Figure 6 show that water uptake of the HPC/silica hybrids is strongly related to the concentration of silica as well as to its curing temperature. The increase of the concentration of silica from 5 wt. % to 25 wt. % decreases the swelling ability. A similar effect is obtained by an additional curing at 230 ºC.

The status of water filling the interstitial space of HPC/silica hybrids was estimated analysing the Raman spectra of the bulk water and water within HPC/silica hybrids after swelling. The Raman bands for the liquid water in the range 2800 –3800 cm^{-1} consist of four overlapping components peaking at 3247 cm^{-1}, 3435 cm^{-1}, 3535 $cm^{-1}$and 3622 cm^{-1}. Walrafen [14] has shown that these components exhibits different temperature dependencies: the intensities of the 3247 cm^{-1} and 3435 cm^{-1} components decrease on increasing temperature, while the two other components, at 3535 cm^{-1} and at 3622 cm^{-1}, increase in intensity. There is an isosbestic point near 3460 cm^{-1}. The integrated intensity ratio of the two former components (I_{3400}/I_{3200}) reflects the orientation order of H–bonds of water molecules [15]. A deviation of the integrated intensity ratio I_{3400}/I_{3200} from the value of 0.86 characteristic of liquid water can be taken as a measure of changes in the water structure.

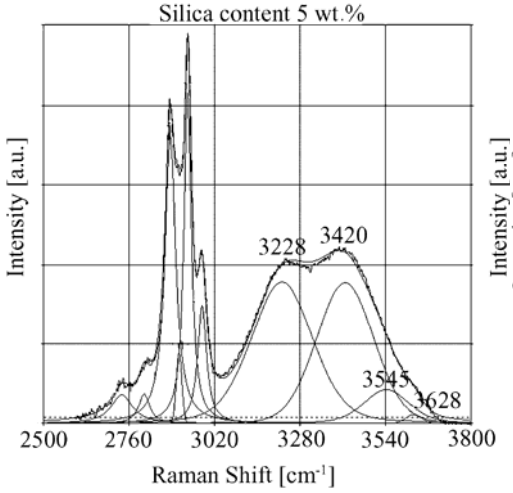

Fig. 7. Deconvolution of the O–H stretching Raman band for water within the HPC/silica hybrids (5 wt. % of silica, h = 1.5)

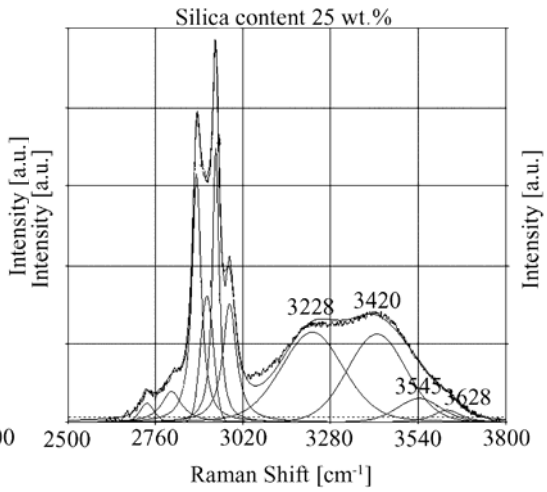

Fig. 8. Deconvolution of the O–H stretching Raman band for water within the HPC/silica hybrids (25 wt. % of silica, h = 0.67)

Figures 7 and 8 show a deconvolution of the OH stretching Raman band of water within the HPC/silica hybrids containing 5 wt. % and 25 wt. % of silica after swelling. The integrated intensity ratios I_{3400}/I_{3200} of the two investigated samples are equal to 0.86 and 0.87, respectively. This means that water in the HPC/silica hybrids has the same microstructure as liquid water in bulk samples.

4. Conclusions

Phase transitions of (2-hydroxypropyl)cellulose (HPC) are sensitive to the presence of silica within the HPC/silica hybrids. The glass transition of HPC in the hybrids is moved to higher temperatures in comparison with bulk HPC. The HPC/silica hybrids maintain the birefringence to temperatures much higher than the isotropisation temperature of bulk HPC. The X-ray measurements reveal a microstructure with *d*-spacing equal to 6.5 nm. It seems that the long range organisation in HPC/silica hybrids is related to surface-induced ordering of HPC in the silica pores.

Curing of the HPC/silica hybrids at elevated temperature affects their swelling behaviour. The curing at the 200 °C strongly suppresses the swelling ability of HPC/silica hybrids, probably due to temperature induced crosslinking.

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