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Determination of the molecular orientation in the polymeric liquid crystalline systems by low frequency Raman spectroscopy

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Abstract

Anisotropic polymer composites with fixed, oriented liquid crystalline organisation prepared by in situ photopolymerisation of acrylic or methacrylic acids in several cellulose derivatives were investigated by low frequency Raman scattering. The results were interpreted basing on a model of non-continuous structure of polymer glasses. The Raman investigations have shown that the macromolecules of the non-mesogenic (acrylic) component are oriented in the anisotropic composites, and that the orientation of the polyacrylic chains is more pronounced in the composites with higher concentration of the liquid crystalline cellulose derivative. It was found, that the interactions between the components play a crucial role in the formation of the composites (template-like photopolymerisation) and they determine their supramolecular structure. The liquid crystalline cellulose derivatives able to form hydrogen bonds play a role of specific cross-linking agents, while the cellulose derivatives with aliphatic side chains work as plasticisers.

Keywords: Polymer composites; Liquid crystalline cellulose derivatives; Low frequency Raman scattering

1. Introduction

The anisotropic composites obtained by photopolymerisation of vinyl monomers in oriented mesophase of liquid crystalline cellulose derivatives (LC-CDs) are known for ca. 20 years [1]; however, they attracted particular attention from both scientific and application point of view only in the last years [2–6]. The reversibility of the optical anisotropy is one of the most interesting properties of these composites: they become isotropic during heating, but their birefringence regenerates after cooling [4–6]. Such behaviour suggests that, besides the macromolecules of LC-CDs, the chains of the non-mesogenic (acrylic) component are also oriented. This seems to be possible taking into account that the polyacrylic chains grow in the oriented phase of CD. The IR and Raman spectroscopy investigations at the frequency range of 1500–1800 cm^{-1} [6,7] have shown significant influence of the medium on the polymerisation of acrylic monomers and have supported the hypothesis of a template character of such processes proposed by Chapiro [8].

Earlier studies [5,9,10] have shown that the low frequency range (below 200 cm^{-1}) of Raman spectrum could be helpful in determination of the orientation of polymer chains. It is due to the fact that the low-frequency Raman scattering (LFRS) provides information about the morphology and the structural relaxation in polymeric materials. Generally, the LFRS of glasses consists of two components: boson peak and quasielastic light scattering [11]. The boson peak is a result of the harmonic (or vibrational) motions, and the anharmonic (or relaxation) motions are a source of the quasielastic scattering. The Stokes LFRS intensity $I(\omega)$ is given by the following formula [12]:

$$I(\omega) = \frac{C(\omega)g(\omega)[n(\omega,T)+1]}{\omega} \qquad (1)$$

where: ω is the wavenumber, $C(\omega)$ is the light-vibrational coupling coefficient, $g(\omega)$ is the density of vibrational states,

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and $n(\omega, T)$ is the bose factor. Analogously as for the inorganic glasses, also for polymer glasses (amorphous polymers) the excess of the $g(\omega)$—observed by Raman scattering at the low frequency range (boson peak) [11,12], as well as by inelastic neutron scattering [13]—correlates with an anomaly in characteristics of specific heat [14] and thermal conductivity [15]. Duval et al. [16] have proposed an explanation of these anomalies based on a model of non-continuous structure of polymer glasses. This model will be discussed later.

In this paper, we focus our interests on the determination of the orientation of non-mesogenic component: poly(acrylic acid) (pAA) and poly(methacrylic acid) (pMAA) in anisotropic composites with LC-CDs.

2. Experimental

2.1. Materials

(Hydroxypropyl)cellulose (HPC) was supplied by Aldrich Chemical Co. The esters of cellulose derivatives: ((propionyloxy)propyl)cellulose (PPC) and ((hexanoyloxy)-propyl) cellulose (HxPC) were obtained by esterification reaction of HPC with adequate acid chloride [17]. ((Cyanoethyl)propyl)cellulose (CEPC) was obtained from HPC by reaction with acrylonitrile. Pure pAA and pMAA were synthesised by photopolymerisation of ca 200 μm thick layers of appropriate monomers with UV light, using xenon lamp 150 W with a band filter of $\lambda_{\max} = 365$ nm.

The composites were prepared from lyotropic solutions of suitable CD in acrylic or methacrylic acid. Small droplet of solution was placed between two glass plates, mechanically oriented by shearing, and then the orientation was fixed by photopolymerisation of the acrylic component as described in details elsewhere [4–6].

2.2. Low frequency Raman scattering

The low frequency Raman spectra were collected using the five-grating monochromator (Dilor Z-40), equipped with argon laser (514.5 nm; 150 hmW of power), as a source of light. Two different configurations of set-up were used: vvv—corresponds to the vertical (v) direction of: polarisation of the laser light, shear direction of the sample, and polarisation of the detected scattered light, respectively; and vhv where h means the horizontal direction of shearing. In the case of unoriented samples, the indices x and y were used. They correspond to the arbitrary defined directions parallel to the surface of the sample and perpendicular to each other.

All spectra were normalised by two steps. In the first one, the direct spectra (the $I(\omega)$ value) have been reduced by dividing them by the Bose factor, yielding the reduced spectrum I_{red} :

$$I_{\text{red}} = \frac{I(\omega)}{[n(\omega, T) + 1]} \tag{2}$$

Then normalised spectrum I_{n} were obtained by dividing I_{red} by ω :

$$I_{\text{n}} = \frac{I_{\text{red}}}{\omega} \tag{3}$$

3. Results

3.1. The low frequency Raman study of pure components

The normalised (upper graphs) and reduced (lower graphs) Raman spectra of pure pAA and pMAA samples at low frequency range are presented in Fig. 1. For both polymers the boson peak is well visible in the normalised spectra. For the pAA a maximum of the boson peak was found at 26 cm^{-1}, and for the pMAA—at 17 cm^{-1}. In the reduced spectrum of pAA two features are seen: a maximum at 55 cm^{-1} and the shoulder at ca. 25–30 cm^{-1}; the last one corresponds to the boson peak. Analogous features were found for pMAA at 70 cm^{-1} and at ca. 20 cm^{-1}, respectively. The broad bands in the reduced spectra of polymers are probably a consequence of the scattering from the acoustic modes localised by the disorder [10].

Figs. 2 and 3 present the low frequency Raman spectra obtained for unoriented and oriented HPC and CEPC samples. For the unoriented sample (Fig. 2), the Raman spectra are identical for both vxv and vyv configurations. For the oriented CEPC sample (Fig. 3), the maximum of the reduced spectrum appears at 60 cm^{-1} for the vhv configuration and it is similar to that found for the unoriented

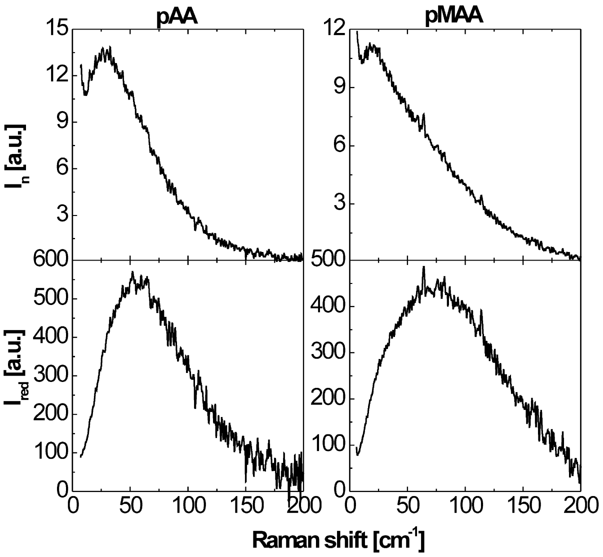

Fig. 1. The normalised (upper graphs) and reduced (lower graphs) low frequency Raman spectra of the unoriented pure pAA and pMAA.

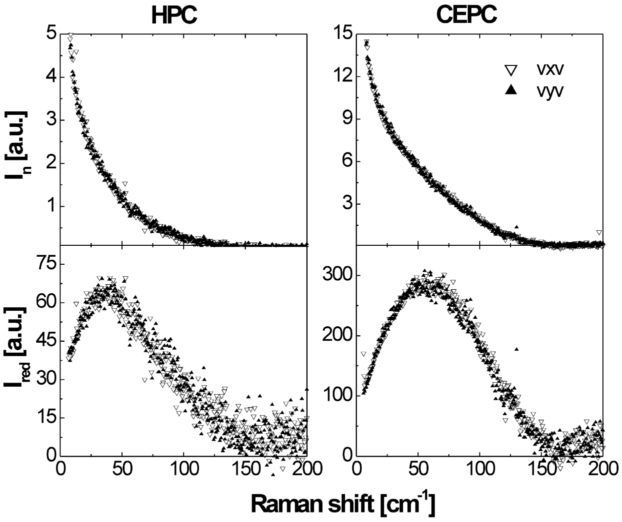

Fig. 2. The normalised (upper graphs) and reduced (lower graphs) low frequency Raman spectra of the unoriented samples of HPC (left panel) and CEPC (right panel).

sample. For the vvv configuration the maximum of the reduced spectrum is shifted to the higher frequency; moreover, a decrease in the intensity of the Raman signal is visible comparing to the vhv configuration.

Also for the HPC orientation induces the changes of the Raman scattering detected for the vhv and vvv configurations. However, the experimental points are more scattered and the differences between vhv and vvv configurations are less pronounced for HPC than for CEPC.

3.2. The low frequency Raman study of the composites of pAA with LC-CDs

Fig. 4 presents the LFRS spectra for the HPC/pAA composites with different content of HPC. The 1:4 system is isotropic because an amount of the HPC in the acrylic acid solution was lower than the critical concentration required to form the lyotropic phase. The Raman spectra for this composite obtained for the vxv and vyv configurations are identical. Additionally, for the HPC/pAA 2:3 system, we have prepared also unoriented samples, the spectra for these samples are presented in Fig. 5; one can see that the Raman spectra for vxv and vyv configurations are also identical. For the oriented samples, HPC/pAA 2:3 and HPC/pAA 3:2 (with 40 and 60% of HPC, respectively), the intensity of the Raman scattering recorded for the vhv configuration (the polarisations of the excitation and scattering light are perpendicular to the direction of the sample orientation) is higher than that for the vvv configuration (Fig. 4).

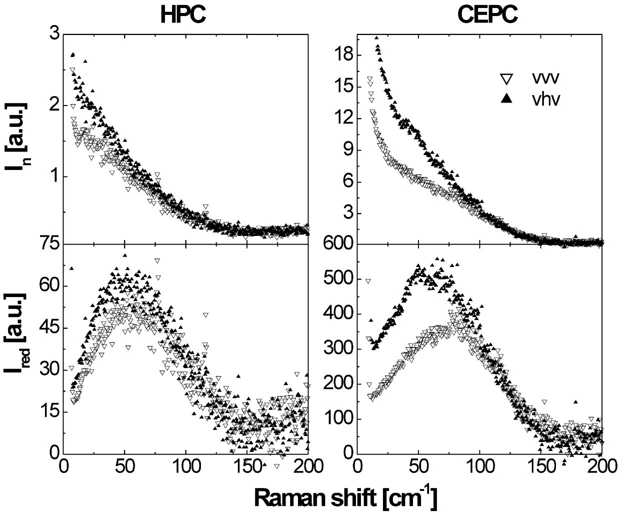

Fig. 3. The normalised (upper graphs) and reduced (lower graphs) low frequency Raman spectra of the oriented samples of HPC (left panel) and CEPC (right panel).

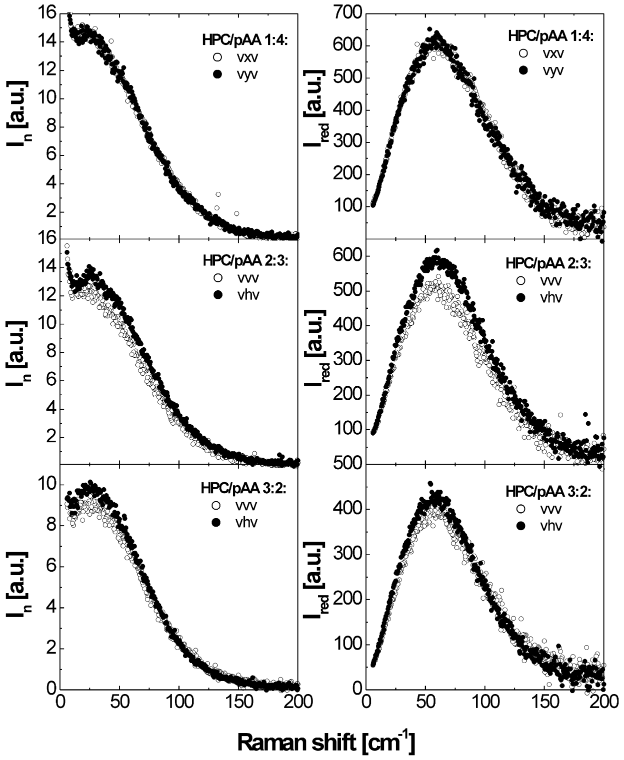

Fig. 4. The normalised (left panel) and reduced (right panel) low frequency Raman spectra of the HPC/pAA composites with different weight ratio of the components.

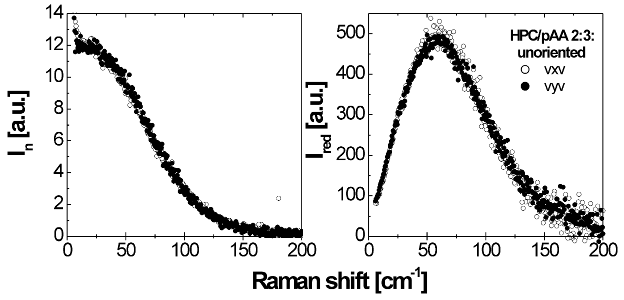

Fig. 5. The normalised (left panel) and reduced (right panel) low frequency Raman spectra of the unoriented HPC/pAA 2:3 composite.

In the case of the CEPC/pAA systems, analogous differences between the LFRS spectra for different concentrations of CD are observed as for the HPC/pAA systems (compare Figs. 4 and 6). The Raman spectra for the unoriented CEPC/pAA 1:4 sample are identical for both vxv and vyv configurations (Fig. 6, upper panels). For the other oriented CEPC/pAA 2:3 and CEPC/pAA 3:2 composites the intensity of the Raman scattering recorded for the vhv configuration is higher than that for the vvv configuration.

3.3. The low frequency Raman study of the composites of pMAA with LC-CDs

The normalised and reduced Raman spectra of the PPC/pMAA, HxPC/pMAA, HPC/pMAA and CEPC/pMAA composites at low range of frequency are presented in Figs. 7 and 8. The boson peak of the pMAA component in the oriented HPC/pMAA sample (Fig. 7, upper panels) is shifted to higher frequency, as compared with the spectrum of pure pMAA (cf. Fig. 1, left panels), and it appears at 25 cm^{-1}. Moreover, the intensity of the quasielastic scattering decreases. Also for other systems similar shift of the boson peak is visible, however, relatively strong quasielastic scattering makes determination of the position of the boson peak impossible. Intensities of the LFRS spectra obtained for the vhv configuration are higher, compared with the vvv configuration, for all the investigated composites with pMAA. Moreover, the reduced spectra differ in a shape for the vvv and vhv configurations in the range between 20 and 60 cm^{-1}. Such differences result from the orientation of the macromolecules in the composites, as it will be discussed below.

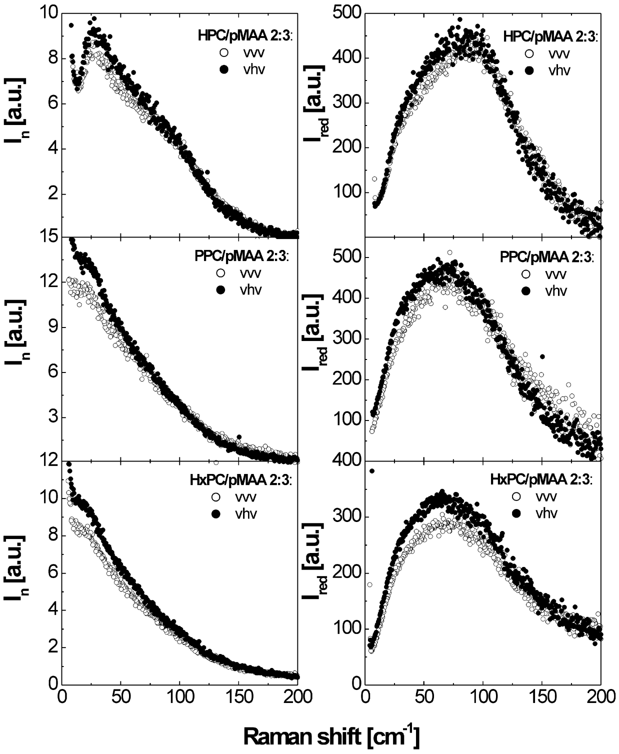

Fig. 7. The normalised (left panel) and reduced (right panel) low frequency Raman spectra of the oriented composites of pMAA with 40% of CD: HPC (upper graphs), PPC (middle graphs) and HxPC (lower graphs).

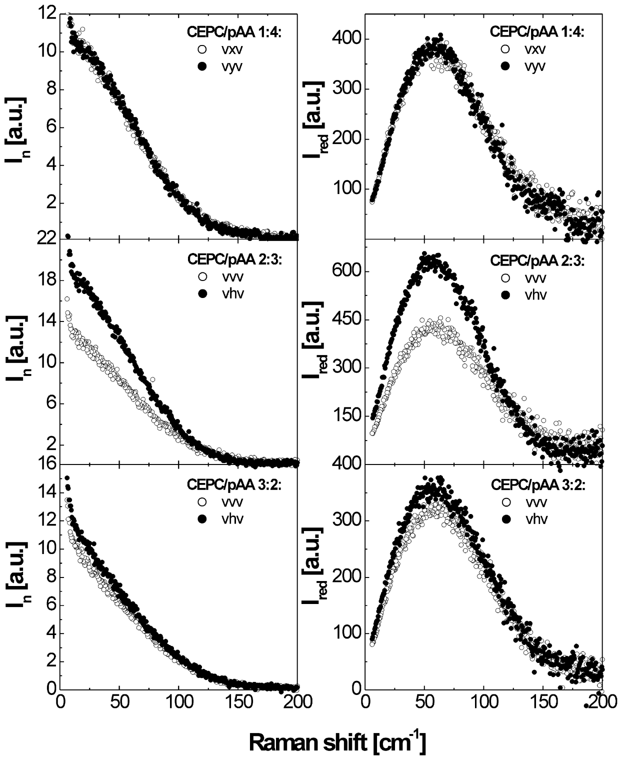

Fig. 6. The normalised (left graphs) and reduced (right graphs) low frequency Raman spectra of the CEPC/pAA composites with different weight ratio of the components.

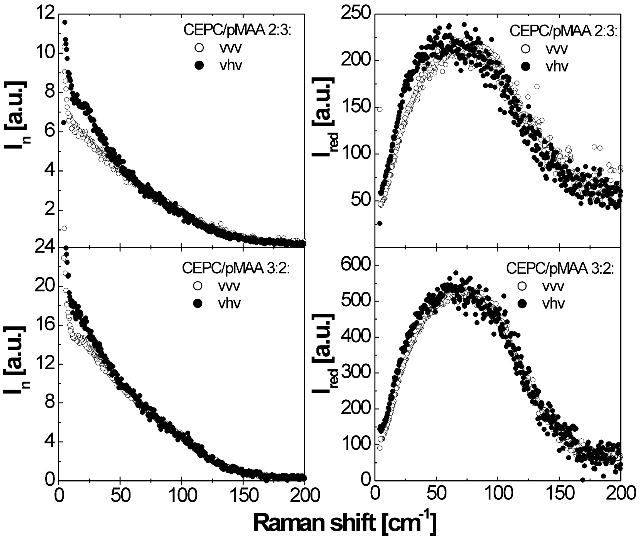

Fig. 8. Normalised (left panel) and reduced (right panel) low frequency Raman spectra of the oriented composites CEPC/pMAA: 2:3 (upper graphs) and 3:2 (lower graphs).

4. Discussion

The model of non-continuous structure of polymer glasses, proposed by Duval et al. [16] for explanation of a presence of the boson peak in the LFRS of amorphous polymers, assumes that the entangled structure of a melt is frozen in the glassy state. It leads to a presence of two kinds of zones in polymeric glasses: more and less cohesive. This model allows to calculate an average size ($2a$) of the more cohesive domains:

$$2a = \frac{SE^{0.5}}{c\omega_B \rho^{0.5}} \tag{4}$$

where: S is a shape factor, E, Young modulus, ρ, density, c, light velocity and ω_B wavenumber corresponding to the position of the boson peak. The Young modulus of pAA and pMAA were recently determined by Okrasa [18] (see Table 1). Density of polyacids (Table 1) was determined by pycnometry using the cyclohexane as non-solvent. Assuming that the shape factor is equal 0.65 (it is the average values of S; $S = 0.8$ correspond to spherical shape, while the $S = 0.5$ correspond to linear objects [5,9,16]), the size of the high cohesive domain is 24 and 32 Å for the unoriented samples of pAA and pMAA, respectively (see Table 1). These values are similar to those found for other polymers by Duval et al. [16]. It should be remembered that the above size estimation is not precise due to the arbitrary assumption of the shape factor. Moreover, the determined Young modulus and density values correspond to the average macroscopic values, since the values for the high cohesive domains one not known. However, such qualitative estimation is sufficient to conclude that the cohesive domains formed in pMAA are larger than those in pAA, probably due to the stronger interactions between the pMAA macromolecules resulting from stabilising role of the methyl groups.

For the unoriented samples of the LC-CDs (Figs. 2 and 3), the Raman spectra are identical for both vxv and vyv configurations. It proves that the samples are isotropic. The shearing induces considerable changes in the Raman spectra. The lower intensity at the vvv configuration and the shift of the maximum in the reduced spectra suggest the orientation of the CDs macromolecules. These effects can be explained if we consider morphology of the HPC and the CEPC liquid crystalline sample induced by shearing. Most LC-CDs form so called polydomain chiral-nematic texture, where the directors of several domains are oriented randomly, and the domains have sphere-like shape [19]. Under shearing, the coalescence and elongation of the domains take place, which leads to formation of the quasi nematic structure. New domains, formed by shearing, have elliptical shape, and their long axes are parallel to the shear direction. Further action of the shearing forces induces the formation of the nematic structure, where the macromolecules are totally straightened; this state is unstable because of the strong conformational strain. Fast relaxation processes lead to reconstruction of the domain structure and formation of the anisotropic zig–zag conformation, visible as the so called band textures in the dark pool of polarizing microscope [1,2,20]. It means that the shearing sets the domains in order. If one assumes that the appearance of the broad band in the reduced spectrum is caused by the scattering from the acoustic modes localised by the disorder, the changes of the Raman spectra induced by shearing indicate a decrease of the disorder. Probably, the decrease of the quasielastic scattering in the spectra of the oriented samples is a direct outcome of better order of the molecules inside the sample. Analogous changes in the LFRS were observed by Achibat et al. [10] for the PET drawn films, and by Mermet et al. [9] for the PMAA drawn films.

Table 1
Size of high cohesive domains ($2a$) calculated from Eq. (4) for the unoriented pAA and pMAA. The Young modulus values (E) are taken from Ref. [18]

Acrylic polymer	Shape factor (S)	ρ (g/cm^3)	E (MPa)	$2a$ (Å)
PAA	0.65	0.93	7000	24
PMAA	0.65	0.97	6000	32

The above described effect of decreasing LFRS intensity due to orientation is also visible for the CEPC and for the HPC samples (compare Figs. 2 and 3). Unfortunately, it was impossible to perform analogous investigations for the oriented pure HxPC and PPC samples because of very fast relaxation of their orientation.

For the isotropic composites (HPC/pAA 1:4 and CEPC/pAA 1:4 systems, cf. Figs. 4 and 6, upper panels), as well as for the unoriented sample HPC/pAA 2:3 (Fig. 5), the Raman spectra obtained at the vxv and vyv configurations are identical. It was expected since such samples are optically isotropic on the macroscopic scale. For the oriented samples the intensity of the Raman scattering recorded at the vhv configuration is always higher than that found for the vvv configuration.

In our previous paper, we have presented similar effect for the PPC/pAA system [5]. The PPC/pAA composites were studied at different temperatures and higher intensity of the LFRS at the vhv configuration was observed even at temperatures above the temperature of the optical isotropisation, i.e. at ca. 400 K. Moreover, the intensity ratio I_{vhv}/I_{vvv} was constant over the whole temperature range. The Thermo-Optical Analysis has shown that the optical anisotropy of the composites decays at the temperature of isotropisation, but during the cooling it is reconstructed almost in 100% [4]. Such behaviour was explained by the formation of the anisotropic network by the pAA chains in the composites [4–6]. Unfortunately, the Raman investigations on such materials can be carried out only up to ca. 400 K, because of a strong fluorescence appearing at higher temperatures. For the other investigated systems the temperatures of isotropisation are still higher than for the PPC/pAA system.

One should notice that the effect of the orientation of the acrylic polymer is better visible in the case of the composites with lower amount (40%) of the CD component (see Figs. 4, 6 and 8). They can be two reasons for such behaviour. The first one can be simply due to a concentration effect of the polyacids: if the concentration of the acrylic component is higher, the boson peak is also higher and its changes are better visible. The second reason may result from higher viscosity of the lyotropic solution with higher concentration of the CD in the acrylic monomer, which is the precursor for the composite. The higher viscosity of the lyotropic solution makes their mechanical orientation more difficult.

For the composites with HPC one can see, that with increasing concentration of this cellulose derivative the quasielastic scattering is decreasing (cf. Figs. 4 and 5). It suggests that the interactions between the HPC and the acrylic component increase with an increase of the HPC concentration. Our earlier Raman investigations in the frequency range of 1500–1800 cm^{-1} confirm this hypothesis [6]. The carbonyl groups of pAA or pMAA are able to form hydrogen bonds with hydroxyl groups of HPC. The number of such bonds (strength of interactions between pAA or pMAA and HPC) depends on a ratio of the carbonyl to the hydroxyl groups in the composites, which is shown in the Table 2 for the HPC/pAA systems. Obviously not all functional groups form the hydrogen bonds, and the steric hindrance are especially important in this case. In the composites with HPC, the hydroxyl groups of the LC-CD component are limiting factor because of their relatively smaller amount (the carbonyl groups of polyacids are in an excess). Moreover, the OH groups joined directly to the cellulose rings are difficult to access [21], which leads—in practice—to an increase in the effective ratio of the carboxyl to the accessible hydroxyl groups, compared with the values presented in Table 2.

The CEPC, which contains nitrile groups within its chemical structure is also able to form the hydrogen bonds with polyacids. The composites with CEPC show behaviour analogous to that observed for the materials with HPC, but the dependence of the quasielastic scattering versus concentration of CD component has opposite tendency due to the stronger quasielastic scattering of CEPC.

It is necessary to remark that the broad band at 100 cm^{-1} assigned to the acoustic modes localised by the disorder appears in the normalised Raman spectra only for the CEPC/pMAA and HPC/pMAA systems. An appearance of this band in the Raman spectra of the pMAA composites can be explained if one assumes that the pMAA interacts stronger with CDs than pAA does. This is in agreement with our previous Raman studies at the frequency range of 1500–1800 cm^{-1} [6,22]. The stronger intermolecular interactions lead to better homogenisation of the samples, and the intensity of boson peak decreases. The lower the boson peak, the better is visible the broad band at 100 cm^{-1}, and vice versa, this band is masked in the spectra of the composites with pAA by stronger boson peak.

This hypothesis may explain also, why in the LFRS spectra of the PPC/pMAA and HxPC/pMAA systems the band at 100 cm^{-1} is invisible. The macromolecules of PPC and HxPC have the aliphatic side chains and only the carbonyl groups of the esters bonds are able to form hydrogen bonds. However, they are difficult to access because of steric effects, and the probability of the formation of the hydrogen bonds with them is low. According to our hypothesis, if the intermolecular interactions are weaker, the boson peak is more intense and it masks the band of acoustic mode at 100 cm^{-1}. The effect is similar to that induced by plasticiser, observed before for poly(methyl methacrylate) with dibuthylphtalate [23].

As discussed above, the orientation of the macromolecules in the composites is visible in Raman spectroscopy as a difference in the intensity between the spectra recorded at vvv and vhv configurations. Moreover, in the case of the composites of pMAA, the reduced spectra have different shape for vvv and vhv configurations between 20 and 60 cm^{-1}. Similar effect was observed before for other polymers [9,10]. These differences are invisible for the composites with pAA, what proves that the described above effects are induced by the orientation of the pMAA macromolecules and not only by LC-CDs. This effect also suggests that the pMAA molecules are better oriented in the composites than the pAA molecules, what can be explained by the mechanism of the composite formation. When the lyotropic solution is sheared, the macromolecules of LC-CD are oriented. If the acrylic monomers interact strongly with CD macromolecules, the mechanism of photopolymerisation can be consider as a template polymerisation, where the oriented CD macromolecules play a role of the template [8]. Therefore, the stronger the interaction between the methacrylic acid and CD macromolecules leads to the better orientation of the growing pMAA chains.

Table 2
Ratio of the carboxyl groups of pAA to the hydroxyl groups of HPC in the HPC/pAA composites with different concentration of HPC

Concentration of HPC (% w/w)	Moles of COOH in 1000 g of material	Moles of OH in 1000 g of material	Ratio of the moles of COOH to the moles of OH
20	11.11	1.79	6.21
40	8.33	3.57	2.33
60	5.56	5.36	1.04

5. Conclusion

1. Comparison of positions of the boson peaks, found for pAA at 26 cm^{-1} and for pMAA at 17 cm^{-1}, shows that the morphology of these polymers is different. Assuming the model of non-continuous structure of polymer glasses, one can conclude that the size of the more cohesive domains is larger in pMAA than in pAA. This is probably the effect of the stronger interaction (hydrogen bonds) between the pMAA macromolecules due to stabilising role of the methyl groups.
2. The macromolecules of the non-mesogenic compounds (pAA, pMAA) are oriented in the anisotropic composites with liquid crystalline cellulose derivatives, which confirm the hypothesis of formation of the anisotropic network by acrylic acids in the lyotropic solutions of LC-CDs. The stronger the LC-CD interacts with acrylic component, the higher is its orientation. It means that the LC-CDs able to form hydrogen bonds (HPC, CEPC) play a role of template for polymerisation of acrylic acids. Moreover, the HPC and CEPC macromolecules act as the specific cross-linking agents, while the CDs with aliphatic side chains (PPC, HxPC) work like plasticisers.
3. The low frequency Raman scattering is useful technique in investigations of the orientation of non-mesogenic components in composites with liquid crystalline macromolecules.

Acknowledgements

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