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Molecular relaxation in anisotropic composites based on (hydroxypropyl)cellulose and acrylic polymer

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Abstract

The birefringence and molecular dynamic of the anisotropic polymer composites obtained by photopolymerisation of the lyotropic liquid-crystalline systems composed of (hydroxypropyl)cellulose and photopolymerisable acrylic acids are studied. Molecular relaxations in such composites were investigated by means of dielectric and mechanical spectroscopies. The molecular relaxation processes, characteristics of pure components, are modified in the composites due to strong intermolecular interactions between the macromolecules. These interactions are also responsible for stabilisation of the structure and the optical properties of the composites. In dielectric spectroscopy two representations were used: temperature dependences of dielectric loss ε'' and of electric modulus M''. This latter one was especially useful in a high temperature range where the ionic conductivity dominates the dielectric response. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: 2-(Hydroxypropyl)cellulose; Polymer composites; Molecular relaxations

1. Introduction

One of the modern trends in materials science is towards building ordered structures with tailor-made optical, electrical, magnetic, mechanical and transport properties. Wide class of such materials, with ordered polymeric structures, can be obtained using self-organising systems such as liquid crystals (LCs). Macroscopically ordered solid structures of LCs with anisotropic properties can be produced in different ways, but usually it is not all that simple to obtain stable structures.

Composites based on LC cellulose derivatives (CDs) constitute one of the most interesting groups of LC materials. Cellulose is a semirigid polymer and glass transition temperature of its derivatives depends on length and structure of side chains. Many cellulose derivatives are known to form thermotropic mesophase. CDs can form also lyotropic phases in various vinyl solvents [1]. It makes possible the preparation of highly anisotropic cellulose-based composites with preserved and thermally stable mesomorphic structure by photopolymerisation of the vinyl monomer in the mechanically oriented lyotropic mesophase [2,3]. By proper choice of the acrylic solvent and of the cellulose derivative (kind and length of side groups), it is possible to select several pairs of polymers, which are able to form different, specific intermolecular interactions [4]. Chosen by us 2-(hydroxypropyl)cellulose (HPC), which has hydroxyl groups, can form hydrogen bonds with organic acids.

Dielectric relaxation measurements as well as dynamic mechanical analysis (DMA) seem to be suitable methods for studying the relaxation motion in LC–CD systems. However the dielectric measurements of this polymer class were often limited to temperatures below the glass transition, because of high conductivity due to ionic impurities [4,5], which were difficult to remove. In this case, the classical representation of the dielectric relaxations, e.g. dielectric losses can be used only at low-temperature range, where the ionic conductivity is very low. It is known that in some cases it is possible to detect the relaxation processes in a temperature range in which the ionic conductivity is high by analysis of the complex electric modulus ($M^* = 1/\varepsilon^*$) defined by Macedo et all [6]. The real (M') and imaginary (M'') parts of electric modulus are given by:

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}; \qquad M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}$$

where ε' and ε'' are real and imaginary parts of the complex dielectric permittivity ε^*.

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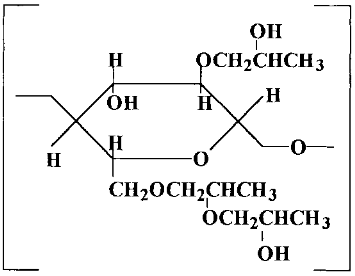

Fig. 1. Idealised structure of 2-(hydroxypropyl)cellulose.

Such duality of representation is well known in dynamic mechanical relaxations as compliance and modulus. Although permittivity representation is easier in an interpretation, modulus representation can be very useful when the conductivity processes are involved. One can expect that the M'' maxima can be correlated with the relaxation processes; this can be rationalised by the fact that molecular relaxations can facilitate the charge-carrier transport [7,8], particularly in respect to ionic conductivity. In our dielectric investigations, it appeared to be the only way to detect the relaxation processes taking place at higher temperatures.

In this work, we describe thermooptical properties and molecular dynamics of anisotropic polymer networks based on the lyotropic LC-solutions of HPC in polymerisable solvents such as acrylic acid (AA) or methacrylic acid (MAA). The main goal of these investigations was to understand an influence of intermolecular interactions (hydrogen bonds) in the composites on optical properties and molecular relaxations of these multicomponent polymer anisotropic systems.

2. Experimental

2.1. Materials

2-(Hydroxypropyl)cellulose (HPC) (see Fig. 1) ($M_w = 100\,000$), AA and MAA were supplied by Aldrich Chemical Co. The HPC:poly(AA) and HPC:poly(MAA) composites were obtained by photopolymerisation of the lyotropic solution of HPC in the acrylic monomer. The alignment state of the lyotropic LC-solution of the cellulose derivative prior to photopolymerisation was achieved by manual mechanical shearing. The preparation details of the polymer composites of the cellulose derivatives have been already reported [2,3].

2.2. Measurements

Thermooptical analysis (TOA) consists of recording of intensity of the light transmitted through the sample placed under a microscope between crossed polarisers, I/I_0 (where I_0 is the initial intensity), as a function of temperature. In our study, TOA experiments were conducted using the Mettler FP 82 Microscope Hot Stage and were performed for the sample orientation yielding the highest transmission of polarised light, i.e. when the angle between the shearing direction of the sample and the polarisation plane of the polariser was about 45°. The heating rate was always 2 K/min.

The DMA were carried out with a Dynamic Mechanical Thermal Analyzer Type DMA 2980 TA Instruments at fixed frequencies (1, 1.5, 5, 10, 30 Hz) with a heating rate of 2 K/min. The experiments were performed under tension mode on the samples about $15 \times 5 \times 0.1$ mm.

Dielectric relaxation spectroscopy (DRS) was performed in a Polymer Laboratories cell using the Hewlett Packard 4284A Precision LCR Meter at fixed frequencies in the range of 30–1 MHz and in the temperature range 210–460 K with a heating rate of 2 K/min. For the dielectric investigations, the 20 μm thick samples were prepared between two plates of conductive ITO glass with Teflon spacers.

3. Results

3.1. Thermooptical behaviour and morphology of HPC systems

The unoriented samples of the cellulose derivatives observed at room temperature under a microscope through crossed polarisers show a grainy structure. Such a structure is characteristic of cholesteric liquid crystals. In the oriented by shearing LC layers of both thermotropic and lyotropic

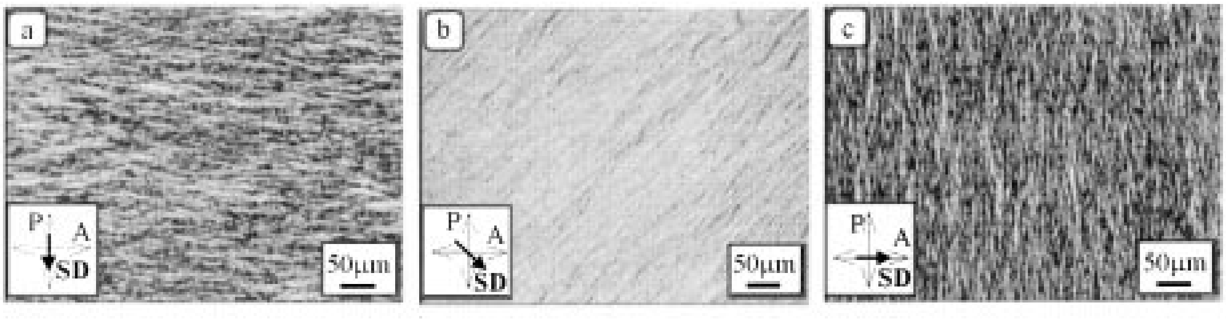

Fig. 2. Polarised micrographs of oriented HPC layer at 300 K, with different angles between the shearing direction (SD) and the polarisation plane of the polariser (P): (a) 0°; (b) 45°; and (c) 90°.

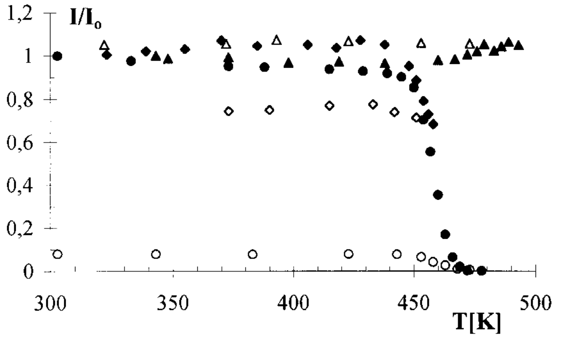

Fig. 3. TOA for (○) pure HPC, and for (△) HPC:poly(AA) (60:40) and (◇) HPC:poly(MAA) (60:40) composites (filled symbols — heating, empty symbols — cooling).

HPC systems, a texture evolution occurs (following cessation of the shearing) and bands are formed perpendicular to the shearing direction [9,10]. An example of such metastable texture is shown in Fig. 2. The bands are distinct only under crossed polarisers. In non-polarised light, the samples are clear and transparent in visible light. The brightness and darkness of the bands varies with the angle between the shearing direction and the polarisation plane of the polariser. The intensity of transmitted light is the strongest when this angle is 45° and the weakest when it is 0° or 90°.

In the oriented lyotropic HPC systems, the polymer chains relax and the anisotropic morphology disappears with time. However, the complete relaxation of the band texture at room temperature takes several days or even weeks, depending on the solvent and concentration. In composites the band structure can be stabilised by the photopolymerisation of the acrylic solvent present in the lyotropic solution of CD. The oriented composite films have similar band texture as the LC layers before the polymerisation. The width of the bands depends, among other things, on the time at which the orientation is 'frozen' by polymerisation.

Fig. 3 presents the TOA results of oriented samples of pure HPC and its composites. It is seen that the optical anisotropy of pure HPC is stable up to high temperature, i.e. around 450 K. Then, after isotropisation above 470 K, the HPC sample returns during cooling to their original macroscopically isotropic, grainy structure, which is much less birefringent than the oriented band structure (see Fig. 4.1). A different behaviour is observed in the HPC: poly(AA) composites. The anisotropic, birefringent band texture of these films is stable up to the degradation temperature, which is much higher than the isotropisation temperature of pure HPC. Fig. 4.2 shows the polarised micrographs for the HPC:poly(AA) (60:40) composite at different temperatures, and it is seen that the band structure does not change with temperature. The same situation is observed for the HPC:poly(AA) (40:60) composite. The third investigated composition of this composite, HPC: poly(AA) (20:80), is below the critical concentration and is not birefringent.

The HPC:poly(MAA) composites are less stable thermally than the composites with poly(AA) and the decrease of birefringence at about 440 K is observed (see Fig. 3). This can be caused by disorientation of macromolecular chains, but also by the thermodegradation of poly(MAA) component, which occurs above 450 K, while the thermodegradation of poly(AA) starts only above 490 K.

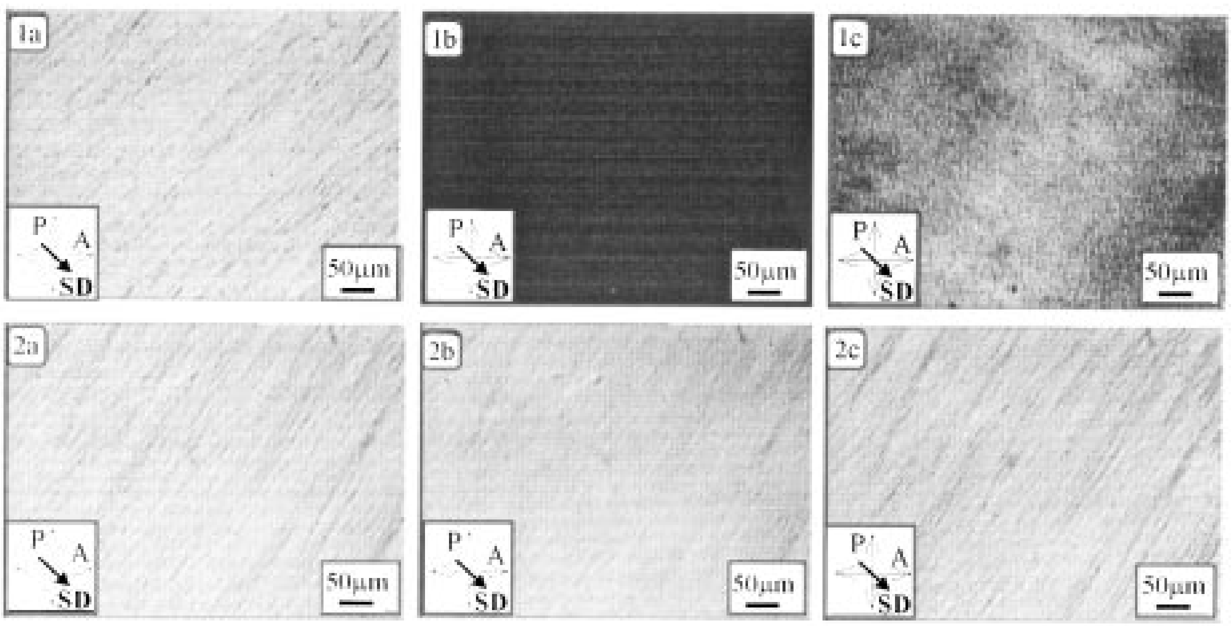

Fig. 4. Polarised micrographs for (1) pure HPC and (2) HPC:poly(AA) (60:40) composite at different temperatures: (a) 300 K before heating; (b) 503 K; and (c) 300 K after cooling.

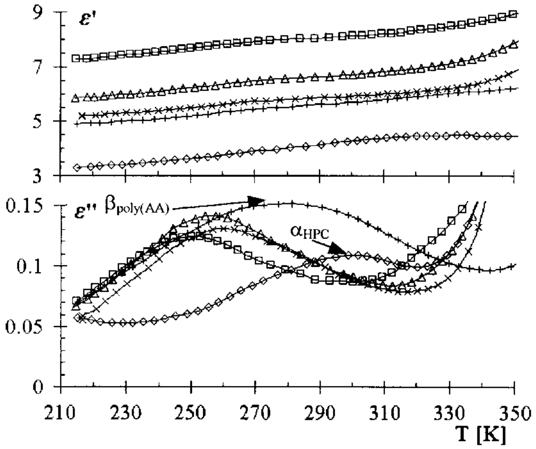

Fig. 5. Temperature dependencies of dielectric permittivities (ε') and dielectric loss (ε'') at 1 kHz for HPC:poly(AA) systems with different compositions: (◇) pure HPC, (□) 60:40, (△) 40:60, (×) 20:80 and (+) pure poly(AA).

3.2. Molecular relaxation phenomena in HPC:poly(AA) composites

3.2.1. Dielectric relaxation spectroscopy

The HPC undergoes glass transition at 292 K as determined by DSC. This phenomenon can be observed also in dielectric spectroscopy as the so-called α-relaxation. Fig. 5 shows the temperature dependencies of dielectric permittivities (ε') and losses (ε'') for HPC and its composites measured at 1 kHz. The maxima of the $\varepsilon''(T)$ plots occur at slightly higher temperatures than the corresponding T_g, due to the frequency effect. Generally, one assumes that the maxima of the $\varepsilon''(T)$ plots occur at the T_g temperature, when the relaxation time is equal to 100 s. The value of T_g estimated in this way for HPC is 284 K and it is not very different from that obtained from DSC. This relaxation phenomenon can be observed also on the diagram of electric modulus $M''(T)$ presented in Fig. 6. At higher temperature (above 350 K), the spectra of the $\varepsilon''(T)$ are dominated by conduction phenomena, which are probably caused by ionic impurities and the high temperature relaxations can be observed only in the $M''(T)$ diagrams. For pure HPC, the second maximum appears at temperatures much higher than T_g. This is the so-called α′-relaxation and it can be assigned to the transition from a frozen anisotropic phase to a mobile liquid crystal phase, while the first α-relaxation is associated with the devitrification process of a disordered amorphous phase.

The second component of the composites, poly(AA) shows also two relaxation phenomena in the investigated temperature range. In the temperature range corresponding to the α-relaxation process of HPC, poly(AA) shows a β-relaxation phenomenon, associated with local segment motions of its chains. This relaxation appears to be a complex process; the β-peak in the $\varepsilon''(T)$ (Fig. 5) as well as in $M''(T)$ (Fig. 6) plots is broad and probably is composed of two maxima. The β-relaxation processes are thermally activated, i.e. the temperatures at which the maxima of the ε'' and M'' peaks occur at different frequencies are shifted according to the Arrhenius equation (see Fig. 7). The values of the activation energy (E_a) of β-relaxation of poly(AA), determined from different relaxation spectra, are shown in Table 1. The relaxation processes at higher temperature are hidden by ionic conductivity, as in the case of pure HPC. For this reason the α-relaxation of poly(AA) (T_g determined by DSC equals 381 K) is visible only in the $M''(T)$ diagram (Fig. 6).

In the dielectric spectra of the HPC:poly(AA) composites, shown in Fig. 5, the α-relaxation of the HPC, which is already poorly seen in pure HPC, is completely masked by the β-relaxation of poly(AA). The maximum of the β-relaxation of poly(AA) in the composites is modified. One could say that the β-relaxation peaks are narrower and shifted to lower temperatures, but it may result also from the fact that the high-temperature parts of the maxima are damped and only the low-temperature part remains. Fig. 7 shows that the Arrhenius law is fulfilled for the β-relaxation in all the compositions of the HPC:poly(AA) composite. The activation energies calculated from these diagrams are given in Table 1. The E_a of the β-relaxation of poly(AA) in the composites is practically the same as in pure poly(AA) photopolymerisated in the bulk. This supports

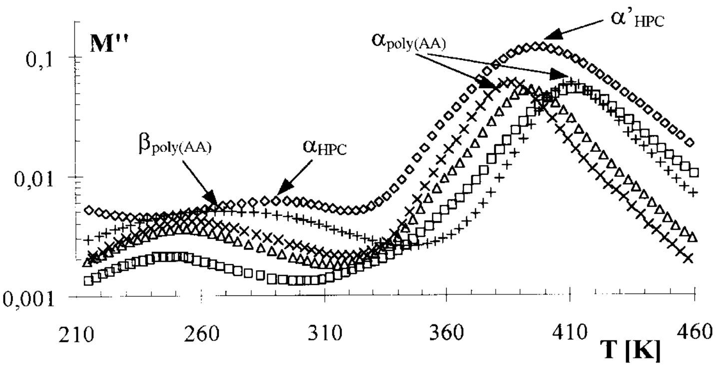

Fig. 6. Temperature dependencies of electric modulus (M'') at 1 kHz for HPC:poly(AA) systems with different compositions: (◇) pure HPC, (□) 60:40, (△) 40:60, (×) 20:80 and (+) pure poly(AA).

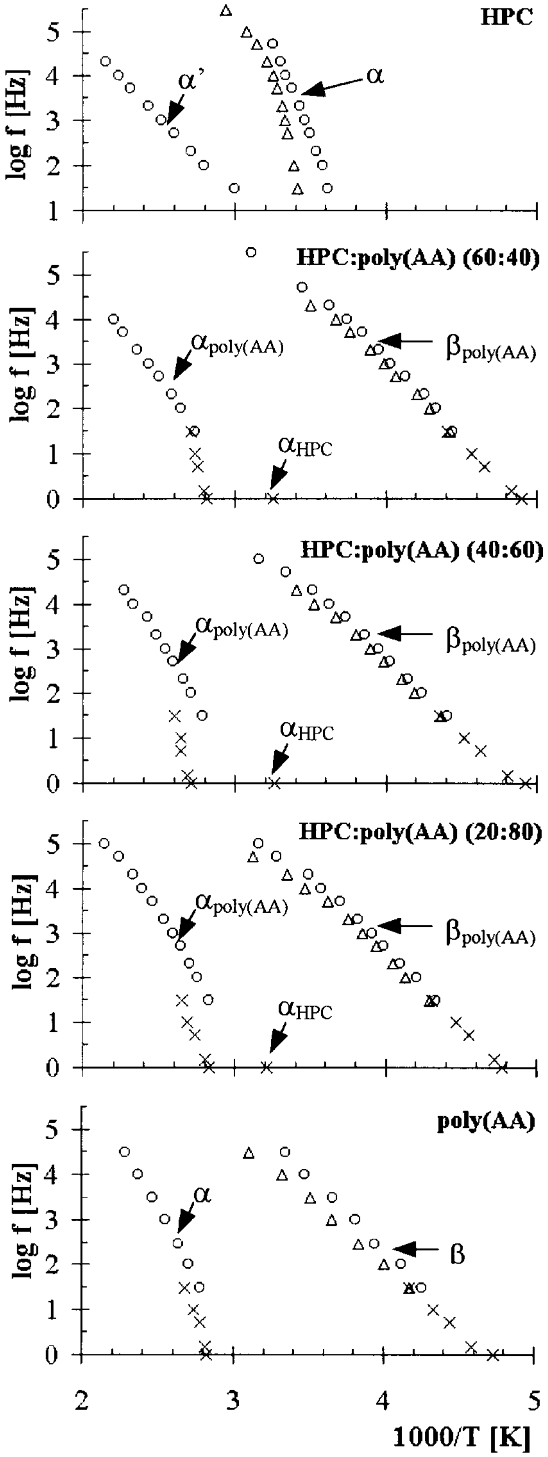

Fig. 7. Arrhenius plots of the relaxation processes for different HPC: poly(AA) systems with different compositions. The point are taken from the $\varepsilon''(T)$ — (△), $M''(T)$ — (○) and $E''(T)$ — (×) diagrams.

our hypothesis that the β-relaxation of poly(AA) in the composites is modified in a specific way.

In the $M''(T)$ diagrams of the composites also the high temperature relaxations can be observed. The α′-relaxation of HPC and α-relaxation of poly(AA) are placed in the same temperature range, however the high temperature relaxations in composites are dominated by the α-relaxation of poly(AA), in spite of that the amplitude of the α′-relaxation in pure HPC is bigger than this of the α-relaxation in pure poly(AA). Only for the highest concentration of HPC (60 wt.%) the α-relaxation process of poly(AA) is affected by the α′-relaxation of HPC.

Table 1
Activation energy of the β-relaxations in the poly(AA) and HPC:poly(AA) composites, calculated from Arrhenius plots for data obtained from $\varepsilon''(T)$, $M''(T)$ and $E''(T)$ diagrams

	E_a (kJ/mol)		
	From $\varepsilon''(T)$	From $M''(T)$	From $E''(T)$
HPC:poly(AA) (60:40)	59 ± 2	57 ± 2	57 ± 2
HPC:poly(AA) (40:60)	57 ± 2	56 ± 2	53 ± 3
HPC:poly(AA) (20:80)	53 ± 2	57 ± 2	60 ± 3
Poly(AA)	55 ± 1	56 ± 3	52 ± 4

3.2.2. Dynamic mechanical analysis

The temperature dependencies of the storage modulus (E'), the loss modulus (E'') and the loss tangent (tan δ) at 1 Hz for the series of HPC:poly(AA) composites with different compositions are presented in Fig. 8. Three transitions are apparent in the $E''(T)$ plots of the HPC:poly(AA) composites within the experimental temperature range. The α and β-relaxation processes found in pure poly(AA) are present in the HPC:poly(AA) composites. They are modified by the presence of the second component, HPC, in a similar way, as it was visible in the dielectric measurement. In the composites, the high-temperature parts of the β-relaxation maxima of the poly(AA) are damped and similarly to the DRS results only the low-temperature part remains. This effect can be better seen in the inset in the $E''(T)$ diagram in Fig. 8, showing expanded low-temperature range. The activation energy of the β-relaxation process of poly(AA) in the composites amounts to about 53–60 kJ/mol, in agreement with the results from the dielectric studies (cf. Table 1). The α-relaxation maxima of poly(AA) in the composites are shifted to slightly higher temperatures, as compared with pure poly(AA). Such a tendency was also found in the dielectric studies on the $M''(T)$ plots (Fig. 6).

Contrary to the dielectric spectroscopy results, the second component of the composites-HPC is also visible in the DMA spectra. The α-relaxation process of HPC, although poorly seen and only marked here, evidently can be detected, both in the $E''(T)$ and the tan $\delta(T)$ plots.

3.3. Molecular relaxation phenomena of HPC:poly(MAA) composites

3.3.1. Dielectric relaxation spectroscopy

In the low-temperature range, the behaviour of the HPC:poly(MAA) composites is similar to that of the

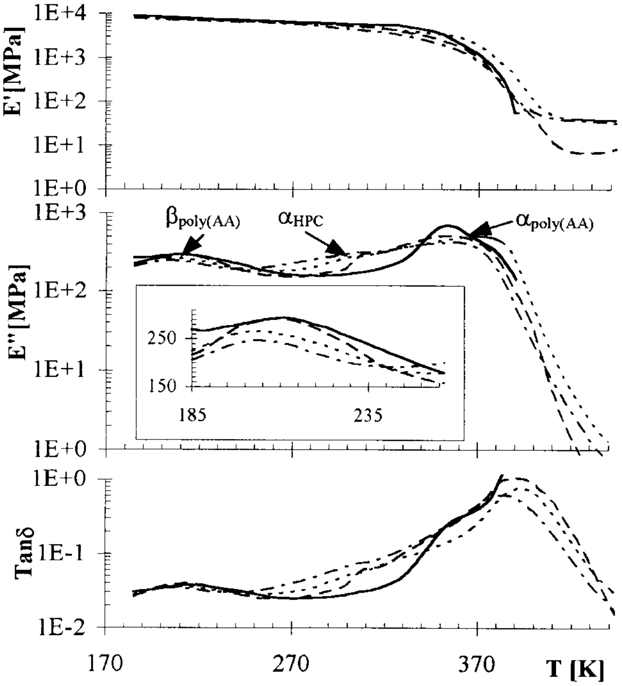

Fig. 8. Temperature dependencies of storage modulus (E'), loss modulus (E''), and loss tangent ($\tan\delta$) at 1 Hz for HPC:poly(AA) systems with different compositions: ----- (60:40); --- (40:60); ——— (20:80); and —— poly(AA). The inset shows a magnified region of the β-relaxation of the poly(AA).

Table 2
Activation energy of the β-relaxations in the poly(MAA) and HPC:poly(MAA) composites, calculated from Arrhenius plots for data obtained from $\varepsilon''(T)$, $M''(T)$ and $E''(T)$ diagrams

	E_a [kJ/mol]		
	From $\varepsilon''(T)$	From $M''(T)$	From $E''(T)$
HPC:poly(MAA) (60:40)	54 ± 2	47 ± 1	55 ± 2
HPC:poly(MAA) (40:60)	50 ± 2	46 ± 1	55 ± 1
HPC:poly(MAA) (20:80)	53 ± 2	47 ± 1	52 ± 2
Poly(MAA)	46 ± 3	45 ± 1	–

composites with poly(AA). Only the β-relaxation of poly(MAA) is visible in the composites, while the α-relaxation of HPC disappears. This can be seen in Figs. 9 and 10, showing the temperature dependencies of the electric modulus and the Arrhenius plots for HPC:poly(MAA) composites with different concentrations. The activation energies of the β-relaxation process are shown in Table 2. The E_a calculation base of the $\varepsilon''(T)$ diagrams for the β-relaxation of poly(MAA) in the composites is slightly higher than in pure poly(MAA) polymerised in the bulk. This can be caused by a presence of the LC component, which can affect the polymerisation process, or simply by the ionic conductivity that changes the $\varepsilon''(T)$ diagrams slightly already in this temperature range. The energies calculated from the $M''(T)$ diagrams are also given in Table 2. In this case the E_a values for β-relaxation of poly(MAA) in composites are the same as in pure poly(MAA). This indicates that higher E_a values obtained from the $\varepsilon''(T)$ diagrams for the composites are rather artefacts — the data can be distorted due to ionic conductivity.

Figs. 9 and 10 show also the second relaxation process in the HPC:poly(MAA) composites. This is most probably the α′-relaxation of HPC shifted to higher temperatures. The α-relaxation of pure poly(MAA) occurs at higher temperatures ($T_g = 488$ K) above our investigation range. At such temperature poly(MAA) undergoes already thermal degradation.

3.3.2. Dynamic mechanical analysis

In HPC:poly(MAA) composites, the β-relaxation process of polyacid is also observed in the DMA results, what is shown in Fig. 11. The activation energy of these processes is slightly higher than the E_a calculated on the basis of dielectric measurement (cf. Table 2). We should note, however that these values are determined with lower accuracy, because of fewer experimental points of DMA.

In the HPC:poly(MAA) composites (with an exception of the 60:40 composition), the α-relaxation of the poly(MAA), connected with its glass transition, can be seen. This process

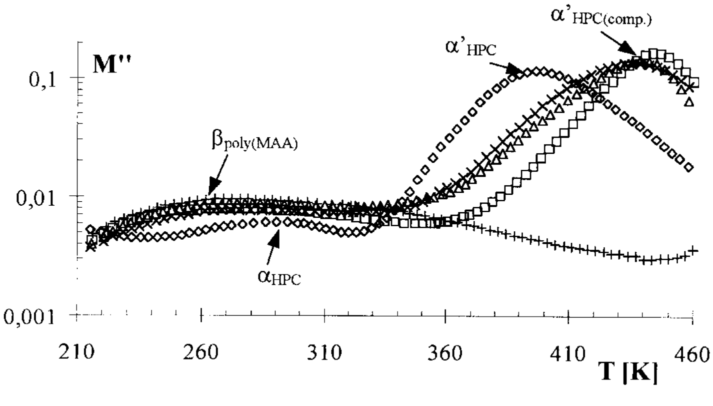

Fig. 9. Temperature dependencies of electric modulus (M'') at 1 kHz for HPC:poly(MAA) systems with different compositions: (◇) pure HPC; (□) 60:40; (△) 40:60; (×) 20:80; and (+) pure poly(MAA).

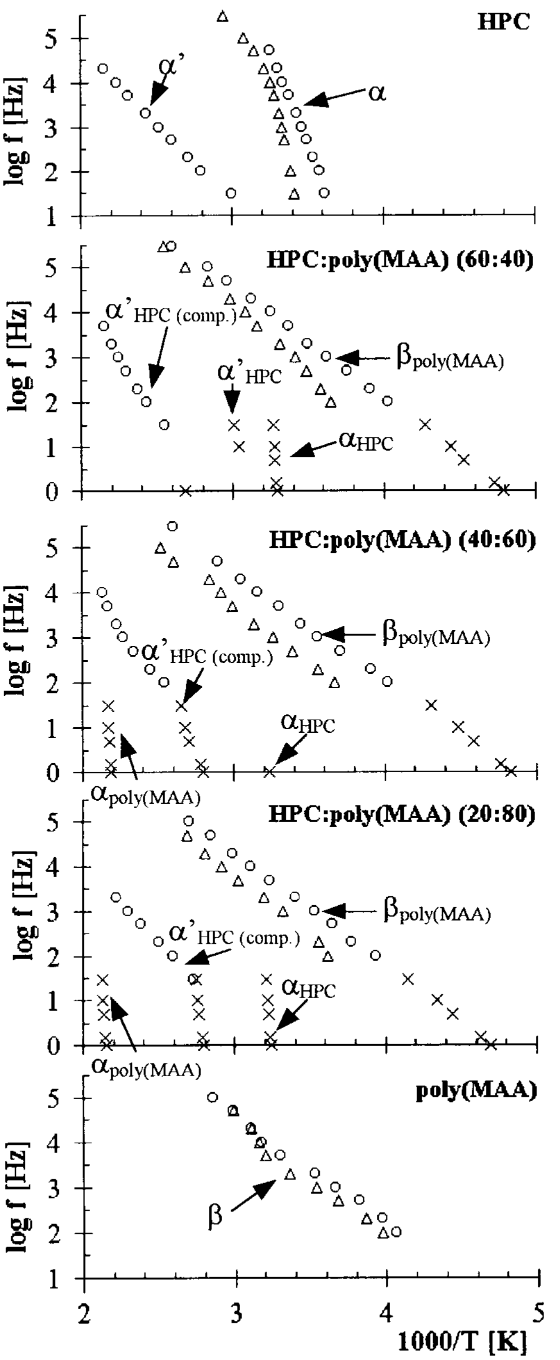

Fig. 10. Arrhenius plots of the relaxation processes for different HPC and poly(MAA) systems with different compositions. The point are taken from the $\varepsilon''(T)$ — (△); $M''(T)$ — (○); and $E''(T)$ — (×) diagrams.

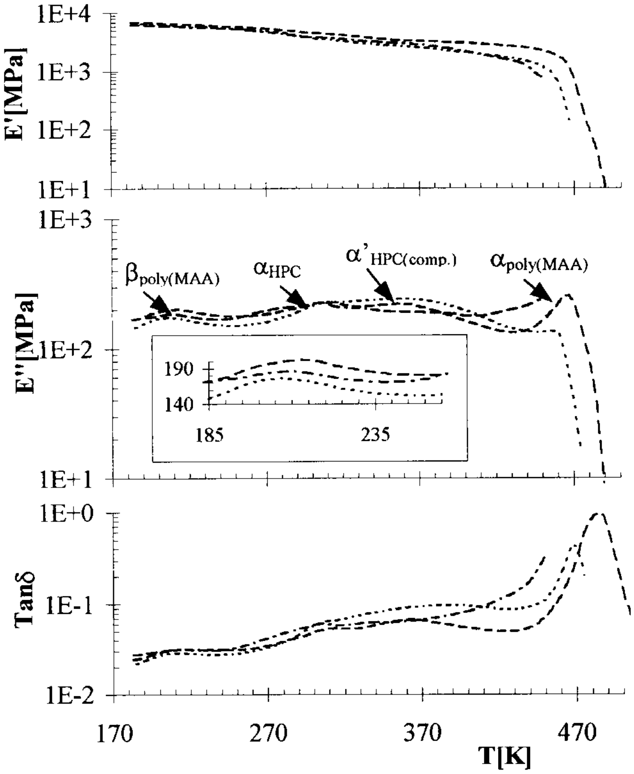

Fig. 11. Temperature dependencies of storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) at 1 Hz for HPC:poly(MAA) composites with different compositions: --- (60:40); ------ (40:60); and ---- (20:80). The inset shows a magnified region of the β-relaxation of the poly(MAA).

was not observed in the dielectric measurements because the temperature range of the dielectric investigations was not large enough. Unfortunately the DMA measurements for pure poly(MAA) were not possible using the accessible apparatus because of high fragility of the poly(MAA) films. We therefore cannot compare the α-relaxation of pure poly(MAA) to that in the composites. For the composite with the highest content of HPC (60:40), the measurements at a higher temperature (which allowed for an analysis of the α-process of poly(MAA)) were not possible because of the destruction of sample.

Besides the β- and α-relaxations of the poly(MAA) there are also relaxation processes related to HPC in the HPC: poly(MAA) composites. The α-relaxation of HPC in the composites with poly(MAA) is better visible than in the composites with poly(AA), but even here for the 40:60 composition the α-peak can be observed only for the lowest frequency, namely 1 Hz.

The α'-relaxations of HPC in the HPC:poly(MAA) composites with compositions 20:80 and 40:60 can be seen in the $E''(T)$ spectra, and they are consistent with the dielectric results. In the Arrhenius plot in Fig. 10 they are labelled $\alpha'_{\mathrm{HPC(comp.)}}$. In the case of the 60:40 composite the α'-relaxations split into two modes. One labelled α'_{HPC} (at 333 K for 30 Hz) appears in the same temperature range as the α'-relaxations in pure HPC detected by means of dielectric spectroscopy (at 337 K for 30 Hz). The other one (labelled $\alpha'_{\mathrm{HPC(comp.)}}$), occurring at higher temperatures, is characteristic of the composites and is visible only at the lowest frequencies (single point on the Arrhenius plot). It agrees with the dielectric spectra, where it was found that the α'-relaxation of HPC in all the HPC:poly(MAA) composites was strongly affected by the presence of the polyacid, and that it was shifted to a higher temperature. DMA shows that in the composites with the highest content of HPC, there is not only the strongly affected mesophase present, but some regions of not affected mesophase of HPC remains as well.

4. Discussion

TOA results show that optical anisotropy is much more stable in HPC:poly(AA) than in HPC:poly(MAA) composites. Partially responsible for this result is thermodegradation of poly(MAA), but decreasing of the transmission of polarised light starts earlier than the thermal destruction of the samples. It means that disorientation of HPC chains occur at temperature close to the isotropisation temperature characteristic for pure HPC. It can be explained by the fact, that the hydrogen bonds present in HPC:poly(MAA) composites are weaker (and/or less numerous) than in the composites with poly(AA).

Other relaxation phenomena of macromolecules are also more modified in the composites with poly(AA) than in those with poly(MAA). For both kinds of composites, the α-relaxation of HPC, related to its glass transition, is not visible in the dielectric spectroscopy. However, this relaxation is well visible in HPC:poly(MAA) composites in DMA; it is shifted to higher temperatures, which can be explained by the immobilisation of HPC chains by hydrogen bonds with more stiff, glassy poly(MAA) ($T_g = 488$ K). Such an effect is similar to the antiplasticisation effect observed in amorphous polymers and caused by intermolecular interactions, e.g. by charge–transfer complexes. The α-relaxation of HPC is only slightly marked in the DMA spectra for HPC:poly(AA) composites. The fact that this relaxation is almost invisible in HPC:poly(AA) composites suggests that here the hydrogen bonds fix stronger the HPC chains than in the HPC:poly(MAA) composites, damping the α-relaxation. This behaviour can be connected with presence of strong hydrogen bond between chains of both components. Due to these intermolecular interactions the three-dimensional network is formed.

The subglassy β-relaxations of polyacids can be well seen in HPC:poly(AA) as well as in HPC:poly(MAA) composites in both DRS and DMA spectra. The activation energy of the β-relaxation in the composites is practically the same as in pure polyacids photopolymerised in the bulk. However, in the composites the β-relaxation peaks of polyacids are strongly modified. The high-temperature parts of the maxima are damped and only the low-temperature part remains. This modification of β-relaxation can be associated with various factors. The first one may be the different nature of the hydrogen bonds (which immobilise some of the –COOH groups) in the composites as compare with pure polyacids. The other reason for the modification of the β-relaxation in the composites with HPC can be a different conformation of the polyacid chains obtained by photopolymerisation in bulk and in the presence of the LC–CD. This can be due to the fact that hydrogen bonding between HPC chains and AA monomers can affect the polymerisation process, resulting in some sort of matrix polymerisation.

At high temperatures in dielectric relaxation spectra, all relaxation processes are hidden by conduction phenomena, which are caused by ionic impurities. In some cases it was possible to detect the relaxation processes in a high temperature range by analysis of the electric modulus. We have found that the α-relaxation processes of CDs observed in the $\varepsilon''(T)$ diagrams at lower temperatures were also observed in the $M''(T)$ plots. The temperature at which the $M''(T)$ plot shows a maximum is slightly lower in comparison with that for the $\varepsilon''(T)$ plot, but the Arrhenius plots have the same character. Therefore, one can say that the same process is visible in both representations. The β-relaxation of polyacids can be also analysed on the basis of $M''(T)$ diagrams as well as $\varepsilon''(T)$, or the $E''(T)$ plots (in DMA), and show the same E_a values. Some other relaxation processes (such as α-relaxation of poly(AA) in pure poly(AA) and in composites with HPC; α′-relaxation of CD component in HPC:poly(MAA) composites) occurring at high temperature demonstrate also similar behaviour in the $M''(T)$ spectra in DRS to that observed in the $E''(T)$ spectra in DMA. This allows us to believe that the $M''(T)$ maxima (associated with conductivity processes) reflect some molecular relaxations. This founding can be very useful in investigations of materials showing high conductivity. In our investigations, this appeared in some cases to be the only way to analyse the relaxation processes in dielectric spectra at higher temperatures.

The α-relaxation process of poly(AA) is visible at high temperature in both DRS and DMA techniques, and the α′-relaxation of HPC is dominated by this relaxation. In the HPC:poly(MAA) composites, the α-relaxation of poly(MAA) occurs at higher temperatures ($T_g = 488$ K) at which poly(MAA) already undergoes thermal degradation and can be seen only in DMA for HPC:poly(MAA) composites with the highest contents of poly(MAA). Due to this, the α′-relaxation of HPC is seen in DRS as well as in DMA. However it is affected by the presence of a second component, poly(MAA), and the maximum is shifted to higher temperatures. In the composite with the highest content of HPC (60 wt.%), additionally the second, unaffected α′-relaxation of HPC can be seen in the DMA spectrum. This indicates the presence of two mesophases of HPC in this composite: one, characteristic of pure HPC, and the second, modified by the interactions with poly(MAA). Our conclusion that intermolecular interaction between chains of HPC and of poly(MAA) are weaker and/or less numerous than in the case of HPC and poly(AA) can be rationalised by analysis of steric hindrance both composites. In the HPC/poly(MAA) composites the steric hindrance is higher because of additional $-CH_3$ groups in poly(MAA) in comparison with poly(AA).

5. Conclusions

The photopolymerisation of oriented lyotropic solutions of cellulose derivatives in polymerisable solvents yield polymer composites with a thermally stable anisotropic structure. The most characteristic feature of these composites is their specific band texture and optical anisotropy. Strong intermolecular interactions influence the thermo-optical behaviour of these composites. In HPC:poly(AA) composites, where strong hydrogen bonds are present, the anisotropy is stable and the isotropisation process cannot be observed in the accessible temperature range up to 520 K. In HPC:poly(MAA) composites, the decrease of birefringence is observed at lower temperatures (already at 440 K), what can be caused by thermal degradation of poly(MAA) component and by disorientation of macromolecular chains, easier in this case because of weaker intermolecular interactions.

The intermolecular interactions in the investigated composites have a strong influence on the molecular relaxations of both components. The larger modification of the molecular relaxation processes is observed in the HPC: poly(AA) composites, where the stronger intermolecular interactions are present. In the HPC:poly(MAA) composites, where intermolecular interaction are weaker (or not so numerous) because of steric hindrance, relaxation processes characteristic on both components are visible, however they are modified.

It has also been demonstrated that the results of DMA agree well with the dielectric measurements. At high temperatures, ionic conductivity dominates the dielectric spectra of the composites. It has been proven that the electric modulus representation in dielectric spectroscopy can be used to detect changes in molecular relaxations in the investigated systems. This means that the molecular relaxations can be investigated complementarily by dielectric spectroscopy and by DMA.

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