Morphology and Rheology of Composites Based on Anisotropic Polymer Matrix and Different Clays

G. B. Vasilyev,[1] V. V. Makarova,[1] A. V. Rebrov,[1] S. J. Picken,[2] N. M. Smirnova,[1] A. Ya. Malkin,[1] V. G. Kulichikhin[1]

[1]A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Science, Moscow 119991, Russia
[2]Department of Chemical Engineering, NanoStructured Materials, Delft University of Technology, 2628 BL Delft, The Netherlands

ABSTRACT: Structure and rheological properties of hybrids with polymer matrix and layered silicates as filler were studied. Solution containing 60% wt of hydroxypropylcellulose (HPC) in oligomeric polyethyleneglycol (PEG) was used as a matrix. The peculiarity of this study is that the matrix depending on temperature can form different phase states including liquid-crystalline (LC). So, a possibility of coexistence and superposition of different ordered structures can be realized at different temperatures. Three different fillers were used: natural Na-montmorillonite (MMT) and organoclays obtained by treating MMT with surfactants varying in polarity of their molecules. Depending on the type of clay, materials with different morphology can be obtained. X-ray data showed that PEG intercalates all types of clay used whereas penetration of HPC macromolecules into clay galleries during mixing does not occur. Clay modified with more polar surfactant should be treated as the most convenient material to be intercalated by PEG. Rheological studies (included steady-state and dynamic shear properties in a wide temperature range) demonstrate that composites are viscoplastic materials and the yield stress is observed already at 5% fillers loading. The level of the yield stress depends on the phase state of the matrix being induced by the superposition of structures formed by clay particles as well as by the LC phase (if it exists). The same conclusion can be made on the base of linear oscillatory measurements because the existence of the LC phase and/or the presence of filler lead to a pseudo solid-like behavior of a system as whole. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3642–3653, 2011

Key words: liquid-crystalline polymer; nanocomposite; clay; viscosity

INTRODUCTION

Composites containing different kinds of layered silicates (clays) as filler have attracted an increased attention in the recent decade. One the one hand, due to high specific surface ($\sim$ 700 m^2/g) loading of polymers with even small amount of clay (usually up to 5 wt %) leads to a remarkable improvement in mechanical properties of a material when compared with the polymer matrix or conventional microcomposites.[1–3] In addition, an inorganic origin and high aspect ratio of clay platelets provide a set of special features such as an increasing thermal resistance,[4] depressing gas permeability[5] and flammability.[6] On the other hand, polymer/layered silicate nanocomposites (PLSN) are also suitable as convenient model objects for investigation of polymer chains dynamics in confined environment.[7]

By now, PLSN with most of industrial plastics and rubbers as matrix have been intensively investigated in the aspect of their structural, thermodynamic, and rheological properties.[6,8–10] In the latter case, it was established that clay particles restrict relaxation of matrix polymer chains. As a result, PLSNs demonstrate the absence of the terminal zone in oscillatory tests. Besides, the solid-like plateau at low frequencies and the yield stress have been registered when the percolation threshold has overcome. The application of strong shear field to polymer melt with distributed anisometric filler particles aligns them along the flow direction, and the matrix response dominates in viscous properties of the systems.[11] Extension deformation is not as sensitive to the presence of nanoparticles as shear one. So, the change of strain-hardening effect is the main effect observed during elongation flow of PLSNs. Controversial results have been obtained in this field. On the one hand, a strong increasing of the strain-hardening effect along with the increase of the

clay content was observed in.[12] On the other hand, it was reported[13,14] that clay particles suppress strain-hardening and this suppression the stronger the higher filler content. In[13] such kind of behavior was related to the intensive aggregation of clay particles at extension.

Composite morphology is another feature strongly affects the rheological behavior of PLSNs. Fine dispersion on nanoscale (intercalated or exfoliated) level gives rise to pronounced effect in rheological properties of materials. Strong interaction between clay and macromolecules of polymer matrix provides a fine dispersion of particles in the matrix, and the best effect occurs when matrix macromolecules are bonded with functional groups of the platelets surface.[8]

All these publications are referred to nanocomposites with isotropic polymer matrices. Meanwhile there is a group of polymers demonstrating the anisotropy of properties. Liquid-crystalline (LC) polymers and block copolymer under order–disorder transition can be referred to this group. The yield point at low shear stresses,[15] the anisotropy of viscosity[16] and viscoelasticity[17] are the main peculiarities of this kind of systems. Articles concerning nanocomposites with anisotropic matrix are rather scarce. There are a few articles reported structural and thermodynamic properties of such systems.[18,19] Oscillatory shear tests showed that when the matrix is in the ordered state, its domain structure determines the viscoelastic response of the nanocomposites, and silicate particles give a small input. When the matrix becomes isotropic, the formation of a percolation network by clay particles results in development of the solid-like viscoelastic behavior.[20,21] In our recent paper[22] rheological behavior of polymer/layered silicate composites based on LC solution of hydroxypropylcellulose (HPC) in polyethyleneglycol (PEG) and unmodified Na-montmorillonite (MMT) was studied and we came to the same conclusion.

The aim of the work was to investigate the effect of the Na-montmorillonite modification consisted in replacing of Na^+ ions on surfactants containing different substituents on the structure and rheological behavior of composites based on HPC/PEG lyotropic system under shear deformation. This system is of interest because it can be used as a component for pressure sensitive hydrocolloid adhesives.[23,24] Addition of structurizing fillers also influences some technological properties of compositions (for example, improves cold flow of adhesives).

EXPERIMENTAL

Materials

HPC (Trade mark Klucel EF) produced by Hercules Co with weight-average molecular weight, $M_w =$ 80,000 g/mol and PEG (Spectrum Co) with $M_w =$ 400 g/mol were used for preparation of the matrix solution. It was established[25] that HPC and the liquid oligomeric PEG can form LC solutions above certain concentration of HPC. In the composition under study the ratio HPC/PEG was equal to 60/40. According to the phase diagram,[25] this system is completely LC in the range 40° to 91°C. At higher temperatures an isotropic phase appears and the system passes into a biphasic state containing both LC and isotropic phases. The system becomes completely isotropic at 127°C.

Three types of clay produced by Southern Clay Products were used as a filler. The first one was unmodified Na-montmorillonite (Cloisite Na^+). Two other types of clay were organophilic MMTs Cloisite 20A and Cloisite 30B, that is natural montmorillonite modified with surfactants. In both clays the quaternary ammonium salts were used for modification: dimethyl, hydrogenated tallow (65% C18, 30% C16, and 5% C14) in the case of Cloisite 20A and methyl, bis-2-hydroxyethyl tallow in the case of Cloisite 30B. The main dissimilarity between modified clays consisted in different polarity of surfactant molecules. An origin of the difference owing to the presence of hydroxyethyl groups in hydrophilic head of surfactant molecules in the case of Cloisite 30B.

Preparation of composites

The following procedure was used for preparation of composites. On the first stage clays were swelled in PEG. For this aim the necessary amount of dried clay powder was immersed in PEG for about 8 h at periodic stirring and room temperature. On the second stage the obtained suspensions were mixed with preliminary dried at 80°C for 24 h HPC powder in double rotary mixer "HAAKE Polydrive" ("ThermoHaake," Germany) at 120°C (30 rpm, 15 min).

Composites with 5.0 wt % of clay were prepared and marked as C5MMT, C5cl20A, and C5cl30B for systems containing Cloisite Na^+, Cloisite 20A, and Cloisite 30B, respectively.

X-ray diffraction

X-ray diffraction was used to verify the interlayer distance of clay platelets. "RU-200 Rotaflex" X-ray difractometer ("Rigaku" Japan) based on 12-kW generator with rotating copper anode was used to obtain X-ray scattering data in the transmission mode. The beam was CuK_α radiation (wavelength λ = 0.1542 nm) generated at 140 mA and 40 kV. Standard goniometer equipped with a nickel filter was applied. Diffraction patterns over 2θ range of 1.0 to 10° were registered.

Optical microscopy

A polarizing microscope "Boetius" (former DDR) equipped with hot stage was used to examine dispersity of clay particles on the micron level and phase behavior of composites. Temperature scanning rate was 4°C/min.

Rheological tests

Steady-state shear flow experiments at high shear stresses and rates were carried out on a capillary microviscometer MV-3M of the melt-indexer type.[26] In this case constant load is applied to the sample through a lever and plunger displacement is digitally recorded. The ratio of capillary length to its diameter was equal to 20 and 30. The calculation of the results was performed using the standard procedure.[27] Viscous properties at low shear stresses and rates were measured with rotational rheometer "RheoStress 600" ("ThermoHaake," Germany). A cone-plate operating unit with diameter 20 mm and the angle at the cone tip equals to 1° was used. The same apparatus allows to perform the oscillatory shear deformation regime. Frequency dependences of storage and loss moduli were recorded. Parallel plates (diameter 20 mm) geometry was applied in this case.

RESULTS AND DISCUSSION

Structure of composites

X-ray data

It was established[22] that swelling of Cloisite Na$^+$ in PEG leads to the shift of basal reflex d_{001} of the clay from $2\theta = 7.59°$ to $4.95°$, that is interlayer distance increases from 11.7 Å up to 17.7 Å. The distance is not changed at further mixing of prepared suspension with HPC. The conclusion was: only PEG intercalates MMT during process chosen for composite preparation.

The results of X-ray diffraction measurements for composites containing organoclays are presented in Figure 1. The basal reflex d_{001} of Cloisite 20A is located at $2\theta = 3.72°$ that corresponds to interlayer distance equal to 23.6 Å [Fig. 1(a)]. For PEG/Cl.20A suspension this reflex shifts to $2.26°$ that is the interlayer distance increases up to 38.9 Å. This means that PEG intercalates the clay. A weak peak at $2\theta = 4.64°$ can be attributed to d_{002} reflex of intercalated clay. These values are in agreement with results obtained for composites of high molecular weight PEG (PEO) and Cloisite 20A.[28] For the final composite d_{001} peak is observed at the same position ($2\theta = 2.26°$) as in the case of suspension. So, one can conclude that a deeper intercalation of clay due to penetration of HPC macromolecules into galleries does not occur.
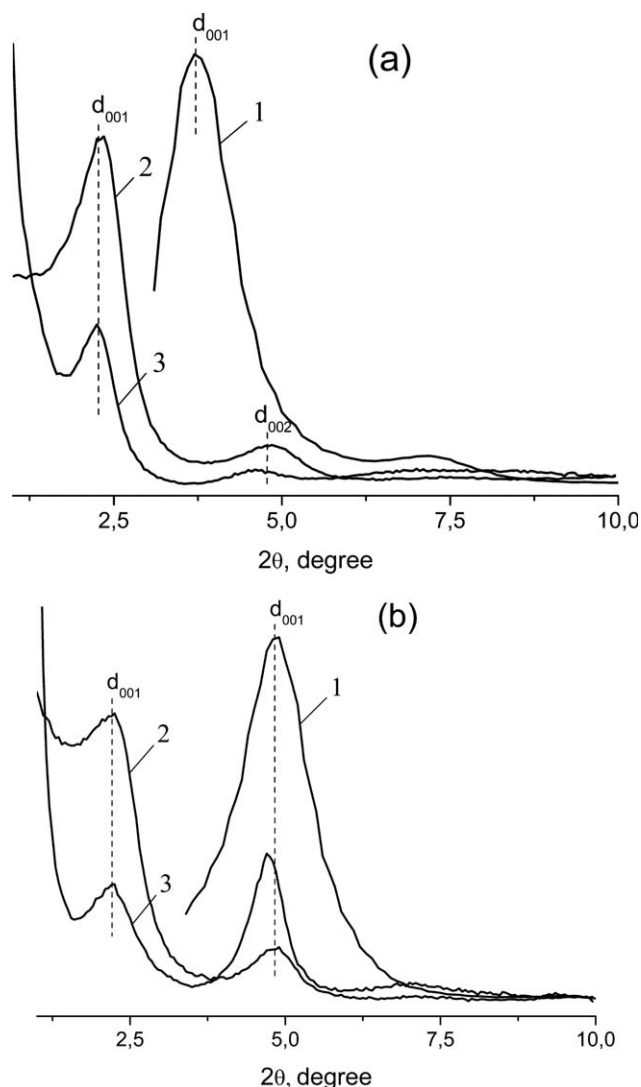

Figure 1 Difractograms of the neat clays (1), suspensions used for composite preparation (2), and final composites (3) for composite C5cl20A (a) and C5cl30B (b).

For Cloisite 30B the basal reflex is situated at $2\theta = 4.83°$ i.e., the interlayer spacing equals to 18.3 Å. Swelling of the clay in PEG leads to the increase of gallery height up to 39.9 Å ($2\theta = 2.21°$) and it keeps unchanged after mixing of suspension with HPC. There is a specific feature for this system. A peak at $2\theta = 4.83°$ that is at the same position as d_{001} reflex for pure Cloisite 30B has appeared for suspension and composite. Similar result was obtained in[29] for exfoliated nanocomposites of PEO with Cloisite 30B at clay content higher than 2.5% wt. In authors' opinion there was a threshold level for the clay concentration above which the amount of the clay becomes too high for complete exfoliation.

Thus, on the base of X-ray data one can conclude that PEG intercalates all type of clays used in this
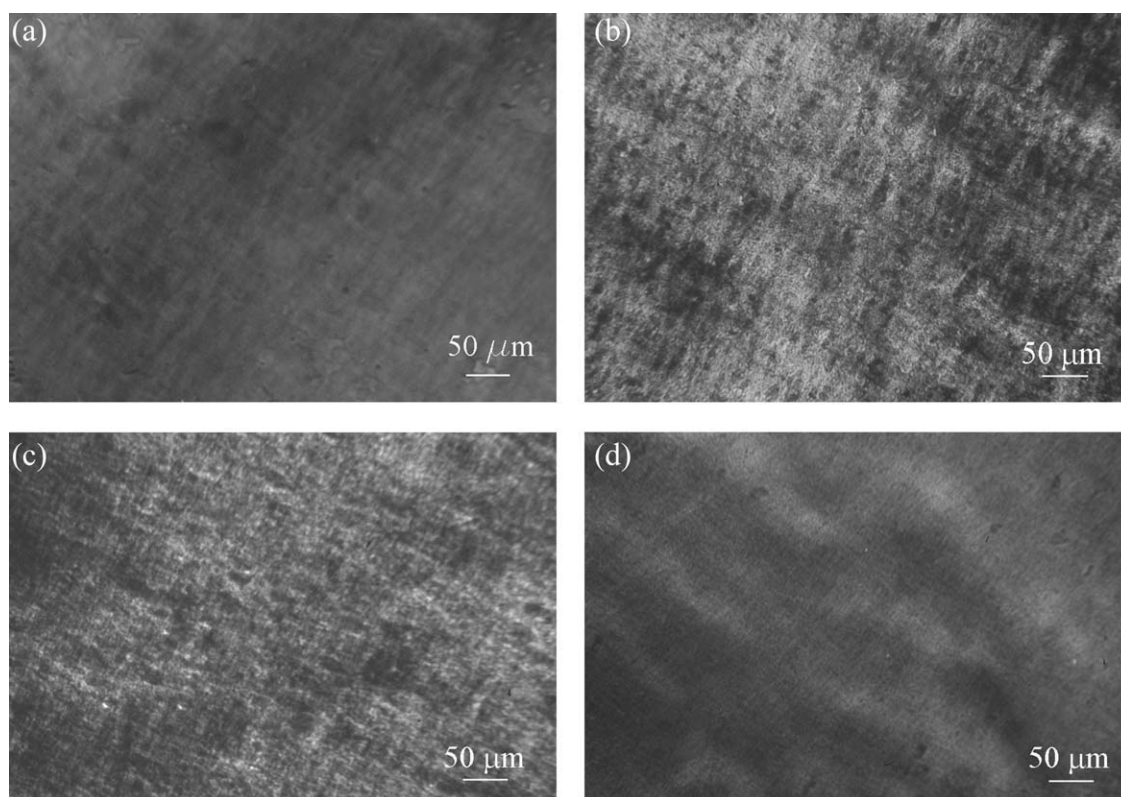
Figure 2 Micrograph of thin films of HPC/PEG (a) and composites C5MMT (b), C5cl20A (c), and C5cl30B (d) in polarized light.

study, whereas penetration of HPC macromolecules into clay galleries during following mixing does not occur. Interlayer distance growth (Δd_{001}) in clays increases in the row Cloisite Na^+ < Cloisite 20A < Cloisite 30B (6.0 Å, 15.3 Å, 21.6 Å). This result shows that the scale of attractive interaction between matrix macromolecules and molecules of clay modifier is more important factor for intercalation than initial interspace distance. So, not Cloisite 20A which has the largest interlayer distance, but Cloisite 30B should be treated as the most convenient clay got the PEG intercalation. A similar conclusion was made in Ref. 30. The gallery distance of organoclay may influence the degree of exfoliation of clay aggregates only when polymer matrix and organoclay are compatible.

Optical, polarizing, and transmission electron microscopy

In general, high clay loading leads to the restriction of chains ability for orientation and ordered structures formation. This can result in significant loss in the LC order[20] or even complete suppression of LC structure.[18] When looking at the matrix solution through crossed polarizers, the optical field colored in dark orange. According to Ref. 31, it is a reliable indicator of the cholesteric LC phase. Thin films (~ 100 μm) of HPC/PEG in crossed polarizers

are colored in gray gradations [Fig. 2(a)]. Addition of clay could lead to disruption of cholesteric structure and formation of less ordered nematic one. Similarity of micrographs of the matrix and composites indicates that cholesteric liquid crystals also were formed in the case of composites [Fig. 2(b–d)]. So, one can conclude that loading HPC/PEG with 5% of different clays in our case does not change the LC structure of the matrix.

Darkening of the field of vision starts at 90 to 93°C for both the matrix and composites that reflects the appearance of isotropic phase. The area becomes completely black at 125 to 130°C. This means that the systems pass into a fully isotropic state. Hence, addition of clays does not affect significantly the phase behavior of HPC/PEG too and the phase diagram built for the HPC/PEG system is valid for composites.

Optical microscopy was used to estimate filler particles dispersion on the micron size level. Figure 3 demonstrates microphotos of three composites. Addition of unmodified montmorillonite in HPC/PEG provides a rather rough dispersion of filler particles in the matrix. There are large aggregates with dimensions up to 30 to 40 μm in composite C5MMT [Fig. 3(a)]. This means that MMT is weakly compatible with HPC/PEG system and more severe mixing conditions is needed to obtain a better dispersion of clay particles.
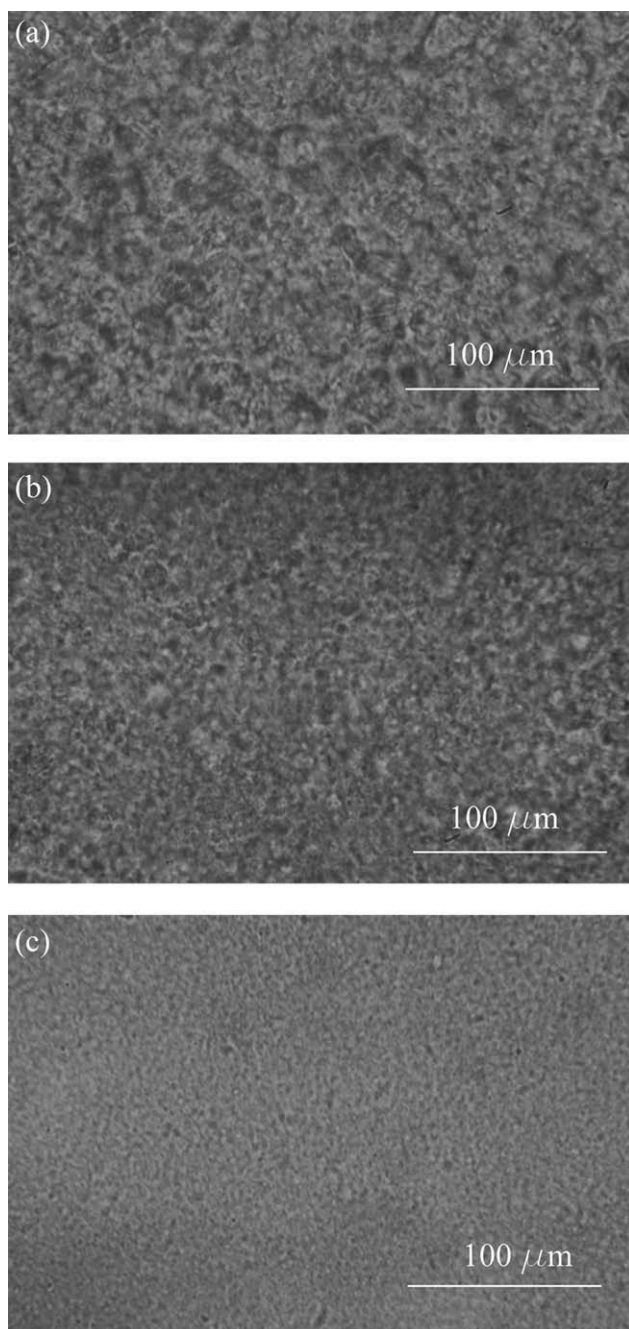
Figure 3 Micrographs of composites C5MMT (a), C5cl20A (b), and C5cl30B (c).

Loading the matrix solution with modified clays makes the dispersion finer. Nevertheless, the presence of large aggregates in composite can be registered when Cloisite 20A was used [Fig. 3(b)]. These aggregates are not as numerous as in the previous case and have a maximum size of about 20 μm. It should be remembered that Cloisite 20A has nonpolar aliphatic substituents in both hydrophilic head and hydrophobic tails of modifier molecules. Presumably, interaction between PEG and modifier molecules as well as high gallery distances

that Cloisite 20A has provide a better filler particles dispersion. The finest particles dispersion was achieved for composite C5cl30B. Probably, the presence of polar hydroxyethyl groups in surfactant molecules and its interaction with end hydroxyl groups of PEG macromolecules are responsible for better compatibility of Cloisite 30B and the matrix. There is homogeneous particle distribution and aggregates size does not exceed a few microns in this case [Fig. 3(c)]. Similar effect of the improved dispersion quality was reported in[30,32] when polar polymers was mixed with layered silicate modified by surfactant containing polar groups.

Transmission electron microscopy (TEM) was applied to observe composite morphology on nanoscale level (LEO 912 AB Omega electron microscope (Carl Zeiss SMT AG, Oberkochen, Germany) operated at 120 kV). Figure 4 demonstrates TEM image of C5cl30B at high magnification. It is evident that there are particles of about 100 to 200 nm in the composite. These dimensions are typical for montmorillonite platelets.[33]

Thus, the structure of composites has been elucidated by three different methods: X-ray diffraction, optical polarizing microscopy, and TEM. Optical microscopy allows to visualize uniformity of clay particles distribution in the matrix and roughly estimating agglomerates dimension, whereas TEM provides a qualitative understanding of system microstructure on the nanosized level. X-ray diffraction is a convenient method to determine the interlayer distance due to the periodic arrangement of clay platelets in the native clay and in the intercalated polymer/clay composites.
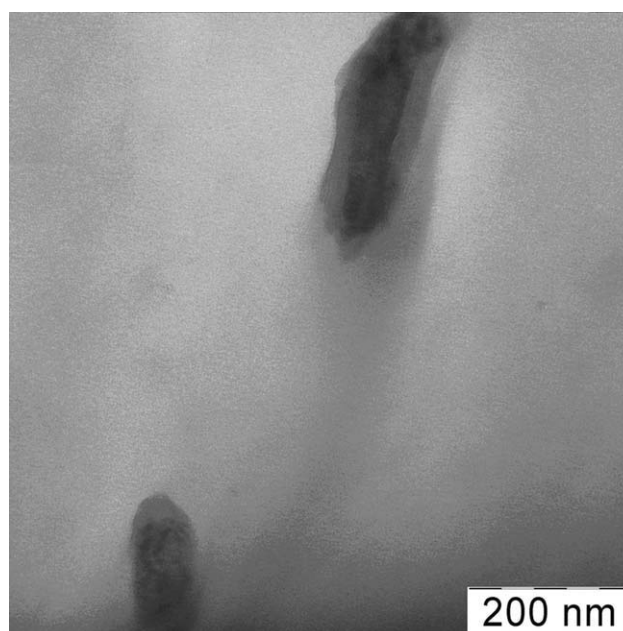

Figure 4 TEM micrographs of composite C5cl30B.

TABLE I
Phase Composition of HPC/PEG at Different Temperatures

T (°C)	71	101	111	118	134–174
LC phase (%)	100	75	50	25	0
Isotropic phase (%)	0	25	50	75	100

Rheological properties of composites

Steady-state shear flow

The choice of experimental temperature was determined by the phase behavior of the HPC/PEG system. According to phase diagram the composition of systems under investigation was (Table I).

Figure 5(a) shows flow curves for the matrix and composites at 134°C corresponding to the isotropic state of HPC/PEG. Viscosity versus shear rate ($\dot{\gamma}$) dependences consist of two domains. At low shear rates a very weak shear thinning takes place. It can be treated by approaching to the Newtonian viscosity limit as well as a small yield stress value.

It is not a typical behavior for unfilled isotropic polymer, but similar results were obtained for isotropic solutions of some other cellulose derivatives.[34] Addition of 5% of unmodified MMT and Cloisite 20A to the matrix does not change significantly the character of the rheological response. The degree of viscosity anomaly is practically unchanged in comparison with the pure matrix. However, a moderate viscosity increase ($\sim$ 30%) should be noted for these composites.

The situation looks different for the composite C5cl30B, which definitely demonstrates the existence of the yield stress. The viscosity of the composite is approximately three fold higher than the matrix one (at $\dot{\gamma} = 0.05$ s^{-1}). Apparently, the difference in yield behavior of composites arises from the nature of clay used. As was said above, strong interaction between modifier molecules and matrix in the case of Cloisite 30B provides finer particles dispersion. The smaller the particles size the less interparticle distance and the higher interparticle interactions. Thus Cloisite 30B forms the most robust structural network in HPC/PEG which contributes significantly in the viscous response of composite. In general, yield stress existence or viscoplastic behavior is typical for filled polymers with strong interparticle interaction. It is attributed to the formation of the percolation network by filler particles when a certain concentration is overcome. Regularly, rather high filler concentration (10–30 vol. %) is needed to provide viscoplastic behavior in the case of conventional microcomposites,[35–37] but a small amount (2–5% wt) of nanofiller is enough to ensure this kind of material response.[38,39]

A strong shear thinning takes place in the region of high shear rates for all compositions under study. The reorganization of temporary junctions and
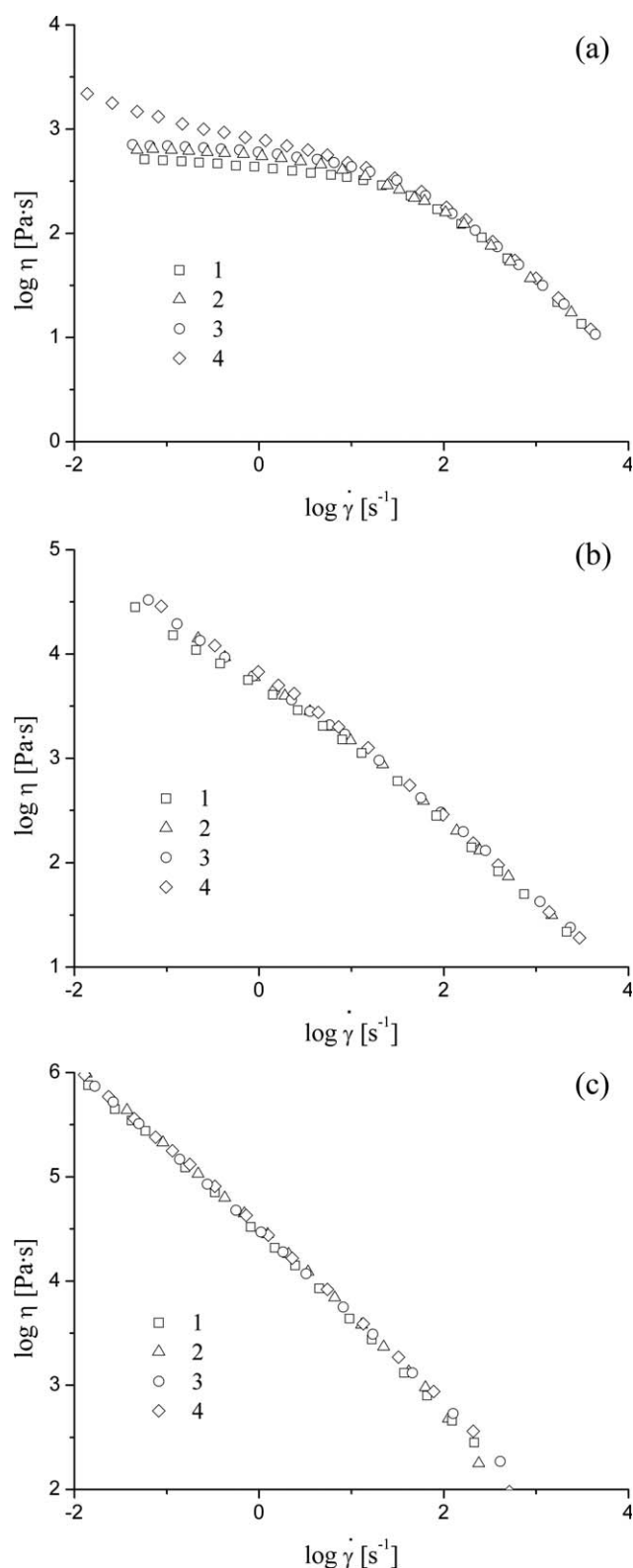

Figure 5 Apparent viscosity versus shear rate for the matrix (1) and composites C5MMT (2), C5cl20A (3), and C5cl30B (4) at 134°C (a), 101°C (b), and 71°C (c).
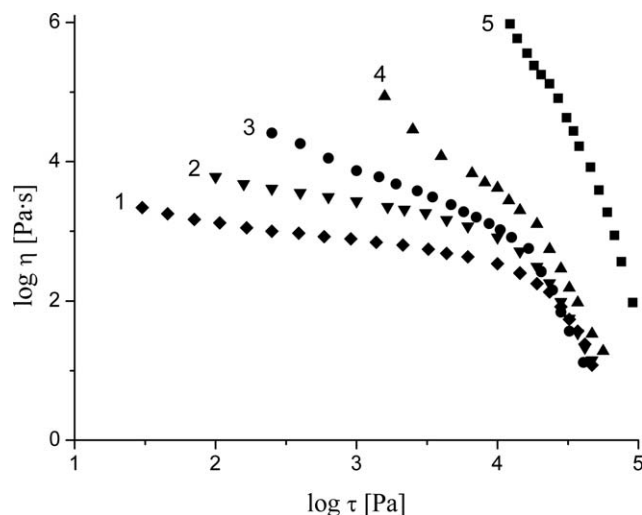
Figure 6 Steady shear viscosity versus shear stress for composite C5cl30B at 134°C (1), 118°C (2), 111°C (3), 101°C (4), and 71°C (5).

polymer chains orientation are responsible for this phenomenon. A transition to non-Newtonian flow occurs at lower shear rates and shear thinning is higher for composites than for the matrix that is typical for filled systems.[40] Filler particles structure destruction is responsible for the behavior. Flow curves for all composites and the matrix practically coincide at $\dot{\gamma} > 100$ s^{-1}. High shear rates provide alignment of clay particles. These particles, probably, do not contribute to the total hydrodynamic resistance to the flow due to their high anisometricity. The same results were obtained in[11,41] for intercalated and exfoliated PLSNs.

The character of viscous response changes drastically when the temperature of experiment was lowered and the matrix becomes biphasic (LC + isotropic). It has been established that HPC/PEG demonstrates unusual rheological behavior for nematic or cholesteric systems.[14,22] This behavior consists in the significant viscosity rise when phase separation takes place and a LC phase appears. In[14] this behavior was explained as a result of reorganization of H-bond network formed between terminal hydroxyl groups of PEG and the ones of hydroxypropyl groups in HPC macromolecules. In this case PEG molecules can act as both intradomain crosslinks and interdomain bridges.

Flow curves of systems under investigation at 101°C are shown in Figure 5(b). As was said, the HPC/PEG system contains 75% of LC phase at this temperature. Thus, the matrix can be considered as a filled system and LC domains play a role of filler. H-bond network density growth leads to a considerable viscosity increase. Besides, a stronger shear thinning takes place in the whole investigated range of shear rates. Probably, the synergism of two simul-

taneous processes can be responsible for the behavior. On the one hand, destruction of temporary linking of polymer chains as in the case of isotropic melts occurs. On the other hand, the orientation of LC domains in the shear field intensifies shear thinning.

Addition of clay does not affect essentially the behavior of the matrix regardless the clay type and composite morphology realized. As the dependences under discussion practically coincide at higher shear rates, one can conclude that the structure formed by the LC domains of the HPC/PEG system governs the rheological behavior of these systems. Small amount (up to 5%) of clays only slightly strengthens the yield behavior.

Further temperature decrease leads to the matrix transition to the complete LC state. Log η versus log $\dot{\gamma}$ dependences at 71°C are depicted on Figure 5(c). It should be mentioned that the shape of the curves is not a classical three region curve[15,42] which is common for many lyotropic and thermotropic LC polymers.[43,44] The complete flow curve demonstrates only a single strong shear thinning. Earlier, curves of this kind were obtained for thermotropic HPC[45] and smectic side-chain LC polymer.[46]

In general the curves shown on Figure 5(b,c) are qualitatively similar. Identical scales on Figure 5(a–c) help to highlight the quantitative influence of such features as the matrix phase state and the type of clay on the rheological behavior of systems under investigation. Transition of the HPC/PEG system being completely in the LC state leads to the viscosity growth by ~ 400 and ~ 10 times (at $\dot{\gamma} = 0.1$ s^{-1}) in comparison with isotropic and biphasic state, respectively. At high shear rates (100 s^{-1}) this difference diminishes and equal to ~ 3 and ~ 2, respectively.

The yield stress value (τ_y) is often used as a quantitative measure of strength of structural network formed in polymer systems. Determination of τ_y is an ambiguous task and the result strongly depends on the method of calculation.[47] The Casson equation was used to estimate the τ_y value in this study:

$$\tau^{0.5} = \tau_y^{0.5} + \alpha\dot{\gamma}^{0.5} \tag{1}$$

where τ is the shear stress, $\dot{\gamma}$, shear rate, and α, constant.

It is rather instructive to follow the yield properties evolution depending on phase state of the matrix for composite C5cl30B. The dependences of viscosity on shear stress at different temperatures for this composite are presented on Figure 6. All curves are S-shaped that is typical for viscoplastic systems.[47] The structural network formed by clay particles is responsible for the observed behavior when the matrix is in isotropic state. On the other hand, a joint effect of the network mentioned above

TABLE II
The τ_y Values at Different Temperatures

T (°C)	71	101	111	118	134
Yield stress (Pa)					
HPC/PEG	6300	700	53	–	0.12
C5cl30B	8300	1100	94	13.6	4.5

and the LC domain structure determines visco-plasticity of the composite when the matrix is either in biphasic or completely LC state.

The curves 1 to 3 practically coincide at high shear stresses (>20 kPa). This occurs in the temperature range 134 to 111°C that is when the share of the LC phase does not exceed the one of isotropic phase. One can conclude that both clay particles and LC domains are strongly aligned in the shear field direction and the isotropic phase of the matrix determines viscous properties of composite. Reasonable viscosity increase can be observed when the LC phase in the matrix dominates (curve 4). Transition of the matrix to the complete LC state provides a very strong sharpening of the effect (curve 5).

A fan-shaped cleavage of the curves can be seen in the region of low shear stresses. This reflects τ_y growth as the content of the LC phase in the matrix increases and the system becomes more and more structurized. The results of the τ_y calculation made according to the Casson equation are presented in Table II. The yield stress value for unfilled HPC/PEG containing 75% of LC phase (101°C) equal to ∼ 0.7 kPa. Transition to a complete LC state (71°C) leads to the τ_y increase up to ∼ 6.3 kPa. The addition of the clay leads to formation of complementary structure which increases the total strength of a matter. As a result, the τ_y values rise up to 1.1 kPa and 8.3 kPa, respectively. An enhancement factor amounts to 1.3 for composite with LC matrix and further 1.6 and 1.8 in the case when the matrix contains 75 and 50% of the LC phase, respectively. So, it is evident that ordered domain structure of HPC/PEG is strengthened in comparison with the structure formed by clay particles. The input of the latter to the total yield behavior increases as the temperature rises providing gradual isotropization of the matrix. This clearly illustrates Figure 7. Nevertheless, a fine dispersion of Cloisite 30B by itself also provides formation of a stable clay particles network. This network is reflected in viscoplastic behavior of C5cl30B even if the matrix is in the isotropic state.

Viscoelastic properties

Oscillatory shear deformation regime was applied to investigate viscoelastic properties of matrix and composites. Frequency sweep tests at constant strain amplitude 2% were carried out at temperatures corre-

sponding to different phase state of the matrix. The preliminary set of experiments confirmed that all systems under investigation demonstrate linear viscoelastic behavior at this amplitude of deformations. The decrease of moduli starts at lower amplitude values for compositions with high LC phase content but the threshold did not exceed 5% in all cases.

Frequency dependences of components of complex dynamic modulus (G^*) – storage (G') and loss (G'') moduli for the matrix at different temperatures are presented on Figure 8. A gradual transformation of the shape of the curves along with the temperature increase can be observed. At 71°C when HPC/PEG is in the LC state (curve 1) a rather weak frequency dependence of moduli can be observed in the low frequency region. Elastic response of material dominates ($G' > G''$) and a slope of the curves is 0.2 for $G'(\omega)$ and 0.23 for $G''(\omega)$. So, pseudo solid-like behavior for the system takes place. Highly ordered LC structure resulting from formation of dense H-bond network between HPC and PEG macromolecules is responsible for this behavior. Much stronger frequency dependences (with slope 0.7–1.0) for G' and G'' were obtained for nematic LC polymers.[48,49] As a rule, dissipative component of G^* dominated for those LC structures. Nevertheless results similar to ours were obtained in[50] for highly ordered smectic polyesters.

Progressive moduli decrease (curves 2 and 3) in the whole range of frequencies takes place as the temperature rises. This effect is much more pronounced in the low frequencies region. The slope of the initial portion of $G'(\omega)$ curve increases up to 0.76 and 1.09 for 101° and 118°C, respectively. G'' prevail over G' in this temperature domain. The melting of an appropriate part of the ordered phase which determines the system strength and
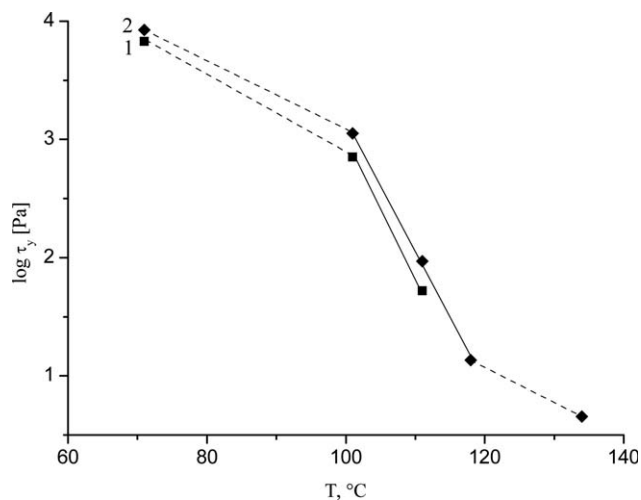

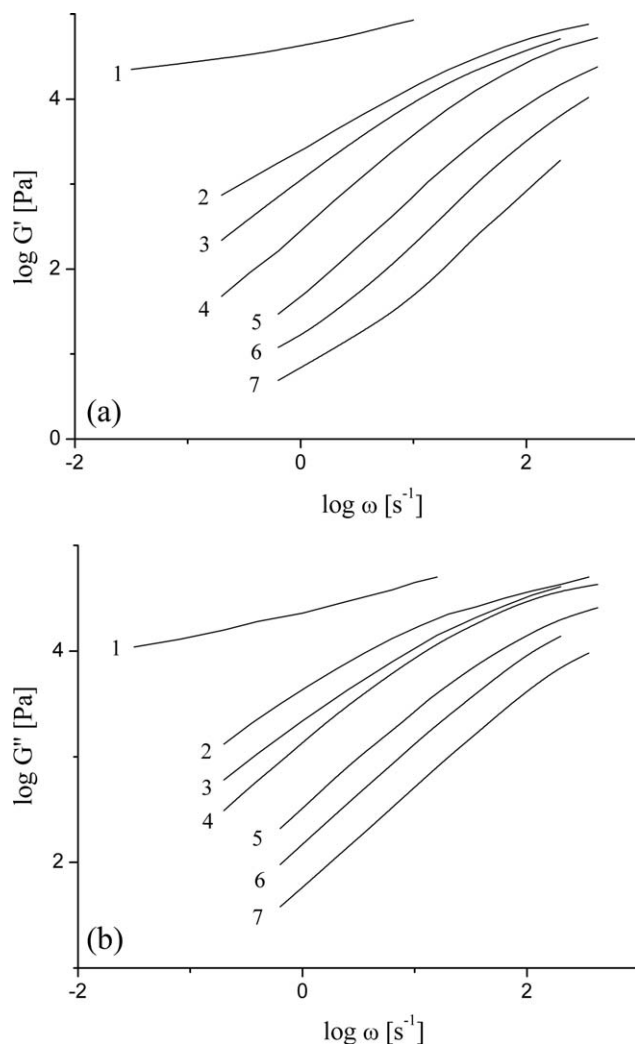**Figure 7** Temperature dependence of the yield stress for HPC/PEG (1) and composite C5cl30B (2).

Figure 8 Frequency dependences of storage (a) and loss moduli (b) for HPC/PEG at 71°C (1), 101°C (2), 111°C (3), 118°C (4), 134°C (5), 154°C (6), and 174°C (7).

transition of the matrix to the biphasic state is responsible for these effects.

Further temperature increase up to 134°C leads to full isotropization of HPC/PEG (curve 4). However, the viscoelastic response of the solution in the isotropic state is different from characteristic for flexible chains polymers. The storage modulus does not hold characteristic terminal behavior ($G' \sim \omega^2$) and the exponent value equals to 1.19 in this region. Nevertheless the exponent value for loss modulus practically coincides with the value typical for linear viscoelastic behavior ($G'' \sim \omega$). Gillmor investigating viscoelastic properties of thermotropic random co-polyether obtained similar results.[51] Namely, both the storage and loss moduli were roughly proportional to $\omega^{0.85}$ at low frequency in the isotropic state. The possibility of a remnant LC structure in the isotropic state as had been suggested,[51] was excluded by direct observation through a polarizing light microscope in the present study. Also Wewerka

et al.[52] obtained $G' \sim \omega^{0.94}$ for short side chain nematic liquid crystals in the isotropic state. In authors' opinion a broad MWD of the polymer was responsible for the behavior. In our case HPC is a commercial grade and broad MWD is typical for materials of this kind. Perhaps it was one of the possible reasons of such abnormal G' behavior.

It should be mentioned that time-temperature superposition[53] is valid for both the matrix and composites when HPC/PEG is in isotropic state that is at $T > 134°C$ (curves 5–7). The same results were obtained in[54] for polystyrene/clay nanocomposites. This reflects a similarity of relaxation mechanism in the temperature range. When the matrix becomes anisotropic time-temperature superposition is failed. It is rather evident result because the formation of a new phase state radically changes a relaxation spectrum of a material.

Figure 9(a–c) represents the effect of filling on storage modulus which is the most sensitive component of G^* to structural changes in polymeric systems. Loading isotropic matrix with 5% of different clays leads to dynamic moduli rise in the whole frequency range [Fig. 9(a)]. The ratio of enhancing differs for various types of clay. The situation reminds the case of steady-state shear flow. Unmodified MMT provides the least G' increase due to poor dispersion of particles in the matrix. The strongest matrix strengthening was achieved when Cloisite 30B was used. The scale of the effect is quite noticeable. G' increases by about one decimal order in the low frequencies region. Fine dispersion of the clay and structural network formation are evidently responsible for the behavior.

The plasticity of both the HPC/PEG and composites becomes stronger, as temperature lowers [Fig. 9(b,c)]. This is evidenced from the change of the slope of low frequency portion of the $G'(\omega)$ dependence. Formation of the ordered LC phase in the matrix is responsible for the behavior. The value drops from 1.19 to 0.76 as the LC phase content increases up to 75% for the matrix. These values become equal to 1.02 and 0.42, respectively, for composite C5cl30B. Thus elastic properties are more sensitive to systems structurization than viscous ones and can "feel" the input of a rather weak structure such as in the case of C5MMT containing unmodified Na-montmorillonite.

Figure 10 illustrates an influence of the clay loading on elastic properties of HPC/PEG in different phase states. The storage modulus against temperature in the low frequency domain is presented. It is evident that the picture analogous to the case of steady-state shear flow takes place. At high temperature when the matrix is in isotropic state the significant G' value increase can be seen. Storage modulus of C5cl30B is approximately seven times
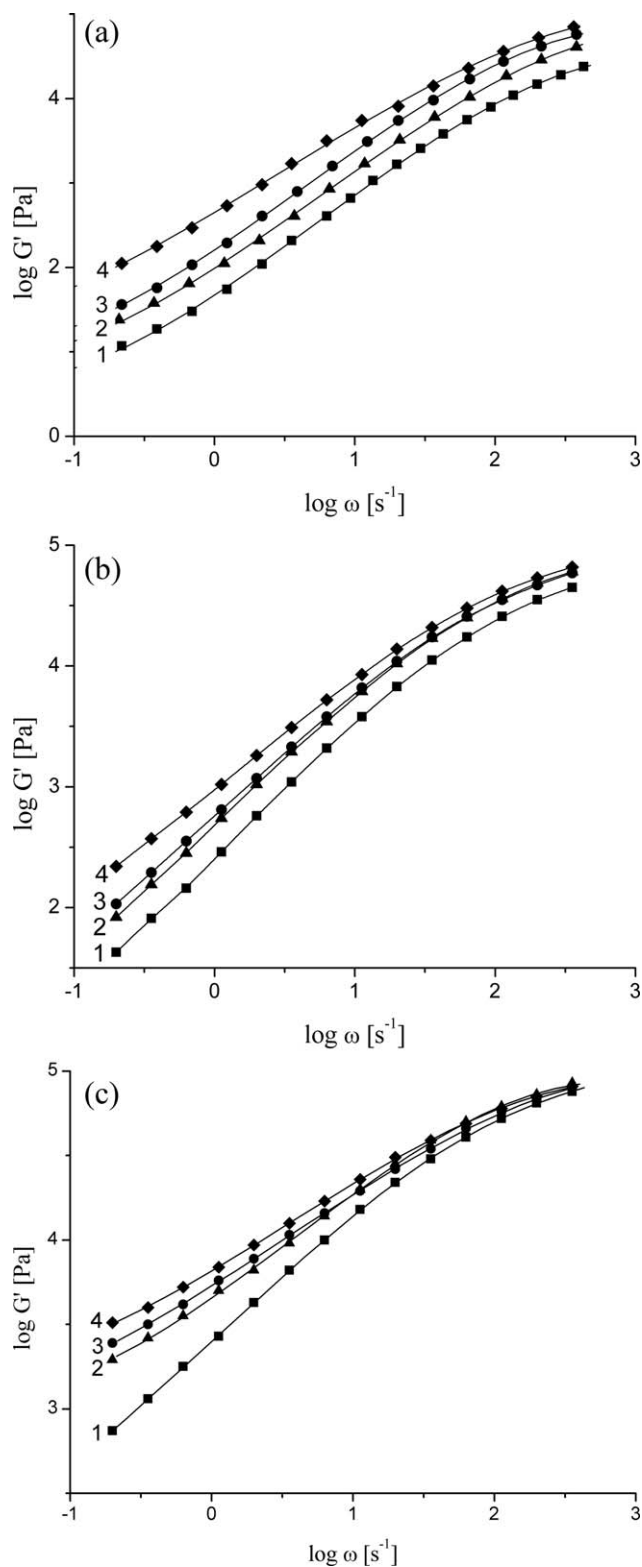
the temperature lowering when the matrix passes in biphasic state containing isotropic and anisotropic phases. Further temperature decrease leads to a formation of the completely LC structure in the HPC/PEG solution. Then the enhancement diminishes and only the 20% G′ growth is observed. Similar results were obtained by authors of Ref. 21 in the study of viscoelastic properties of styrene triblockcopolymers/clay nanocomposites in the different phase state of the matrix.

CONCLUSIONS

Structure and rheological properties of composites based on HPC in oligomeric PEG solution at different shear deformation modes have been investigated. The matrix can exist in different phase state depending on temperature. Three grades of montmorillonite were used as a filler: hydrophilic unmodified Cloisite Na$^+$, organophilic Cloisite 20A, and organophilic Cloisite 30B modified with more polar surfactant than in the previous case. In all case the composites can be attributed to the intercalated ones. Intercalation was achieved by penetration of PEG molecules into interlayer clay galleries. HPC macromolecules likely do not interact with the clays. A weak compatibility of filler and the matrix provides a rough clay dispersion with the presence of large aggregates when unmodified clay and Cloisite 20A were used. The finest morphology was obtained for composite with Cloisite 30B. Apparently, strong interaction between polar hydroxyethyl groups of modifier molecules and polar groups of PEG macromolecules leads to a good dispersive ability of this clay in HPC/PEG. Addition of small (5% wt) amount of clays does not affect the structure and phase behavior of the
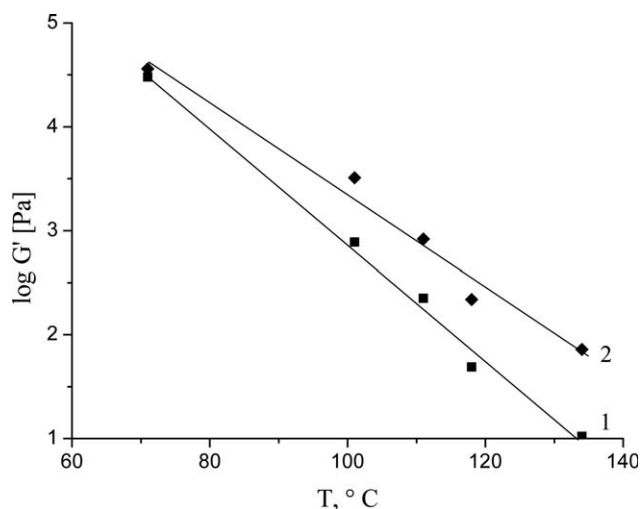
Figure 9 Frequency dependences of storage modulus for the matrix (1) and composites C5MMT (2), C5cl20A (3), and C5cl30B (4) at 134°C (a), 118°C (b), and 101°C (c).

higher than that of the matrix. Formation of structural network by clay particles is responsible for the enhancement. This difference decreases along with

Figure 10 Temperature dependences of storage modulus for HPC/PEG (1) and C5cl30B (2) at $\omega = 0.2$ s^{-1}.

matrix. Rough estimation shows that due to intercalation of PEG fraction into clay structure the matrix solution concentration increases on not more than ~ 1.0%. This does not influence on location of phase equilibrium lines.

Two main features affect rheological behavior of composites under consideration at steady-state and oscillatory shear deformation. The phase state of the matrix system plays a key role when HPC/PEG solution is in anisotropic state. An ordered domain structure of the matrix is more robust then the structure formed by clay particles. It provides yield behavior and strong shear thinning at steady-state shear flow as well as pseudo solid-like behavior observed at the oscillation deformation mode. Addition of the clay only slightly enhances these responses almost independently on the clay type. The influence of a supplementary structure constituted by clay becomes stronger in biphasic region. The yield stress growth and pseudo solid-like behavior enhancement for composites occur at this phase state. The scale of these effects increases as the LC phase content in the matrix solution decreases.

The morphology of composites being strongly dependent on clay type is a major factor determining rheological behavior of a composite if the matrix is isotropic. The formation of rough morphology with large filler aggregates does not change the character of rheological response providing only moderate viscosity growth in the low shear rate domain. However, the fine particle dispersion when Cloisite 30B was used creates conditions for the formation of a stable clay particles network. It leads to the clearly expressed viscoplastic behavior of a composite with rather high yield stress.

References

1. Shariatpanahi, H.; Sarabi, F.; Mirali, M.; Hemmati, M.; Mahdavi, F. J Appl Polym Sci 2009, 113, 922.
2. Nayak, S.K.; Mohanty, S. J Appl Polym Sci 2009, 112, 778.
3. Liu, X.; Wu, Q. Polymer 2001, 42, 10013.
4. Agag, T.; Koga, T.; Takeichi, T. Polymer 2001, 42, 3399.
5. Ray, S. S.; Okamoto, K.; Okamoto, M. J Appl Polym Sci 2006, 102, 777.
6. Lee, Y. H.; Park, C. B.; Sain, M.; Kontopoulou, M.; Zheng, W. J Appl Polym Sci 1993 2007, 105.
7. Zax, D. B.; Yang, D. K.; Santos, R. A.; Hegmann, H.; Giannelis, E. P.; Manias, E. J Chem Phys 2000, 112, 2945.
8. Krishnamoorti, R.; Giannelis, E. P. Macromolecules 1997, 30, 4097.
9. Kulichikhin, V. G.; Tsamalashvili, L. A.; Plotnikova, E. P.; Barannikov, A. A.; Kerber, M. L.; Fischer, H. Polym Sci 2003, 45, 564.
10. Usuki, A.; Tukigase, A.; Kato, M. Polymer 2002, 43, 2185.
11. Kim, T. H.; Lim, S. T.; Lee, C. H.; Choi, H. J.; Jhon, M. S. J Appl Polym Sci 2003, 87, 2106.
12. Kotsilkova, R. Mech Time-Dependent Mater 2002, 6, 283.
13. Pasanovic-Zujo, V.; Gupta, R. K.; Bhattacharya, S. N. Rheol Acta 2004, 43, 99.
14. Vasilyev, G. B.; Makarova, V. V.; Picken, S. J.; Rebrov, A. V.; Kulichikhin, V. G. Polym Eng Sci 2010, 50, 789.
15. Kulichikhin, V. G. In Liquid-Crystal Polymers; Platé, N. A., Ed.; Plenum Press: New-York, London, 1993; Chapter 9.
16. Malkin, A. Ya.; Vasil'eva, N. V.; Belousova, T. A.; Kulichikhin, V. G. Kolloid Zh 1979, 61, 200 (In Russian).
17. Volkov, V. S.; Tereshin, A. K.; Kulichikhin, V. G. Polym Sci 2004, 46, 1141.
18. Chang, J-H.; Ju, C.H.; Kim, S.H. J Polym Sci Part B: Polym Phys 2006, 44, 387.
19. Bandyopadhyay, J.; Ray, S. S.; Bousmina, M. Macromol Chem Phys 1979 2007, 208.
20. Huang, W.; Han, C. D. Macromolecules 2006, 39, 257.
21. Carastan, D. J.; Demarquette, N. R.; Vermogen, A.; Masenelli-Varlot, K. Rheol Acta 2008, 47, 521.
22. Vasilyev, G. B.; Makarova, V. V.; Rebrov, A. V.; Malkin, A. Ya.; Kulichikhin, V. G. Polym Sci 2010, 52, 60.
23. Kulichikhin, V. G.; Antonov, S. V.; Semakov, A. V.; Makarova, V. V.; Tereshin, A. K.; Singh, P. In Pressure-Sensitive Adhesives, Formulations and Design; Benedek, I., Ed.; VSP: Leiden, Boston, 2006; Vol.1, Chapter 7.
24. Kulichikhin, V.; Parandoosh, S.; Feldstein, M.; Antonov, S.; Cleary, G. US Pat.7,217,853 B2. 2007.
25. Makarova, V. V.; Gerasimov, V. K.; Tereshin, A. K.; Chalykh, A. E.; Kulichikhin, V. G. Polym Sci 2007, 49, 433.
26. Dreval', V. E.; Hayretdinov, F. N.; Litvinov, I. A.; Kerber, M. L.; Kulichikhin, V. G. Polym Sci 1995, 37, 79.
27. Malkin, A. Ya.; Chalykh, A. E. Diffusion and Viscosity of Polymers. Methods of Measurements; Khimiya: Moscow, 1979; Chapter 1.
28. Hyun, Y. H.; Lim, S. T.; Choi, H. J.; Jhon, M. S. Macromolecules 2001, 34, 8084.
29. Loyens, W.; Jannasch, P.; Maurer, F. H. J Polym 2005, 46, 903.
30. Lee, K. M.; Han, C. D. Macromolecules 2003, 36, 7165.
31. Hongladarom, K.; Burghardt, W. R. Rheol Acta 1998, 37, 46.
32. Li, X.; Ha, C. -S. J Appl Polym Sci 1901 2003, 87.
33. Ray, S. S.; Okamoto, M. Progr Polym Sci 2003, 28, 1539.
34. Kulichikhin, V. G.; Kostikova, E. B.; Ginzberg, M. A. Khim Volokna 1971, 4, 27 (In Russian).
35. Dreval', V. E.; Borisenkova, E. K. Rheol Acta 1993, 32, 337.
36. Suetsugu, Y.; White, J. L. J Appl Polym Sci 1983, 28, 1481.
37. Vinogradov, G. V.; Malkin, A. Ya.; Plotnikova, E. P.; Sabsai, O. Yu.; Nikolaeva, N. E. Intern J Polym Mater 1972, 2, 1.
38. Chae, D. W.; Kim, B. C. Compos Sci Technol 2007, 67, 1348.
39. Vlasveld, D. P. N.; de Jong, M.; Bersee, H. E. N.; Gotsis, A. D.; Picken, S. J Polym 2005, 46, 10279.
40. Malkin, A. Ya. Adv Polym Sci 1990, 96, 69.
41. Gupta, R. K.; Pasanovic-Zujo, V.; Bhattacharya, S. N. J Non-Newtonian Fluid Mech 2005, 128, 116.
42. Onogi, S.; Asada, T. In Rheology; Astarita, G., Marrucci, G., Nicolais, L., Eds.; Plenum Press: New York, 1980, 122.
43. Tolstykh, M. Yu.; Makarova, V. V.; Vasilyev, G. B.; Kulichikhin, V. G. In Proceeding of VII International Conference "Lyotropic Liquid Crystals and Nanomaterials;" Ivanovo State University Publishing House: Ivanovo, Russia, 2009; p 156.
44. Kulichikhin, V. G.; Shumskii, V. F.; Semakov, A. V. In Rheology and Processing of Liquid Crystal Polymers; Acierno, D., Collyer, A. A., Eds.; Chapman & Hall: London, New York, 1996; Chapter 5.
45. Fujiyama, M. J Appl Polym Sci 1990, 40, 67.

46. Lee, K. M.; Han, C. D. Macromolecules 2003, 36, 8796.
47. Malkin, A. Ya.; Isayev, A. I. Rheology. Conceptions, Methods and Applications; ChemTec: Toronto, 2006,; Chapter 3.
48. Driscoll, P.; Masuda, T.; Fujiwara, K. Macromolecules 1991, 24, 1567.
49. Wewerka, A.; Floudas, G.; Pakula, T.; Stelzer, F. Macromolecules 2001, 34, 8129.
50. Colby, R. H.; Ober, C. K.; Gillmor, J. R.; Connelly, R. W.; Duong, T.; Galfi, G.; Laus, M. Rheol Acta 1997, 36, 498.
51. Gillmor, J. R.; Colby, R. H.; Hall, E.; Ober, C. K. J Rheol 1994, 38, 1623.
52. Wewerka, A.; Viertler, K.; Vlassopoulos, D.; Stelzer, F. Rheol Acta 2001, 40, 416.
53. Vinogradov, G. V.; Malkin, A. Ya. Rheology of Polymers; Mir: Moscow, 1983; Chapter 3.
54. Tanoue, S.; Utracki, L. A.; Garcia-Rejon, A.; Sammut, P.; Ton-That, M. -T.; Pesneau, I.; Kamal, M. R.; Lyngaae-Jørgansen, J. Polym Eng Sci 2004, 44, 1061.