

# Phase State and Rheology of Organosilicon Nanocomposites with Functionalized Hyperbranched Nanoparticles

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**Abstract**—The phase equilibrium in a system of linear polydimethylsiloxane–functionalized nanoparticles 1.2–2.2 nm in size with a core made of hyperbranched silica and a periphery of decyl groups has been studied by laser interferometry method. Phase diagrams of the studied systems fit the amorphous phase equilibrium with UCST increasing with the nanoparticle size. The mixtures present nanoparticle solutions in the linear polymer or emulsions of a saturated solution of one component in a saturated solution of other component depending on the components ratio. Dilute, concentrated, or highly concentrated dispersions show individual features of the rheological behavior. For each colloid chemical and phase states of mixtures, the viscosity and viscoelastic properties have been investigated in a wide temperature range. The obtained results have been compared with the previous data for mixtures of decylated nanoparticles and polyisobutylene.

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## INTRODUCTION

The grafting of functional groups to the particle surface must allow one to improve their dispersity (i.e., to reduce the agglomeration) in the polymer medium and, as a result of the enhanced chemical affinity of components, in order to obtain a composite material with a new [1–6] or an improved complex of properties [1, 7–11]. In this case, one should bear in mind that both the surface modification of nanoparticles and their small size may be responsible for the unusual behavior of liquid and solid blends. Nanoparticles may act both as solid fillers and plasticizers [12] and can be considered as core–shell objects with peripheral functional groups soluble in polymer forming the interfacial layer of composite. Moreover, for small nanoparticles (on the order of nanometers), the controversial question arises of whether elementary nanoparticles distributed in the medium form of a heterogeneous dispersion or a true solution?

A priori, it can be suggested that the transition from macromolecular to solid particles behavior of nanoparticles can be realized, not only through changes in their size, but via variations in the concentration in the medium or in environmental conditions, e.g., temperature. Thus, to predict nanocomposite characteristics, the understanding of the phase equilibrium between components, which immediately affects their rheological behavior, acquires a special importance [13–20]. It follows from this that rheology

is a sensitive method that allows one to trace the phase transitions and special features of the thermodynamic state of the necessary systems needed to choose their processing methods in order to obtain materials [21].

In our previous work, the phase diagrams were obtained and the rheological behavior of model blends of polyisobutylene (PIB) with nanoparticles of hyperbranched silica coated by grafted and complementary to polymer decyl groups were studied [22]. Due to the low molecular mass and the presence of grafted non-polar groups, the array of nanoparticles demonstrated the properties of viscoelastic liquids soluble in the polymer under specific conditions. The phase state of composites was characterized by the amorphous equilibrium with the UCST. The mutual solubility of components was decreased with growing of their molecular masses and was dependent on the applied mechanical field. The phase state of the above blends determined the rheological properties of nanocomposites, which can behave as Newtonian or pseudoplastic liquids according to the composite morphology.

This work continues the aforementioned cycle of investigations with the aim of accumulating data on the phase equilibrium and rheological properties of macromolecule–particles and linear macromolecules blends according to the chemical affinity of components, their molecular masses, and temperature. For this purpose, decylated silica nanoparticles studied previously in the blends with PIB will be considered in

Characteristics of studied nanoparticles

Nanoparticles	$M \times 10^{-3}$	Diameter, nm	$\eta_{20^\circ\text{C}}$ , Pa s	$n_{25^\circ\text{C}}$
S1	1.5	1.2	0.037	1.4455
S2	3.0	1.6	0.28	1.4500
S3	8.0	2.2	55.0	1.4585

blends with polydimethylsiloxane characterized by the chemical structure similar to the nanoparticle core.

## EXPERIMENTAL

Nanoparticles were prepared via the following stages: the synthesis of hyperbranched polyethoxysilane [23] and the substitution of ethoxy groups for dimethylhydridesilyl groups, followed by their hydrosilylation with 1-decene [22]. Thus, the surfaces of the obtained silica nanoparticles were enriched with grafted *n*-decyl groups. Their consistencies were liquids and, hence, in the literature, they are frequently called *silicasols* [12]. Three fractions of nanoparticles were prepared, the characteristics of which are discussed in detail in [22] and shown in the table.

For blends with nanoparticles, polydimethylsiloxane (PDMS) SKTN E (Penta-91, Russia,  $M_n = 72.2 \times 10^3$ , polydispersity index of 1.7, and refractive index  $n_{25^\circ\text{C}} = 1.406$ ) was used. The viscosity of PDMS was as high as 89 Pa s at 20°C. Compositions with nanoparticles were prepared by the mechanical mixing of components at 100°C for no less than 24 h. Blends containing 5, 10, 15, 20, 30, and 40 wt % particle fraction S1 were obtained. Because of the small amount of synthesized nanoparticles, a blend with the maximum desired content of particles was prepared first and after testing, it was diluted by polymer for further experiments.

The blends were transparent colorless liquids or white low-viscosity and turbid resin-like dispersions depending on the component ratio and temperature. The phase equilibrium of nanoparticles–linear polymer systems was studied by laser interferometry technique at 20–280°C following the evolution of the interference bands in the diffusion zone; helium–neon laser with wavelength of 632.8 nm was used as a light source. The diffusion cell formation and experiments were performed via the procedure described previously [24, 25], and the interference pattern was recorded with a MYscope 500M digital video camera. The temperature of experiments was changed by steps with a delay of no less than 30 min at each step. To confirm the equilibrium and reversible character of the resulting boundary concentrations, the measurements were carried out in both the modes of rising and decreasing temperature.

The compositions were studied on a Physica MCR 301 rotary rheometer (Anton Paar, Austria) with the

cone–plane geometry of the working unit. The rheological measurements were carried out in two modes, i.e., at steady shear with an increase in the shear rate by steps to obtain the flow curves and at small amplitude oscillatory shear in order to determine the viscoelastic characteristics. The temperature dependences were recorded at a heating rate of 5 K/min.

## RESULTS AND DISCUSSION

Upon the contact of the medium of nanoparticles with silicone, the initial linear interference bands near the interface are distorted as a result of a change in the refractive index due to interdiffusion of components (Fig. 1a). In the PDMS zone, the distortion was much more pronounced, which suggests a higher solubility of particles in the polymer than that of polymer in the particle medium. The interface only disappears upon heating the blends above 260°C. Thus, the solubility of the polymer and nanoparticles in each other is limited and their mutual solubility improves with temperature, i.e., the nanocomposite is characteristic of the amorphous equilibrium with the UCST.

The solubility of particles in the polymer medium is presumably determined by both the presence of peripheral relatively long decyl groups that interact with the neighbor macromolecules and by a gain in entropy due to the distribution of particles in the liquid medium. Since the nanoparticle size of the order of 1–2 nm (Table) corresponds to the arbitrary boundary between colloid dispersions and true solutions, the questions of whether these nanoparticles can be considered to be fully soluble as a whole or is the solubility solely a property of their peripheral groups remain open.

The increase in the particle size is accompanied by a smaller distortion of bands in the contact zone (Fig. 1b), which is indicative of the poorer solubility of coarser particles. Nevertheless, their solubility is beyond question, as the cooling of cell results in the amorphous phase separation well pronounced in the zone saturated with polymer (Fig. 1c).

The known refractive indexes of diffusing components and the interference band profiles, which are essentially of a concentration type, allow one to construct phase diagrams of nanocomposites (Fig. 2). Diagrams characteristic of the UCST are qualitatively similar to the diagrams obtained for blends of these particles with PIB [22]. The quantitative distinction is a lower UCST for the composites with PIB due to the better affinity of grafted decyl groups to the hydrocarbon chain. Thus, the substitution of the hydrocarbon matrix for siloxane one deteriorates the mutual solubility of polymer medium and functionalized nanoparticles.

An analysis of the rheological demonstration of the phase state of nanocomposites will be carried out for a system with the best miscibility of components. The

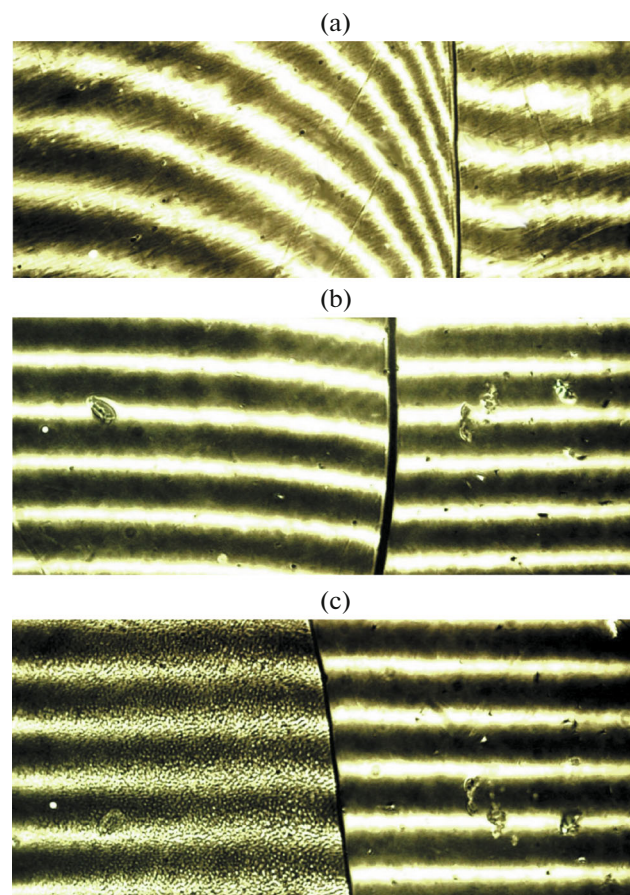
maximum content of particles S1 distributed in the PDMS medium was as high as 40 wt %, which is comparable with 40 vol % because of the close densities of the organosilicon polymer and nanoparticles. The attempt to introduce a higher content of particles into the polymer medium results in an instable dispersion that separates into the initial components upon the completion of stirring.

The flow curves obtained at three temperatures demonstrate a variety of the rheological behavior of blends (Fig. 3). Nanoparticles S1 hardly dissolve PDMS and have a viscosity that is three orders lower than the viscosity of PDMS. Thus, the reduction in the viscosity with an increasing content of nanoparticles in the series of systems with 20–40% concentrations studied at 20°C, which are heterogeneous according to the phase diagrams, may suggest with a high probability that the nanoparticles present true dispersion medium.

The composition with 5% particles is similar to PDMS with almost constant viscosity independently of temperature (Fig. 3, curves 1; curves for PDMS are not shown because of overlapping). The blend with 10% particles at 20°C in contrast to the above mentioned blend exhibited non-Newtonian behavior with a sharp reversible drop of viscosity at a shear stress of approximately 600 Pa that was apparently due to the change in the shape of dispersed drops S1. As the temperature increased to 100°C, the milky white sample became transparent, with a Newtonian flow curve and viscosity below the values for PDMS or 5% composite.

Sample with 15% nanoparticles demonstrated varied behavior depending on the history (Fig. 3, curves 3 and 3'). Upon long-term storage at room temperature for several days, the sample became resin-like with very high viscosity, which remained constant up to stress of the order of 30 kPa (Fig. 3a, curve 3). The reduction in viscosity with increasing stress was limited and accompanied by the disruption of the sample's continuity.

On the temperature increase up to 100 or 200°C, the viscosity of this composition reduced by three orders, which was in contrast to the behavior of samples with a greater number of particles. Similar to the 15% blend, the samples with 20 and 30% S1 had a high viscosity at 20°C, which decreased sharply at the approximately equal stresses (Fig. 3a, curves 4 and 5). In the concentration series from three samples, the system viscosity increased as the nanoparticle fraction diminished. Thus, it can be concluded that the viscosity in the series of dispersions enhanced due to the increasing fraction of disperse phase consisted of polymer drops. In this case the drops of disperse phase represent a saturated solution of PDMS in nanoparticles. For example, according to the phase diagram (Fig. 2), at 100°C, only about 10% of the nanoparticles were soluble in PDMS. Thus, under these conditions, the sample with a total content of particles as high as 30%

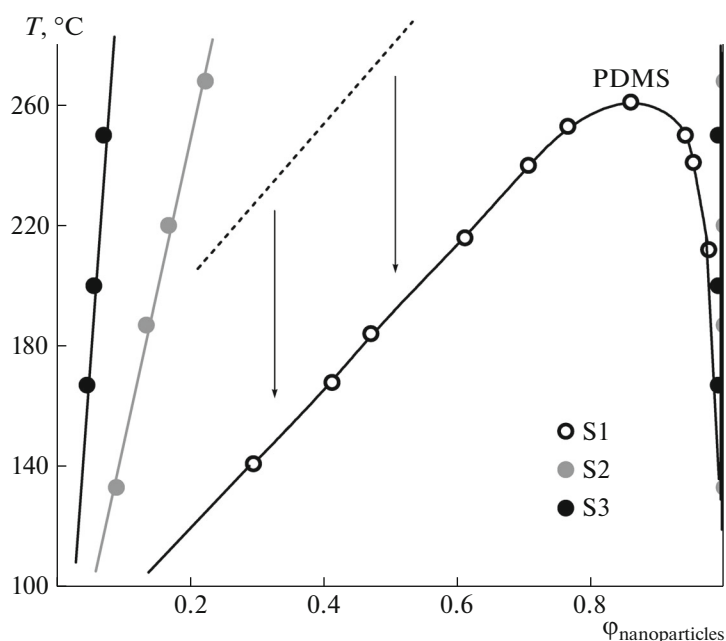


**Fig. 1.** (Color online) Interference pattern in the contact zone of PDMS (left) and nanoparticles S1 (right) at (a) 240°C, (b) S2 at 190°C, as well as (c) S2 at 25°C after the preliminary heating up to 250°C. The width of microphotograph corresponds to 1 mm diffusion zone.

will be a 73% ( $100\% - 30\% \times 0.9$ ) dispersion of 10% solutions of nanoparticles in PDMS emulsified in the nanoparticles medium (in which, based on the data of Fig. 2, PDMS is almost insoluble).

Upon an increase in temperature to 100°C, the samples with 20 and 30% particles retained a high viscosity and, at 200°C, became even incapable of flow at low shear stresses; their flow curves were transformed up to the appearance of the yield point (Fig. 3c, curves 4 and 5). In contrast, the viscosity of 15% system at high temperatures was lower than the viscosity of more concentrated systems; furthermore, became low at 20°C and retained this value in the case of temperature pretreatment.

The above-mentioned phenomena can apparently be explained by the enhancement of the mutual solubility of components with temperature. As a result, the content of dispersion medium, which consists of nanoparticles with a negligibly small amount of dissolved polymer and is present in the lower content compared to that of disperse phase, becomes less and



**Fig. 2.** Phase diagrams for compositions of decylated nanoparticles and PDMS. Shift in binodal relative to true position is shown by dotted line and arrows. See text.

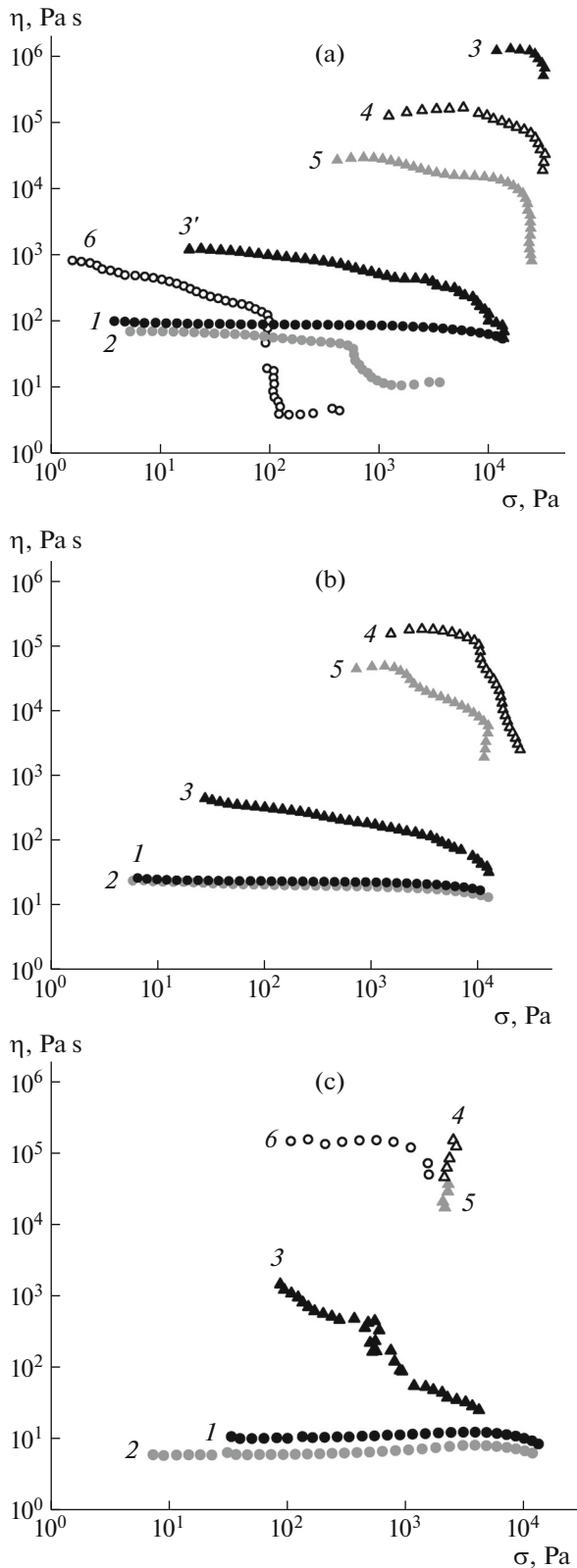
less as temperature increases. Thus, the volume fraction of disperse phase grows with temperature and the emulsions become highly concentrated, with the loss of fluidity of 20 and 30% samples. At 20°C, for example, the solubility of nanoparticles in PDMS is of the order of 5% (by the rheology data, see below) and, at 200°C, according to the phase diagram, even 55% nanoparticles are dissolved in polymer. The sample with 20% S1 at 20°C consists of 81% ( $100\% - 20\% \times 0.95$ ) emulsion and, at 200°C, even 91% ( $100\% - 20\% \times 0.45$ ) emulsion. For 15% sample, even the phase inversion takes place and the dispersion medium changes from the saturated solution of polymer in nanoparticles for the saturated solution of nanoparticles in PDMS.

The aforementioned behavior of samples does not correspond to the phase diagram (Fig. 2), which suggests that, at 200°C, these samples must be homogeneous. This discrepancy can be explained by the idealization of the diagram typical of monodisperse components. Actually, the phase diagram should be presented by multiple binodals, which in this case were averaged by the experimental method of obtaining the interference patterns. The recording of diffusion at the specified wavelength gives the experimental criterion for classifying the systems as homogeneous or heterogeneous. The system will be considered to be arbitrarily homogeneous, if the disperse phase particle size will be below the half-wavelength of the laser used in the unit, i.e., below ~300 nm. As a result, the binodals with the UCST will be shifted to lower temperatures. By the rheological data, the shift can be no less than 80°C (shown by arrows in Fig. 2).

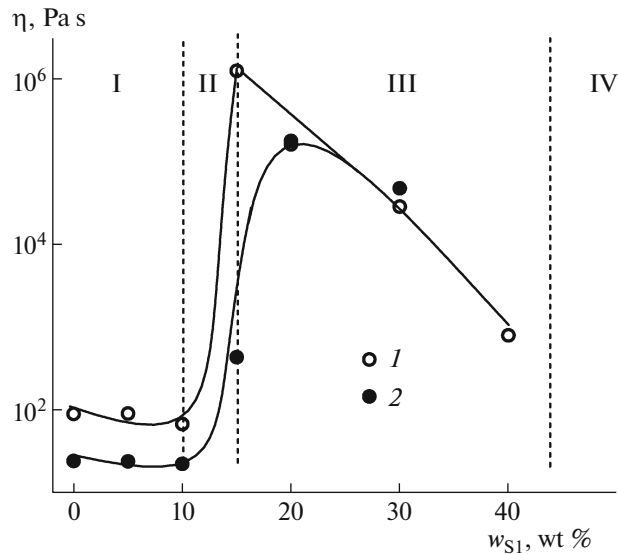
In a 15% composition, if the saturated solution of nanoparticles in PDMS becomes the dispersion medium, the viscosity of this sample is higher by an order of magnitude than the viscosity of a 10% sample with the same dispersion medium and it decreases in a smoother manner with the shear stress (Fig. 3a, curves 2 and 3'). Therefore, at a content of nanoparticles increased by 5%, the dispersion becomes much more concentrated and its viscosity can decrease with shear stress not only due to the extension of drops in flow, but as a result of breaking of coagulation contacts between them. In any case, the disruption of the dispersion structure is reversible and, after the cessation of deformation, they return to the initial state.

The flow curve of the most concentrated 40% sample at 20°C is similar to the curve for a sample with 10% particles; the smooth decrease in viscosity at low stresses and a jumpy drop of viscosity at ~100 Pa (Fig. 3a, curves 2 and 6). It is evident that, at the first stage, the shape of drops oriented in flow is changed and, above this stress, the disruption of coagulation contacts (or generally the physicochemical interaction) between drops takes place. Thus, the change in the dispersion medium enriched with polymer for the medium saturated by nanoparticles does not result in radical variations in the rheological behavior of dispersions.

On heating to 200°C, the viscosity of a 40% sample increases as for other emulsions, probably due to enhanced energy of interaction between drops. However, unlike systems with 20 and 30% particles, which do not flow at low stresses, the 40% composition



**Fig. 3.** Flow curves at (a) 20, (b) 100, and (c) 200°C for PDMS with (1) 5, (2) 10, (3, 3') 15, (4) 20, (5) 30, and (6) 40 wt % S1. Sample with 15% particles was tested (3) without temperature history and (3') after preliminary heating up to 200°C.



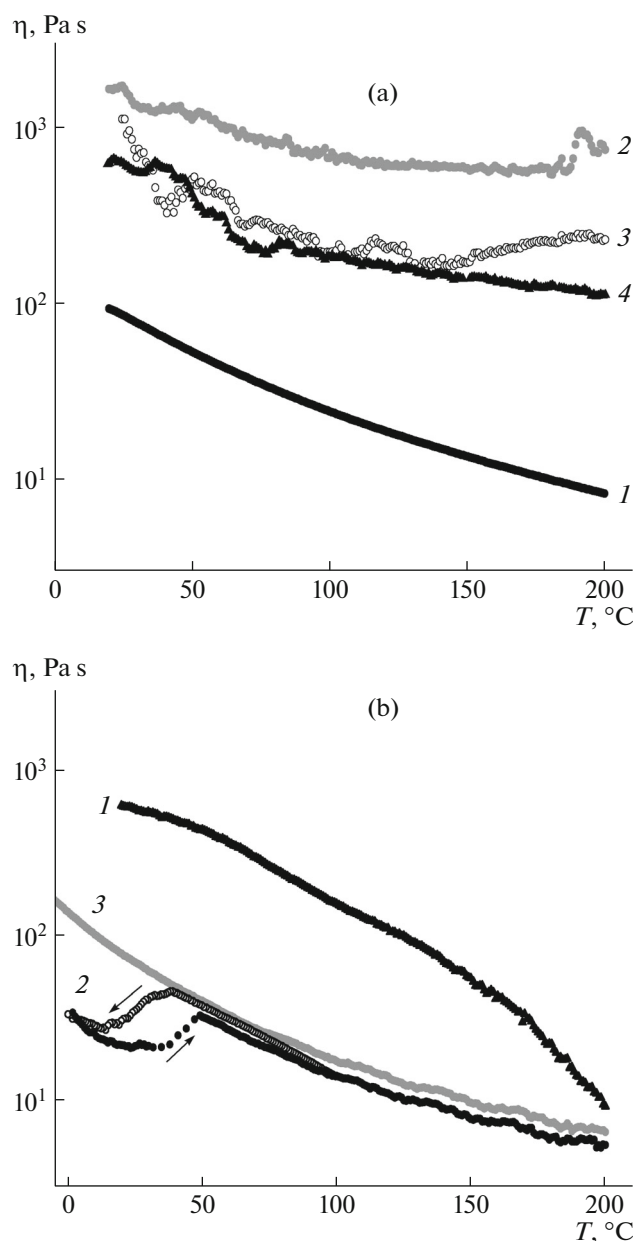
**Fig. 4.** Concentration dependencies of zero shear viscosity at (1) 20 and (2) 100°C for PDMS and S1 blends. (I) Zone of S1 solution in PDMS, (II) zone of emulsion S1 in PDMS, (III) zone of emulsion PDMS in S1, and (IV) zone of immiscibility of components.

exhibits the region of maximum Newtonian viscosity, presumably due to the smaller fraction of disperse phase.

Figure 4 shows the generalized data on the phase state of compositions by their viscosity characteristics. At low contents of particles, they are dissolved in PDMS almost without changes in its viscosity. At a particle content of 10–15%, they form drops of disperse phase (with negligibly small concentration of PDMS) in the PDMS medium with approximately 10% dissolved nanoparticles. The viscosity of these emulsions with low contents of disperse phase enhances the viscosity of the composition as a whole by no more than an order of magnitude.

At particle contents above 15%, dispersions are formed that contain drops of nanoparticle solution in polymer distributed in the medium of nanoparticles almost free of polymer. The concentration phase inversion in dispersions seems to be due to a lower viscosity of the array of nanoparticles compared to PDMS, and the temperature phase inversion is explained by the approaching viscosity values for nanoparticles and polymer on heating as well as by the reduced fraction of nanoparticles not dissolved in polymer.

The failure to prepare systems with concentrations of particles that exceed 40% can be explained by a low fraction of emulsifying PDMS and a low viscosity of particles S1. In other words, the high viscosity of disperse phase due to its coagulation in the concentrated 15–40% systems enhances its sedimentation stability and prevents the macroscopic phase separa-



**Fig. 5.** Temperature dependences of effective viscosity. (a) (1) PDMS, (2–4) PDMS with (2) 30, (3) 20, and (4) 15 wt % S1; (b) PDMS with (1) 40, (2) 10, and (3) 5 wt % S1. Shear rate was equal to  $10 \text{ s}^{-1}$  except for the system with 10% S1 measured at shear rate of  $100 \text{ s}^{-1}$ . Arrows show the direction of temperature change.

tion. The viscosity of concentrated emulsions is determined by the contacts between drops, which do not disappear with temperature changes. Thus, the viscosity of heterogeneous compositions is weakly dependent on temperature unlike, for example, PDMS (Fig. 5a). The wide scatter of the experimental points for emulsions is due to the high shear rates both as a result of the instable layer-by-layer flow of the con-

centrated colloid systems characterized by yield stress [26] and due to the slip of emulsion over the surface of the measuring unit [27].

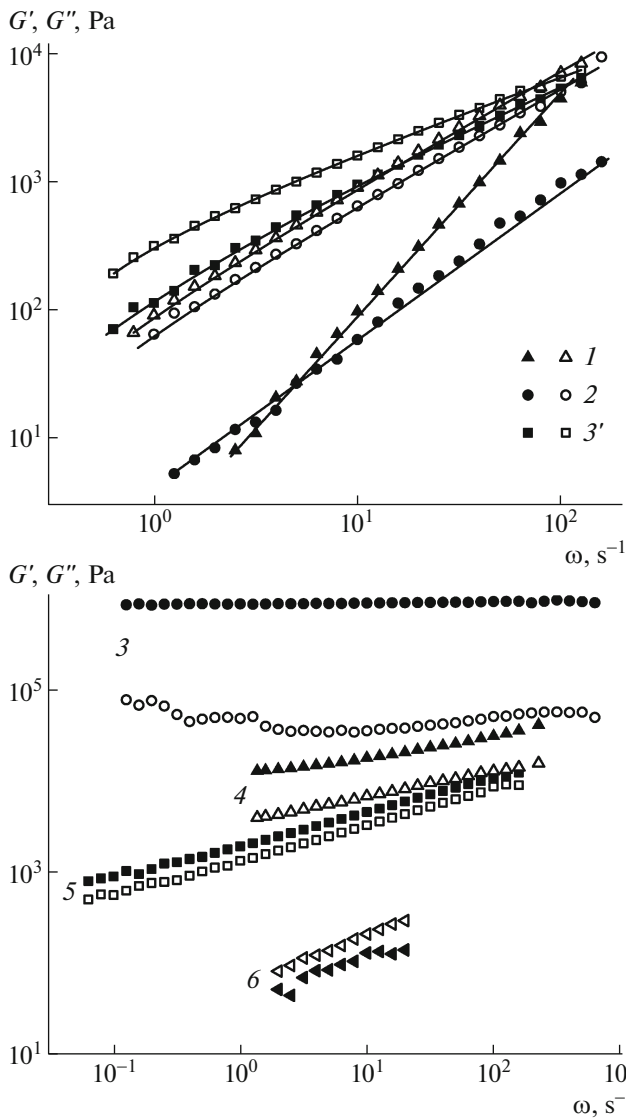
In samples with 15% nanoparticles, two characteristic zones may be distinguished: the zone of unsteady flow in the low-temperature region and the zone of smooth decrease of viscosity on the sample heating above  $80^\circ\text{C}$ . It is evident that the transition is related to the phase inversion and the transformation of composition into a less concentrated emulsion according to the flow curves of the system (Fig. 3, curves 3). In other words, the dispersion is a living system with variations in the composition and morphology along the temperature scale.

The samples with the contents of particles not suitable for the formation of concentrated emulsions are characteristic of different behaviors (Fig. 5b). The viscosity of the composition with the maximum particle content (40%) decreases with an increase in temperature that approaches the viscosity of PDMS. According to the phase diagram, the homogenization of the above blend must occur at a temperature in the vicinity of  $170^\circ\text{C}$ . Thus, as temperature rises, the volume content of drops in the medium decreases due to their dissolution, which reduces the composition viscosity. In the region of  $170^\circ\text{C}$ , the plot of the temperature dependence of viscosity shows a pronounced inflection, and the smooth curve pattern may be due to the polydispersity of both components.

The well-defined phase transition exhibits a composition with a low particle content (10%). Its viscosity changes in the temperature range of  $25\text{--}50^\circ\text{C}$ , which is clearly pronounced upon testing a sample with the intensive deformation due to the lower viscosity of emulsions with deformed drops compared to homogeneous samples (Fig. 3, curves 1 and 2). This seems to be explained by the dissolution of emulsified drops S1 in PDMS, which is confirmed by the visual recording of the sample turbidity.

The composition with 5% nanoparticles shows the optical transparency and the temperature dependence of viscosity similar to that for PDMS. As the viscosity of even dilute emulsions must be higher than the viscosity of medium, the viscosity of the system with 5% particles proved to be equal to the PDMS viscosity within the measurement error, and the gain in the particle content by further 5% results in a decrease in viscosity (Fig. 5b, curves 2 and 3). In this case, nanoparticles act as solvent for PDMS and the above-mentioned composition is homogeneous.

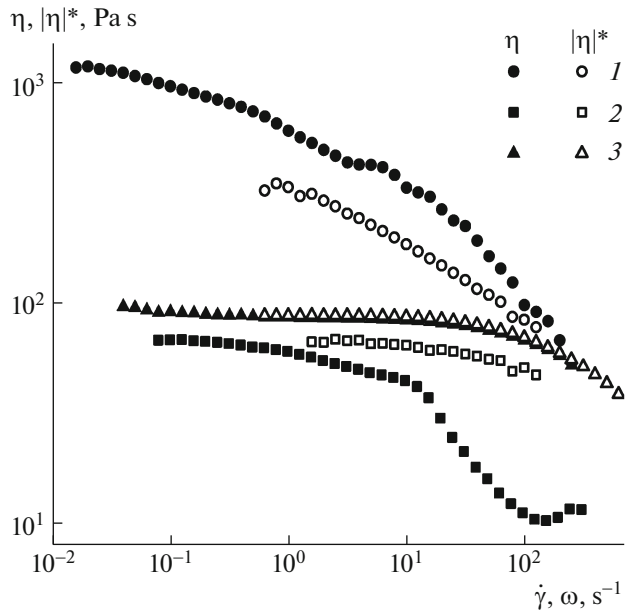
The phase state of samples affects their viscoelastic properties. Elastic and loss moduli of concentrated emulsions increase in the same manner as the deformation frequency grows (Fig. 6a). The absolute moduli and the ratio between the elastic and loss moduli enhance with the disperse phase fraction, whereas the tangent of the slope angle of the plot of elastic modulus logarithm versus frequency logarithm decreases.



**Fig. 6.** Frequency dependences of elastic modulus (dark circles) and loss modulus (open circles) for PDMS with (1) 5, (2) 10, (3, 3') 15, (4) 20, (5) 30, and (6) 40 wt % S1 at 20°C. Sample with 15% particles was tested without temperature history (3) and after preliminary heating up to 200°C (3').

Thus, as the concentration of disperse phase grows, the emulsions become more and more similar to solids [28, 29] like the sample with 15% particles, which consists of a highly concentrated emulsion with a disperse phase content of no less than 86% (100%–15% × 0.95).

The same 15% sample after the temperature pretreatment and phase inversion became a moderately concentrated emulsion with the dynamic modulus lower by three orders compared to the modulus of its solid-like alternative. The loss modulus of the composition exceeded the elastic modulus throughout the entire frequency range under investigation and, thus,



**Fig. 7.** Shear (dark circles) and complex (open circles) viscosity vs. shear rate and angular frequency, respectively, for PDMS with (1) 15, (2) 10, and (3) 5% S1.

this composition is similar to other systems with lower nanoparticle contents (Fig. 6b).

However, there are some peculiarities that distinguish these emulsions from true homogeneous samples. The tangent of the slope angle of the plot of the logarithmic frequency dependence of elastic modulus of homogeneous solution agrees with the tangent for PDMS equal to 2.0. For emulsions with 10 and 15% particles, the tangent values are significantly lower and are equal to 1.2 and 1.0, respectively. The 2.0 value is conform to the generalized Maxwell model true for solutions and melts of noncrosslinked polymers and the deviation from 2.0 suggests that it is not only the relaxation mobility of macromolecules that is responsible for the elasticity of 10–15% samples.

The second peculiarity is related to the fulfillment of the Cox–Mertz rule, i.e., the coincidence of the steady and dynamic viscosities for the homogeneous samples which is absent for colloid samples (Fig. 7). Both of the latter facts suggest that, in the emulsion samples, not only the polymer nature of the dispersion medium, but also the discrete elements of disperse phase are responsible for the elasticity of system [30, 31].

The additional elasticity of dilute emulsions may be related to the elasticity of drops owing to interfacial tension, and, in concentrated emulsions, the elasticity of coagulation contacts may be added. Note that the complex viscosity is higher than the shear viscosity for dilute emulsion and is lower for the concentrated emulsion. The decrease in viscosity on the shear of the dilute emulsion is due to a change in the shape of

drops, whereas, at low-amplitude dynamic shear, their shape remains unchanged and, as a result, the complex viscosity proves to be higher. For the concentrated emulsion, the low-amplitude dynamic shear does not result in the disruption of structure, which is responsible for the additional resistance at flow and enhances the shear viscosity compared to the dynamic viscosity.

## CONCLUSIONS

Hyperbranched silica nanoparticles with grafted decyl groups show limited solubility in the organosilicon medium. The phase equilibrium is characteristic of the UCST, which increases with the molecular mass of particles. Thus, the behavior of decylated nanoparticles in the PDMS medium is similar to their behavior in the PIB medium distinguishing in the lower UCST value for nanoparticles in the medium of PIB complementary to the grafted groups.

Despite that the rheometry is not a direct structural or thermodynamic method of investigation, the study of the rheological properties of the compositions allows one to significantly extend the understanding of the phase state of systems by adding colloid chemical details. As the content of nanoparticles in the PDMS medium increases, the system is successively transferred from a dilute solution of nanoparticles in polymer to their dilute and concentrated emulsion and passes through the phase inversion to the highly concentrated emulsions of swelled polymer in the particles medium. The dilution of highly concentrated emulsion by nanoparticles is only possible in a limited range and on the transition to dilute emulsions of swelled polymers the system becomes kinetically unstable with the macroscopic phase separation.

The dissolved nanoparticles do not change the viscosity of PDMS and the viscosity of nanoparticle emulsions is somewhat higher than the polymer viscosity. In contrast, the emulsions of swelled polymer drops in the nanoparticle medium show great viscosities and behave like gels at a content of the disperse phase on the order of 90%.

The following distinctions in the rheological behavior of decylated nanoparticles in the organosilicon polymer medium compared to their behavior in the PIB medium can be observed. First, no effect of the mechanical field on the phase equilibrium of nanocomposites in the PDMS medium was fixed presumably because of the poor affinity of decylated groups to PDMS and, as a result, a lower entropy component of the total energy of nanocomposite. Second, in the PIB medium, concentrated emulsions were not obtained, probably due to the higher mutual solubility of decylated nanoparticles and hydrocarbon polymer.

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