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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Rheological Characteristics and Relaxation Properties of Polymer–Nanodiamond Composites

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Abstract—The effect of modifying additives of nanodispersed substances on rheological and relaxation properties of composite materials based on polydimethylsiloxane was examined. The effect of modifying additives on relaxation properties of polymeric composite materials was considered within the framework of elastic strain theory using the Mooney–Rivlin model.

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The development of composite materials modified with nanosized substances is a promising way to enhance the strength parameters of polymeric materials. However, the available experimental data are very contradictory, and some authors cast doubt on the prospects of this field of polymeric materials science [1].

The goal of our study was to compare the properties of composite materials filled with finely dispersed substances of different origins. Our work is based on Rebinder's studies [2] where it was shown that not all finely dispersed substances cause structurization of polymer solution, as judged from differences in the rheological parameters of the corresponding solutions.

We intended to find experimental criteria for differentiation between finely dispersed and nanostructured substances. Presumably, such a criterion is associated with fine morphological features of the particles. This difference can be revealed most clearly by comparing the surface energies.

EXPERIMENTAL

As finely dispersed modifiers we chose well-studied substances with the particle size in the nanometer range: nanocarbon from detonation synthesis (DND), finely dispersed silica (A-300, Degussa), and fullerene C_{60}. As a relatively coarse filler we chose Plazmas glass microspheres of size 1–3 μm.

The surface energy was calculated by the procedure suggested in [3]. This procedure is based on inverse gas chromatography (IGC) as applied to studies of interphase interactions and allows calculation of the surface energies for finely dispersed substances distributed in a polymeric matrix.

The calculation of thermodynamic quantities in the IGC method is based on the experimentally determined specific retention volumes V_g^0:

$$V_g^0 = K_L\nu_L + K_L\left[-(K_e/2) + (K_e/2)\frac{1 + N_0/(c_n^0 + K_eK'h)}{\left(1 + \dfrac{4K_eK'hN_0)}{(c_n^0 + K_eK'h)^2}\right)^{1/2}}\right]S_A, \quad (1)$$

where N_0 is the concentration of adsorbed segments of the dispersion medium on the surface of domains (mol cm^{-1}); c_n^0, concentration of segments of the dispersion medium in the interphase layer (mol cm^{-3}); h, peak height (mm); K', detector sensitivity (mol cm^{-3} mm^{-1}); S_A, surface area of domains of the hard phase in 1 cm^3 of the dispersion medium; $K_L\nu_L$, contribution from sorbate dissolution in the dispersion medium; ν_L, specific volume of the dispersion medium; K_L, sorbate distribution coefficient characterizing the dissolution process; and K_e, constant of the adsorption equilibrium for the general case of a polymeric microheterogeneous system.

Analysis of (1) shows that, in the limiting cases of $h \to \infty$ and $h \to 0$, V_g^0 is independent of the sample size. For example, at $h \to \infty$,

$$(V_g^0)_{h\to\infty} = K_L v_L = L, \quad (2)$$

and with infinitely small samples ($h \to 0$),

$$(V_g^0)_{h\to 0} = K_L v_L + K_L K_e (N_0/c_n^0) S_A. \quad (3)$$

It follows from (3) that $K_A = K_L K_e N_0/c_n^0$, the adsorption equilibrium constant, depends on the concentration ratio of adsorbed segments of the dispersion medium on the domain surface (N_0) and in the interphase layer (c_n^0).

Consider the case of an inorganic nanodispersed filler. It is natural to assume in this case that $N_0/c_n^0 = 1$. Then expression (3) will be simplified to

$$(V_g^0)_{h\to 0} = K_L v_L + K_L K_e S_A. \quad (4)$$

The adsorption contribution is calculated as

$$A = K_A S_A = V_g^0 - (V_g^0)_{h\to\infty}. \quad (5)$$

If it is experimentally possible to reach the level of sorbate concentration (sample size) at which V_g^0 is independent of the sample size, the data of inverse gas chromatography can be principally used for calculation of the partial contributions of dissolution and adsorption.

Within the framework of our problem, it is also important to calculate the surface tension of hard block domains. Being guided by the assumption that the London term of the work of adhesion W_A is identical to the Gibbs free energy of desorption from the unit surface of the methylene group of a molecular sample, we have

$$W = \Delta G[A(CH_2)]/N_A a(CH_2), \quad (6)$$

where N_A is the Avogadro number and $a(CH_2)$ is the area occupied by the methylene group on the adsorbent surface.

The Gibbs free energy per mole of methylene groups can be calculated by the equation

$$\Delta G[A(CH_2)] = -RT \ln \frac{V_R^{n+1}}{V^n}, \quad (7)$$

where R is the gas constant; T, temperature; V_R^{n+1} and V^n, retention volumes for n-alkanes with $(n + 1)$ and n carbon atoms, respectively.

With n-alkanes taken as sorbates, only nonpolar forces contribute to $\Delta G^0[A(CH_2)]$ Hence, this quantity corresponds to the work of adhesion between a nonpolar liquid and a solid surface.

The work of adhesion is described by the well-known Fowkes relationship

$$W_A\, 2\,(\gamma_1 \gamma_2^L)^{1/2}, \quad (8)$$

where γ_1 is the surface tension of the nonpolar liquid and γ_2^L, London term of the surface tension of the second component.

Combination of Eqs. (6) and (8) gives an expression for calculating γ_2^L:

$$\Delta G[A(CH_2)]/Na(CH_2) = 2(\gamma_{CH2}\gamma^L)^{1/2}. \quad (9)$$

The viscosity of polymeric nanocomposites based on grade A polydimethylsiloxane (number-average molecular weight 30000 Da) was determined by the standard procedure with a Hoeppler rotary viscometer.

The calculated surface energies γ^L of aggregates of particles of finely dispersed substances at T = 49.4°C are given below:

Substance	SiO_2	DND	Fullerene C_{60}
γ^L, mN m^{-2}	30.6	22.1	27.4

It can be seen that the surface energies are relatively low. To compare, for polymer in the glassy state they are in the range 40–50 mN m^{-2} [4]. The value obtained for the surface energy of finely dispersed silica is close to the published value, 26.3 mN m^{-2} [5]. The low surface energies of the finely dispersed clusters under consideration are consistent with the trend predicted by the theory of nanocrystals: decrease in the surface energy with increasing dispersity. Thus, Aerosil can be considered as a finely dispersed, rather than nanostructured, substance, and polymeric composites filled with Aerosil will hardly exhibit any unusual properties. This conclusion coincides with the conclusions made previously in analysis of the effect of modifying additives of finely dispersed substances on the set of elastic and strength parameters [6].

To examine the effect of modifying additives of nanodispersed substances on rheological parameters of composite materials, we took polydimethylsiloxane (PDMS) modified with appropriate amounts of nanomodifiers. The results are shown in Figs. 1a and 1b.

As seen from Fig. 1a, addition of a minimal amount of DND (0.005 wt %) leads to a decrease in the viscosity by approximately 20%. The subsequent increase in the DND concentration leads to an increase in the viscosity to the initial level. A different pattern is observed in modification of PDMS with fullerene

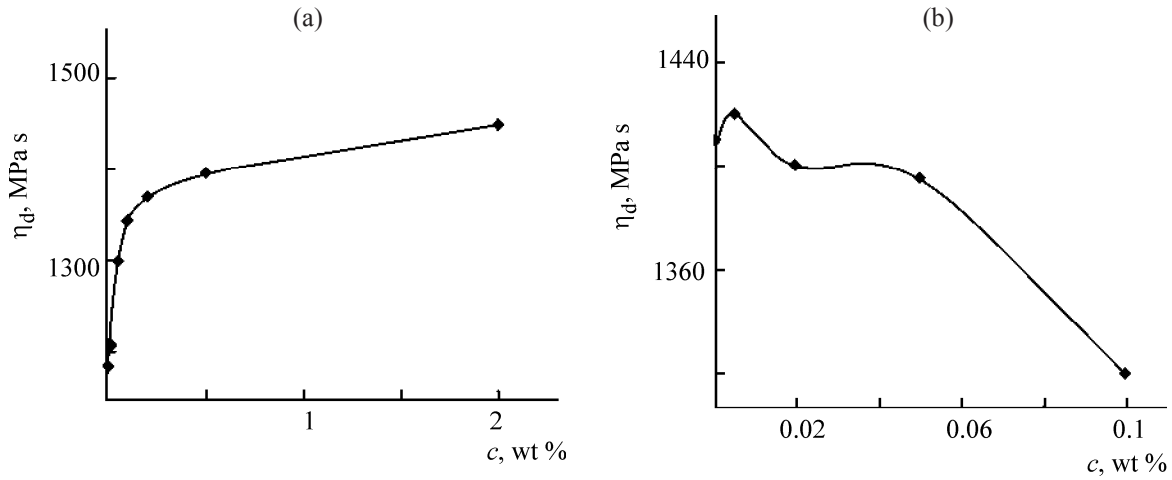

Fig. 1. Dynamic viscosity η_d of siloxane nanocomposites as a function of the concentration c of modifying additive: (a) DND and (b) fullerene C_{60}.

C_{60} (Fig. 1b). With an increase in the C_{60} concentration, the viscosity of the polymeric nanocomposite monotonically decreases. Thus, it can be concluded that the nature of the modifying additive exerts a decisive effect on the supramolecular organization of the polymeric matrix and correspondingly affects the polymer viscosity. Presumably, addition of minimal amounts of DND leads to the formation of a supramolecular organization characterized by the presence of primary aggregates of PDMS macrochains with the nucleus of the DND cluster. With an increase in the amount of DND clusters in the polymeric matrix, the aggregates become coarser, which is manifested in an increase in the viscosity.

With fullerene C_{60}, an increase in the concentration of clusters (aggregate nuclei) leads only to an increase in their amount, with the geometric size preserved.

Data on elastic strain of polymers at uniaxial extension are very useful in studying rheological properties of polymer films and parameters of three-dimensional chemical network. In the case of uniaxial extension, the stress–strain relationship is often described by the Mooney–Rivlin equation [7]

$$f^* = \sigma(\lambda^2 - 1/\lambda) = C_1 + C_2\lambda^{-1}, \qquad (10)$$

where f^* is the reduced mechanical stress; λ, relative elongation; and C_1 and C_2, constants.

From the linear portion of the dependence of f^* on λ^{-1} in the range of initial strains, by extrapolation to $\lambda^{-1} \to 1$ ($\varepsilon \to 0$), it is possible to determine the quantity $f_0^* = C_1 + C_2$ characterizing the thickness of the network of intermolecular contacts. The coefficient C_2 associated with deviation of the network of intermolecular contacts from the ideal network can be estimated from the slope of the linear portion for which the Mooney–Rivlin equation is valid.

Of considerable practical interest is the effect of nanomodifiers on the character of elastic strain of a composite material. As modifiers we used finely dispersed glass spheres (GS), technical-grade diamond-containing carbon from detonation synthesis (TDC), and their combinations in various proportions.

Figure 2a shows that modification of PDMS with TDC (up to 0.05 wt %) does not significantly enhance the set of elastic and strength parameters relative to the initial polymer. It should be noted, however, that the plots of f^* vs. λ^{-1} for PDMS modified with various concentrations of TDC lie above those for neat PDMS.

Filling of the polymer with GS (20–100 wt %) leads, as expected, to enhancement of the strength parameters, but the deformation characteristics sharply decrease (Fig. 2b).

Very interesting results were obtained with the two modifiers taken simultaneously (Fig. 2c).

Addition of 0.1 wt % TDC (the largest amount in this experiment) to 100 wt % GS leads to an appreciable decrease in f^*. Simultaneously, the elasticity of the composite material somewhat increases. Addition of 0.024 wt % GS (the smallest amount in this experiment) cardinally changes the rheological characteristics of the polymeric nanocomposite.

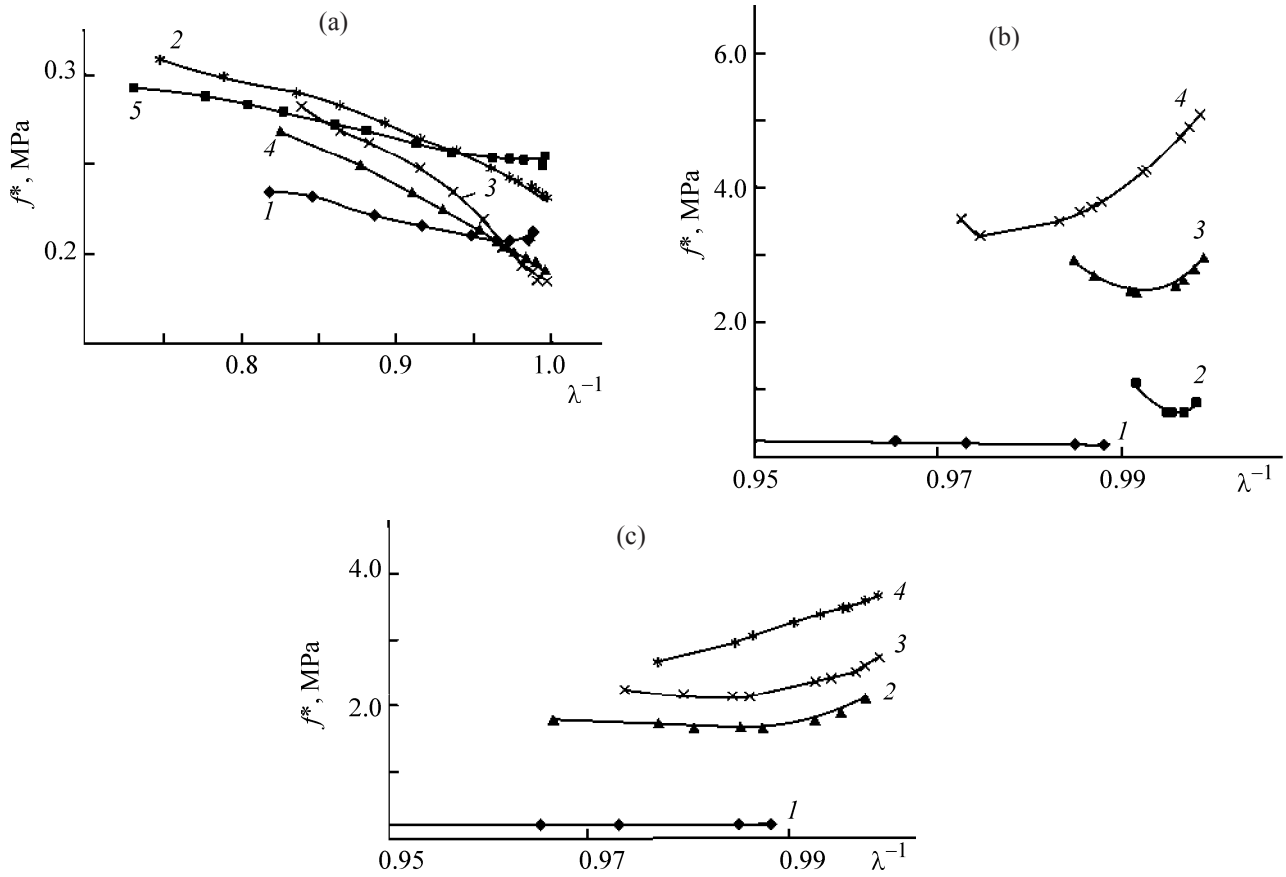

Fig. 2. Reduced mechanical stress f^* as a function of reciprocal relative elongation λ^{-1} for PDMS films modified with (a) TDC, (b) GS, and (c) GS + TDC. (a) TDC content, wt %: (*1*) 0, (*2*) 0.006, (*3*) 0.0125, (*4*) 0.025, and (*5*) 0.05. (b) GS content, wt %: (*1*) 0, (*2*) 20, (*3*) 50, and (*4*) 100. (c) GS + TDC content, wt %: (*1*) 0, (*2*) 100 + 0.024, (*3*) 100 + 0.05, and (*4*) 100 + 0.1.

The experimental results can be interpreted using a model based on the theory of dispersion-reinforced composites. This theory considers dispersion-filled elastomeric materials as certain hierarchically built systems with well-defined different levels. The polymer volume incorporating at least one filler particle with the adjacent matrix layer is considered as the lowest size level.

In this case, the topological pattern of the distribution of structural units throughout the volume (taking into account the real polydispersity of TDC particles) will be characterized by the presence of ensembles formed by large structural units of particles H, surrounded by small structural units of particles L. It is natural to assume that the supramolecular structure thus formed is more isotropic than that formed with an individual H-type filler. The supramolecular structure formed and the improved rheological parameters of the composite can favor formation of a more perfect supramolecular organization of the polymer and, correspondingly, attainment of higher service parameters.

CONCLUSIONS

(1) The nature of the modifying additive exerts a decisive effect on the viscosity characteristics of a nanocomposite. Presumably, addition of minimal amounts of nanocarbon from detonation synthesis leads to the formation of a supramolecular organization characterized by the presence of primary aggregates of polydimethylsiloxane macrochains with the nucleus of a nanocarbon cluster. An increase in the amount of clusters in the polymer matrix leads to coarsening of the aggregates, which is manifested in the viscosity growth. With fullerene C_{60}, an increase in the concentration of clusters leads only to an increase in their amount, with the geometric size preserved.

(2) A combination of low- and high-dispersity substances was suggested as a significant factor for

formation of the desirable supramolecular organization. Addition to finely dispersed glass spheres of even hundredth fractions of percent of nanocarbon significantly changes the relaxation properties.

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