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ScienceDirect

Procedia Chemistry 10 (2014) 2 – 6

Procedia Chemistry

XV International Scientific Conference "Chemistry and Chemical Engineering in XXI century" dedicated to Professor L.P. Kulyov

Study of shear properties of nanoparticle suspensions

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Abstract

Low-frequency complex shear modulus of the colloidal suspensions of nanoparticles Nd:YAG in ethylene glycol was measured for the first time by using acoustic a resonance method with piezoquartz vibrator. Dependence of viscoelastic properties of the colloidal suspensions on nanoparticles sizes and their concentrations has been carried out.

Peer-review under responsibility of Tomsk Polytechnic University

Keywords: Suspension; nanoparticles; concentration; particle size; shear elasticity.

1. Introduction

For the first time low-frequency (10^5 Hz) shear elasticity of liquids[1,2] has been found by acoustic resonance method. Elasticity can be explained by the fact that in liquids there is unknown earlier low-frequency viscoelastic relaxation process. Therefore, detail investigation of the shear elasticity has fundamental importance for the correct understanding of the nature of liquid state as a whole. The resonance method[3-7] has high sensitivity to inhomogeneities of structure of investigated objects. Now viscoelastic properties of colloidal suspensions of nanoparticles are studied by this method. Colloidal suspensions of nanoparticles have certain structural and mechanical properties depending on the concentration and size of nanoparticles.

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Peer-review under responsibility of Tomsk Polytechnic University
doi:10.1016/j.proche.2014.10.002

2. Experimental

The acoustic resonance method is based on the study of influence of forces of the additive connection realized by liquid interlayer on resonance parameters of a quartz resonator. The tested liquid is placed between surfaces of piezoelectric quartz oscillated on a resonance frequency and a fixed solid cover plate. Piezoelectric quartz has X-18,5^o cut and the liquid possesses purely shear deformations. Stagnant shear waves are installed in the tested liquid. The problem of interaction of the resonator with the liquid interlayer and the solid cover plate[2] produces following expression for complex shear of resonance frequency ($\Delta f^* = \Delta f' + i\Delta f''$):

$$\Delta f^* = \frac{SG^*\kappa}{4\pi^2 M f_o} \cdot \frac{1+\cos(2\kappa H - \varphi)}{\sin(2\kappa H - \varphi)}, \qquad (1)$$

where $G^* = G' + iG''$ - a complex shear modulus of the liquid, S - square of the cover plate, H - thickness of the liquid interlayer, M - resonator mass, f_o - its resonance frequency, $\kappa = \beta - i\alpha$ - a complex wave number, φ - a complex phase shift at reflection of shear wave from boundary liquid – cover plate. According to the theory of research technique shift of resonance frequency of piezoelectric quartz Δf^* should be proportional to an inverse value of the thickness of liquid interlayer, when the cover plate is practically in rest ($\varphi = 0$), and when the interlayer thickness much less than wavelength in liquid ($H << \lambda$). Then the complex shear modulus will be determined by expression:

$$G^* = \frac{4\pi^2 M f_o \Delta f^* H}{S}, \qquad (2)$$

The tangent of mechanical losses angle is determined as $\tan\theta = G''/G' = \Delta f''/\Delta f'$. Thus, viscoelastic properties of tested liquid can be calculated by measuring of real and imaginary frequency shifts of piezoquartz.

The real and imaginary shear modulus of colloidal suspensions of nanoparticles Nd:YAG (yttrium and aluminum garnet doped by neodymium) in ethylene glycol are measured by an acoustic resonance and rheological methods. Colloidal suspensions of nanoparticles in ethylene glycol are obtained by an ultrasonic method. Nanoparticles of Nd:YAG of 40 and 300 nanometers have been used. Nanopowder of Nd:YAG is obtained by a chemical fluid method[8]. Ethylene glycol ($C_2H_6O_2$) of Merck company (Germany) was used as solvent (purity of 99.5 %, the molar mass M = 62.07 g/mole and density ρ = 1.11/cm^3). Density of ethylene glycol allows using it in the experiments with Nd:YAG nanoparticles without loss of particles in the sediment. Suspensions have been prepared with use of ultrasonic disperser Sonoswiss SW 1H.

3. Results and Discussion

Results of nanoparticle suspension research by resonance method have shown a linear dependence of the real and imaginary frequency shifts on the inverse value of the thickness of the liquid interlayer. The piezoquartz of X-18,5^o cut with a main resonance frequency of 73.2 kHz and with a mass of 6.24 g were used in the experiment, with the cover-plate area being 0.2 cm^2, the area of the cover-plate was 0.2 cm^2. The linear dependence confirms that the tested liquid has a bulk shear modulus, i.e. not depending on a thickness of the liquid interlayer. Figures 1 and 2 show experimental results for suspension of 40 nm particles with 0.62 wt% concentration and 300 nm particles of 0.4 wt% concentration.

Measurements of real and imaginary frequency shifts for suspensions of nanoparticles Nd: YAG with the size of 300 nm and 40 nm in ethylene glycol depending on their concentration were obtained experimentally. With increasing concentration of nanoparticles the value of the shear moduli increases. Probably, the nanoparticles of a certain concentration of the solution contribute to hardening of the liquid structure with the maximum on the curves indicate the optimal content of the dispersed phase. Reduction in the shear modulus with certain concentrations can be explained by the fact that in this case, the nanoparticles behave as a plasticizer. Such a transition role of nanoparticles in solution is confirmed by the maximum of the damping system, and for the 40 nm nanoparticles with a maximum attenuation is occured at higher concentrations.

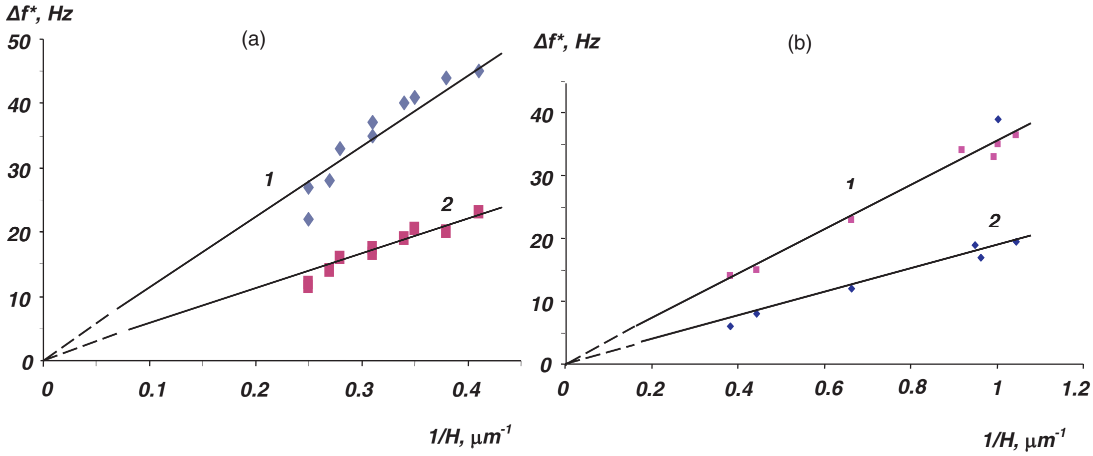

Fig. 1. Dependences of the real (1) and imaginary (2) shifts of frequencies on inverse value of the thickness of liquid layer for suspension of (a) 0.62wt%, 40 nm particles and (b) 0.4wt%, 300 nm particles.

The values of the shear moduli of suspensions of the same concentration show the dependence of the size of nanoparticles: for suspensions of 40 nm particles magnitudes is higher than that of suspensions with a particle of 300 nm. The values of the real shear modulus and a tangent of mechanical loss angle are presented in Table 1.

Table 1. The values of the real shear modulus and a tangent of mechanical losses angle

c, wt%	$G' \cdot 10^{-5}$, Pa	$\tan\theta$	f_{rel}, Hz	η_{ef}, Pa·s
		ND:YAG/ethylene glycol, 300 nm		
0.4	0.37	0.4	29264	0,23
0.5	1.07	0.49	35848	0,59
0.6	1.169	0.5	36580	0,64
0.8	0.97	0.35	25606	0,68
1	0.49	0.47	34385	0,28
1.2	0.38	0.71	51943	0,18
		ND:YAG/ethylene glycol, 40 nm		
0.4	0.33	0.89	65112	0,14
0.62	1.063	0.72	52675	0,49
0.8	1.21	0.8	58528	0,54
1	0.86	0.38	27800	0,56
1.2	0.197	0.75	54870	0.09

From the Table 1 it is shown that the tangent of mechanical losses angle $\tan\theta$ is less than unity for all tested liquids. If the mechanism of the viscoelastic relaxation can be explained by the rheological model of Maxwell the frequency of relaxation process should be less than the frequencies of the experiment, $f_{rel} = f_o \cdot \tan\theta$. Effective viscosity is calculated on the rheological model of Maxwell under formula $\eta_{ef} = G'(1+\tan^2\theta)/2\pi f_o \tan\theta$.

A study of nonlinear viscoelastic properties of suspensions of nanoparticles on the angle of the shear deformation is significantly different from that for the base liquid, i.e. dispersion medium. As shown in Fig.1, the real shift of the resonance frequency for the suspension of Nd:YAG nanoparticles with a mass fraction of 1% in ethylene glycol shows no significant dependence on the angle of the shear deformation in contrast from that for ethylene glycol[3] (inset in Figure 2). An increase in the shear modulus of elasticity in reducing the size of the nanoparticles is observed. These results indicate the formation of a solid structure of a colloidal suspension of nanoparticles in comparison with the pure liquid.

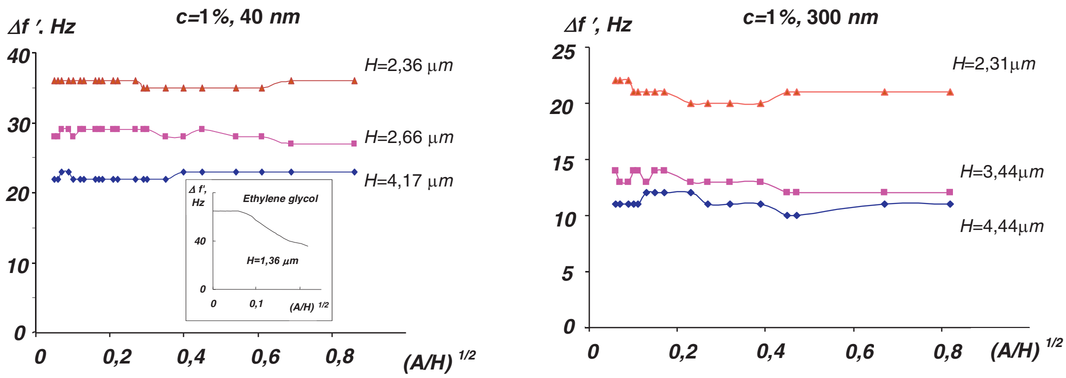

Fig.2. The dependence of the real frequency shift on the angle of the shear deformation for suspensions of nanoparticles Nd:YAG/ethylene glycol for different thicknesses *H*.

Colloidal suspensions of nanoparticles Nd:YAG in ethylene glycol have been also investigated by means of dynamic oscillatory methods (Rheometer Gemini) on frequencies of 0.1-100 Hz. In rheological experiments, unlike the acoustic resonance method, the studied fluid finds space between two round disks, one of which makes oscillations. The dynamic and imaginary shear modulus of a fluid are calculated from dependence of shear stress on a shear deformation. The suspensions of 300 and 40 nm of nanoparticles in ethylene glycol have been researched.

Figure 3 (a) shows the dependencies of imaginary shear modulus of the studied suspensions on the frequency for different concentrations of 40 nm nanoparticles of Nd:YAG. It is seen that with increasing particle concentration the maximum of the imaginary modulus shifts to higher frequencies (Fig. 3(b)). This is due to apparently with the change of the relaxation frequency of a suspension.

Thus the experimental study of colloidal suspensions of nanoparticles showed that their structure has some sensitive properties such as shear modulus and viscosity dependent not only on the frequency and on amplitude of the shear effects, but also on the size and concentration of nanoparticles.

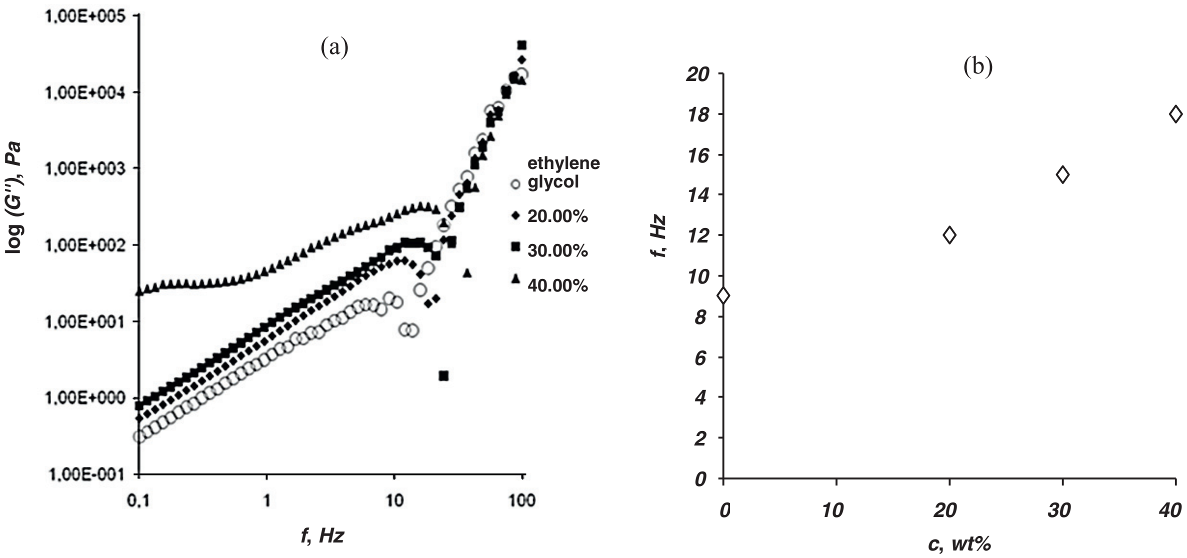

Fig. 3. (a) Frequency dependencies of G″ for suspensions of 40 nm Nd:YAG nanoparticles in ethylene glycol. (b) Position of G″ maximum in dependence on concentration of 40 nm Nd:YAG

Acknowledgements

The authors thank Prof. W. Schranz and Mag. M. Reinecker (University of Vienna, Austria) for assistance. The reported study particularly was supported by RFBR grant No.12-02-98012-r_sibir_a.

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