

Studying mechanical, acoustical and dielectric properties of SiO₂-filled polyester resin nanocomposites

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Concentration effects of fumed silica on mechanical (static Young modulus, compression strength limit), acoustic (Lame constant, shear modulus, Young modulus, compression modulus, and Poisson's ratio), and dielectric parameters of an unsaturated styrene-containing polyester resin have been experimentally studied. The degree of filling $C_{f,m}$ was ranged from 0.5 to 5.0 w. %. $C_{f,m}$ -dependences of all the parameters are proved to be non-regular, with their maximal deviations from initial values being at $C_{f,m} \leq 1.5$ %.

Экспериментально исследованы концентрационные эффекты влияния наноразмерного диоксида кремния (аэросил) на механические (статический модуль Юнга, предел прочности на сжатие), акустические (постоянная Ламэ, модуль сдвига, модуль Юнга, модуль всестороннего сжатия и коэффициент Пуассона) и диэлектрические параметры ненасыщенной стирол-содержащей полиэфирной смолы. Степень наполнения $C_{f,m}$ изменялась от 0.5 до 5 % (по массе). Зависимости всех параметров от $C_{f,m}$ немонотонные, наибольшие отклонения их значений от начальных наблюдаются при $C_{f,m} \leq 1.5$ %.

1. Introduction

Unsaturated polyester resins (UPR) that belong to a class of thermosetting polymers [1, 2] show a good combination of mechanical, electrical, chemical-resistant properties and relatively low production cost [3]. Both UPR and its microcomposites are widely used in various industrial and domestic applications as structural or functional materials [4, 5]. In recent years the development of nanotechnology stimulates researches on the structure, chemical, and physical properties of the particle-filled UPR-based polymer nanocomposites (PNC) [6–10]. Fumed silica (aerosil) is widely used as nano-sized filler not only in UPR but also in other polymer matrices [11–13].

A large variety of components used for creating PNC-materials and variety of cooking techniques complicates greatly the generalization of the results obtained by various researches. It does not allow to form a holistic view on the interaction mechanisms among SiO₂-nanoparticles and polymer macromolecules and to build a quantitative model for structure-property relationships of PNC-materials. The purpose of this work is to study the effects of SiO₂-loading on both mechanical and dielectric properties of styrene-cross-linked UPR.

2. Experimental

The orthophthalic styrene-cross-linked unsaturated polyester resin "Polylite 640-

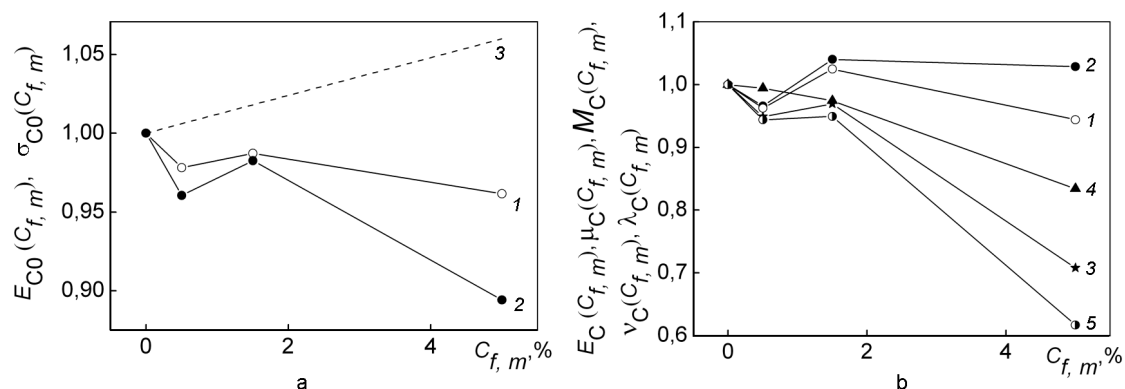


Fig. 1. Normalized concentration dependences of mechanical (a) and acoustical (b) parameters of the unfilled UPR ($C_{f,m} = 0$) and its SiO₂-nanocomposites: a) E_{C0} (1); σ_{C0} (2); E_{C0} , calculated by the model of Christensen and Lo [14] (3); b) E_C (1); μ_C (2); M_C (3); $\nu_C(C_{f,m})$ (4); $\lambda_C(C_{f,m})$ (5).

M888" (Finland) has been used as a matrix for preparing PNC.

The nanofiller was aerosilica A-300 (Ukraine) of a high surface reactivity and of specific surface area $S_f \sim 280$ m²/g. Particle's diameter was ranged from 5 to 20 nm (average size $R_f \sim 10$ nm). Filler's mass concentrations $C_{f,m}$ were 0, 0.5, 1.5, 3.0, and 5.0 %.

Nanocomposite samples were obtained from UPR-dilutions mixed with the filler into mixtures of homogeneous consistency. The polycondensation process took place at room temperature for 48 h.

Static mechanical properties of the samples, namely, Young's modulus (E_{C0}), compression strength (σ_{C0}); dynamic elastic moduli (DEM), namely, — Lamé constant (λ_C), shear modulus (μ_C), compression modulus (M_C), dynamic Young's modulus (E_C); and complex dielectric permittivity ($\epsilon^* = \epsilon_1 - j\epsilon_2$) of both the unfilled resin and its SiO₂-nanocomposites have been measured by using methods of static mechanical loading technique, ultrasonic pulsed echo technique and dielectric spectroscopy, respectively. Measurements of both static and dynamic mechanical parameters have been carried out at room temperature. Dielectric parameters have been measured within the temperature range from -50 to $+70^\circ\text{C}$ at fixed frequencies ranged from 60 Hz to 1.2 MHz. The measurement accuracy did not exceed 10 % for the static parameters, 2 % for the dynamic moduli, and 5 % for the dielectric parameters.

3. Results and discussion

The behavior of the mechanical parameters with increasing $C_{f,m}$ is non-monotonous

(Fig. 1). For the unfilled resin it was found that $E_{C0} = 0.78 \cdot 10^4$ kg/cm² and $\sigma_{C0} = 1087$ kg/cm². When $C_{f,m} = 0.5$ % both σ_{C0} and E_{C0} are reduced, when $C_{f,m} = 1.5$ % they increase and decrease again with increasing $C_{f,m}$ to 5 %.

A straight line in Fig. 1 describes the theoretical dependence $E_{C0}(C_{f,m})$ calculated within the self-consistent micromechanical model of Christensen and Lo [14] via the parameters of the matrix and filler such as compression moduli (M_m and M_f), shear moduli (μ_m and μ_f) and Poisson's ratios (ν_m and ν_f). The following values of the above-mentioned UPR-parameters were chosen for numerical calculations: $\rho_m = 1.20 \cdot 10^6$ g/m³, $E_m = 3.5 \cdot 10^9$ N/m², $\mu_m = 1.4 \cdot 10^9$ N/m², $\nu_m = 0.25$ [1]. For SiO₂-nanoparticles we used the following values: $\rho_f = 2.2 \cdot 10^6$ g/m³, $M_f = 36.7 \cdot 10^9$ N/m², $\mu_f = 31.3 \cdot 10^9$ N/m², $\nu_f = 0.17$ which correspond to an amorphous silica glass [15]. This model does not account for changes in the polymer structure near the particle-polymer interfaces and shows a linear increase in E_{C0} with increasing $C_{f,m}$ — $E_{C0}(0.05)/E_{C0}(0) \sim 1.05$.

The non-monotonous decrease in E_{C0} can be attributed to changes in the molecular structure of the nanocomposites in the interphase region (IPR) formed around SiO₂-nanoparticles [16]. The data obtained from thermodesorption mass spectrometry study [10] show that SiO₂-nanoparticles with active surface centers cause rebuilding of NPC's molecular structure in two ways — first, by forming chemical bonds to both polyester macromolecules and styrene molecules, and, second, by preventing formation of long macromolecular chains as well as binding them to styrene molecules, thus re-

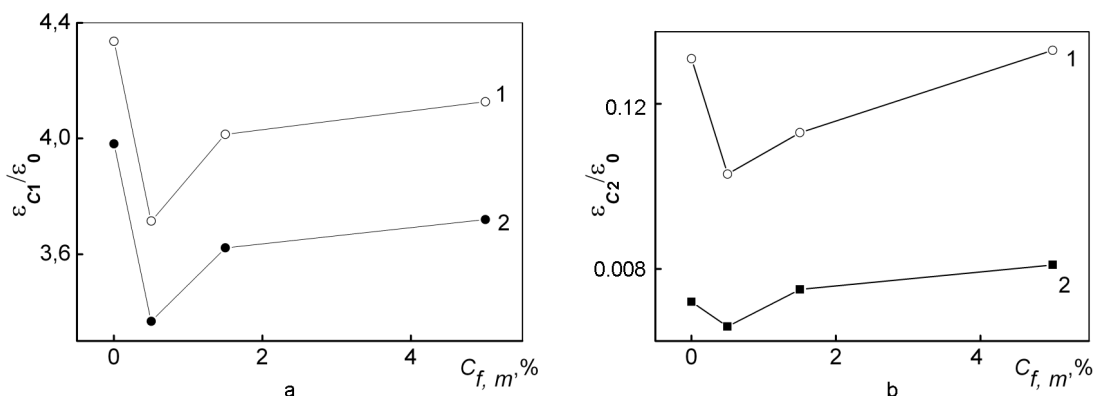


Fig. 2. Concentration dependences of relative dielectric permittivity ϵ_{C1}/ϵ_0 (a) and dielectric loss factor ϵ_{C2}/ϵ_0 (b) of the unfilled UPR and their SiO₂-nanocomposites measured at 300 K at fixed frequencies of 1.2 kHz (1) and 1 MHz (2).

sulting in appearance of free styrene molecules and short polyester macromolecular segments.

For the unfilled UPR ($C_{f,m} = 0$) phase velocities of elastic waves are $V_L(0) = 2566 \pm 11$ m/s and $V_S(0) = 1231 \pm 11$ m/s which are in a good agreement with literature data [17]. In nanocomposites at $C_{f,m} = 0.005$ V_L and V_S are reduced by 2 %, at $C_{f,m} = 0.015$ they returned to their original values. With increasing $C_{f,m}$ to 0.05 V_S remains unchanged whereas V_L reduces by 10 %. Numerical calculations of composite's density ρ_C versus $C_{f,m}$ indicates that changes in both V_S and V_L with changing $C_{f,m}$ are related only with changes in composite's elastic moduli.

From the measured values of V_S and V_L and calculated values of ρ_C both DEM (E_C , M_C , μ_C , and λ_C) and Poisson's ratio (ν_C) have been evaluated by using well-known relations for the plate-shaped samples [18] (Fig. 1b). Here one can see that the concentration dependences of the DEM are non-monotonous. When $C_{f,m} = 0.005$ they decrease by 4–5 %; at $C_{f,m} = 0.015$ both E_C and μ_C increase by 4.5 % as compared to their initial values (i.e. for the unfilled resin), whereas M_C and λ_C suffer no changes; at $C_{f,m} = 0.05$ $E_C(0.05) \approx E_C(0.005)$, $\mu_C(0.05) \approx \mu_C(0.015)$, $M_C(0.05)/M_C(0) \approx 0.7$, and $\lambda_C(0.05)/\lambda_C(0) \approx 0.6$. In general, $C_{f,m}$ -dependences of both E_C and E_{C0} are qualitatively similar to each other, the ratio of $E_C(C_{f,m})/E_{C0}(C_{f,m})$ suffers negligible changes relative to its initial value ($E_C(C_{f,m} = 0)/E_{C0}(C_{f,m} = 0) = 7.3$). It should be noted that the concentration dependencies obtained for DEM cannot be described using a long-wavelength approximation of the

multiple scattering model of elastic wave propagation (MSEWP-model) through a random-particulate composite material [19]. This may indicate that changes in both density and elastic properties of nanocomposites occur in IPRs due to rebuilding of their molecular structure — effects that are not included in the MSEWP-model.

Concentration dependences of both the real and imaginary components of the complex dielectric permittivity of the nanocomposites are also non-monotonous (Fig. 2) reaching its minimal values at $C_{f,m} = 0.005$. In the frequency range studied the electric polarization of both UPR and its SiO₂-nanocomposites is governed by two main mechanisms — the dipole orientation polarization and the hopping polarization [20], each of which is associated with the motion of charged particles and dipole molecules in an external electric field. In accordance with the classic (Debye) polarization theory [20] the former mechanism contributes at the frequency range from 10^5 to 10^9 Hz, and the latter — from 1 to 10^5 Hz. Due to the hopping polarization mechanisms low-frequency values of ϵ_{C1} and ϵ_{C2} (curves 1 on Fig. 2) are somewhat higher than ones at high-frequency (curves 2).

It should be noted that dependences of $\epsilon_{C1}(C_{f,m})$ and $\epsilon_{C2}(C_{f,m})$ do not obey the well-known mixing rules [21] for calculating complex dielectric permittivity $\epsilon_C = \epsilon_{C1} - j\epsilon_{C2}$ of a mixture composed of spherical particles of a dielectric material (of the permittivity $\epsilon_f = \epsilon_{f1} - j\epsilon_{f2}$) which are distributed uniformly in dielectric matrix ($\epsilon_m = \epsilon_{m1} - j\epsilon_{m2}$). This rules predict linear concentration dependences for ϵ_C at low $C_{f,m}$ -values. In our case $\epsilon_{f1} = 3.75$ at 1 MHz [22] and $\epsilon_{m1} \approx 4.0$ at 1 MHz (Fig. 2)

and the classical mixing rules predict a linear decrease in ε_{CI} with increasing $C_{f,m}$ at $C_{f,m} \leq 0.05$. Numerical calculations made in accordance with the Bottcher formula, the Maxwell-Garnet formula, the Bruggeman formula, and the Lichtenecker-Rother logarithmic formula give the following values for $\varepsilon_{CI}(C_{f,m})/\varepsilon_{m1}$ at $C_{f,m} \leq 0.05$ —0.99681, 0.99681, 0.99681, and 0.99678, respectively, whereas the experimental values obtained at 1 MHz are $\varepsilon_{CI}(0.005)/\varepsilon_{m1} = 3.72/3.98 \approx 0.846$ and $\varepsilon_{CI}(0.05)/\varepsilon_{m1} = 3.72/3.98 \approx 0.935$. This discrepancy between the theoretical and our experimental data can be explained by the fact that filling UPR with SiO₂-nanoparticles results in rebuilding internal molecular structure of the nanocomposites, particularly within IPR due to binding both polyester and styrene molecules to the nanoparticles. Therefore this rebuilding is accompanied with changes in polyester chain mobility [16] and also with formation of the electrical double layer [23] around nanoparticles which may affect local conductivity at the SiO₂-resin interfaces. These phenomena, in turn, cause local changes in ε_m which are not taken into account by the classical mixing rules.

4. Conclusions

The effects of nano-sized silicon dioxide on both the mechanical and dielectric properties of polymer nanocomposites based on a styrene-cross-linked unsaturated polyester resin have experimentally been investigated in the range of filler's mass concentrations $C_{f,m}$ from 0.5 to 5.0 %. It was found that the concentration dependences of static mechanical parameters (static Young modulus, compression strength limit), the dynamic elastic moduli (Lame constant, shear modulus, Young modulus, compression modulus, and Poisson's ratio) and the components of the complex permittivity are non-monotonous. The $C_{f,m}$ -dependence of the static Young's modulus cannot be described within the traditional micromechanical model of Christensen and Lo, and $C_{f,m}$ -dependence of nanocomposite's dielectric permittivity are different from one predicted by the traditional mixing formula for a two-component matrix mixture of dielectric materials.

These results enable to conclude that complicated interactions among polyester macromolecules and styrene molecules and SiO₂-nanoparticles occur which resulted in forming interphase regions around nanopar-

ticles where rebuilding of the polymer molecular structure is accompanied with redistribution of bounded charges.

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Дослідження механічних, акустичних та діелектричних властивостей нанокомпозитів поліефірної смоли з діоксидом кремнію

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Експериментально досліджено концентраційні ефекти впливу нанорозмірного діоксиду кремнію (аеросил) на механічні (статичний модуль Юнга, межа міцності на стискання), акустичні (стала Ламе, модуль зсуву, модуль Юнга, модуль всебічного стискання та коефіцієнт Пуассона) та діелектричні параметри ненасиченої стиролвмісної поліефірної смоли. Ступінь наповнення $C_{f,m}$ змінювався у межах від 0,5 до 5 % за масою. Концентраційні залежності усіх параметрів виявилися немонотоними, найбільші відхилення значень параметрів від початкових спостерігаються при $C_{f,m} \leq 1.5$ %.