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AGING OF AQUEOUS LAPONITE DISPERSIONS IN THE PRESENCE OF SODIUM POLYSTYRENE SULFONATE

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Aqueous suspensions of Laponite with discotic particles are well-studied and find a wide range of applications in industry. A new direction of their implementation is polymer composites that can exhibit improved physical properties. We have studied the aging of aqueous suspensions of Laponite and sodium polystyrene sulfonate (PSS-Na) and both their microscopic (small-angle X-ray scattering, SAXS) and macroscopic (small amplitude oscillatory shear (SAOS) rheometry) properties. The concentration of Laponite, C_L , was fixed at 2.5% wt and concentration of PSS-Na, C_p , was varied within 0–0.5% wt (0–24.2 mM). It is shown that the adding of PSS-Na significantly accelerates the aging. Nevertheless, the systems were stable against the sedimentation, and the flocculation didn't occur. Polyelectrolyte induced the appearance of large-scale fractal heterogeneities, which became more compact in the course of the aging.

Keywords: laponite, PSS-Na, aqueous suspensions, rheology, SAXS, aging.

1. Introduction

Laponite is a synthetic clay, which consists of discotic colloidal particles with the diameter $d \approx 30$ nm and the thickness $h \approx 1$ nm [1]. In aqueous media, their faces have a large negative charge (≈ -700 e), while their edges are positively charged ($\approx +50$ e at $\text{pH} \leq 11$) due to the protonation of OH groups [2]. Aqueous suspensions of Laponite display a very rich phase behavior that includes sol, gel, glass, and nematic states [3–5]. The gelation transition was observed at a Laponite volume fraction of $\approx 0.7\%$ ($\approx 1.8\%$ wt). It was accompanied by the thixotropic response to a stress [6].

The structure of a gel is described as the spanning network of discs connected via the so-called T -bonds or edge-to-face bonds (“house-of-cards” model)

[7]. Moreover, it was assumed that the gel structure is fractal, whereas the structure of the glassy state has a uniform density [8]. Recently, the time-dependent self-organizing processes in the so-called low-energy states [9] have obtained a considerable attention. The various aging processes such as the phase separation (coacervation), gelling, and glassing, which depend on the particle type, salt concentration, and presence of adsorbed substances (surfactants and polymers), were reported in [10].

The kinetics of a gel aging is known to depend on the potential of interaction between nanodisks that is a sum of the van der Waals attraction and the electrostatic double-layer repulsion. It was demonstrated that the addition of a monovalent salt such as NaCl increases the dominance of the attraction between Laponite particles in face-to-edge configurations [9]. In addition, the additional attraction or repulsion between Laponite particles can be finely

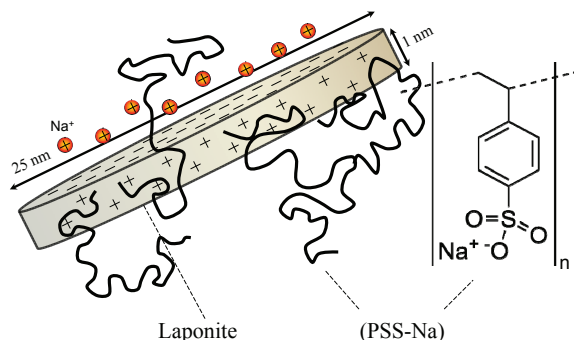


Fig. 1. Structure of Laponite and polystyrene sulfonic acid-sodium salt (PSS-Na) system

tuned, by using various additives. For example, it was shown that the adsorption of cationic CTAB on Laponite particles induced the additional attraction between them owing to the enhancement of hydrophobic interactions [11], and the adsorption of non-ionic polyethylene glycol (PEG) hindered the gelation of Laponite owing to the steric repulsion between molecules of the polymer adsorbed on Laponite [12–17]. The interactions between PEG and Laponite result in the appearance of the so-called “shake-gel” phenomenon even at a rather low concentration of the polymer [18, 19].

For more complex pluronic tri-block copolymers, the preferential segregation of hydrophobic segments at the surface of Laponite with hydrophilic segments dangling into a solution was observed [20]. Electrostatic interactions between Laponite and gelatin-A (polyelectrolyte) was shown to drive the complex spinodal decomposition and coacervation with the formation of ellipsoidal domains [21, 22]. However, the mechanism of aging of the electrolyte-containing Laponite gel can depend on many details of interactions between Laponite and a polymeric electrolyte, and it is still debated.

This work is devoted to the study of the aging of an aqueous Laponite suspension in the presence of PSS-Na. The concentration of Laponite, C_L , in all the experiments was fixed at 2.5% wt, which is just near the boundary between the agings into the attractive gel and the repulsive “Wigner” glass in the salt-free aqueous solution (below 10^{-4} M concentration of Na^+ ions) [5]. At $C_L \approx 2.5\%$ wt, the Debye screening length in a salt-free aqueous solution is rather large, $\lambda \approx 4.2$ nm [9], and the estimations show that the negative potential can affect practically all the parti-

cles [16]. A glass-like state is preferably formed in a salt-free solution, and an increase of the concentration of Na^+ ions leads to the formation of a gel-like state. The concentration of polymeric salt PSS-Na in our experiments was below 0.5% wt, which corresponds to a Na^+ concentration of $\leq 2.4 \times 10^{-2}$ M. The choice of polymeric salt PSS-Na was stipulated by the following circumstance: PSS-Na is a strong water-soluble polyelectrolyte with repeating chains that have both hydrophobic and hydrophilic parts with attached negative charge (anionic chains) [23]. The electrostatic attraction between these anionic chains and positively charged edges of Laponite particles is assumed to be very small at small concentrations of PSS-Na. However, at high concentrations of PSS-Na, the Na^+ ions effectively screen the negative charges on Laponite particles. This enhances the attractive interactions between the polymer and Laponite and can result in changes in the dynamics of aging and the state of the system. In our work, the aging processes were studied by the methods of small amplitude oscillatory shear (SAOS) rheometry and small-angle X-ray scattering (SAXS).

2. Experimental

The Laponite RD (Rockwood Additives Ltd., UK) was used as-received. Its empirical formula is $\text{Na}_{0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.4})\text{O}_{20}(\text{OH})_4]$, and the solid density is ≈ 2.53 g/cm³ [24, 25]. Poly (styrene sulfonic acid-sodium salt) (PSS-Na) ($\text{C}_8\text{H}_7\text{SO}_3\text{Na}$)_n with the molecular mass of a single chain $m = 206.2$ g/mol and the average molecular mass $M = 145000$ g/mole (i.e., $n \approx 700$) was prepared by the multiple sulfonation of polystyrene by sulfuric acid. The sulfonation degree was close to 100%. The obtained solution of PSS-Na was cleaned and dried. The structure of Laponite and PSS-Na is schematically presented in Fig. 1.

Two stock solutions of Laponite and PSS-Na were prepared by mixing these substances with deionized ultrapure water (MilliQ) and further ultrasonication of mixtures using a UP 400S ultrasonic disperser (Dr. Hielscher GmbH, Germany) at a frequency of 24 kHz and an output power of 400 W for 15 min. The combined Laponite and PSS-Na suspensions were prepared by mixing the stock solutions of Laponite and PSS-Na according to the required concentration with the further ultrasonication of the mixture for 15 min. The final concentration of Laponite in all the

samples, C_L , was fixed at 2.5% wt, and the concentration of PSS–Na, C_p , was varied within 0–0.5% wt (0–24.2 mM). After the preparation and the cooling to room temperature, suspensions were stirred carefully for 5 min, and the measurements were immediately started.

A small-amplitude oscillatory shear (SAOS) rheometry HAAKE MARS III (Haake, Karlsruhe, Germany) tests were done for measuring the storage and loss G' and G'' shear moduli in the range of 10^{-1} – 10^3 Pa during the total time of 12 h. A cone-plate fixture of 35 mm in diameter with a cone angle of 2.0° was used. The sample was protected from the water evaporation during the experiment by a special cover. The steady pre-shear at 200 s^{-1} was performed for 200 s before each test in order to homogenize the suspension before the aging experiment [16]. The dynamic time sweep test was done at the small oscillation frequency $\omega = 1 \text{ Hz}$, and a deformation rate of 0.01 s^{-1} , which was within the linear viscoelastic regime. The complex viscosity, η^* , was evaluated as

$$\eta^* = \sqrt{G'^2 + G''^2} / \omega. \quad (1)$$

The small-angle X-ray scattering spectra (SAXS) were obtained using a digital detector Elexience, which allowed the range of $q = (0.08 \div 1.6) \text{ nm}^{-1}$ for the scattering vector magnitude. The Cu–K α source of radiation with the wavelength $\lambda_r = 0.154 \text{ nm}$ was used. The “effective” structure factor $S(q)$ was estimated by the substitution of the measured scattering intensity $I(q)$ to the relation

$$S(q) = \frac{I(q)}{K C_L M P(q)}, \quad (2)$$

where $K = 0.0445 \text{ Mol/g}^2$ is the constant accounting for the contrast between Laponite and the solvent, $M = 930 \pm 190 \text{ kg/Mol}$ is the molecular mass of platelets, and $P(q)$ is the form factor. The term “effective” was used because relation (2) is only valid for spherical particles.

The form factor $P(q)$ of discotic particles with diameter d and thickness h was calculated using the Guinier equation [26]:

$$p(q) = \int_0^{\pi/2} \frac{4J_1^2(0.5qd \sin x) \sin(qh \cos x)}{4J_1^2((qh \cos x)^2 (0.5qd \sin x)^2)} \sin x dx, \quad (3)$$

where J_1 is the first-order cylindrical Bessel function.

The effect of polydispersity in the particle diameter was taken into account by the convolution of relation (2) with a normalized Gaussian distribution [27],

$$\Psi(d) = (\Delta\sqrt{\pi})^{-1} \exp\left(-\frac{(d - \langle d \rangle)^2}{\Delta^2}\right), \quad (4)$$

where $\langle d \rangle$ is the mean particle diameter and the standard deviation Δ is the polydispersity parameter. The values of $\langle d \rangle = 25 \pm 0.5 \text{ nm}$ and $\Delta = 8 \pm 2 \text{ nm}$ were used as the best fit parameters [27].

In the present experiments, the scattering length density (SLD) contrast between macroions and water was very low, and the observed scattering patterns reflected the input of Laponite particles or their aggregates.

The temperature was fixed at $T = 298 \text{ K}$ in all measurements, and all the experiments were repeated at least three times. The Table Curve 2D (Jandel Scientific, San Rafael, CA) software was used for smoothing the data and for the estimation of their standard deviations. Means and standard deviations are shown in the figures by error bars.

3. Results and Discussion

Note that the transition from $G' < G''$ to $G' > G''$ was observed for all the studied samples in the course of the aging. This behavior is typical of the fluid-to-gel transition in suspensions of Laponite [16]. The characteristic time t_g , at which $G' = G''$, can be defined as the time of transition into an arrested state.

Figure 2 presents the time dependences of the complex viscosity, η^* , during the aging at various concentrations of polyelectrolyte C_p . The data show that the viscosity can change by many orders of magnitude during the time of observation $t = 0$ –12 h. The complex viscosity also shows a typical power-law type dependence on the age [8]

$$\eta^* \propto t^\alpha, \quad (5)$$

with different slopes α at small and long times of aging t .

The characteristic time t_g^* , at which the slope changes, can be also used for the characterization of the time of transition into an arrested state. The corresponding dependences of t_g , t_g^* , and the power-law exponent α (for a long time of aging) versus the polyelectrolyte concentration C_p are presented in

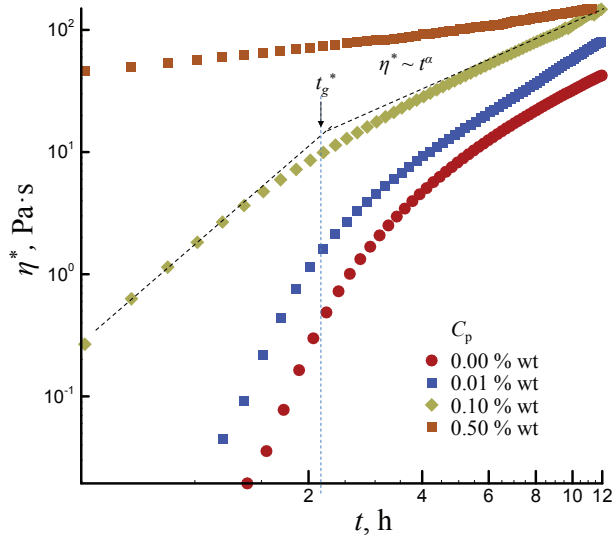


Fig. 2. Complex viscosity η^* versus the aging time t at various concentrations of PSS-Na, C_p

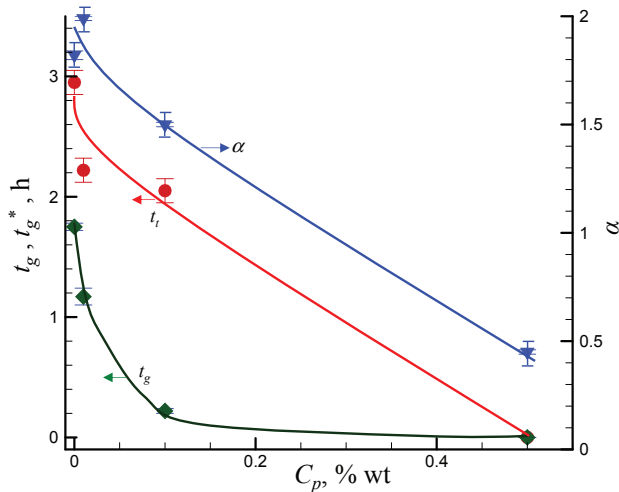


Fig. 3. Characteristic times, t_g and t_g^* , and the power-law exponent α (for a long time of aging) versus the concentration of PSS-Na, C_p

Fig. 3. It can be seen that the introduction of PSS-Na results in a decrease of both t_g , and t_g^* , and the transition into the arrested state was observed practically instantly after the preparation of a suspension at the highest concentration of C_p ($=0.5\%$ wt). Moreover, the complex viscosity shows a weaker dependence on the age with increase in C_p .

Note that the effect of the polyelectrolyte on the viscosity of a solvent (i.e., at $C_L = 0\%$ wt) is ex-

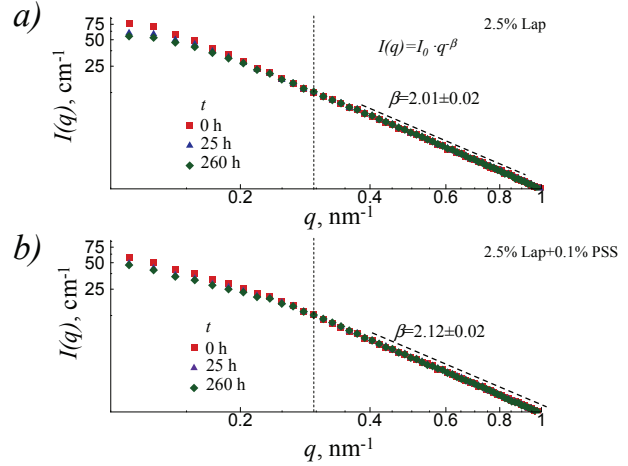


Fig. 4. Evolution of SAXS spectra during the aging of the PSS-Na free suspension (a) and the suspension with $C_p = 0.1\%$ wt (b)

pected to be low even at the maximum concentration of PSS-Na, $C_p = 0.5\%$ wt ($=24.2$ mM). The used range of concentrations corresponds to the unentangled semidilute regime, when the experimental data follow the scaling dependence $\eta \propto C_p^{0.5}$. According to [28], the estimated level of η should be of the order of $(2-3) \eta_w$ ($=0.75 \times 10^{-3}$ Pa·s at 25°C), where η_w is the viscosity of water. In general, the observed behavior at different concentrations of PSS-Na was rather similar to that observed in Laponite suspensions at different concentrations of monovalent NaCl salt [8]. This was explained by a decrease of the electrostatic screening length associated with Laponite discs with increase in the salt concentration.

Figure 4 shows the evolution of SAXS spectra during the aging of Laponite suspensions in the absence (a) and in the presence (b) of PSS-Na. At large q , the decay of the scattered intensity $I(q)$ follows roughly a $q^{-\beta}$ power-law with $\beta = 2.01 \pm 0.02$ (Fig. 4, a) and $\beta = 2.12 \pm 0.02$ (Fig. 4, b). Note that the value of $\beta \approx 2$ is expected for randomly oriented thin disks [27].

To extract more useful information from the scattering patterns, we have calculated the structure factor $S(q)$ by the method as described above. The function $S(q)$ was previously used for determining the origin of two different non-ergodic states: gel and Wigner glass [5]. It was shown that $S(q)$ grew significantly at small q -values in suspensions with Laponite

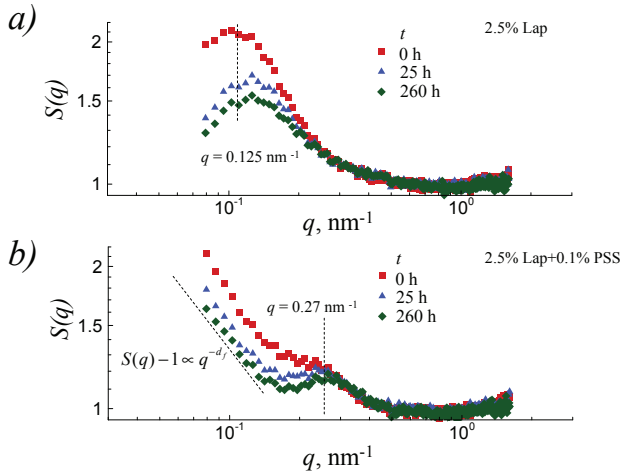


Fig. 5. Static structure factor $S(q)$ calculated from SAXS data for the pure 2.5-% Laponite suspension (a) and for the Laponite suspension containing 0.1 %wt PSS-Na (b)

concentration under 2% wt, which is an evidence of large-scale (over 200 nm) heterogeneities, which are typical of the gel state. Moreover, for samples with Laponite concentrations above 2%, $S(q)$ was flat in the range of low q values, which is the evidence of a homogeneous glass state.

For the pure 2.5-% Laponite suspension, we observe a clear peak of the structure factor $S(q)$ at $q = 0.125 \text{ nm}^{-1}$ (Fig. 5, a). This value obviously corresponds to the average interparticle distance, which is about 50 nm (two times larger than the mean diameter of Laponite platelets). The value of $S(q)$ was decreased continuously at low q ($q < 0.1 \text{ nm}^{-1}$). The observed behavior was in correspondence with the formation of a glass state in the pure 2.5-% Laponite suspension [5].

However, the peak of the static structure factor of the 2.5-% Laponite suspension containing 0.1% wt PSS-Na (Fig. 5, b) was shifted to larger q -value, if compared with the pure Laponite suspension. Such peak matches the mean Laponite particle diameter of 25 nm. It can evidence the presence of T-bonds in Laponite aggregates. Moreover, a significant increase of $S(q)$ was observed in the range of low q -values. It indicates large-scale inhomogeneities, which are typical of a gel network.

We used the power-law approximation

$$S(q) - 1 \propto q^{-d_f}, \quad (6)$$

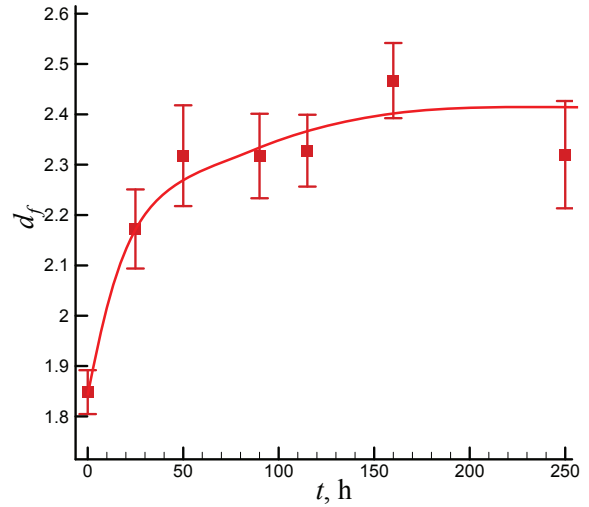


Fig. 6. Fractal dimension d_f versus the aging time for the 2.5-% Laponite suspension containing 0.1% wt PSS-Na

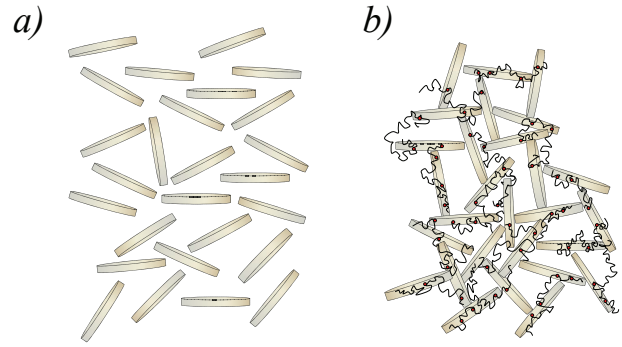


Fig. 7. Schemes of a glass state in the pure 2.5-% Laponite suspension (a) and a fractal gel network in the 2.5-% Laponite suspension in the presence of 0.1% wt PSS-Na

to determine the fractal dimension of a gel structure d_f in polyelectrolyte-containing samples with various aging times (Fig. 6). The picture shows that value of d_f grows with the aging time t , which means that the gel structure becomes more homogeneous and stabilizes at $t \geq 150$ hours.

The obtained results allow to conclude that the addition of a polyelectrolyte induces the transition in the 2.5-% Laponite suspension from originally glass state to gel (Fig. 7), which is typical of suspensions with lower clay concentrations ($C_L < 2\%$). This effect can be caused by a decrease of the Debye radius and thus a partial screening of the strong electrostatic repulsion between Laponite particles. However, the high ionic strength didn't induce the floccula-

tion as in the case of the doping by a monovalent salt and samples remained stable to the sedimentation during at least one month. The cross-linking of Laponite platelets by polymer chains, resulting in the formation of dense fractal aggregates by clay particles, can be the other cause of the gel network structure origin.

4. Conclusions

This paper presents the results of studies of the aging in aqueous Laponite-PSS-Na suspensions. The concentration of Laponite, C_L , was fixed at 2.5% wt, and the concentration of PSS-Na, C_p , was varied within 0–0.5% wt (0–24.2 mM). The samples remained stable to the sedimentation and transparent at all PSS-Na concentrations. Both visual observations and rheology tests have shown that sodium polystyrene sulfonate decreases the ergodicity-breaking time of Laponite suspensions by the factor of 2 at a PSS-Na concentration of 0.01% and by the factor of 10 at a PSS concentration of 0.1%. The flocculation didn't appear even at the PSS-Na concentration $C_p = 0.5\%$, which corresponds to an ionic strength of 24.2 mM, in contrast to Laponite suspensions doped by a monovalent salt, where the flocculation was starting immediately even at an ionic strength of 20 mM. The mechanism of acceleration of the aggregation may reflect not only a decrease of the Debye length, but also the cross-linking of Laponite particles by PSS⁺ macroions. SAXS experiments have shown that the addition of a polyelectrolyte induced the transition in the 2.5%-Laponite suspension from a homogeneous glass state to a gel network with a fractal structure, and the fractal dimension d_f increased during the aging.

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СТАРІННЯ ВОДНИХ
СУСПЕНЗІЙ ЛАПОНІТУ В ПРИСУТНОСТІ
ПОЛІСТИРОЛ СУЛЬФОНАТУ НАТРІЮ

Резюме

Водні суспензії лапоніту, що складаються з дископодібних частинок, добре вивчені і знаходять широке застосування в промисловості. Новим напрямком їх застосування є полімерні композити, які можуть мати поліпшені фізичні властивості. В даній роботі вивчено процеси старіння во-

дних суспензій лапоніту в присутності полістирол сульфонату натрію (PSS-Na). Дослідження проведено на мікроскопічному (малокутове розсіяння рентгенівських променів) і макроскопічному (малоамплітудна зсувна реометрія) рівнях. Концентрація лапоніту була фіксованою, $C_L = 2,5\%$ ваг. а концентрація PSS-Na, C_p , варіювалася в інтервалі 0–0,5% ваг. (0–24,2 ммоль). Було показано, що додавання PSS-Na істотно прискорює старіння. Проте, вивчені системи були седиментаційно стійкими і флокуляція не спостерігалася. Крім того, в присутності поліелектроліту виникали великомасштабні фрактальні неоднорідності, які ставали більш гомогенними в процесі старіння.