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Microstructure, microrheology, and dynamics of laponite® and laponite®-poly(ethylene oxide) glasses and dispersions

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Abstract

We utilize dynamic light scattering (DLS)-based passive microrheology to probe the dynamics and structural evolution of laponite® and laponite®-polymer glasses and dispersions at the microscale. The results reveal an increase in the dynamic heterogeneity of laponite® dispersions with an increase of laponite® concentration and aging time. In neat laponite® dispersions, the degree of stiffness is enhanced and the dynamics are retarded at higher laponite® concentration due to the formation of a repulsive glass. In the presence of PEO with a moderate molecular weight of 20 kg/mol, the microviscoelastic properties of 2 wt% laponite® dispersions show non-monotonic effects with PEO concentration upon aging, which agrees with the results obtained previously from bulk rheology. However, the magnitudes of the viscoelastic moduli (G' and G'') of dispersions beyond the gel point obtained from DLS-microrheology is lower than that obtained from conventional rheology. Our results suggest that the DLS-microrheology can be used to qualitatively study dynamic transitions and the microviscoelastic properties of gels and soft solids.

Keywords Colloidal glass · Clay · Clay-polymer · Nanoparticle · Nanocomposite · Re-entrant

Introduction

Complex fluids consisting of colloids and polymers often feature hierarchical microstructures with multiple relaxation time scales, which lead to complex rheological properties (Sohn and Rajagopalan 2004). Conventional rheometry provides viscoelastic information over a limited frequency range and measures rheological properties under external perturbations, which may destroy the microstructure of materials. Recent instrumental improvements of microrheology techniques allow us to investigate the rheological properties of complex fluids on microscopic length scales by measuring the motion of probe particles (Amin et al. 2014; Amin et al. 2012; Hassan et al. 2005; Liang et al. 2015). Microrheology has been utilized to study structure and dynamics of polymers, colloids, emulsions, and proteins (Amin et al. 2012) (Elmendorp 1986; Moschakis 2013; Moschakis et al. 2006; Puertas and Voigtmann 2014; Xia et al. 1989), and it has advantages in terms of the (1) small amount of sample required, (2) short

acquisition times, (3) extended range of frequencies, and (4) sensitivity to the local microenvironment (Furst and Squires 2017; Krajina et al. 2017). Dynamic light scattering (DLS)-microrheology measures thermal fluctuations of probe particles with coherent laser light. The motion of the probe particles reflects the microstructure of the material, and is presented as the mean square displacement (MSD or $\langle \Delta x^2(t) \rangle$) as function of time (t) (Furst and Squires 2017):

$$\text{MSD} = \langle \Delta x^2(t) \rangle = 2dDt$$

where d is dimensionality of the motion and D is the diffusion coefficient of the probe particle. For a purely viscous medium, the diffusion coefficient of the probe particle can be estimated using the Stokes-Einstein relation (Furst and Squires 2017; Mason et al. 1996):

$$D = \frac{k_B T}{6\pi a \eta}$$

where k_B is Boltzmann's constant, T is temperature, a is the radius of probe particle, and η is the viscosity of the material. For a viscoelastic material, the time-dependent behavior of the MSD is bounded between that of a viscous Newtonian fluid and an elastic solid. If a material is purely viscous, the MSD will linearly increase with time. By contrast, if the probe

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particle is embedded in a purely elastic material, the MSD of the probe particle remains constant with time.

Laponite® has long been studied as a model colloid to probe properties of glasses and gels, owing to its rich physical properties. It has been used as a rheological modifier in a variety of industrial formulations such as coating, painting, and personal care products (Dávila and d'Ávila 2017; Gallegos and Franco 1999). Laponite® is a disk-shaped synthetic particle with an approximate thickness of 1 nm and diameter of 25 nm. The face of laponite® particles is negatively charged, while the charge of the rim of laponite® particle depends on pH (Thompson and Butterworth 1992). At $\text{pH} < 9$, the rim is partially positively charged, whereas at $\text{pH} > 9$, the rim is negatively charged. Laponite® dispersions exhibit rheological properties and aging behavior that are highly sensitive to pH, ionic strength, particle concentration, and the presence of polymers (Bandyopadhyay et al. 2006; Knaebel et al. 2000; Pozzo and Walker 2004; Ruzicka and Zaccarelli 2011; Shahin and Joshi 2012). During the aging process, the structure and properties of laponite® dispersions evolve with time due to local particle rearrangements to reach a structurally arrested state. At basic and low salt conditions, the interactions between laponite® particles are dominated by electrostatic repulsion, and the system evolves slowly to form a repulsive glassy state. However, the aging process is highly dependent on the particle concentration. Under salt-free conditions, 1 wt% laponite® in D.I. water reaches an attractive gel state over several weeks, while 3 wt% laponite® dispersion forms a repulsive glass within 24 h. At intermediate concentration, laponite® dispersion reaches an arrested state either by forming an attractive gel or a repulsive glass (Suman and Joshi 2018). Many researchers have investigated the aging behavior of laponite® dispersions using X-ray photon correlation spectroscopy (XPCS), small angle X-ray scattering (SAXS), rheological measurements, dynamic light scattering (DLS), and Monte Carlo simulations (Angelini et al. 2014; Atmuri et al. 2012; Baghdadi et al. 2008; Kishore et al. 2015; Li et al. 2005). The interactions between laponite® particles are found to be dominated by long-range screened electrostatic repulsion during the short-term aging process, and then dominated by orientational attraction, leading to the formation of attractive glasses at longer aging times. The interaction of laponite® particles can be also tuned by addition of a weakly absorbing polymer which influences the dynamics of aging process. Our group previously investigated the effects of aging behavior of laponite® dispersion in the presence of polyethylene oxide (PEO) at various molecular weights and concentrations using rheological measurements and DLS (Baghdadi et al. 2005, 2008; Zheng and Bhatia 2017). Studies have shown that the addition of high-molecular-weight PEO accelerated the aging process due to polymer-particle bridging. Whereas, addition of low-molecular-weight PEO slows down the aging process due to a polymer-induced depletion attraction.

In this study, we used DLS-microrheology to probe the microscale rheological behavior of laponite® dispersions at different laponite® concentrations and in the presence of PEO ($M_n = 20$ kg/mol). We first study the degree of heterogeneity of laponite® dispersions using a Gaussian function fit to the MSD distribution at a constant lag time. The MSD and microviscoelastic properties of laponite® dispersions in water at 1 wt%, 2 wt%, and 3 wt% are presented to explore the effects of particle concentration on aging behavior over 28 days. In addition, the aging behaviors of laponite® dispersions with the addition different amount of PEO are also examined. Our results show that the particle concentration and PEO concentration have significant effects on the aging process. In addition, there is some evidence for a phenomenon similar to a re-entrant glass transition at the microscale, although the properties measured via conventional bulk rheology and microrheology differ in magnitude.

Materials and methods

Materials

Laponite® RD was purchased from Southern Clay Products (Gonzales, TX). Sodium hydroxide (NaOH) was obtained from Sigma-Aldrich. A total of 640 nm carboxyl polystyrene was purchased from Invitrogen. Polyethylene oxide was purchased from Aldrich. All chemicals were used without purification.

Sample preparation

A total of 1 M NaOH solution was prepared by dissolving NaOH in 10 mL of D.I. water, and 200 mL of D.I. water was adjusted to pH 10. Laponite® was added to 20-mL water to reach the desired concentrations of laponite®, 1 wt%, 2 wt%, and 3 wt%. A T25 Basic UltraTurrax homogenizer was applied for 1 min to fully disperse laponite® in the water. Laponite® dispersions were stirred at a constant stirring rate for 20 min before filtering by a 0.45- μm filter to remove large aggregates. For the laponite® dispersions with PEO, a desired amount of PEO was added to 2 wt%-filtered laponite® dispersion and stirred for 30 min until PEO was fully dissolved. One drop of 0.65- μm carboxyl polystyrene (0.00975 solid%) was added to each sample as probe particles. Although we did not explore the impact of probe particle concentration, this is much lower than the concentration of laponite particles, and we expect that the probe particles will not impact the rheology. Approximately, 3 mL of each sample was transferred to a DLS cuvette and capped for microrheology measurements. These test tubes were stored in a drawer at room temperature. The time when the test tubes were placed in the sealed area was considered $t = 0$ for aging time. Throughout the paper, sample

names are given as $xLyPEO$, where x and y are the concentrations in wt% (e.g., 3 L for a dispersion of 3 wt% laponite, 2L0.25PEO for a dispersion containing 2 wt% laponite and 0.25 wt% PEO).

DLS-microrheology

DLS-microrheology employs a light source to scatter probe particles and a photon detector to detect the scattered intensity of the probe particle. In order to generate a normalized autocorrelation function ($g_1(\tau)$):

$$g_1(\tau) = g_1(0)e^{-q^2 \langle \Delta r(\tau)^2 \rangle / 6}$$

where τ is delay time, $g_1(0)$ is the autocorrelation function at $\tau = 0$, q is scattering vector, $q = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2}$, and $\Delta r(\tau)^2$ is the MSD of the probe particle.

For complex materials, the viscoelastic modulus $G^*(\omega)$ can be estimated using the generalized Stokes-Einstein relation (GSER) (Mason 2000; Mason and Weitz 1995),

$$G^*(\omega) = \frac{k_B T}{\pi a \langle \Delta r(\frac{1}{\omega})^2 \rangle \Gamma(1 + \alpha(\omega))}$$

where Γ is a gamma function due to Fourier transformation, ω is frequency ($\omega = \frac{1}{\tau}$), and $\alpha(\omega)$ is a variable between 0 and 1. The storage modulus (G') and viscous modulus (G'') of the complex materials can be expressed by the following:

$$G' = G^*(\omega) \times \cos\left(\frac{\alpha(\omega)\pi}{2}\right)$$

$$G'' = G^*(\omega) \times \sin\left(\frac{\alpha(\omega)\pi}{2}\right)$$

The limits $\alpha(\omega) = 1$ and $G' = 0$ indicate a purely viscous material. By contrast, $\alpha(\omega) = 0$ and $G'' = 0$ suggest a purely elastic material.

Microrheological measurements

The microrheological measurements of laponite® dispersions and laponite®-PEO dispersions were performed using the NanoBrook Omni (Brookhaven Instrument Inc., Holtsville, NY). The instrument is equipped with a 640-nm 35-mW diode laser, and all measurements were conducted at 25 °C. Before each measurement, the sample was placed in the sample holder in the instrument for 5 min to assure that there was no motion from sample loading. The measurements were performed for samples after 1 day and 28 days of storage at room temperature.

Bulk rheological measurements

The rheological measurements were conducted using a stress-controlled rheometer (TA Instruments, ARG2) using a 20-mm parallel plate geometry, after the samples were aged for 28 days. Amplitude sweeps were performed to determine the linear viscoelastic (LVE) regime. Frequency sweeps were performed within the LVE regime to determine the dynamic moduli (G' and G''). All experiments were conducted at 25 °C, and all samples were equilibrated for 5 min to assure that the samples were stabilized before measurements. Solvent traps were applied during measurements to prevent water evaporation.

Results and discussion

Dynamic heterogeneity of laponite® dispersions

To determine dynamic heterogeneity of laponite® dispersions, samples were measured 12 times using DLS-microrheology, varying the position of the sample, and the MSD of the 640 nm probe particle at 100 μ s was utilized to generate an ensemble-averaged MSD distribution (Xu et al. 2002). Figure 1 shows the MSD of probe particles in laponite® dispersions as a function of lag time at different laponite® concentrations after 1 day of storage. The insets are the ensemble-averaged MSD distribution of each sample at 100 μ s fitted by a Gaussian distribution function. For 1 L and 2 L after 1 day of aging, MSD of these repeating measurements were overlapping, and the ensemble-averaged MSD distribution was narrow and symmetric (Fig. 1a and b). This observation indicates that the dynamics of probe particles in these samples are homogeneous. By comparison, the MSD for 3 L deviated between each measurement, and the ensemble-average MSD distribution possessed two major peaks at 0.9 and 1.1 and displayed an unsymmetrical distribution, indicative of a dynamically heterogeneous structure in the 3 L dispersion.

The dynamic heterogeneity of laponite® dispersions after 28 days of storage was also investigated as shown in Fig. 2. The curves of MSDs of 1 L were overlapping, while the curves of MSDs for 2 L and 3 L varied between measurements. The ensemble-average MSD distribution of 1 L displayed a narrow but unsymmetrical distribution, the ensemble-average MSD distribution of 2 L showed a wider and unsymmetrical distribution, and the ensemble-average MSD distribution of 3 L displayed a wide and unsymmetrical distribution. These results indicate a higher degree of dynamic heterogeneity of laponite® dispersions upon aging. Our results are in agreement with a report by Jabbari-Farouji (Jabbari-Farouji et al. 2012), where they found a growing dynamic heterogeneity in an aged laponite dispersion. The

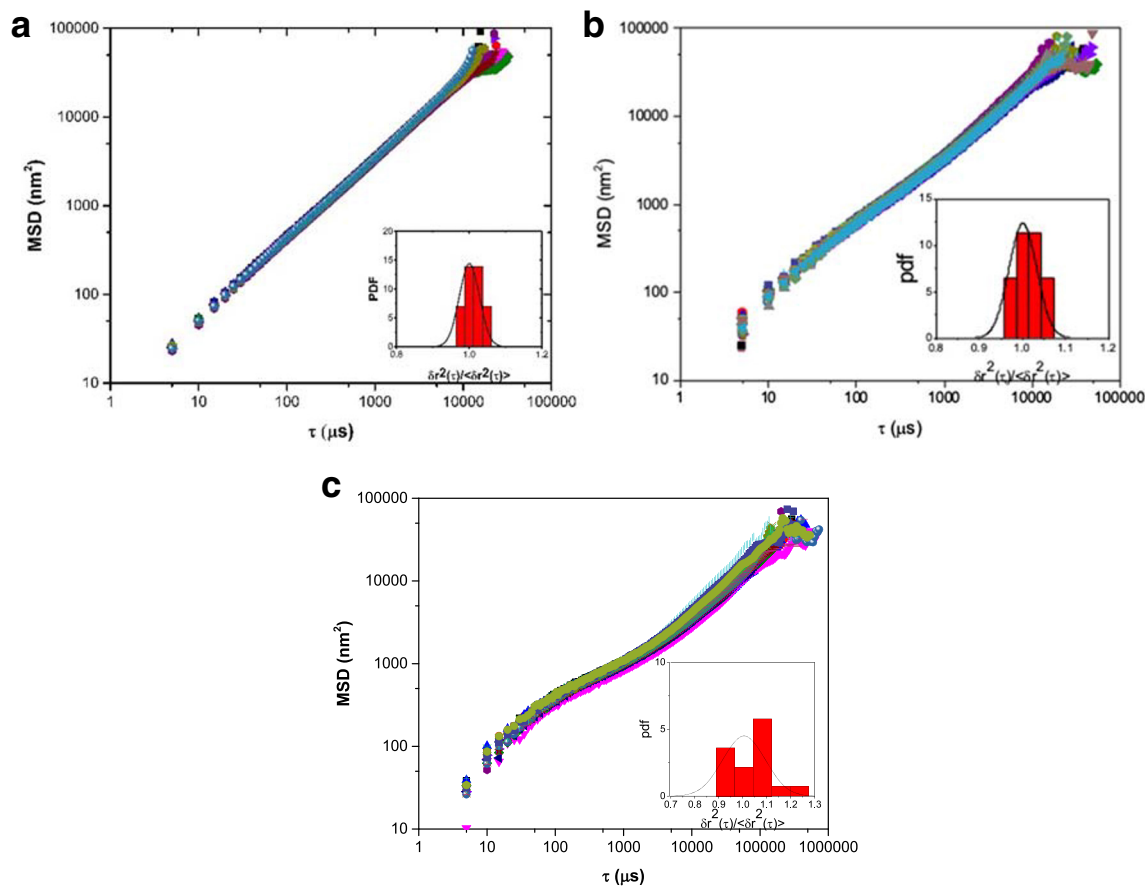


Fig. 1 MSD of probe particle of 12 measurements in (a) 1 L, (b) 2 L, and (c) 3 L at pH 10 after 1 day of aging at several positions and repeats within the sample. The insets are ensemble-average single particle distribution of MSD at 100 μs fitted with a Gaussian distribution function (black curve)

heterogeneity is attributed to particle rearrangements during aging process, whereby particles overcome cage formed by the neighboring particle due to the local structure and form a new configuration which would be discussed in the next section. These results suggest that laponite® in aqueous dispersions forms a heterogeneous structure at 3 wt% and after 28 days of storage, which could be due to the formation of a structurally arrested state after particle rearrangement. In the following sections, the microstructure and dynamics of laponite® dispersions and laponite®/PEO mixtures were monitored using average MSD and viscoelastic properties measured by DLS-microrheology to study the aging behavior of laponite® dispersions.

The effects of laponite® concentration on the aging behavior of laponite® dispersions

Figure 3 shows the dependence of MSD of probe particles on laponite® concentration after 1 day of storage. As shown in Fig. 3a, the MSD of 1 L and 2 L increased linearly with respect to time, which correlates to the free diffusion of particles in these dispersions and is consistent with characterizing them as Newtonian fluids. At a laponite® concentration of 3 wt%

(3 L), the MSD displays three regimes of time dependence, $MSD \approx \tau^\alpha$ ($0 < \alpha < 1$). At short lag time, the logarithmic MSD of probe particles increases linearly with lag time with slope close to 1, denoted as a sub-diffusive regime. In this regime, the particle freely diffuses in the local environment, and the motion of particle is dominated by Brownian motion. As time evolves, the MSD gradually curves with lag time, becoming more weakly dependent on time. We refer to this as the constrained regime. The reduction of the motion in this regime is ascribed to the motion of probe particle restrained by the surrounding environment, which also determines the viscoelastic properties of the material. At longer lag times, the MSD increases rapidly with time, which is defined as a super-diffusive regime. In this region, probe particles move faster than Brownian motion due to a rising non-Brownian force from the local environment. The framework of continuous-time random walks (CTRW) predicts this super-diffusive motion due to the breaking of the local structure allowing particle flow (Puertas and Voigtmann 2014; Schroer and Heuer 2013). Below, we discuss the motion of the probe particles in the first two regimes, the sub-diffusive regime and the constrained regime, to elucidate the microstructure and dynamics of laponite® dispersions.

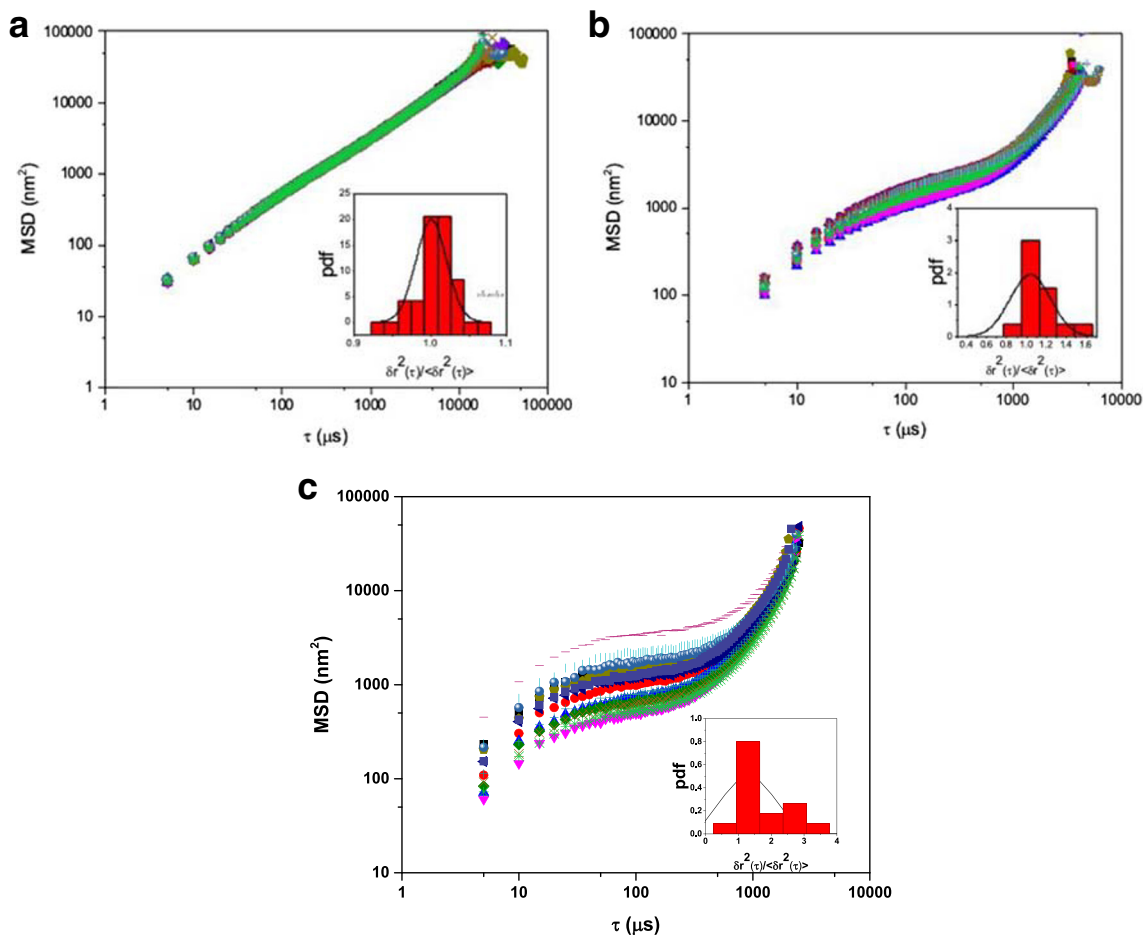
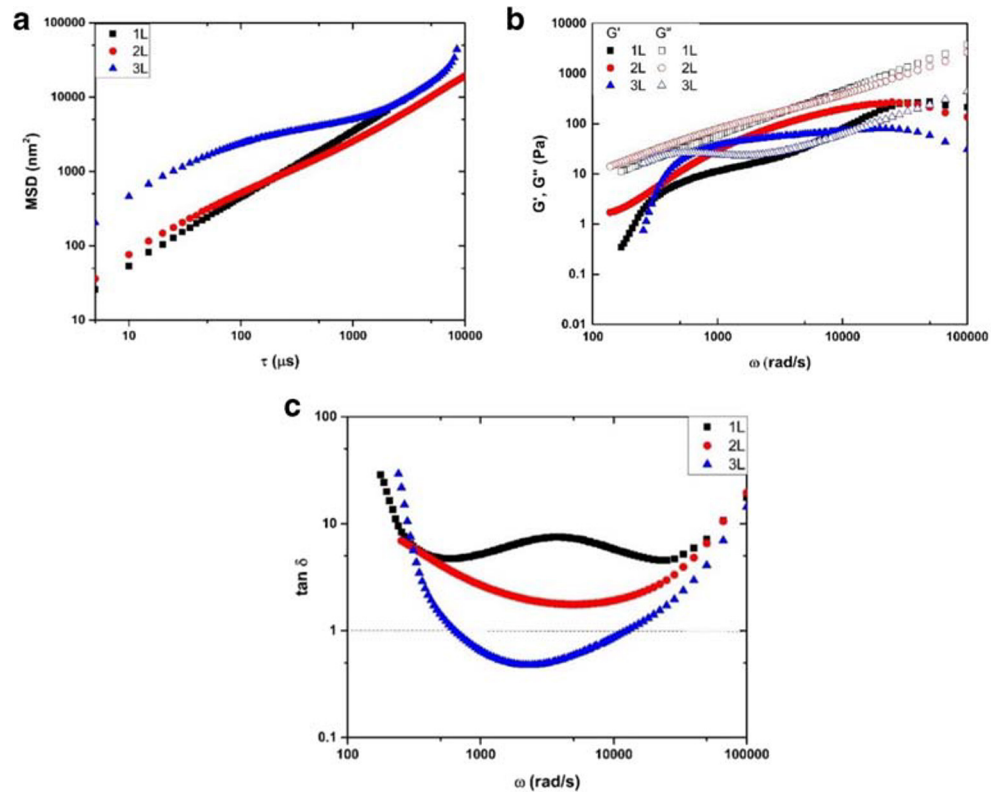


Fig. 2 MSD of probe particle at several positions and repeats within the sample for (a) 1 L, (b) 2 L, and (c) 3 L at pH 10 after 28 days of aging. The insets are ensemble-average single particle distributions of MSD at 100 μs fitted with a Gaussian distribution function (black curve)

To investigate the aging behaviors of laponite® dispersions, G' and G'' derived from DLS-microrheology of laponite® dispersions are plotted as a function of frequency after 1 day of storage (Fig. 3b). As discussed above, the motion of the probe particle in the constrained regime was governed by the microviscoelastic properties of the materials, where the motion of particle solely relies on the local structure of the material. For 1 L and 2 L, $G'' > G'$ over the measured range, indicative of predominantly viscous behaviors. On the other hand, 3 L possesses $G' > G''$ at intermediate frequency regime (constrained regime), indicative of an elastic solid. However, $G'' > G'$ at high frequency (sub-diffusive regime), reflecting a viscous behavior of internal structure. This results suggests that 3 L forms a glassy state after 24 h, which is consistent with our previous bulk rheology studies (Baghdadi et al. 2008). To have a more direct observation whether the tested systems behave as elastic solids or viscous liquids, $\tan \delta$ is presented in Fig. 3c. Over the measured frequency range, $\tan \delta$ values for 1 L and 2 L are greater than 1. On the other hand, $\tan \delta$ values for 3 L showed both elastic solid and viscous liquid behaviors.

Figure 4 illustrates the MSD, dynamic moduli, and $\tan \delta$ of probe particle in various concentrations of laponite® dispersions after 28 days of storage. The MSD of 1 L, 2 L, and 3 L clearly shows three distinct regimes of time dependence (Fig. 4a) that vary with the concentration of laponite®. In the sub-diffusive regime, the probe particle freely diffuses in all samples. The MSD of 3 L in the constrained regime becomes independent of the lag time due to the probe particle being entrapped by the surrounding environment. By contrast, the MSD of 1 L and 2 L moderately depend on the lag time in the constrained regime, suggesting that the motion of probe particle is slowed by the surrounding environment, but is not arrested or entrapped. In the super-diffusive regime, the particle motion dramatically increases again. Figure 4b and c show the microviscoelastic properties of these laponite® dispersions after 28 days of storage. In the intermediate frequency range, G' of 2 L and 3 L showed a weak dependence on frequency, and G'' displayed a minimum at higher frequency, which is often observed in glassy structures (Atmuri et al. 2012). Over this range, $G' > G''$ and $\tan \delta < 1$, reflecting an elastic solid behavior. At high frequency,

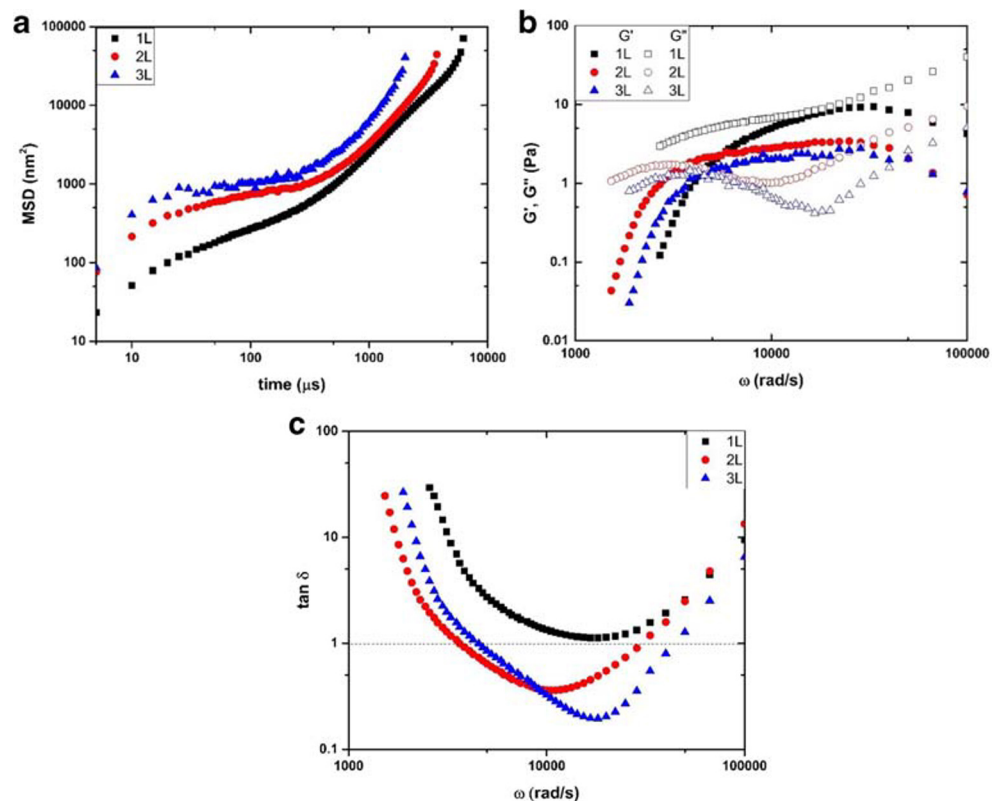
Fig. 3 The (a) MSD of probe particle in various concentrations of laponite® dispersions, (b) $G'(\omega)$ and $G''(\omega)$, and (c) $\tan \delta$ of laponite® dispersions at pH 10 after 1 day of aging. The concentrations of laponite dispersions are listed in the legend



$G'' > G'$ and $\tan \delta > 1$ for 2 L and 3 L, indicative of viscous liquid behaviors. Interestingly, although three different regimes of MSD were also observed for 1 L after

28 days of storage, $G'' > G'$ and $\tan \delta > 1$ over measured frequency range. This observation indicates that 1 L exhibited a viscous liquid behavior after 28 day of aging.

Fig. 4 The (a) MSD of probe particle in various concentrations of laponite® dispersions, (b) $G'(\omega)$ and $G''(\omega)$, and (c) $\tan \delta$ of laponite® dispersions at pH 10 after 28 days of aging. The concentrations of laponite dispersions are listed in the legend



To have a detailed understanding of microstructure and microdynamics of laponite® dispersions, α in the sub-diffusive regime and the constrained regime was calculated for all samples after 1 day and 28 days of storage (Table 1). At low concentration (1 wt% and 2 wt%), only a diffusive regime was observed at day 1 with $\alpha \approx 1$, $G'' > G'$, and $\tan \delta > 1$ over the measured range. Laponite® dispersions exhibited liquid-like behavior, where the motion of particles is dominated by Brownian motion. As particle concentration increases, reduction in α of the sub-diffusive regime and the constrained regime was observed and $G'' < G'$ and $\tan \delta < 1$, indicative of a rheological solid-like behavior. We attribute the transition from a liquid-like behavior to a solid-like behavior at high concentration to the repulsive interparticle interactions. At low concentration, laponite® dispersions form isotropic liquids, where the probe particles freely diffuse. As the particle concentration increases, a glassy state is formed due to electrostatic repulsive interactions between laponite® particles, and the probe particles are trapped by the neighboring particles (Mongondry et al. 2005; Ruzicka and Zaccarelli 2011). After 28 days of storage, α of all samples reduces in the sub-diffusive regime (α_{sub}) and the constrained regime (α_{cons}) corresponding to further restriction of motion of the probe particle by the surrounding structure. The reduction in α in the constrained regime suggests increasing of “hardness” of the local structure owing to its aging behavior. The decrease of α in the sub-diffusive regime correlates to an increase in the bulk viscosity of laponite® dispersion upon aging which limits the motion of probe particle. Nevertheless, 1 L after 28 days of storage behaves as a rheological liquid featuring three regimes of MSD. The motion of probe particle can be affected by particle clusters formed by a weak attraction between particles (Sciortino et al. 2004). By contrast, 2 L and 3 L exhibited solid-like behaviors ($G'' < G'$ and $\tan \delta < 1$) after 28 days of storage (Baghdadi et al. 2008). Baghdadadi proposed two different mechanisms for the formation of glassy states in 2 L and 3 L upon aging. At 2 wt%, laponite® dispersion transition from an anisotropic liquid to a glassy state due to the coexistence of short-range electrostatic attraction and long-range electrostatic repulsion. At short aging time, laponite® dispersions form interparticle clusters/aggregates

by short-range electrostatic attraction. Upon aging, the formation of repulsive glass is a result from a large effective particle size after the dissociation of the interparticle aggregates. At high concentration, the formation of a glassy state is driven by the electrostatic repulsion between laponite® particles resulting in a large effective size of laponite® particle.

In addition to the study of microstructure, DLS-microrheology can be used to investigate the microdynamics of the laponite® dispersions. Previous studies showed a two-step relaxation processes for glassy colloid-polymer systems (Baghdadi et al. 2008; Bellour et al. 2003; Kishore et al. 2015; Knaebel et al. 2000; Zheng and Bhatia 2017). Theoretically, a fast relaxation process is attributed to the diffusion of a particle in the cage formed by the nearest neighboring particles, while a slow relaxation process describes the potential of a particle to break the cage and diffuse away. In DLS-microrheology, the relaxation time (τ) for the fast relaxation process and the slow relaxation process is determined by the frequency at crossover points, $\tau = \frac{1}{\omega}|_{G'=G''}$ (Cardinaux et al. 2002). The first crossover point characterizes the slow relaxation time (τ_2), whereas the second crossover point estimates the fast relaxation time (τ_1). At day 1, 3 L behaves as a rheological solid with $\tau_1 = 89 \mu\text{s}$ and $\tau_2 = 1495 \mu\text{s}$. Upon 28 days of aging, both 2 L and 3 L exhibit solid-like behaviors. The τ_1 and τ_2 for 2 L are $35 \mu\text{s}$ and $283 \mu\text{s}$, while the τ_1 and τ_2 for 3 L are $23 \mu\text{s}$ and $218 \mu\text{s}$. Both fast and slow relaxation times decrease with an increase in concentration and aging time. This is somewhat unexpected, because as the samples age, the structure consolidates, which would result in the increase in the relaxation time. However, it may be that these denser domains constrict the motion of the probe particles, leading to the decrease observed.

The effects of PEO concentration on the aging behavior of laponite® dispersions

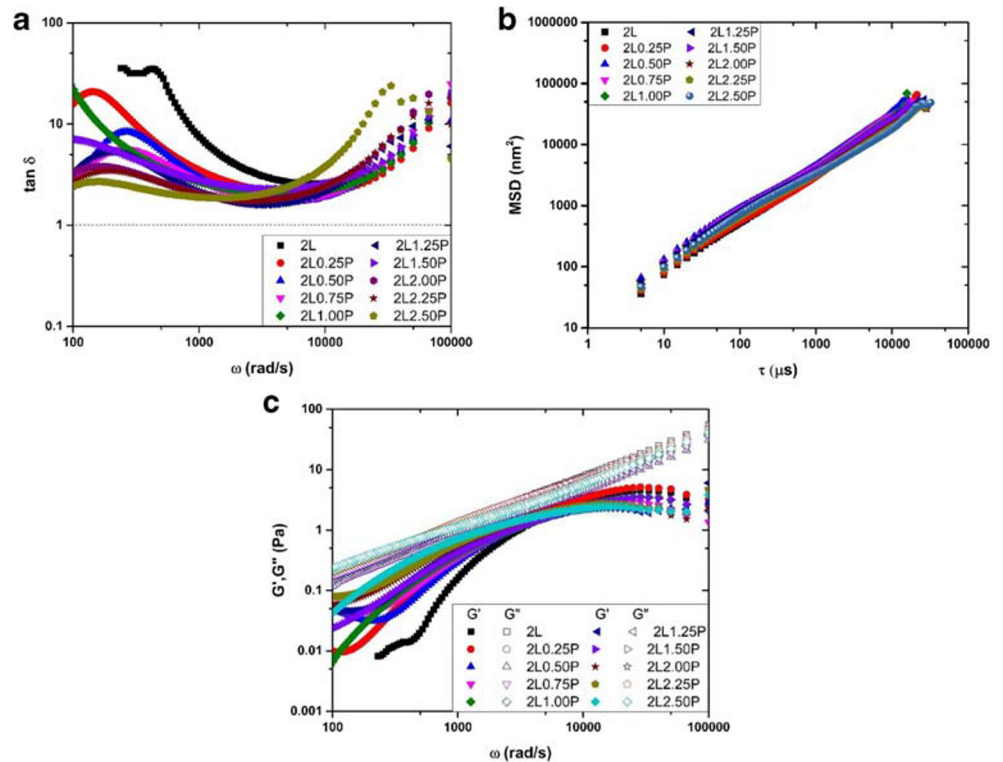
The aging behavior of laponite® dispersions can be retarded or accelerated in the presence of weakly absorbing PEO. The absorption of PEO on laponite surfaces tailors the microstructure and microdynamics of laponite® dispersions, resulting in a change in the aging behaviors of laponite® dispersions. In this section, the effects of 20 K PEO on the microstructure and microdynamics of laponite® dispersions were explored.

The microrheological results for 2 wt% laponite with various concentrations of 20 K PEO after 1 day and 28 days of storage are reported in Figs. 5 and 6. After 1 day of storage, MSD of each sample displayed a linear increase with lag time with $\alpha \approx 0.8$, $G'' > G'$, and $\tan \delta > 1$ over the entire frequency range. The motion of probe particles is dominated by Brownian motion, representative of viscous fluid behavior. After 28 days of storage, three different regimes of MSD were observed. The motions of probe particles in the lap/PEO

Table 1 The parameter α for 1 L, 2 L, and 3 L at 1 day and 28 days of aging

(Lap) (wt%)	Day 1		Day 28	
	α_{sub}	α_{cons}	α_{sub}	α_{cons}
1	0.92	N/A	0.71	0.58
2	0.79	N/A	0.54	0.28
3	0.73	0.30	0.32	0.25

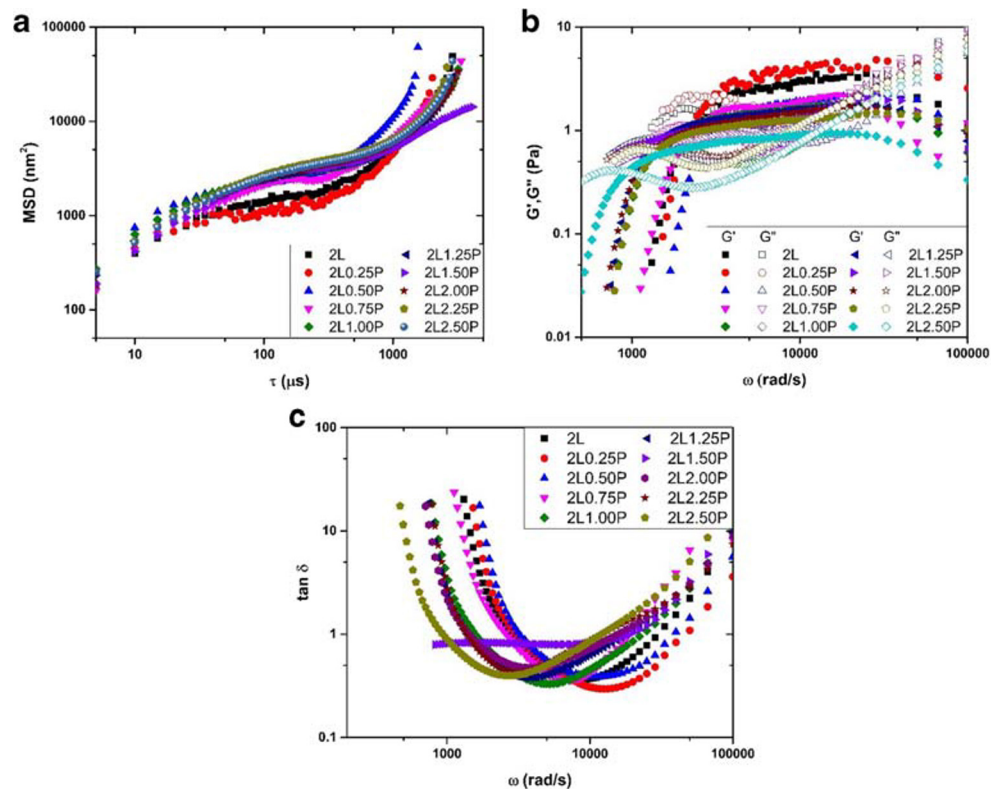
Fig. 5 **a** MSD of probe particle in lap/PEO systems, and **(b)** $G'(\omega)$ and $G''(\omega)$ of lap/PEO dispersions at a constant laponite concentration and varying PEO concentration at pH 10 after 1 day of storage. The concentrations of PEO are listed in the legend



systems are significantly influenced by PEO concentrations, showing that the microstructure and microdynamics of lap/PEO dispersions are strongly dependent on the PEO concentration. The MSD of 2 L and 2L0.25PEO in the constrained

regime are slightly dependent on the lag time, and the MSD of remaining samples in the constrained regime evolve with lag time. The microviscoelastic properties of lap/PEO samples are presented in Fig. 6b and c. All samples exhibited $G' > G''$ and

Fig. 6 **a** MSD of probe particle in lap/PEO systems, **b** $G'(\omega)$ and $G''(\omega)$, and **c** $\tan \delta$ of lap/PEO dispersions at a constant laponite concentration and varying PEO concentration at pH 10 after 28 days of storage. The concentrations of PEO are listed in the legend



tan $\delta < 1$ in the constrained regime and $G' < G''$ and tan $\delta > 1$ in the sub-diffusive regime, suggesting the formation of glassy states upon aging. Interestingly, in the presence of 1.50PEO, $G' \approx G''$ and tan δ remained constant at lower frequency which is characteristics of sol-gel transition (Suman and Joshi 2018; Winter and Chambon 1986). The α parameters in the sub-diffusive regime and the constrained regime, in combination with τ_1 and τ_2 after 28 days of storage, were estimated and utilized to elucidate PEO effects on the aging behavior of laponite® dispersion.

The non-monotonic effects of PEO concentration in the aging behavior of laponite® dispersions are illustrated in Fig. 7a. In the neat laponite dispersion, 2 L formed a repulsive glassy state with $\alpha_{sub} = 0.2$ and $\alpha_{cons} = 0.54$. The neat laponite dispersion formed a repulsive glassy state after 28 days of storage. As 0.25 wt% PEO added to the laponite system, the decreases in α_{sub} and τ_1 reflect restriction of particle motion within the microstructure. As the PEO concentration increases to 0.50 wt%, α_{sub} and τ_1 increase, suggesting that the particles diffuse more quickly within the microstructure. Nevertheless, α_{cons} and τ_2 exhibit a different PEO concentration dependence at low PEO concentration. In the presence of a small amount of PEO, α_{cons} and τ_2 increase, which may indicate a more fluid or “looser” microstructure at low PEO concentration. As the concentration of PEO increased to 0.75 wt%, α_{cons} decreases

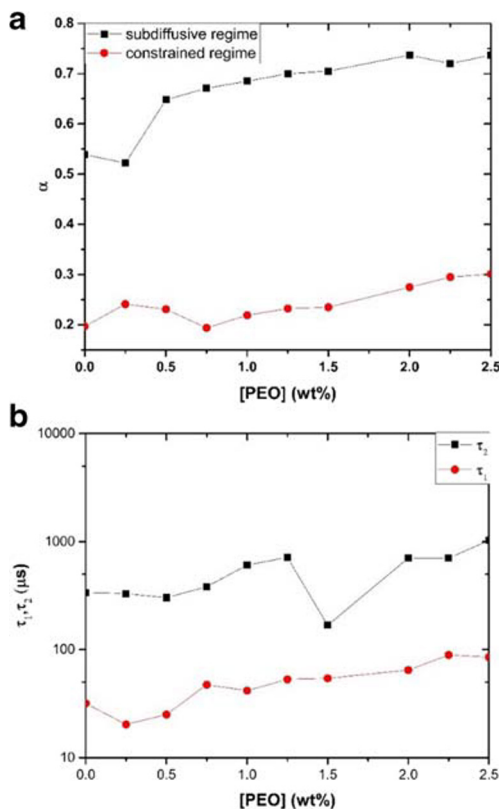


Fig. 7 Variation of (a) α of the sub-diffusive regime and the constrained regime and (b) τ_1 and τ_2 on the PEO concentration for 2 wt% laponite and PEO samples after 28 days of storage

owing to the formation of more compact, denser microstructure. As the PEO concentration further increases, α_{cons} and τ_2 again increase. This type of non-monotonic dependence of the dynamics on PEO concentration has also been observed via conventional rheology (Kishore et al. 2015)

We speculate that the interactions between PEO chains and laponite® particles change the microstructure and microdynamics of laponite®/PEO dispersion. The neat laponite dispersion forms a repulsive glassy state after 28 day of storage due to coexistence of short-range attraction between laponite® particles and long-range repulsion between laponite aggregates. In the presence of PEO, PEO chains “wrap” around the laponite surface forming a steric barrier (Baghdadi et al. 2005; Mongondry et al. 2004; Nelson and Cosgrove 2004). Initial addition of PEO screens the electrostatic repulsion and reduces the effective size of the particle, leading to a softer local structure (higher α_{cons}). As PEO concentration increases to 0.75 wt%, PEO chains surround around the aggregates and form a denser network. Upon adding more PEO, laponite® particles tend to rearrange and

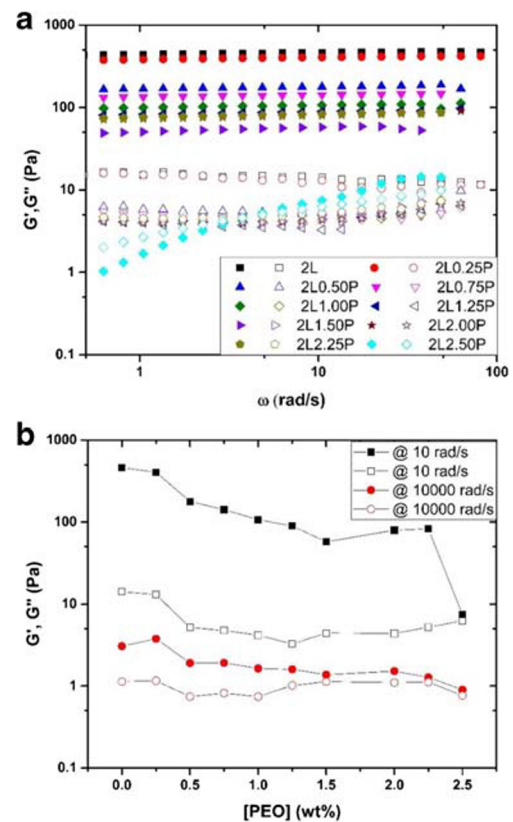


Fig. 8 a Bulk rheological measurement of 2 wt% laponite® and various concentrations of PEO after 28 day of aging. G' (closed symbol) and G'' (open symbol) are plotted as a function of frequency, with the concentration of PEO listed in the legend. b Comparison of microrheology (red) and bulk conventional rheology (black) results. Viscoelastic moduli at the frequencies indicated in the legend, 10 rad/s and 10,000 rad/s, as a function of PEO concentration

escape from the laponite® aggregates, leading to weaker local structure and retarding the aging behavior.

The bulk rheology of 2 wt% laponite® and various concentrations of PEO after 28 days of storage was also investigated to study the bulk rheological behavior of lap/PEO system. As shown in Fig. 8a, all samples behave rheologically as elastic solids; G' remains constant over the measured frequency range, and G'' exhibits a shallow minimum which is commonly found for soft glassy systems (Cipelletti and Ramos 2005). However, as PEO concentration reaches 2.5%, the system behaves as a viscous fluid due to phase separation. Additionally, G' and G'' of bulk rheology at 10 rad/s and G' and G'' of microrheology at 10000 rad/s are plotted in Fig. 8b to compare the bulk viscoelastic properties to the microviscoelastic properties. Both bulk rheology and microrheology results show addition of 20 K g/mol. PEO decreases the elasticity and retards the aging behavior. However, the dynamic moduli of bulk rheology are 2 orders of magnitude higher than that of microrheology of lap/PEO samples. This is not unexpected for passive microrheology of glassy and gel-like systems; Furst and Squires discuss possible causes of this and describe the use of microrheology as more of an indexing measurement to detect the onset of gelation or follow liquid-gel transitions in these types of systems (Furst and Squires 2017). Our results confirm that DLS-microrheology can be used to qualitatively study the microrheological properties of samples beyond the gel point.

Conclusions

We show that DLS-microrheology can be used to monitor the aging behaviors of laponite® dispersions at various laponite® particle concentrations and in the presence of PEO. The use of DLS-microrheology enables us to probe the structure and dynamics of laponite® dispersions on microscopic length scale. An increase in the dynamic heterogeneity of laponite® dispersions after 28 days of aging was observed. Laponite® dispersions formed repulsive glassy states at high concentration and long aging times. Increasing particle concentration accelerates the aging process and leads to the formation of dense microstructures. However, the addition of 20 kg/mol PEO shows non-monotonic effects on the microstructure and microdynamics of laponite® dispersions. All samples reach a structural arrested state after 28 days of storage. Initial addition of PEO melts the glassy state. Increasing PEO concentration to 0.75 wt% leads to the formation of a denser structure. Further increase PEO concentration further decreases the elasticity of the material.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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