ELECTRONIC SUPPLEMENTARY INFORMATION

Influence of medium structure on the physicochemical properties of aging colloidal dispersions investigated using the synthetic clay Laponite®

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1. EFFECTS OF ADDITIVES

1(a) Photon correlation spectroscopy study

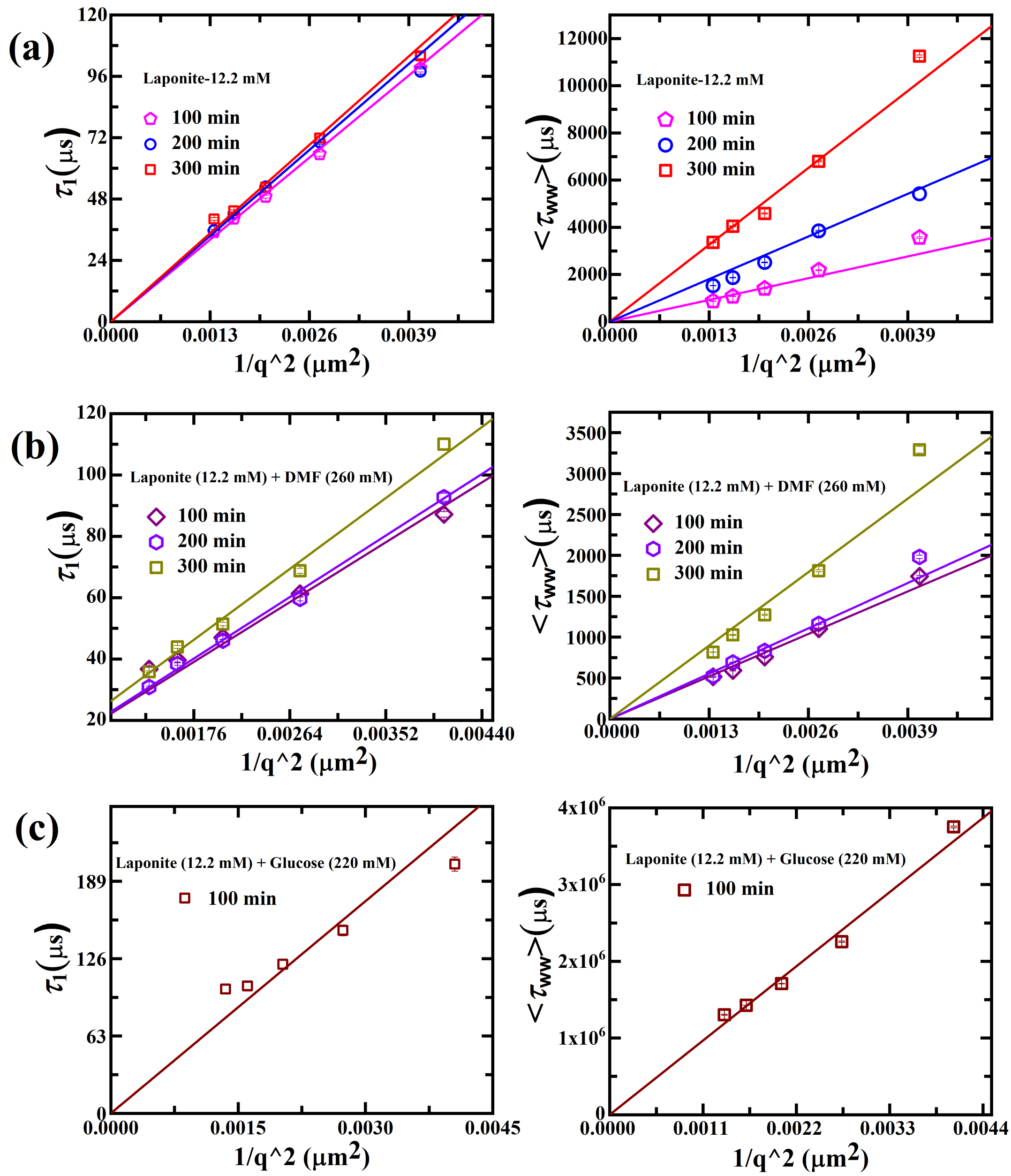

Figure S1: The diffusive nature of the fast β- relaxation time, τ_1, and mean slow α- relaxation time, $< \tau_{ww} >$ (left and right panels respectively), are shown for (a) a 12.2 mM Laponite dispersion and Laponite dispersions in the presence of (b) DMF (260 mM), (c) glucose (220 mM) at different waiting times t_w. The solid lines are linear fits passing through the origin.

The straight line fit passing through the origin demonstrates the diffusive nature of both relaxation processes [1]. The reciprocal of the slope of each plot provides diffusion coefficients for both relaxation processes i.e. $D_1 = 1/\tau_1 q^2$ and $D_{ww} = 1/ < \tau_{ww} > q^2$, where D_1 and D_{ww} are the diffusion coefficients corresponding to β- (diffusion inside the cage) and α- (cooperative diffusion) relaxation processes respectively.

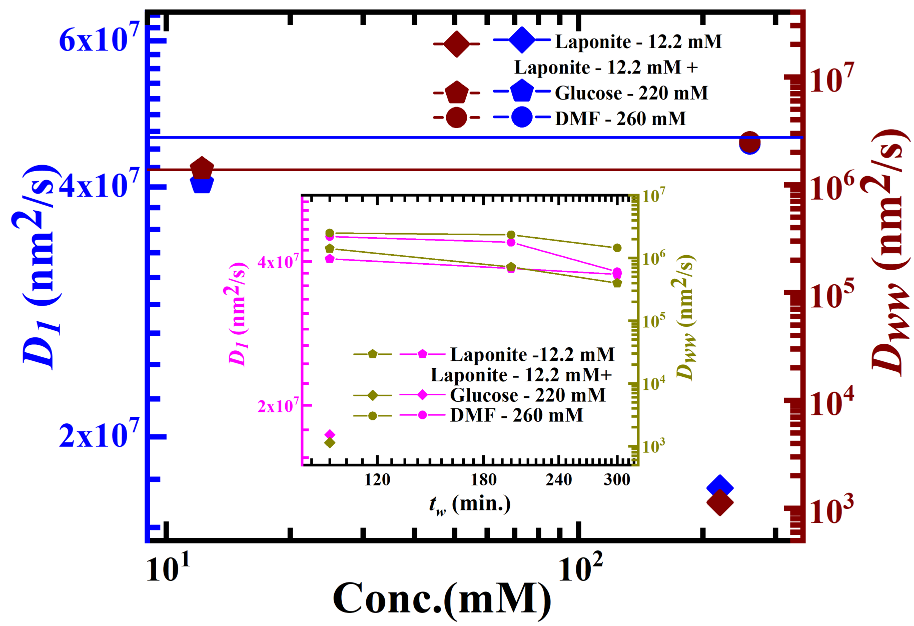

Figure S2: Diffusion coefficients corresponding to β- (D_1) and slow α- (D_{ww}) relaxation processes for 12.2 mM aqueous Laponite dispersions and Laponite dispersions in the presence of 220 mM glucose and 260 mM DMF at $t_w = 100$ min. The inset shows D_1 and D_{ww} *vs.* waiting time t_w for 12.2 mM aqueous Laponite dispersions and Laponite dispersions in the presence of glucose and DMF.

1(b) Debye screening lengths calculation

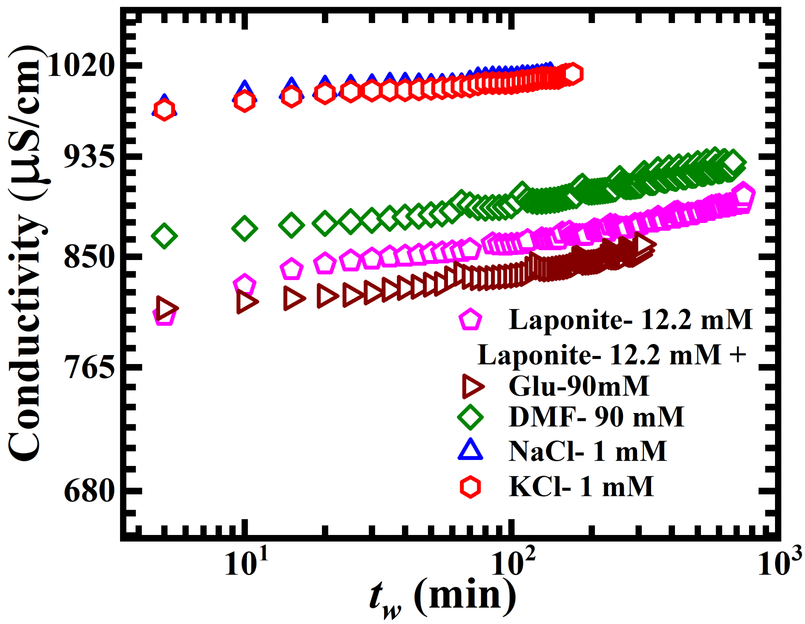

Figure S3: Conductivity of 12.2 mM aqueous Laponite dispersions in the presence of different additives as a function of waiting time t_w.

The Debye screening lenghts can be estimated using the relation: $\kappa^{-1} = (\epsilon_0 \epsilon_r k_B T / \Sigma_i (z_i e)^2 n_i)^{1/2}$ [2], where ϵ_0, ϵ_r, k_B, z_i, n_i and e are the permittivity of free space, relative permittivity, Boltzmann constant, valency of ith ion, total number density of the ith ion and electron charge respectively. The Na^+ ions in the Laponite dispersions are contributed by the externally added NaCl and the dissociation of Na^+ from the Laponite surface. The concentration of Cl^- (which is contributed only by the added salt) can be computed from the concentration of the added salt. Concentration of Na^+ can be calculated using the relation: $\sigma = e(\mu_{Na} n_{Na} + \mu_{Cl} n_{Cl})$ [3], where σ is the conductivity of the system and mobilities of Na^+ and Cl^- are given by $\mu_{Na} = 5.19 \times 10^{-8}$ m^2/sV and $\mu_{Cl} = 5.19 \times 10^{-8}$ m^2/sV [4] respectively. In the presence of KCl, the concentration of Na^+ can be estimated using: $\sigma = e(\mu_{Na} n_{Na} + \mu_K n_K + \mu_{Cl} n_{Cl})$, where mobility of K^+ is $\mu_K = 7.62 \times 10^{-8}$ m^2/sV [4].

1(c) Rheometry

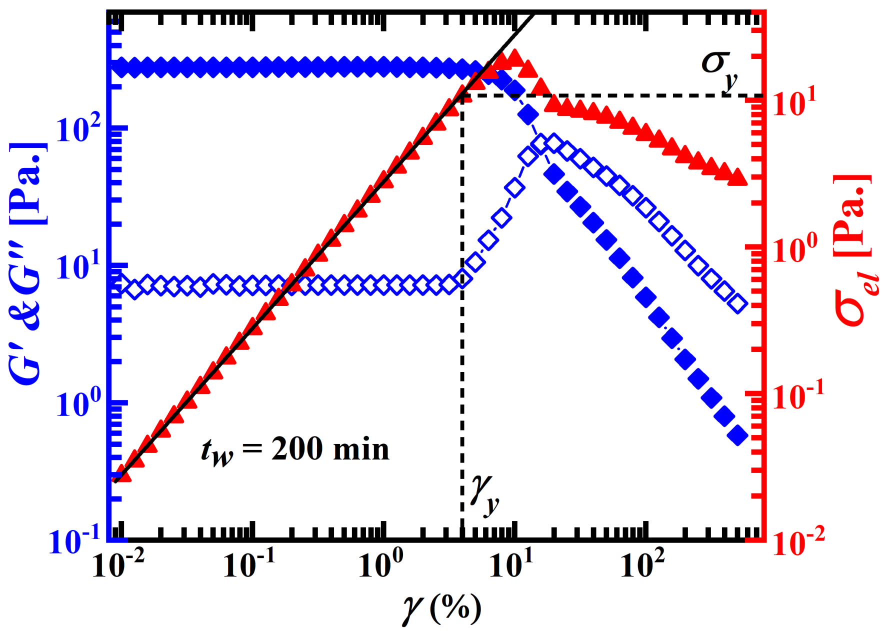

Figure S4: Viscoelastic moduli, G' and G'' (represented by solid and open symbols in blue respectively), and elastic stress, σ_{el} (red), of 12.2 mM aqueous Laponite dispersions in the presence of 2 mM NaCl at $t_w = 200$ min. The horizontal and vertical dashed lines represent yield stress, σ_y, and yield strain, γ_y, respectively.

The elastic stress, $\sigma_{el} = G' \times \gamma$, which separates the contribution of the elastic stress from the total stress, is plotted as a function of γ (Figure S4). The value of σ_{el} at which the straight line fit to σ_{el} *vs.* γ deviates by more than 3% from the prediction of Hooke's law is defined as the yield stress, σ_y, while the corresponding γ is the yield strain, γ_y.

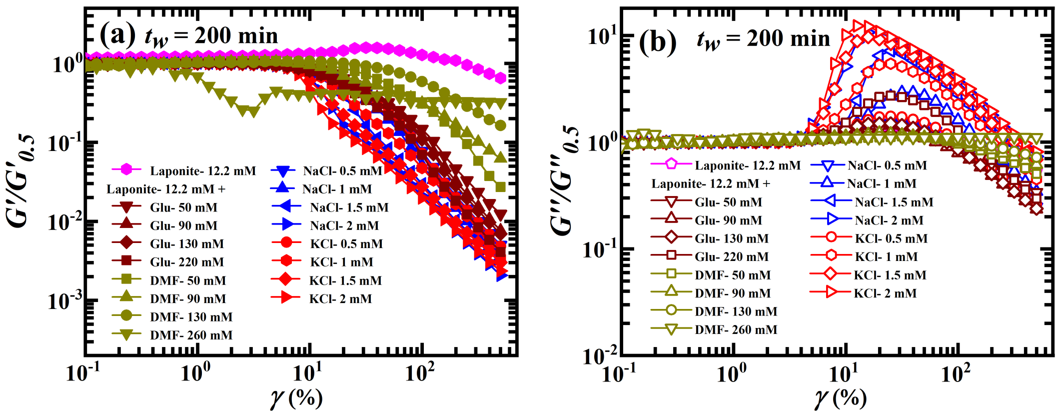

Figure S5: (a) and (b) Normalized storage ($G'/G'_{0.5}$) and loss ($G''/G''_{0.5}$) moduli *vs.* applied strain amplitude γ for aqueous Laponite dispersions with and without additives at $t_w = 200$ min. Here, $G'_{0.5}$ and $G''_{0.5}$ are the values of the storage and loss moduli at strain 0.5%. The strain amplitude sweep data has been normalized following the procedure proposed in [5].

1(d) Cryo-SEM Images

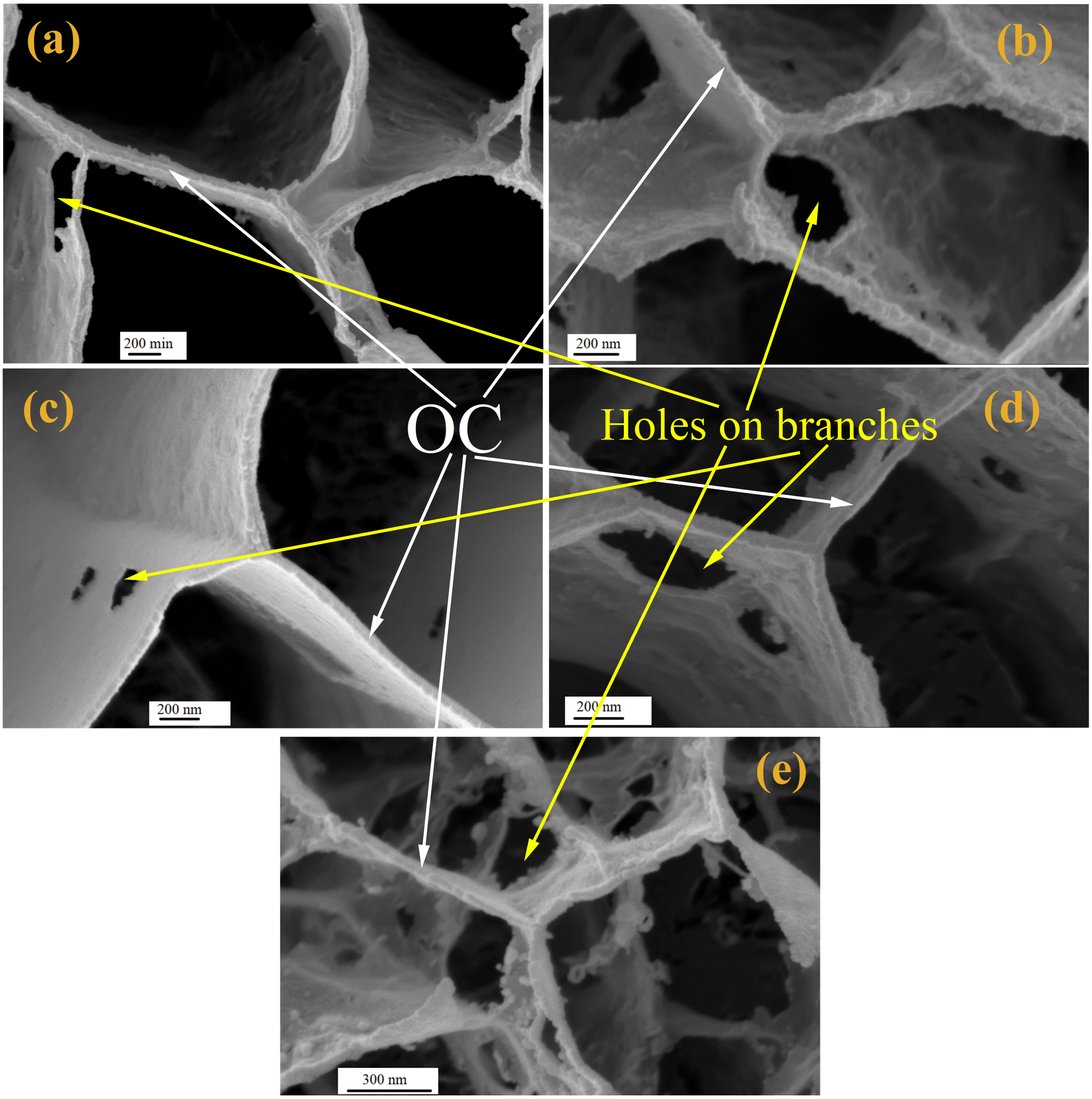

Figure S6: Magnified cryo-SEM micrographs for (a) a 12.2 mM aqueous Laponite dispersion and Laponite dispersions with (b) 90 mM glucose, (c) 90 mM DMF, (d) 1 mM NaCl and (e) 1 mM KCl at $t_w = 24$ h. OC refers to overlapping coin configurations of Laponite platelets.

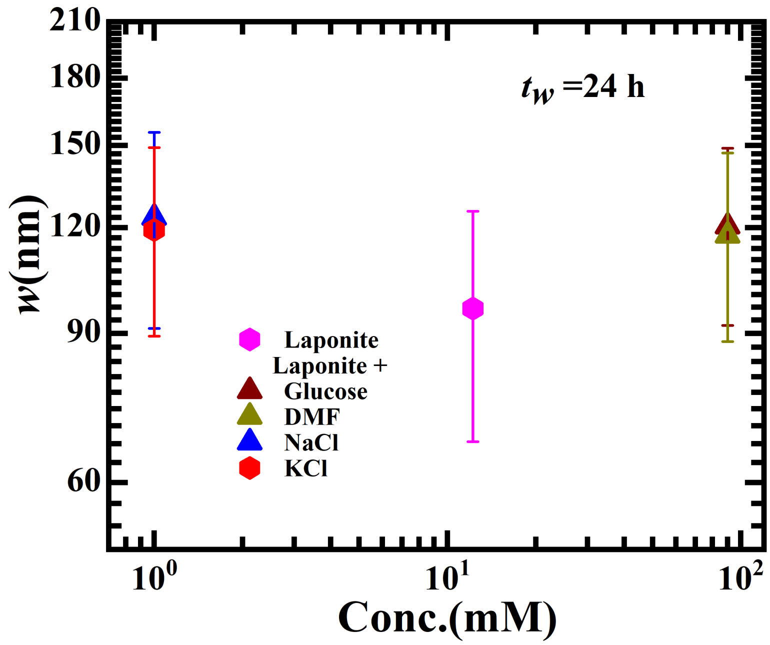

Figure S7: Network branch thickness for 12.2 mM Laponite dispersions with and without additives at $t_w = 24$ h.

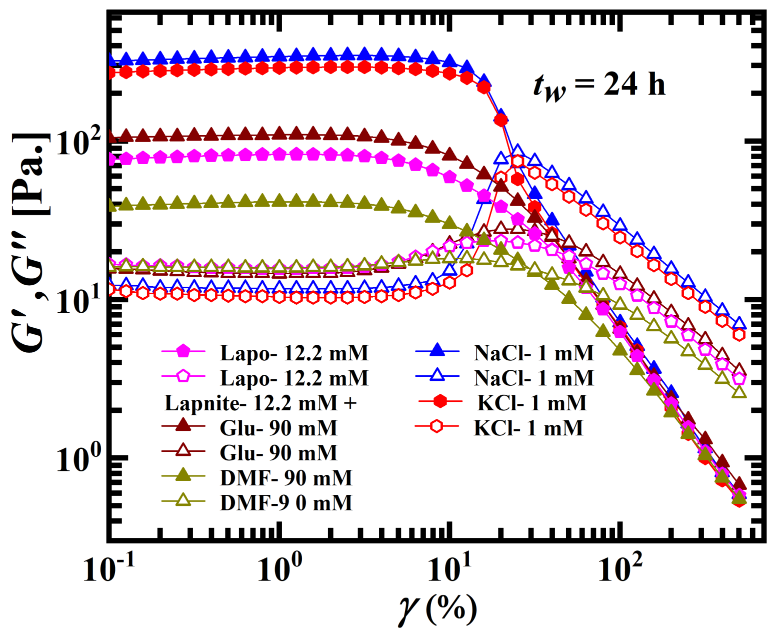

Figure S8: Storage modulus G' (solid symbols) and loss modulus G'' (open symbols) as a function of applied strain amplitude γ for 12.2 mM aqueous Laponite dispersion in the presence of different additives at $t_w = 24$ h.

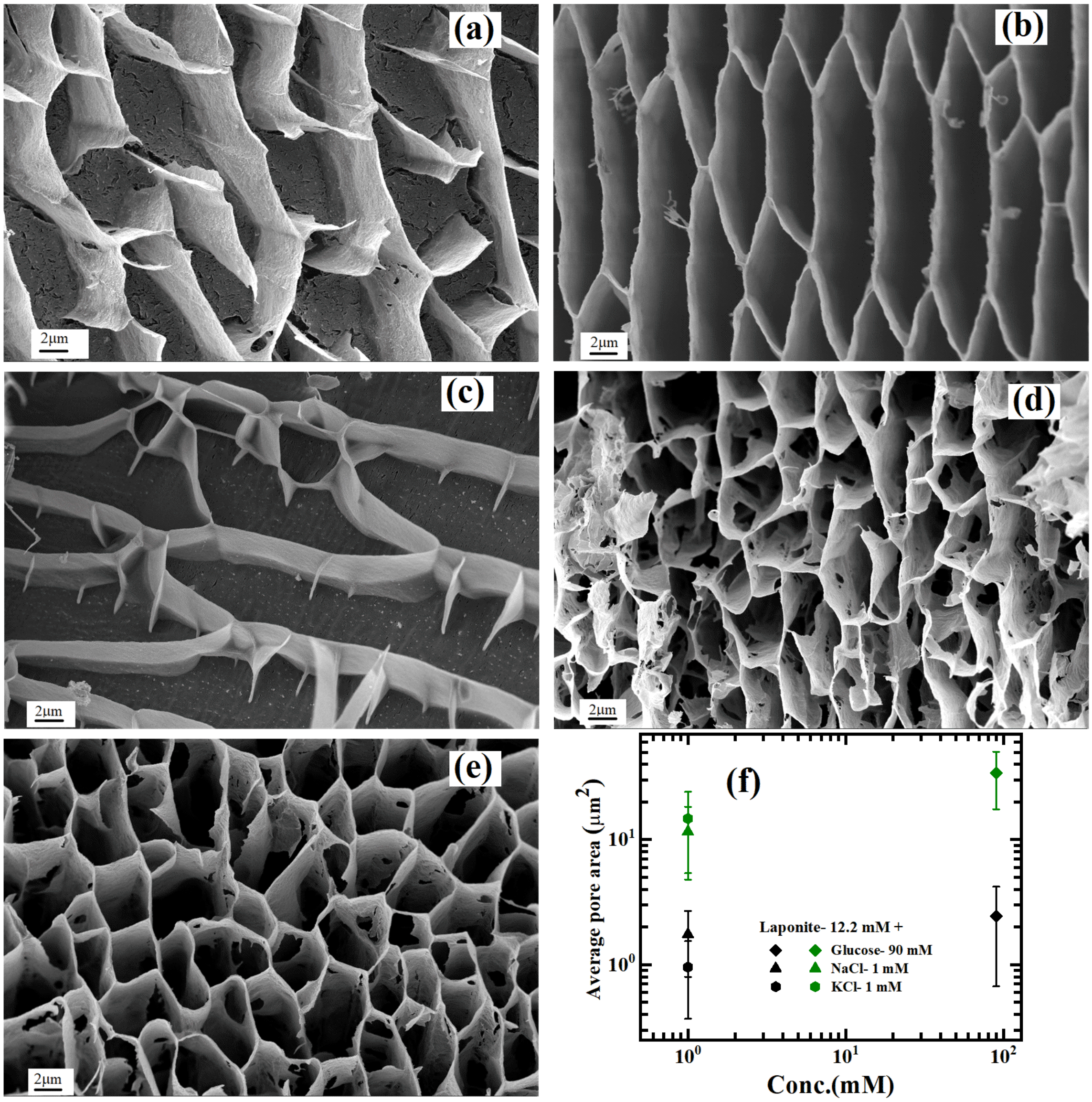

Figure S9: Cryo-SEM micrographs for (a) a 12.2 mM aqueous Laponite dispersions without additives and with (b) 90 mM glucose, (c) 90 mM DMF, (d) 1 mM NaCl and (e) 1 mM KCl at t_w = 200 min. (f) Average pore area for 12.2 mM aqueous Laponite dispersions in the presence of 90 mM glucose, 1mM NaCl and 1 mM KCl at waiting times 24 h (black) and 200 min (olive).

2. EFFECTS OF TEMPERATURE

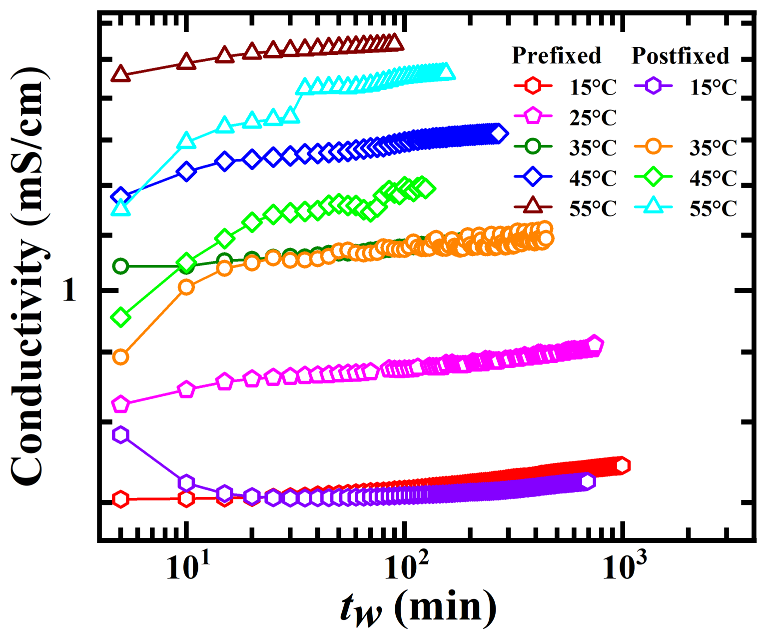

Figure S10: Conductivity for prefixed and postfixed temperature experiments for 12.2 mM aqueous Laponite dispersions as a function of t_w.

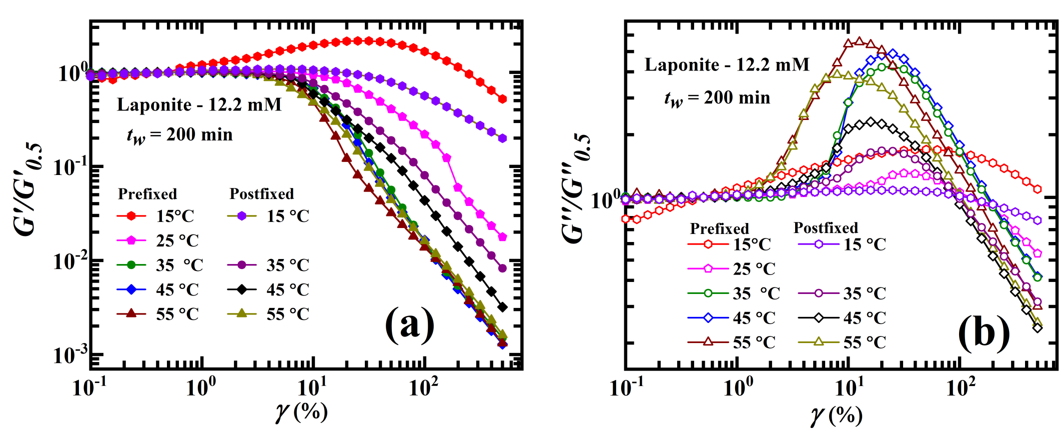

Figure S11: (a) and (b) Normalized storage ($G'/G'_{0.5}$) and loss ($G''/G''_{0.5}$) moduli *vs.* applied strain amplitude γ for dispersions with prefixed and postfixed temperatures at t_w = 200 min. $G'_{0.5}$ and $G''_{0.5}$ are the values of the storage and loss moduli at strain 0.5%.

REFERENCES

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