Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Spatial inhomogeneity, Interfaces and Complex Vitrification Kinetics in a Network Forming Nanocomposite

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Calculation of the scattering length density (SLD)

The chemical structure of the epoxy matrix was approximated by

$C_{41.5\,\%}\,H_{49.9\,\%}\,O_{7.7\,\%}\,N_{0.9\%}$.

The chemical structure of the LDH was approximated by

$Mg_2\,O_{13}\,H_{13}\,Al_3\,N_2$

The scattering length densities were calculated for an X-ray wavelength of 1.542 Å by the NIST scattering length density calculator (https://www.ncnr.nist.gov/resources/sldcalc.html) to:

Expoy : $10.310\ 10^{-6}$ Å^2

TLDH : $23.743\ 10^{-6}$ Å^2

Conventional DSC – Analysis of the heat flow curves

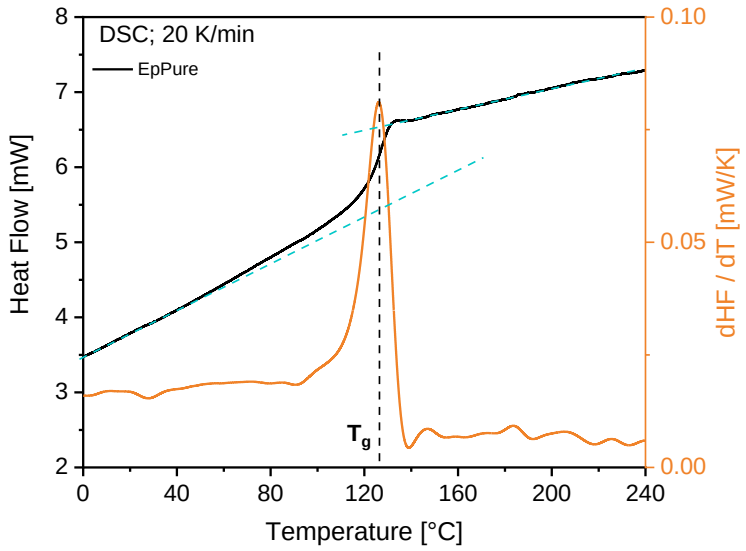

Figure S1: Heat flow curve for the unfilled epoxy at the heating rate of 20 K min^{-1} The orange curve is the first derivative of the heat flow curve with respect to temperature. The maximum of the peak is taken as the glass transition temperature (T_g).

Temperature Modulated DSC – composition dependence of specific heat capacity

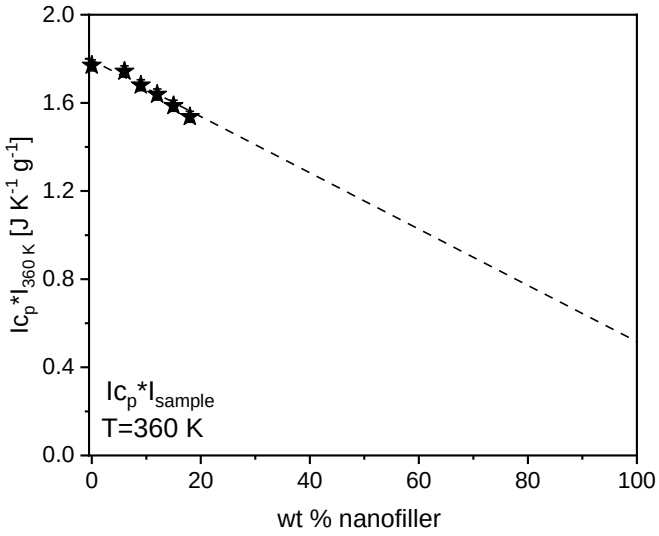

Figure S2: Specific heat capacity $|c_p^*|$ value at frequency of 0.0083 Hz at 360 K as ~~a~~ function of the concentration of the nanofiller. The line is a guide to the eyes.

Broadband Dielectric Spectroscopy – Analysis in the temperature domain

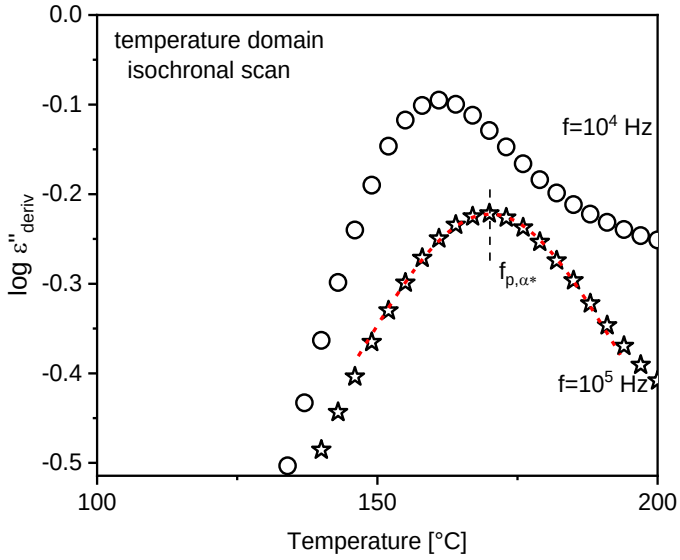

Figure S3: Temperature dependence of ε''_{deriv} for the pure epoxy at fixed frequencies of $f = 10^4\ Hz$ (black circles) and $f = 10^5\ Hz$ (black stars) (temperature domain). The red line is a Gaussian fit to the data.

Combined Relaxation Maps

EP/T-LDH9

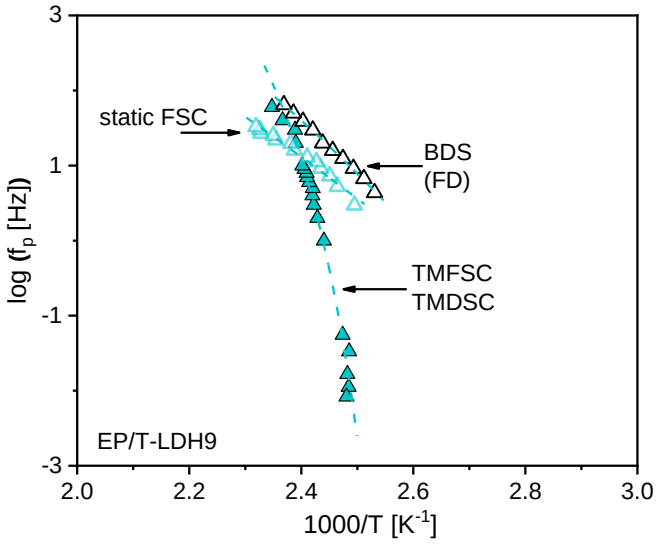

Figure S4: Relaxation map for epoxy/T-LDH nanocomposite with 9 wt % of the nanofiller. Blue filled triangles – temperature modulated DSC and FSC data, blue empty triangles – static FSC data, black empty triangles – BDS data taken from ref. 1. Blue dashed lines are VFT fits to the data.

EP/T-LDH12

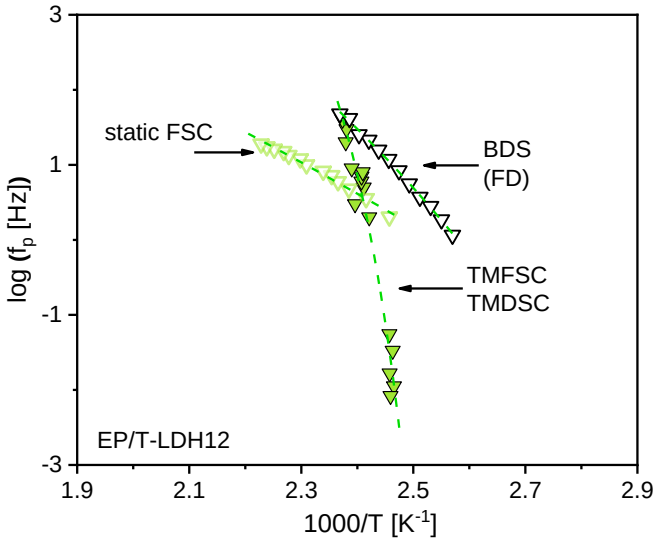

Figure S5: Relaxation map for epoxy/T-LDH nanocomposite with 12 wt % of the nanofiller. Green filled down-sided triangles – temperature modulated DSC and FSC data, green empty down-sided triangles – static

FSC data, black empty down-sided triangles – BDS data taken from ref. 1 Green dashed lines are VFT fits to the data.

EP/T-LDH18

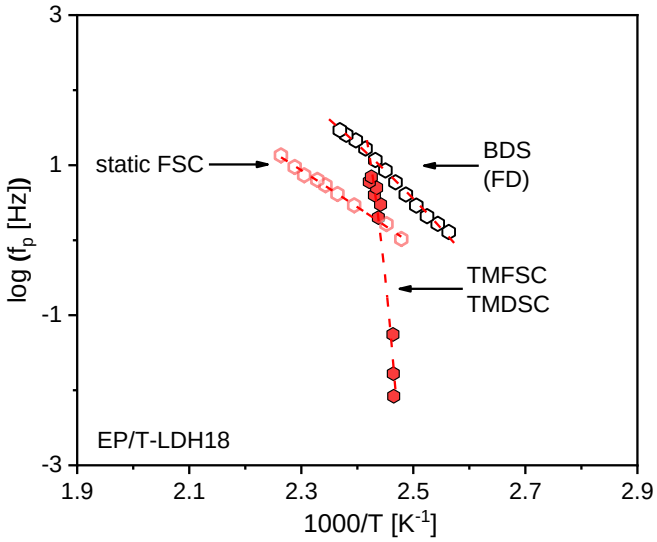

Figure S6: Relaxation map for epoxy/T-LDH nanocomposite with 18 wt % of the nanofiller. Red filled hexagons – temperature modulated DSC and FSC data, red empty hexagons – static FSC data, black empty hexagons – BDS data taken from ref. 1 Red dashed lines are VFT fits to the data.

Flash DSC – temperature modulated approach

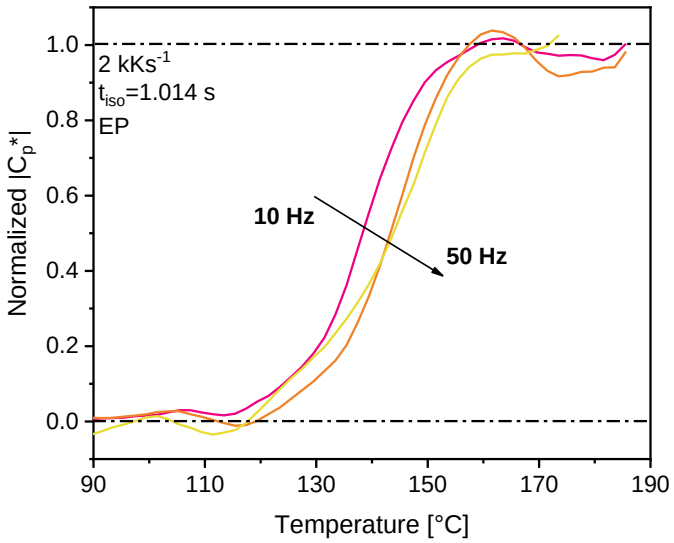

Figure S7: Normalized reversing heat capacity for the unfilled epoxy at different frequencies from 10 Hz to 50 Hz. The curve at 10 Hz corresponds to the base frequency, while the other curves are due to higher harmonics.

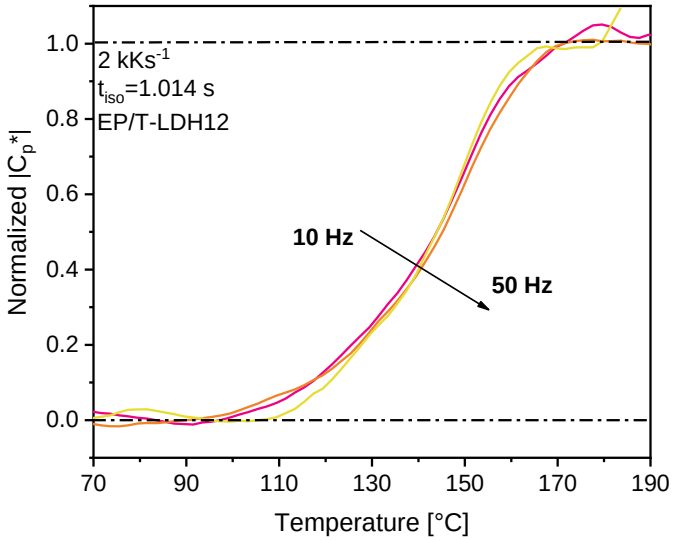

Figure S8: Normalized reversing heat capacity for the nanocomposite with 12 wt % T-LDH nanofiller (EP/T-LDH12) at different frequencies from 10 Hz to 50 Hz. The curve at 10 Hz corresponds to the base frequency, while the other curves are due to higher harmonics.

Concentration dependence of the cooperativity length scale

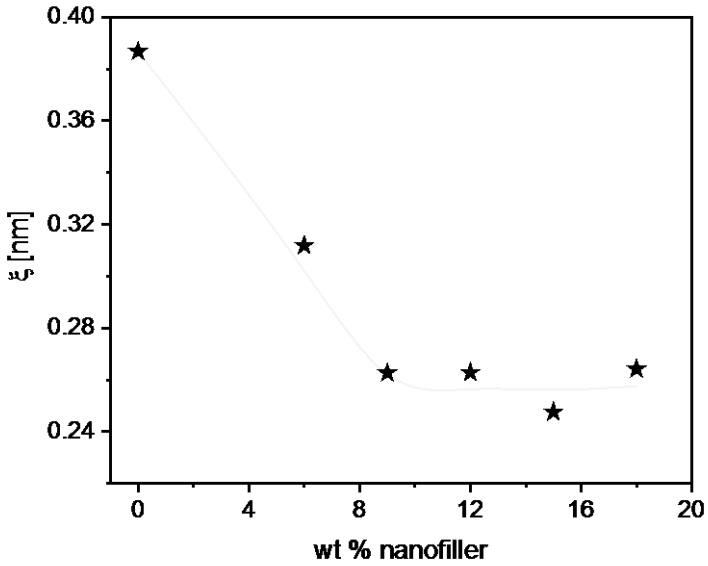

Figure S9: Cooperativity length scale ξ of the α*-process vs the concentration of the nanofiller.

Temperature Modulated DSC – normalized specific heat capacity

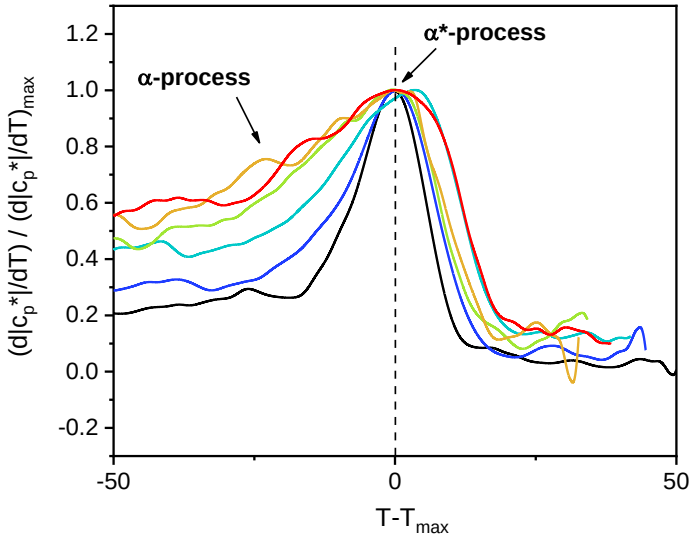

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Figure S10: Normalized derivative of the specific heat capacity $|c_p^*|$ $(d|c_p^*|/dT)/(d|c_p^*|/dT)_{max}$ at frequency of 0.0083 Hz versus temperature normalized by the value of the frequency dependent glass transition temperature ($T_{max,\alpha}$) for pure epoxy (EP – black) and the nanocomposites: EP/T-LDH6 – dark blue, EP/ T-LDH9 – blue, EP/

T-LDH12 – green, EP/ T-LDH15 10 – orange and EP/ T-LDH18 – red.

Sample	log (f_∞ [Hz])	A	T_0 [K]
EP	9	537.1	342.4
EP/T-LDH6	9	494.4	351.2
EP/T-LDH9	9	428.12	362.8
EP/T-LDH12	9	365	371.8
EP/T-LDH15	9	474.5	363.3
EP/T-LDH18	9	214.4	385.8

Table S1: VFT parameters obtained from fitting temperature modulated DSC data (TMDSC and modulated FSC). To reduce the number of free fit parameters, log f_∞ was fixed to 8

References:

1 Szymoniak, P.; Li, Z.; Wang, D-Y.; Schönhals, A. Dielectric and flash DSC investigations on an epoxy based nanocomposite system with MgAl layered double hydroxide as nanofiller Thermochim. Acta 2019, 677, 151.