Supporting Information:

Enhanced Resilience to Thermal Decay of Imprinted Nanopatterns in Thin Films by Bare Nanoparticles Compared to Polymer-Grafted Nanoparticles

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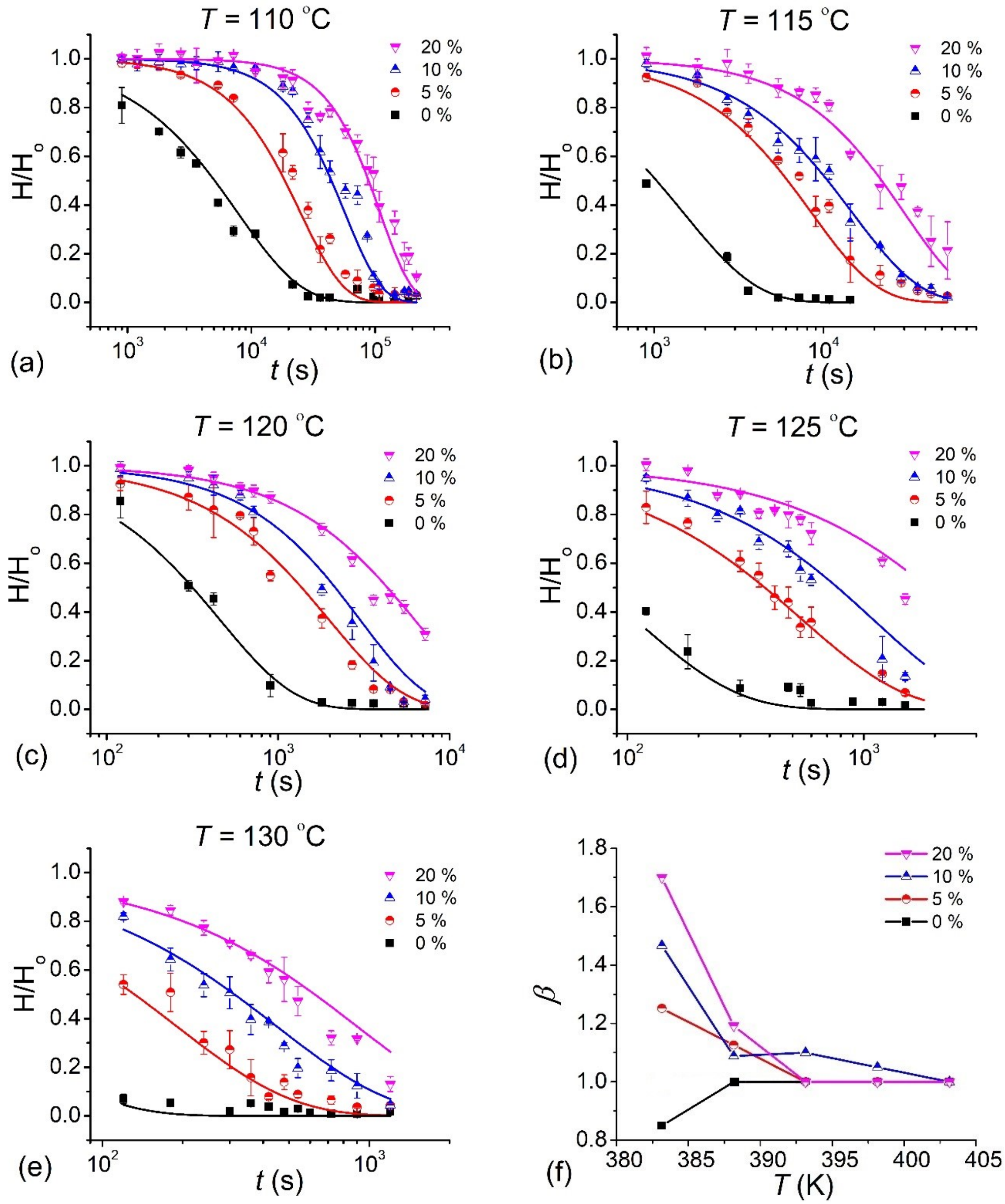
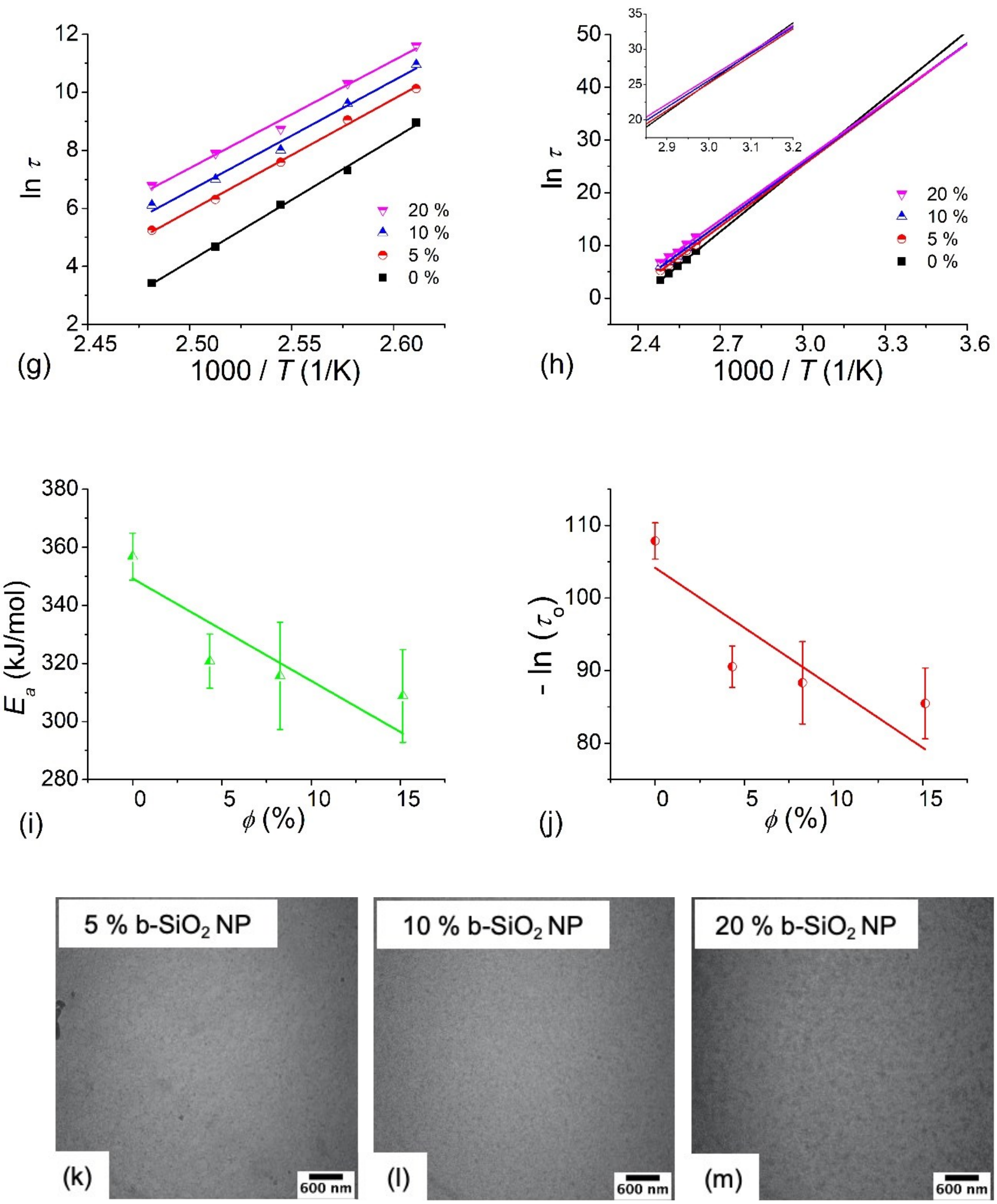
Slumping Relaxation Dynamics for bare unmodified SiO2 NP within PMMA Matrix

Unmodified bare SiO_2 nanoparticle (b-SiO_2 NP) (4 nm to 5 nm nominal radius) were purchased from Nissan Chemicals and used as received. Figure S1a-e depicts the pattern height decay behavior at different slumping temperatures. Figure S1f shows the variation of the exponent β characterizing the degree of non-exponentiality of the relaxation process as a function with the of nanoparticle concentration and temperature. Figure S1g, h depicts the Arrhenius behavior of the relaxation time constant and the convergence of the extrapolated linear fits yielding a compensation. Figure S1i, j shows the concentration dependence of the activation parameters, E_a and - ln τ_o respectively. Figure S1k-n depicts the dispersion of a 5%, 10%, 20 % mass fraction (relative to the PMMA matrix) b-SiO_2 NP film captured by TEM.



T = 110 °C
T = 115 °C
T = 120 °C
T = 125 °C
T = 130 °C
20 %
10 %
5 %
0 %
H/Ho
t (s)
T (K)
β
(a)
(b)
(c)
(d)
(e)
(f)



ln τ
1000 / T (1/K)
20 %
10 %
5 %
0 %
(g)
(h)
E_a (kJ/mol)
ϕ (%)
(i)
- ln (τ_o)
(j)
5 % b-SiO_2 NP
10 % b-SiO_2 NP
20 % b-SiO_2 NP
(k)
(l)
(m)
600 nm

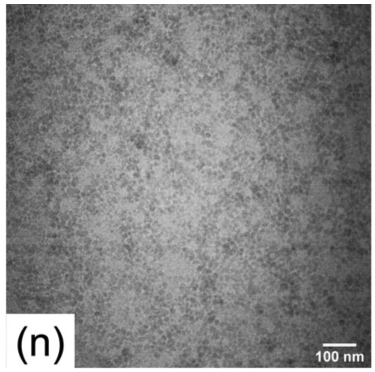
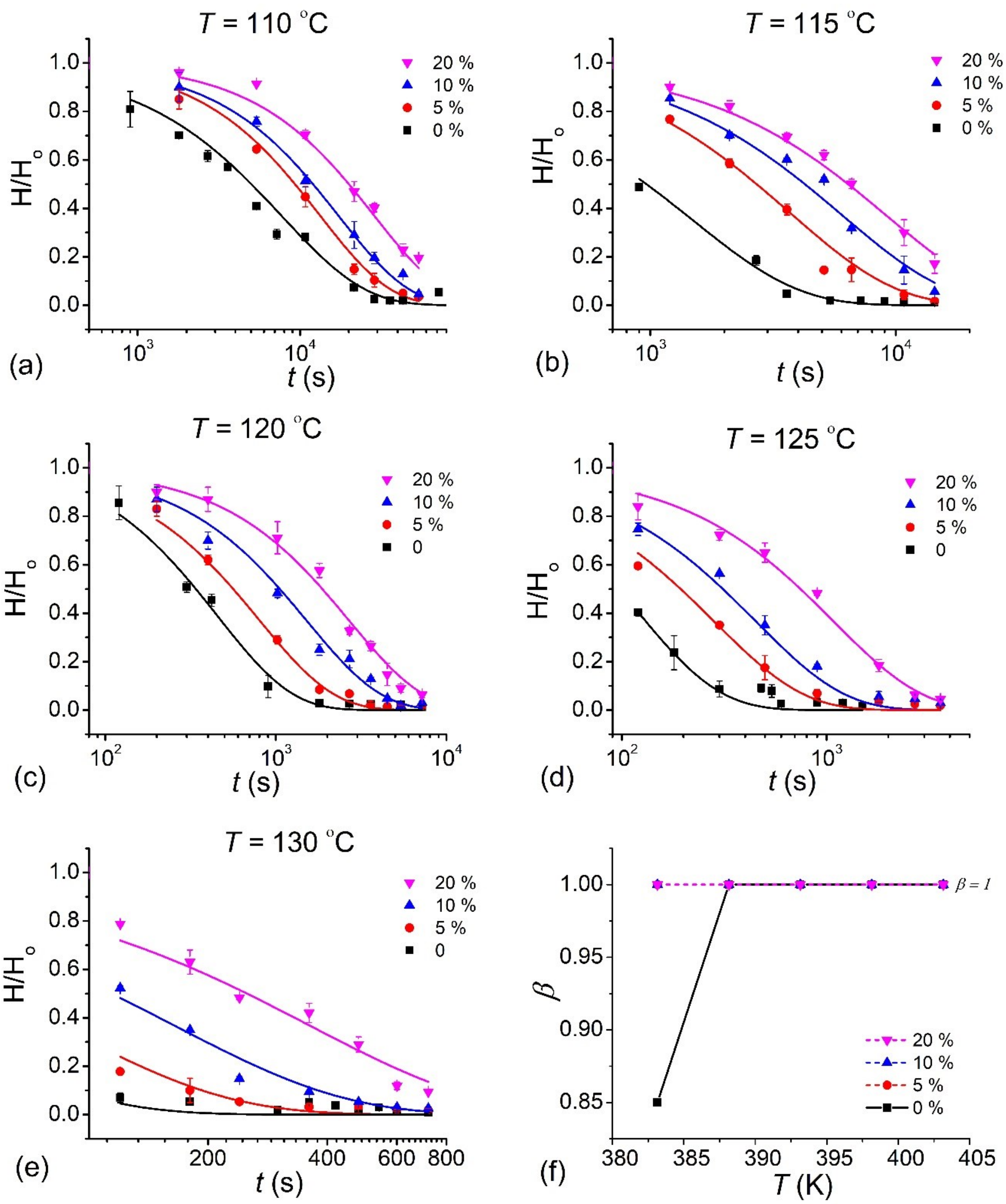


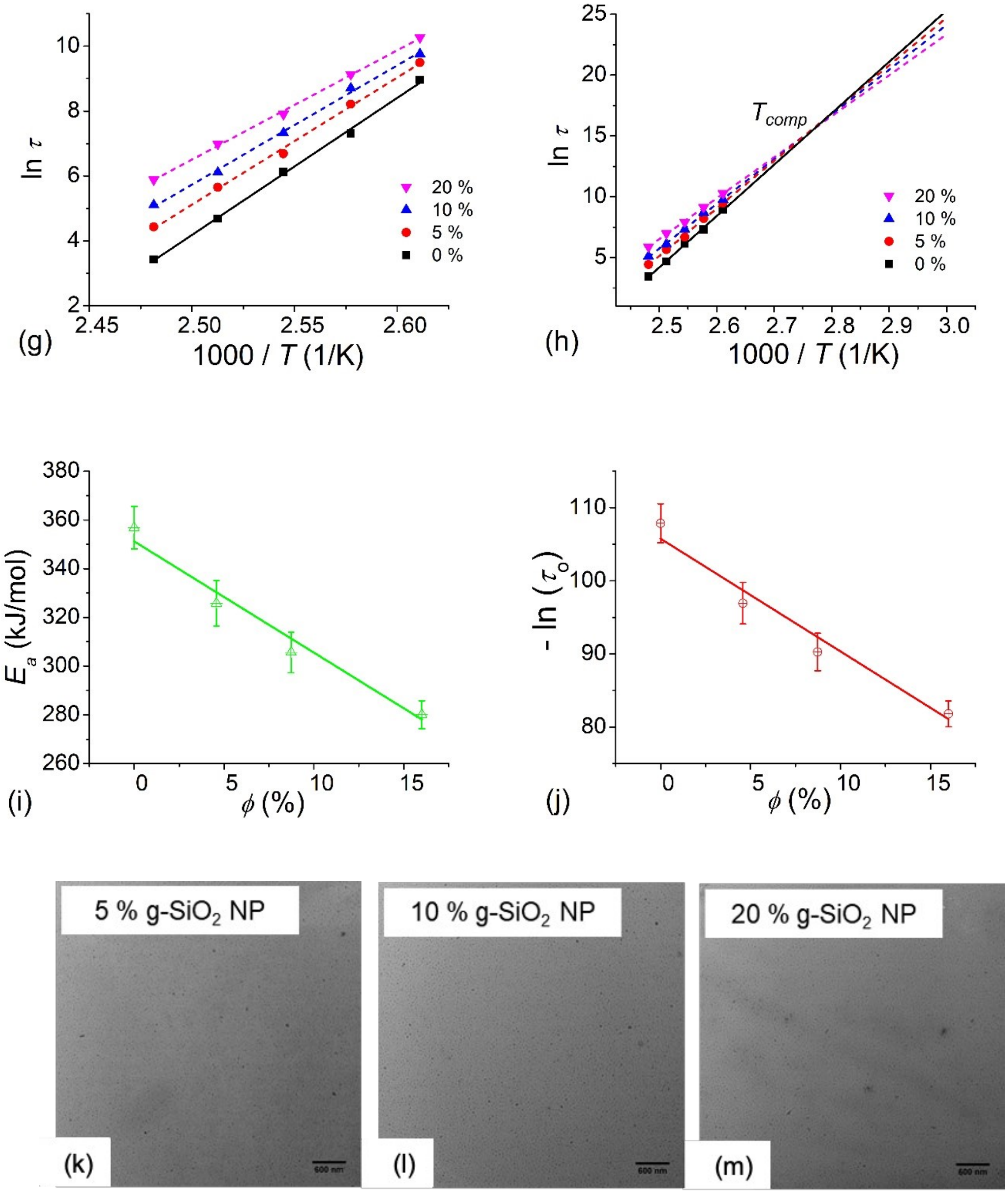
Figure S1. *Relaxation kinetics of bare unmodified SiO_2 NP system.* Normalized pattern height decays at (a) 110 °C, (b) 115 °C, (c) 120 °C, (d) 125 °C, and (e) 130 °C in patterned neat PMMA thin film (0 % - black filled squares) and PMMA thin films containing b-SiO_2 NP at mass fractions of 5 % (upper-filled red circles), 10% (upward upper-filled blue arrow) and 20 % (downward upper-filled purple arrow). Solid lines denote non-exponential fits to the data. The uncertainty intervals represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement. (f) Variation of the exponent β from the slumping relaxation curves as a function of T and different concentrations of b-SiO_2 NP within PMMA matrix. (g) Arrhenius plots for the temperature dependence of the relaxation time, ln τ. Solid lines show linear Arrhenius fits to the data. (h) Extrapolation of the linear fits leads to a point of convergence, near ≈ 57.43 °C to 64.69 °C, a temperature approximately 32.5 °C to 40 °C lower than the $T_{g,\ bulk}$ ≈ 97.24 (± 0.23) °C as computed from this plot. (i) E_a (kJ/mol) (light-green left-filled upward arrow, $R^2 \approx 0.59$) as a function of volume fraction (ϕ) of the bare SiO2 NP. (j) $-\ln(\tau_o)$ (red left-filled circle, $R^2 \approx 0.56$) as a function of volume fraction (ϕ) of the bare SiO2 NP respectively. Error bars denotes the standard error of fitting. (k, l, m) TEM image for a 5%, 10% and 20 % mass fraction (relative to the PMMA matrix) b-SiO_2 NP filled film annealed at 180 °C for 1 h. Scale bar is 600 nm. (n) Zoomed-in TEM image for a 20 % mass fraction (relative to the PMMA matrix) b-SiO_2 NP filled film. Scale bar is 100 nm.

Slumping Relaxation Dynamics for PMMA grafted SiO_2 NP within PMMA Matrix

The PMMA grafted Silica nanoparticles (g-SiO_2 NP) had an average radius of 7.7 (± 2) nm after grafting as measured by transmission electron microscopy (TEM). The number average molecular mass (M_n) of the grafted PMMA chains was measured to be 19.4 kg/mol using GPC with a polydispersity of 1.17. PMMA grafting density, was estimated to be ≈ 0.65 chains/nm^2 based on organic mass loss from TGA[2]. Figure S2a-e depicts the pattern height decay behavior at different slumping temperatures. Figure S2f shows the variation of the exponent β characterizing the degree of non-exponential relaxation with the concentration of the NP and temperature. Figure S2g, h depicts the Arrhenius behavior of the relaxation time constant and the convergence of the extrapolated linear fits yielding a compensation. Figure S2i, j shows the volume fraction ϕ dependence of the activation parameters, E_a and - ln τ_o , respectively. Figure S2k-n depicts the dispersion of a 5%, 10%, 20 % mass fraction (relative to the PMMA matrix) g-SiO_2 NP film captured by TEM.



T = 110 °C
T = 115 °C
T = 120 °C
T = 125 °C
T = 130 °C
H/H_o
t (s)
20 %
10 %
5 %
0 %
0
(a)
(b)
(c)
(d)
(e)
(f)
β
β = 1
T (K)



ln τ
20 %
10 %
5 %
0 %
(g)
1000 / T (1/K)
T_comp
ln τ
20 %
10 %
5 %
0 %
(h)
1000 / T (1/K)
E_a (kJ/mol)
(i)
ϕ (%)
- ln (τ_o)
(j)
ϕ (%)
5 % g-SiO2 NP
10 % g-SiO2 NP
20 % g-SiO2 NP
(k)
(l)
(m)
600 nm
600 nm
600 nm

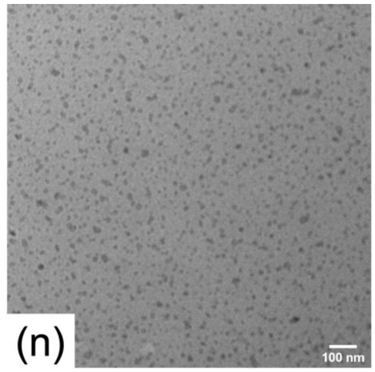


Figure S2. *Relaxation kinetics of grafted SiO_2 NP system.* Normalized pattern height *H* decays at (a) 110 °C, (b) 115 °C, (c) 120 °C, (d) 125 °C, and (e) 130 °C in patterned neat PMMA thin film (0 % - black filled squares) and PMMA thin films containing g-SiO_2 NP at mass fractions of 5 % (filled red circles), 10% (upward filled blue arrows) and 20 % (downward filled purple arrow). Solid lines denote non-exponential fits to the data. The error bars represent one standard deviation of the data, which is taken as the experimental uncertainty of the measurement. (f) Variation of the exponent β from the slumping relaxation curves as a function of *T* and different concentrations of g-SiO_2 NP within the PMMA matrix. (g) Arrhenius plots for the temperature dependence of the relaxation time, ln τ. Solid lines show linear Arrhenius fits. (h) Extrapolation of the linear fits leads to a point of convergence, near ≈ 89.16 °C to 94.49 °C, a temperature approximately 2 °C to 8 °C lower than the $T_{g,\ bulk} \approx 97.24$ (± 0.23) °C, as computed from this plot. (i) E_a (kJ/mol) (light-green cross-centered upward arrow, $R^2 \approx 0.92$) as a function of volume fraction (ϕ) of the grafted SiO_2 NPs. (j) − ln(τ_o) (red cross-centered circle, $R^2 \approx 0.92$) as a function of volume fraction (ϕ) of the grafted SiO_2 NP respectively. Uncertainty intervals denotes the standard error of fitting. (k, l, m) TEM image for a 5%, 10% and 20 % mass fraction (relative to the PMMA matrix) g-SiO_2 NP filled. (n) Zoomed-in TEM image for a 20 % mass fraction (relative to the PMMA matrix) g-SiO_2 NP filled film. Scale bar is 100 nm.

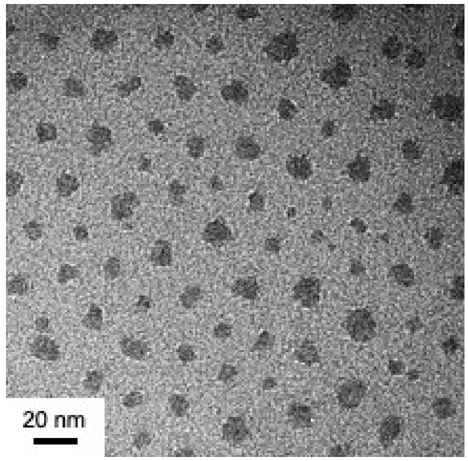


Figure S3. TEM micrograph of SiO_2 NP post grafting

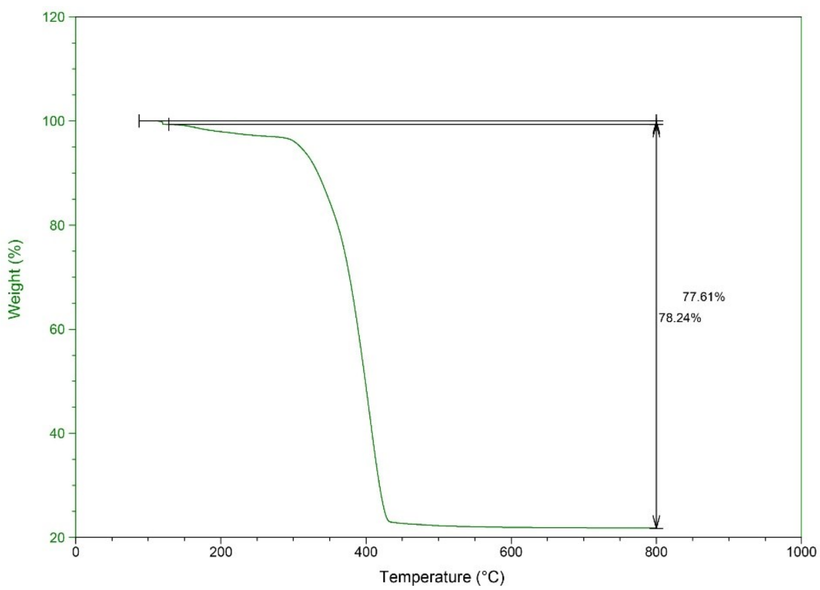


Figure S4. TGA curve showing the organic mass loss for the SiO_2 NP post grafting

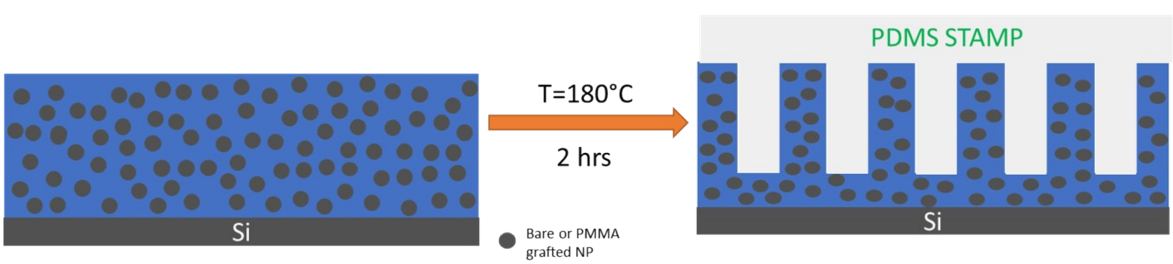


Figure S5. Schematic of imprinting nanocomposite films utilizing capillary force lithography

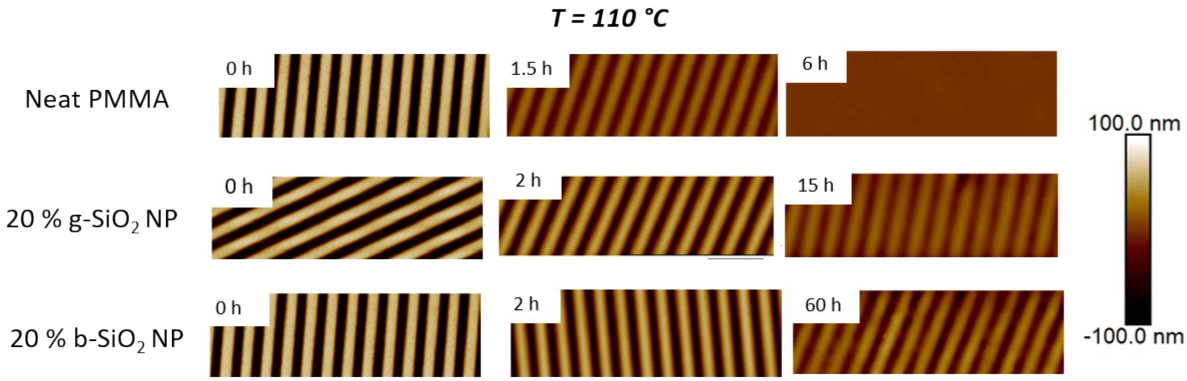


Figure S6. AFM micrographs for neat PMMA, 20% g-SiO_2 NP + PMMA and 20% b-SiO_2 NP + PMMA slumping at 110 ºC