Bimodal Surface Ligand Engineering: The Key to Tunable Nanocomposites

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Supporting Information

The grafting density of each PDMS brush was calculated from the corresponding weight loss ratio determined by TGA (Figure 1S), the number of grafting chains, and surface area of NPs using:[1]

$$\sigma = (wN_\mathrm{A}/M_\mathrm{n})/(4\pi a^2 \mathrm{n}) = \mathrm{a\rho z}N_\mathrm{A} \times 10^{-21}/3(1-z)M_\mathrm{n}$$

where w, N_A, n and z are the weight of organic polymers, Avogadro's number, the number of NPs and weight loss of polymer chains respectively.

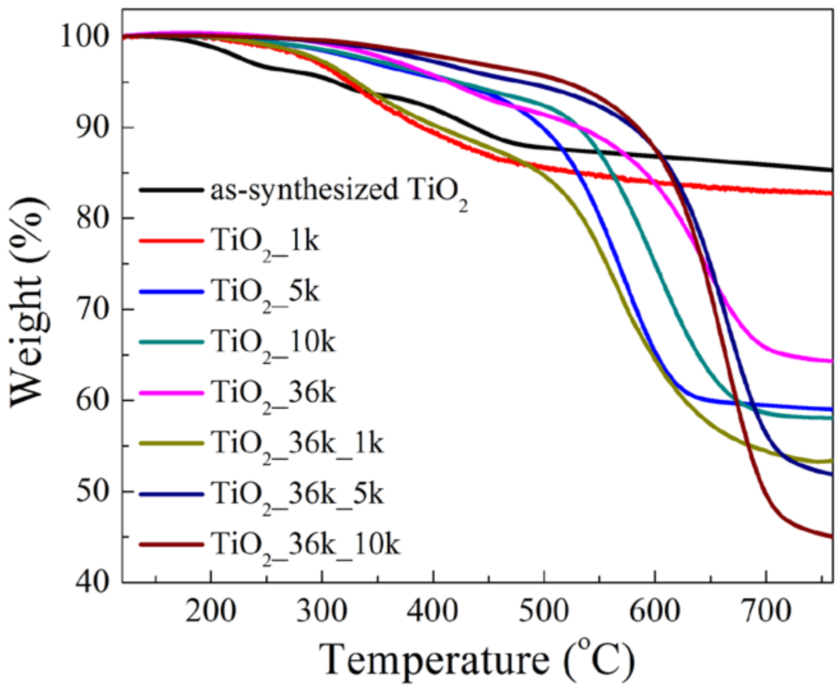

Figure 1S. Normalized TGA curves for various PDMS-brush-grafted TiO_2 NPs.

Parameters used in theoretical calculations

We reiterate that the phase diagram was determined by four dimensionless parameters:[2] the energetic gain, χ, resulting from the contact of NPs, the excluded volume parameter $\nu N^2/R_g{}^3$ where R_g is the radius of gyration of the brush chain and ν is an excluded-volume-interactions-related parameter (which can be approximated as $b^3\, N/P$ when the brush and matrix chains have same chemistry and b is their Kuhn segment length, 1.06 nm in our case[2, 3]), the total number of grafted chains for each particle n_p, and r/R_g with r being the particle core radius. Bulk parameters used in modeling are listed in Table 1S–4S.

Table 1S. Bulk parameters for various media used in mono–modal-brush-grafted NPs modeling.

Component	Dielectric Constant ε	Refractive Index n	Hamaker Constant A at 298.15 K (10^{-20} J)	Density (g/cm^3)
Silicone matrix	2.65	1.41	5.04	-
TiO_2	85.00	2.50	37.50	3.50
Oleic acid	2.50	1.46	6.12	0.89

The van der Waals attraction V_{vdW} between two particle cores can be calculated from the Hamaker Constants using:[4]

$$V_{\mathrm{vdW}} \simeq -\frac{r}{12}\left[\frac{\left(\sqrt{A_{\mathrm{Silicone}}}-\sqrt{A_{\mathrm{OA}}}\right)^2}{d}+\frac{\left(\sqrt{A_{\mathrm{OA}}}-\sqrt{A_{\mathrm{TiO2}}}\right)^2}{d+2L}+\frac{\left(\sqrt{A_{\mathrm{Silicone}}}-\sqrt{A_{\mathrm{OA}}}\right)\left(\sqrt{A_{\mathrm{OA}}}-\sqrt{A_{\mathrm{TiO2}}}\right)}{d+L}\right]$$

Here the distance between the outer edges of two NPs d was taken to be 0.165 nm typically.[4, 5]

The radius of gyration of grafted PDMS chains can be estimated by:[6]

$$R_{\mathrm{g}} = \sqrt{0.077 \times N_{\mathrm{PDMS}}}\ \text{(nm)}$$

Table 2S. Modeling parameters for mono–modal-PDMS-brush-grafted NPs.

Grafted brushes	N	R_{g} (nm)	n_{p}	$\mathrm{r}/R_{\mathrm{g}}$
1k PDMS	16.67	1.13	17.04	2.21
5k PDMS	83.33	2.53	6.50	0.99
10k PDMS	166.67	3.58	4.12	0.70
36k PDMS	600.00	5.80	1.08	0.37

Table 3S. Bulk parameters of three types of short brushes in the hybrid layers of bimodal-PDMS-brush-grafted NPs.

PDMS short brush layer	Dielectric Constant ε	Refractive Index n	Density (g/cm^3)	Weight Percentage
1k PDMS	2.65	1.41	0.96	0.33
5k PDMS	2.65	1.41	0.97	0.57
10k PDMS	2.65	1.40	0.98	0.64

The effective Hamaker constant for the hybrid OA/PDMS short brush layer is calculated from:

$$A_{\text{eff}} = \frac{3}{4} k_B T \left(\frac{\varepsilon_{\text{eff}} - \varepsilon_{\text{Vac.}}}{\varepsilon_{\text{eff}} + \varepsilon_{\text{Vac.}}} \right)^2 + \frac{3h\nu_{\text{e}}}{16\sqrt{2}} \frac{(n_{\text{eff}}^2 - n_{\text{Vac.}}^2)^2}{\left(n_{\text{eff}}^2 + n_{\text{Vac.}}^2\right)^{3/2}}$$

Table 4S. Bulk parameters of various hybrid layers used in bimodal-PDMS-brush-grafted NPs modeling.

Hybrid layer	ε_{eff}	n_{eff}	A_{eff} at 298.15 K (10^{-20} J)
OA+1k PDMS	2.55	1.44	5.77
OA+5k PDMS	2.58	1.43	5.46
OA+10k PDMS	2.59	1.43	5.37

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