Supporting Information

Nano-dimensional Spheres and Worms as Fillers in Polymer Nanocomposites: Effect of Filler Morphology

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Experimental

Materials
Poly(ethylene glycol) methyl ether methacrylate, M_n = 950 g mol^{-1} (PEGMA, Sigma-Aldrich), methacrylic acid (MAA, Sigma-Aldrich, 99%), hexadecane (HD, Sigma-Aldrich, 99%), sodium dodecyl sulfate (SDS, Ajax Finechem), 4,4′-azobis(4-cyanovaleric acid) (ACPA, Sigma-Aldrich, ≥97%), sodium hydroxide (NaOH, Chem-Supply), 1,3,5-trioxane, tetrahydrofuran (THF, Sigma-Aldrich, ≥99.9%) and N,N-dimethylacetamide (DMAc, 99.9%, Sigma-Aldrich) were used as received. Tri(methylsilyl)diazomethane solution was used as a methylation agent (in 2 M hexane, Sigma-Aldrich). Deuterated NMR solvent (DMSO) was purchased from Cambridge Isotope Laboratories. Methyl methacrylate (MMA, >99%, Sigma-Aldrich), styrene (St, 99%, Sigma-Aldrich), *n*-butyl acylate (nBA, 99%, Sigma-Aldrich) and ethylene glycol dimethacrylate (EGDMA, 98%, Sigma-Aldrich) were deinhibited by passing through a column of activated basic alumina. Deionized (DI) water was produced by a Milli-Q reverse osmosis system and had a resistivity of 18.2 mΩ cm−1. The RAFT agent, 4-cyano-4-thiothiobutylsulfanylpentanoic acid (CTBPA) was synthesized according to the literature.[1]

Synthesis of P(St-*stat*-*n*BA) base latex
P(St-*stat*-*n*BA) base latex (solids content = 7 wt%) was prepared by miniemulsion polymerization of styrene (0.525 g, 5.04 mmol) and *n*BA (0.525 g, 4.10 mmol) (weight ratio = 50/50) using milli-Q water (15 g) as a solvent in the presence of AIBN (0.051 g, 0.31 mmol), SDS (0.011 g, 0.04 mmol), hexadecane (0.0525 g, 0.23 mmol). The solution was mixed in 25 mL glass vial at ambient temperature for 15 min, and then ultrasonicated for 10 min in an ice bath (Branson Digital Sonifier at 10% amplitude). Subsequently, the solution was purged for 20 min with nitrogen in an ice bath. The polymerization was carried out at 70 °C in an oil bath with stirring speed of 500 rpm for 24 h. The polymerization mixture was subsequently

quenched by putting the flask in an ice bath. The final conversion of styrene and nBA was determined by gravimetric analysis.

Synthesis of P(MAA-*stat*-PEGMA)-*b*-PMMA non-crosslinked worms, crosslinked spheres, and crosslinked worms

The worm synthesis procedures were adapted from the literature.[2, 3] The crosslinked worms/spheres were synthesized as follows:

Step 1. RAFT polymerization of PEGMA and MAA using CTBPA. PEGMA (0.9792 g, 1.03×10^{-3} mol), MAA (0.0887 g, 1.03×10^{-3} mol), CTBPA (0.02 g, 0.07×10^{-3} mol) as RAFT agent, and ACPA (3.9 mg, 1.4×10^{-4} mol) as initiator were dissolved in water (5.2 mL) to give a [monomers]:[RAFT]:[initiator] molar ratio of 30:1:0.2. An aliquot (18.6 mg) of 1,3,5-trioxane was added as an internal standard to determine the monomer conversion by ^{1}H NMR. The polymerization mixture was purged with nitrogen gas for 30 min before being placed in an oil bath at 80 °C for 3 h. The polymerization was stopped by placing the 25 ml glass vial in an ice bath. The overall conversion was determined to be ~98% via ^{1}H NMR in d_6-DMSO. This macroRAFT agent was used in Step 2 without purification. For SEC analysis, samples were methylated using trimethylsilyldiazomethane in THF/H$_2$O mixture (90/10 by volume).

Step 2. Synthesis of crosslinked worms and spheres with P(PEGMA-stat-MAA) macroRAFT agent. The amount of EGDMA was varied to find the optimum condition. The typical condition is as follows: The solution prepared above (containing macroRAFT agent, 1 g, 0.066 mmol) was mixed with MMA (1.81 g, 18.1 mmol), EGDMA (39 mg, 0.20 mmol), ACPA (3.6 mg, 0.013 mmol), NaHCO$_3$ (3.9 mg, 0.046 mmol) and 4 g of water in a 25 ml glass vial. For the synthesis of spheres, pH was adjusted to 5 by adding 1 M NaOH dropwise. The mixture was purged with nitrogen gas in an ice bath for 30 min before being placed in an oil bath at 80 °C with constant stirring at 350 rpm. After 3 h, the polymerization was stopped by placing the vial in an ice bath. The monomer conversion was determined by gravimetry. The synthesis conditions and GPC data are summarized in Table 1 and Figure 1.

Film formation
The obtained worm and sphere dispersions were diluted in milli-Q water to 5 wt% and stirred for 7 days at ambient temperature prior to use. The base latex corresponding to 0.8522 g of dried latex, or base latex mixtures containing 2, 5 and 8% worms and 5% spheres with respect to dried latex were stirred overnight at ambient temperature before film formation. Milli-Q water (5 g) was subsequently added to the latex (approx. base latex 14 g + 5 wt% worm or sphere latex) to adjust the volume of latex to ensure the latex covers the mold, followed by stirring at ambient temperature for 5 min. Films were prepared by solvent casting in a square silicone mold ($70 \times 70 \times 30$ mm^3). Square silicone mold was placed in a desiccator for 30 min to remove the trapped air bubbles, followed by drying overnight at 40°C in an incubator. Films with approximately 0.3 mm thickness were obtained after drying.

Tensile tests
Films were cut into dumbbell shape with a standard cutting die (ISO 527-2-Type 5B). Length, width, and thickness of tensile test specimens were measured using a digital vernier caliper. Uniaxial tensile tests were performed at 22°C and 70% humidity using a tensile testing instrument (Mark-10, ESM 303) with a 25 N load cell. Nominal stress (σ_n) and strain (ε_n) values were calculated from the force (F) and elongation in the tensile direction. Young's modulus (E) was determined by calculating the slope of the elastic region of the stress-strain curve. The

toughness (U_T) of the films was calculated by integrating the total area under the stress-strain curve. At least five specimens from each film were tested at a constant loading rate of 20 mm min^{-1}.

Stress (σ_n, MPa) was determined by eqn (2):

$$\sigma_n = \frac{F}{A} \tag{2}$$

where F (N) is the load applied perpendicular to the cross-sectional area of the specimen, and A (m^2) is the original cross-sectional area of the specimen before load is applied.

Strain (ε_n, %) was determined by eqn (3):

$$\varepsilon_n = \frac{\Delta l}{l_0} \times 100 \tag{3}$$

where Δl is the absolute increase in length and l_0 is the initial length of the specimen before load is applied.

Characterization techniques

Gravimetric Analysis. The total conversion of styrene, nBA, and MMA was determined by gravimetric analysis. 950 µL of latex was weighed in a pre-weighed aluminium pan and dried at 50°C overnight in a vacuum oven.

Nuclear Magnetic Resonance (NMR). The final total conversion of MAA and PEGMA at t = 3 h was determined by ^{1}H NMR spectroscopy using a Bruker Avance III 300 MHz NMR with 1,3,5-trioxane used as an internal reference. Samples were prepared by dissolving 50 µL of the reaction mixture (t = 0 h and t = 3 h) in 600 µL of deuterated dimethyl sulfoxide (d_6-DMSO).

Gel Permeation Chromatography (GPC). Number-average (M_n) and weight-average (M_w) molecular weights and dispersity ($Đ$) were determined by gel permeation chromatography (GPC) using a Shimadzu modular system, comprising an SIL-10AD autoinjector, an LC-10AT pump, a DGU-12A degasser, a CTO-10A column oven, and an RID-10A differential refractive index detector. A column arrangement consisting of a Polymer Laboratories 5.0 µm bead size guard column (50 × 7.8 mm), followed by four linear PL column (300 × 7.8 mm, 500, 10^3, 10^4, and 10^5 Å, 5 µm pore size) was used for the analysis. N,N-Dimethylacetamide (DMAc, 0.03% w/v LiBr, 0.05% w/v 2,6-dibutyl-4-methylphenol(BHT)) at 50 °C or tetrahydrofuran (THF) at 40 °C were used as the mobile phase at a flow rate of 1 mL min^{-1} with an injection volume of 100 µL. The GPC system was calibrated using linear polystyrene standards ranging from 500 to 10^6 g mol^{-1} (Polymer Laboratories). Chromatograms were processed using Cirrus 2.0 software (Polymer Laboratories). MacroRAFT agent and non-crosslinked worm were methylated to modify the carboxylic group in methacrylic acid to reduce the interaction with the column. The dried latex (10 mg) was added to 1 mL of milli-Q water in a 25 mL glass vial and HCl was added to adjust to pH 3-4. Then, 20 mL of THF was added to the mixture. Trimethylsilyldiazomethane methylating agent was added into the vial drop by drop. The mixture was stirred at room temperature for 4 h. After methylation, the solution was dried in an aluminum pan at ambient temperature overnight. It was further dried at 35°C using high vacuum oven for 1 h to remove water. Samples were dissolved in DMAc and filtrated using a syringe filter (0.45 µm) prior to injection into the DMAc GPC system. Dried latex (3 mg) of P(St-*stat*-nBA) base latex synthesized via miniemulsion polymerization was dissolved in 1 mL

of THF and filtrated using a syringe filter (0.45 μm) prior to injection into the THF GPC system.

Scanning Electron Microscopy (SEM). SEM samples were prepared by dropping 10 μL of diluted latex (10 μL of latex in 1 mL of THF) on a silicon wafer. Samples were dried under ambient temperature overnight, and subsequently kept in desiccator prior to coating to remove water. The samples were coated with chromium and platinum. SEM images were obtained using a FEI Nova NanoSEM 450 at a working distance of approximately 5 mm and an accelerating voltage of 5 kV.

Transmission Electron Microscopy (TEM). TEM samples were prepared by dropping 10 μL of diluted latex (10 μL of latex in 1 mL of milli-Q water) on a glow-discharged formvar-coated copper grid, which was dried at ambient temperature. The grid was glow-discharged to modify the grid surface from hydrophobic to hydrophilic to avoid accumulation of block copolymer nanoparticles on the periphery of the grid. The samples were subsequently stained with uranyl acetate for 2 min at room temperature. The TEM images were obtained under an accelerating voltage of 100 kV using a JEOL 1400 transmission electron microscope.

Dynamic light scattering (DLS). The particle size and size distribution were measured using a Malvern ZetaSizer Nanoseries. DLS samples were prepared by diluting 10 μL of latex in 1 ml of milli-Q water. A total of three measurements were conducted. In each measurement, the number of runs, attenuator, and path length used were automatically adjusted by the instrument, depending on the quality of the sample. The presented results are averages of the three measurements.

Differential Scanning Calorimetry (DSC). DSC measurements to determine the glass transition temperatures of the films were performed on a NETZSCH DSC 204 F1 Phoenix under nitrogen flux. The temperature ranged between −40 and 150 °C with a heating rate of 10 °C/min.

Table S1. Synthesis of macroRAFT agents (M1-3) via solution polymerization of MAA and PEGMA using CTBPA as RAFT agent at 80 °C, molar ratio of MAA/PEGMA/RAFT/ACPA = 15/15/1/0.2 and non-crosslinked worms via emulsion polymerization of MMA in the presence of M2.

Entry	Time (h)	Conv.[a] (%)	$M_{n,th}$[b] (g/mol)	$M_{n(GPC)}$[c] (g/mol)	$Đ$[d]
M1	3	98	15,500	16,700	1.08
M2	3	98	15,700	15,800	1.10
M3	3	98	15,300	15,400	1.19
NCLW	4	91	42,400	36,500	1.23
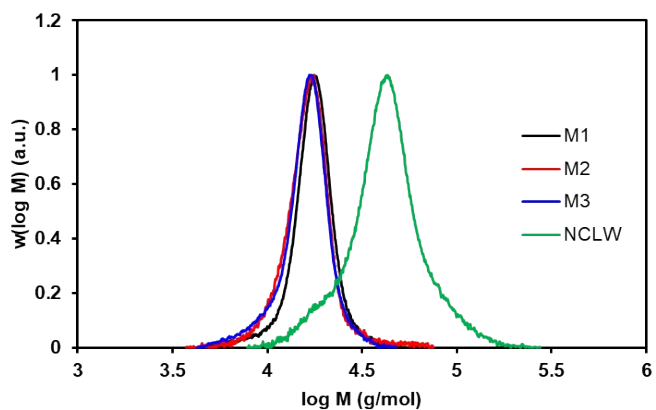
Fig. S1 Molecular weight distributions of macroRAFT agents and non-crosslinked worms.
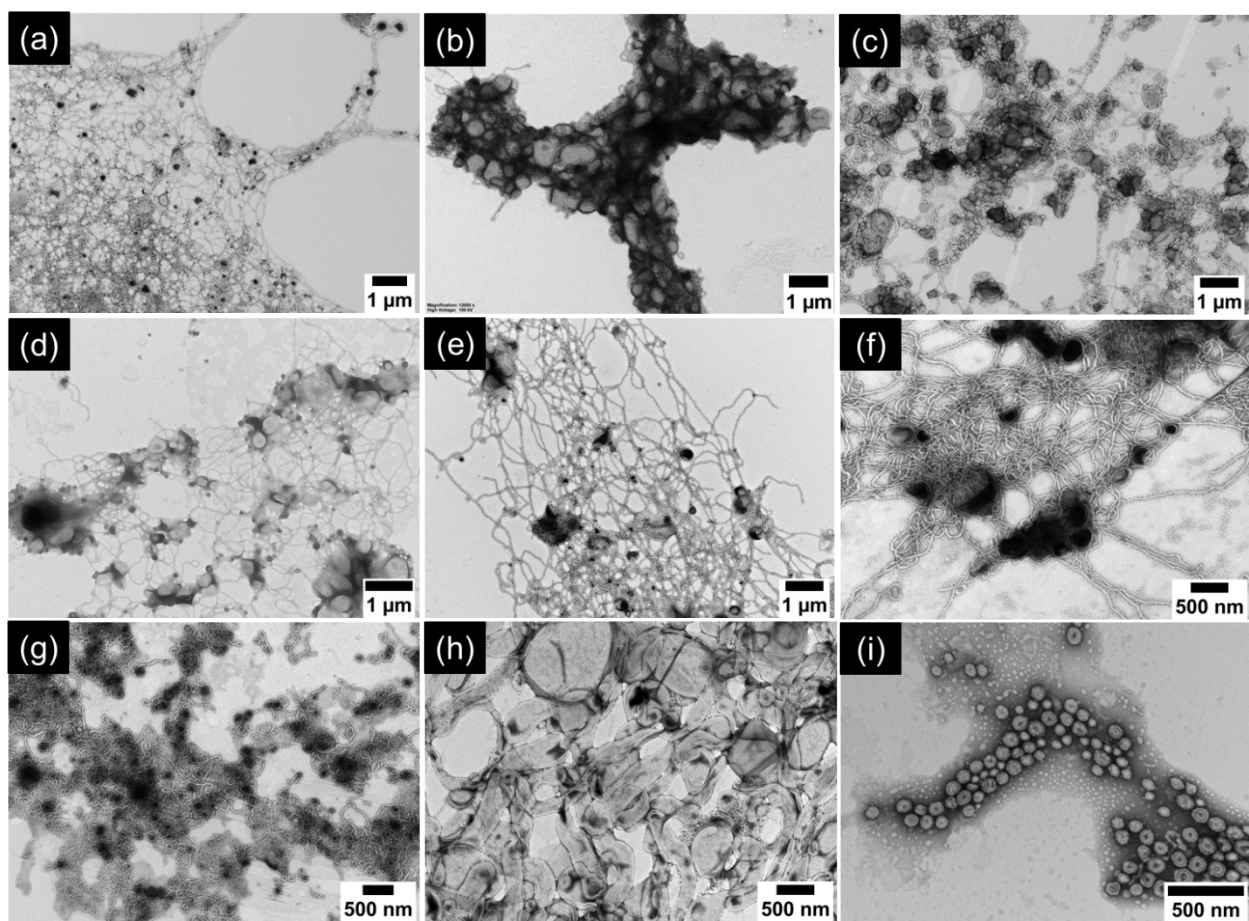
Fig. S2 TEM micrographs of crosslinked particles at various [MMA]:[EGDMA]:[RAFT] molar ratio: (a) 300:0:1 (NCLW), (b) 300:5:1, (c) 300:3:1, (d) 290:3:1, (e) 280:3:1 (CLW), (f) 270:3:1, (g) 250:3:1, (h) 270:10:1, (i) 270:15:1. (Note: e is the same as Figure a in the main part.)

**Table S2.** Results of tensile testing.

| #	wt% filler	σ_{max}[a] /MPa	U_T[b] /MJ·m^{-3}	U_T/U_{T0}[b]
Entries I: P(St-stat-nBA) base film				
1	–	1.3 ± 0.2[e]	6.0 ± 1.1[e]	–
Entries II: Non-crosslinked worm film				
2	5	2.2 ± 1.2	7.7 ± 3.4	1.3
Entries III: Crosslinked worm film				
3	2	2.5 ± 0.6	7.0 ± 1.2	1.2
4	5	6.6 ± 1.7	24.5 ± 7.6	4.1
5	8	1.9 ± 0.6	4.4 ± 3.8	0.7
Entries IV: Crosslinked sphere film				
6	5	2.0 ± 0.3	7.3 ± 1.0	1.2

[a] σ_{max} = tensile strength.
[b] U_T = toughness of material = total area under the stress-strain curve, U_{T0} = toughness of the reference P(St-*stat-n*BA) film prepared without fillers.
[c] Standard deviations on at least 5 samples.
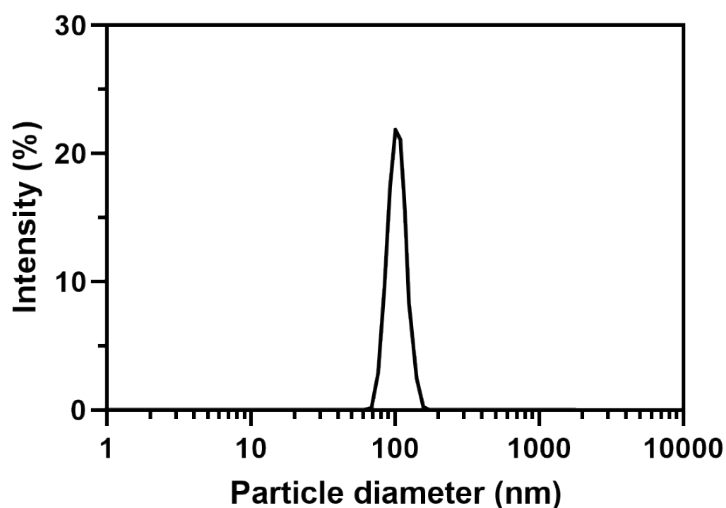
Fig. S3 Particle size distribution of base latex prepared via miniemulsion polymerization.
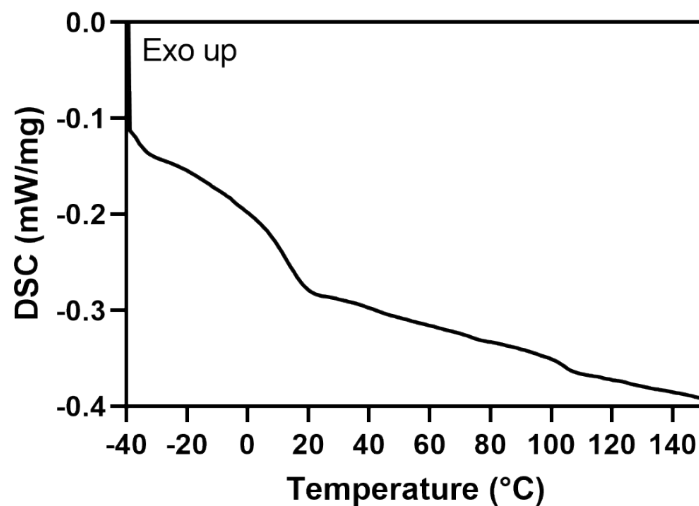
Fig. S4 DSC curve of base matrix prepared via miniemulsion polymerization of styrene and *n*BA.
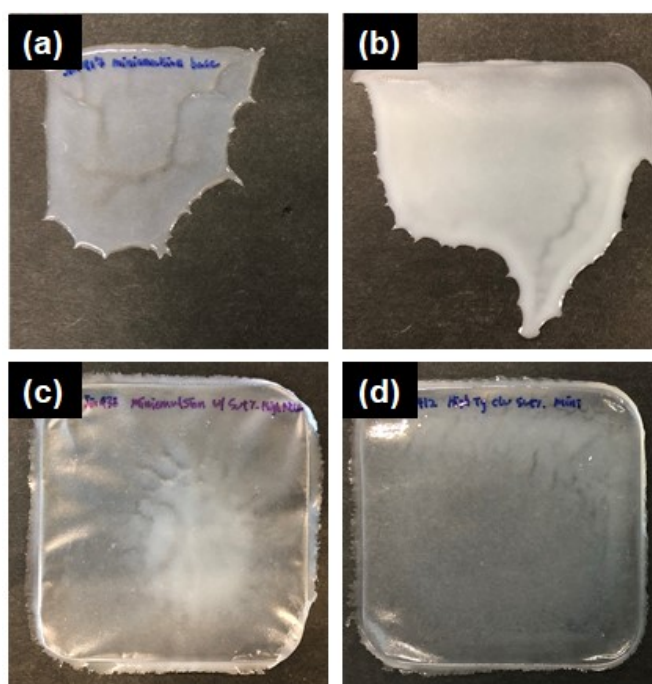
Fig. S5 Images of film surfaces (a) P(St-*stat*-*n*BA) base only film, (b) 5 wt% crosslinked sphere film, (c) 5 wt% non-crosslinked worm film, (d) 5 wt% crosslinked worm film.

References
1.   S. W. Thompson, T. R. Guimarães and P. B. Zetterlund, *Biomacromolecules*, 2020, **21**, 4577-4590.
2.   W. J. Zhang, B. Charleux and P. Cassagnau, *Soft Matter*, 2013, **9**, 2197-2205.
3.   W. J. Zhang, F. D'Agosto, P. Y. Dugas, J. Rieger and B. Charleux, *Polymer*, 2013, **54**, 2011-2019.