Supporting Information

Understanding the Rheology of Polymer-Polymer Interfaces Covered with Janus Nanoparticles: Polymer Blends versus Particle Sandwiched Multilayers

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S1. Linear viscoelasticity of commercial PMMA and PS polymers

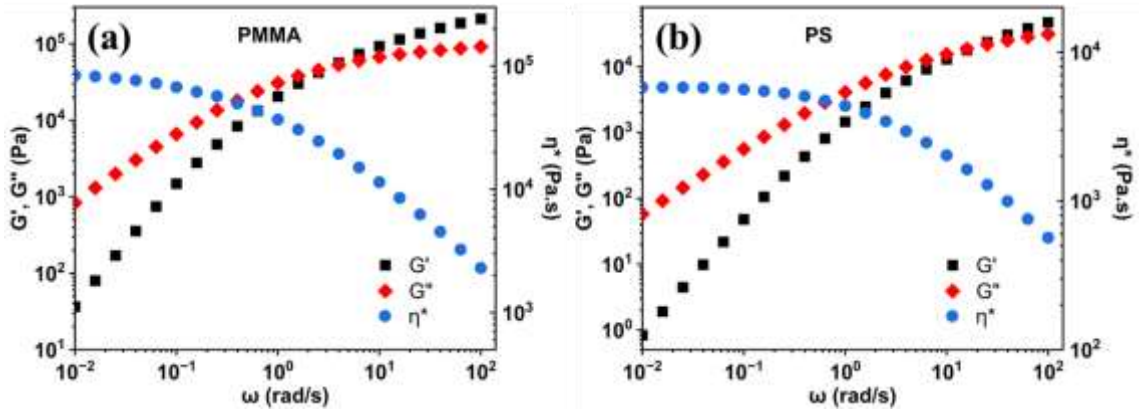

Fig. S1. Variation of G', G'' and η^* with frequency for (a) PMMA and (b) PS at 200 °C.

S2. Synthesis of PMMA-PS dumbbell-shaped JNPs

PMMA-PS dumbbell-shaped JNPs were prepared by seed emulsion polymerization method [1], with PMMA nanoparticles first synthesized as seeds for following growth of PS nanoparticles. A typical synthesis procedure of PMMA seed nanoparticles is shown in Fig. S2. 1.5 g sodium dodecylbenzenesulfonate (SDBS) was firstly dissolved in 353 g deionized (DI) water under magnetic stirring in a three-necked flask, before 100 g of MMA monomer was added. The mixture was bubbled with nitrogen gas for 0.5 h and heated up to 70 °C, then potassium persulfate aqueous solution (KPS, 0.4 g dissolved in 20 g DI water) and divinylbenzene (DVB, 5 wt% of MMA) were slowly added through a cannula, and the mixture was allowed to react at 70 °C for 15 h under N_2 atmosphere protection. After completion of the reaction, the system was purified by dialysis (7 days) to remove impurities till the conductivity reached a value less than 20 μS/cm.

In the second stage, seed emulsion polymerization of styrene (St) monomer based on the above PMMA emulsion was carried out. St monomer (13.5 g), KPS initiator (0.3 g dissolved in 15 g DI water) and DVB crosslinker (5 wt% of St) were added dropwise to 100 mL of the as-obtained PMMA seed emulsion (solid content 3.23 wt%) at 60 °C under magnetic stirring and N_2 bubbling. Then the polymerization reaction was allowed to continue at 70 °C for 2 h before being cooled down to the ambient temperature. The resultant emulsion product was repeatedly washed with ultrapure water via centrifuging at least 3 times and finally freeze-dried to obtain dumbbell-shaped JNPs powders for subsequent use.

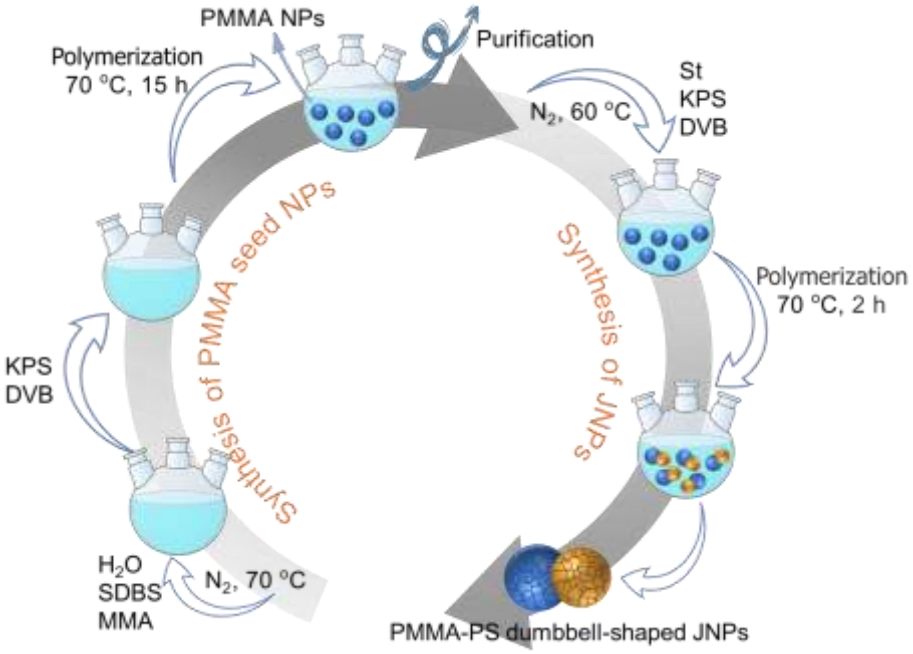

Fig. S2. Schematic illustration of the synthesis of dumbbell-shaped JNPs.

S3. Loading of PMMA-PS dumbbell JNPs onto layer film

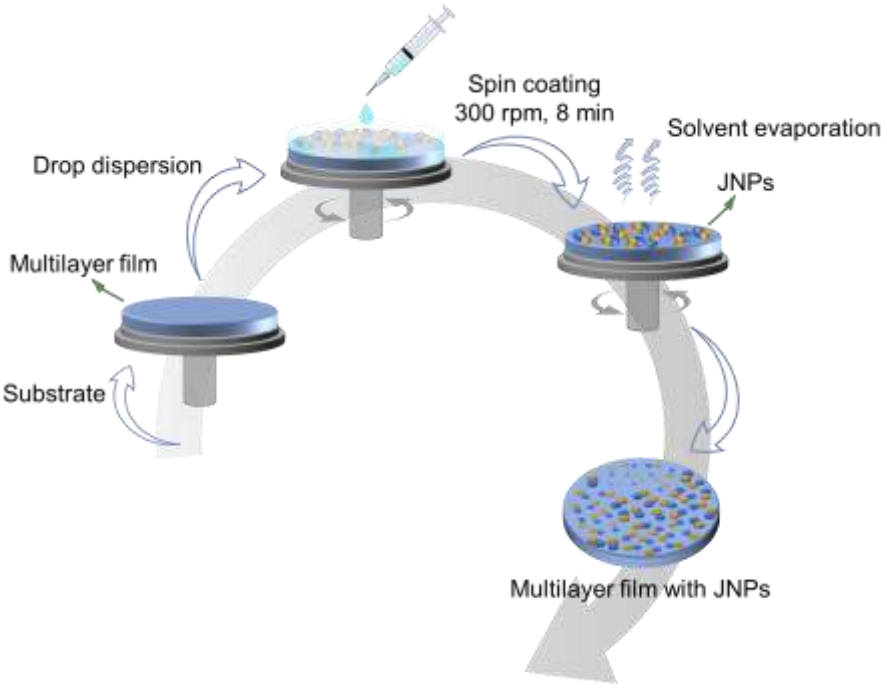

Fig. S3. Schematic illustration of spin coating of JNPs on a multilayer film.

S4. Thermal stability of neat polymers

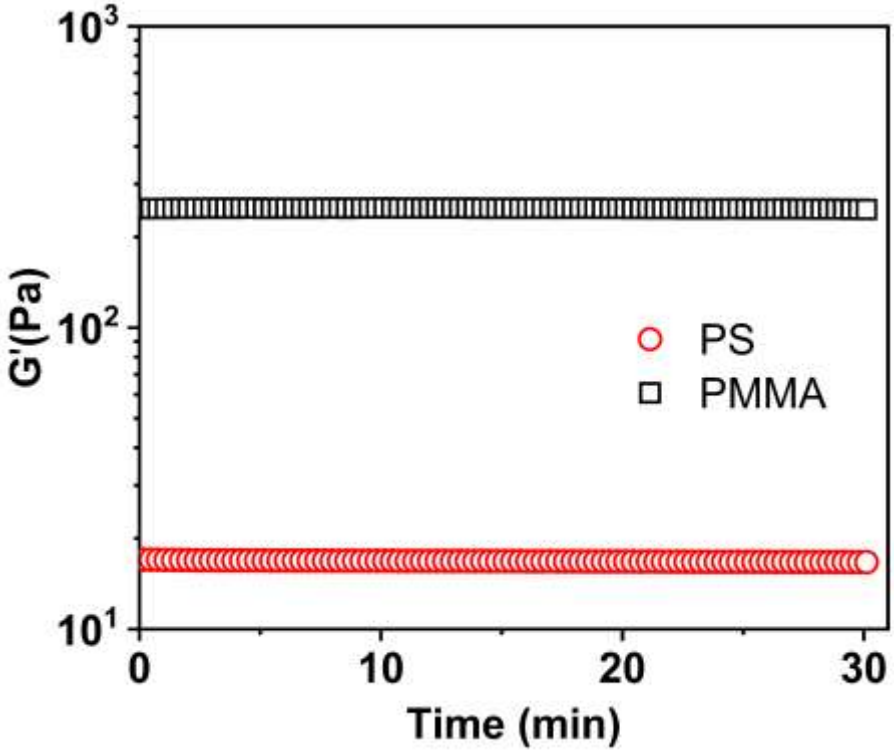

Fig. S4. Variation of storage modulus G' with time for PMMA and PS at 220°C and 1 rad/s.

S5. FTIR data of PS-PMMA dumbbell JNPs

As shown in Fig.S5, the FTIR spectra of PMMA seed NPs and dumbbell-shaped JNPs both exhibit distinct characteristic peaks at 2949 cm^{-1} and 1725 cm^{-1} attributed to the stretching vibrations of -CH_3 and -C=O in PMMA seed NPs, respectively. The PMMA-PS dumbbell-shaped JNPs shows a distinct characteristic peak at 3067 cm^{-1} assigned to the aromatic -C-H stretching vibration in PS NPs, and the aromatic -C=C stretching vibration absorption shows three absorption peaks at 1610 cm^{-1}, 1492 cm^{-1} and 1450 cm^{-1}. Such results fully demonstrate the successful preparation of JNPs.

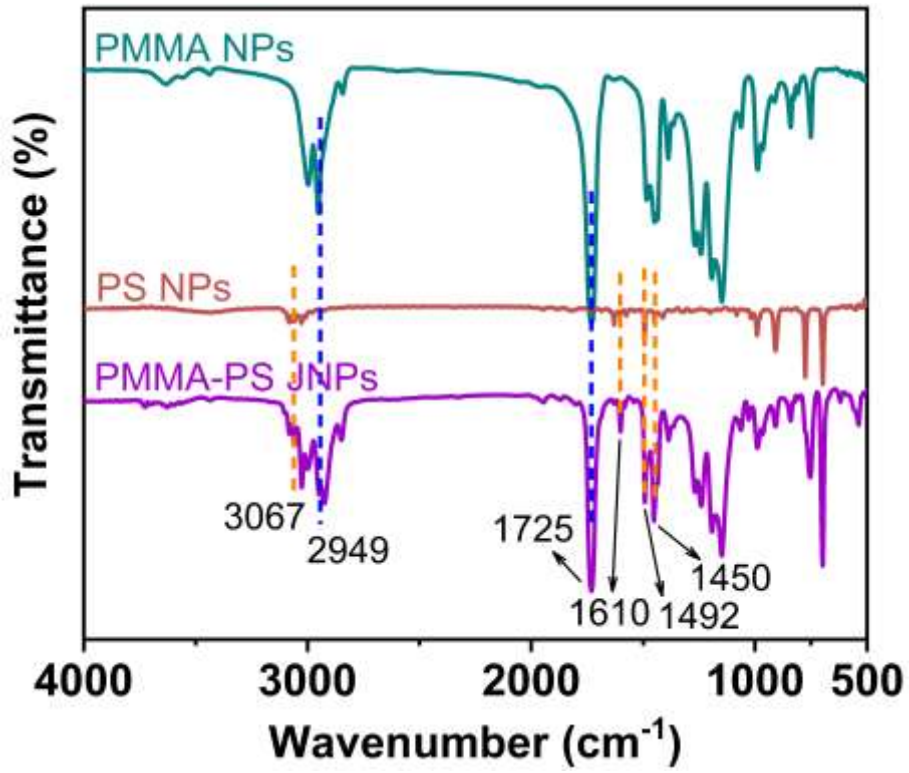

Fig. S5. FTIR spectra of PMMA seed NPs, PS NPs and PMMA-PS dumbbell-shaped JNPs.

S6. Rheology data of PS-PMMA dumbbell JNPs

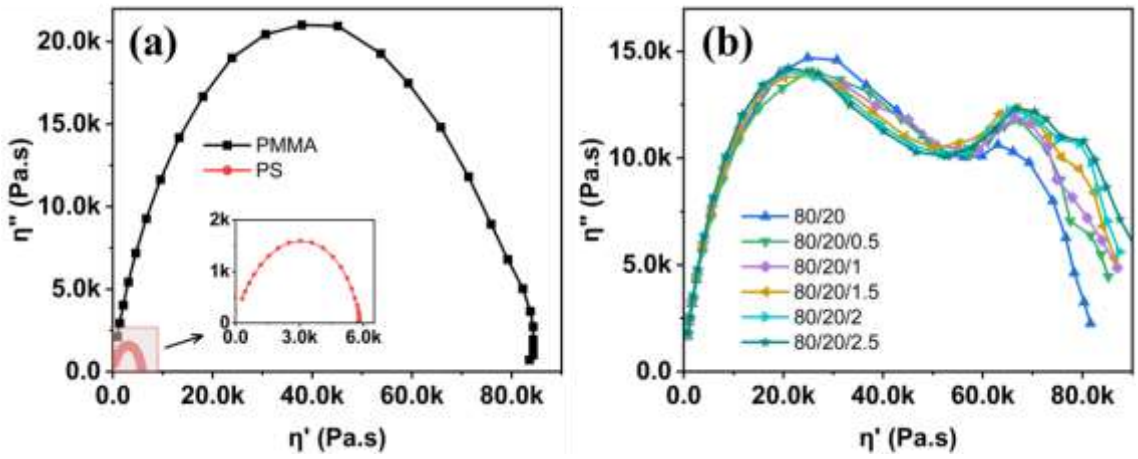

Fig. S6. Cole-Cole plots of (a) neat PS and PMMA polymers and (b) PMMA/PS blends with

various JNPs amounts at 200 °C.

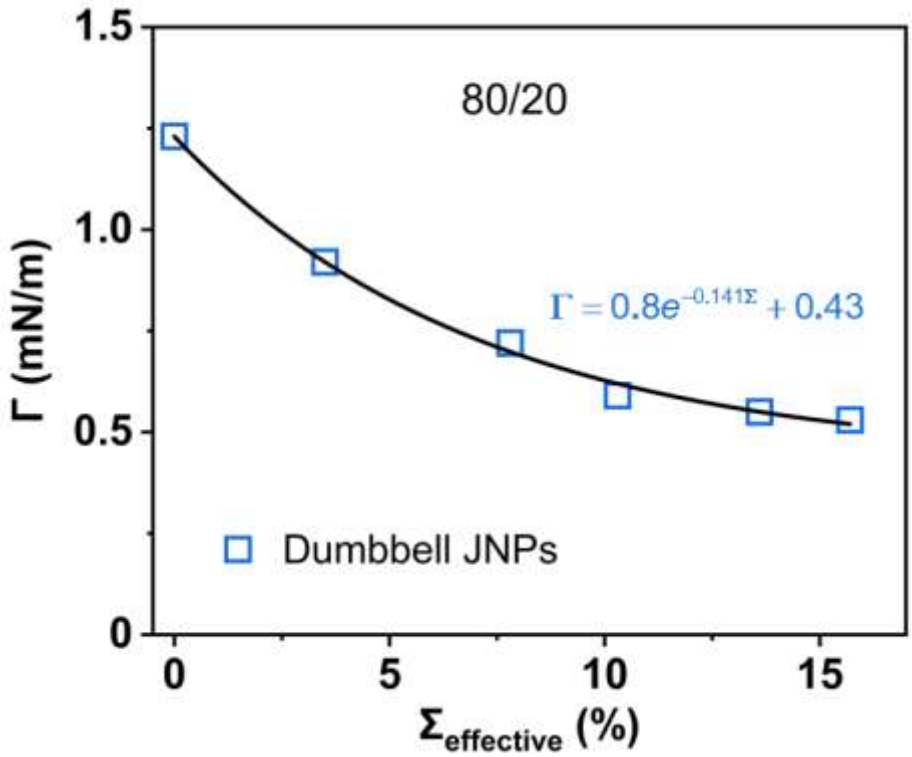

Fig. S7. The Γ of PMMA/PS 80/20 blends as a function of $\Sigma_{effective}$ of the JNPs. The line is the fitting result of Eq. 5 but having w replaced by $\Sigma_{effective}$.

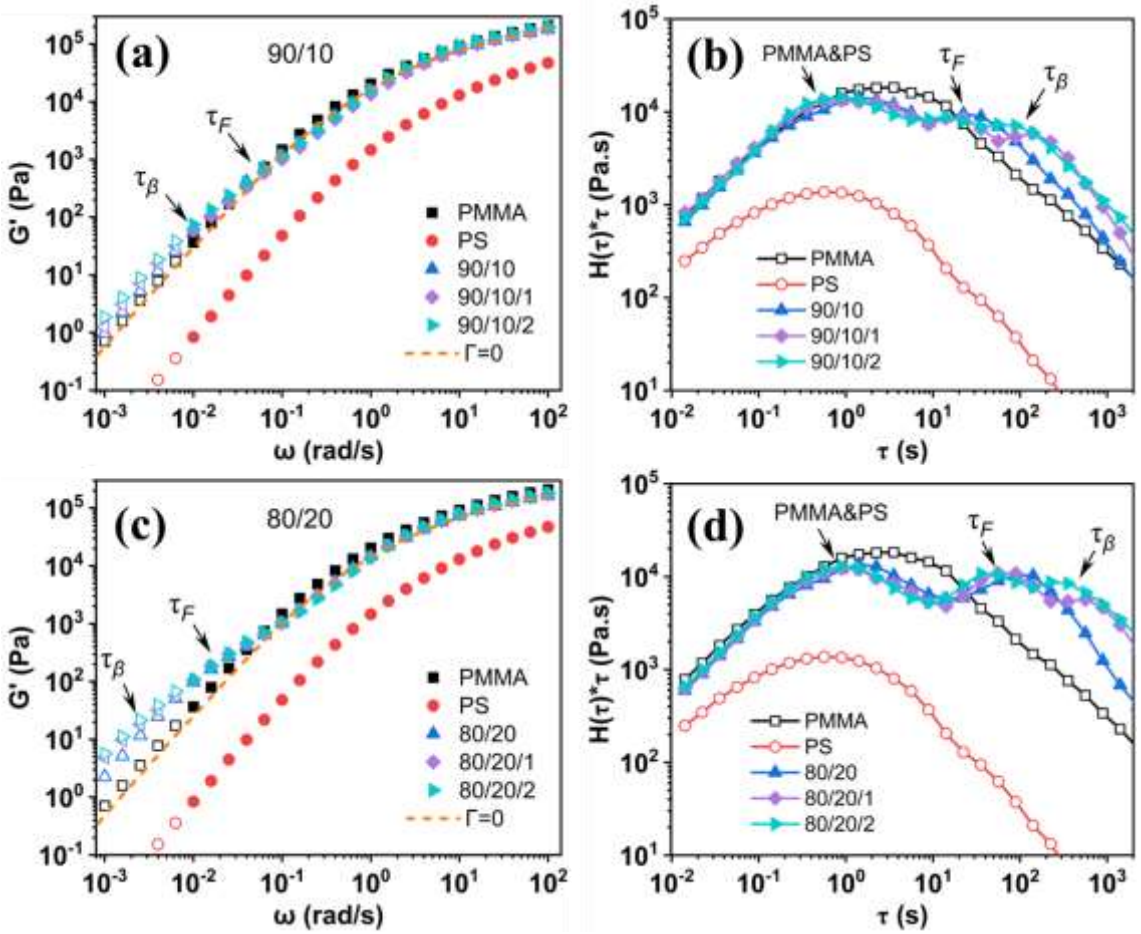

Fig. S8. (a, c) Storage moduli and (b, d) relaxation spectra of PMMA/PS 90/10 and 80/20 blends at 200 °C with various JNPs amounts. The solid symbols are the results from dynamic tests and the hollow symbols are the conversion data from creep tests. The dashed line is the contribution of the blend components at Γ = 0 based on Kerner's model (Eq. 4).

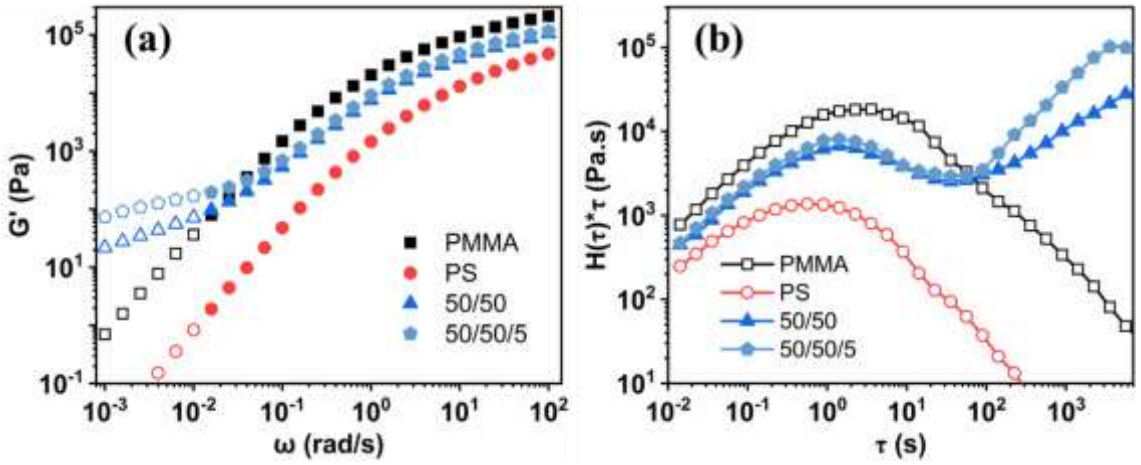

Fig. S9. (a) Storage moduli G' and (b) relaxation time spectra of PS/PMMA 50/50 and PS/PMMA/JNPs 50/50/5 blends at 200 °C with neat polymers presented as reference.

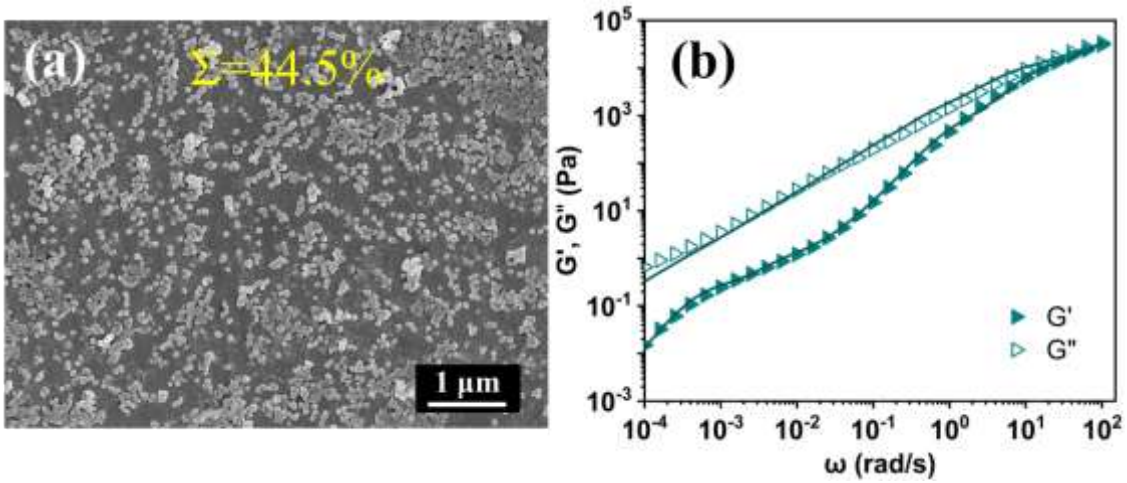

Fig. S10. (a) SEM morphology of the interface of a PMMA/PS multilayer (PS films selectively etched) exhibiting a statistics of the interfacial coverage of JNPs (mostly the PS sphere parts exposed at the interface) to be Σ = 44.5%. (b) Frequency dependence of G' and G'' at 220 °C of 12 layer samples sandwiched with JNPs at Σ = 44.5%. The solid lines represent predictions of the Maxwell model with six modes.

References

[1] M. Hoffmann, Y. Lu, M. Schrinner, M. Ballauff, L. Harnau, Dumbbell-Shaped Polyelectrolyte Brushes Studied by Depolarized Dynamic Light Scattering, The Journal of Physical Chemistry B, 112 (2008) 14843-14850.