Supporting Information for

"House-of-cards" Structures in Silicone Rubber Composites for Superb Anti-collapsing Performance at Medium High Temperature

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Fig. S1. The influence of TPM/PEA ratio on the resultant structures of the composite particles. TEM images of composite particles with different ratios of TPM and PEA: (a) LHCP-1, (b) LHCP-2, (c) LHCP-3, (d) LHCP-4.

The influence of different ratios of TPM and PEA on the resultant structure of the composite particles was established, as shown Fig. S1. When the ratio of TPM and PEA was 0.1, no stable emulsion was obtained; consequently no individual LHCPs was produced but only free Laponite platelets were found in the final products (Fig. S1a). Although LHCPs were obtained with increasing the ratio to 0.2, the LHCPs turned out to be larger than 200 nm with some aggregates of Laponite platelets and PTPM remained (Fig. S1b). As the ratio reached to 0.4, relatively uniform LHCPs with smaller diameter (~100 nm) were obtained (Fig. S1c), suggesting the emulsion system was much more stable at this ratio. Solid particles with diameter of ~50 nm and Laponite armored on the surface were prepared in the absence of PEA (Fig. S1d).



Fig. S2. Free-standing nature of the LHCPs after heat treatment: SEM images of the LHCPs after heating at (a_{1-2}) 500°C, (b_{1-2}) 700°C, (c_{1-2}) 900°C, (d_{1-2}) 1100°C.



Fig. S3. Dispersion of Laponite, modified Laponite and the LHCPs in silicone matrices: (a) Optical images of S-L, S-ML and S-LHCP composites, SEM images of the fracture surfaces of (b) the S-L, (c) the S-ML and (d) the S-LHCP before pyrolysis.

The compatibility between fillers and silicone rubber matrix was examined by visual check and microscopic observation (Fig. S3). Solution co-blending was used to mix the composite particles and rubber matrix. The composite particles were dispersed in THF to generate a homogenous dispersion, while the silicone rubber was also dissolved in THF. The particle dispersion was added to silicone rubber solution under stirring, and the solvent was removed afterward by rotary evaporation. Finally, the samples were dried in vacuum oven at ambient temperature for 2 days.

When unmodified Laponite platelets were used (S-L), obvious phase separation was observed (Fig. S3a), and large aggregates were formed (Fig. S3b). For both S-ML and S-LHCP, when mixed with silicone rubber, no macroscopic phase separation (Fig. S3a) or microscopic aggregates (Fig. S3c and S3d) were observed, manifesting their good compatibility with silicone rubber matrix.



Fig. S4. N₂ adsorption and desorption isotherms (a) and pore size distribution of S-LHCP composites after pyrolysis at 700°C.

Fig. S4 represents the N_2 adsorption and desorption isotherms and pore size distribution of S-LHCP composites after pyrolysis at 700°C. It showed an obvious hysteresis as a result of the presence of mesopores, with a specific surface area of 172 m².g⁻¹ (Fig. S4a). In addition, the mesopores showed a broad distribution centered at around approximately 22 nm, exhibiting a pore volume of 0.716 cm³.g⁻¹. The narrow distribution around 3.8 nm was attributed to the tensile strength effect (TSE) owing to the application of the BJH model.¹ The porosity measurements further confirmed the shape retention property of the S-LHCP composites after heat treatment.



Fig. S5. SEM images of the pyrolyzates of (a) the neat silicone, (b) the S-L composite.

The neat silicone and the S-L composite were converted to powder-like residues after pyrolysis, with small particles loosely agglomerated (Fig. S5).

Reference

J. C. Groen, L. A. A. Peffer and J. Pérez-Ramírez, *Micropor. Mesopor. Mat.*, 2003, 60, 1-17.