

Liyang Shen¹, Tung-ping Wang¹, Sri Harsha Kalluru¹, Sabrina Torres², Thomas Robison², Eric W. Cochran¹

All-polymer-based anti-aging, lightweight block copolymer modified polysiloxane composites

Introduction

Silica is widely used for liquid silicone thickening and silicone rubber reinforcement because of the high modulus and strong matrix-filler bonding. Fresh silica filled silicone compounds usually require few weeks' storage for stabilization before direct use or subsequent processing, because the compounds tend to have aging phenomena, which refers to changes in the viscosity, over this storage time. It pushes up the production cost and more importantly, decreases the process repeatability. Silicone materials are commonly used in areas such as aviation and aerospace, which value lightweight materials, but the relative density of silica is above 2.1. Polystyrene-block-Polydimethylsiloxane(PS-b-PDMS) block copolymers have attracted great attention in nanolithography due to the strong self-assembly. Nevertheless, we applied the well-known block copolymers acting as compatibilizers along with homopolystyrene to create the new lightweight silicone composites, since both polymers have relative density close to 1. The relatively large interaction parameter χ of PS/PDMS ensures the anti-aging ability. The structure and size of the fillers depend on the molecular characteristics and filler content. PS-b-PDMS-b-PS triblock copolymer is also added to promote the filler-filler interaction. The mechanical characterization of the glassy polymer reinforced PDMS has been able to prove the feasibility of silica substitution by polymer. Surprisingly, the block copolymer filled composites display noticeable mechanical performance comparing with silica filled composites, even though the modulus of PS is much smaller than silica.

Experimental

Vinyl-terminated polydimethylsiloxane (Gelest, DMS-V31 28 kDa) was used as the polymer matrix. 30 wt% silica filled PDMS composites (Cabot, CAB-O-SIL® Fumed Silica MS-75D) were prepared as reference. The polymer fillers included a homopolystyrene (Sigma-Aldrich) and self-synthesized block copolymer by anionic polymerization(PDMS-b-PS, PS-b-PDMS-b-PS), which are shown in following table.

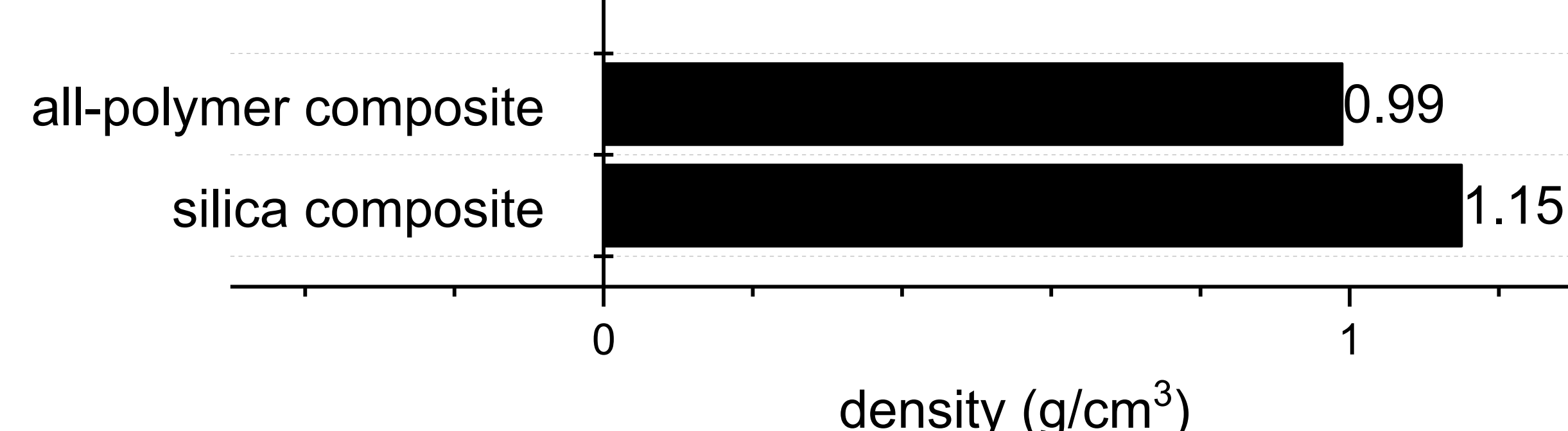
Molecular characteristics of PDMS homopolymer and polymer fillers

Sample	M _n (kg/mol)	Mw/Mn	f _{PS%}	w _{PS%}
Vinyl-terminated PDMS	28	1.57	--	--
Polystyrene(PS)	23	1.52	--	--
PDMS-b-PS (Di)	61	1.08	0.47	0.49
PS-b-PDMS-b-PS (Tri)	121	1.10	0.47	0.49

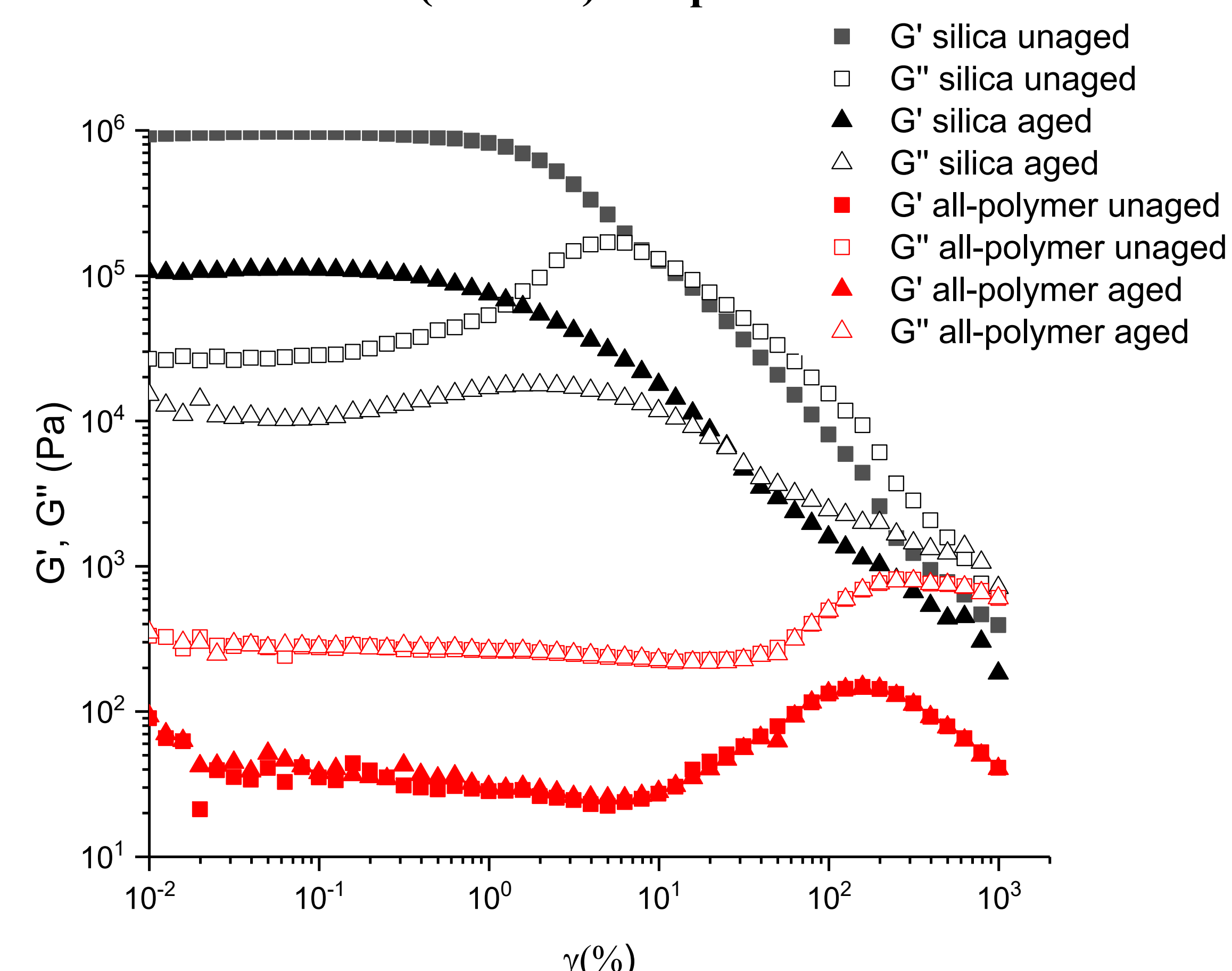
The raw materials and the crosslinking agent methylhydrosiloxane-dimethylsiloxane copolymer (Gelest, HMS-301) were mixed at 160 °C, 200 rpm for 30 minutes in twin-screw micro-compounder. After the platinum catalyst (Gelest SIP6832.2) was added and mixed, the mixture was put under vacuum again. The final step was compression molding at 5000 lbs, 150 °C for 3 h.

The density measurement of the cured composites were performed according to ASTM D297-15. The rheological measurement of the pre-cure compounds were performed on TA ARES-G2 rheometer at 25°C, $\omega=6.28$ rad/s. The aged samples were storage at room temperature for 120 days. A special designed SER universal testing platform were used for mechanical characterization. The strips used for tensile test have a dimension of 30mm (length) ×8mm (width) ×1mm (thickness). The strain rate was 0.1 s⁻¹. All samples were stretched until breakage to collect ultimate tensile strength and elongation at break. The TEM specimens with a thickness of about 90 nm were microtomed below -140°C by cryo-ultramicrotomy (Leica Ultracut 125UCT). The morphological characterization was performed by JEOL 2100 scanning and transmission electron microscope at 200 kV.

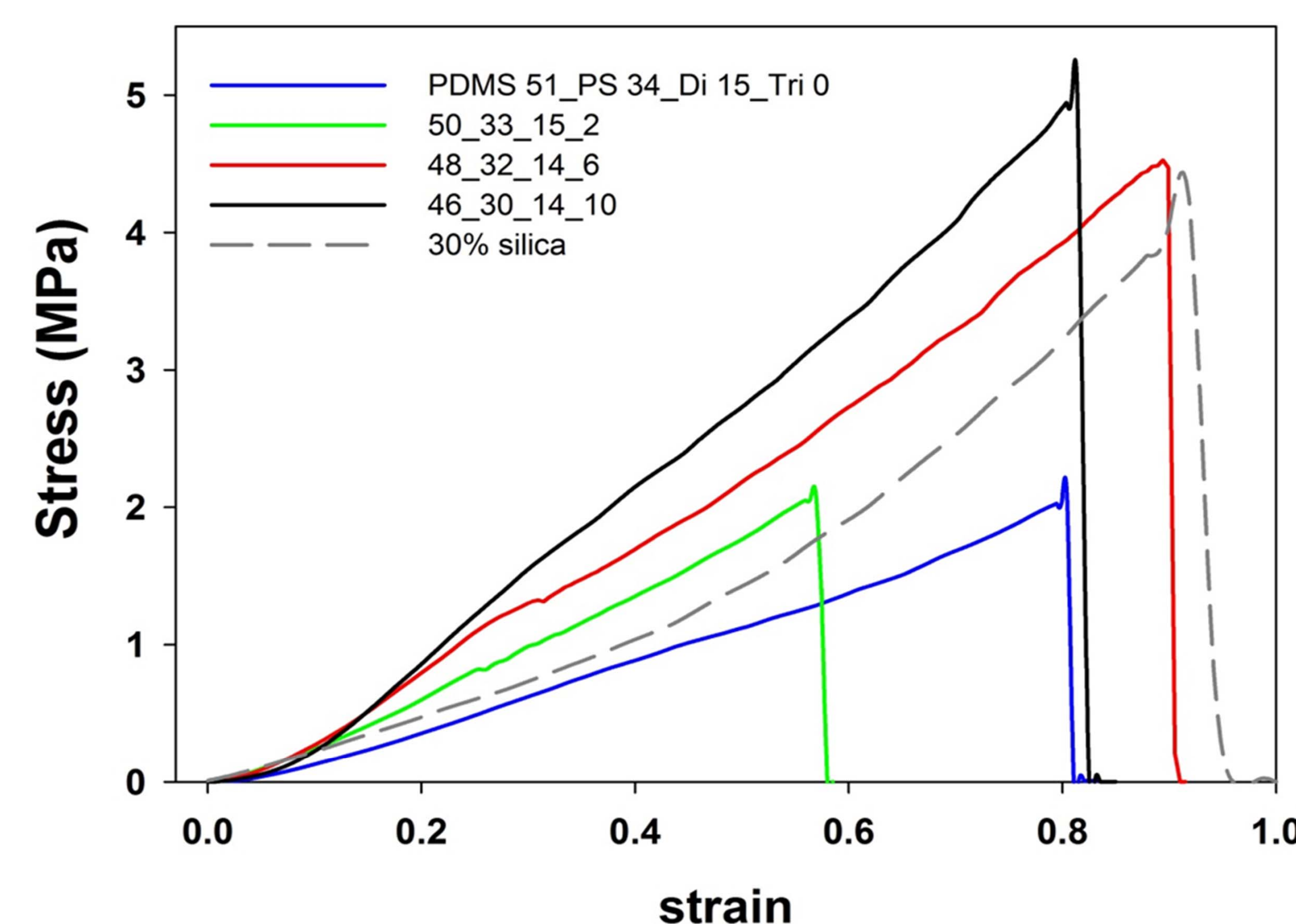
Results



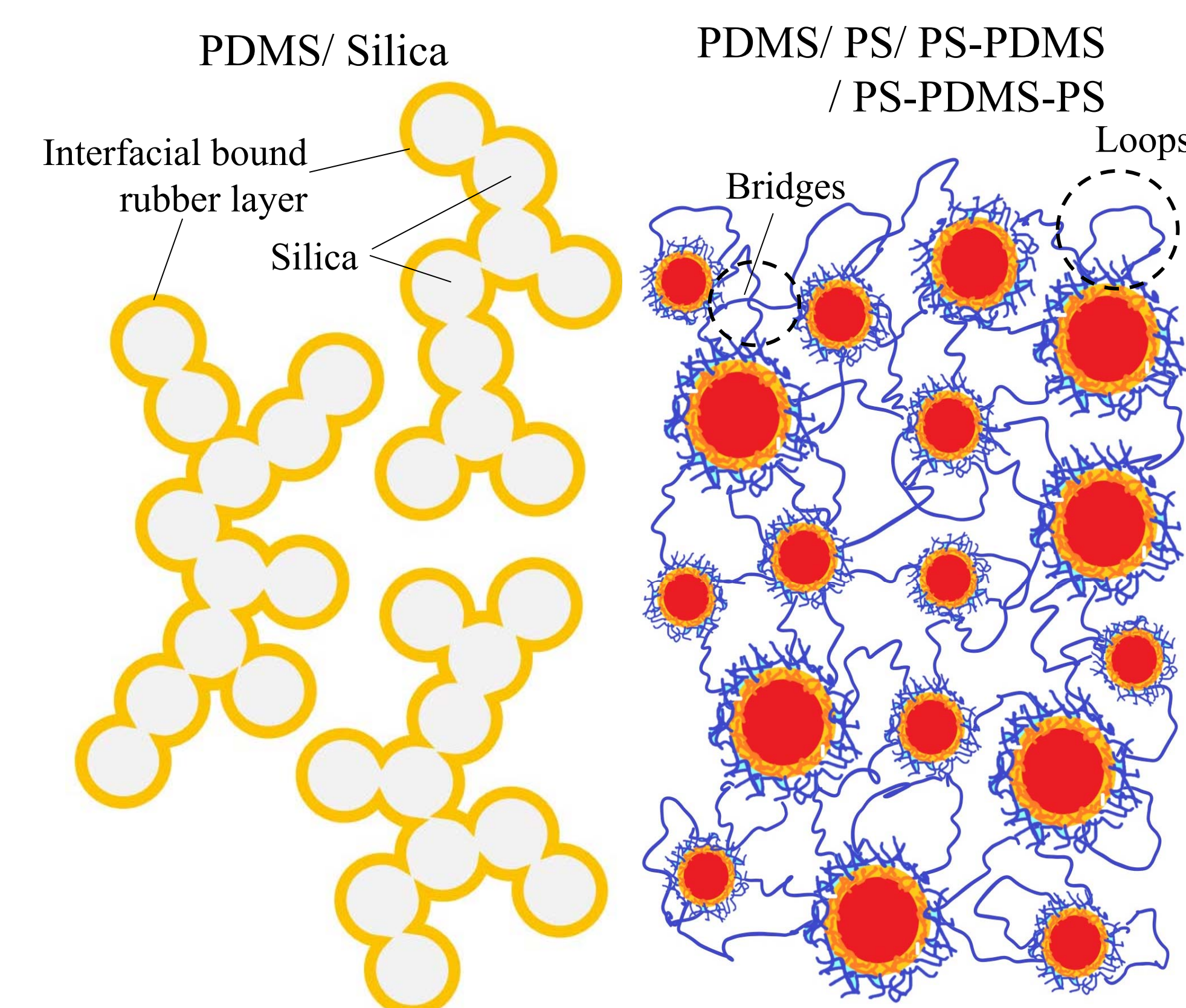
Density comparison of all-polymer (PS 30/ Di 14/ Tri 10 wt%) and silica (30 wt%) composites



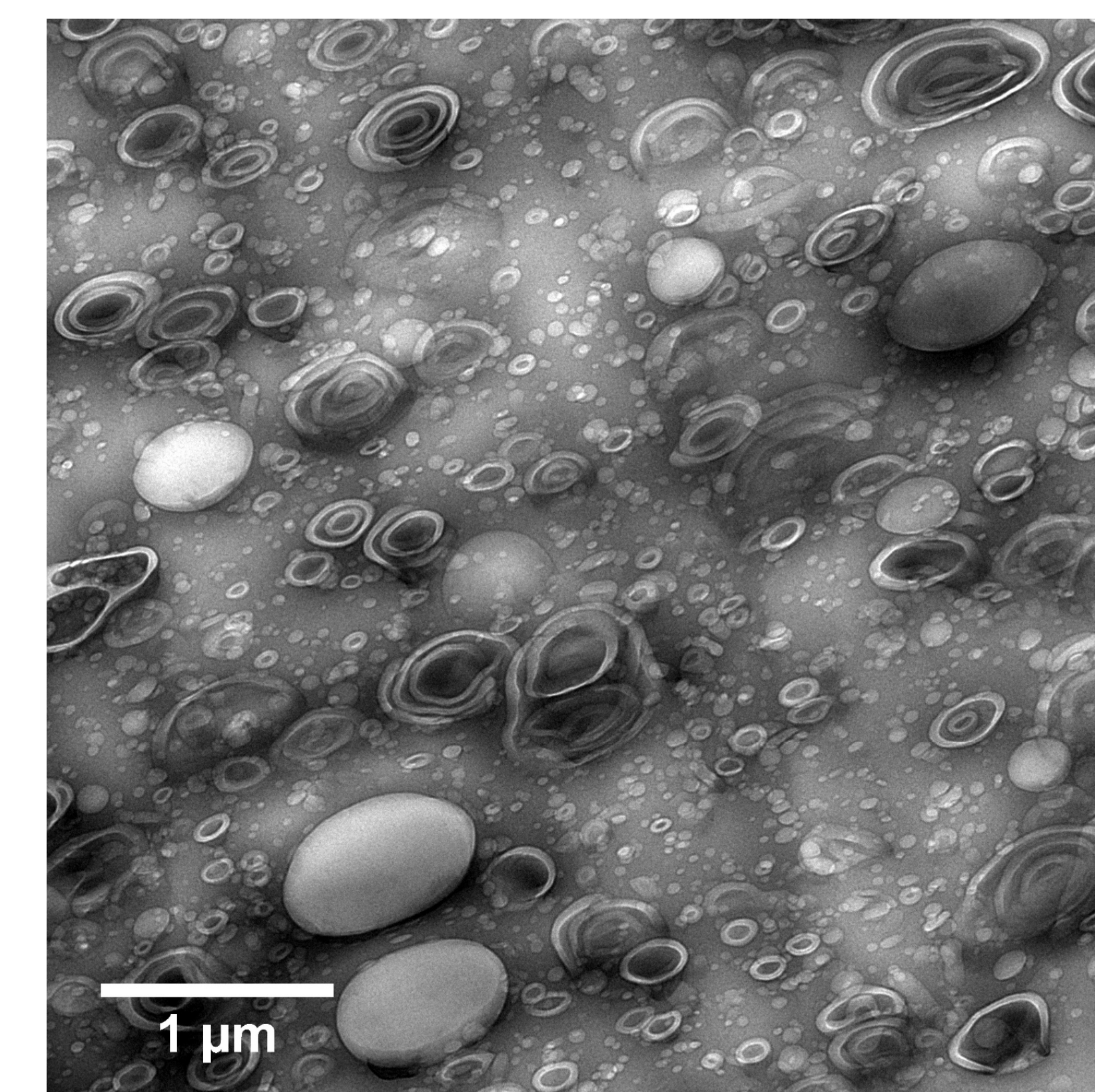
Influence of aging on G' (solid symbols) and G'' (hollow symbols) of silica (30 wt%) and all-polymer (PS 30/ Di 14/ Tri 10 wt%) compounds at 25°C, 6.28 rad/s



Stress-strain curves of silica and all-polymer (both in wt%) composites, strain rate 0.1 s⁻¹



Cartoon hypothesized morphology of silica and all-polymer composites



Representative TEM images of and all-polymer (PS 30/ Di 14/ Tri 10 wt%) composites

Conclusions

This work exhibits that the lightweight, easy-processable all polymer reinforced polysiloxane composites are able to rival the traditional silica filled composites, while the pre-cure all-polymer compounds do not age after long-term storage.

Acknowledgement

This work is funded by the Department of Energy's Kansas City National Security Campus, operated by Honeywell Federal Manufacturing & Technologies, LLC under contract number N000217245 and N000254419.