Polyurethane microparticles for stimuli response and reduced oxidative degradation in highly porous shape memory polymers

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SUPPLEMENTAL MATERIALS

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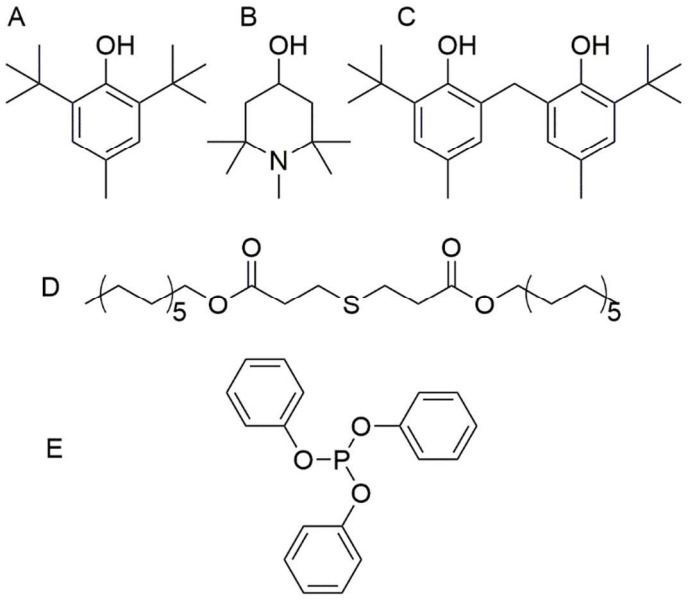
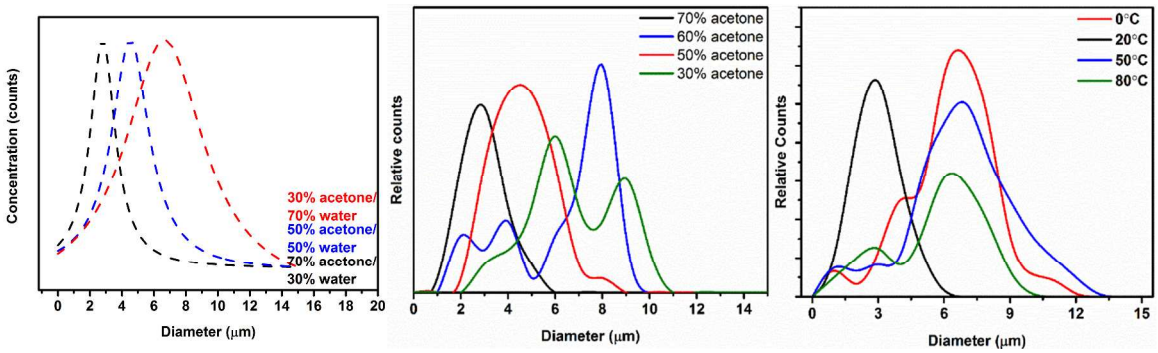
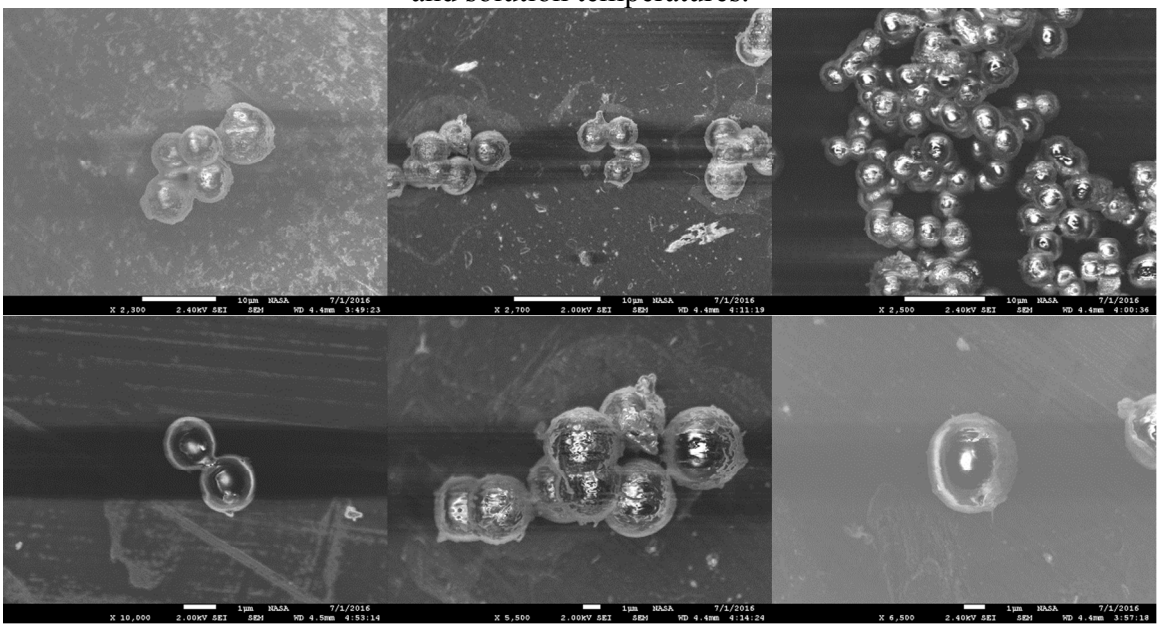


Species	*Starting Material (%) at conclusion*	*Urethane formation (%)*	*Urea formation (%)*
Control (EtOH)	3.7	70.2	26.1
Piper	45.7	31.7	22.6
Methyl	32.8	28.0 (19.5)*	19.5
BHT	100	0	~100
Thio	100	0	~100
Triphen	100	0	~100

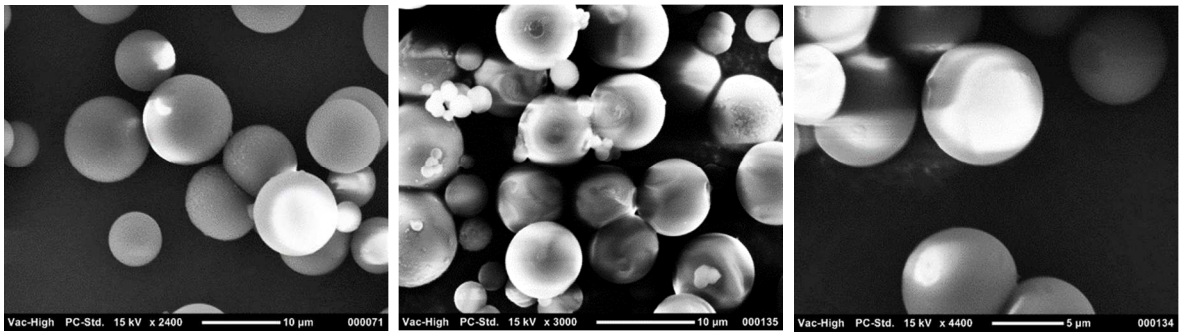
SI Figure 1. Antioxidant structures used to synthesize oxidatively stable porous SMPs. (A) butylated hydroxytoluene, (B) 2,2,6,6 tetramethyl piperidinol, (C) 2,2'-methylenebis(6-tert-butyl-methylphenol), (D) didodecyl 3,3 thiodipropionate, (E) triphenyl phosphite, and their reactions with hexyl isocyanate in model compound studies with quantified urethane and urea concentrations determined. * denotes where two urethane linkages were formed as determined by LCMS.



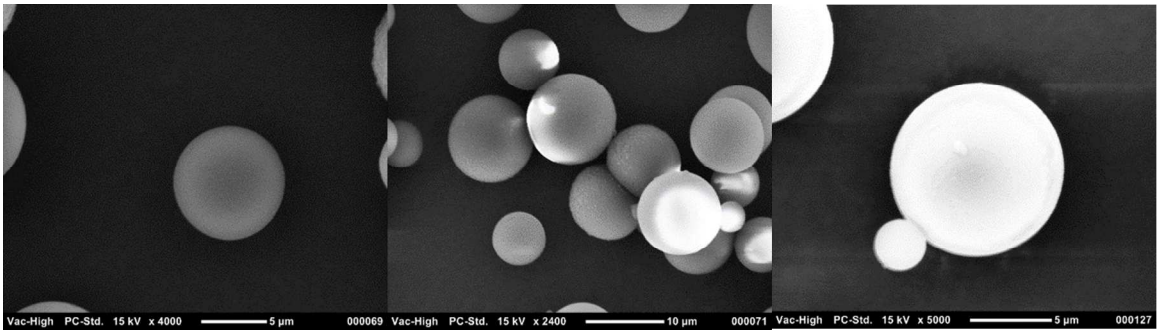
SI Figure 2. Size distribution of IPDI TEA particles synthesized at varied solvent percentages and solution temperatures.



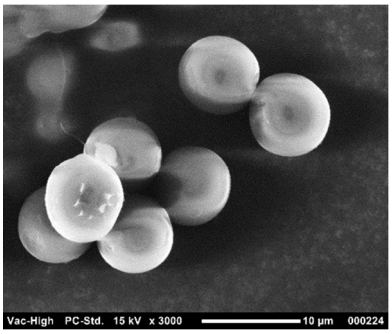
SI Figure 3. SEM images of particles synthesized containing BHT (top) and Piper (bottom).



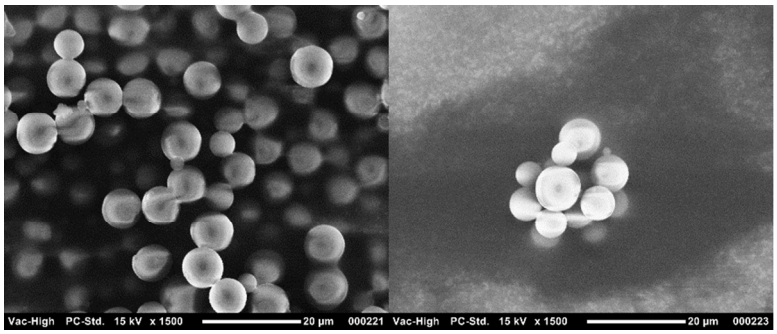
SI Figure 4. SEM images of microparticles made from TEA (left), HPED (middle) and DEA (right).



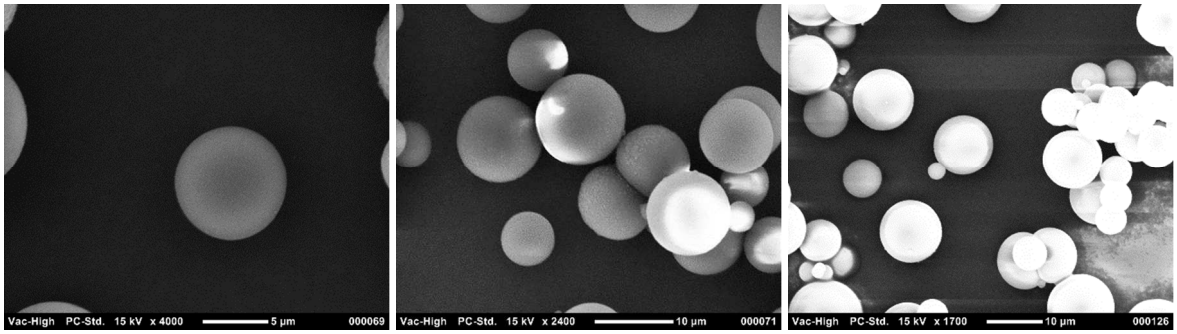
SI Figure 5. SEM images of particles synthesized from IPDI and TEA at 20°C.



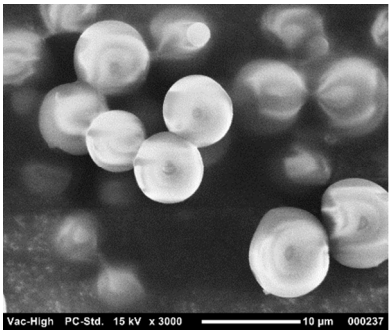
SI Figure 6. SEM images of particles synthesized from IPDI and TEA 0°C



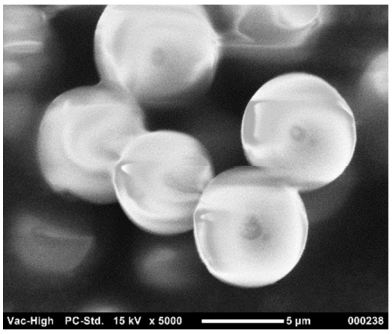
SI Figure 7. SEM images of particles synthesized from IPDI and TEA at 80°C



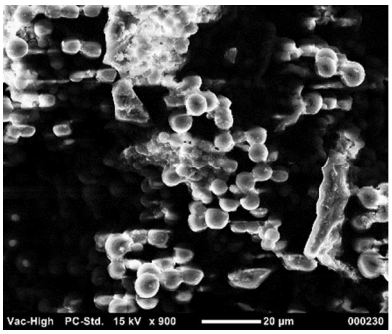
SI Figure 8. SEM images of particles synthesized from IPDI and TEA at 65°C



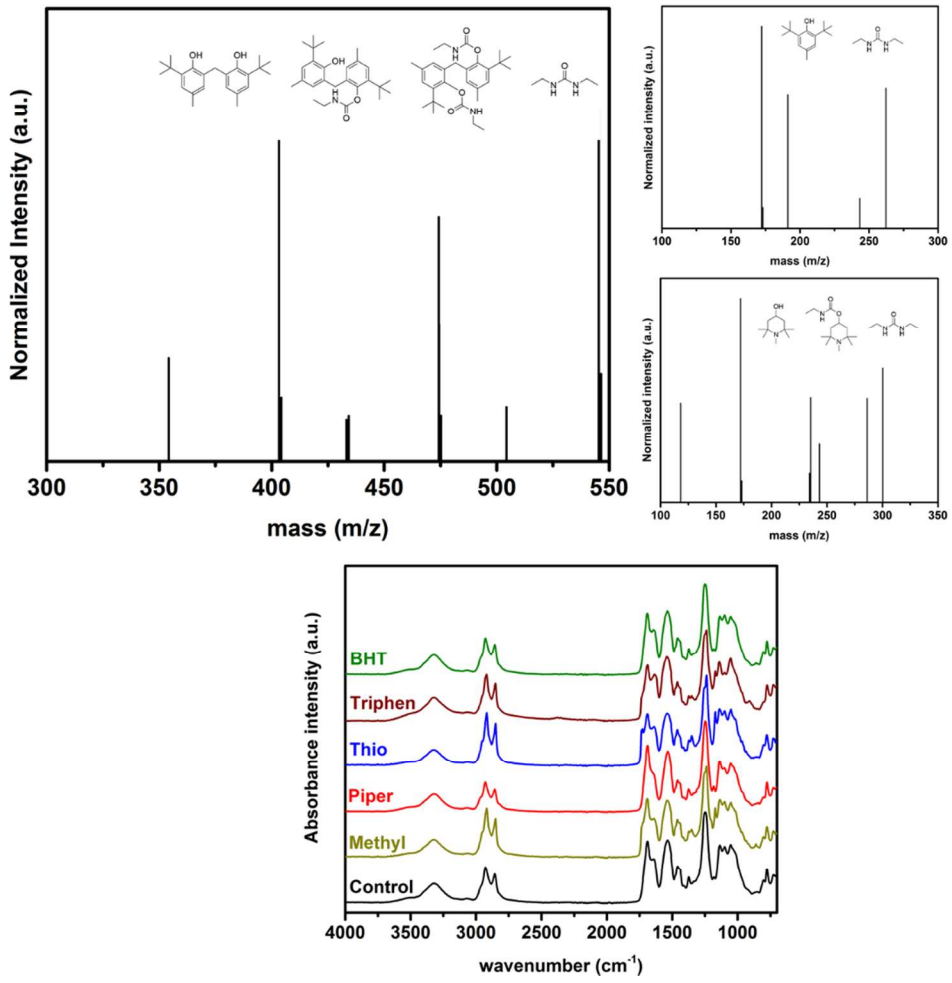
SI Figure 9. SEM image of particles synthesized from IPDI and TEA, 60% acetone



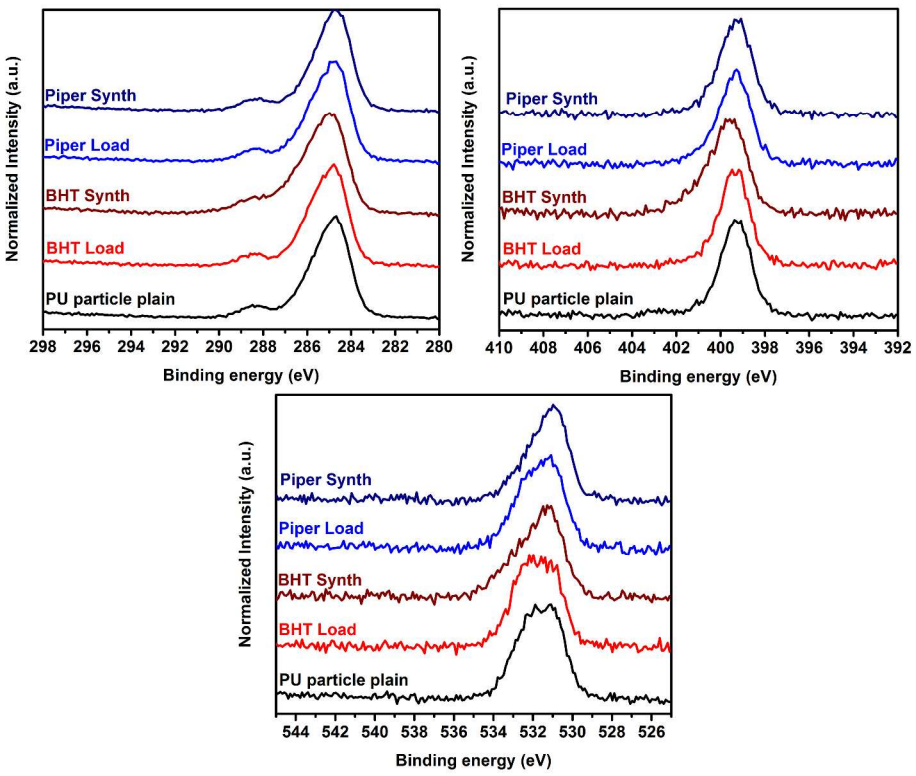
SI Figure 10. SEM image of particles synthesized from IPDI and TEA 50% acetone



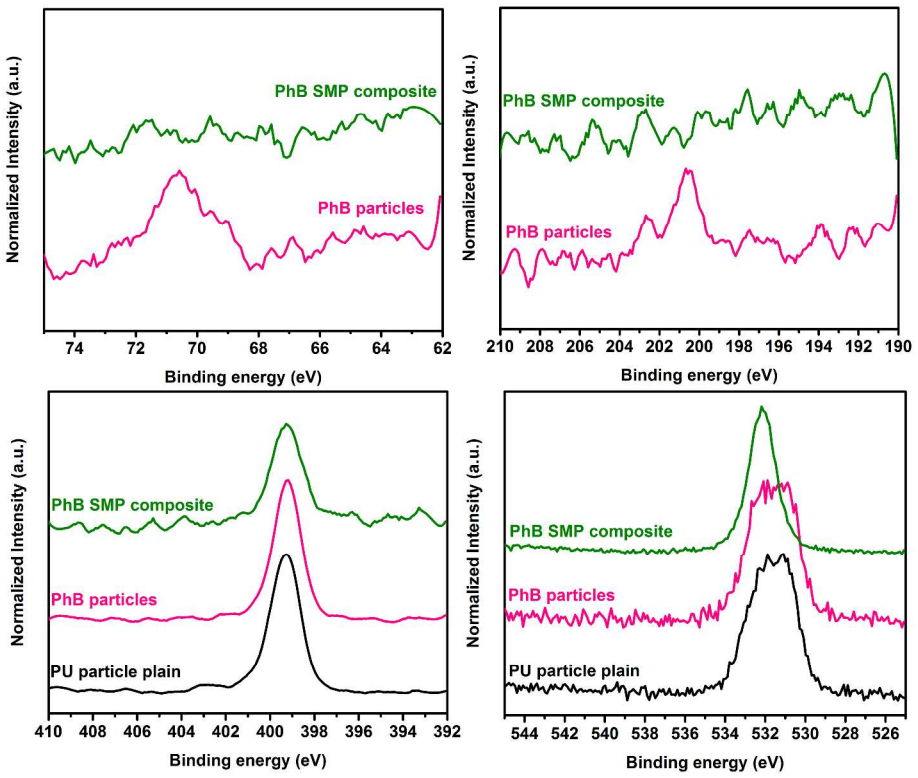
SI Figure 11. SEM image of particles synthesized from IPDI and TEA 30% acetone



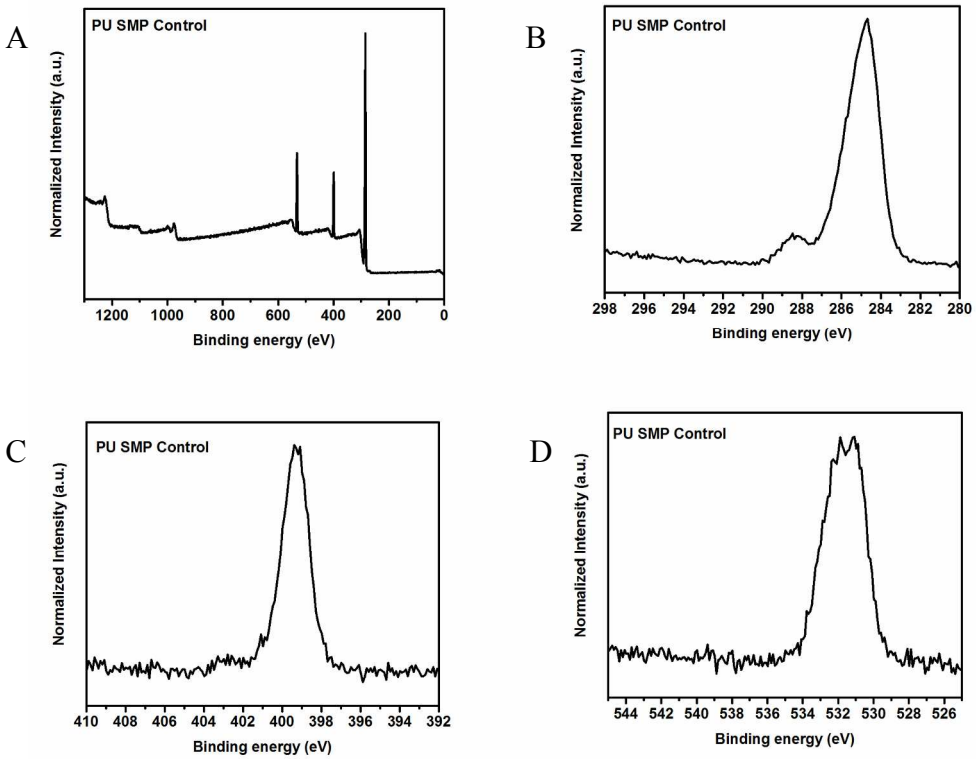
SI Figure 12. Spectroscopic analysis of the antioxidant reactions with isocyanates using model compounds BHT, Methyl and Piper (top), and FTIR-ATR of the antioxidant-containing SMPs (bottom).



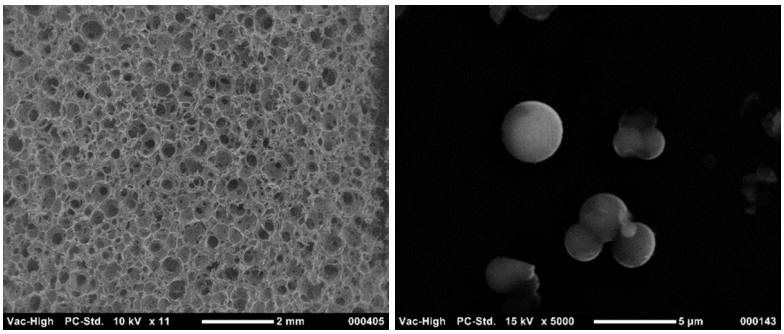
SI Figure 13. XPS spectra of example particles comparing the effects of loading during synthesis compared with post synthesis of Piper and BHT antioxidants. (C1s (298-280 eV), N1s (410-392 eV), O1s (545-525 eV)).



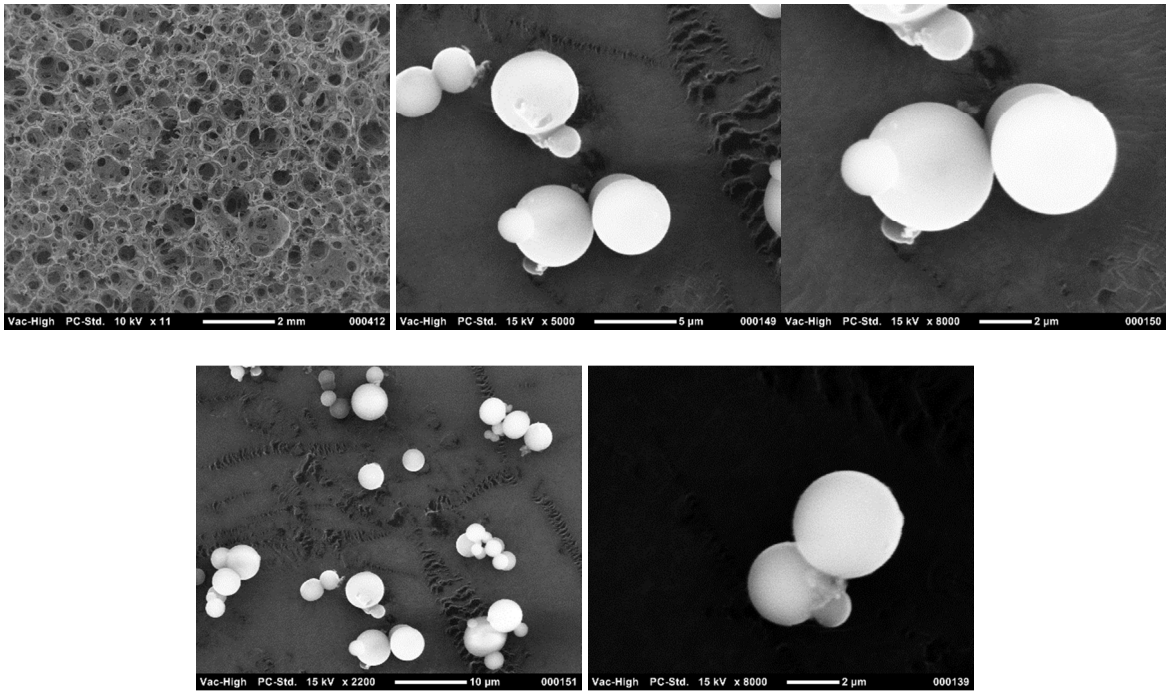
SI Figure 14. XPS spectra of Br3p (75-62 eV), Cl2s (210-190 eV), N1s (410-392 eV), O1s (545-525 eV) for PhB-containing SMPs and particles.



SI Figure 15. XPS spectra displaying control SMP formulations, displaying the survey scan (A) and specific elemental scans (C1s (298-280 eV, B), N1s (410-392 eV, C), O1s (545-525 eV, D)).



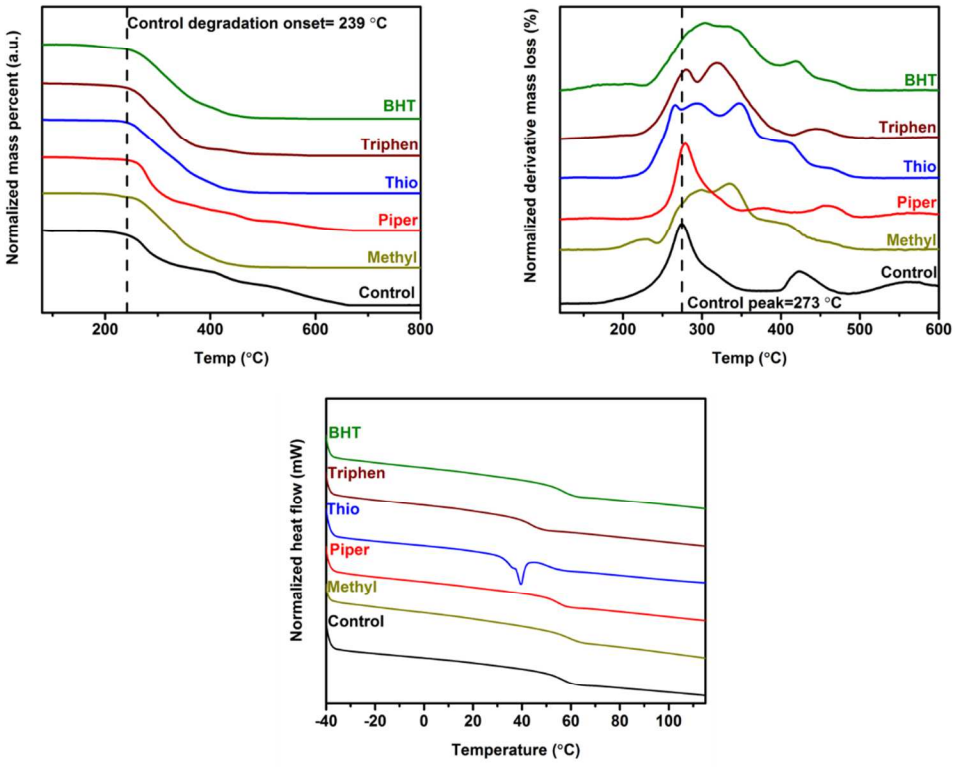
SI Figure 16. SEM image of Nile particle SMP composite of foam pores containing microparticles in struts (left), and individual particles (right).



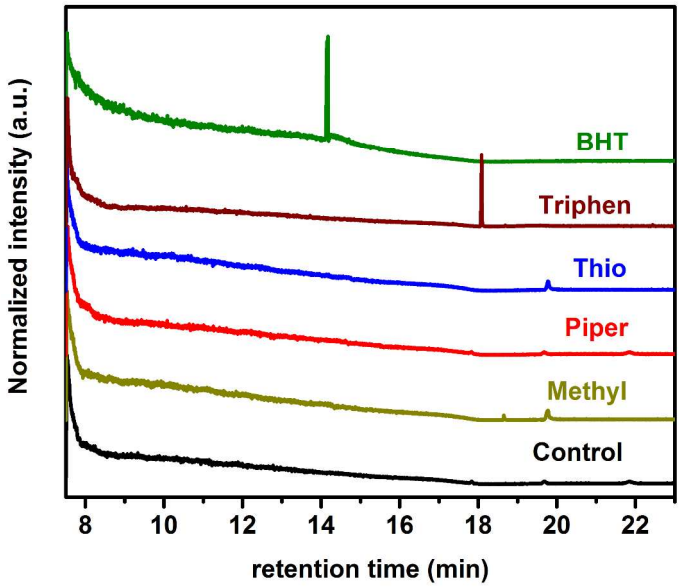
SI Figure 17. SEM image of PhB particle SMP composite (top left) and SEM images of particles (top center, top right, and bottom).

SI Table 1. Mechanical properties of small molecule antioxidant-containing SMPs using HDI and 60% TEA/40% HPED alcohol ratio; all samples were tested at room temperature at 5 mm/min for ASTM Type IV dogbones.

Foam Composition	*Elastic Modulus (MPa)*	*Strain-to-Failure (%)*	*Tensile Strength (MPa)*	*Toughness (J*m^4)*
Control	0.25 ± 0.06	165 ± 21	0.41 ± 0.08	333.1
Piper	0.28 ± 0.19	167 ± 27	0.61 ± 0.23	786.9
Methyl	2.32 ± 0.44	104 ± 27	1.77 ± 0.46	1263.8
BHT	0.24 ± 0.06	176 ± 39	0.97 ± 0.14	940.1
Thio	0.24 ± 0.06	181 ± 49	0.81 ± 0.21	722.6
Triphen	0.11 ± 0.02	131 ± 21	0.35 ± 0.06	204.5



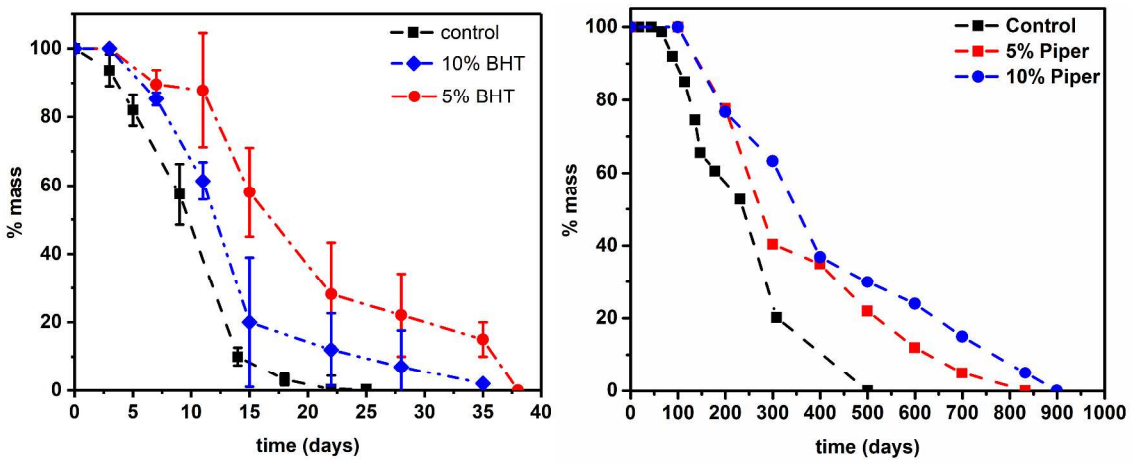
SI Figure 18. Thermal analysis of antioxidant-containing foams, displaying TGA (top) and DSC (below) thermograms. BHT, Piper, Thio, and Methyl seemed to delay thermal oxidation; after extractions, Thio still appeared to be in the SMP matrix, as did Methyl, Piper, and BHT (Triphen seemed to have been extracted out).



SI Figure 19. GCMS chromatographs for antioxidants extracted from SMPs.

SI Table 2. Mass and concentration of antioxidants added during synthesis and extracted during cleaning, determined using GC/MS.

	Additive Mass (g)	Additive Concentration (mol)	Extract Mass (g)	Extract Concentration (mol)
Piper	2.000	0.012	0.080	0.000
Methyl	2.000	0.006	0.155	0.000
Thio	2.000	0.004	0.149	0.000
Triphen	2.000	0.007	1.928	0.006
BHT	2.000	0.009	1.629	0.007



SI Figure 20. Accelerated oxidation of TMHDI SMPs containing BHT (left) and predicted real time oxidative mass loss of antioxidant (Piper) containing HDI-based SMPs (equivalent of 2% H_2O_2 at 37°C).