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Mechanically Tunable PDMS-based polyHIPE acoustic materials

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Contents **Page**

Materials. The polymers [13-17% (mercaptopropyl) methylsiloxane]–dimethylsiloxane copolymer (thiolated-PDMS), vinyl terminated polydimethylsiloxane (vinyl-PDMS), and (30-35% dodecylmethylsiloxane-[7-10% hydroxy(propethyleneoxy (6-9) propyl) methylsiloxane] – (55-65% dimethylsiloxane) terpolymer (Silube J208-812) were purchased from Gelest (Morrisville, PA, USA) and used as received. The photoinitiator 2,2-Dimethoxy-2-phenylacetophenone (DMPA) and reagent grade dichloromethane (DCM) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received.

Section II. Methods. PolyHIPEs were polymerized using UV irradiation of the emulsions by pouring the emulsion or emulsions into custom-built molds and then irradiating (λ_{max} =365 nm, 48 W, 6 min) from all sides in a mirrored enclosure. Total porosity calculations and density measurements were obtained from dried polyHIPE samples using a home-built Archimedes balance. Average pore morphology observations were obtained by analysis of scanning electron microscopy (SEM) images using a Scanning Electron Microscope (Low-Vac) (FEI XL-30) equipped with an EDAX detector. Cross sections of the materials were cut from dried polyHIPEs or non-porous films fixed onto aluminum stubs, sputter coated with gold/palladium, and imaged at an accelerating voltage of 15 kV. Viscoelastic properties of dried polyHIPEs were obtained using dynamic mechanical analysis (DMA) by a Perkin Elmer Dynamic Mechanical Analyzer 8000 and processed using Pyris software. Sections of dried polyHIPEs and films were cut to ~ 3 mm thick, ~ 5 mm wide, and ~ 8 mm long. Rectangular tension frequency sweep experiments (0.1-70 Hz; 0.01 mm strain) were run on three replicate samples for each formulation. The acoustic characterization of samples was performed at ultrasonic frequencies. For each material, two samples (32 mm in diameter) with different thicknesses *d* (1 and 2 mm) were used. Each sample was placed between two identical broadband ultrasonic (US) transducers (emitter and receiver,

Olympus V301) with a diameter of 30 mm and a central frequency of 500 kHz. The US transducers were placed face to face and mounted on a linear manual stage, allowing the precise measurement of the sample thickness, i.e., the propagation distances d with an uncertainty of about 100 μm. The emitting transducer was excited with short (broadband) pulses generated by a pulser/receiver (Olympus, 5077PR) that was also used to amplify the electric signal recorded by the receiving transducer before its acquisition on a computer via an oscilloscope.

Synthesis of PDMS polyHIPE foams. PolyHIPEs were prepared using a protocol from our lab.[32] The continuous phase was first prepared in an appropriately sized glass vial. For a polyHIPE with a 1:1 thiol to alkene functional group ratio, thiolated-PDMS (0.75 g, 0.858 mmol thiol-functional group), vinyl-PDMS (2.57 g, 0.858 mmol alkene-functional group), and Silube (34 mg, 1.0 wt% with respect to weight of continuous phase) were combined and vortexed to mix. In a separate glass vial the photoinitiator DMPA (34 mg, 1.0 wt% with respect to weight of continuous phase) was dissolved in approximately 0.2 mL of DCM. This solution was added to the continuous phase and the mixture vortexed until homogenous. The dispersed phase consisting of a 1.5% wt/vol NaCl solution in Mili-Q water was added in small portions and vortexed until a viscous emulsion formed. The emulsion was poured into a template and irradiated with UV light (λ_{max} = 365 nm) for 6 minutes before being removed and placed into a vacuum oven and dried for ~ 48 h at 24 °C. There was no further purification method performed after drying.

Synthesis of non-porous PDMS films. Crosslinked PDMS films were prepared following the same protocol as polyHIPE synthesis with some modifications. The polymerizable phase (continuous phase as detailed previously) was prepared under the same conditions and with the same reagents. Thiolated-PDMS, vinyl-PDMS, Silube, and DMPA were added to a vial and vortexed until homogenous. This viscous PDMS mixture was poured into a template and irradiated with UV light (λ_{max} = 365 nm) for 6 minutes before being removed and placed into the vacuum oven. Although these films do not require any surfactant, we chose to still add Silube to the mixture to ensure direct comparisons can be made between materials as surfactants can act as a plasticizer and impact the viscoelastic properties.

Table S1. Measured density, total porosity, and acoustic velocities of non-porous PDMS films ($NP_{3:1}$ – $NP_{1:3}$).

Sample ID	Measured Density (g/mL)	Total Porosity[a] (+/- 2%)	Longitudinal velocity (m/s)
$NP_{3:1}$	0.979	0.0%	1000
$NP_{2.5:1}$	0.972	0.4%	1100
$NP_{2:1}$	0.984	0.0%	1050
$NP_{1.5:1}$	0.981	0.0%	1090
$NP_{1:1}$	0.970	0.5%	1040
$NP_{1:1.5}$	0.977	0.0%	1050
$NP_{1:2}$	0.989	0.0%	1040
$NP_{1:2.5}$	0.974	0.1%	1030
$NP_{1:3}$	0.967	0.8%	1030

[a]Calculated from Equation 1