Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Ductile Adhesive Elastomers with Force-Triggered Ultra-High Adhesion Strength

Xiao Zhao[a], Zoriana Demchuk[a], Jia Tian[b], Jiancheng Luo[a], Bingrui Li[c], Ke Cao[a], Alexei P. Sokolov[a,d], Diana Hun[e,*], Tomonori Saito[a,c,*], and Peng-Fei Cao[b*]

[a]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA, saitot@ornl.gov

[b]State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China, caopf@buct.edu.cn

[c]The Bredesen Center for Interdisciplinary Research and Graduate Education, University of Tennessee, Knoxville, TN 37996, USA.

[d]Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA.

[e]Buildings and Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830 USA, hunde@ornl.gov

Experimental Methods

1.1. Materials.

MDI-prepolymer Mondur® 1522 (NCO content: 31.5-32.4 wt. %, Covestro, Pittsburg, PA), Poly(propylene glycol) bis(2-aminopropyl ether) Jeffamine© D-2000 (Sigma-Aldrich, St. Louis, MO), gum arabic from acacia tree (spray dried, Sigma-Aldrich, St. Louis, MO), DTAB (> 98.0%, Sigma-Aldrich, St. Louis, MO), and glycerol (>99.0%, Sigma-Aldrich, St. Louis, MO) were used as received. Methyl methacrylate (99%, stabilized, Sigma-Aldrich, St. Louis, MO), butyl acrylate (>99%, Sigma-Aldrich, St. Louis, MO), and 2-ethylhexyl acrylate (>98%, Sigma-Aldrich, St. Louis, MO) were purified from inhibitors before use. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Sigma-Aldrich, St. Louis, MO) was purified with recrystallization from methanol.

1.2. Synthesis and characterizations of isocyanate-based microcapsules

The range of isocyanate-based microcapsules was synthesized using an interfacial polymerization process. In a typical synthesis, the aqueous phase was first prepared by dissolving 6 g of gum arabic and 0.1 g of DTAB in 200 ml of distilled water in a 500 ml conical flask equipped with a mechanical stirrer. 18 g of MDI-prepolymer was added dropwise to the aqueous phase during vigorous stirring to form an emulsion. The prepared emulsion was heated to 50 ºC and glycerol as shell extender was added in the amount of 3 g. The reaction mixture was heated to 70 ºC and the reaction continued for 50 min. The obtained microcapsules were filtered out from the reaction mixture using distilled water 3 times and dried in the vacuum oven for 24 h at 25 ºC.

Fourier-transform infrared spectroscopy (FT-IR) was measured on a Nicolet iS50 FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The spectra of each sample were obtained with 64 scans and signals were averaged.

Scanning electron microscopy (SEM) was applied to evaluate the surface morphology of microcapsules using a scanning electron microscope (Zeiss Auriga focused ion beam–SEM system, Carl Zeiss Microscopy GmbH, Germany), with an acceleration voltage of 5 kV. The non-conductive samples of microcapsules were sputter-coated with gold for 10 s before testing, using a high vacuum turbo evaporator.

Differential scanning calorimetry (DSC) measurements were performed on a TA instrument DSC 2500. The samples were sealed into aluminum hermetic pans, and a heating scan was conducted at a rate of 10 °C/min in the range of -80 °C to 120 °C, where the heating scan was taken to analyze its T_g; no equilibration at high temperature was conducted to avoid the curing of reactive MDI-prepolymer.

Solvent extraction was conducted by adding 1 gram of broken microcapsules into 20 ml acetone, followed by 5 min of vortex mixing. The mixture was filtered using the 100 μm-size filtration paper, and the residual was oven-dried and weighed as the mass of the microcapsule shell. The percentage of shell material (w_{shell}) was calculated using the following formula:

$$w_{shell} = \left(1 - \frac{m_{mc} - m_{dr}}{m_{mc}}\right) \times 100\ \%$$

where m_{mc} denotes the mass of broken microcapsules, and m_{dr} denotes the mass of dried residuals.

1.3. Synthesis of matrix polymer and characterization

Matrix polymer was synthesized using free radical polymerization in solution. Methyl methacrylate (0.35 mole part), butyl acrylate (0.30 mole part), and ethyl hexyl acrylate (0.35 mole part) (total molar concentration – 1M) were purified from inhibitors and added to the 250 ml round-bottom flask equipped with a magnetic stirrer. AIBN was used as a thermal initiator in the amount of 1.5 wt. % based on monomer feed. Toluene was added as a solvent to the reactor and the reaction mixture was purged with argon for 30 min before starting. The polymerization was carried out overnight at 68 ºC. The obtained polymer was precipitated by a large excess of methanol and then purified by multiple precipitations from toluene in methanol.

^{1}H NMR spectra were recorded on a Bruker instrument (400 MHz) with CDCl3 as a solvent. Gel permeation chromatography (GPC) measurements were performed on a Tosoh Ecosec 8320 GPC system to estimate the molecular weights. The samples were dissolved in tetrahydrofuran (THF) at 1 mg/mL concentration. DMA measurements were performed on a TA Discovery DMA850. The amplitude and frequency in the oscillation model were set to 20 µm and 1 Hz, respectively. The samples were ramped from -75 to 150 °C at a rate of 3.0 °C/min.

1.4. Fabrication of ultra-adhesive elastomer and characterization

The ultra-adhesive elastomer was fabricated by combining microcapsules, curing agent, and matrix polymer in the ratio of 50:40:10 mass ratio, respectively. In a typical formulation, 4 g of prepared precursor mixture was placed in the groove-shape kit and the required compression force was applied. The prepared sample was cured for 3 days at 25 ºC until completely cured. Tensile, peel, and lap shear tests were performed on the Instron 3343 Universal Testing System.

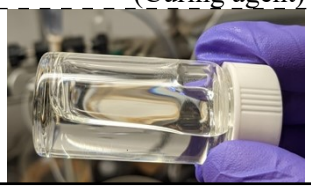
The tensile strength and elongation at break were determined according to the stress/strain results obtained using the above-mentioned Instron Testing System with a crosshead speed of 5mm/min at ambient

temperature. The tensile samples with a size of approximately 20 mm of length and 2.5 mm of neck width were used.

The peel test (Figure 4A) was conducted using a customized groove-shape geometry that obeys ASTM C961. The groove is 1 by 1.6 inches. Approximately 0.12-inch thick precursor was placed at the bottom of the groove, followed by adding a stainless steel mesh, and another approximately 0.12-inch thick precursor layer was added on the top of the metal mesh. Then, a 0.12-inch thick Teflon sheet with a width and length of 1 and 1.6 inches was added to the top precursor layer. The compression was exerted onto the Teflon sheet, followed by removing the Teflon sheet to cure the precursor.

The lap shear test (Figure 4B) was conducted using a customized groove-shape geometry that obeys ASTM C794. The groove is 1 by 1.6 inches with one side able to be separated from the groove. The dosing of the precursor was similar to the method of preparing peel test samples except that a wood/metal stick was used instead of the metal mesh; the wood/metal stick was used to create the lap shear event. After removing the Teflon sheet, the separable part was also removed.

Table S1. Candidate selection matrix of the reactive and curing agents, and curing time of selections. In all pre-screens, reactive and curing agents are stoichiometrically fed.

Bisphenol A diglycidyl ether (Reactive agent)	**PPG-triamine** (Curing agent)
No solidification after 24 hours at room temperature.	

Unsaturation-modified epoxy (Reactive agent)	**Polyethyleneimine (PEI)** (Curing agent 1)	**PPG-triamine** (Curing agent 2)
Not cured 		Cured 

wt% PEI in curing agents	0	2.5	5	10	20
At 73 °F	> 2 days	16 hours	5 hours	2 hours	30-45 min
At 0 °F	N/A	N/A	3-4 days	1-2 days	< 24 hours

Hexamethylene diisocyanate prepolymer (Reactive agent)	**PPG-diamine** (Curing agent 1)	**PPG-di-OH** (Curing agent 2)

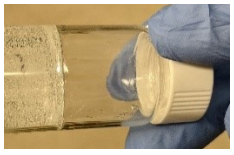
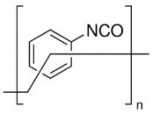
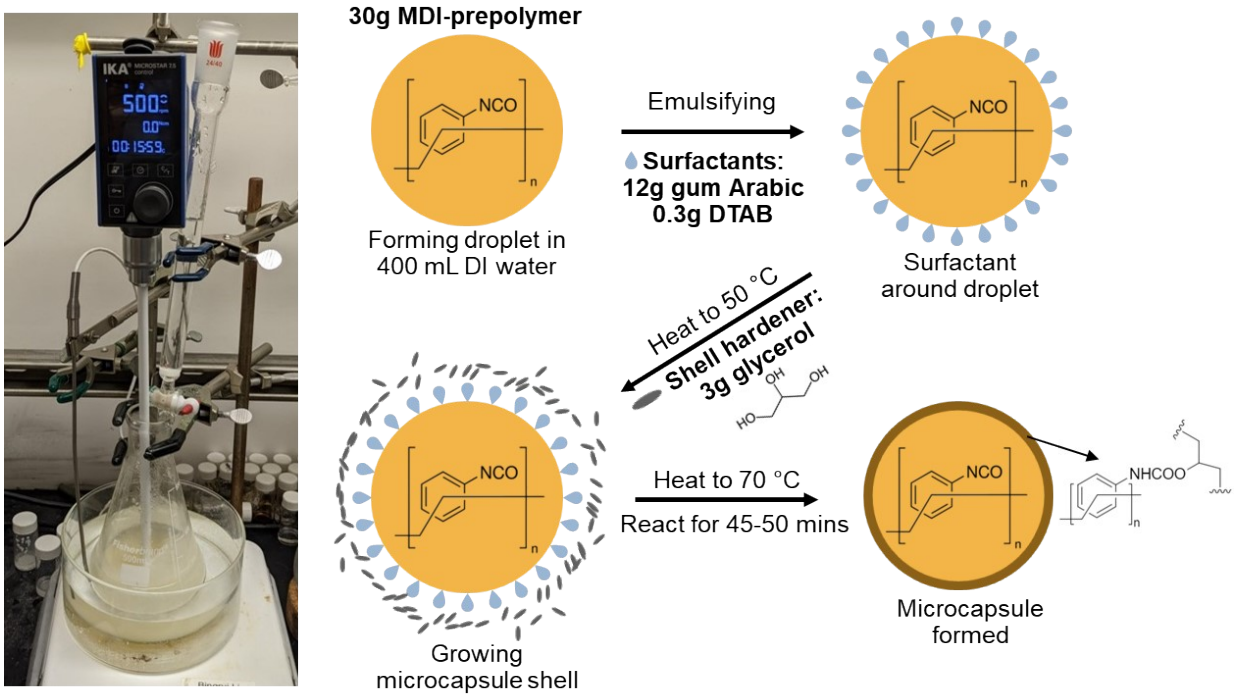
	wt% PPG-diamine in curing agents	40	60	80
Cured 	At 73 °F	24 hours	4 hours	45 min
	At 0 °F	N/A	1-2 days	14 hours

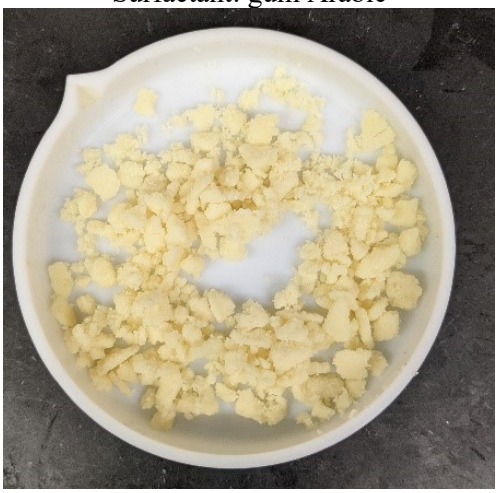
Table S1 continued

Methylene diphenyl diisocyanate prepolymer		**PPG-diamine**		**PPG-di-OH**	
					
(Reactive agent)		(Curing agent 1)		(Curing agent 2)	
	wt% PPG-diamine in curing agents	40	60	80	90
Cured 	At 73 °F	> 1 day	8 hours	2-3 hours	1 hour
	At 0 °F	N/A	N/A	1-2 days	< 24 hours



Scheme S1. Synthesis protocol and setup for encapsulated MDI-prepolymer.

Surfactant: gum Arabic



Poor separation
Microcapsules stick to each other

Surfactant: gum Arabic + DTAB

Good separation
Easy to mix with polymer matrix and curing agent

Figure S1. Visualizations of synthesized microcapsules using surfactants with/without DTAB. DTAB effectively prevent agglomeration of microcapsules.

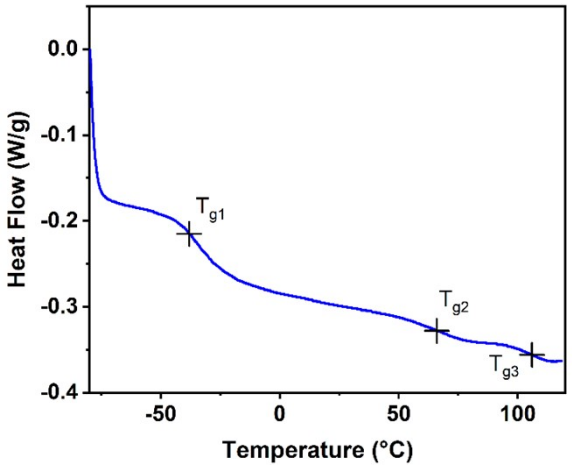


Figure S2. DSC result of the encapsulated MDI-prepolymer. T_{g1} is -38 °C that corresponds to T_g of MDI-prepolymer. T_{g2} is 66 °C that corresponds to a partially crosslinked MDI-prepolymer as it has the broadest glass transition region. And T_{g3} is 106 °C that corresponds to the T_g of shell, the fully crosslinked urethane. The change of heat flow at each T_g is proportional to the mass of each phase, and we found out that the weight percent of T_{g3} phase is roughly 12% that agrees very well with the dry mass of broken microcapsule that could not be dissolved in acetone.

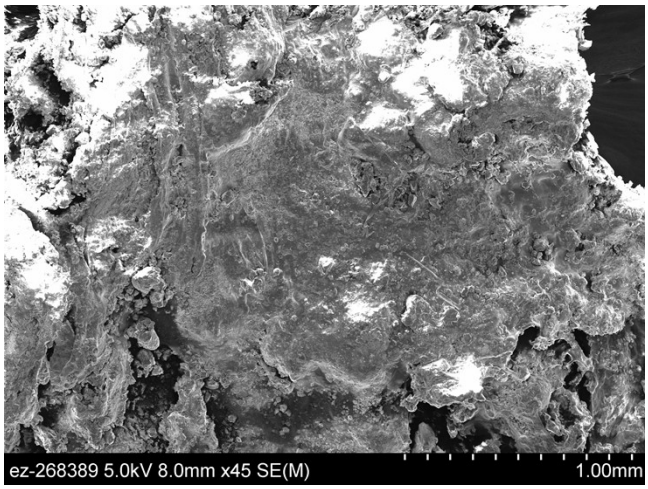


Figure S3. SEM visualization of the encapsulated MDI-prepolymer paste after finger compression, where microcapsules are broken, and no obvious boundaries are observed.

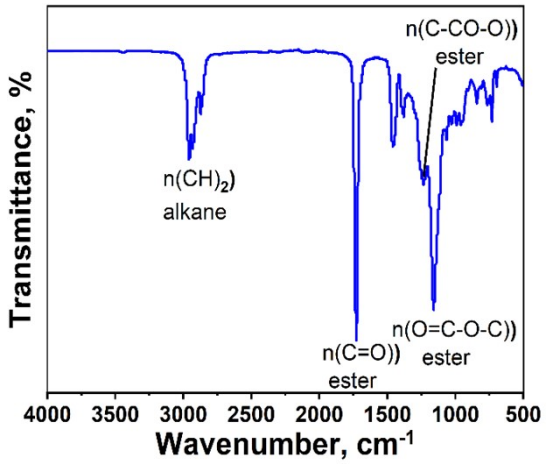


Figure S4. FTIR spectrum of the matrix polymer synthesized by free radical polymerization among methyl methacrylate, butyl acrylate, and ethylhexyl acrylate. Characteristic peaks are: 2995 cm^{-1}, C-H stretching (asymmetric); 2935 cm^{-1} (symmetric); 1730 cm^{-1}, C=O stretching; 1271 cm^{-1}, 1240 cm^{-1}, C-O-C stretching (asymmetric); 1190 cm^{-1}, 1148 cm^{-1}, C-O-C ester; and 989 cm^{-1}, 842 cm^{-1}, ester skeletal vibrations. Other prominent absorption peaks are at 1454 cm^{-1} and 1400 cm^{-1}, and they are due to asymmetrical and symmetrical bending vibrations of $C\text{-}CH_3$.

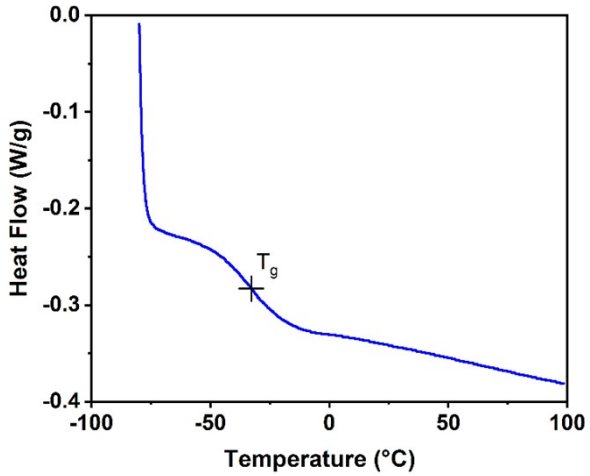


Figure S5. DSC result of the matrix polymer synthesized by free radical polymerization among methyl methacrylate, butyl acrylate, and ethylhexyl acrylate.

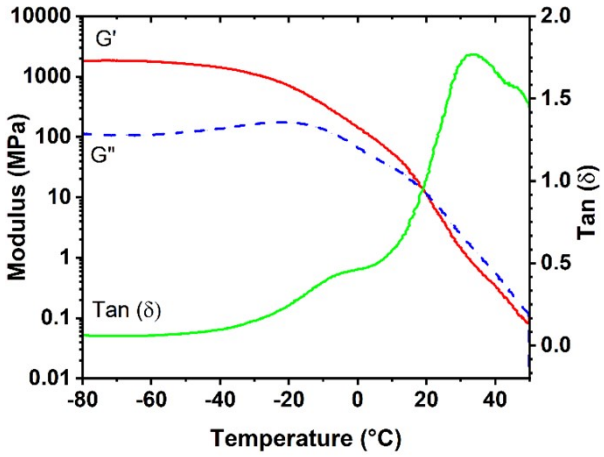


Figure S6. Temperature sweep result *via* DMA for the matrix polymer synthesized by free radical polymerization among methyl methacrylate, butyl acrylate, and ethylhexyl acrylate.

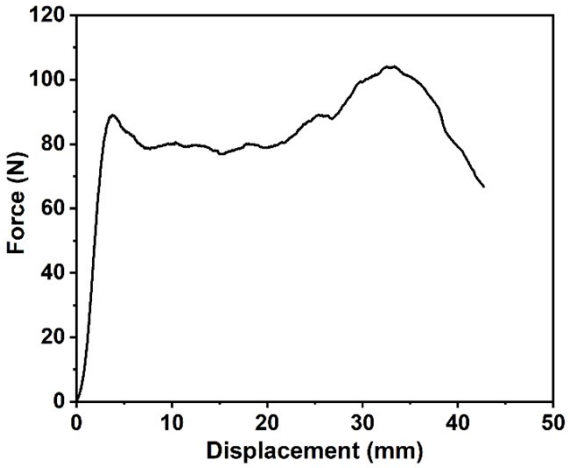
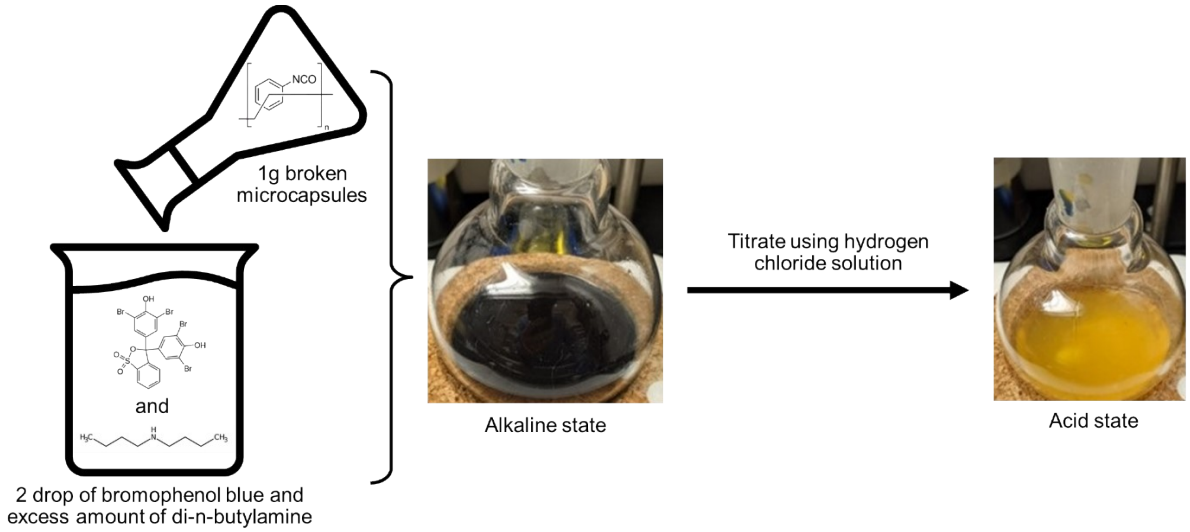


Figure S7. The tensile test result of 180° peel on the cured elastomer using the initial formulation: 60 wt% encapsulated MDI-prepolymer, 30 wt% PPG-diamine, and 10 wt% matrix polymer.



Scheme S2. Titration protocol to determine the active MDI component in the encapsulated microcapsules.

Table S2. Photos of precursors before and after various compression forces. The microcapsules were synthesized under 300 RPM.

Before compression				
Compression force (N)	50	150	300	500
After compression				

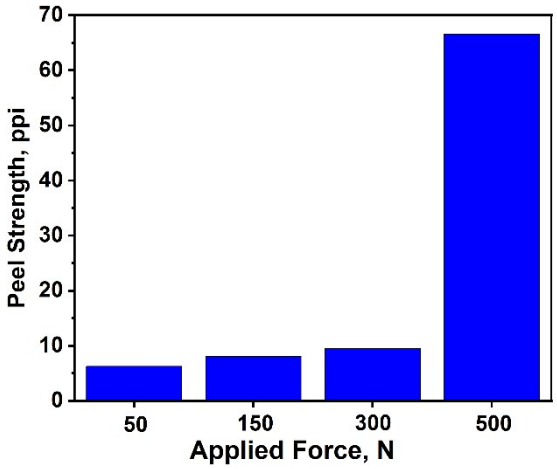
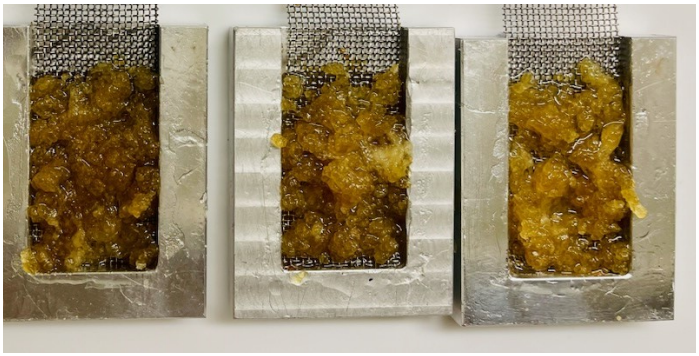
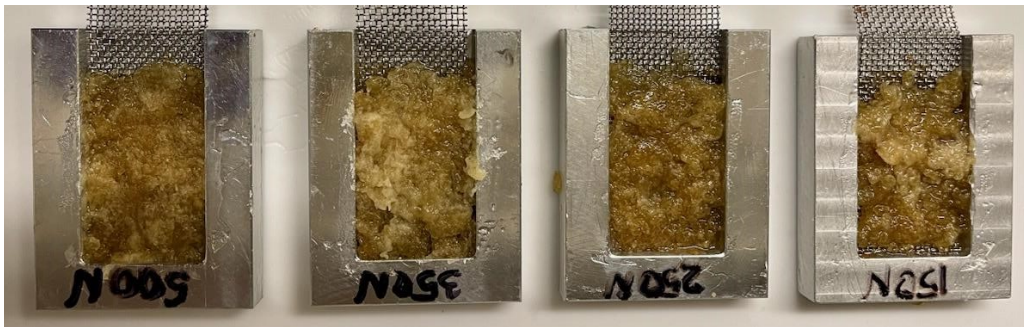


Figure S8. Peel strength of cured adhesive elastomer after different compression forces. The microcapsules were synthesized under 300 RPM.

Table S3. Photos of precursors before and after various compression forces. Microcapsules were synthesized under 200 RPM.

Before compression				
Compression force (N)	500	350	250	150

After compression



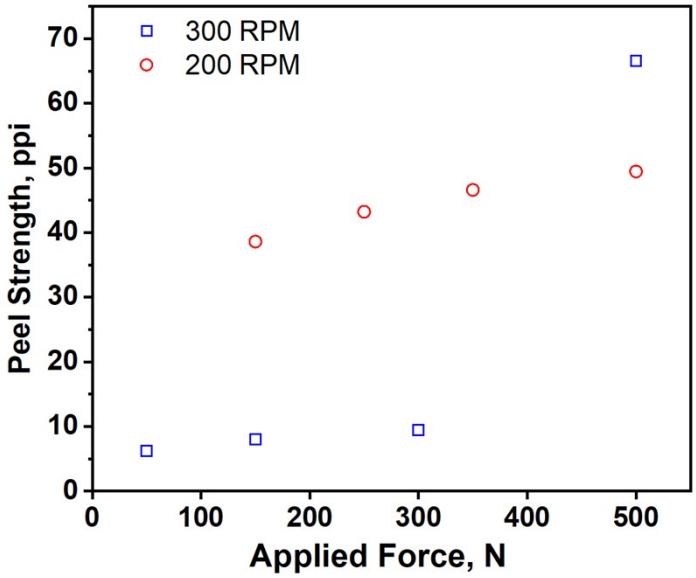


Figure S9. Peel strength of cured adhesive elastomer after different compression forces for precursors that use microcapsules synthesized under 200 and 300 RPM.

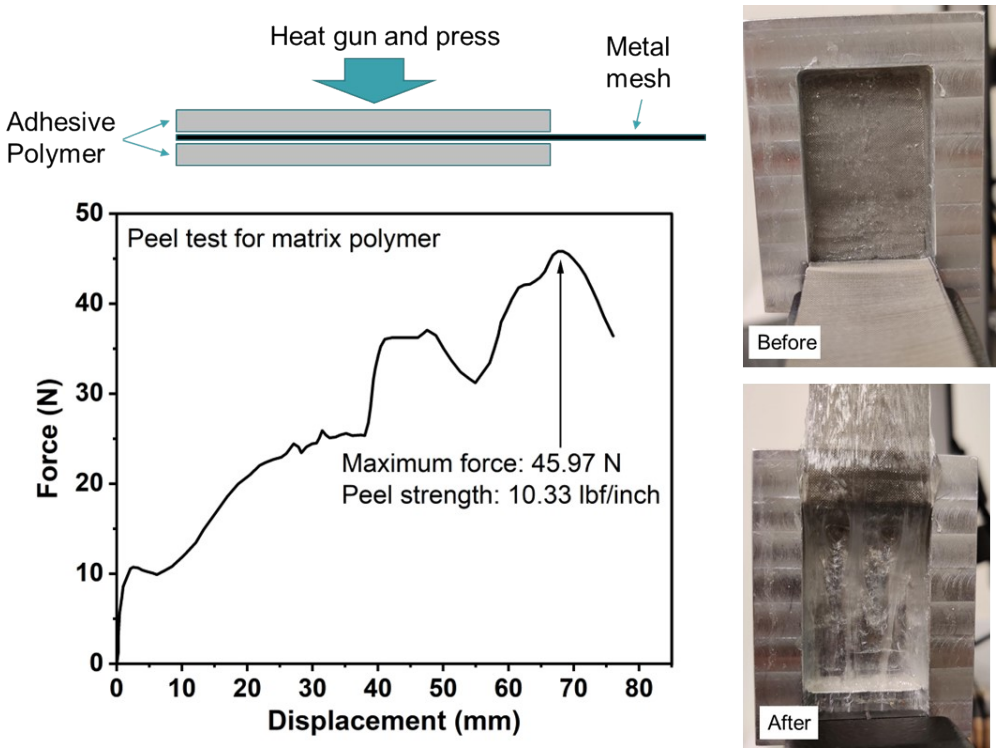


Figure S10. Peel test on the matrix polymer itself. The method is consistent with ASTM C794 and the method that was applied for the elastomer.