Supporting Information

# A hyperbranched polymer elastomer-based pressure sensitive adhesive

*Chunyan Cui, Bo Liu, Tengling Wu, Yang Liu, Chuanchuan Fan, Ziyang Xu, Yuan Yao, Wenguang Liu**

C. Cui, B. Liu, T. Wu, Y. Liu, C. Fan, Z. Xu, Y. Yao, Prof. W. Liu

School of Material Science and Engineering, Tianjin Key Laboratory of Composite and Functional Materials, Tianjin University, Tianjin 300350, China

*Corresponding author (E-mail: wgliu@tju.edu.cn)

# Experimental Section

*Materials:* Pentaerythritol tetraacrylate (PETEA, 99%), and poly(ethylene glycol) diacrylate (PEGDA-200, 98%) were purchased from TCI (Shanghai, China). Agarose (Sigma-Aldrich, Shanghai, China), and thioctic acid (TA, 99 %, Macklin, Shanghai, China) were used as received. All the other reagents are of analytical grade and used without further purification.

*Characterizations of elastomer adhesives:* The nuclear magnetic resonance spectra of the TA, PETEA, PEGDA and elastomer samples were measured in dimethyl sulfoxide-d6 (10% w/v) on a Varian Inova-400 MHz NMR Spectrometer. Raman spectra were recorded on a DXR Microscope with 532 nm excitation. The surface chemical compositions of the elastomers were measured using an X-ray photoelectron spectrometer (Thermo Scientific ESCALAB 250 Xi). A monochromatic Al Kα X-ray was used as an excitation source (hν = 1486.6 eV) running at 15 kV and 150 W. The neutral C1s peak (C-C (H), set at 284.4 eV) was used as a reference for charge correction. The contact angles were measured at room temperature on an optical contact goniometer (Harke-SPCA, China) after 5 μL drop of deionized water was placed carefully on the elastomer surface. Herein, at least four different spots were measured on each sample. The average value of contact angle was calculated from at least 4 times measurements for each sample using Image J software (NIH USA, 2008). The crystal structure of the elastomer PSA at different temperature was determined using an XRD (D8 Advanced, Bruker, Germany). XRD data were obtained from 5° to 60° (2θ) using Cu Kα radiation with a scan rate of 1° $min^{-1}$. The tan δ and modulus of the elastomers were measured on a dynamic mechanical analyzer (Q800, TA). For all the samples, the dynamic temperature sweep was performed in a submersion tensile mode at 0.1% strain, 1 Hz frequency over a temperature range of -60-50 °C. DSC analysis was performed on a DSC instrument (200 F3, Netzsch, Germany) over a temperature range from −40 °C to 150 °C at a heating rate of 5 °C $min^{-1}$ under nitrogen atmosphere. The test process was heated twice to eliminate heat history and remove the influence of other factors. The surface morphology of PSAs after adhering dust surface was observed

using a field-emission SEM (FEI Quanta S-4800 FE-SEM). Before test, the tested PSAs were sprayed with gold for 50 seconds.

*Subcutaneous implantation of the elastomer PSA:* All the protocols for animal experiments were carried out according to the guidelines of the Council for the Purpose of Control and Supervision of Experiments on Animals, Ministry of Public Health, China. The animal experiments were approved by the Animal Ethical Committee of Institute of Radiation Medicine, Chinese Academy of Medical Sciences, China (Approval NO. IRM-DWLL-2019043). Prior to surgery, rats were anesthetized with 8% chloral hydrate solution. The back of the rat was subsequently shaved and washed with betadine. An incision was made with surgical scissors on the back of the rats. The polyTA-PETEA-PEGDA-Agar elastomer PSA was placed in the incision, and then the wound was sutured with a 3-0 silk thread. The rats were sacrificed after 1, 3, 10, 20 and 30 days with an overdose of chloral hydrate. The surrounding tissues of the polyTA-PETEA-PEGDA-Agar elastomer PSA were surgically removed and strained with hematoxylin-eosin or Masson trichrome and photographed by inverted fluorescent microscope (TiU inverted, Nikon, Japan).

*3D Printing of the elastomer PSA:* Elastomer constructs were fabricated by a 3D bioprinter (ZDBP-B, Tianjin, China) with a low-temperature deposition platform. The desired 3D models designed from the CAD/CAM software or reconstructed from the Micro-CT data via Mimics Research 20.0 software were used for obtaining the corresponding G-code files through the CuraEngine slice software, which directed the layer-by-layer stack protocol to build up the designed architectures.[1] Subsequently, the polyTA-PETEA-PEGDA-Agar elastomer PSA ink was printed according to the following procedures: the elastomer was firstly loaded into the syringe and heated to 90 °C to soften the elastomer. Then, the polyTA-PETEA-PEGDA-Agar based elastomer PSA ink was extruded through the needle under a temperature of 90 °C and the air pressure of 0.3 MPa. The printed threads were deposited on various substances at 15 °C to cool the elastomer quickly and the 3D printed structure was obtained.

*Rheological measurements of elastomer PSA:* Rheological properties were measured on a rheometer (MCR-302, Anton-Paar) with a 20 mm-diameter parallel steel plate.

Frequency sweeps were performed at a strain amplitude of 0.1% in a frequency range from 0.01 to 100 rad $s^{-1}$ and temperature sweeps were performed at a frequency of 1 Hz in a temperature range from 20 to 100 °C. The disk sample with a diameter of 20 mm was pressed to the sandblasted parallel plate with a force of 5 N to avoid slippage.

*Creep behavior test of elastomer PSA*：Taking ceramics as a representative substrate. First, the maximum adhesion force of PSA to the ceramic substrate was determined by lap shear test, and then different weights were hung on the adhered ceramic sheets, starting at the maximum strength measured on the mechanical testing machine and then different fractions of the maximum, and photos of the creep process and the time to failure were recorded.

*Cytotoxicity Assay:* The cytotoxicity of the polyTA-PETEA-PEGDA-Agar elastomer PSA was evaluated using the co-culture method with mouse fibroblast cells (L929, obtained from Peking Union Medical College). The L929 cells were seeded in a 96-well plate with a concentration of 2 × 104 cells per well and incubated for 24 h. Then the culture medium was refreshed with 200 μL extraction medium (the concentration is 0.1 g/mL) from the PSA. After culturing 24 h, the medium was replaced with 180 μL fresh complete medium and 20 μL MTT (5 mg mL-1 in PBS), and the plate was further incubated for 4 h. Next, all medium was removed and washed with 150 μL DMSO per well and shaking for 30 min at 37 ℃. The absorbance (Abs) of each well was measured at 570 nm on a ∑960 plate-reader (Metertech). Non-treated cell was used as a control and the relative cell viability (mean%±SD, n=5) was expressed as Abssample/Abscontrol×100%.

**Table S1.** Preparation schemes of TA-base elastomer PSAs with different compositions.

| Name | TA (M) | PETEA/TA (mol%) | PEGDA/TA (mol%) | Agarose/TA (wt%) |
|---|---|---|---|---|
| polyTA-PETEA-1 | 0.02 | 5 | 0 | 0 |
| polyTA-PETEA-2 | 0.02 | 7.5 | 0 | 0 |
| polyTA-PETEA-3 | 0.02 | 10 | 0 | 0 |
| polyTA-PEGDA-1 | 0.02 | 0 | 10 | 0 |
| polyTA-PEGDA-2 | 0.02 | 0 | 15 | 0 |
| polyTA-PEGDA-3 | 0.02 | 0 | 20 | 0 |
| polyTA-PETEA-PEGDA-1 | 0.02 | 5 | 10 | 0 |
| polyTA-PETEA-PEGDA-2 | 0.02 | 5 | 15 | 0 |
| polyTA-PETEA-PEGDA-3 | 0.02 | 5 | 20 | 0 |
| polyTA-PETEA-PEGDA-Agar-1 | 0.02 | 5 | 15 | 3.75 |
| polyTA-PETEA-PEGDA-Agar-2 | 0.02 | 5 | 15 | 5 |
| polyTA-PETEA-PEGDA-Agar-3 | 0.02 | 5 | 15 | 6.25 |

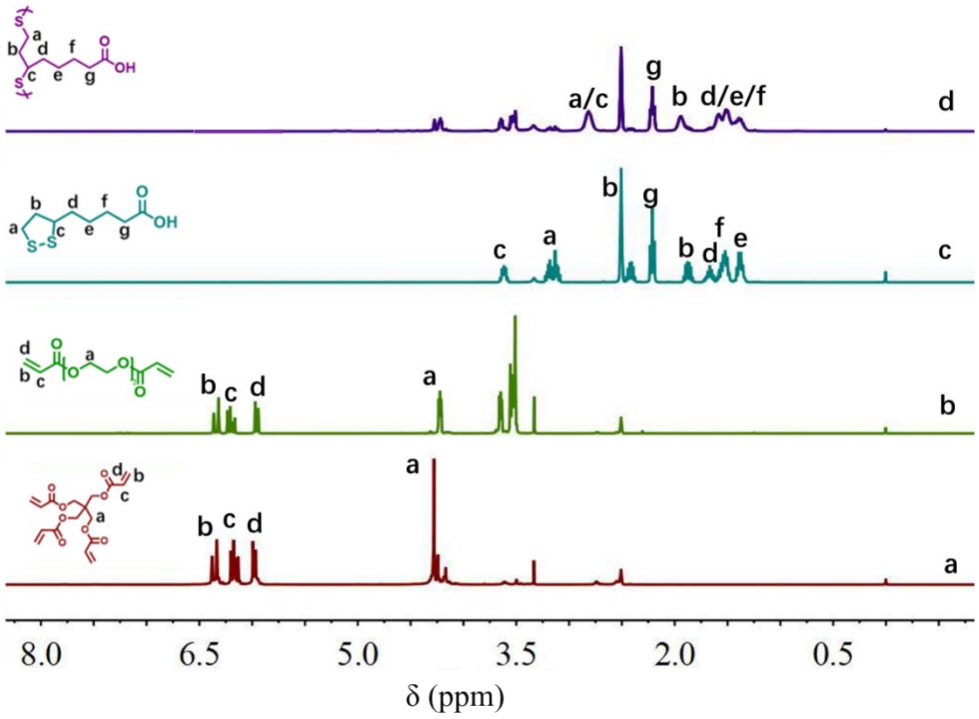


**Figure S1.** $^{1}$H NMR spectra of the PETEA (**a**), PEGDA (**b**), TA (**c**) and polyTA-PETEA-PEGDA elastomer (**d**) in DMSO-d6. The double bond peaks of vinyl group in PETEA and PEGDA disappear, indicating that the free radical reaction between double bond and terminal diradicals is completed, while the peaks of disulfide bond on the five-membered ring of TA at 3.58-3.65 and 3.1-3.25 ppm shift to 2.93 ppm, meaning that TA has undergone ring-opening polymerization.[2-4]

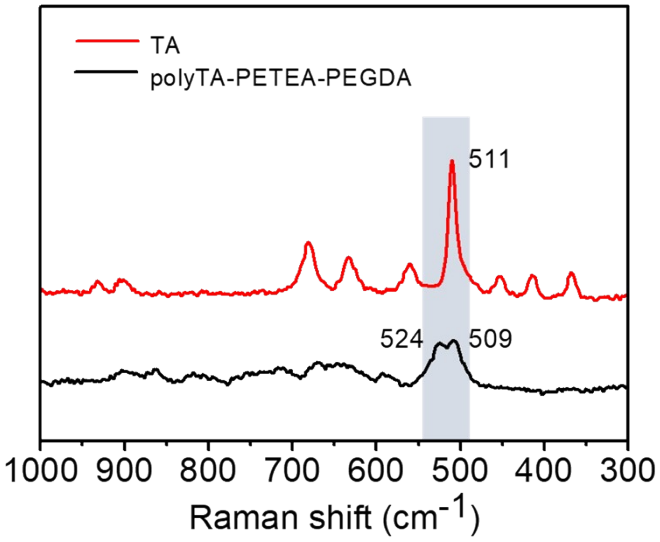


**Figure S2.** Raman spectra of the TA and polyTA-PETEA-PEGDA elastomer. The peak at 511 $cm^{-1}$ in TA splits into two peaks at 509 $cm^{-1}$ and 524 $cm^{-1}$ after polymerization, indicating complete polymerization of TA in the elastomer.[5]

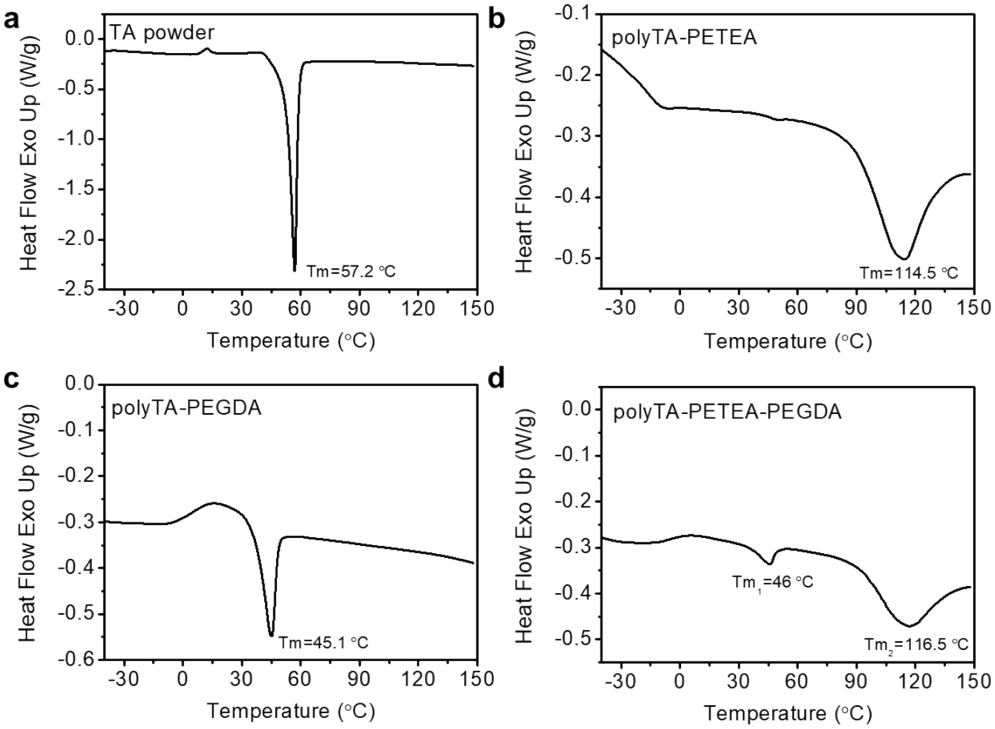


**Figure S3.** DSC thermograms of TA powder, polyTA-PETEA, polyTA-PEGDA and polyTA-PETEA-PEGDA elastomer.

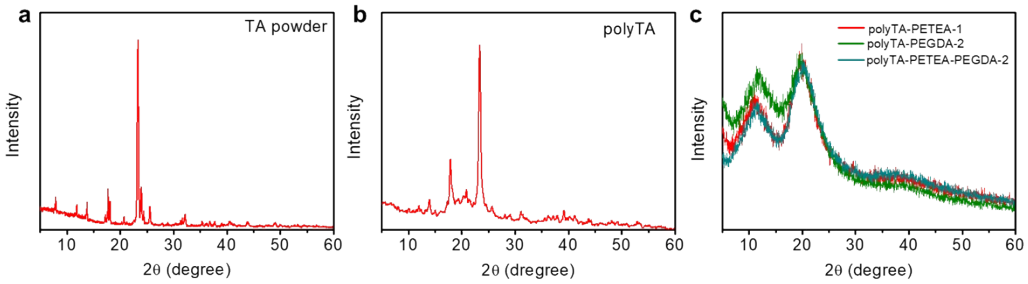


**Figure S4.** XRD patterns of TA powder (**a**), polyTA (**b**) and polyTA-based elastomers (**c**).

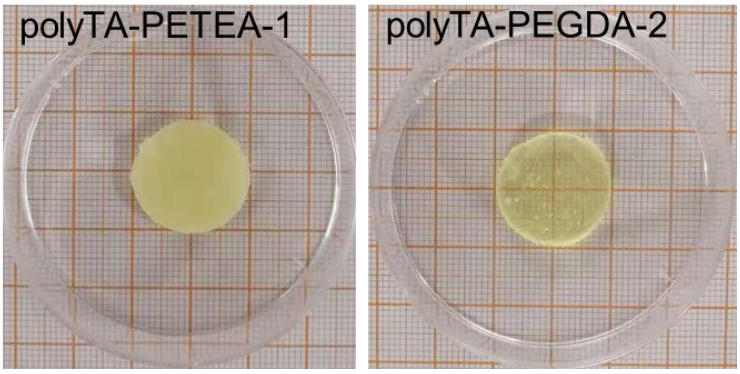


**Figure S5.** Photographs of the polyTA-PETEA-1 and polyTA-PEGDA-2 elastomer.

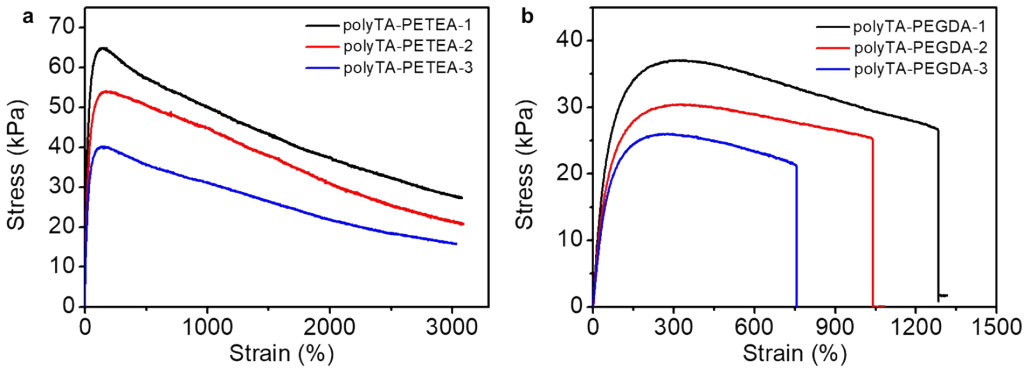


**Figure S6.** Tensile stress-strain curves of the polyTA-PETEA elastomers (**a**) and polyTA-PEGDA elastomers (**b**).

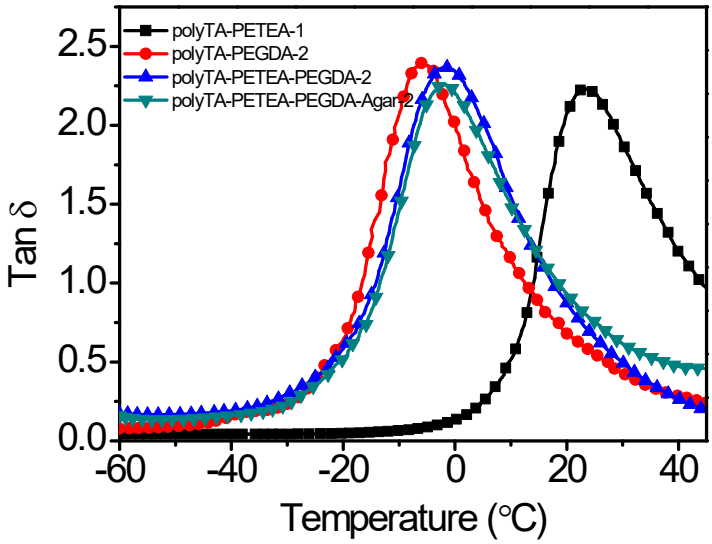


**Figure S7.** DMA curves of polyTA-PETEA, polyTA-PEGDA, polyTA-PETEA-PEGDA and polyTA-PETEA-PEGDA-Agar elastomer.

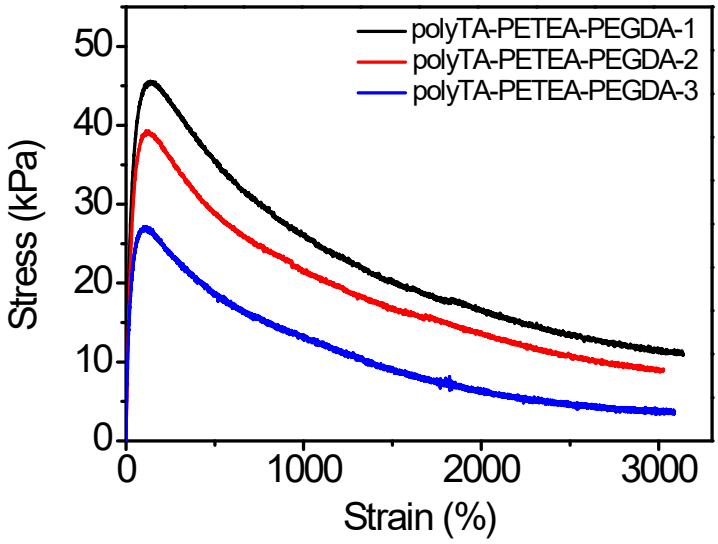


**Figure S8.** Tensile stress-strain curves of the polyTA-PETEA-PEGDA elastomers.

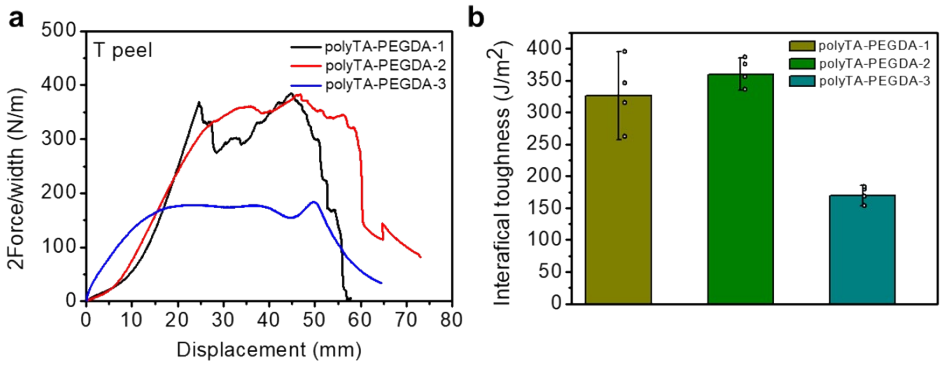


**Figure S9. a**: T peel curves of the polyTA-PEGDA elastomers in bonding to pig skin; **b**: Interfacial toughness of the polyTA-PEGDA elastomers in bonding to pig skin.

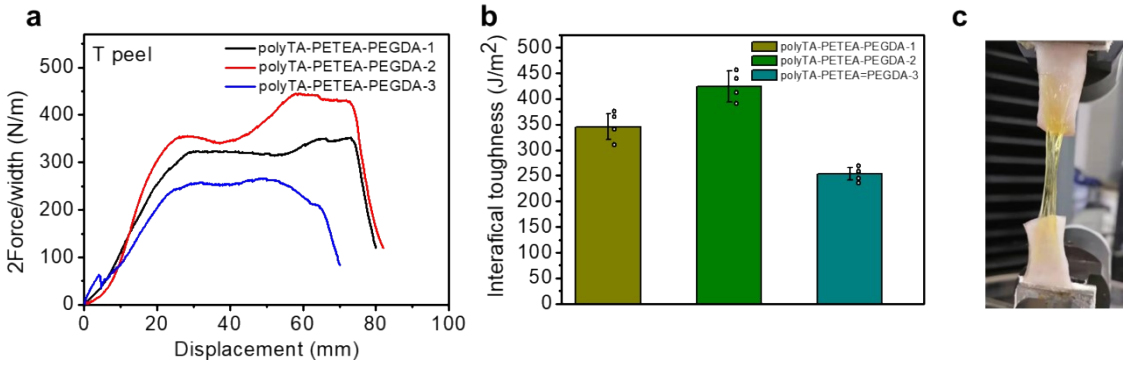


**Figure S10. a**: T peel curves of the polyTA-PETEA-PEGDA elastomers to in bonding to pig skin; **b**: Interfacial toughness of the polyTA-PETEA-PEGDA elastomers in bonding to pig skin; **c**: Digital images displaying T peel process of the polyTA-PETEA-PEGDA elastomer in bonding to pig skin with occurrence of bulk failure.

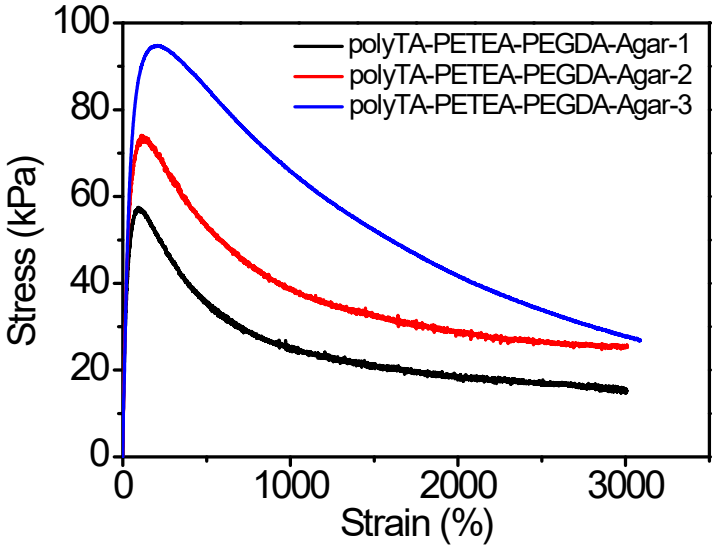


**Figure S11.** Tensile stress-strain curves of the polyTA-PETEA-PEGDA-Agar elastomers.

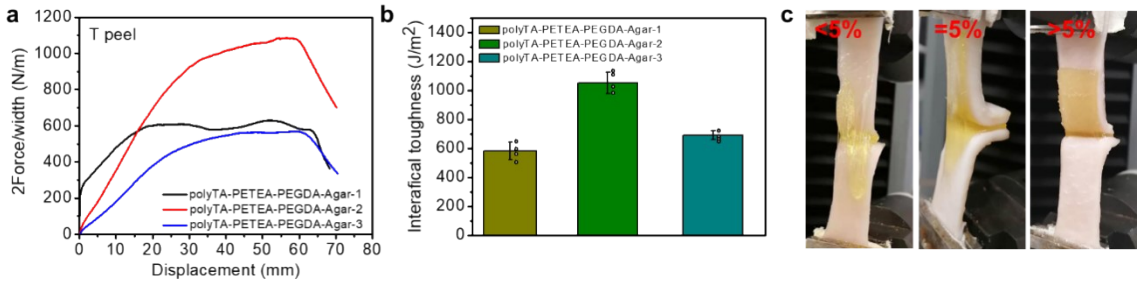


**Figure S12. a**: T peel curves of the polyTA-PETEA-PEGDA-Agar elastomers in bonding to pig skin; **b**: Interfacial toughness of the polyTA-PETEA-PEGDA-Agar elastomers in bonding to pig skin; **c**: Digital images displaying T peel process of the polyTA-PETEA-PEGDA-Agar elastomers in bonding to pig skin with different contents of agarose.

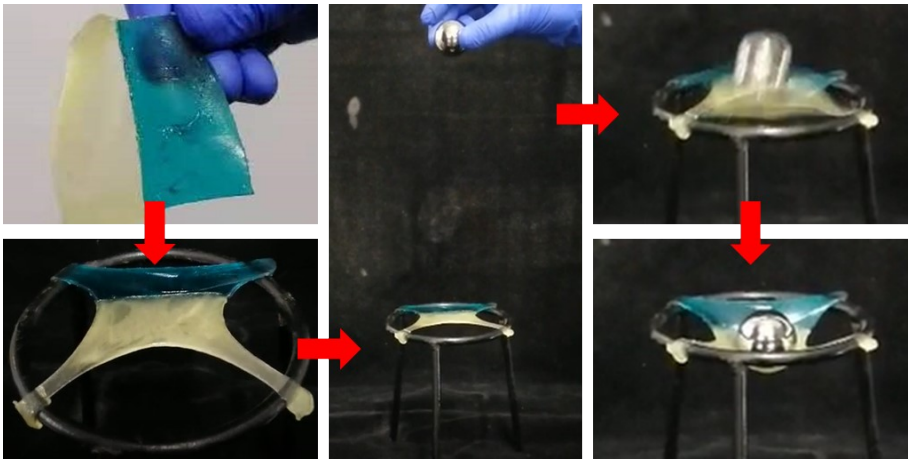

**Figure S13.** Digital images showing the super self-healing ability of elastomer PSA. Two elastomer PSA were re-contacted and placed for 1 min at room temperature, and then the healed elastomer was glued to a metal frame and a ball (50 g) was thrown on the surface of the elastomer. The ball was caught to the healed elastomer without occurrence of the interface damage.

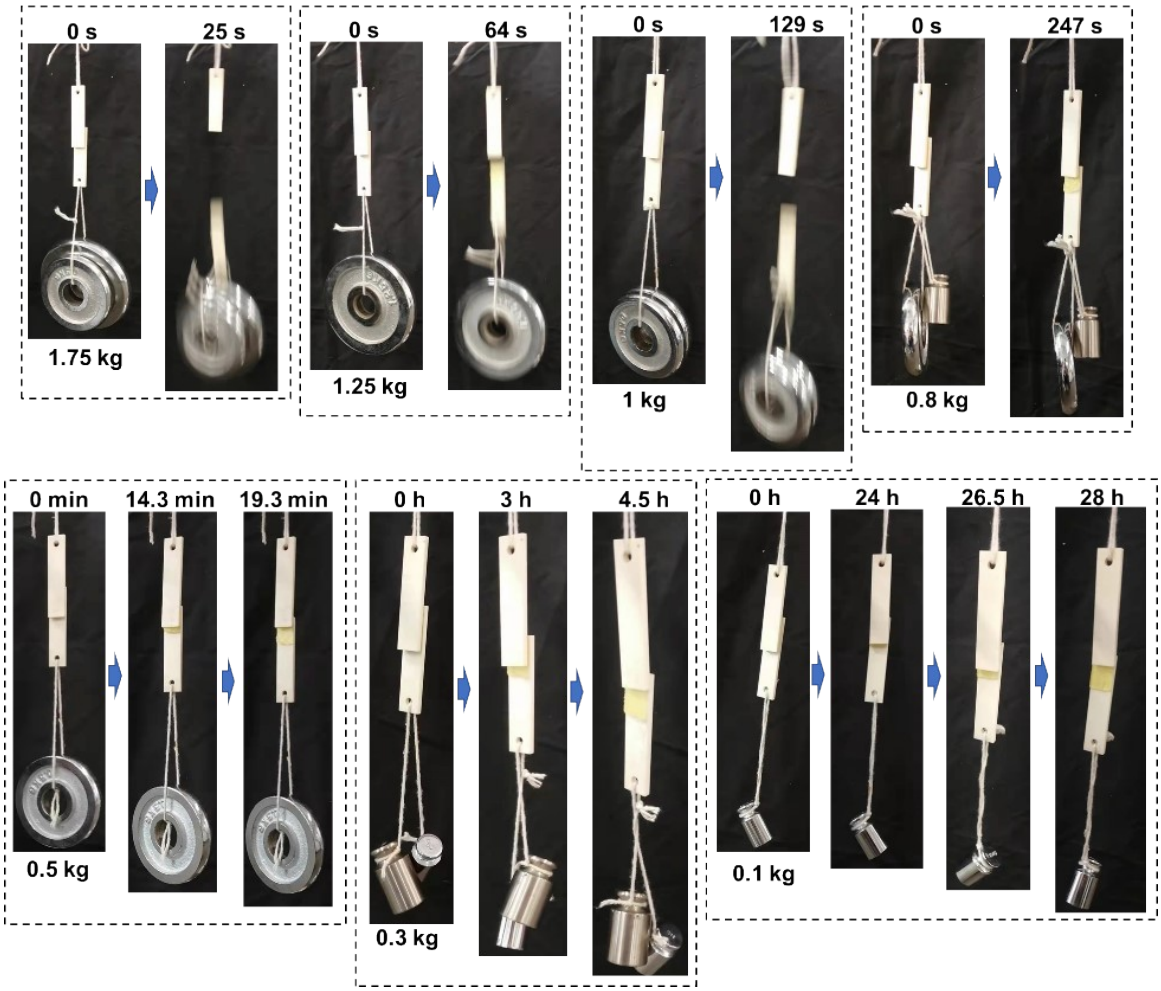


**Figure S14**. Creep behavior of PSA as an adhesive after bearing different weights.

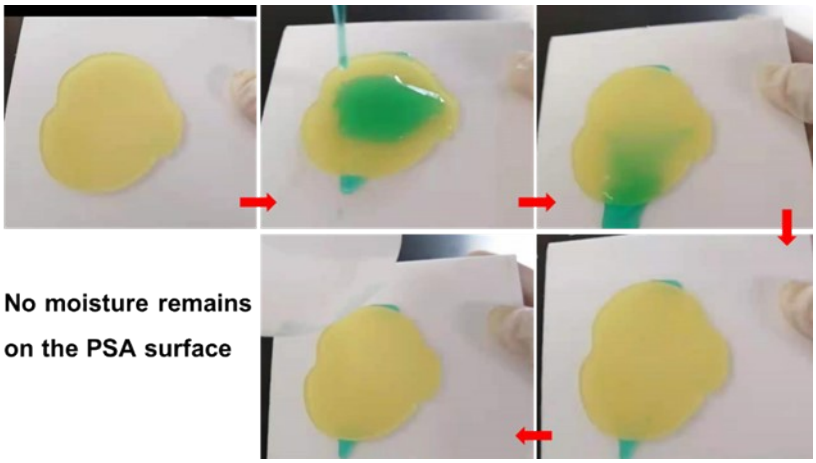


**Figure S15.** Picture displays of surface drainage capacity of hyperbranched elastomer PSA.

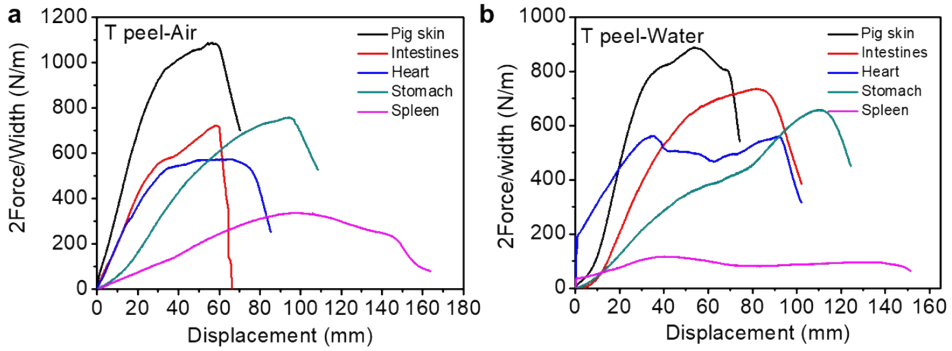


**Figure S16. a**: T peel curves of the polyTA-PETEA-PEGDA-Agar elastomer PSA to various tissues adhered in air condition; **b**: T peel curves of the polyTA-PETEA-PEGDA-Agar elastomer to various tissues adhered in water environment.

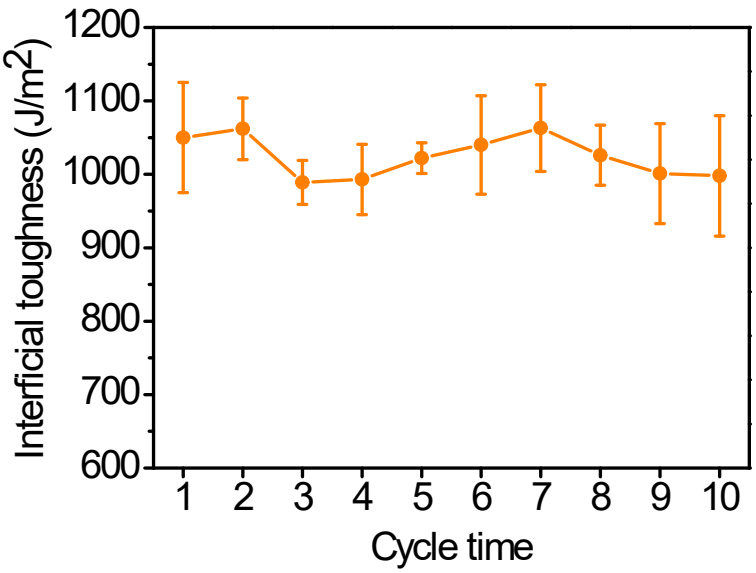


**Figure S17.** Interfacial toughness of continuous ten-time cycle peel test of the adhesion of polyTA-PETEA-PEGDA-Agar to pig skin in air.

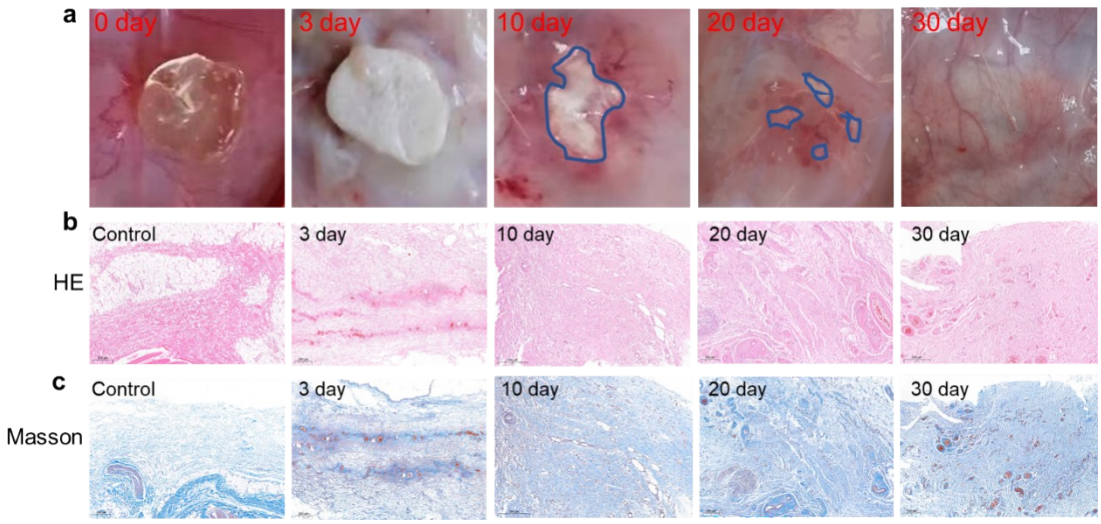


**Figure S18. a:** Degradation of the elastomer at different time points in vivo. Blue circle denotes the location of the elastomer

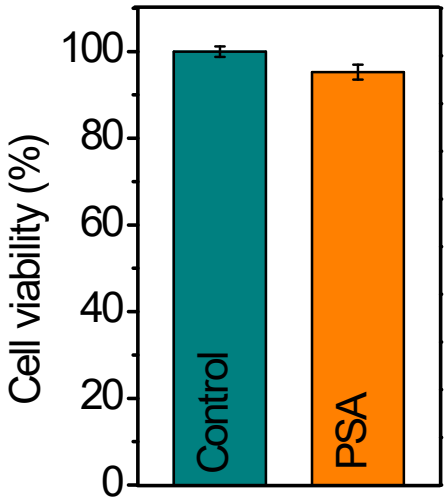


**Figure S19.** In vitro cytocompatibility of the hyperbranched elastomer PSA assayed with mouse fibroblast cells (L929) after 24 h of culture.

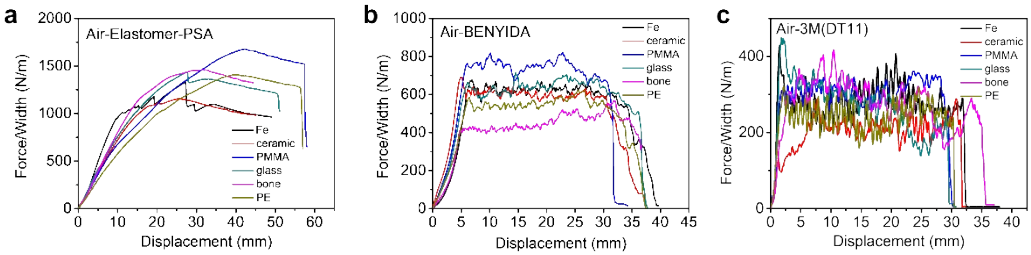


**Figure S20. a**: 90° peel curves of the elastomer PSA to different substrates in air condition; **b**: 90° peel curves of the BENYIDA to different substrates in air condition; **c**: 90° peel curves of the 3M (DT11) to different substrates in air condition.

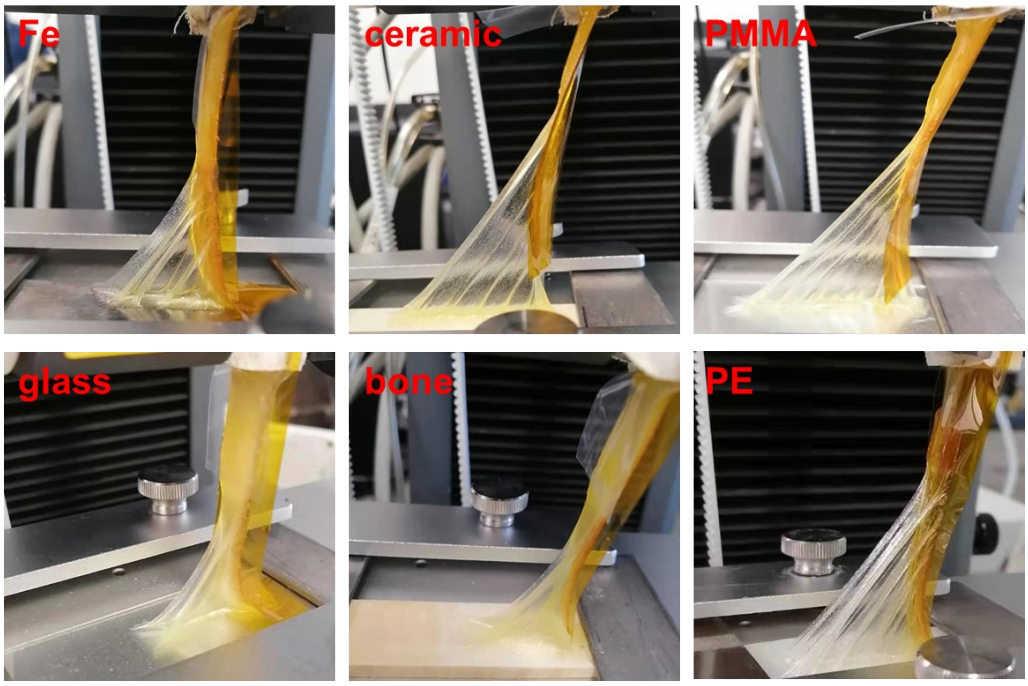


**Figure S21.** Photographs showing the crack and stripping lag at the interface between the polyTA-PETEA-PEGDA-Agar elastomer PSA and different substrate in 90° peel test.

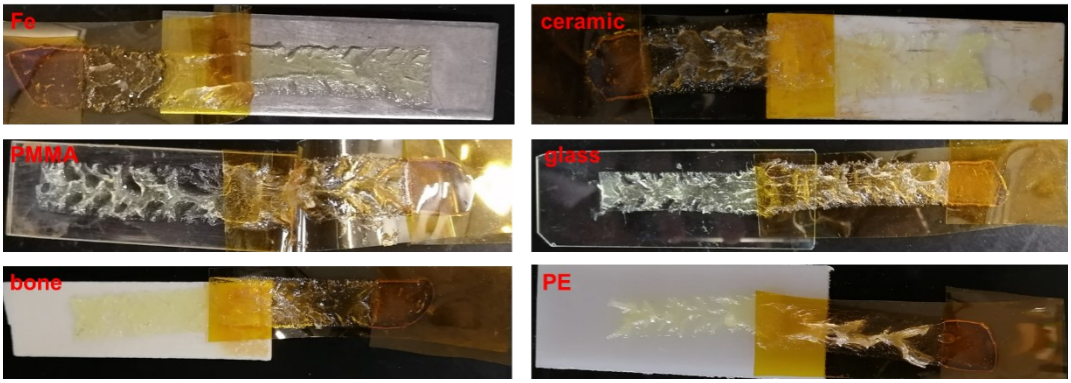


**Figure S22**: Pictures of various adhered substrates after 90° peeling.

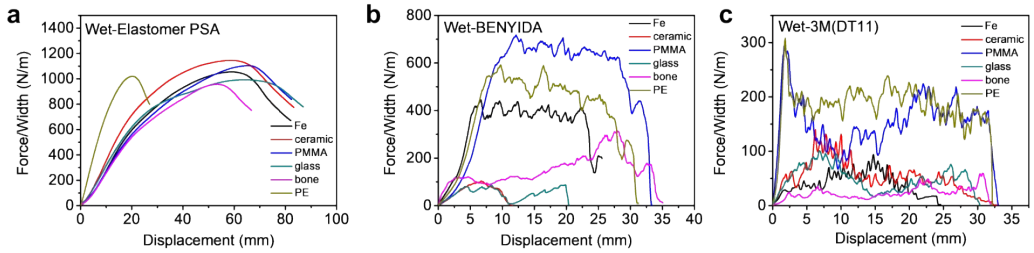


**Figure S23.** **a**: 90° peel curves of the elastomer PSA to different substrates in wet condition; **b**: 90° peel curves of the BENYIDA to different substrates in wet condition; **c**: 90° peel curves of the 3M (DT11) to different substrates in wet condition.

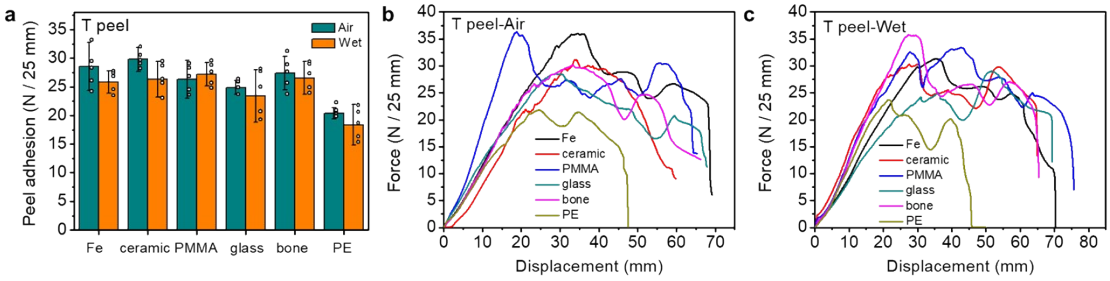


**Figure S24. a**: T peel strength of the elastomer PSA to various substrates in both air and wet condition; **b**: T peel curves of the elastomer PSA to various substrates in air condition; **c**: T peel curves of the elastomer PSA to various substrates in wet condition.

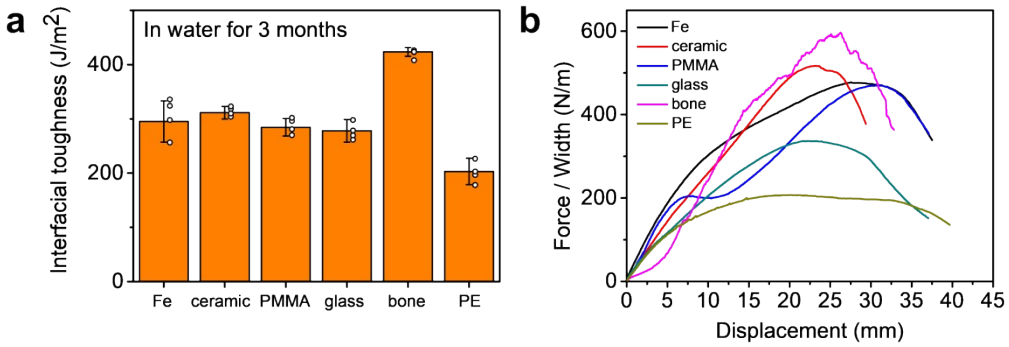


**Figure S25. a**: Interfacial toughness of the elastomer PSA to various substrates after soaking in water for 3 months; **b**: 90° peel adhesion curves of the elastomer PSA to various substrates after soaking in water for 3 months.

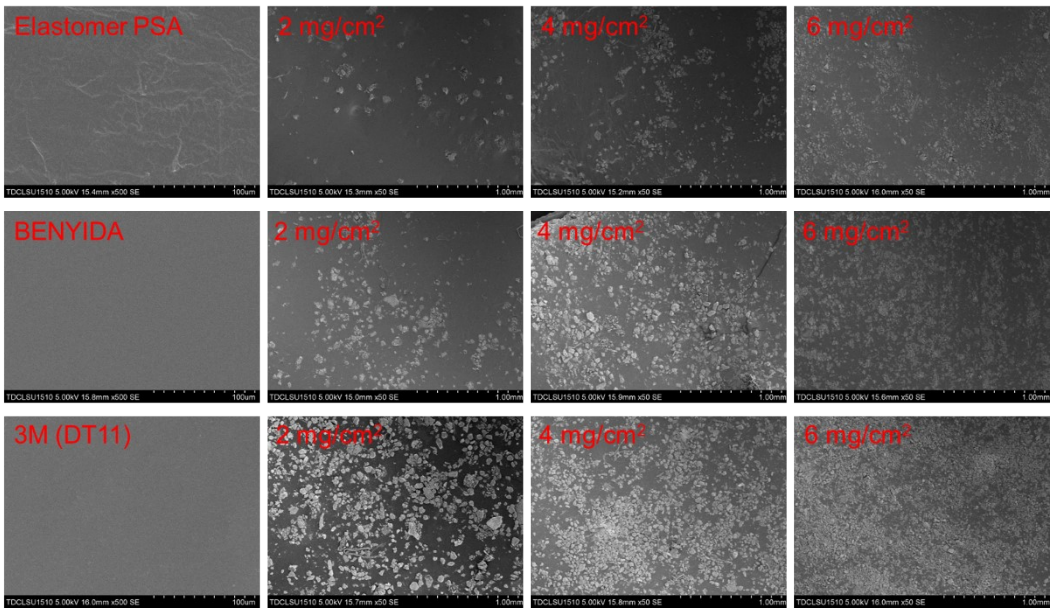


**Figure S26.** SEM surface morphologies of the elastomer PSA, BENYIDA and 3M (DT11) with adsorbed dust.

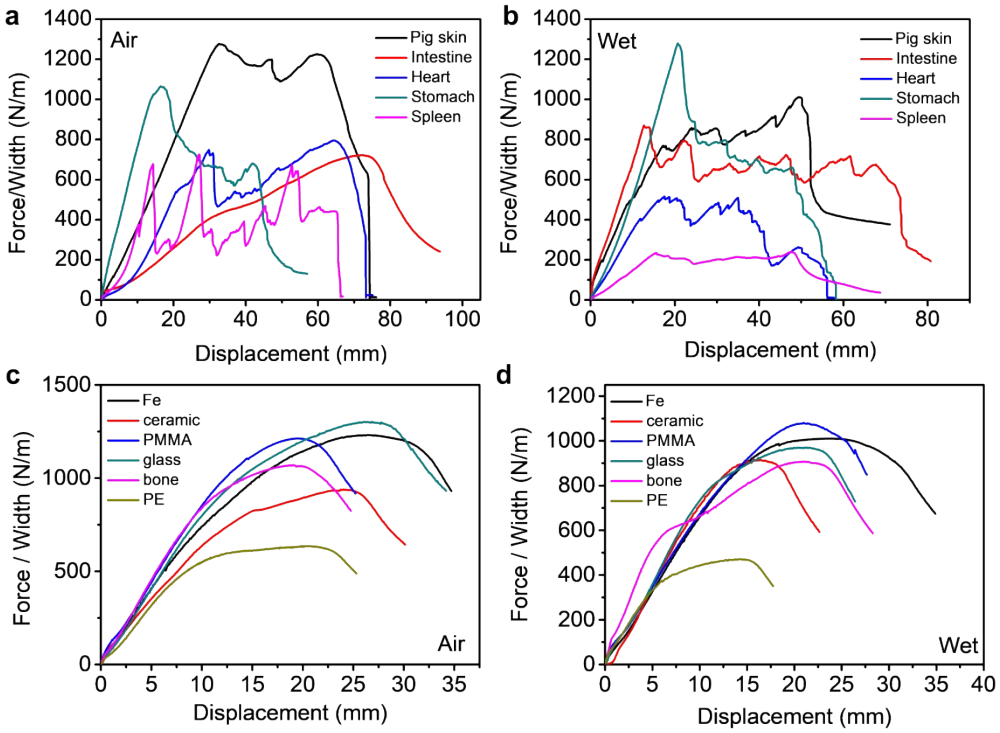


**Figure S27.** T peel curves of the elastomer PSA to different tissues in air condition (**a**) and water condition (**b**) after placing in air for 2 months; 90° peel curves of the elastomer PSA to different substrates in air condition (**c**) and water condition (**d**) after placing in air for 2 months.

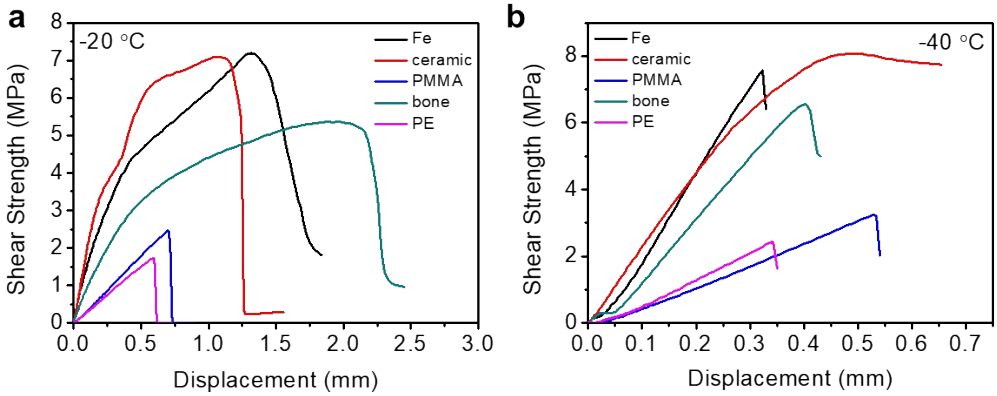


**Figure S28. a**: Lap shear adhesion curves of the elastomer PSA to different materials at -20 °C; **b**: Lap shear adhesion curves of the elastomer PSA to different materials at -40 °C.

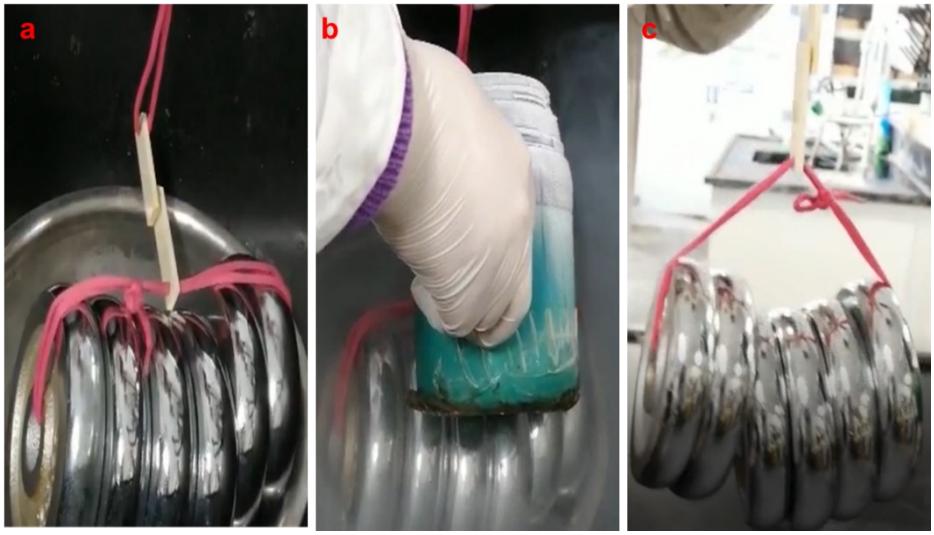


**Figure S29. a**: Two ceramic pieces were adhered by the elastomer PSA (adhesion area is about 2 $cm^2$); **b**: Pouring liquid nitrogen on the adhered ceramic pieces; **c**: The ceramic pieces frozen by liquid nitrogen can lift a weight of 30 kg without debonding of adhesive.

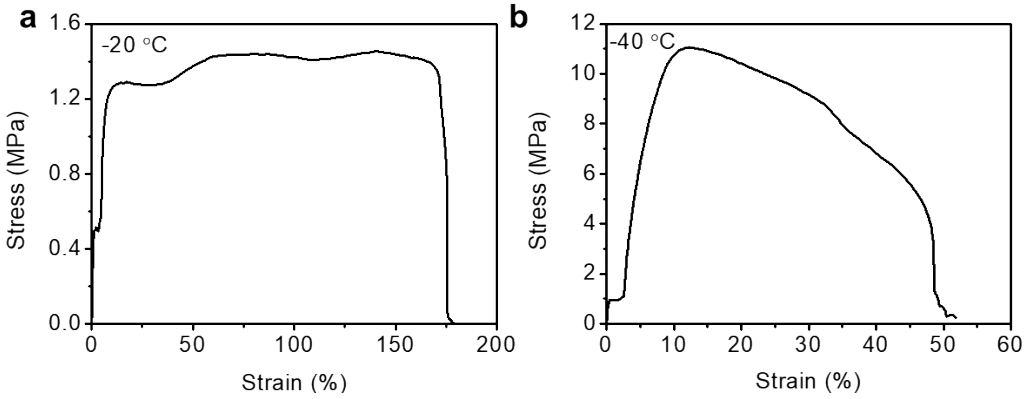


**Figure S30. a**: Tensile stress-strain curves of the elastomer PSA at -20 °C; **b**: Tensile stress-strain curves of the elastomer PSA at -40 °C.

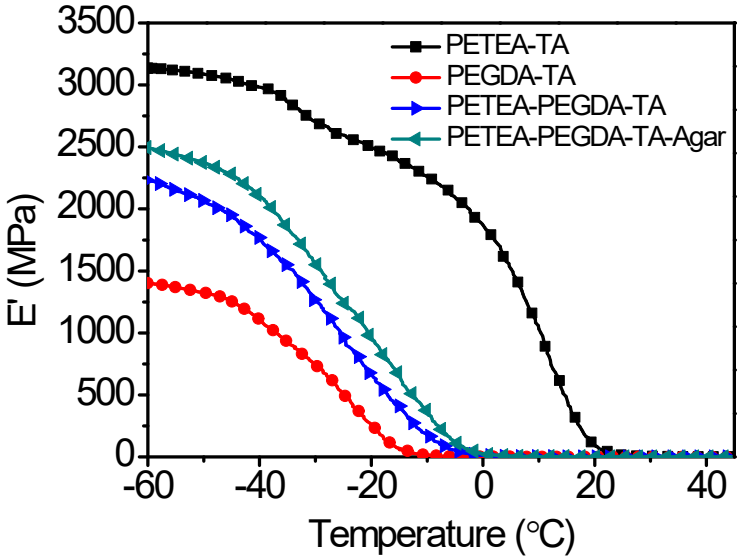


**Figure S31.** Change in modulus curve of the various polyTA-based elastomers as a function of temperature.

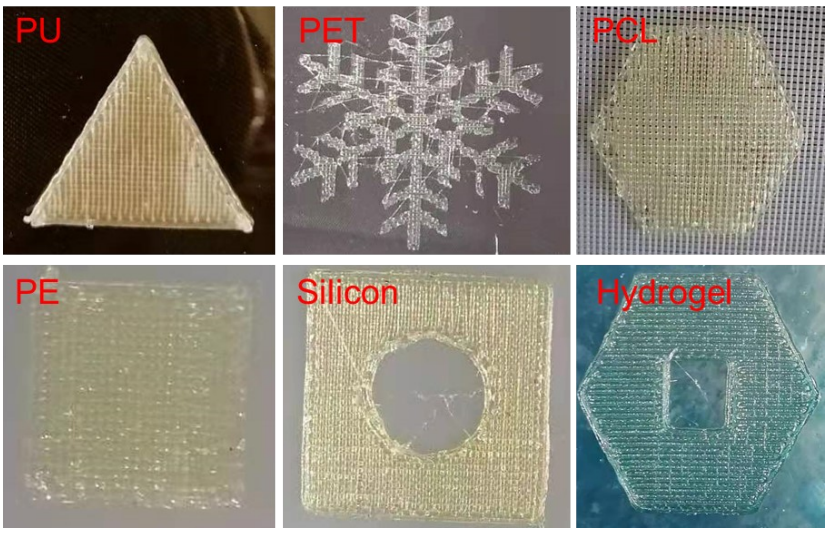


**Figure S32.** Digital images showing the 3D printing of the elastomer PSA. The elastomer PSA can be printed in various patterns and deposited on various surfaces due to its excellent universal adhesiveness. (PU: Polyurethane; PET: Polyethylene terephthalate; PCL: Polycaprolactone; PE: Polyethylene)

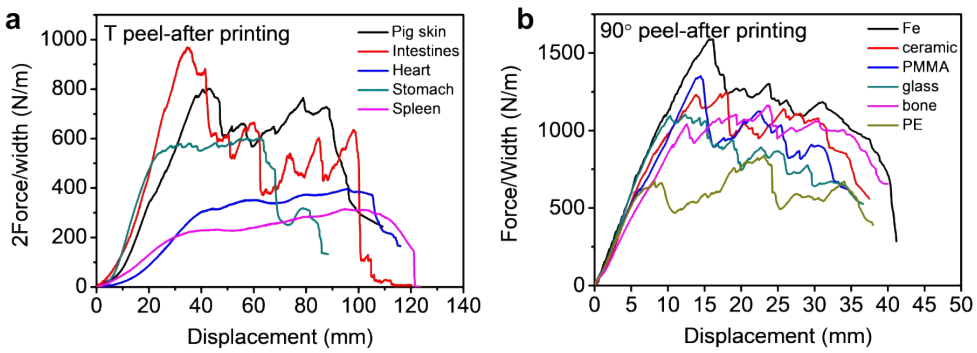


**Figure S33. a**: T peel curves of the printed elastomer PSA coating on PU film to different tissues; **b**: 90° peel curves of the printed elastomer PSA coating on PU film to different solid substrates.

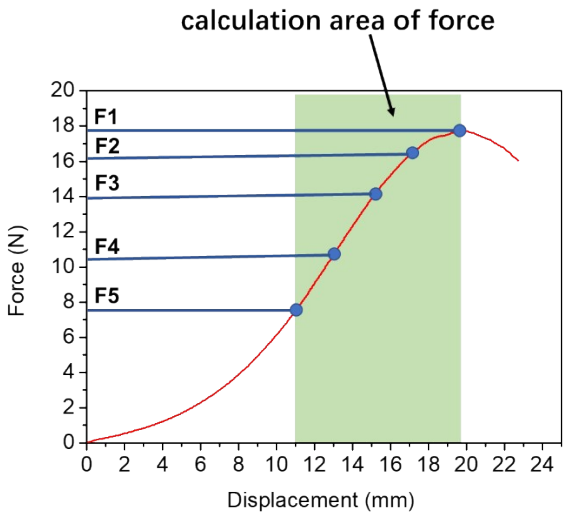


**Figure S34.** Illustration of selecting the average value of the force in the peel test. F1 represents the maximum force generated during the peeling process, and F5 corresponds to the force at 60% the displacement of F1. As the peeling progresses, the adhesive is gradually stretched, so the displacement continues to increase. We choose 3 points on average between the displacements corresponding to F1 and F5, and the corresponding forces are F2, F3 and F4 respectively, and the average value of the force (F) is (F1+F2+F3+F4+F5)/5.

**Movie S1.** The elastomer PSA is stretched to 585 times its original length.

**Movie S2.** The self-healed elastomer PSA can catch an iron ball (50 g) after healed at room temperature for 1 min.

**Movie S3.** Surface drainage display of hyperbranched elastomer PSA.

**Movie S4.** Instant adhesion of the elastomer PSA to tissues underwater and an ability of the glued tissues to lift a weight of 600 g.

**Movie S5.** Instantly repair the broken colon with one piece of the elastomer PSA patch preventing water leakage.

**Movie S6.** Elastomer PSA repairs cracked iron barrel preventing water leakage.

**Movie S7.** Elastomer PSA repairs cracked wood barrel preventing water leakage.

**Movie S8.** Elastomer PSA repairs cracked PC plastic barrel preventing water leakage.

**Movie S9.** Elastomer PSA repairs cracked glass barrel preventing water leakage.

**Movie S10.** Stretched elastomer PSA repairs 5 holes of iron barrel at the same time preventing water leakage.

**Movie S11.** Ultralow temperature adhesion of elastomer PSA. The adhered ceramic can lift a 30 kg weight after experiencing the violent impact of splashing liquid nitrogen.

**Movie S12.** 3D printing process of the elastomer PSA.

**References**


1. Z. Y. Xu, C. C. Fan, Q. Zhang, Y. Liu, C. Y. Cui, B. Liu, T. L. Wu, X.P. Zhang, W. G. Liu, *Adv. Funct. Mater.,* 2021, 2100462.
2. Q. Zhang, C. Y. Shi, D. H. Qu1, Y. T. Long, B. L. Feringa, H. Tian, *Sci. Adv.,* 2018, ***4***, eaat8192.
3. K. Endo, T. Yamanaka, *Macromolecules,* 2006, ***39***, 4038.
4. J. Y. Chen, T. Yuan, Z. Z. Liu, *Biomater. Sci.,* 2020, **22**, 6235.
5. A. Attia a, F. Lehmann, M. Kern, *Dent. Mater.,* 2011, **27**, 207.