Supporting Information for:

Mussel-inspired load bearing metal/polymer glues

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Contents:

A) General information

B) Synthesis of p(DMA-co-MMA)

C) MALDI-ToF of p(DMA-co-MMA)

D) Preparation of the PMMA cements

E) Metal-polymer adhesion tests

F) Synthesis of p(VC-co-MMA)

G) Tensile bonding strength of p(VC-co-MMA)

H) Photographs of the cross-sections

A) General information

Matrix-assisted laser desorption-ionization (time of flight) mass spectrometry (MALDI-ToF) was measured on a Ultraflex II system (Bruker Daltonics, Germany), with a SmartBeam laser II, with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyl-idene]–malononitrile (DCTB; Aldrich, >99%) as matrix.^{1}H NMR spectra were recorded on a Bruker-250 MHz NMR spectrometer at ambient conditions, T = 298 K.

B) Synthesis of p(DMA-co-MMA)

Three different ratios of DMA to MMA were used: 1:20, 1:10 and 1:5. The molar ratio 1:20 revealed tensile bonding strength values not significantly higher than non-treated titanium cylinders (4.4 ± 2.4 MPa). 1:5 resulted in non-stable film upon spin-coating the metal cylinders. The following procedure was used to prepare p(DMA-co-MMA) for 1 to 10 monomers ratio:

1.175 g of MMA (Sigma-Aldrich, 99%) (11.75 mmol) and 64 mg of azobisisobutyronitrile (Sigma-Aldrich, 98%) (0.38 mmol) were added to 0.26 g of DMA (1.175 mmol), dissolved in 30 ml of toluene in an airtight flask and bubbled with Ar. The solution mixture was heated up to 70 °C and stirred overnight. The reaction mixture was dissolved in 5 ml of dichloromethane, precipitated in an excess of hexane (300 ml), filtered and dried *in vacuo*. The white solid was obtained as 50% yield. ^{1}H NMR (250 MHz, DMSO): δ 8.72(s, 1H, -O*H*), 8.63 (s, 1H, -O*H*), 6.65-6.40 (m, 3H, Ar-*H*), 3.55 (s, 15H, -O-CH_3), 3.24 (m, 2H, Ar-CH$_2$-CH_2(NH)-), 2.50 (m, 2H, Ar-CH_2-CH$_2$(NH)-), 1.25-0.9 (m, 18H, -C-CH_3). According to MALDI-ToF, the resulting molar ratio of DMA to MMA in the copolymer was 1:5.

C) MALDI-ToF of p(DMA-co-MMA)

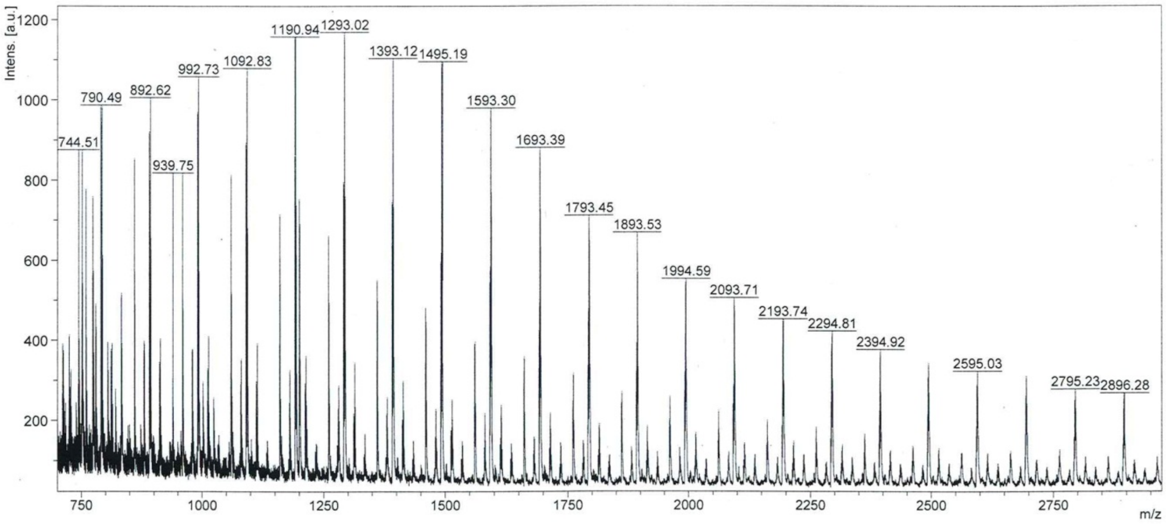


Fig. S1 MALDI-ToF of p(DMA-co-MMA).

D) Preparation of the PMMA cements

The PMMA cements were prepared following the procedure commonly used in the medical applications:

Briefly, each specimen was prepared by mixing powder and liquid within the ratio of 2:1, similar to commercial acrylic cements (Palacos ®). Powder consisted of 99 mg of prepolymerized PMMA particles (Sigma-Aldrich, M_w = 350.000) and 1 mg of benzoyl peroxide (Sigma-Aldrich, 98%). The liquid part contained 2% wt. of N,N-dimethyl-p-toluidine (Fluka, 98.5 %) in methyl methacrylate (Sigma-Aldrich, 99%). The two components were manually mixed together for 30 seconds until homogenous paste was achieved and applied on the prepared metal substrate.

E) Metal-polymer adhesion tests

The adhesion of the polymers on metal surfaces was tested on an Instron 4411 (Instron corporation, Canton, MA, USA)) by measuring tensile bonding strength[1], (for scheme see Figure S2). The tensile strength measurements (5 samples each) were performed at ambient conditions with a cross-head speed of 1 mm min^{-1}.

The p(DMA-co-MMA) polymer was dissolved in dimethyl sulfoxide within 10 % wt. The solution was applied on metal substrates using spin-coating (Laurell Technologies Corp., WS-650SZ, USA). A drop of approximately 500 µl was pipetted onto the substrate and then spun for 120 s at 2500 rpm and 30 s at 1000 rpm with an acceleration of 1000 rpm/s (see Scheme 2). Subsequent heating for 60 min at 110 °C in an air circulation oven (Memmert GmbH, Germany) lead to solvent evaporation and resulted in transparent polymeric films strongly adherent to metal surface.

The aluminum and titanium (technical grade) rods were cut into cylindrical forms (20 × 10 mm). As control polymer adhesive, commercially available Palacos R ® acrylic bone cement (Heraeus, Medical) was used. The polydopamine coating of the metal cylinders was performed following the protocol by Lee et al.[2]

Scanning electron microscope (SEM; LEO 1530 Gemini, Zeiss, Germany) images characterized the morphology of coated samples and the cross-section of the metal cylinders after the pull-out experiments. The labeling of the PMMA cement was performed by dyeing liquid monomer MMA with coumarin based Macrolex® Fluorescent Yellow (Lanxess, Germany) within the concentration of 2 mg/ml before gluing to metal cylinders. Area count of the adhered PMMA on the metal surface was performed by ImageJ (ver. 1.6.0).

All data for tensile bonding strength and attached areas are stated as mean values ± standard deviation. Statistical significance ($p < 0.05$) between different primers and control samples was evaluated by Student's *t*-test for tensile bonding strength experiments. Results were taken as significant at $p < 0.05$.

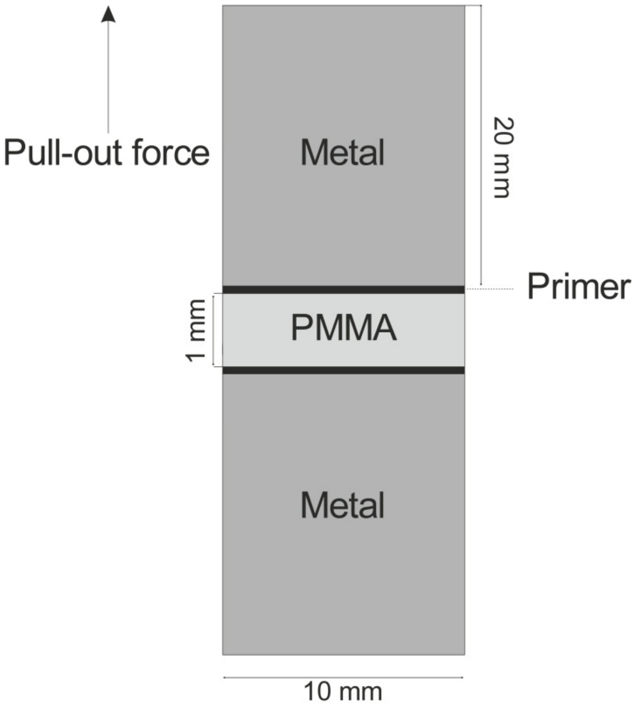


Fig. S2 Scheme of the tensile bonding strength setup.

F) Synthesis of p(VC-co-MMA)

5-vinylbenzo[d][1,3]dioxole (VD) (Scheme 1B, **4**) was prepared according to Aslam et al.[3] 1.687 g of MMA (Sigma-Aldrich, 99%) (16.78 mmol) and 91.4 mg of azobisisobutyronitrile (Sigma-Aldrich, 98%) (0.55 mmol) were added to 0.25 g of VD (1.678 mmol) mixed with 1.937g of toluene in an airtight flask and bubbled with Ar. The solution mixture was heated up to 70 °C and stirred overnight. The reaction mixture was dissolved in 20 ml of toluene, precipitated in an excess of hexane (300 ml), filtered and dried *in vacuo*. P(VD-co-MMA) was obtained as a yellow solid (20%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.66 (s, br, 1H, Ar-*H*), 6.54 (m, br, 2H, Ar-*H*), 5.94 (s, 2H, -O-CH_2-O-), 3.64 (s, 15H, -O-CH_3), 2.0-0.75 (m, 28H, -C-CH_2-C-, -C-CH_3).

To deblock the catechol groups, the 0.4 g of derived copolymer was dissolved in 64 ml of dichloromethane and further treated under Ar with 4.8 ml of 1M boron tribromide in dichloromethane (ABCR-Chemicals) according to modified procedure by Daly and Moulay.[4] The reaction mixture was stirred for 36 h at room temperature and afterwards poured in 500 ml of deionized water, washed with dichloromethane, dried and recrystallized from hexane. p(VC-co-MMA) (**5**) was obtained as a white powder (40%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.90-8.75(m, br, 2H, -O*H*), 6.66-6.30 (m, br, 3H, Ar-*H*), 3.56 (s, 18H, -O-CH_3), 2.0-0.75(m, 28H, -C-CH_2-C-, -C-CH_3).

G) Tensile bonding strength of p(VC-co-MMA)

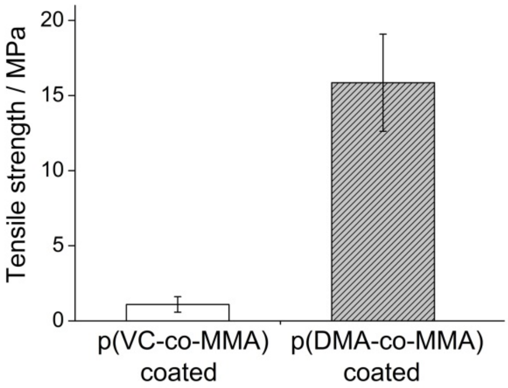
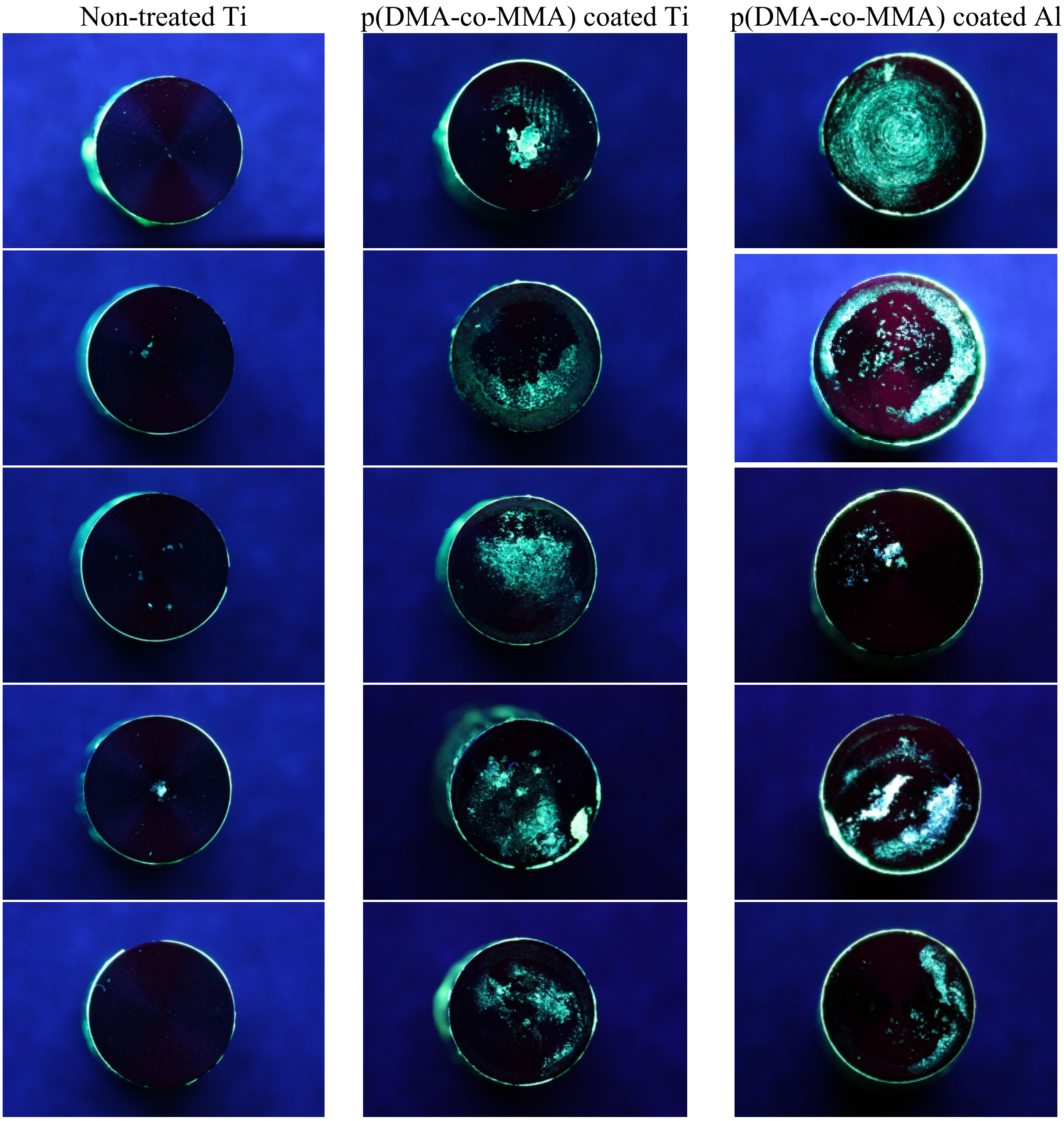


Fig. S3 Tensile strength values upon pull-out experiments for p(VC-co-MMA) and p(DMA-co-MMA) samples.

H) Photographs of the cross-sections

Table S1. Photographs of the coumarin labeled cross-sections of the metal cylinders after the breakup/rupture upon tensile bonding measurements.



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