

Supplementary Materials

# Mucoadhesive and Rheological Studies on the Co-Hydrogel Systems of Poly(Ethylene Glycol) Copolymers with Fluoroalkyl and Poly(Acrylic Acid)

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**Citation:** Sun, Y.; Perez, A.F.; Cardoza, I.L.; Baluyot-Reyes, N.; Ba, Y. Mucoadhesive and Rheological Studies on the Co-Hydrogel Systems of Poly(Ethylene Glycol) Copolymers with Fluoroalkyl and Poly(Acrylic Acid). *Polymers* **2021**, *13*, 1956. <https://doi.org/10.3390/polym13121956>

Academic Editor: Elisabetta Ranucci

Received: 16 April 2021

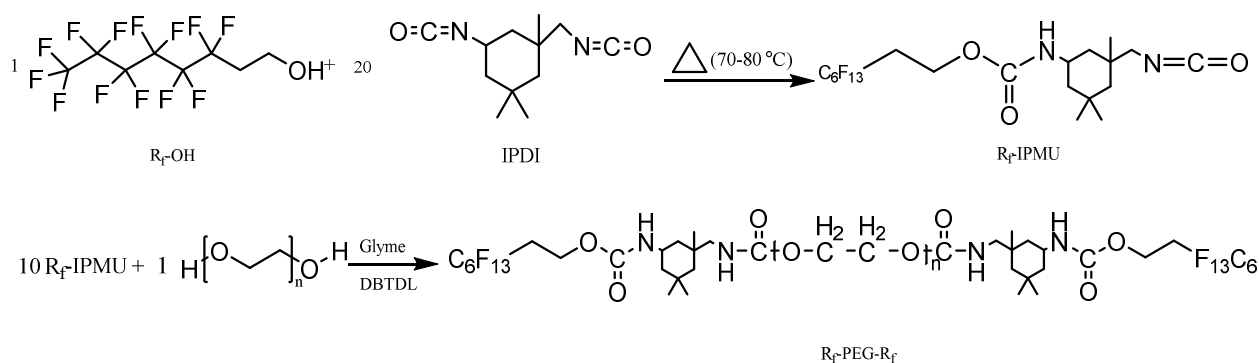
Accepted: 10 June 2021

Published: 12 June 2021

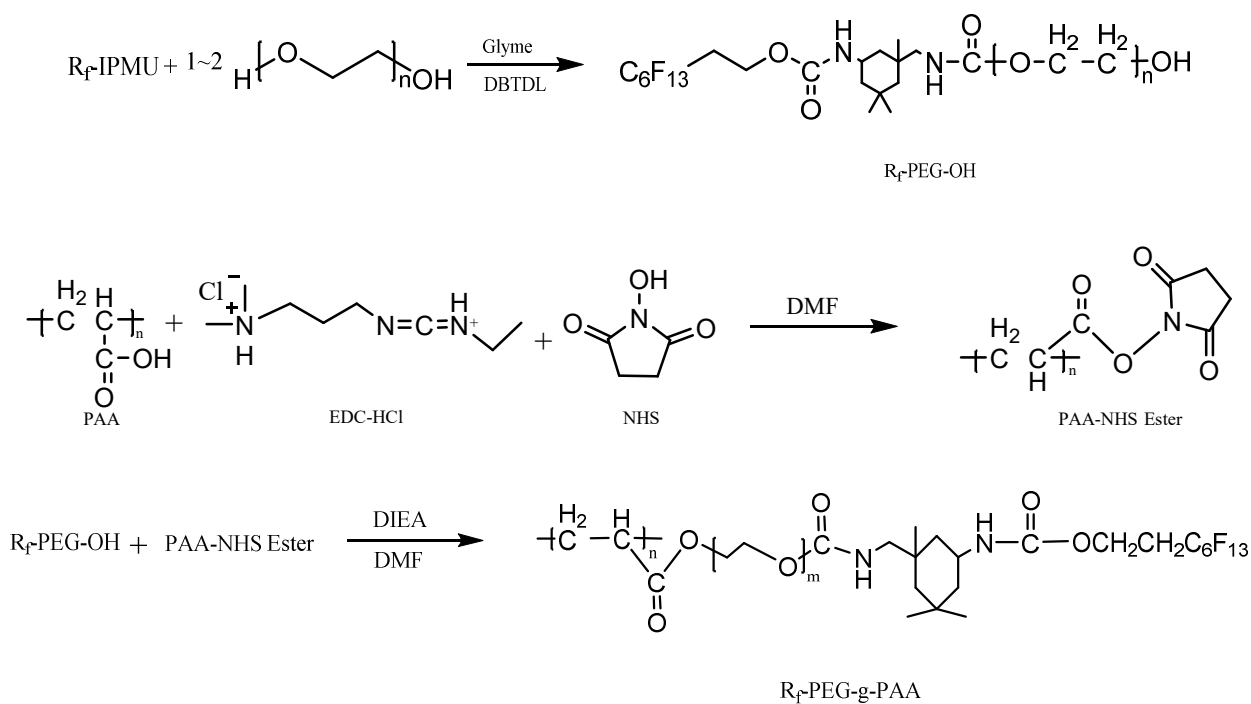
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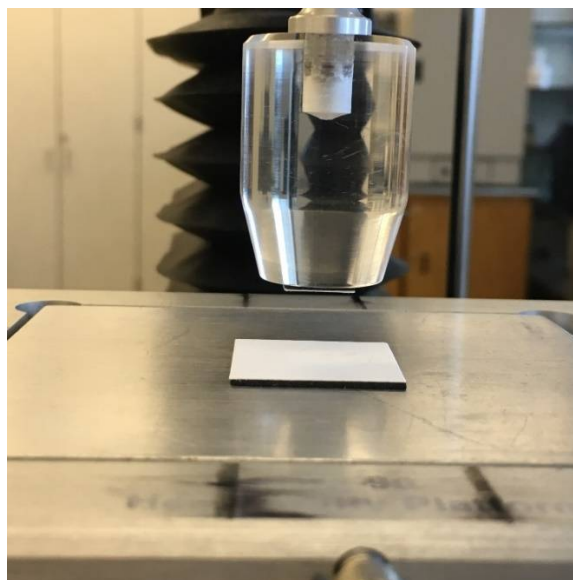
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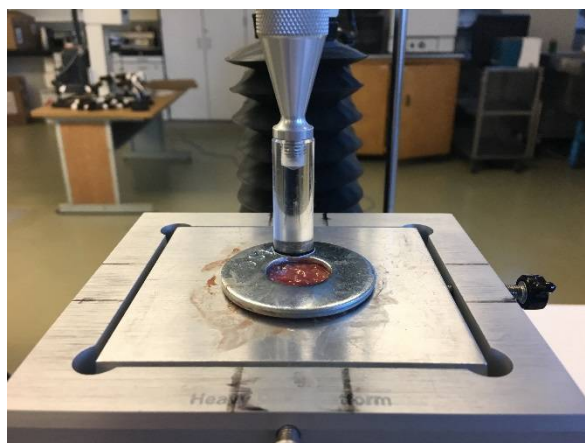
**Scheme S1.** Route of synthesis of  $\text{R}_f\text{-PEG-R}_f$ .



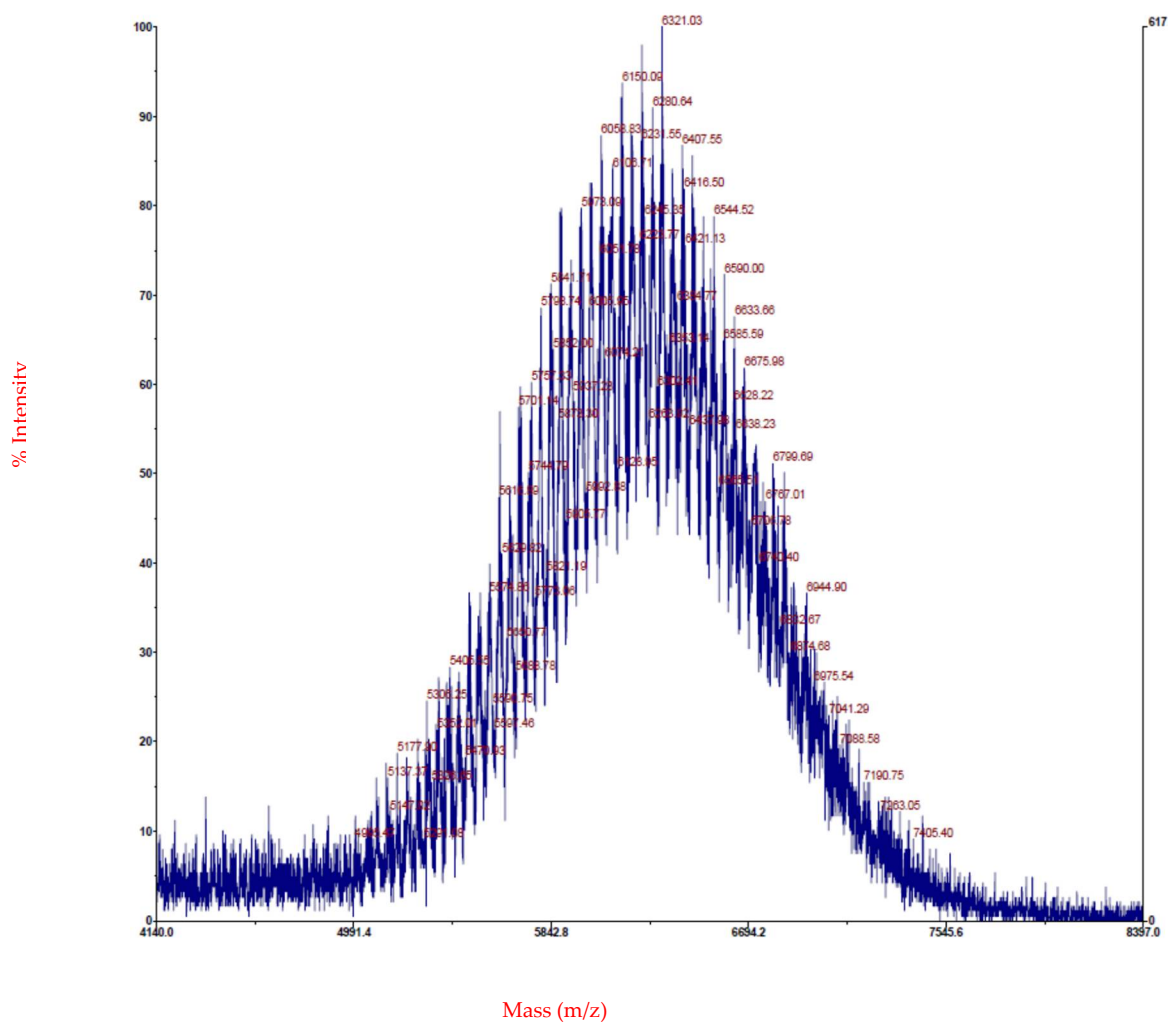
**Scheme S2.** Route of synthesis of  $\text{R}_f\text{-PEG-g-PAA}$ .



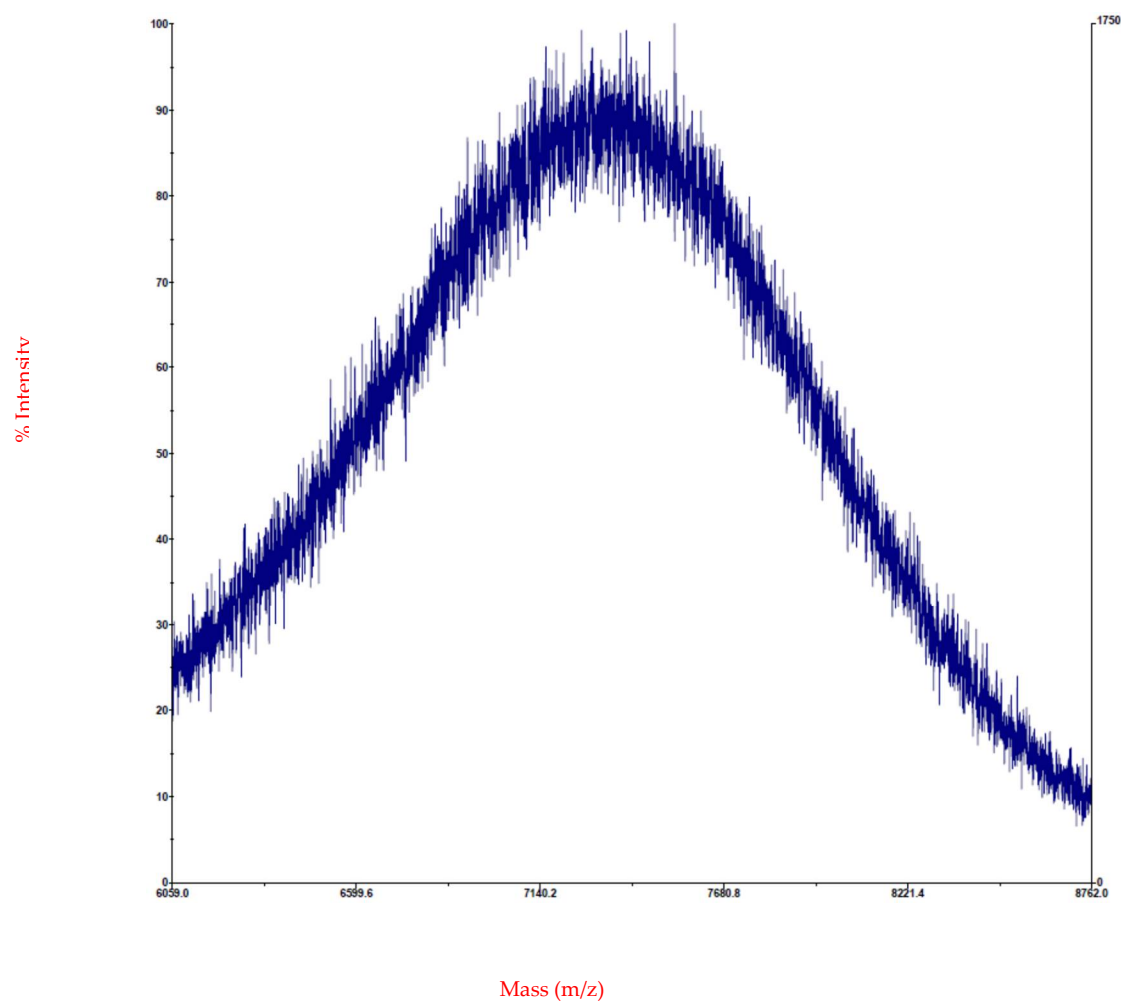
**Figure S1.** Photo picture of the Texture Analyzer experimental setting.



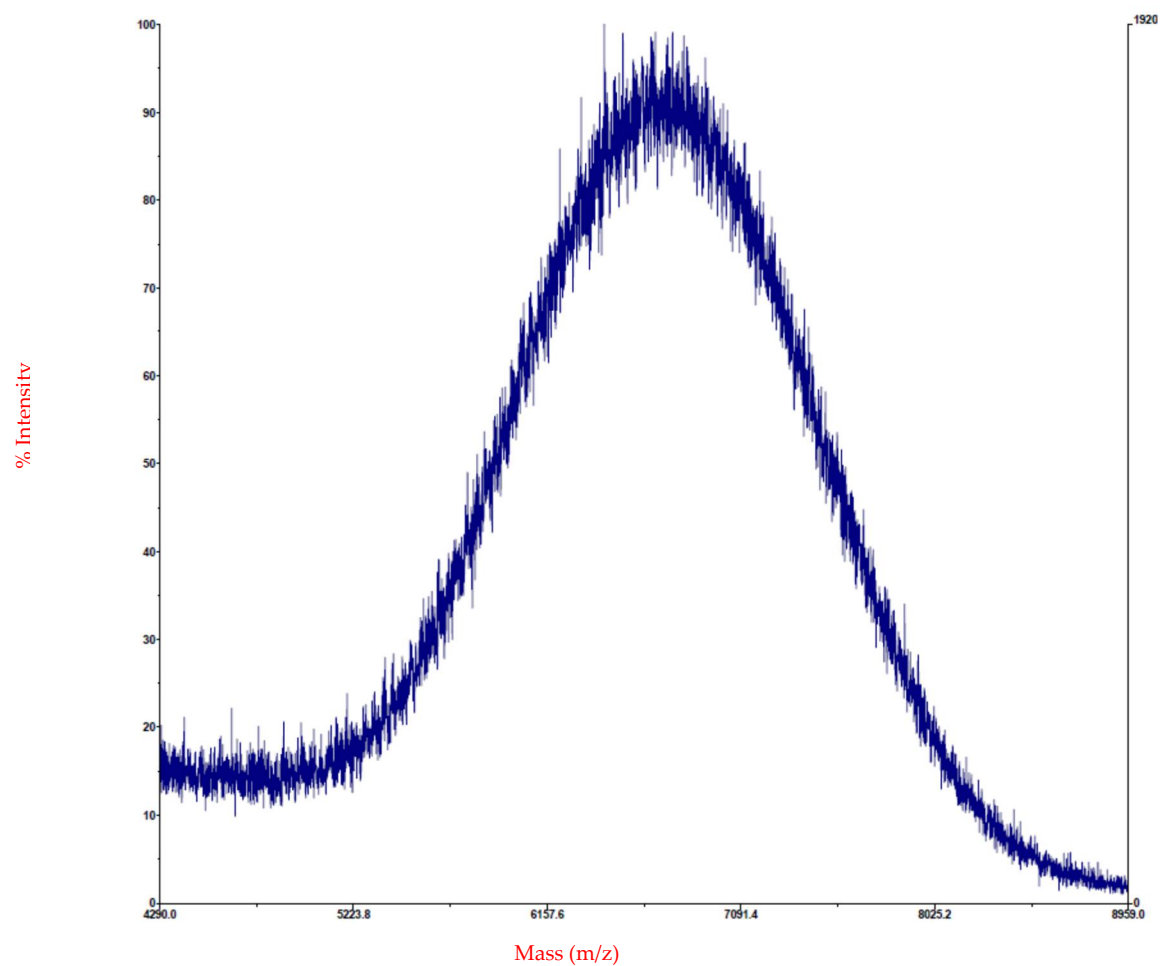
**Figure S2.** The lower plate shows the sample setting of the pig small intestine on the surface of the platform of the texture analyzer. The upper component shows the TA-10 probe on the surface of which a filter paper soaked with R<sub>f</sub>-PEG-R<sub>f</sub>/R<sub>f</sub>-PEG-g-PAA co-hydrogel was glued on.



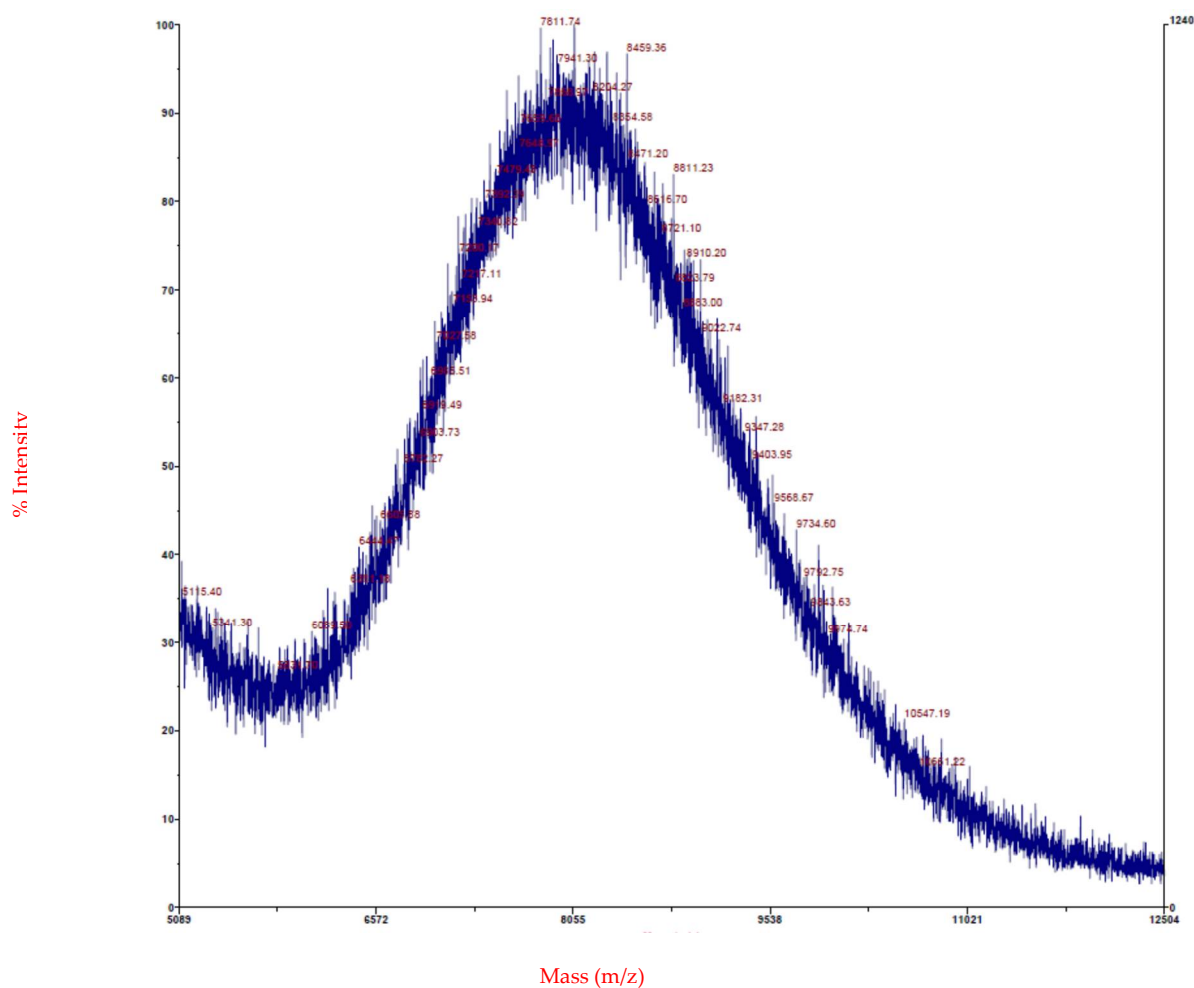
**Figure S3.** MALDI-TOF MS spectrum of the PEG showing an average molecular weight of  $6.2 \times 10^3$ .



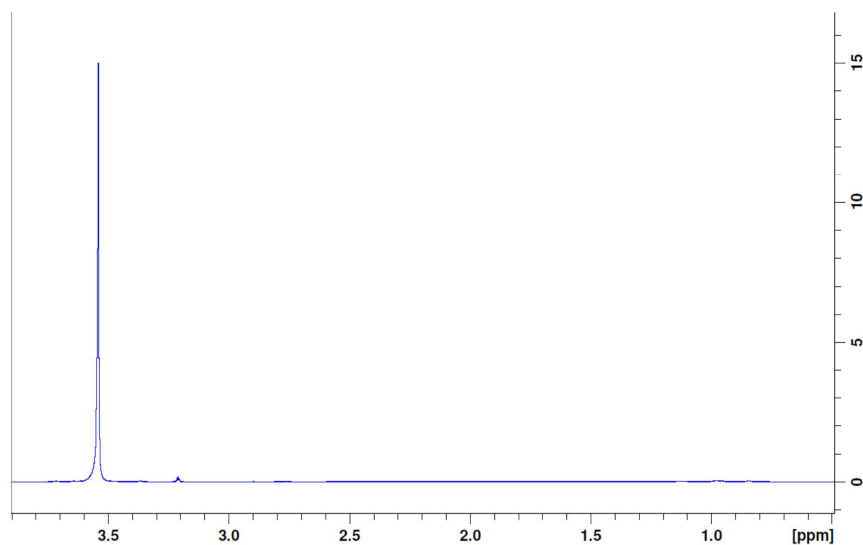
**Figure S4.** MALDI TOF mass spectrum of the R<sub>f</sub>-PEG-R<sub>f</sub> showing an average molecular weight of  $7.4 \times 10^3$ .



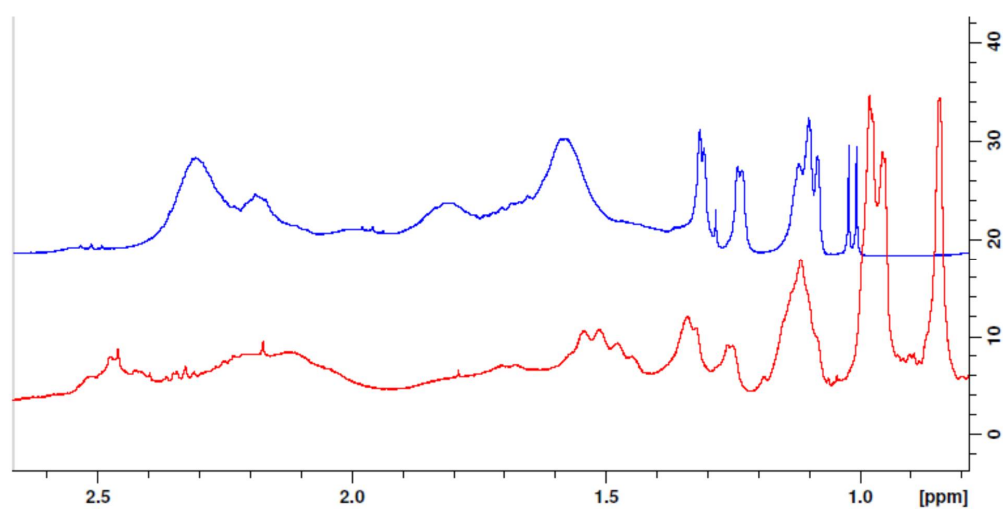
**Figure S5** MALDI TOF mass spectrum of the R<sub>f</sub>-PEG-OH showing an average molecular weight of  $6.8 \times 10^3$ .



**Figure S6.** MALDI TOF mass spectrum of the R<sub>f</sub>-PEG-g-PAA showing an average molecular weight of  $8.0 \times 10^3$ .



**Figure S7.** <sup>1</sup>H NMR spectrum of the R<sub>f</sub>-PEG-g-PAA. The sharp peak at 3.5407 ppm is from the PEG block.



**Figure S8.** Comparison of PAA region of the  $^1\text{H}$  NMR spectrum of PAA (top, blue) and  $\text{R}_f\text{-PEG-g-PAA}$  (bottom, red).



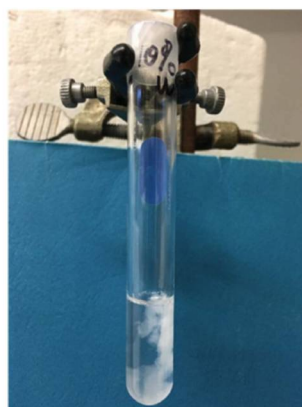
A



B

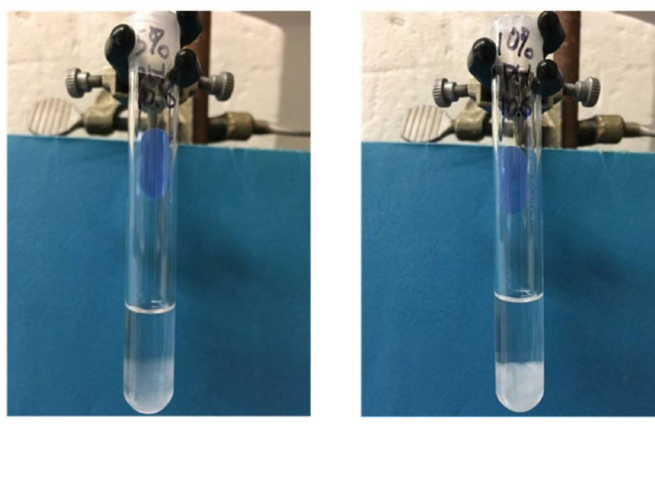


C

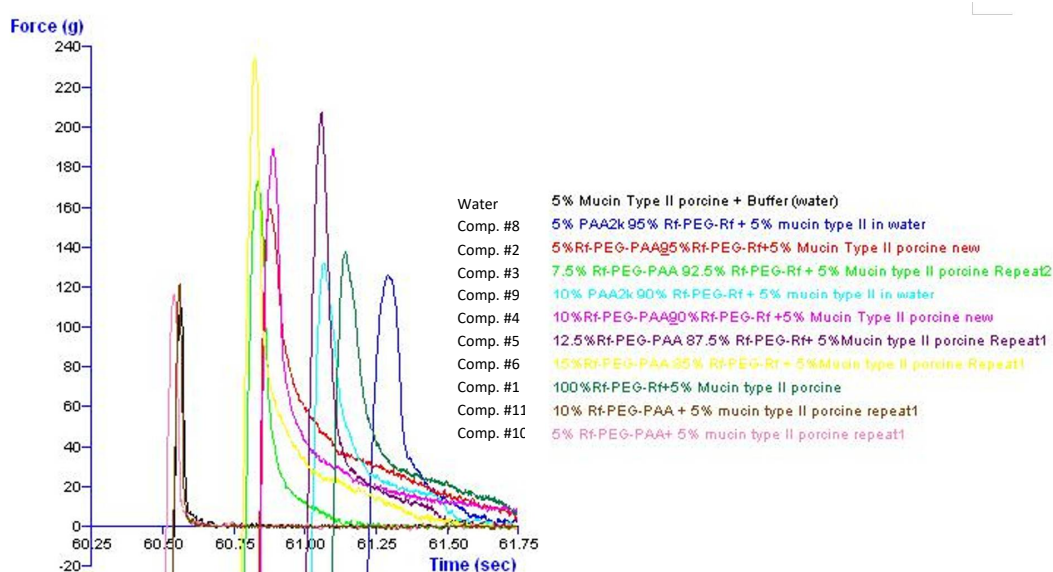


D

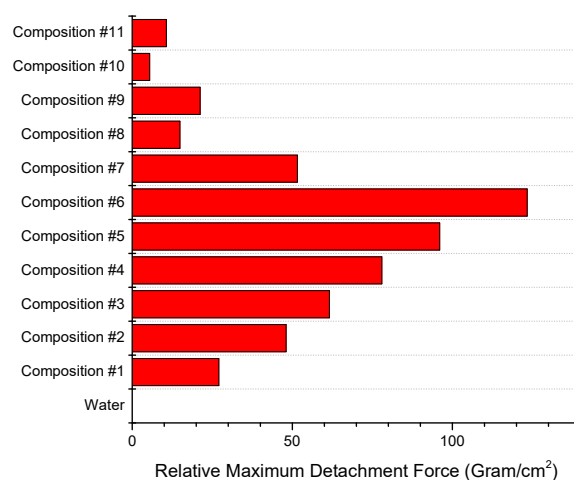




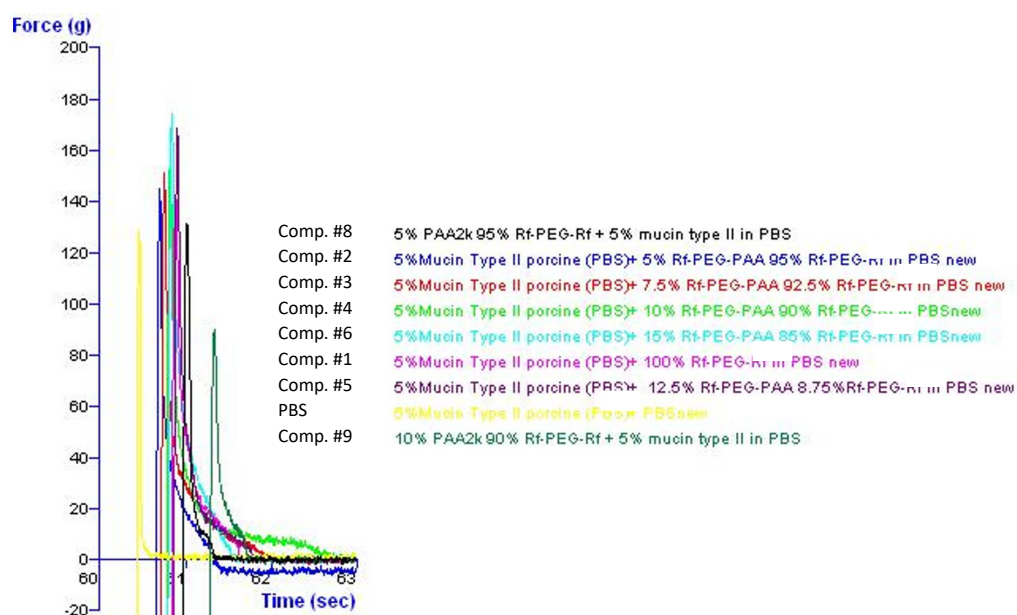
**Figure S9.** Photo pictures of the sol-gel two-phase coexistences of the 5% R<sub>f</sub>-PEG-g-PAA/95% R<sub>f</sub>-PEG-R<sub>f</sub> (composition #2 in Table 1), and the 10% R<sub>f</sub>-PEG-g-PAA/90% R<sub>f</sub>-PEG-R<sub>f</sub> (composition #4 in Table 1), respectively, prepared in the following solutions at 37 °C after 11 days: (A) and (B) in PBS buffer (pH=7.2); (C) and (d) in DI water (pH=4-5); and (E) and (F) in the glycine/sodium hydroxide buffer (pH=10.6).



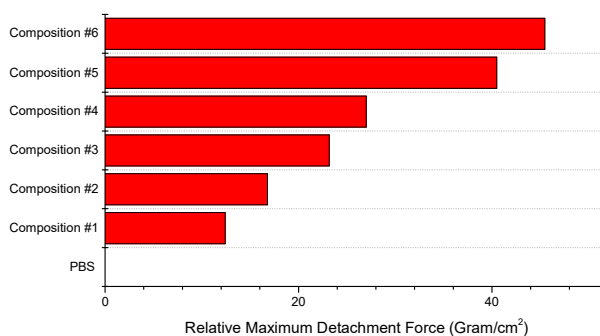
**Figure S10.** Force (g) vs. time (s) curves for the 5.0% mucin Type II sample interacting with the R<sub>f</sub>-PEG-R<sub>f</sub>/R<sub>f</sub>-PEG-g-PAA (here the -g- was omitted in the inset) co-hydrogels and the control samples prepared in water.



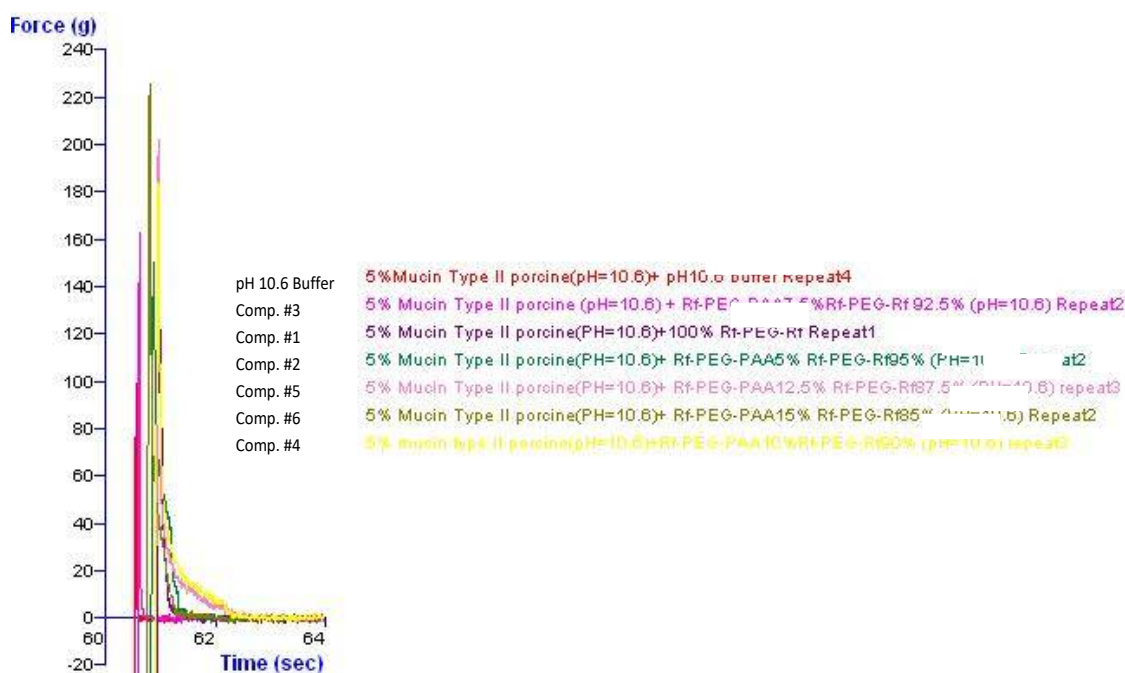
**Figure S 11.** Bar graph representation of the relative MDSs with respect to the MDS of the water sample for the 5.0% mucin Type II sample interacting with the R<sub>f</sub>-PEG-R<sub>f</sub>/R<sub>f</sub>-PEG-g-PAA co-hydrogels and the control samples prepared in water.



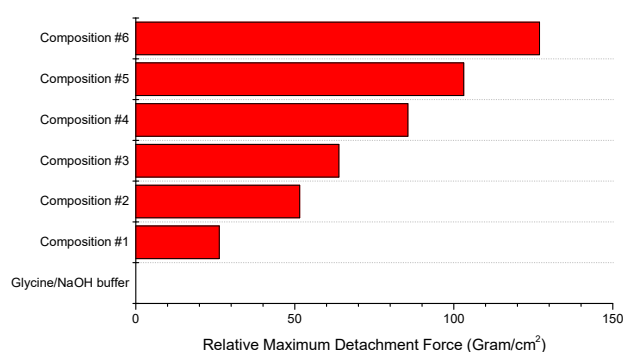
**Figure S12.** Force (g) vs. time (s) curves for the 5.0% mucin Type II sample interacting with the R<sub>f</sub>-PEG-R<sub>f</sub>/R<sub>f</sub>-PEG-g-PAA (here the -g- was omitted in the inset) co-hydrogels prepared in the PBS buffer.



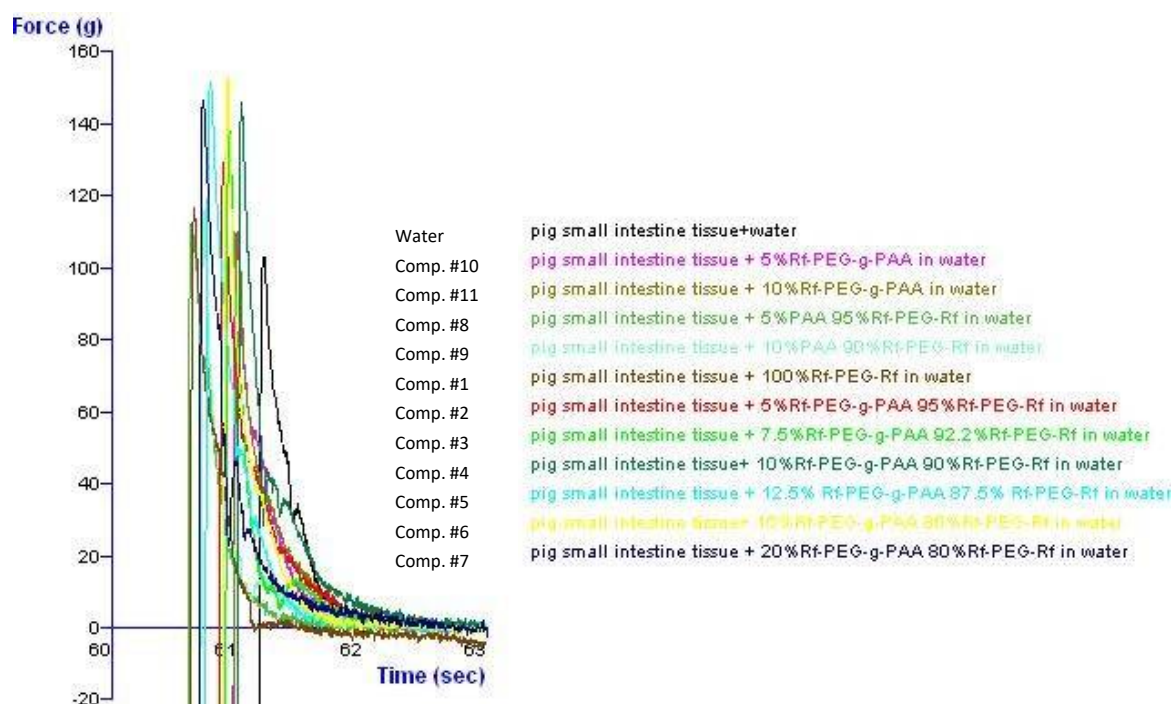
**Figure S13.** Bar graph representation of the relative MDSs with respect to the MDS of the PBS buffer sample for the 5.0% mucin Type II sample interacting with the R<sub>f</sub>-PEG-R<sub>f</sub>/R<sub>f</sub>-PEG-g-PAA co-hydrogels prepared in the PBS buffer.



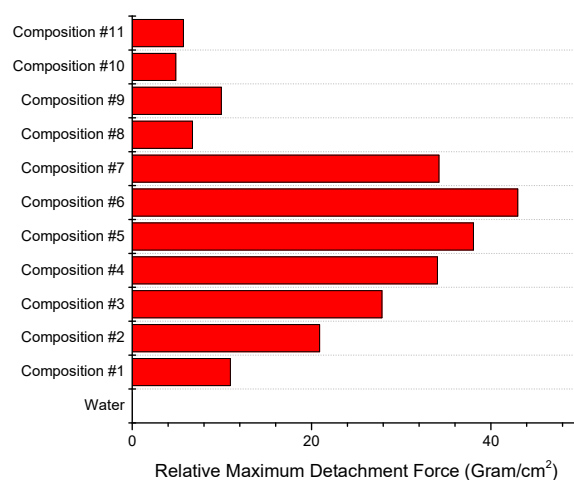
**Figure S14.** Force (g) vs. time (s) curves for the 5.0% mucin Type II sample interacting with the R<sub>f</sub>-PEG-R<sub>f</sub>/R<sub>f</sub>-PEG-g-PAA (here the -g- was omitted in the inset) co-hydrogel prepared in the glycine/NaOH buffer.



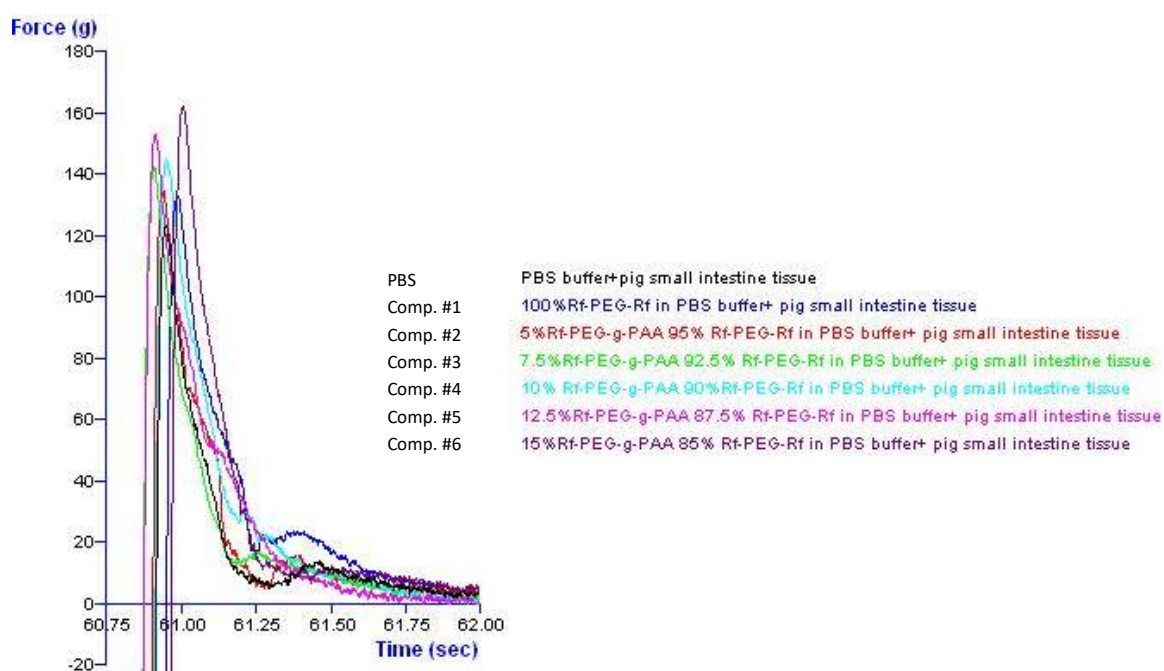
**Figure S15.** Bar graph representation of the relative MDSs with respect to the MDS of the PBS buffer sample for the 5.0% mucin Type II sample interacting with the R<sub>f</sub>-PEG-R<sub>f</sub>/R<sub>f</sub>-PEG-g-PAA co-hydrogel prepared in the glycine/NaOH buffer.



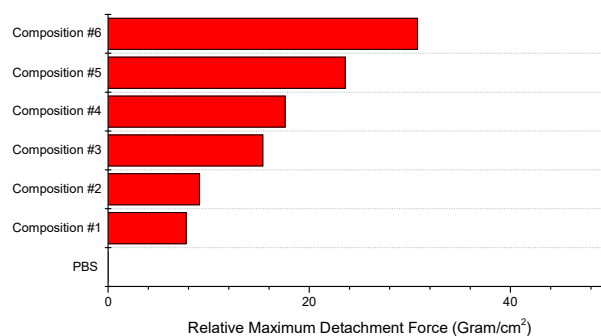
**Figure S16.** Force (g) vs. time (s) curves of the interactions of the various R<sub>f</sub>-PEG-R<sub>f</sub>/R<sub>f</sub>-PEG-g-PAA co-hydrogels and the control samples prepared in water with the pig small intestine surface.



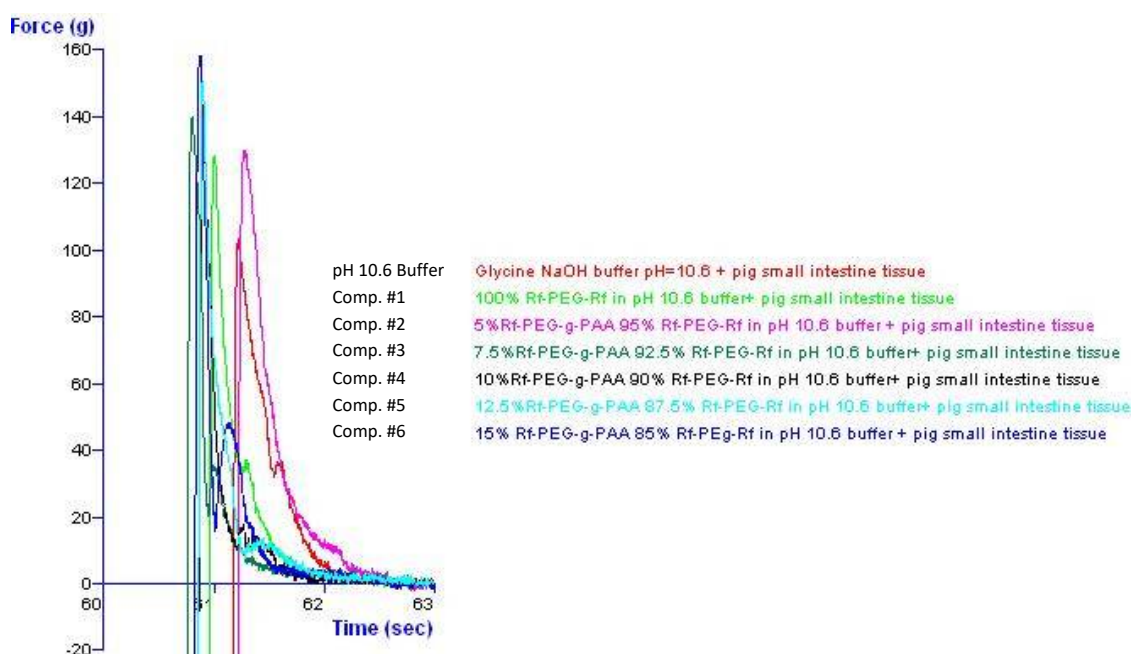
**Figure S17.** Bar graph presentation showing the relative MDSs of various Rf-PEG-Rf/Rf-PEG-g-PAA co-hydrogels and the control samples prepared in water with the pig small intestine surface.



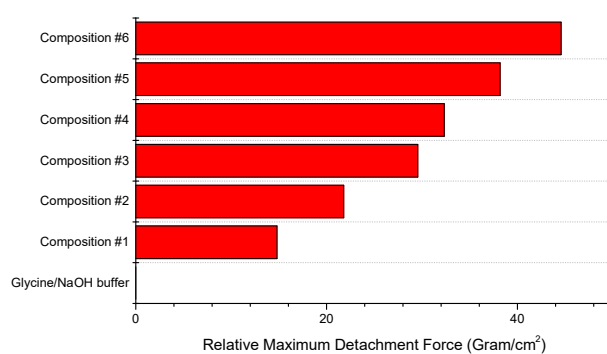
**Figure S18.** Force (g) vs. time (s) curves of the interactions of the various Rf-PEG-Rf/Rf-PEG-g-PAA co-hydrogels and the control sample prepared in PBS buffer with the pig small intestine surface.



**Figure S19.** Bar graph presentation showing the relative MDSs of various R<sub>f</sub>-PEG-R<sub>f</sub>/R<sub>f</sub>-PEG-g-PAA co-hydrogels and the control samples prepared in the PBS buffer with the pig small intestine surface.



**Figure S20.** Force vs. time curves of the interactions of various R<sub>f</sub>-PEG-R<sub>f</sub>/R<sub>f</sub>-PEG-g-PAA co-hydrogels and the control sample prepared in the glycine/NaOH buffer with the pig small intestine surface.



**Figure S21.** Bar graph presentation showing the relative MDSs for various  $R_f$ -PEG- $R_f$ / $R_f$ -PEG-g-PAA co-hydrogels and the control samples prepared in glycine/NaOH buffer interacting with the pig small intestine surface.