Supplementary Materials

Dynamic Glycan Network Engineering of Native Mucin Enables Reversible, Self-Healing, and Adhesive Hydrogel Interfaces

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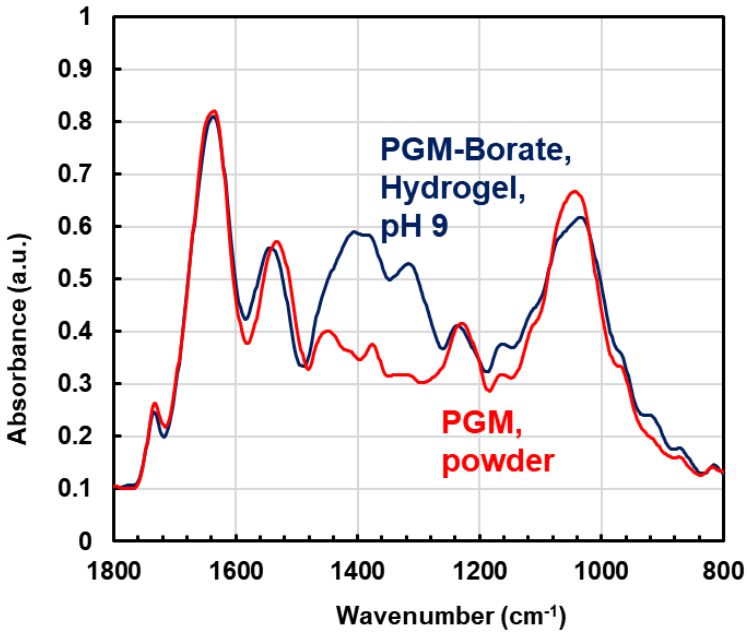

Figure S1. FTIR spectra of native PGM powder (red) and the borate-crosslinked PGM hydrogel prepared at pH 9 (blue).

Results and Discussion

FTIR Analysis

As shown in **Figure S2**, native PGM powder displayed characteristic bands at 1375 cm^{-1} (CH_3 bending), 1448 cm^{-1} (CH_2 scissoring), 1533 cm^{-1} (amide II), and 1635 cm^{-1} (amide I). Upon addition of borate, the spectral pattern changed substantially. The native C–O stretching band at 1030–1050 cm^{-1} decreased in intensity, while absorptions increased at 1180–1200 cm^{-1}. A strong, broad band developed near 1310 cm^{-1} and additional broad features appeared in the 1390–1410 cm^{-1} region.

These changes correspond to established FTIR signatures of borate–diol complexation. The reduction of the 1030–1050 cm^{-1} band indicates consumption of mucin glycan cis-diols during ester formation. The enhanced absorption near 1310 cm^{-1} matches the tetrahedral BO_4-type B–O–C asymmetric stretch reported for PVA–borax and alginate/gelatin–borate hydrogels [1–3], indicating the presence of BO_4-coordinated borate species bound to mucin diols. The strong, broad band around 1400 cm^{-1} aligns with the trigonal BO_3-type B–O–C stretch typically observed at 1409–1420 cm^{-1} in polymer–borate networks [1,2], confirming BO_3-based borate ester formation. The coexistence of BO_3- and BO_4-associated bands indicates mixed coordination states of borate within the mucin matrix.

Overall, the spectral evolution from 1050 to 1450 cm^{-1} demonstrates that borate forms reversible PGM–borate crosslinked domains consisting of B–O–C ester linkages and mixed BO_3/BO_4 coordination. These signatures parallel those of other polysaccharide–borate hydrogels [1–3], indicating that borate reorganizes the PGM network at the molecular scale.

References

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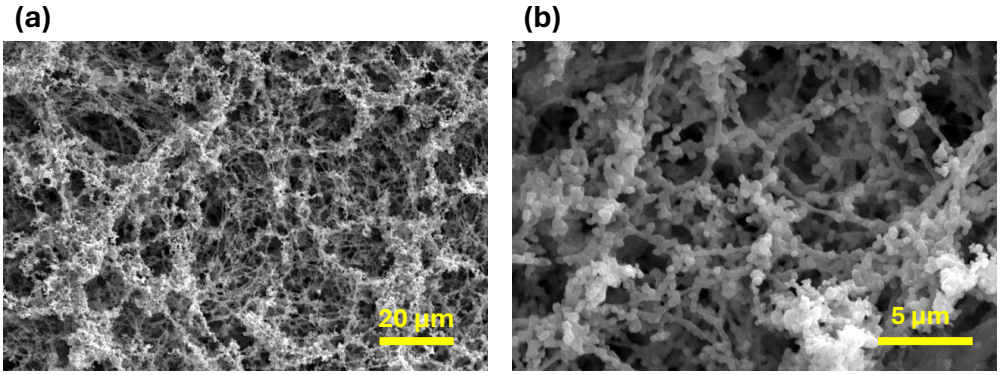

Figure S2. SEM images of PGM–borate hydrogel prepared at pH 9. The hydrogel was solvent-exchanged with ethanol in a stepwise manner, followed by t-butyl alcohol, and subsequently freeze-dried. (a) Low magnification. Bar = 20 µm. (b) High magnification. Bar = 5 µm. These images confirm the formation of an interconnected porous network characteristic of borate–crosslinked systems.

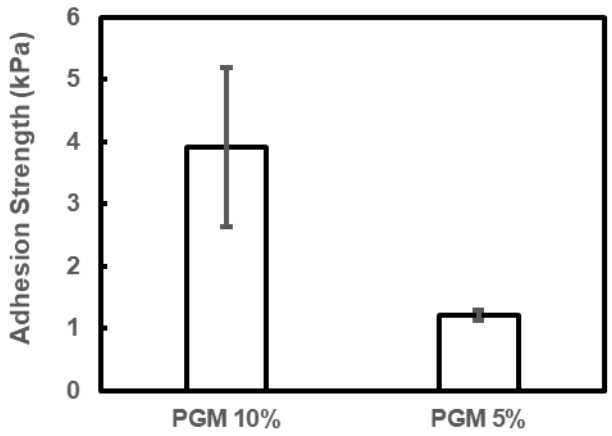

Figure S3. Adhesion strength of PGM–borate hydrogels prepared with different PGM concentrations (5% and 10%). Adhesion strength was measured using a universal testing machine by sandwiching the hydrogel between two oxygen-plasma-treated acrylic plates (diameter 3 mm). The applied load at detachment was normalized by the contact area to obtain the adhesion strength (kPa). Bars represent the mean ± SD (n = 3).

Results and Discussion

Measurement of Adhesion Strength

As shown in **Figure S3**, the adhesion strength of the PGM–borate hydrogels increased with increasing PGM concentration. The 10% PGM hydrogel showed an adhesion strength of approximately 4 kPa, whereas the 5% PGM hydrogel exhibited values around 1 kPa. This concentration-dependent increase demonstrates that the amount of PGM present in the hydrogel directly influences the measured adhesion strength.

The higher adhesion strength observed at 10% PGM suggests that PGM itself plays a central role in establishing adhesion to the plasma-treated acrylic surface. A greater PGM concentration provides more polymer chains and more borate-binding sites, increasing the number of functional groups capable of interacting with the hydrophilic acrylic surface. The polar glycans in PGM can form hydrogen bonds or other polar interactions with oxygen-containing groups introduced on the acrylic by plasma treatment, promoting stronger interfacial contact. These considerations support the conclusion that PGM contributes directly to the adhesion of the PGM–borate hydrogel to the acrylic substrate.

Supplementary Movies

Movie S1 Self-healing behavior of the PGM/BA hydrogel (10% PGM mixed with 300 mM BA, pH 8.0) after a 60 s contact time. Two differently dyed hydrogel pieces were cut and brought into contact, followed by a 60 s healing period. The movie shows the complete self-healing process and the successful stretching of the rejoined gel. This movie corresponds to Fig. 4a.

Movie S2 Self-healing behavior of the PGM/BA hydrogel after a 10 s contact time. The two cut gel pieces were briefly brought into contact for 10 s. The movie shows partial or insufficient healing, with the interface failing during subsequent handling.

Movie S3 Self-healing behavior of the PGM/BA hydrogel with 0 s contact time. The cut gel pieces were placed in brief contact without any holding time, resulting in no observable healing. The movie shows immediate separation upon manipulation.

Movie S4 Adhesive behavior of the PGM/BA hydrogel (10% PGM mixed with 300 mM BA, pH 8.0). A hydrogel sample placed on a glass plate was pressed against the bottom of a glass beaker for 10 s. The movie shows the attachment process and the lifting of the glass plate by holding the adhered beaker. This movie corresponds to Fig. 4b.