Development of debondable dental resin cements containing photodegradable polyrotaxane as a cross-linker

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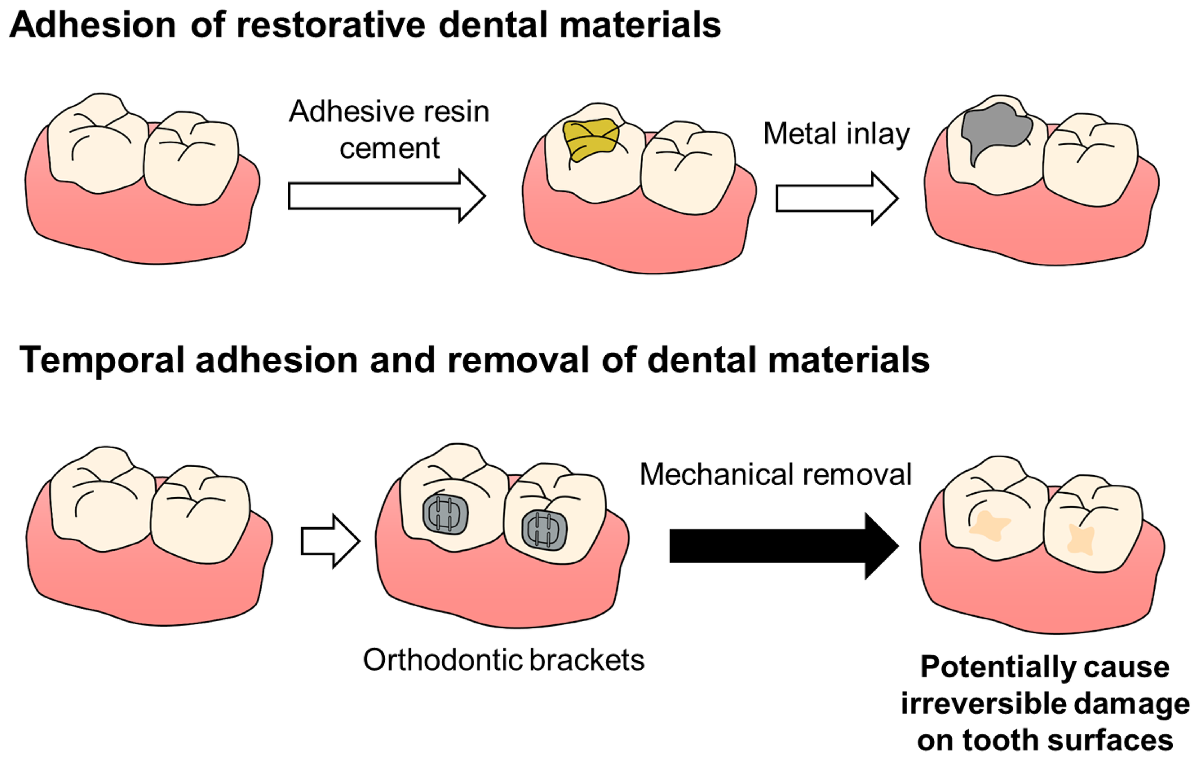
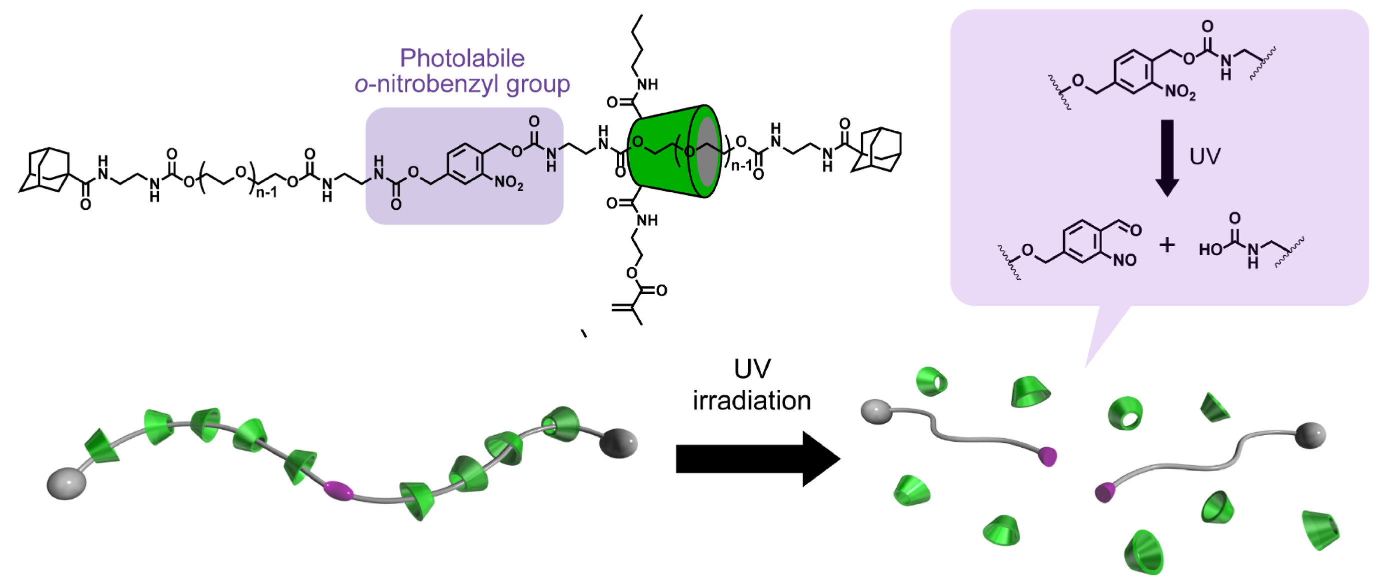
Introduction

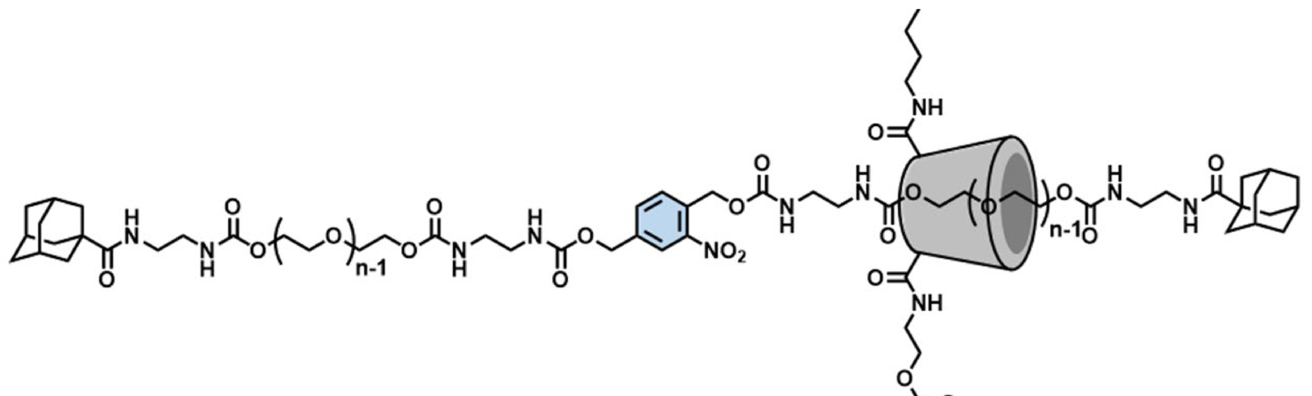
Various dental materials, including metals, ceramics, and polymers are often fixed onto tooth surfaces for the treatment, such as metal and ceramic alloys in fixed prosthodontic treatment, resin composites in caries treatment and crown restorations, and dental brackets in orthodontic treatment. To achieve the current progress in adhesive dentistry, numerous researchers made efforts over the past several decades to fabricate durable dental materials adhesion on tooth surfaces. In some dental treatments, dental materials are temporarily adhered onto the tooth using adhesive resin cements, such as orthodontic brackets. However, the removal of adhered materials from the tooth surfaces still relies on the mechanical detachment or destruction of the materials. The mechanical removal of the adhered materials potentially causes irreversible damage and fracture of enamel layers, such as in the debonding of orthodontic devices. It is envisaged that the development of adhesive materials that can be removed from tooth surfaces provides non-invasive and simple debonding methods in current dental treatments.



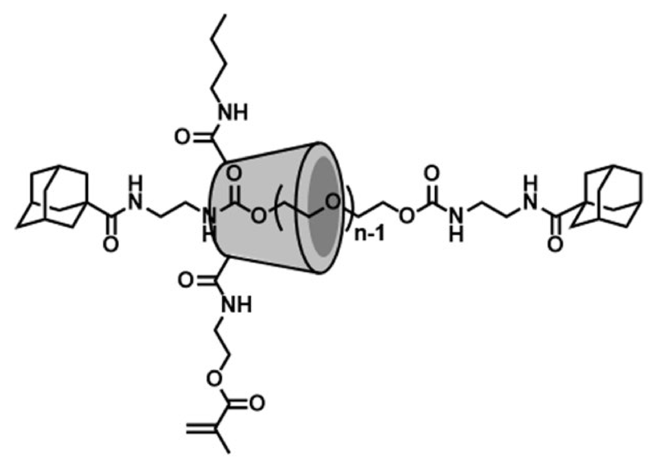
Our group developed photo-degradable polyrotaxanes (PRXs), a supramolecular interlocked polymer composed of α-cyclodextrin (α-CD) threaded along a linear poly(ethylene glycol) (PEG) chain capped with bulky stopper molecules. The photodegradable PRXs containing an *o*-nitrobenzyl ester at the internal chain of the axle polymer, wherein the *o*-nitrobenzyl ester linkage are cleaved via ultraviolet (UV) light irradiation. The cleavage of the *o*-nitrobenzyl ester linker leads to the degradation of PRXs and the release of threaded α-CDs. Note that the stimuli-induced dissociation of PRXs occurs through the cleavage of only one side of the cleavable linkers, which is beneficial for reducing the number of photolabile components in the resins compared with small-molecular photolabile cross-linkers. The UV irradiation is advantageous for oral microenvironment applications, because light irradiation is widely used in current dental treatment (e.g., photo-polymerization of resin cements and resin composites). Using the designed internally *o*-nitrobenzyl ester-introduced PRX (iNB-PRX) as a cross-linker, we prepared adhesive resin cements containing iNB-PRX-based cross-linkers and investigated the adhesive force of poly(methyl methacrylate) (PMMA) blocks adhered with the resin cement cross-linked with the iNB-PRX.



Materials



Photodegradable PRX (MB-iNB-PRX)
M_n = 85,200 (M_n of axle PEG = 10,000)
Number of threading α-CD = 31.0
Number of methacryloyl group = 49.9
Number of *n*-butyl group = 382



Nondegradable PRX (MB-PRX)
M_n = 92,400 (M_n of axle PEG = 10,000)
Number of threading α-CD = 33.6
Number of methacryloyl group = 52.3
Number of *n*-butyl group = 415

Results and discussion

Photodegradability of MB-iNB-PRX

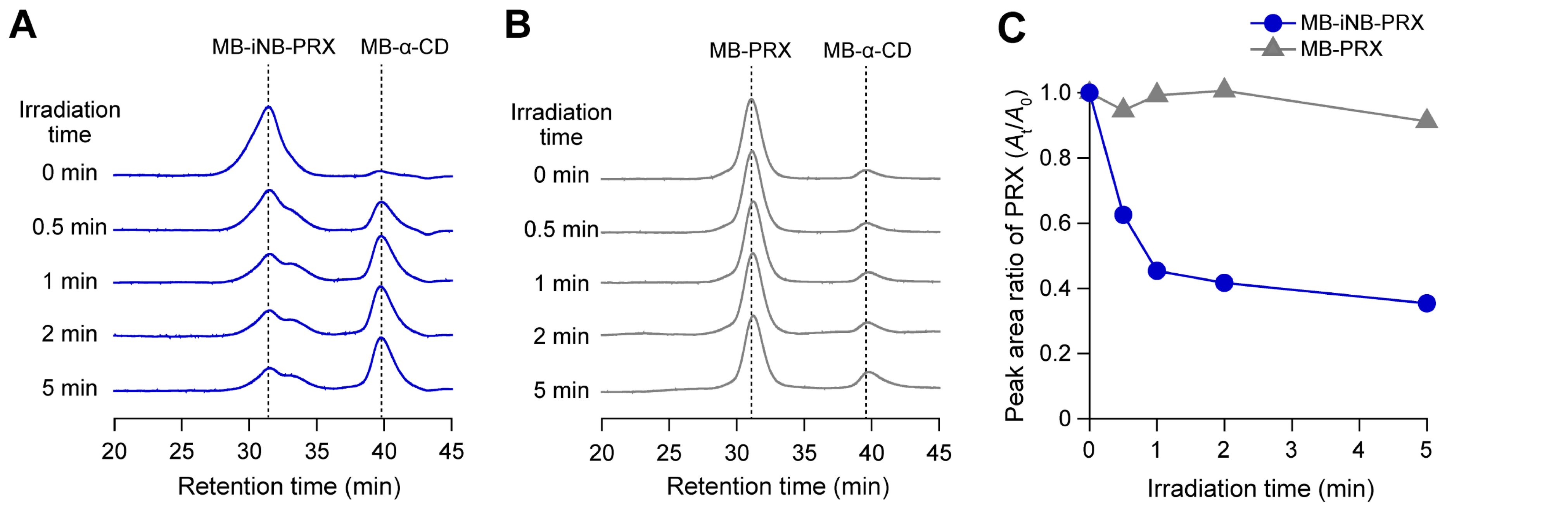


Figure. SEC charts of MB-iNB-PRX (A) and nondegradable MB-PRX (B) after irradiation of UV light. (C) Time courses of the degradation rates of MB-iNB-PRX and nondegradable MB-PRX under UV irradiation. Upon irradiation with UV light, approximately 60% of MB-iNB-PRX degraded within 5 min.

UV-Induced Embrittlement of Adhesive Resin Cements

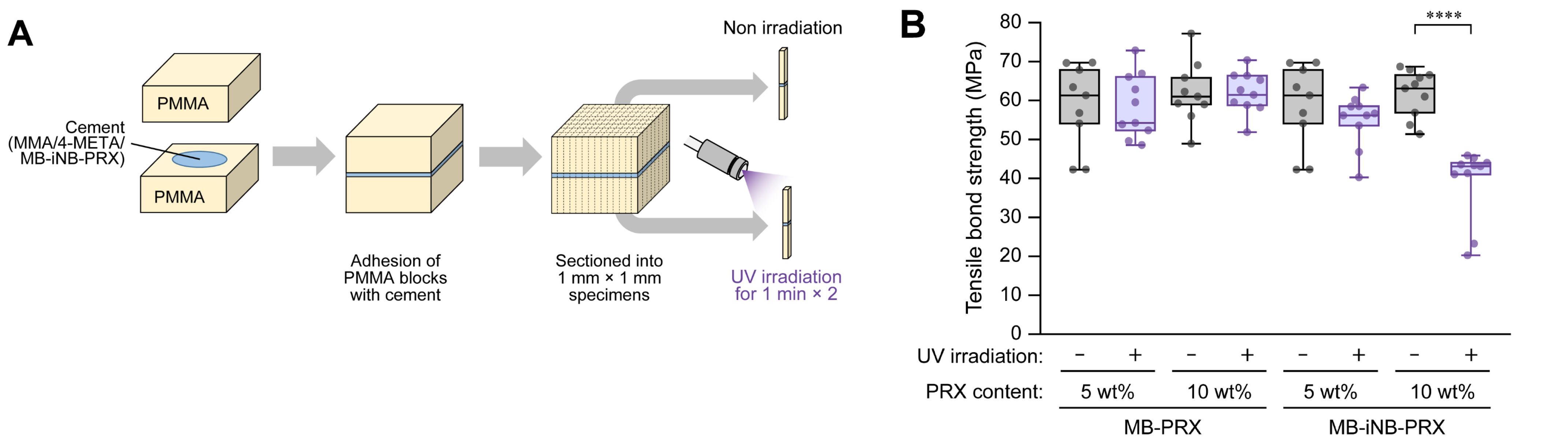


Figure. (A) Schematic illustration of the adhesion of PMMA blocks with adhesive resin cements. (B) Tensile bond strength of the non-irradiated and UV-irradiated specimens comprising PMMA blocks adhered with the adhesive resin cements containing MB-iNB-PRX or MB-PRX (5 or 10 wt %).The tensile bond strength of the resin cement containing 10 wt% MB-iNB-PRX was significantly decreased by UV irradiation. For the resin cement containing 5 wt% MB-iNB-PRX, the tensile bond strength was not changed by UV irradiation. In addition, the tensile bond strength of the resin cements containing the nondegradable MB-PRX was not significantly changed by UV irradiation.

Adhesion of Bovine Dentin

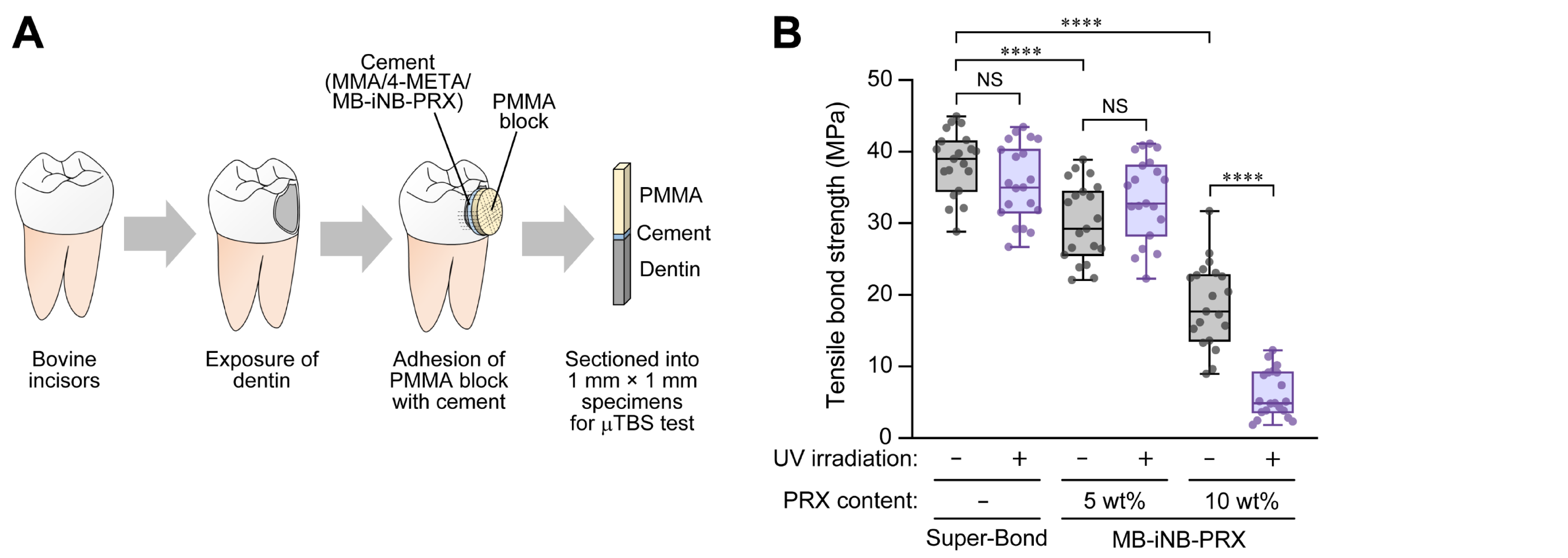


Figure. (A) Schematic illustration of the adhesion of a PMMA block onto a bovine teeth dentin surface with the adhesive resin cement and the preparation of the specimens for the tensile bond strength test. (B) Tensile bond strength of the non-irradiated and UV-irradiated specimens adhered with Super-Bond C&B and the adhesive resin cement containing MB-iNB-PRX (5 and 10 wt %). Two sides of the specimens were irradiated with UV light for 1 min each. The tensile bond strength of the resin cement containing 10 wt% MB-iNB-PRX was significantly decreased by UV irradiation. For the resin cement containing 5 wt% MB-iNB-PRX, µTBS was not changed by UV irradiation. In addition, the µTBS of the resin cements containing the nondegradable MB-PRX was not significantly changed by UV irradiation.

Conclusions

The adhesive resin cement containing the MB-iNB-PRX cross-linker was prepared by dissolving MB-iNB-PRX into a clinically utilized resin cement and used to adhere two PMMA blocks. The tensile strength of the PMMA specimens decreased significantly upon UV irradiation for 2 min owing to the UV-induced degradation of the MB-iNB-PRX cross-linker. Additionally, adhesive resin cement containing the MB-iNB-PRX cross-linker was used to adhere PMMA blocks on the bovine dentin surface. The tensile bond strength of PMMA–dentin specimens decreased significantly upon UV irradiation. Fine-tuning MB-iNB-PRX would resolve these issues to contribute toward the development of clinically applicable light-embrittled dental adhesive resin cements.

S. Matsunaga, A. Tamura, M. Fushimi, H. Santa, Y. Arisaka, T. Nikaido, J. Tagami, N. Yui. ***ACS Appl. Polym. Mater.*** 2, 5756–5766 (2020)