

A Novel Polyurethane-based Root Canal—obturation Material and Urethane-Acrylate—based Root Canal Sealer—Part 2: Evaluation of Push-out Bond Strengths

Bor-Shiunn Lee, DDS, MS, PhD,* Eddie Hsiang-Hua Lai, DDS, MS,* Ken-Hsuan Liao, BS, MS,[†] Chung-Yi Lee, DDS, MS,* Kuo-Huang Hsieh, BS, MS, PhD,[†] and Chun-Pin Lin, DDS, MS, PhD*[†]

Abstract

We have developed a visible-light curable urethane-acrylate/tripropylene glycol diacrylate (UA/TPGDA) oligomer to serve as a root canal sealer and a zinc oxide/thermoplastic polyurethane (ZnO/TPU) composite to serve as a root canal obturation material. The purpose of this study was to compare the push-out bond strengths of the following 8 groups of materials: (1) Tubliseal + gutta-percha (TB/GP); (2) Tubliseal + Resilon (TB/R); (3) Epiphany + gutta-percha (EP/GP); (4) Epiphany + Resilon (EP/R); (5) EndoREZ sealer + EndoREZ cone (ES/EC); (6) EndoREZ sealer + ZnO/TPU (ES/PU); (7) UA/TPGDA + EndoREZ cone (UA/EC); and (8) UA/TPGDA + ZnO/TPU (UA/PU). Eighty 1-mm-thick root slices prepared from extracted human permanent molars were randomly divided into 8 groups with 10 specimens in each group. Root slices were filled with the above obturation materials, and then push-out test was performed with a universal testing machine. The results showed that the UA/EC and UA/PU groups had significantly higher bond strengths than the other groups. (*J Endod* 2008;34:594–598)

Key Words

Push-out bond strength, root canal obturation, ZnO/TPU composite

From the *School of Dentistry & Graduate Institute of Clinical Dentistry, National Taiwan University and National Taiwan University Hospital, Taipei, Taiwan; and [†]Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan.

Address requests for reprints to Chun-Pin Lin, Dean and Professor, School of Dentistry & Graduate Institute of Clinical Dentistry, National Taiwan University, No. 1, Chang-Te Street, Taipei 10016, Taiwan. E-mail address: pinlin@ntu.edu.tw; or Professor Kuo-Huang Hsieh, Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan. E-mail address: khhsieh@ntu.edu.tw. 0099-2399/\$0 - see front matter

Copyright © 2008 by the American Association of Endodontists.

doi:10.1016/j.joen.2008.02.015

A hermetically 3-dimensional obturation plays a crucial role in reducing periapical inflammation and microbial leakage (1). In addition, adhesion of root canal sealers to dentin is important to seal the root canal thoroughly and prevent dislodgement of filling materials (2). The traditional obturation materials used in endodontics are gutta-percha and root canal sealers. However, disadvantages of gutta-percha include no dentinal adhesion, lack of sufficient rigidity, and shrinkage during cooling or solvent evaporation (3). To circumvent these disadvantages, a new polymer-based obturation material, Resilon, in combination with methacrylate-based resin sealers was developed. The manufacturer has claimed that the use of Resilon in combination with self-etching adhesives and methacrylate-based resin sealers offers the advantages of monoblock bonding for the root canal system (4). Resilon has been demonstrated to exhibit less microbial leakage (5) and higher bond strength to root canal dentin (6), reduce periapical inflammation (7), and enhance fracture resistance of endodontically treated teeth (8) compared with gutta-percha. However, previous studies also reported limitations of Resilon including low push-out bond strength (3, 9, 10) and low cohesive strength plus stiffness (11). In addition, Resilon could not achieve a complete hermetic apical seal (4).

We have developed a novel polyurethane-based composite to serve as a root canal obturation material and a visible-light curable urethane-acrylate/tripropylene glycol diacrylate (UA/TPGDA) oligomer to serve as a root canal sealer. The composite is composed of thermoplastic polyurethane (TPU) as well as zinc oxide (ZnO) and exhibits better mechanical properties than Resilon and gutta-percha. In addition, ZnO/TPU composite in combination with UA/TPGDA sealer can bond to the intraradicular dentin. Because strengthening of roots with adhesive materials can be reflected by improved interfacial strength and dislocation resistance (12), the push-out test is one effective method to evaluate the adhesive bond strength of an endodontic obturation material. The purpose of this study was to evaluate the push-out bond strength of our newly developed materials and to compare them with those of other widely used filling materials.

Materials and Methods

Specimen Preparation

The procedures used to synthesize ZnO/TPU composite and UA/TPGDA sealer have been described in the first part of this series of studies. Extracted human permanent molars (Fig. 1A) from subjects aged 16–40 years were used in this study after informed consent was obtained from the donors. Crowns with caries, restorations, or fractures were discarded. Any remaining soft tissues were thoroughly removed from the tooth surfaces with a dental scaler (Sonicflex 2000; KaVo Co, Biberbach, Germany) under running water. All teeth were then stored at 4°C in distilled water containing 0.2% thymol to inhibit microbial growth until use. While fully hydrated, the palatal roots of maxillary molars or distal roots of mandibular molars were first cut down perpendicular to the long axis of the tooth by using a low-speed diamond wafering blade (Isomet; Buehler Ltd, Lake Bluff, IL). Then the apical 3 mm of each root was cut, and the apical portions were discarded (Fig. 1B). Each canal was prepared until the apical opening could be passed by an ISO size 80, 0.02 taper file. The canals were irrigated with 17% ethylenediaminetetraacetic acid (EDTA) and 2.5% sodium hypochlorite during instru-

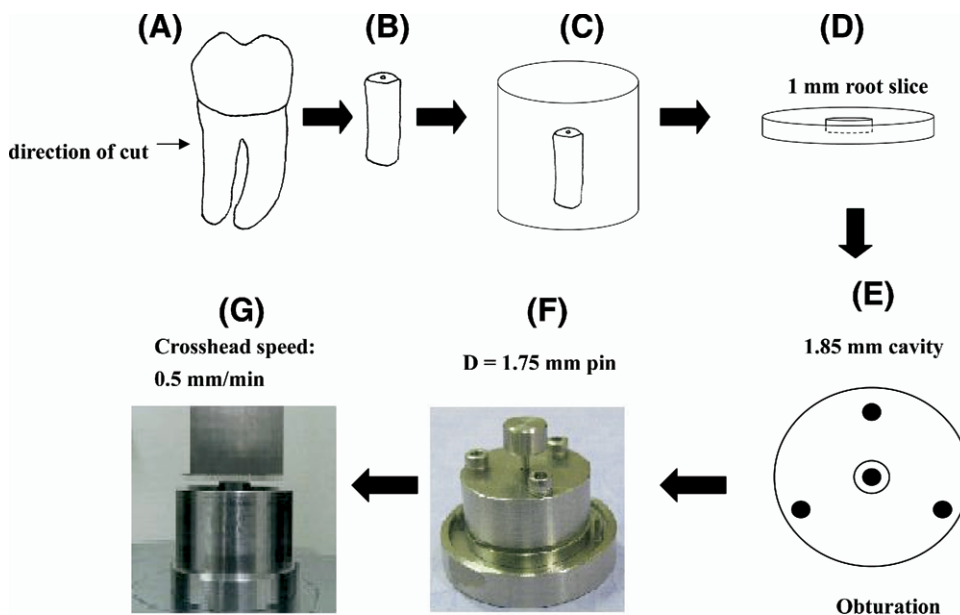


Figure 1. Illustration of the push-out bond test procedure. (A) Extracted human permanent molars were used. (B) Palatal roots of maxillary molars or distal roots of mandibular molars were cut down perpendicular to the long axis of the tooth. The apical 3 mm of each root was cut, and the apical portions were discarded. (C) Each prepared root was mounted vertically in a custom-made aluminum cylinder with self-curing acrylic resin. (D) Each root was serially sectioned to create a root slice of 1-mm thickness. (E) A 1.85-mm diameter hole was centrally prepared in each root slice by using a multi-drilling machine, and the hole was filled with obturation materials. (F) The punch-out apparatus consisted of 2 cylindrical steel dies aligned together with 2 dowels and secured with 3 screws. A 1.80-mm diameter hole and a 1.90-mm diameter hole were centrally positioned at the upper and lower dies, respectively. A cylindrical carbon steel rod 1.75 mm in diameter was used as a plunger. (G) The push-out apparatus was mounted on an Instron universal testing machine.

mentation. A custom-made aligning device was used to mount each prepared root vertically in custom-made aluminum cylinder (3 cm in diameter and 2 cm in height) with self-curing acrylic resin (Tempron; GC Corp, Tokyo, Japan) (Fig. 1C). The aligning device contained a base plate with 3 orientation screws and 1 central guiding pin. Each prepared root was positioned with the central guiding pin, and self-curing acrylic resin was poured to embed the root after application of a thin layer of petroleum jelly on the inner wall of aluminum cylinder. The cylinder was removed after the setting of acrylic resin to obtain resin block with mounted root segment. Each root was serially sectioned to create a root slice of 1-mm thickness by using a high-speed diamond wafering blade (Isomet 2000 Precision High-Speed Saw; Buehler Ltd) (Fig. 1D), and the thickness was verified by using an electronic vernier (CD-10CX; Mitutoyo Co Ltd, Tokyo, Japan). The root slice was restrained by an apparatus consisting of 2 cylindrical steel dies aligned together and secured with 3 screws. Under copious distilled water cooling, a 1.85-mm diameter hole was centrally prepared in each root slice by using a multi-drilling machine (LT-848; Dengyng Instruments Co Ltd, Taipei, Taiwan) (Fig. 1E). The hole was at least 0.5 mm from the edge of the specimen. All specimens were immersed in an ultrasonic cleaner

(Delta; Mandarin Scientific Co Ltd, Taipei, Taiwan) filled with 2.5% sodium hypochlorite for 1 minute, then 17% EDTA for 2 minutes to remove the smear layer, and finally distilled water for 2 minutes 3 times.

Obturation of Root Canal Space

The materials used included gutta-percha (Obtura II; Obtura-Spartan, Fenton, MO), Tubliseal (SybronEndo, Orange, CA), Epiphany (RealSeal; SybronEndo), EndoREZ (Ultradent, South Jordan, UT), Resilon (RealSeal; SybronEndo), ZnO/TPU composite, and UA/TPGDA sealer.

Eighty root slices were randomly divided into 8 groups with 10 root slices in each group. The sealer and cone used in each group are listed in Table 1. All specimens were filled with warm vertical compaction following the manufacturer’s instructions. Briefly, gutta-percha was carried by using Obtura II, and Resilon was carried by using Element obturation unit (SybronEndo). The UA/TPGDA sealer appeared as viscous liquid and was coated on the root canal. It was cured by visible light after the root canal was filled by cone materials. The UA/TPGDA sealer contains D,L-camphorquinone, ethyl 4-dimethylaminobenzoate (EDMAB), and 2,2-azobis-isobutyroni-

TABLE 1. Types of Sealer and Cone Used in Each Group and Fracture Mode

	Sealer	Cone	Abbreviation	Fracture mode
Group 1	Tubliseal	GP	TB/GP	Class I
Group 2	Tubliseal	Resilon	TB/R	Class I
Group 3	Epiphany	GP	EP/GP	Class II
Group 4	Epiphany	Resilon	EP/R	Class II
Group 5	EndoREZ	EndoREZ	ES/EC	Class I
Group 6	EndoREZ	ZnO/TPU	ES/PU	Class I
Group 7	UA/TPGDA	EndoREZ	UA/EC	Class I
Group 8	UA/TPGDA	ZnO/TPU	UA/PU	Class I

GP, gutta-percha; UA/TPGDA, urethaneacrylate/tripropylene glycol diacrylate oligomer; ZnO/TPU, zinc oxide/thermoplastic polyurethane composite.

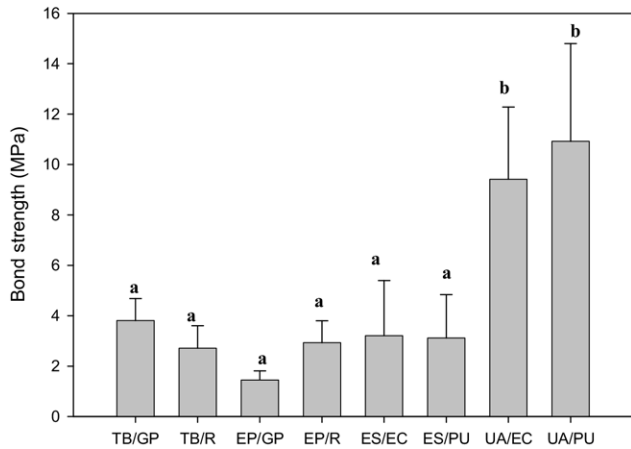


Figure 2. The push-out bond strengths (MPa) of groups 1–8 (n = 10). Different letters indicate a significant difference.

trile (AIBN); therefore, it can be further cured thermally at 37°C temperature. Because no specific heat carrier has been designed for EndoREZ and ZnO/TPU cone materials, a stainless steel carrier (Stopping carrier; Yamaura, Japan) and a burner (Person burner; Phoenix-dent, Japan) were used. All filled specimens were stored at 100% humidity, 37°C for 24 hours.

Push-out Test

The punch-out apparatus (Fig. 1F) consisted of 2 cylindrical steel dies aligned together with 2 dowels and was secured with 3 screws. A 1.80-mm diameter hole and a 1.90-mm diameter hole were centrally positioned at the upper and lower dies, respectively. A cylindrical carbon steel rod 1.75 mm in diameter was used as a plunger. The push-out apparatus was mounted on an Instron universal testing machine (Merlin series, Mini-55; Instron Corp., Canton, MA) (Fig. 1G). A constant crosshead speed of 0.5 mm/min was set to push the filling materials from the root slice, and a linear variable differential transformer (LVDT, Linear Ball Bearing Series, ±5 mm; Half Bridge Model, RDP Electronics, Inc., Pottstown, PA, North America) was used to measure the displacement. Push-out bond strength was calculated by using the following equation (6): Push-out bond strength = Force/π × Diameter × Thickness.

Bond strengths of each group were analyzed with one-way analysis of variance and Tukey test (α = .05) to determine the presence of a significant difference among the groups.

To examine the debonded surfaces and penetration of sealer into dentinal tubules, a groove was prepared by using tapered fissure bur on each specimen to facilitate the sectioning of each specimen with a chisel. The specimens were prepared for observation with scanning electron microscopy (SEM) by serial dehydration of graded ethanol solutions (50%–100%) at 45-minute intervals. Finally, all specimens were mounted on aluminum stubs and sputter-coated with gold. The

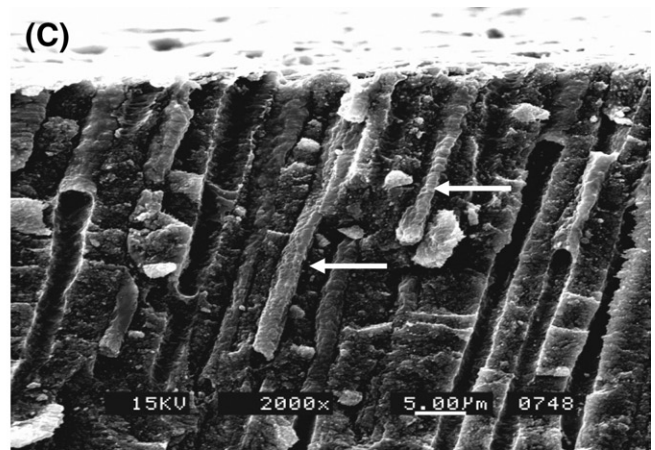
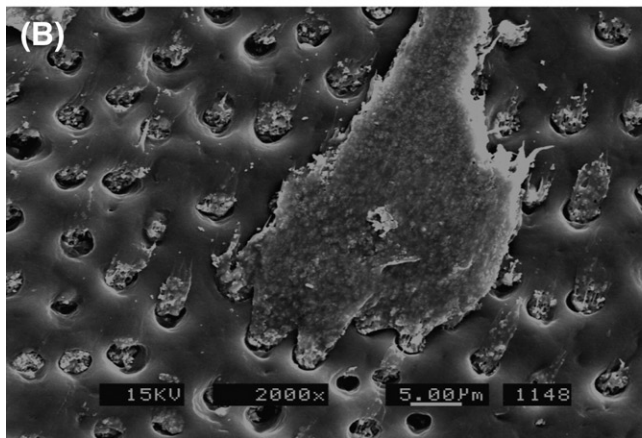
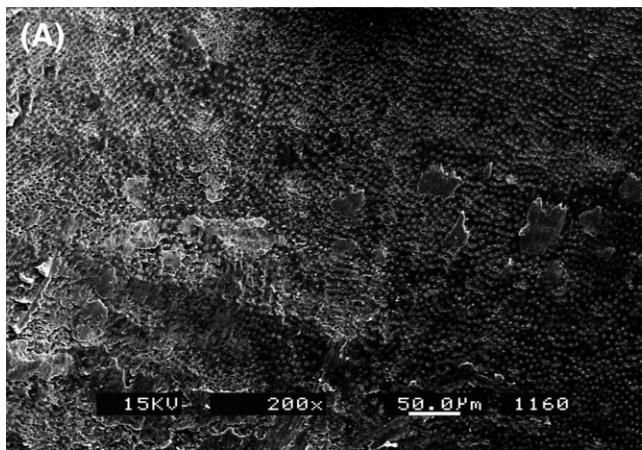


Figure 3. (A) SEM micrographs from the UA/PU group reveal sparse ZnO/TPU composite on the debonded dentin surfaces and (B) occlusion of most of the orifices of dentinal tubules. (C) Deep penetration of UA/TPGDA sealer into the dentinal tubules was observed in the longitudinal section (arrow).

specimens were then observed with SEM (TOPCON ABT-60; Topcon Corp, Tokyo, Japan) at an accelerating voltage of 15 kV. To determine the fracture mode, we adopted the method suggested by Fowler et al. (13) to evaluate debonded surfaces. The type of failure was defined on the basis of the percentage of canal surfaces without sealer remnant. The percentage $\geq 75\%$ was defined as Class I adhesive failure, >25 to $<75\%$ as Class II adhesive-cohesive failure, and $\leq 25\%$ as Class III cohesive failure.

Results

The mean push-out bond strengths (MPa) of groups 1–8 were as follows (Fig. 2): TB/GP, 3.81 ± 0.87 ; TB/R, 2.71 ± 0.89 ; EP/GP, 1.45 ± 0.36 ; EP/R, 2.93 ± 0.87 ; ES/EC, 3.21 ± 2.19 ; ES/PU, 3.12 ± 1.72 ; UA/EC, 9.42 ± 2.86 ; UA/PU, 10.92 ± 3.88 . The UA/EC and UA/PU groups exhibited significantly higher bond strengths than the remaining groups. In addition, there was no significant difference among the mean bond strengths of the TB/GP, TB/R, EP/GP, EP/R, ES/EC, and ES/PU groups.

The fracture modes of all groups are listed in Table 1. Class I adhesive failure was the predominant fracture mode, with only the EP/GP and EP/R groups exhibiting Class II adhesive-cohesive failure.

The SEM micrograph of a representative Class I adhesive failure is shown in Fig. 3A. Scarce remnants of ZnO/TPU composite on the debonded dentin surfaces of the UA/PU group were noted, and most of the orifices of dentinal tubules were occluded (Fig. 3B). The UA/TPGDA sealer could deeply penetrate into the dentinal tubules in the longitudinal section parallel to the alignment direction of the dentinal tubules (Fig. 3C), which was not observed in specimens of the other groups. Fig. 4A shows a representative Class II adhesive-cohesive failure. Remnants of Epiphany sealer could be observed on the debonded dentin surfaces of the EP/GP group (Fig. 4B).

Discussion

The most widely accepted concept of the mechanism of dentin bonding involves the formation of a hybrid layer and hypothesizes that acidic conditioners dissolve the smear layer and demineralize the hydroxyapatite crystals of dentin substrate, followed by infiltration of monomers into exposed collagen fibers (14). The bonding mechanism of commercial products can be grossly divided into 2 types, total-etch and self-etch luting materials. Total-etch luting material is characterized by the complete removal of the smear layer with 37% phosphoric acid, whereas self-etch luting material combines the etchant and primer in one application to achieve simultaneous demineralization and resin infiltration (15). The success of the dentin bonding mechanism has allowed its introduction to the application of endodontic filling materials as a newly developed sealer (ie, RealSeal) whose primer is self-etch and consists of 2-hydroxyethylmethacrylate (HEMA). This sealer is combined with methacrylate-based resin cones to create a monoblock bonding for root canal obturation.

In this study, the push-out bond strengths (Fig. 2) of the UA/EC and UA/PU groups were significantly greater than in the other groups. The smear layer was removed by irrigating the canals with 17% EDTA and 2.5% NaOCl during instrumentation. The greater bond strength of the UA/PU group might be attributable to the inclusion of hydrophilic urethane (-NHCOO-) functional group, which probably could form a stronger bond to the collagen matrix of dentin and consequently form the hybrid layer. In addition, both the side chain of UA/TPGDA sealer and main chain of TPU exhibit urethane group and polybutyleneadipate (PBA). The formation of hydrogen bonds between the hydrogen and nitrogen atoms on urethane groups of UA/TPGDA sealer and ZnO/TPU cone enhances their adhesion of UA/TPGDA sealer to ZnO/TPU cone.

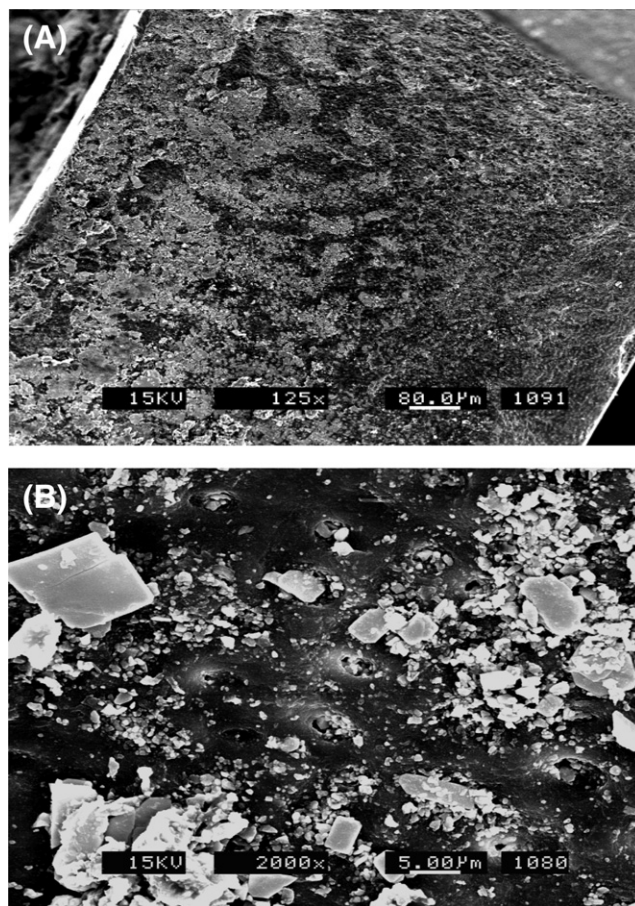


Figure 4. (A) A representative Class II adhesive-cohesive failure. (B) Remnants of Epiphany sealer could be observed on the debonded dentin surfaces of the EP/GP group.

SEM in the UA/PU group revealed that the debonded dentin surfaces had remnants of ZnO/TPU composite, and most of the orifices of dentinal tubules were occluded (Fig. 3A, B). The longitudinal section parallel to the alignment direction of dentinal tubules revealed that the sealer could deeply penetrate into the dentinal tubules (Fig. 3C), which was not observed in the specimens from other groups. The results of SEM examination revealed that mechanical bond might also contribute to the higher push-out bond strength of UA/PU group.

EndoREZ cone is a polybutadiene-diisocyanate-methacrylate resin-coating gutta-percha (16), whereas EndoREZ sealer is a hydrophilic, dual-cured resin sealer containing 30% urethane dimethacrylate (17). When EndoREZ cone was used in combination with UA/TPGDA sealer in this study, a bond strength of the UA/EC group as high as that of the UA/PU group could be achieved. This might be attributable to the high affinity that UA/TPGDA sealer exhibits toward dentin (Fig. 3A–C). In addition, both the UA/TPGDA and EndoREZ sealers are hydrophilic and contain methacrylate functional groups. Thus, the chemical coupling between UA/TPGDA sealer and EndoREZ cone contributed to the high bond strength. However, ZnO/TPU cone does not contain methacrylate groups, and its use with EndoREZ sealer therefore lacks a strong chemical coupling. Moreover, Eldeniz et al. (18) suspected that the cohesive strength of EndoREZ sealer is lower than its adhesive strength, and Tay et al. (19) observed interfacial gaps along the sealer-dentin interfaces that were possibly due to polymerization shrinkage. The low bond strengths of EndoREZ sealer to ZnO/TPU cone and dentin therefore resulted in significantly lower bond strength than those of the UA/EC and

UA/PU groups. The significantly lower bond strength of the ES/EC group might be attributable to poor adaptation of the space along EndoREZ sealer/cone and sealer-dentin interfaces (20, 21).

The push-out bond strengths of EP/GP (1.45 ± 0.36 MPa) and EP/R (2.93 ± 0.87 MPa) groups in this study (Fig. 2) are similar to those from previous studies that reported the bond strength of EP/GP was 2.857 ± 0.523 MPa (10), and the bond strengths of EP/R ranged from 0.50–1.706 MPa (3, 6, 9, 10). It has been suggested that low concentration of dimethacrylates or absence of free radicals within Resilon, leading to ineffective coupling with Epiphany, might be the reason for the low bond strength in EP/R (3, 21). Tubliseal is a zinc oxide–eugenol–based sealer that does not exhibit the ability to adhere to dentin wall. This explains why the TB/GP and TB/R groups did not demonstrate significantly higher bond strength.

To prevent possible non-uniform stress distribution (22) in this study, we modified the push-out test by preparing a 1.85-mm diameter cylinder hole at each root slice by using a multi-drilling machine. Previous studies showed that if the specimens were prepared by enlarging and filling the root canals followed by serial slicing of roots (3, 6, 9), the specimens were non-uniform and did not meet the requirements of the theory of Smith and Cooper (23), which states that the specimens must be in sheet form.

This study showed that the newly developed ZnO/TPU cone and UA/TPGDA sealer had the greatest push-out bond strength of all of the materials tested. Nevertheless, bond strength to intraradicular dentin is only one factor that must be considered when evaluating the quality of root canal sealing. Other features of the new root canal filling materials, such as microleakage test and fracture resistance, need to be further investigated.

Acknowledgments

The authors gratefully acknowledge the financial support from the National Science Council of Taiwan (NSC 96-2628-B-002-061).

References

1. Schilder H. Filling root canal in three dimensions. *Dent Clin North Am* 1967;11:723–44.
2. Tagger M, Tagger E, Tjan AHL, Bakland LK. Measurement of adhesion of endodontic sealers to dentine. *J Endod* 2002;28:351–4.
3. Gesi A, Raffaelli O, Goracci C, Pashley DH, Tay FR, Ferrari M. Interfacial strength of Resilon and gutta-percha to intraradicular dentin. *J Endod* 2005;31:809–13.
4. Tay FR, Loushine RJ, Weller RN, et al. Ultrastructural evaluation of the apical seal in roots filled with a polycaprolactone-based root canal filling material. *J Endod* 2005;31:514–9.
5. Shipper G, Orstavik D, Teixeira FB, Trope M. An evaluation of microbial leakage in roots filled with a thermoplastic synthetic polymer-based root canal filling material (Resilon). *J Endod* 2004;30:342–7.
6. Skidmore LJ, Berzins DW, Bahcall JK. An in vitro comparison of the intraradicular dentin bond strength of Resilon and gutta-percha. *J Endod* 2006;32:963–6.
7. Shipper G, Teixeira FB, Arnold RR, Trope M. Periapical inflammation after coronal microbial inoculation of dog roots filled with gutta-percha or Resilon. *J Endod* 2005;31:91–6.
8. Teixeira FB, Teixeira EC, Thompson JY, Trope M. Fracture resistance of roots endodontically treated with a new resin filled material. *J Am Dent Assoc* 2004;135:646–52.
9. Sly MM, Moore BK, Platt JA, Brown CE. Push-out bond strength of a new endodontic obturation system (Resilon/Epiphany). *J Endod* 2007;33:160–2.
10. Ungor M, Onay EO, Orucoglu H. Push-out bond strengths: the Epiphany-Resilon endodontic obturation system compared with different pairings of Epiphany, Resilon, AH Plus and gutta-percha. *Int Endod J* 2006;39:643–7.
11. Williams C, Loushine RJ, Weller RN, Pashley DH, Tay FR. A comparison of cohesive strength and stiffness of Resilon and gutta-percha. *J Endod* 2006;32:553–5.
12. Goracci C, Fabianelli A, Sadek FT, Papacchini F, Tay FR, Ferrari M. The contribution of friction to the dislocation resistance of bonded fiber posts. *J Endod* 2005;31:608–12.
13. Fowler CS, Swartz ML, Moore BK, Rhodes BF. Influence of selected variables on adhesion testing. *Dent Mater* 1992;8:265–9.
14. Nakabayashi N, Kojima K, Masuhara E. The promotion of adhesion by the infiltration of monomers into tooth substrates. *J Biomed Mater Res* 1982;16:265–73.
15. Bishara SE, Oonsombat C, Ajlouni R, Laffoon JF. Comparison of the shear bond strength of 2 self-etch primer adhesive systems. *Am J Orthod Dentofacial Orthop* 2004;124:348–50.
16. Haschke E. Adhesive endodontic cones and related methods. United States Patent Application 20040202986. US Patent & Trademark Office, October 14, 2004.
17. Jensen SD, Fischer DJ. Method for filling and sealing a root canal. United States Patent & Trademark Office. Patent Number 6,811,400, November 2, 2004.
18. Eldeniz AU, Erdemir A, Belli S. Shear bond strength of three resin based sealers to dentin with and without the smear layer. *J Endod* 2005;31:293–6.
19. Tay FR, Loushine RJ, Monticelli F, et al. Effectiveness of resin-coated gutta-percha cones and a dual-cured, hydrophilic methacrylate resin-based sealer in obturating root canals. *J Endod* 2005;31:659–64.
20. Sevimay S, Kalayci A. Evaluation of apical sealing ability and adaptation to dentine of two resin-based sealers. *J Oral Rehabil* 2005;32:105–10.
21. Burtscher P. Stability of radicals in cured composite materials. *Dent Mater* 1993;9:218–21.
22. Sudsangiam S, Van Noort R. Do dentin bond strength tests serve a useful purpose? *J Adhes Dent* 1999;1:57–67.
23. Smith DC, Cooper WEG. The determination of shear strength. *Br Dent J* 1971;130:333–7.