ESTELITE BULK FILL Flow

Technical Report

Ver. 2.0

Tokuyama Dental

Contents

1. Introduction

Tokuyama Dental has developed various light-curing dental restorative composite resins that take advantage of its proprietary Supra-Nano Spherical filler technology. Represented by Palfique Estelite® Paste, Estelite® Σ, and Palfique Estelite® LV, these products have acquired a reputation for outstanding aesthetics and gloss.

In 2005, Tokuyama Dental launched Estelite Flow Quick®, a new flowable composite resin, based on a new catalyst technology (RAP technology™) and a proprietary filler technology. This approach results in remarkably fast curing compared to conventional flowable resins (requiring approximately 1/3 the time). Due to RAP technology™, Estelite Flow Quick® features high conversion and leading levels of filler content (71 wt%) among flowable composite resins. It offers outstanding scientific and engineering properties not found with conventional flowable composite resins.

In recent years, bulk fill type composite resins, such as Dentsply's SureFill SDR Flow, have appeared and are spreading in the U.S. and European markets through various companies.

Tokuyama Dental has developed Estelite® Bulk Fill Flow through the application of the Supra-Nano Spherical filler, RAP technology™, and a new composite filler. The technological backgrounds, features, and material properties of this new resin are described below.

2. Materials

2.1. Components

- Bis-GMA, Bis-MPEPP, TEGDMA
- Supra-Nano Spherical filler (200nm spherical SiO_2-ZrO_2)
- Composite Filler (include 200nm spherical SiO_2-ZrO_2)
- Filler loading：70 wt% (56 vol%)

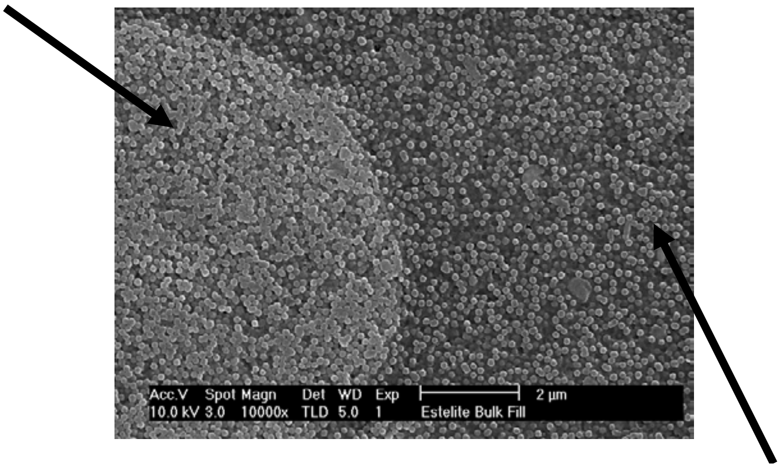
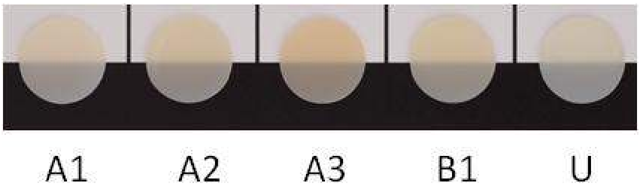


Fig. 1 Estelite Bulk Fill Flow (10,000x)

2.2. Shades

Estelite® Bulk Fill Flow is available in five shades (A1, A2, A3, B1, U (Universal)), and conforms to wide-ranging colors owing to its high chameleon effect. The curing time is 10 seconds of light exposure for all shades (800 mW/cm^2 or greater).



		Tooth shade *1															
		Light															Dark
		W	B1	A1	B2	D2	A2	C1	C2	D4	A3	D3	B3	A3.5	B4	C3	A4
U		E	E	V	G	G	F	G	G	–	F	–	G	F	F	G	–
B1		V	E	V	V	F	G	F	F	F	G	F	G	F	F	–	–
A1		V	V	E	G	G	V	F	F	–	G	F	F	–	–	–	–
A2		G	G	V	G	F	E	–	F	F	V	G	F	F	F	–	–
A3		-	F	G	G	F	V	G	V	G	E	V	V	V	G	F	G

E=Excellent V=Very Good G=Good F=Fair –=Poor

*1 Above tooth shades are selected according to the VITA Shade Guide. VITA is a registered trademark of VITA Zahnfabrik H. Rauter GmbH & Co.KG

2.3 Concept, Features

■ Bulk fill composite resin that can be applied to the outermost layer

- High depth of cure
- Low polymerization shrinkage stress
- Good color matching
- Sufficient strength and wear resistance

2.4 Indications

- Direct anterior and posterior restorations
- Cavity lining
- Blocking out cavity undercuts before fabrication indirect restorations
- Repair of porcelain/composite

3. Background technology

3.1. Radical Amplified Photo-polymerization initiator (RAP technology™)

3.1.1. Mechanism

The catalyst technology adopted for Estelite® Bulk Fill Flow is the Radical Amplified Photo-polymerization initiator (RAP technology™) used in Estelite Σ Quick®. As a major feature, the initiator balances the high polymerization activity needed to cure the resin with short exposure times (1/3 of that required by conventional products) and stability in ambient lighting. These two traits are often regarded as mutually conflicting, since shorter curing times tend to reduce stability. However, this unique catalyst technology achieves a balance of these two factors. Fig.2 is a schematic diagram of RAP technology™.

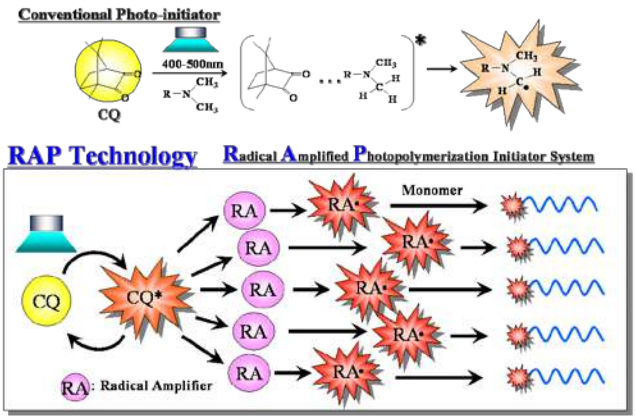


Fig.2 Radical amplified polymerization initiator system

Conventional photo-polymerization initiators consist of camphorquinone (hereafter abbreviated CQ) and amines. The mechanism of action involves the excitation of CQ by irradiation, followed by the abstraction of hydrogen in the alpha-position by the excited CQ, producing amine-derived radicals. The amine-derived radicals function as the polymerization initiator and react with monomers to generate polymers, ultimately producing the curing effect. In this catalyst system, CQ is consumed as it changes to CQ-H in polymerization initiator generation. Unlike CQ, CQ-H is not excited by light. This means a single molecule of CQ can only produce a single polymerization initiator molecule.

With the radical amplified photo-polymerization initiator, the initial stage of CQ excitation by light is the same as in conventional systems. However, energy is transferred to the radical amplifier (hereafter abbreviated RA); the RA is subsequently excited, and then allowed to decompose to produce RA-derived radicals. Theses radicals act as the polymerization initiator and react with monomers to generate polymers, producing the curing effect. After transferring energy to RA, the excited CQ returns to the ground state and is once again excited by irradiation and contributes to the reaction for polymerization initiator species generation. In other words, with RAP technology™, CQ is recycled within the polymerization initiator generation reaction, and a single CQ molecule can produce multiple initiator radicals. Thus, in addition to being highly active, RAP initiators can be used with smaller CQ volumes than conventional catalysts and improve stability in ambient lighting, including dental and fluorescent lights. The present initiator system is also free of chemical reactions between two molecule species, such as hydrogen abstraction in conventional systems, allowing shorter times from the photo-excitation of CQ to initiator radical generation.

To confirm that RAP technology™ increases polymerization rates, we compared the amount of residual monomers after a light cure for two different composite resins: Estelite Flow Quick®, which contains a radical amplified photo-polymerization initiator, and flowable composite, which contains a conventional photo-polymerization initiator composed of CQ and amines. Fig.3, 4 shows the results. Fig.3 indicates that the radical amplified photo-polymerization initiator significantly reduces residual monomers compared to the conventional CQ-amine photo-polymerization initiator for both 10-second and 30-second exposures. This holds true even when comparing Estelite Flow Quick® after 10-seconds of exposure to conventional flowable composite after 30-seconds of exposure. We also found that more radicals are generated in the RAP initiator system than the conventional CQ/amine system (radical concentrations greater by a factor of approximately 2.5) according to Fig.4. These results support the mechanism of action shown in Fig. 2.
RAP technology facilitates a control of polymerization rate. Polymerization rate is slow and material is stable under small light intensity (ambient light such as a dental light), however, polymerization rate becomes quick under large light intensity (light irradiation unit) (Fig.5).

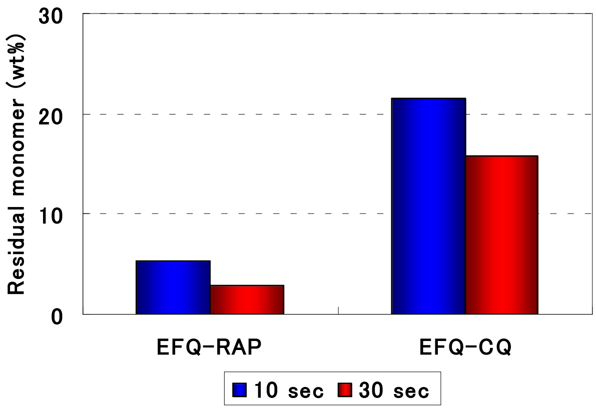


Fig.3 Residual monomer(wt%)

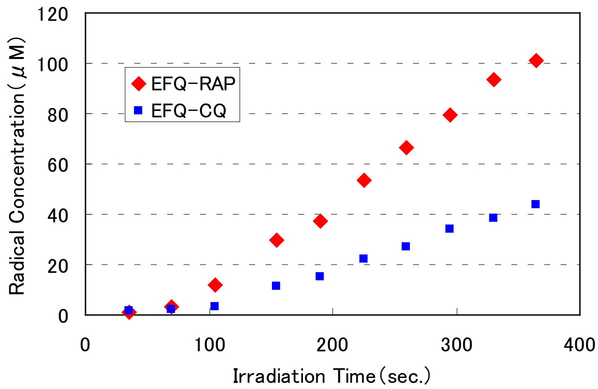


Fig.4 Change of radical concentration

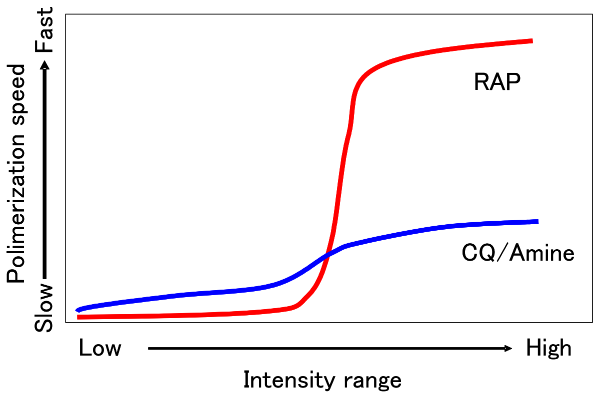


Fig.5 Correlation between intensity range and polymerization speed

3.1.2. Stability in ambient light

In the past, high polymerization activity with short exposures could only be achieved by increasing the amount of photo-polymerization initiator used. However, increasing the amount of the catalyst decreases the stability of the resin in ambient light. Additionally, the viscosity of the paste may increase during the filling step in clinical services, making the resin impossible to sculpt and requiring a second filling attempt. In addition, increasing the amount of catalyst can also exacerbate changes in color before and after polymerization. While increasing the amount of photo-polymerization initiator is believed to result in various undesirable effects, RAP technology™ can provide both polymerization activity and stability in ambient light, as described in detail in 3.1.1. Fig.6 compares stability under ambient light (10,000 lx of dental light) between Estelite® Bulk Fill Flow and other commercially available bulk fill composite resin.

As shown in Fig.6, Estelite® Bulk Fill Flow offers good stability in ambient light compared with products from other manufacturers, in spite of curing in less exposure time. This gives clinicians more time to perform filling and other steps.

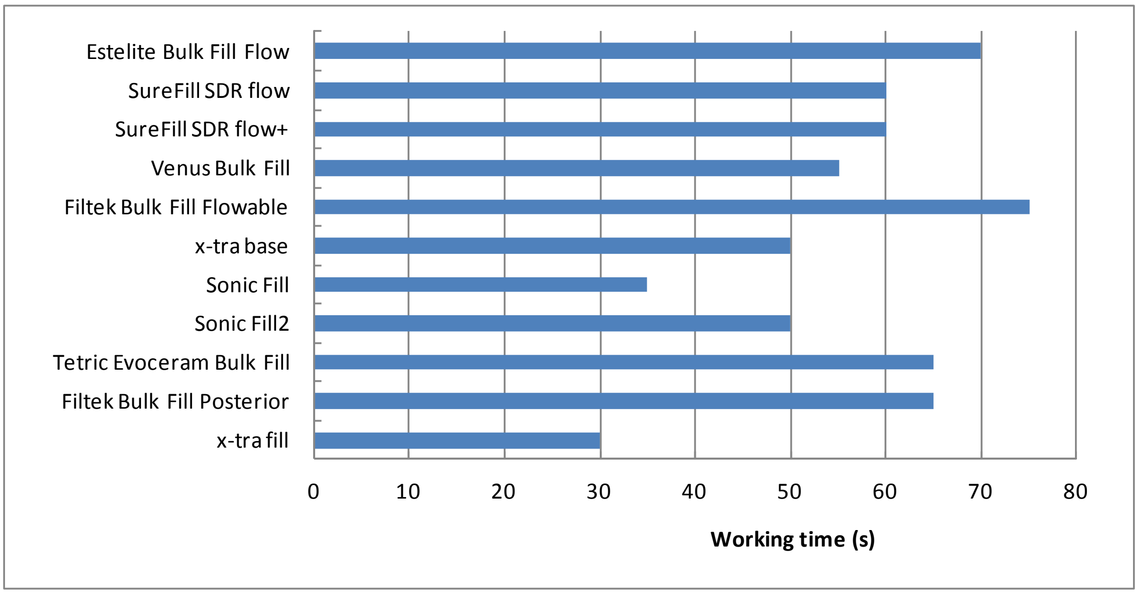


Fig.6 Working time (10,000 lux/dental light)

3.2 Supra-Nano Spherical Filler Technology

Tokuyama Dental synthesizes monodispersing Supra-Nano Spherical fillers by a special technique called the sol-gel method. Unlike the conventional filler manufacturing method, which involves crushing glass materials, fillers with the present method are produced by creating filler cores in organic solvent and allowing the filler to grow gradually from the cores. This method makes it possible to produce uniform, spherical fillers (Fig.7)。

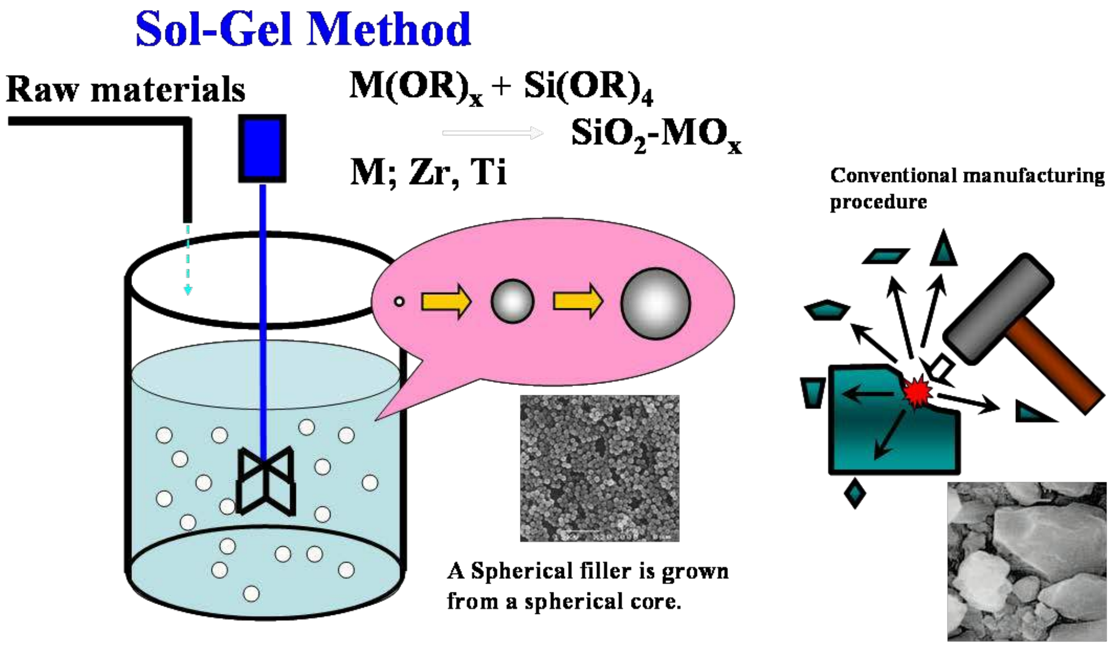


Fig.7 Summary of sol-gel method

A major feature of the sol-gel method is that it allows the filler size to be controlled by adjusting reaction times. In composite resins, filler size significantly affects the physical characteristics of the cured body and its esthetic aspects. Smaller filler sizes produce a superior surface glossiness, but make it difficult to increase filler content, leading to problems such as increased polymerization shrinkage and poor physical characteristics such as reduced flexural strength.

Fig.8 gives the correlation between filler particle size and filler content and compressive strength. Fig.9 gives the correlation between filler particle size and surface roughness and hardness. From Fig.8, we see that filler content begins to fall significantly below 100 nm, but is nearly constant at sizes above that. In addition, we observe maximum compressive strength at particles size ranging from 100 to 500 nm. From Fig.9, we see that surface roughness decreases with particle sizes down to approx. 500 nm but remains constant at sizes below that. Surface hardness attains the highest value at particle sizes ranging from 200 to 300nm. Based on the above results, we conclude that the best balance between esthetics and physical characteristics can be achieved by using Supra-Nano sized particles (200nm).[1)]。

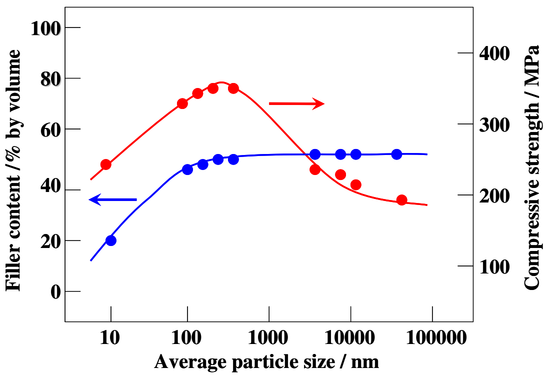


Fig.8 Correlation between particle size, filler content and compressive strength

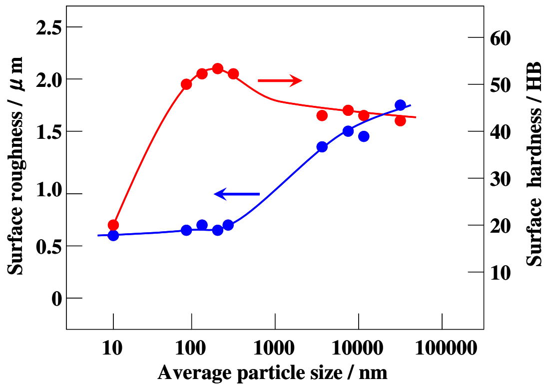


Fig.9 Correlation between particle size, surface roughness and surface hardness

For Estelite® Bulk Fill Flow, we use Supra-Nano Spherical fillers made of silica-zirconia produced by the sol-gel method, with particle sizes of 200 nm (Fig.10)。

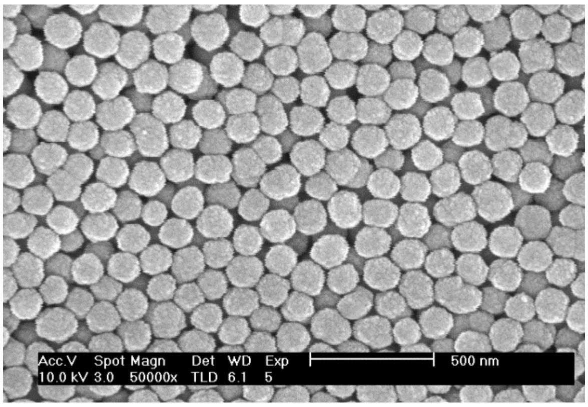


Fig.10 Supra-nano spherical filler

Another major feature of the sol-gel method is that the refractive index of the filler can be controlled by changing the type and fraction of the additive. Composite resins tend to show a strong relationship between the filler refractive index and that of the matrix organic resin. To reproduce the semi-translucent quality of natural teeth using composite resins, we must control the difference between the refractive indices of the filler and the organic resin. Composite resins consist of fillers and organic resins containing catalysts. When the refractive indices of both materials are equal, the composite resin is highly

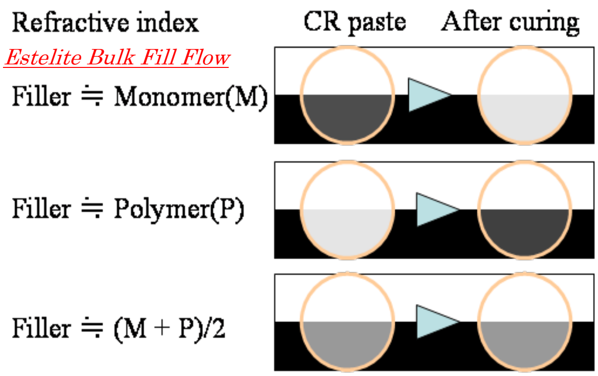
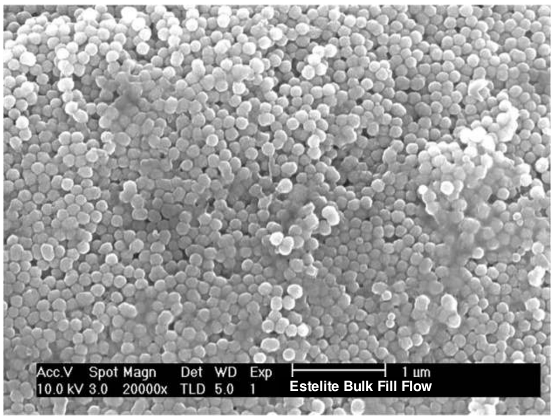


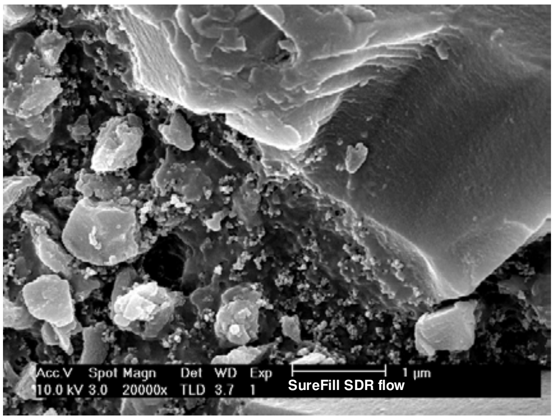
Fig.11 Refractive index

translucent; when they differ significantly, the resin is opaque. The refractive index of resins tends to change from before to after polymerization; the refractive index of the cured resin (polymer) tends to be higher than that of the resin (monomer) before curing.

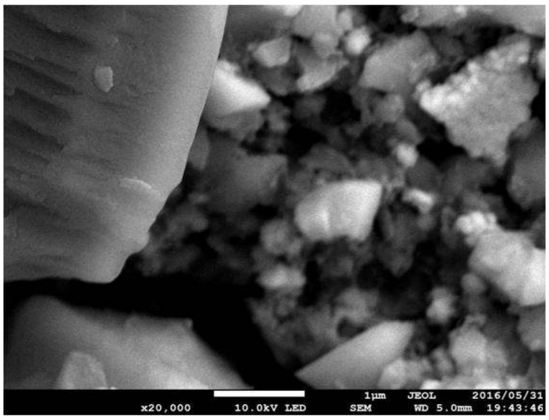
Below are SEM images (20,000X) of fillers used in Estelite® Bulk Fill Flow and in bulk fill composite resins from other manufacturers.



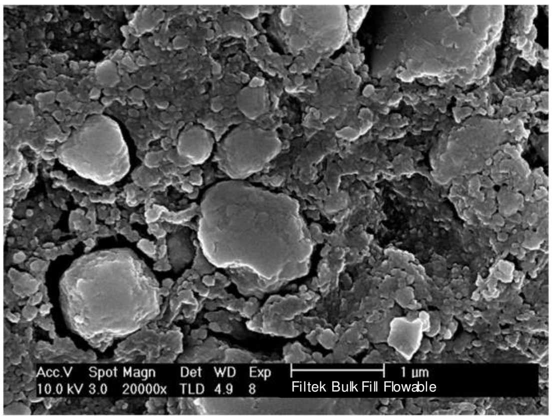
Estelite Bulk Fill Flow



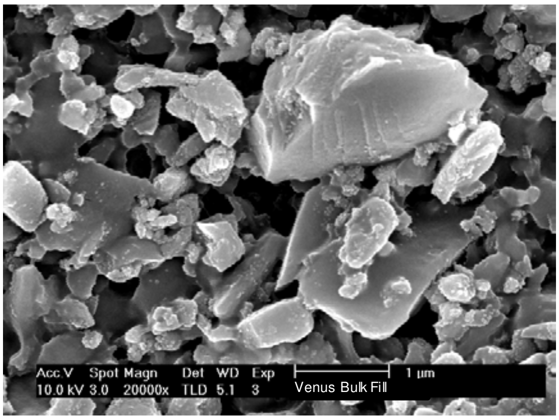
SureFill SDR flow



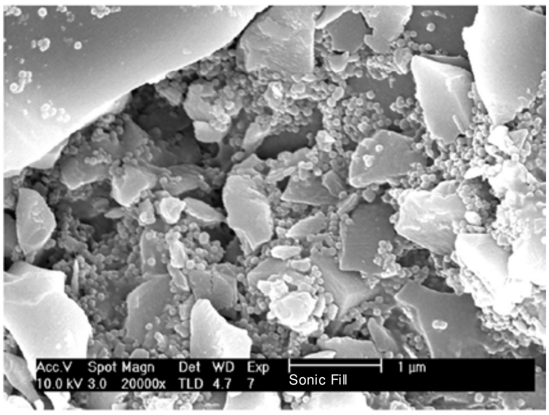
SureFill SDR flow+



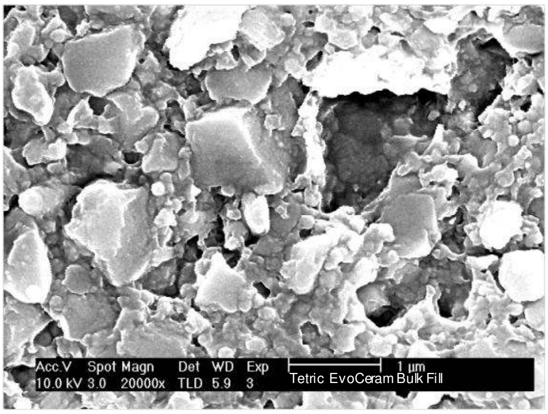
Filtek Bulk Fill Flowable



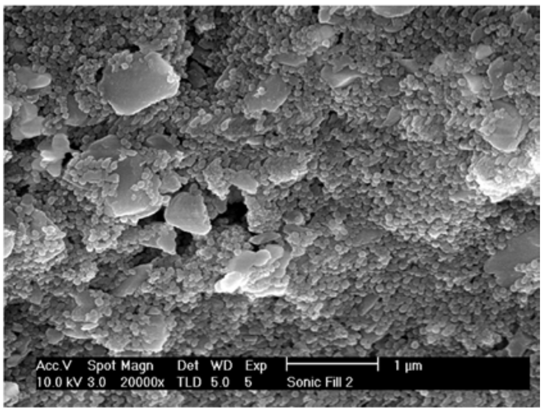
Venus Bulk Fill



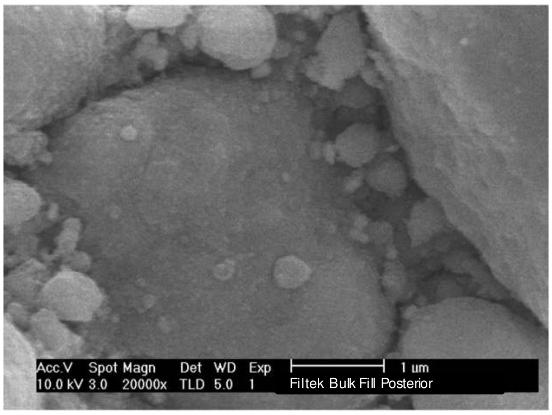
Sonic Fill



Tetric EvoCeram Bulk Fill



Sonic Fill 2



Filtek Bulk Fill Posterior

3.3. Composite Filler Technology

Composite fillers have been adapted for use in a variety of products at Tokuyama Dental, such as Estelite Σ Quick.

As described previously, the controlled particle size of Supra-Nano Spherical filler lends aesthetic properties to composite resins, including polishability, gloss retention, and wear resistance. On the other hand, pastes containing only a filler having a single particle size tend to have low flowability, which makes it difficult to increase filler content while maintaining satisfactory handling. Tokuyama Dental has developed a proprietary composite filler containing Supra-Nano Spherical filler and combined it with Supra-Nano Spherical filler to simultaneously achieve aesthetic properties, handling, and mechanical properties of a composite resin.

A newly developed composite filler was adopted for Estelite® Bulk Fill Flow. This composite filler, like Tokuyama Dental's previous fillers, contains Supra-Nano Spherical filler; however, this filler has an effect of reducing polymerization shrinkage stress while maintaining the excellent features of conventional fillers (aesthetics, handling, and material properties), which has been achieved through the adoption of a round filler shape.

During polymerization of a composite resin, displacement of the filler occurs with shrinkage of the matrix component. In Supra-Nano Spherical filler and the round-shaped composite filler used in Estelite® Bulk Fill Flow, friction between particles and between particles and the matrix is reduced by the effects of their shape and their small surface area, which is less likely to limit the movements of each other; therefore, the shrinkage stress inside the composite resin is dispersed and the maximum shrinkage stress is reduced.

A comparison between the polymerization shrinkage stress of a composite resin containing the new round-shaped composite filler and a composite resin containing a conventional "irregular-shaped" composite filler is shown in Fig. 12. The composite resin containing the round-shaped composite filler exhibited lower polymerization shrinkage stress.

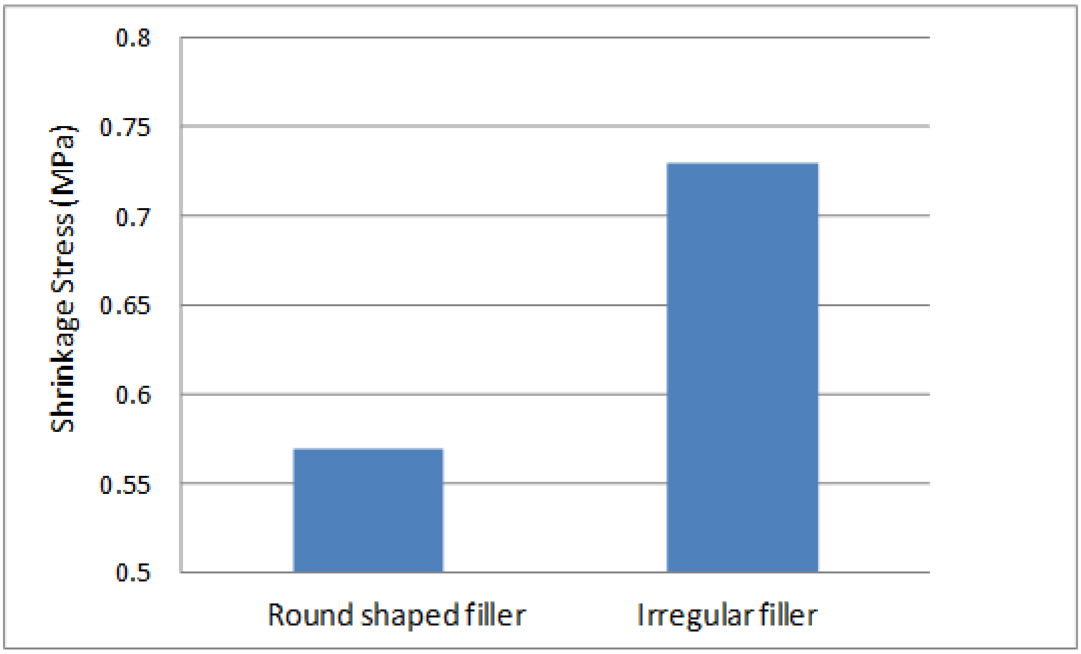


Fig.12 Polymerization shrinkage stress

4. Material properties

4.1. Polymerization shrinkage (%linear)

We measured polymerization shrinkage by our original method. Fig.13 is a schematic diagram of the measurement method. This method can measure shrinkage in the cavity floor (interface between the composite resin and plunger in Fig.13) when the composite resin is placed into a cavity and exposed to light in a clinical procedure. This permits evaluation of shrinkage under conditions closer to those encountered in actual clinical settings.

Fig.14 shows the polymerization shrinkage (%linear) of Estelite® Bulk Fill Flow and other commercially available bulk fill composite resins. The graph indicates shrinkage 3 minutes after the start of light exposure.

The polymerization shrinkage (%linear) of Estelite® Bulk Fill Flow is 2.1%. This is the minimum level among commercially available bulk fill composite resins. This result is due to the high filler volume content made possible by the combination of Supra-Nano Spherical filler and round shaped composite filler.

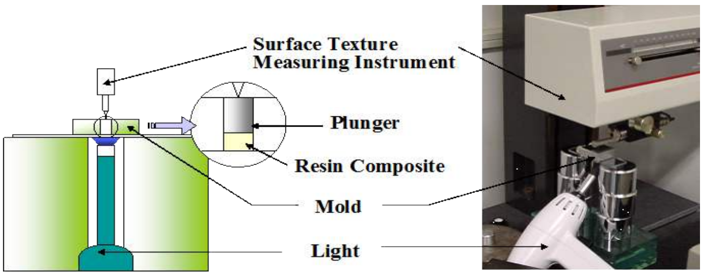


Fig.13 Method of polymerization shrinkage

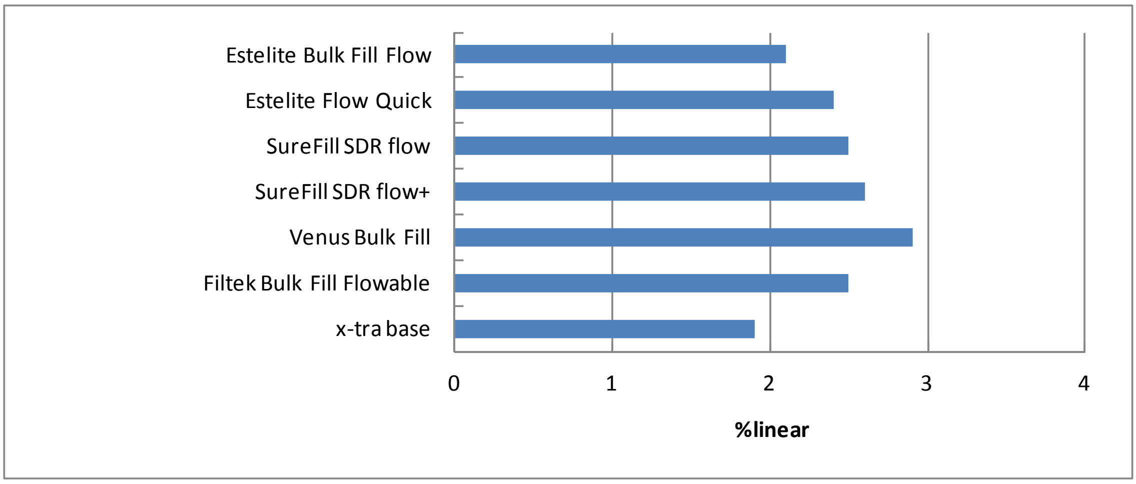


Fig.14 Polymerization shrinkage (%linear)

4.2. Polymerization Shrinkage Stress

The polymerization shrinkage stress was measured using our original method. Fig. 15 is a schematic diagram of the measurement method.

One-Up Bond F Plus was applied to the top portion of a rod with a diameter of 6 mm, and a ring was placed around the rod after light-curing to make a simulated cavity with a depth of 4 mm. This simulated cavity was filled with the composite resin, which was then exposed to light using a dental curing light for a specified period of time. At this point, polymerization shrinkage exerts a downward force, displacing the crosshead securing the load cell. A displacement-sensing device detects the minute displacement of the crosshead, and automatic control is performed to prevent displacement of the crosshead. The force detected by the load cell is regarded as the shrinkage stress.

The result of polymerization shrinkage stress measurement is shown in Fig. 16. The polymerization shrinkage stress of Estelite® Bulk Fill Flow was 0.64 MPa, which is the lowest among commercially available flowable type bulk fill composite resins. This result is believed to be due to the round filler shape's having mitigated the shrinkage stress that occurred during polymerization, in addition to the high filler volume content made possible by the combination of Supra-Nano Spherical filler and a newly developed composite filler.

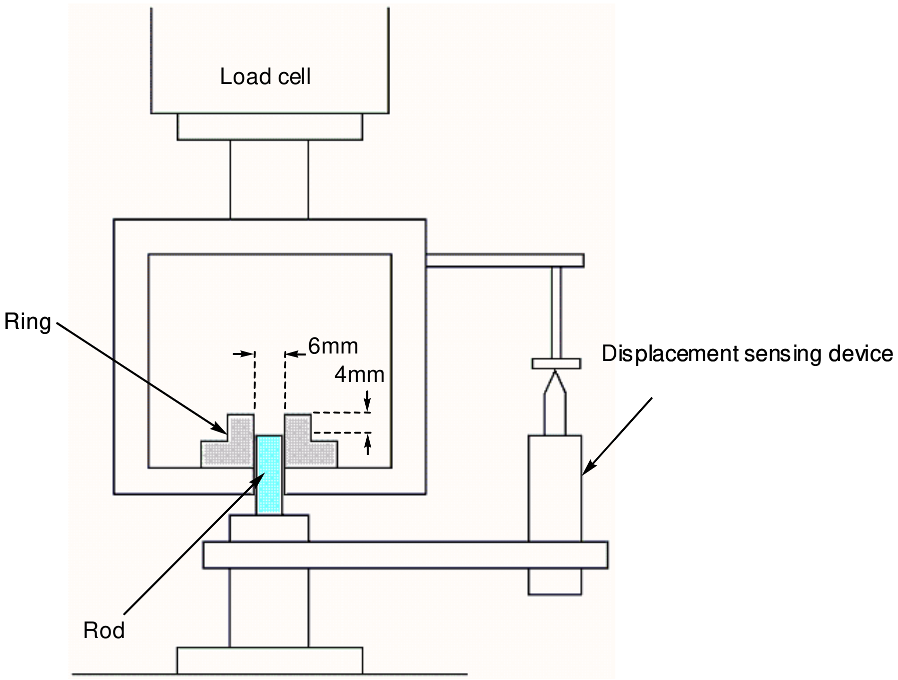


Fig.15 Method of polymerization shrinkage stress

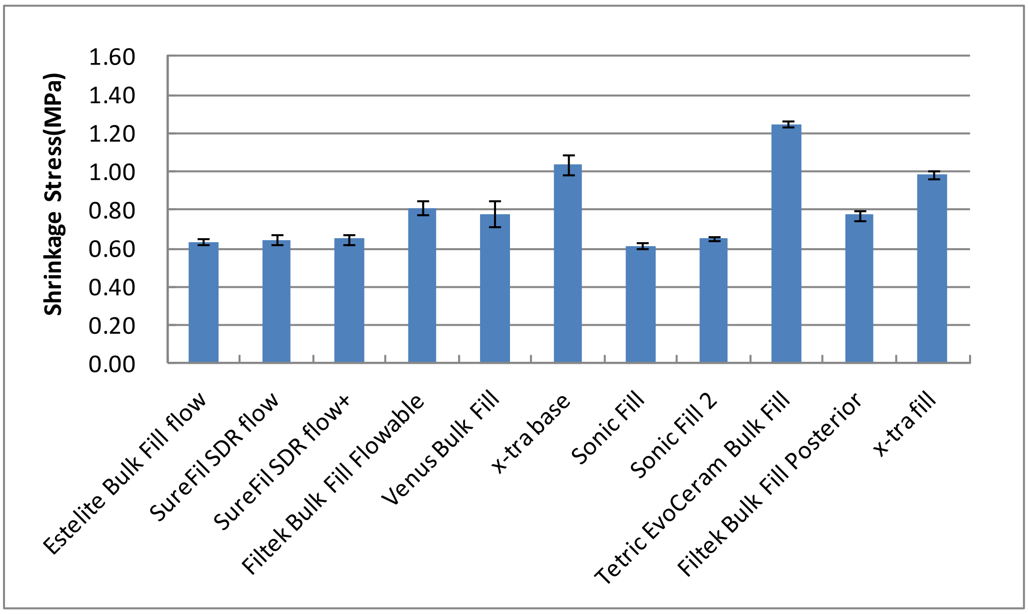


Fig.16　Polymerization shrinkage stress

4.3. Depth Curability

Bulk fill composite resins can be applied to deeper cavities than conventional composite resins can. Therefore, sufficient depth curability is required. To make Estelite® Bulk Fill Flow applicable to cavities with a depth up to 4 mm, it needs to cure sufficiently to the depth of 4 mm. Fig. 17 shows the depth of cure, and Fig. 19 shows the Vickers hardness Number (VHN) ratio (bottom/top) when the resin is cured with a thickness of 4 mm and the Degree of Conversion (DC) ratio (bottom/top). In addition, Fig. 18 shows the fabrication method for the test sample and the calculation method used to obtain the result in Fig. 19. The result shows that the VHN ratio and the DC ratio of Estelite® Bulk Fill Flow are high as compared to those of other commercially available bulk fill composite resins, indicating a high curability up to a depth of 4 mm.

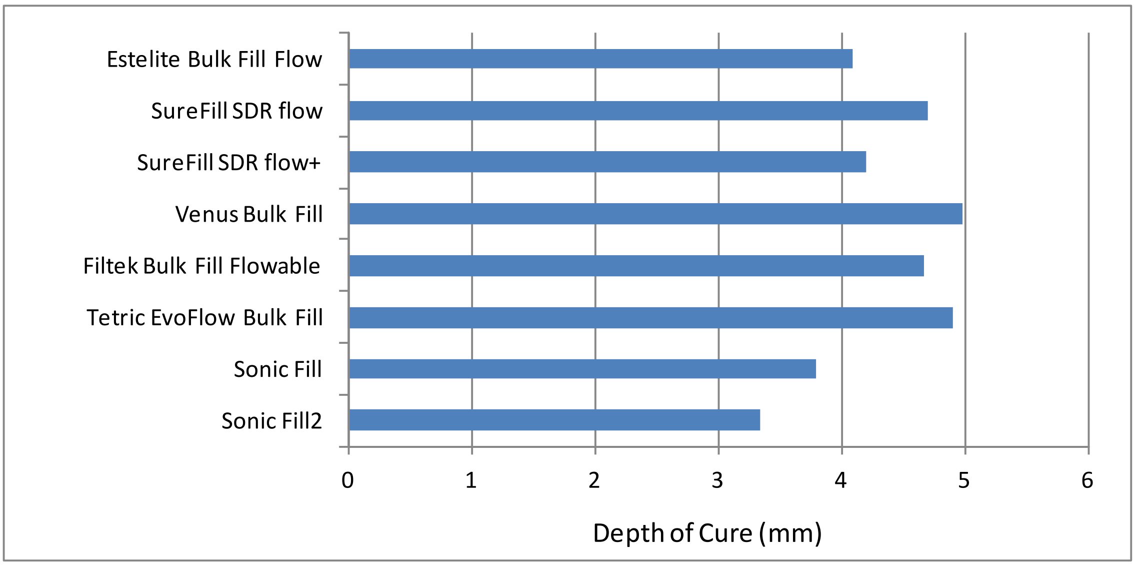
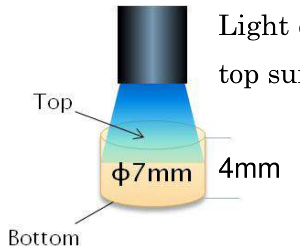


Fig.17 Depth of cure (ISO4049:2009)



$$\frac{\text{ı of DC}}{\text{of DC}} \times 100$$

$$(\%) = \frac{\text{Bottom of VHN}}{\text{Top of VHN}} \times 100$$

Fig. 18 Method of curing, calculation

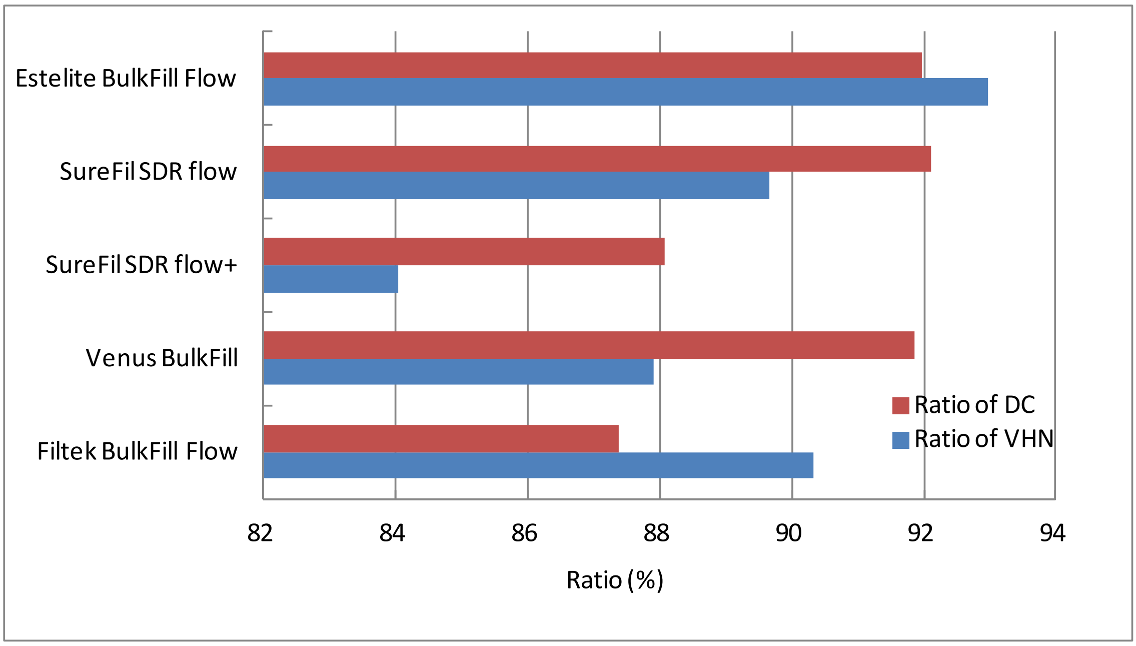


Fig.19 Ratio of DC, VHN

4.4. Cavity Adaptation

Adaptation of Estelite® Bulk Fill Flow to a box cavity with a 4 mm depth and a 4 mm diameter was examined. The results are shown in Fig. 20 and 21. Bovine teeth were used for evaluation; however, it was difficult to secure a depth of 4 mm. Therefore, their height was increased an additional 1.5 mm using a composite resin, and Bond Force II was used as the bonding material.

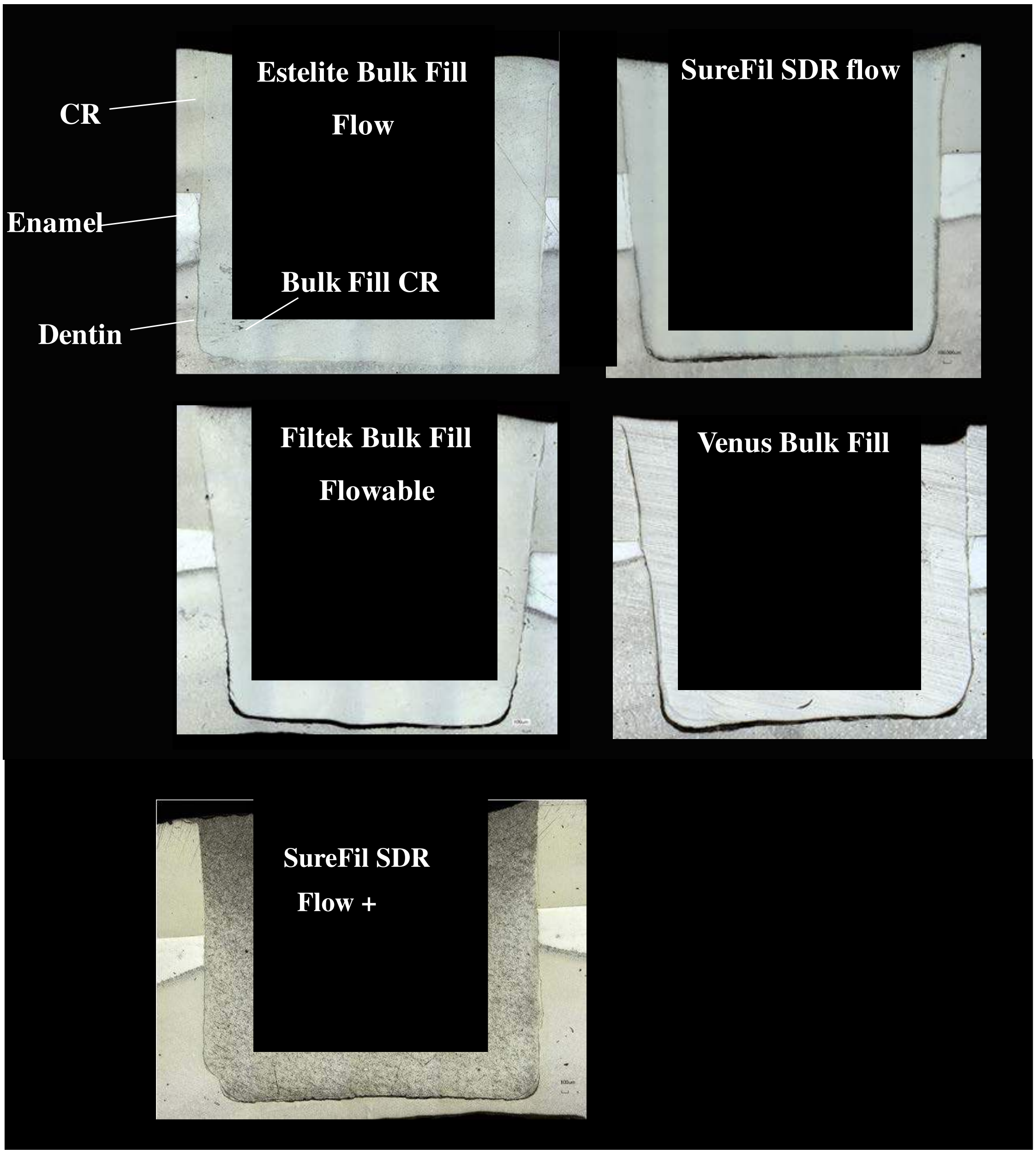


Fig.20 Cavity Adaptation

The results show that Estelite® Bulk Fill Flow exhibits good cavity adaptation compared to other commercially available bulk fill composite resins. In other commercial products, the bond has adhered to the tooth. However, the gap has occurred at the interface of the bond and the bulk fill resin. This result is due to its low polymerization shrinkage and polymerization shrinkage stress, as well as high depth curability.

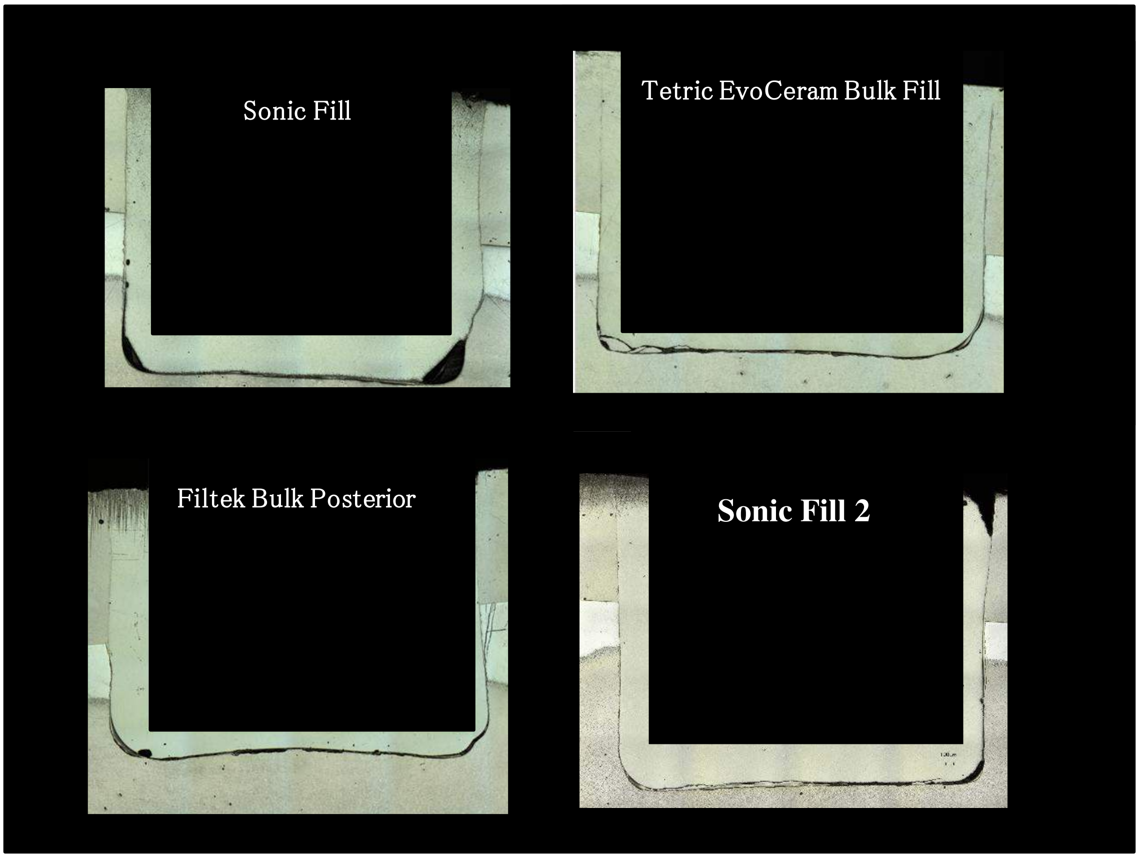


Fig.21 Cavity Adaptation

4.5 Wear Properties (Antagonistic wear test)

Wear resistance of the composite resin against a human tooth was examined using the method shown in Fig. 22. Comparisons were made with a conventional composite resin and a universal type bulk fill composite resin, as commercially available flowable type bulk fill composite resins are not recommended for use on the surface layer. The comparison results are shown in Fig. 23 and 24. The results shows that Estelite® Bulk Fill Flow exhibits an excellent balance between volume loss of the composite resin and wear of the human tooth, which leads to the conclusion that Estelite® Bulk Fill Flow is a composite resin that is less likely to abrade opposing teeth, while not easily becoming abraded, as in the case of Estelite Flow Quick®.

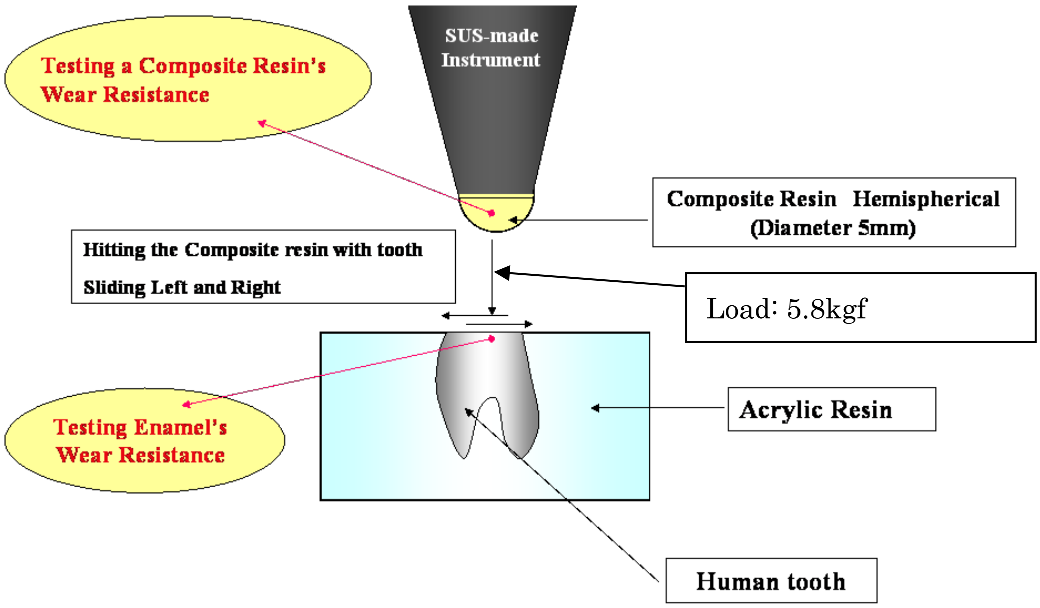


Fig.22 Method of wear resistance

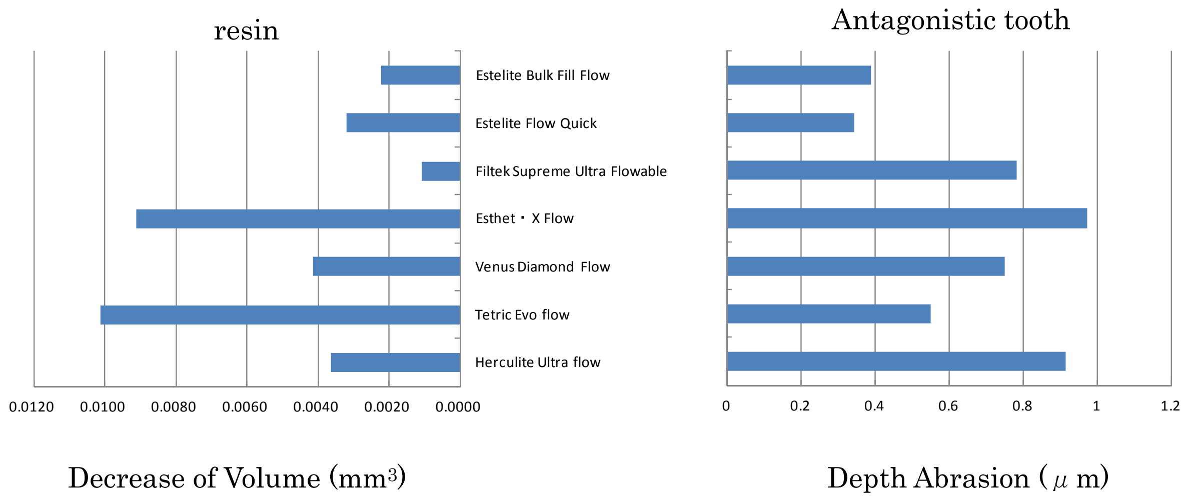


Fig.23 Wear resistance 1 (50,000cycles)

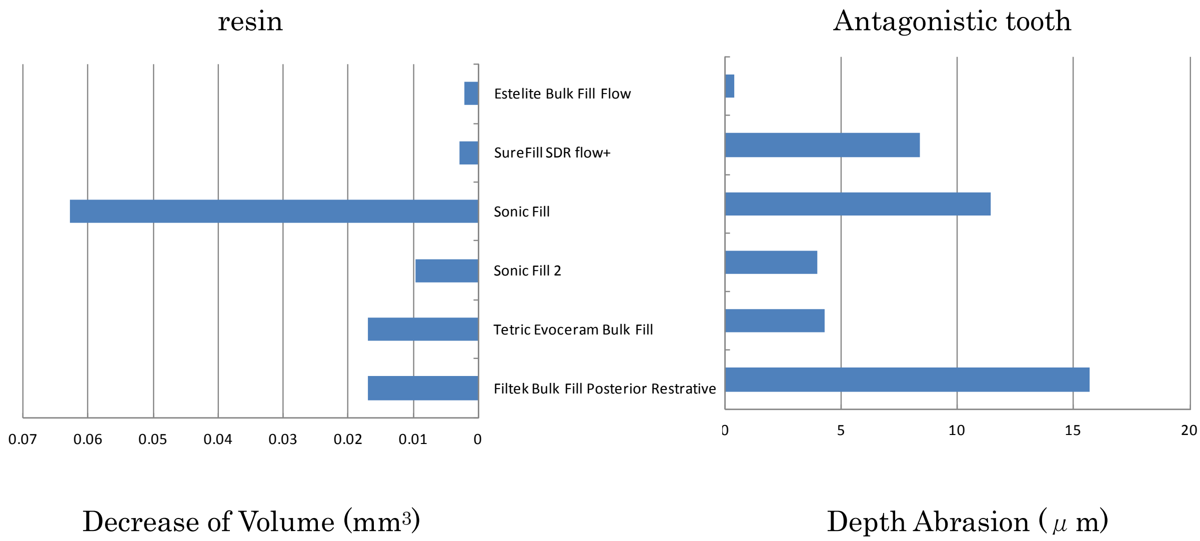


Fig.24 Wear resistance 2 (50,000 cycles)

4.6 Flexural strength and Compressive strength

Fig.25 presents the flexural strength and Fig.26 presents the compressive strength of Estelite® Bulk Fill Flow and other commercially available bulk fill composite resins.

The flexural strength and the compressive strength of Estelite® Bulk Fill Flow are relatively high among commercially available bulk fill composite resins.

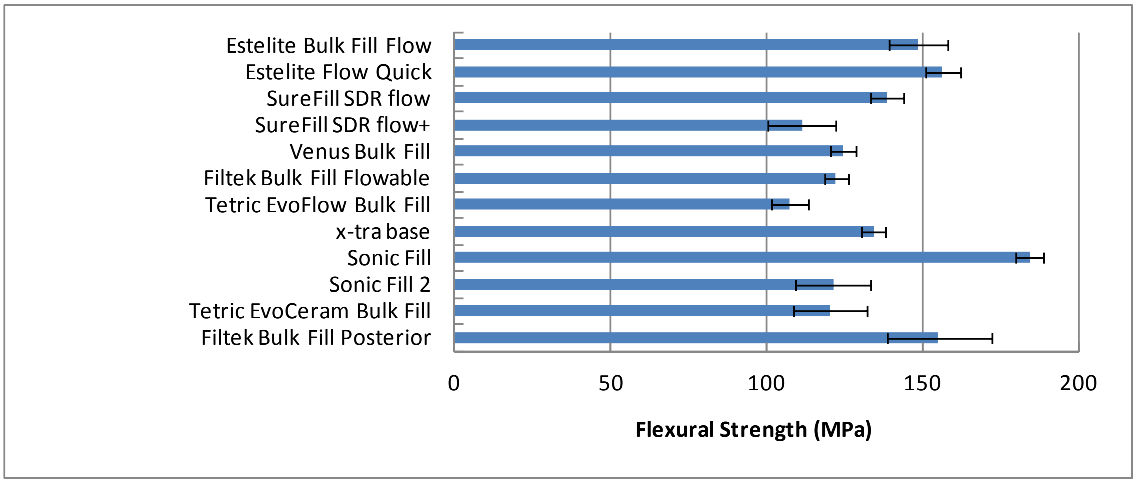


Fig.25 Flexural strength

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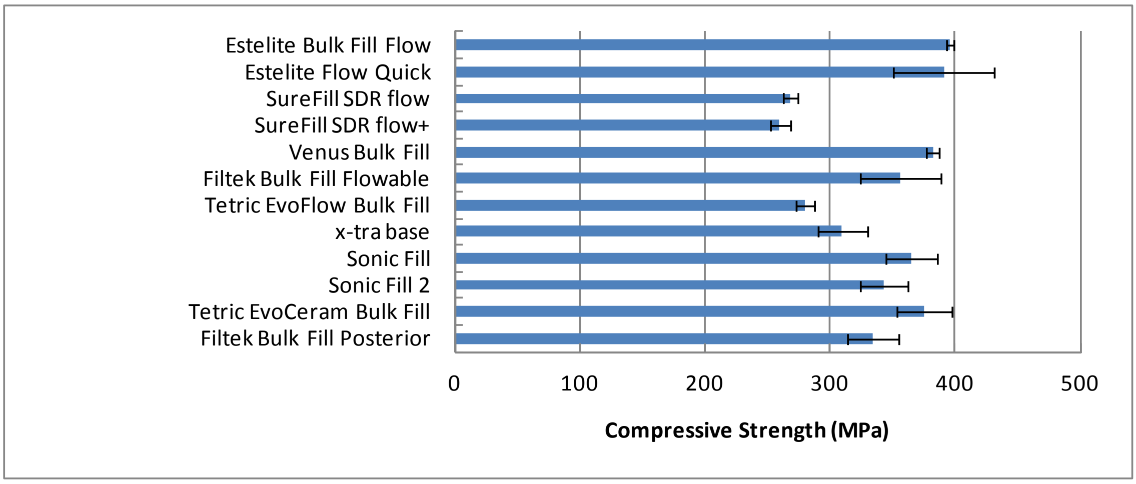


Fig.26 Compressive strength

4.7 Surface Glossiness

Fig.27 shows surface gloss after the surface of cured CR is polished with waterproof abrasive paper (#1500) followed by Soflex super fine (for 60 seconds under running water). Fig.28, 29 shows the relationship between polishing time and surface gloss. The results show that like Estelite Σ Quick®, Estelite® Bulk Fill Flow produces extremely high gloss in short polishing sessions.

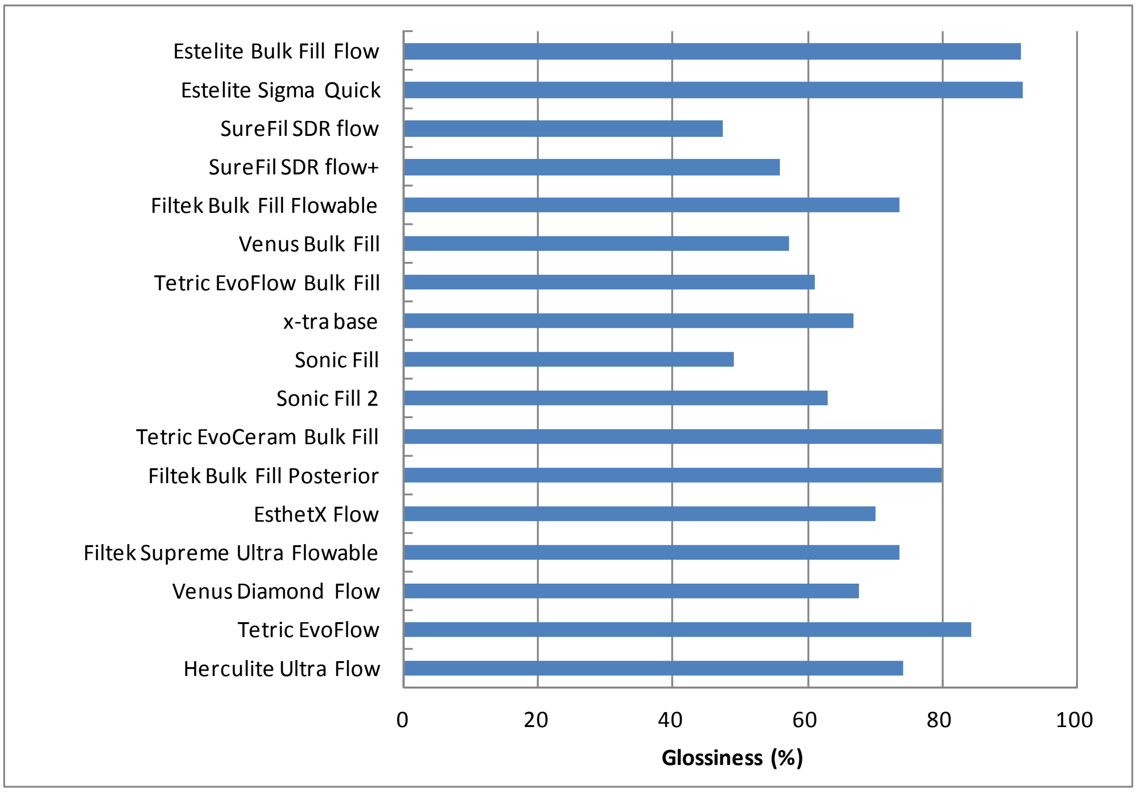


Fig.27 Surface Glossiness

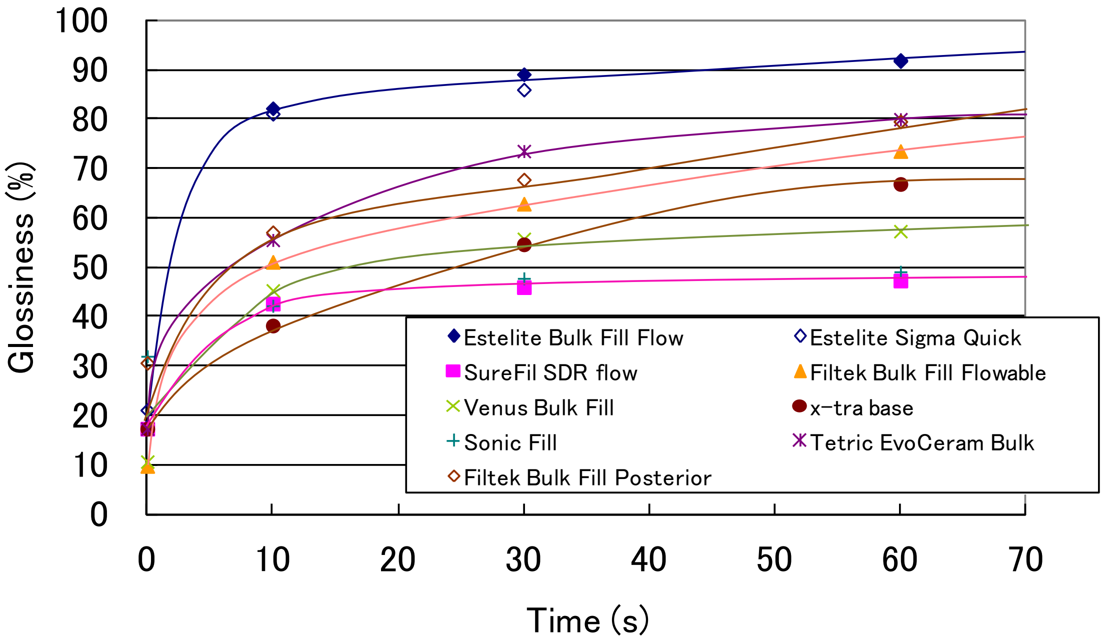


Fig.28 Relationship of glossiness to polishing time（Soflex/superfine）

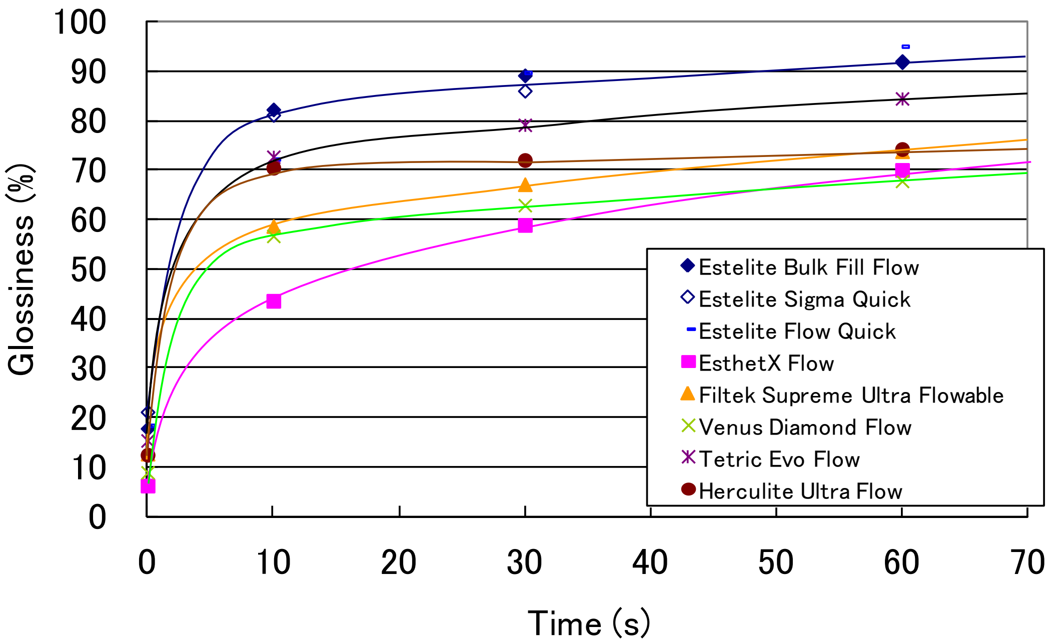


Fig.29 Relationship of glossiness to polishing time（Soflex/superfine）

4.8 Gloss Retention

In addition to exhibiting extremely high gloss with relatively short polishing, Estelite® Bulk Fill Flow features a remarkably persistent gloss.

Fig.30 shows the surface glossiness of cured resin after 0, 3000, 5000, 10000 times thermal cycle test (5℃- 55℃). Fig.31 shows 3D-images of surface of cured resin after 10,000 times thermal cycle test measured by laser-microscope.

These results show that Estelite® Bulk Fill Flow keeps its surface smoothness, resulting in glossing over time.

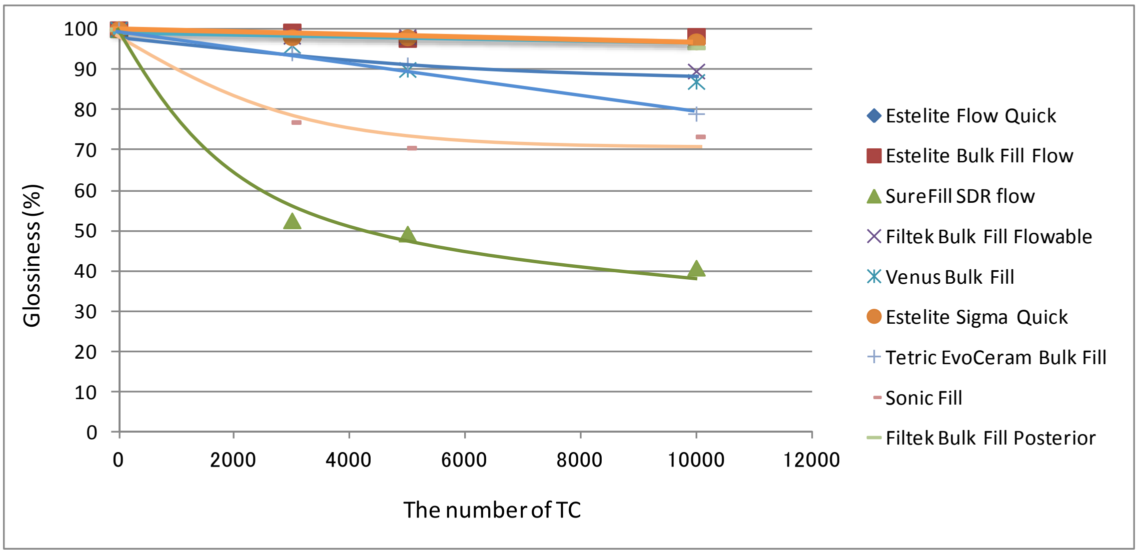
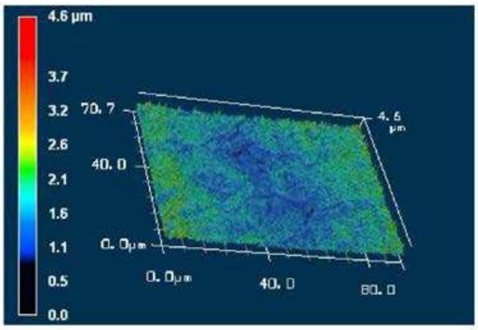
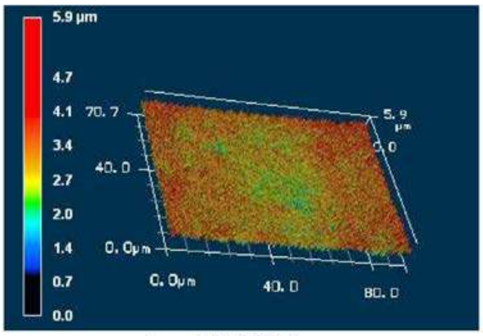


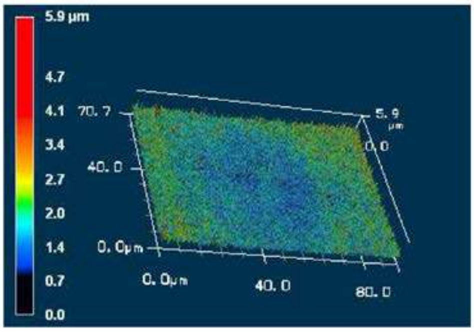
Fig.30 Surface glossiness



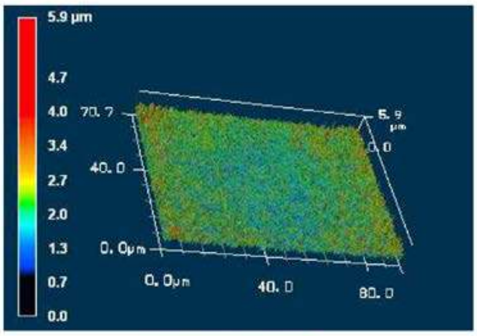
Estelite Bulk Fill Flow



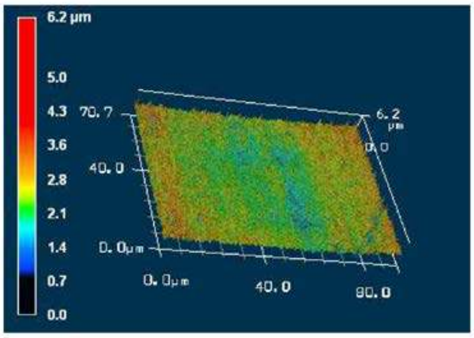
SureFill SDR flow



Filtek Bulk Fill Flowable



Venus Bulk Fill



Filtek Bulk Fill Posterior

Fig.31 Surface observance

4.9 Staining by Coffee

A composite resin used in an oral cavity degrades over time due to the effects of various foods and drinks. If such changes are greater than those of the dentition, the composite resins will be judged as lacking aesthetics when evaluated visually. For this, we examined the degree of staining by coffee (immersed for 24 hours at 80°C). The results are shown in Fig. 32.

The extent of staining for Estelite® Bulk Fill Flow after soaking in coffee was relatively low among commercially available bulk fill composite resins. We believe Estelite® Bulk Fill Flow will retain its color at the time of restoration over a long term.

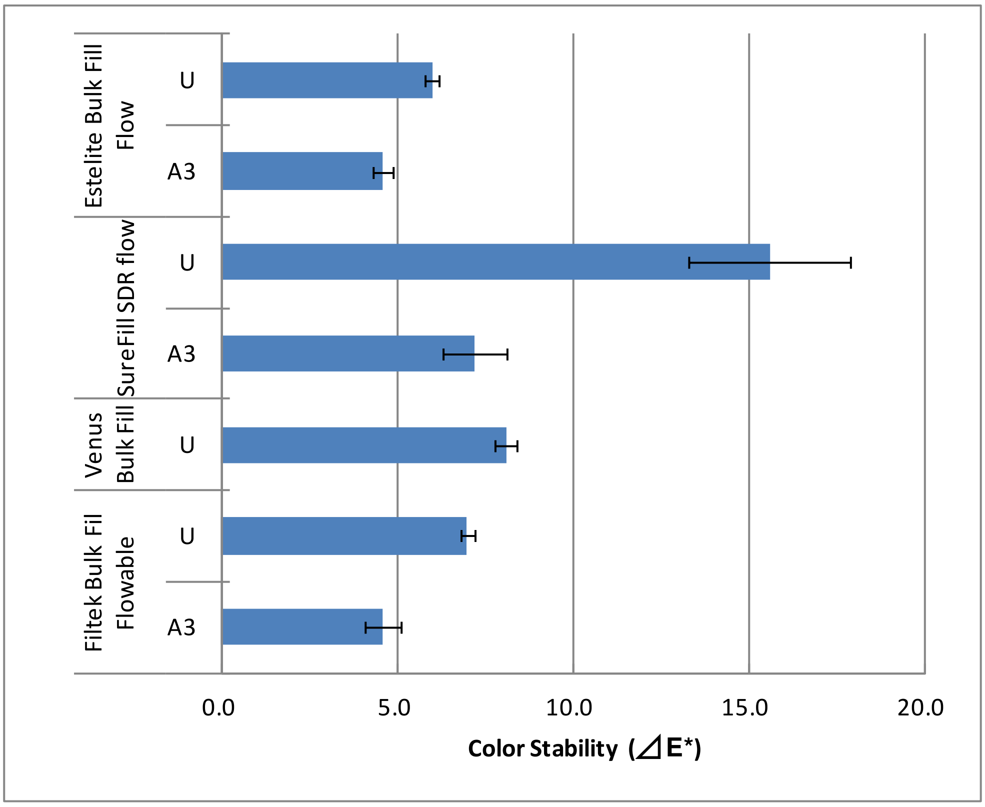


Fig.32 Color stability(⊿E*)

4.10. Color Matching

Color matching was visually checked using artificial teeth in which cavities with a depth of 4 mm were filled with different bulk fill composite resins (Fig. 33 and 34). As a result, Estelite® Bulk Fill Flow retained value and offered good color matching compared to other commercially available bulk fill composite resins owing to its chameleon effect.

Fig. 35 represents the results of value measurement at each position filled with bulk fill composite resins. Estelite® Bulk Fill Flow exhibited a level of value closest to that before cavity formation (Fig. 35).

From the above results, it can be concluded that Estelite® Bulk Fill Flow offers color matching that is superior to other commercially available bulk fill composite resins.

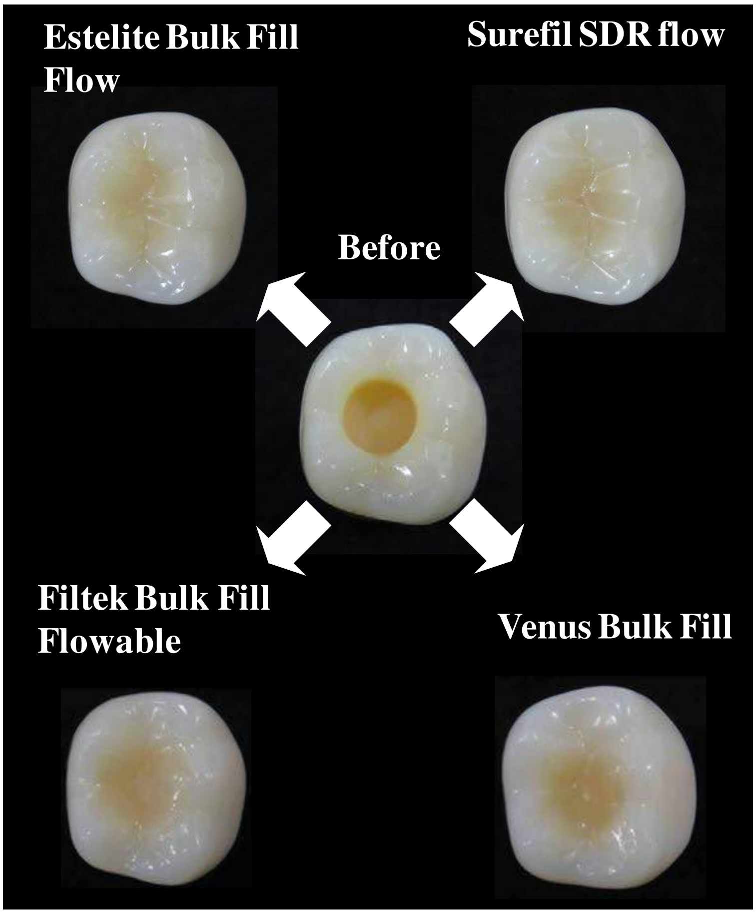


Fig.33 Color adaptation

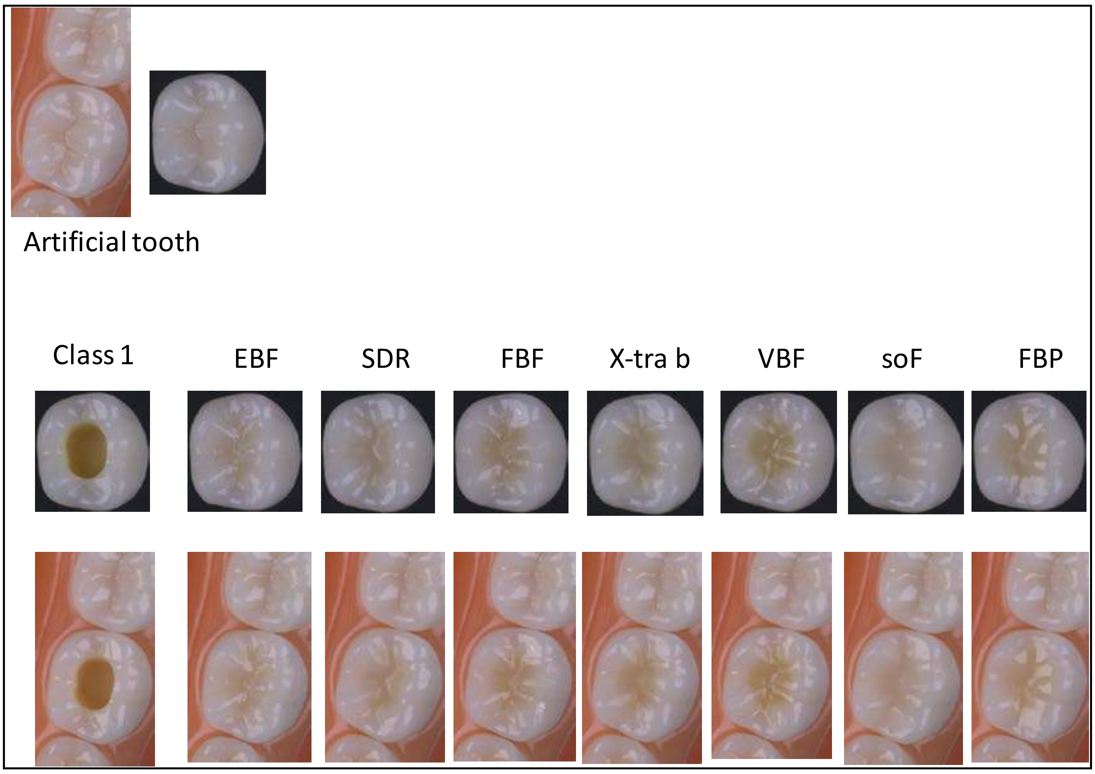


Fig. 34 Color adaptation 2

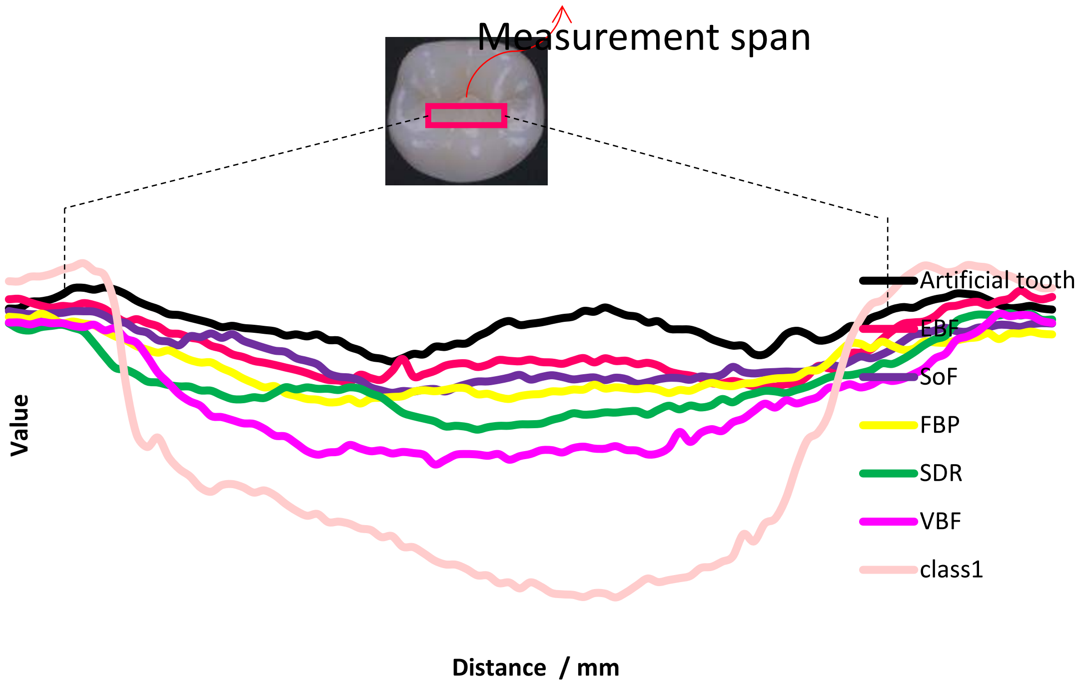


Fig.35 Value of Artificial teeth filled with Bulk Fill Resin Composite

4.11. Radiopacity

Radiopacity is determined by the composition of the inorganic filler and its filler content. The radiopacity of a resin is higher if the composition of the resin includes larger amount of elements with high atomic numbers at higher filler content. However, a filler containing large amounts of elements with high atomic numbers is associated with large refractive indices.

As indicated in 3.2, the inorganic filler used in Estelite® Bulk Fill Flow is designed to minimize difference of refractive indices in filler and monomer and to maximize radiopacity under this constraint. Fig.36 shows the radiopacity of commercially available bulk fill composite resins.

The radiopacity of Estelite® Bulk Fill Flow is equivalent to Estelite® Flow Quick.

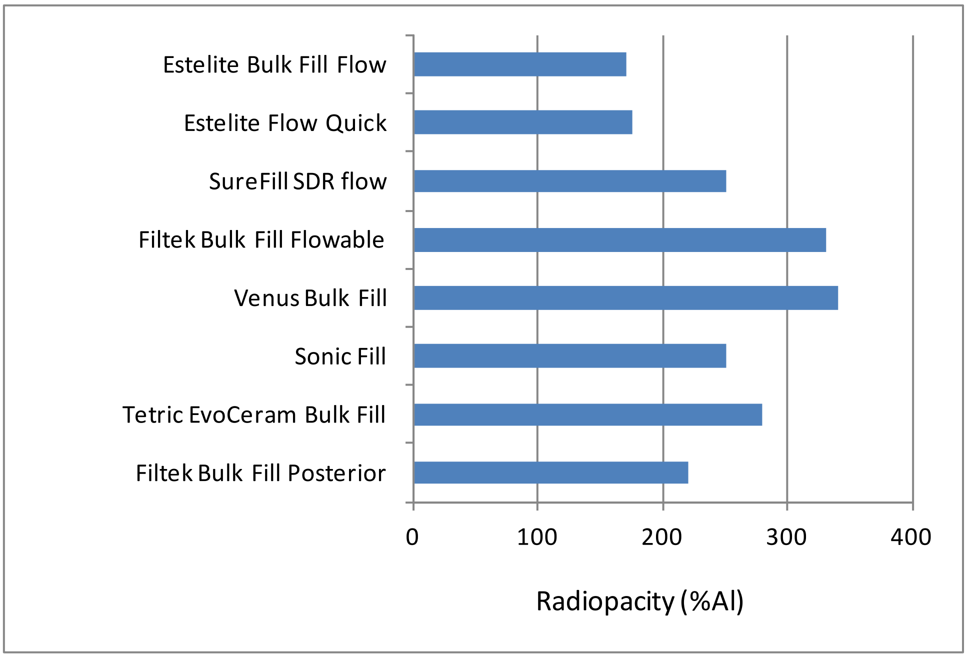
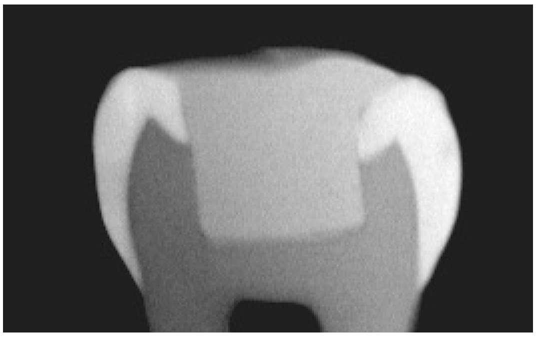


Fig.36 Radiopacity



Estelite Bulk Fill Flow

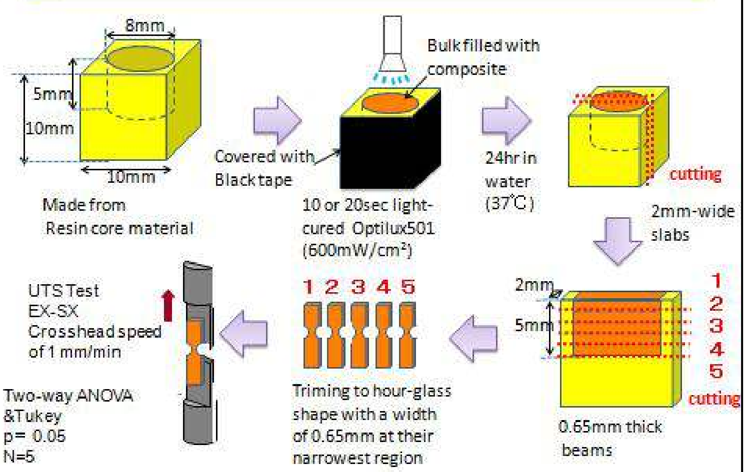
5. External Data

Effect of cavity depth on Ultimate Tensile Strength (UTS) of bulk fill flowable resin

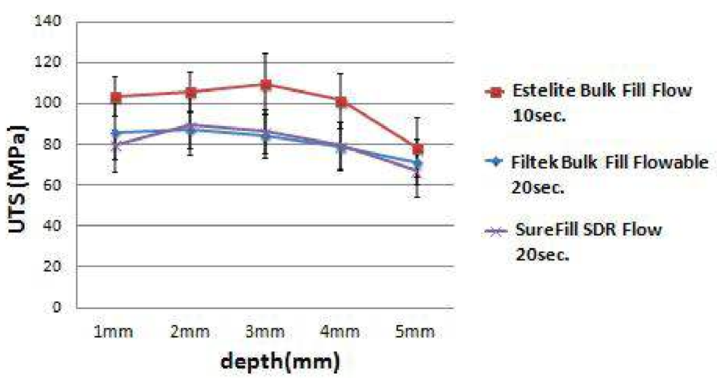
K. Ide, J. Tagami et al
Tokyo Medical and Dental University

The 144th Meeting of the Japanese Society of Conservative Dentistry, 2016

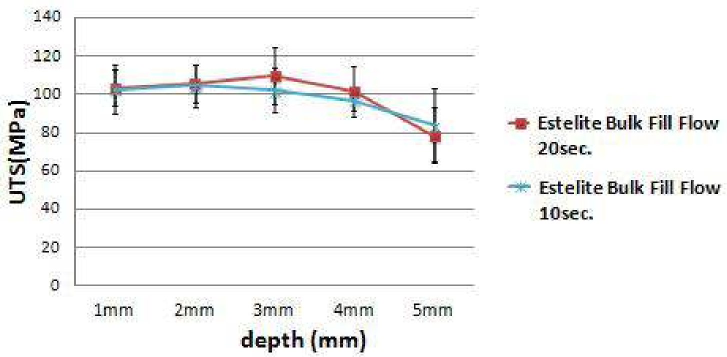
Methods



Results



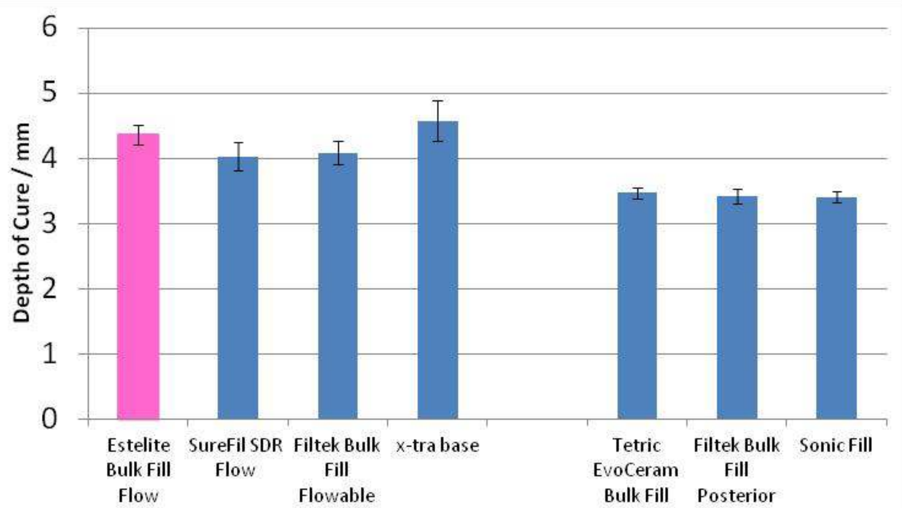
Results

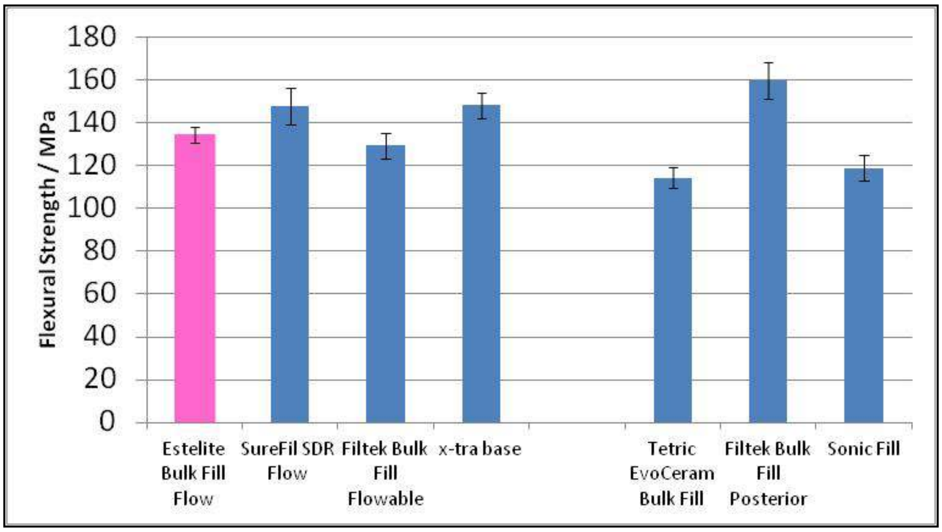


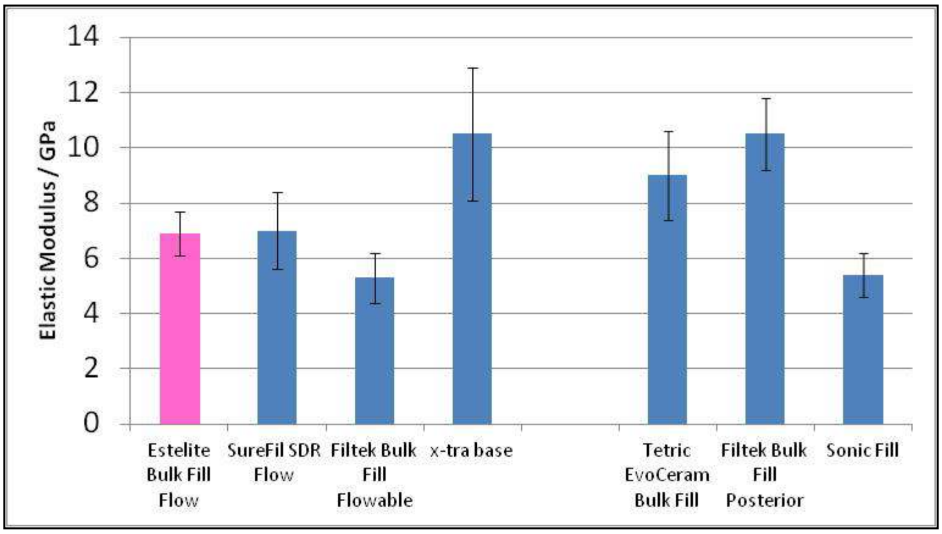
Mechanical Properties of new buil fill composite resin

T. Nojiri, M. Miyazaki et.al
Nihon University

The 144th Meeting of the Japanese Society of




Flexural Strength / MPa
180
160
140
120
100
80
60
40
20
0
Estelite Bulk Fill Flow
SureFil SDR Flow
Filtek Bulk Fill Flowable
x-tra base
Tetric EvoCeram Bulk Fill
Filtek Bulk Fill Posterior
Sonic Fill


Elastic Modulus / GPa
14
12
10
8
6
4
2
0
Estelite Bulk Fill Flow
SureFil SDR Flow
Filtek Bulk Fill Flowable
x-tra base
Tetric EvoCeram Bulk Fill
Filtek Bulk Fill Posterior
Sonic Fill

6. Summary

Estelite® Bulk Fill Flow is a composite resin offering various outstanding traits, including desirable levels of mechanical properties and cosmetics thanks to the Tokuyama polymerization catalyst technology (RAP technology), the Supra-nano Spherical filler technology and new composite filler technology.

① Excellent mechanical properties

- Estelite® Bulk Fill Flow features minimum level of polymerization shrinkage stress among commercially available bulk fill composite resins.
- Estelite® Bulk Fill Flow provides high depth of cure.
- Estelite® Bulk Fill Flow exhibits good cavity adaptation.
- Estelite® Bulk Fill Flow offers superior characteristics with respect to wear resistance and opposing tooth wear.

② Outstanding esthetics

- Estelite® Bulk Fill Flow exhibits good color match to the surrounding dentition.
- Estelite® Bulk Fill Flow provides high gloss with little polishing.
- Estelite® Bulk Fill Flow exhibits high gloss retention.

③ Fast curing

- Estelite® Bulk Fill Flow cures in less exposure time required for commercially available bulk fill composite resins.
- Estelite® Bulk Fill Flow is less sensitive to ambient light.

7. References

1) Shigeki Yuasa, "Composite oxide spherical particle filler"
DE, No.128, 33-36 (1999)