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博士論文

Application of Fourier transform for analysis of surface topographic properties of dental zirconia

(歯科用ジルコニアの表面性状解析への フーリエ変換の応用)

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歯科用ジルコニアの表面性状解析への

フーリエ変換の応用

Ⅰ公表論文

第一部

Naoyoshi Tarumi, Motohiro Uo, Eiji Yamaga, Fumio Watari. SEM observation and wettability of variously processed and fractured surface of dental zirconia, Applied Surface Science, ASPSUSC-24180 (2012)

第二部

Naoyoshi Tarumi, Tsukasa Akasaka, Fumio Watari. Application of Fourier transform for analysis of surface topographic properties of dental zirconia, Nano Biomedicine, accepted (2013年12月)

Ⅱ論文の構成と概要

【目的】
当初、歯科用ジルコニアは陶材で被服する内部フレームとしての使われ方だった。近年、ジルコニア単体での補綴物、やチタン製シリンダーに接着させたハイブリット型アバットメントなど使用例が多様化している。しかし、接着性における嵌合効力への寄与などの表面性状に関与する特性は多岐にわたる。従来、表面粗さとその各種特性への影響評価には、Ra（平均粗さ）等の深さ方向の値が使用されてきたが、平面方向の粗さの周期性（波長）も影響すると考えられる。本研究では、凹凸頻度の周波数解析を可能とするフーリエ変換を応用し、ジルコニア表面粗さの波長を解析し、接着性等に影響する粗さレベルを調べた。また、研磨や陶材被服した表面の SEM 観察および、臨床で破折したケースと実験的に破折させた破断面との比較をして、歯科用ジルコニアを臨床で使用する際の留意点を考察した。

【材料と方法】
第一部
　試料：直径20mm のシリンダー形状の半焼結のジルコニアを厚さ約10mm でカットし、耐水研磨紙（＃800）で観察面を整えた。1350℃で焼結後、シリコーンホイールでの中研磨、アルミナでのサンドブラスト処理、トライボケミカル処理、鏡面研磨、酸処理、陶材被服をした試料を制作した。破断面観察：臨床でのフレームの連結部を想定して、高さ3mm 幅が1.8 から 2mm の断面積で長さを約 50mm の試料を制作し破折させた。試料と臨床で破折した破断面を SEM 観察した。計測：表面粗さ計測器を用いて、各表面処理をした試料の粗さを計測。濡れ性試験は、シリコーンホイールでの中研磨、サンドブラスト処理、トライボケミカル処理の3種を水との接触角を計測し評価した。

第二部
　試料：半焼結のジルコニアから板状(18×20×10mm^3)と(12×12×5mm^3)の2種の試験片を作成し、耐水研磨紙（#1500）を使用し表面を平滑後 1500℃で4時間係留後、10時間の徐冷をした。焼結後、最終的な試料の寸法は約20％収縮した（10×10×4mm^3）,(14×18×8mm^3)。表面処理：ダイヤモンドバー（ファイン）で約 1mm 間隔の溝を付与［低周波粗さ］、アルミナサンドブラスト処理（2atm,50um）［高周波粗さ］、ダイヤモンドバー処理後サンドブラスト処理[低周波＋高周波]、未処理の試験片を準備した。接着：シアノン（シアノアクリレート系モノマー）、歯科用レジンセメント（ビューティーセム：松風）、プライマー（モノボンドプラス：イボクラ）処理後にレジンセメントでジルコニア試験片同士を接着した。大きい試料は保持側、小さい試料は荷重側とした。3)解析：SURFCOM1400A を用いて、評価長さ 8500um,測定速度 60um/sec で粗さ曲線計測をした。Low と Low+High は付与した溝に対して垂直に計測した。濡れ性試験は Drop Muster DMs-200 を用いて水との接触角を計測した（n=10）。Low と Low+High は付与した溝に対して垂直に計測した。インストロンを使用してせん断接着強さ試験を行い、フーリエ解析、SEM 像で評価した。

【結果と考察】
第一部
表面処理後の SEM 観察では、中研磨で残っていた傷は鏡面研磨や陶材被服より平滑な面になり、サンドブラスト、トライボケミカル処理ではわずかな凹凸が付与されていた。凹凸の付与は、濡れ性試験の結果濡れ性の向上がみられ、接着への向上が期待できる。しかし、酸処理では表面の凹凸は付与されるものの、わずかな腐食もあるため、長時間の処理はジルコニアの劣化が予想される。表面粗さは、陶材被服したものが著しく高い結果となったが、陶材の緩く大きな凹凸が反映されたためと思われる。破断面観察では実験での破綻面と異なり、臨床での破断面は鱗状の破断面が観察され、口腔内での応力のかかり方が複雑なものであると考察した。また、実験での破断面にみられたクラックは、ジルコニアのクラックを抑制させる特性であろう、クラックが直進できずに進展してとどまっているものが観察された。

第二部
表面粗さ曲線（実空間）をフーリエ変換し、周波数空間でピークを示した周期を逆フーリエ変換することで、粗さ曲線をマクロな凹凸からなる低周波成分と、その上に乗ったミクロな粗さからなる高周波成分とに分離できた。濡れ性は高周波成分を付与することで向上でき、せん断接着強さは未処理（7MPa）、低周波（5MPa）、高周波（14MPa）、低周波＋高周波（9MPa）となり、Ra が大きい[低周波(波長約1600um)＋高周波(波長約 12um)]より、サンドブラスト処理のみで Ra がより小さい[高周波]の方が高かった。SEM 像では、試料のほとんどが界面破壊をしているのがみられた。大きな嵌合力として期待した低周波要素としての溝には、一部のレジンセメントしか残っておらず、高周波要素として付与したサンドブラスト処理の試料では、ジルコニアとレジンセメントの境界線付近にわずかな凝集破壊が観察された。このことから、ジルコニアには化学的結合は期待できず、また大きな粗さよりは小さな粗さの方が接着には有効と考えられた。

【結論】

表面粗さが影響する物性の検討には、従来使用されてきたRaよりも波長の影響が大きい場合もあると考えられる。接着強さの向上には嵌合力のある大きな凹より、十数ミクロンの短波長の方が影響を与えた。以上より本研究は接着性等の表面性状が関与する各種特性の検討にフーリエ変換を用いた解析が有効である事が示された。また、臨床での破断面観察では、口腔内での応力のかかり方は多様であるため、材料強度に過信をしないで補綴物の設計をしなければいけない。

【謝　辞】
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SEM observation and wettability of variously processed and fractured surface of dental zirconia

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Keywords: Zirconia, Fracture, Surface treatments, Wettability, Dental prostheses, CAD/CAM

a b s t r a c t

Current dental zirconia has several problems in clinical application such as chipping, fracture and detachment. To reduce these problems the surface after various treatments was analyzed by SEM observation, contact angle measurement and surface roughness measurement, and compared. The surface after mirror polishing was smooth. Porcelain layering was smooth except large formed grooves by bubbles. After sandblast and tribochemical treatments, the surfaces showed several micron-sized caving with micron to submicron-level irregularities. Sandblast and tribochemical treatments with the lager roughness had the smaller water contact angle than silicone wheel polishing. Clinically fractured surface of zirconia showed a more complex structure than manually fractured surface, which may be due to the various mode of stress to be imposed repetitively to various direction.

1. Introduction

Recently, all ceramic crowns and bridges using zirconia fabricated by CAD/CAM for core frame have been used more and more for wider cases in dental clinics. They are especially effective in the cases of metallic allergy and esthetic prostheses. However there are some problems such as fracture of frame in certain cases.

Various surface treatments were done onto zirconia in the fabrication process of all-ceramic crowns. Silicone wheel was used to polish the frame surface. Sandblast treatment was done to clean and to make the surface sufficiently rough for adhesion of resin cement and bonding of porcelain [1]. Tribochemical treatment was used as a pretreatment for the silane coupling treatment processing. Acid treatments were done to dissolve porcelain layer on the surface of frame at the rebuilding of used zirconia prostheses.

Chipping or fracture and detachment of zirconia frame are major problems in clinical practice. Wettability of surface has a large influence on the adhesion effect [2]. In this study, the surface after various treatments was analyzed by SEM observation, contact angle measurement and surface roughness measurement, and compared to reduce the problems in clinical application such as chipping, fracture and detachment. The clinically derived and experimentally attained fracture surfaces of zirconia were also observed by SEM and compared.

2. Materials and methods

2.1. Surface processing

Pre-sintered zirconia of cylinder block of 20 mm in diameter (Cercon Base Basic, DeguDent, Germany) was cut into 10 mm thick disks. Disk surface was polished by waterproof paper (#240 &#800). After sintered at 1350◦C in accordance to the sintering program recommended by product company, all samples were polished by (1) SW: silicone wheel (Core Master fine, Shofu, Kyoto, Japan), then these surfaces were variously treated. These surface treatments are (2) SB: sandblast with alumina (Cobra 2 μm at2.5 atm: Renfert, Germany), (3) TC: tribochemical (Rocatec 30μm at 2.5 atm: 3 M ESPE, Minnesota, United States), (4) MP: mirror polishing using the buff with diamond paste (Gradia Diapolisher: GC, Tokyo, Japan). (5) AC: 24-h acid with the solution of 13% HF + 16%H_2SO_4 (Uniclean: Shofu, Kyoto, Japan), and (6) PL: porcelain layering treatments (Cerabien CZR: Noritake, Aichi, Japan).

2.2. Fracture surface

The block of 3 mm high, 50 mm long with the upper surface of 2 mm width and the lower surface of 1.8 mm width was cut from zirconia cylinder and sintered at 1350◦C as recommended by Product Company. The size of cross-section of zirconia block was selected to fit to the clinical fracture case. It was fractured manually through bending by loading from upper to lower surface without any treatment on the sintered surface. Clinically derived fracture zirconia was also used as sample.

2.3. Observation

Variously treated surfaces and fractured cross-sections were observed by FE-SEM (S4000: Hitachi, Tokyo, Japan).

2.4. Contact angle measurement

The contact angles with water were measured for the surface of zirconia after silicone wheel, sandblast and tribochemical treatments with DMs-200 (Drop Master S series: Kyowa Interface Science Co.Ltd, Saitama, Japan) Measurements were performed 10times for each. All experimental results were evaluated by Non-repeated Measures ANOVA ($n = 10$) ($p < 0.001$).

2.5. Surface roughness measurement

The surface roughness was measured using SURFCOM 1400A (Tokyo Seimitu, Japan) after the treatments with silicone wheel, sandblast, tribochemical treatments, mirror polishing and porcelain layering.

3. Results

Fig. 1 shows SEM observation of smoothed zirconia surface. Fig. 1a is silicone wheel polishing, Fig. 1b is mirror polishing, and Fig. 1c is porcelain layering. The surfaces after mirror polishing were smooth except mechanically formed grooves during silicone wheel polishing. Porcelain layering was smooth except large formed grooves by bubbles. Both mirror polishing and porcelain layering look similarly smooth.

Fig. 2 shows SEM observation of roughened zirconia surface, for silicone wheel polishing Fig. 2a, sandblast treatment Fig. 2b and tribochemical treatment Fig. 2c. After sandblast and tribochemical treatments, the surfaces showed several micron-sized caving with micron to submicron level irregularities. When Fig. 2b and c were compared, the latter was slightly rougher.

Fig. 3 is the enlargement of roughened zirconia surface by SEM observation. Fig. 3a is tribochemical treatment, and Fig. 3b is 24-hacid treatment. 24-h acid treatment induced much more surface roughening with the 50–100 nm particulate roughness than tribochemical treatments.

Fig. 4 shows the specimens of dental zirconia. Fig. 4a shows zirconia cylinder supplied for dental CAD/CAM machining and a fabricated bridge. Fig. 4b is the fractured block and matchstick behind for reference of size. Block was obtained by milling from zirconia cylinder. Fig. 4c is fractured zirconia bridge used in clinical case and d is enlargement of pontic with fracture cross-section seen as white plane in right side. Fracture occurred nearly in the center of bridge c.

Fig. 5 is SEM observation of fracture cross-section, Fig. 5a clinically fractured, Fig. 5b enlargement of Fig. 5a, Fig. 5c experimentally fractured, Fig. 5d enlargement of Fig. 5b. Clinically occurred fracture exhibited the scab-like surface. For experimentally attained fracture surface cracks were formed straight in most part and in some places curved or twisted into S or Ω form.

Figs. 6 and 7 show the photographs and the corresponding mean and standard deviation of the contact angle with water, respectively. Fig. 6a is silicone wheel polishing, Fig. 6b is sandblast treatment, and Fig. 6c is tribochemical treatment. In Fig. 7 all these treatments showed a significant difference each other ($p<0.001$). The average contact angles were 91.6 ± 4.8◦ (SW), 65.6 ± 8.0◦ (SB), and 51.4 ± 4.8◦ (TC). Sandblast and tribochemical treatments had the smaller water contact angle than silicone wheel polishing.

Fig. 8 shows the surface roughness of zirconia with various treatments. The measured values of mean surface roughness Ra were 0.12μm for silicone wheel polishing, 0.26 μm for sandblast treatment, 0.32μm for tribochemical treatment, 0.11 μm for mirror polishing and 1.45μm for Porcelain layering. Porcelain layering showed the largest roughness. Mirror polishing roughness had the smoothest surface.

4. Discussion

4.1. Suitable surface treatments for dental zirconia

To have the good adhesion of porcelain onto zirconia, the wettability is important. Sandblast and tribochemical treatments showed the contact angle smaller than silicone wheel treatment (Figs. 6 and 7), which provides the improved wettability. This maybe mainly due to the increased surface roughness granted by sandblast and tribochemical treatments (Fig. 8). Both treatments are effective to enhance the adhesion of zirconia with resin cement to fix on teeth and for bonding of porcelain [3].

Plaque tends to attachment more easily to the rougher surfaces [4]. In the surface roughness measurement, porcelain layering showed the largest mean roughness (Ra 1.45). Only porcelain layering treatment was done manually with the human hands. During the process of condensing of porcelain powders, they contain bubbles inside. By the following glazing process, bubbles go out then the large and gradually sloped grooves are formed. This may cause the larger roughness with the longer periodicity. Except there large grooves, however, the surface is quite smooth with the much less high frequency roughness with the small periodicity. On the other hand, although Ra is smaller, SB and TC had much more high frequency roughness, which leads to the easier plaque attachment. Thus the large Ra value of PL has nothing to do with plaque attachment. From the aspect of plaque attachment, zirconia surface with the high frequency roughness without porcelain layering like SB and TC is recommended to be polished.

The 24-h acid treatment done in this study deteriorated the surface (Fig. 3b). The acid treatment is used to dissolve the porcelain to replace with the new one in such cases that the matching of color shade dose not fit well. When the amount of porcelain is large, the acid treatment needs a longer time. If the acid treatment time is less than 10 min, zirconia suffers little damage. To shorten acid treatment time, it is preferable to remove porcelain mechanically as much as possible before the acid treatment.

When there are possibilities to choose treatments from various ones, it is also important to pay attention to health care in working condition. Some surface treatments produce abraded powders whose nano particles may induce the health risk to human body [5]. Most treatments shown in this study were done under water spray, which decreases the risk to much lower level.

4.2. Fracture of zirconia

In the cross-section of experimentally fractured samples, cracks were formed straight in most part and in some places curved or twisted into S or Ω form. This suggests that crack propagation was obstructed by the fracture toughness of zirconia resulted from martensitic crystalline transformation [6,7].In clinics, complex stress is applied in mouth and it is not a simple bending deformation mode to one direction at one time. Various deformation mode of tension, bending, twist and fatigue in various directions are imposed many times for long time. Therefore fracture was progressed little by little in a long time. This resulted scab-like morphology in fracture surface.

5. Conclusions

This study evaluated the surface morphology and wettability after various treatments done in the fabrication process of dental zirconia. There is the tendency that the larger surface roughness leads to better wettability, which may be one of the factors to con-tribute to the better bonding of porcelain onto the zirconia surface.

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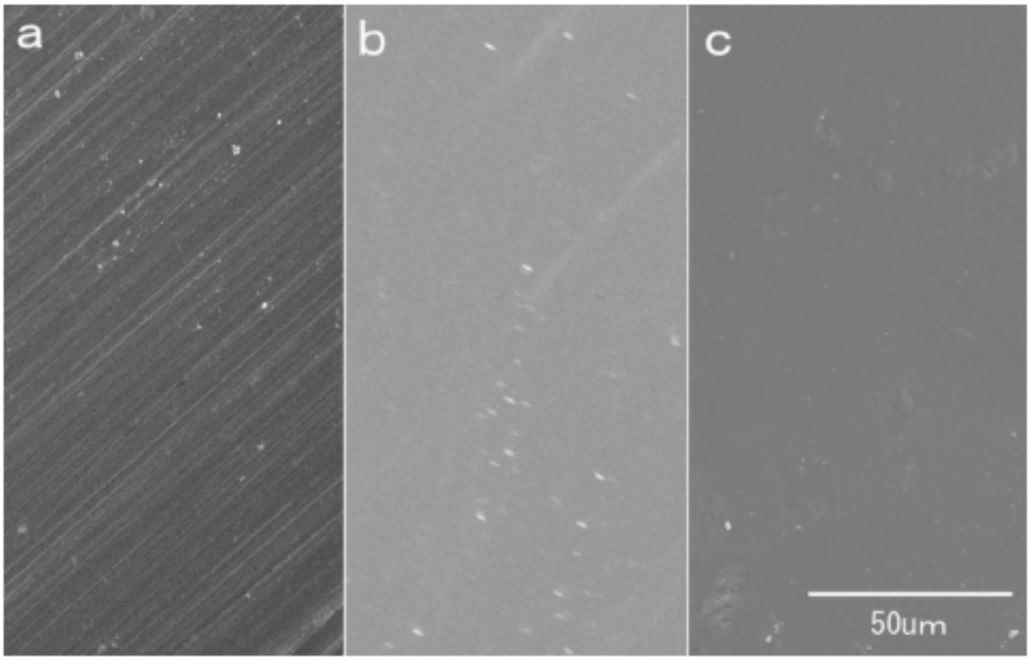

Fig. 1. SEM observation of smoothed zirconia surface. (a) Silicone wheel polishing treatment, (b) mirror polishing, (c) porcelain layering.

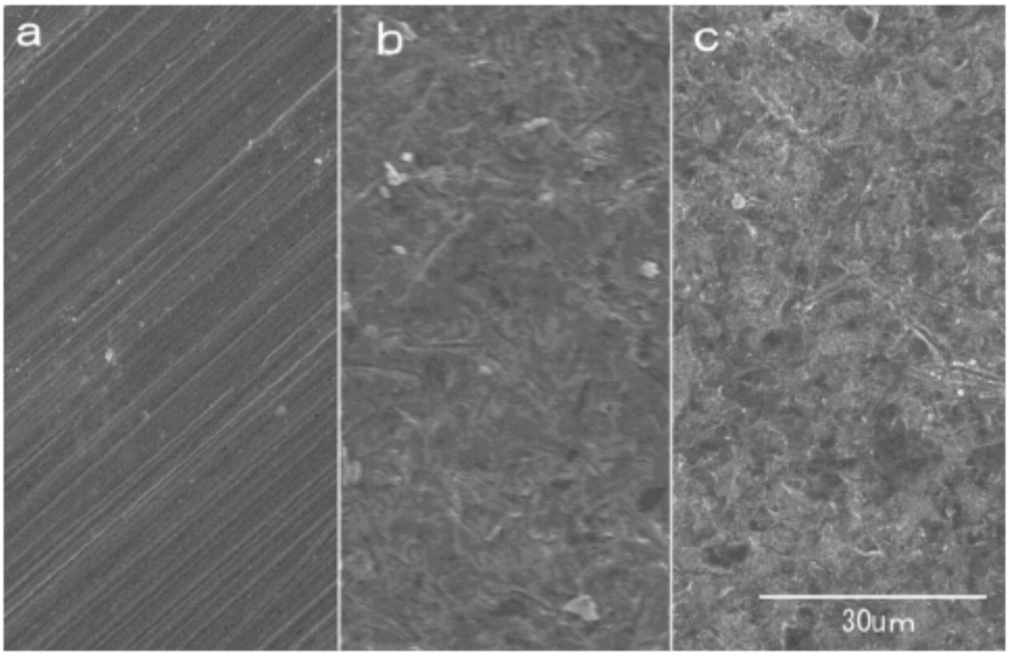

Fig. 2. SEM observation of roughened zirconia surface. (a) Silicone wheel polishing treatment, (b) sandblast treatment, (c) tribochemical treatment.

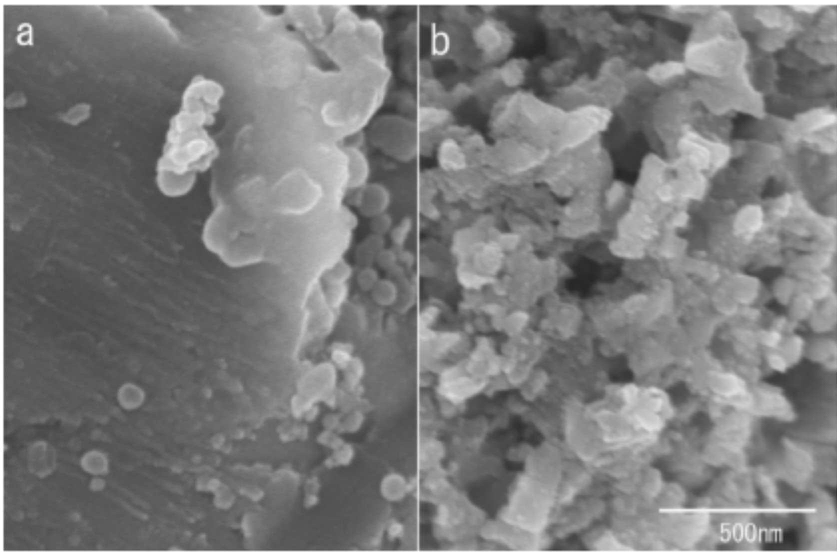

Fig.3.Enlargement of roughened zirconia surface SEM. (a) Tribochemical treatment, (b) 24-h acid treatment.

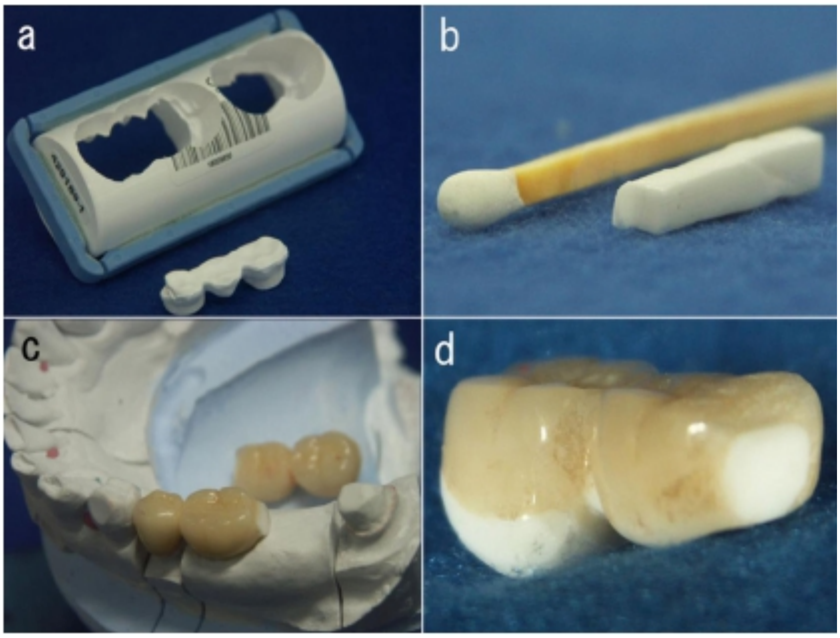

Fig. 4. (a) Zirconia cylinder for dental CAD/CAM and a fabricated bridge, (b) experimentally fractured block obtained by milling from zirconia cylinder, (c) fractured zirconia bridge used in clinical case, (d) enlargement of pontic with fracture cross-sections.

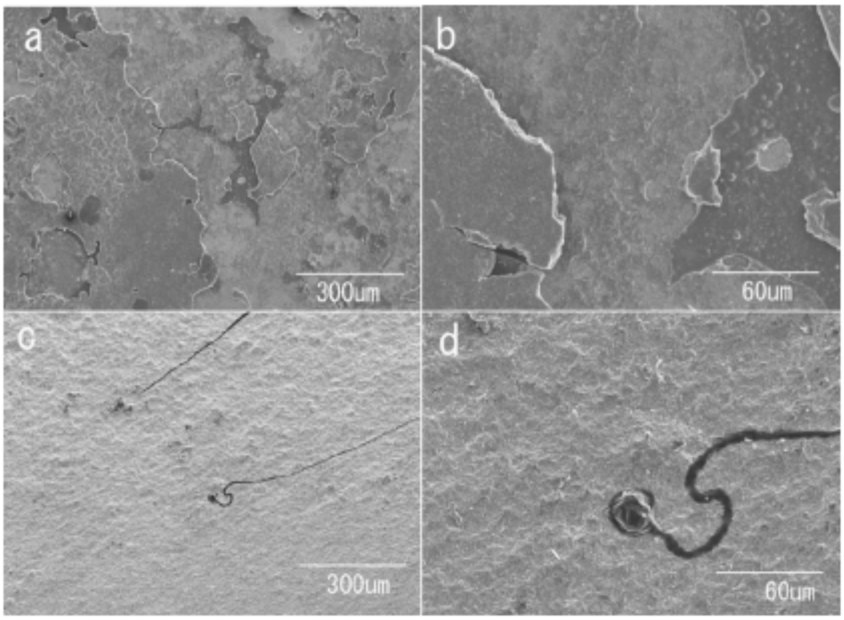

Fig. 5. SEM observation of fracture cross-section. (a) Clinically fractured, (b) enlargement of (a), (c) experimentally fractured, (d) Enlargement of (c).

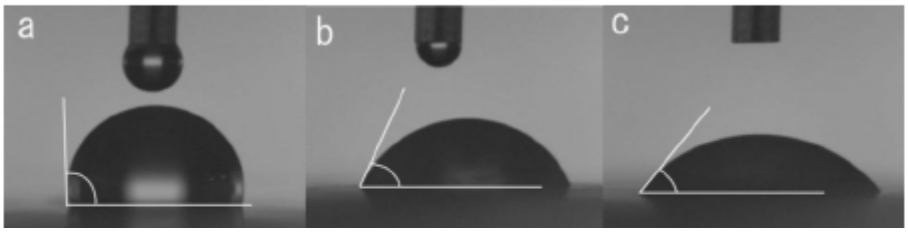

Fig. 6. Contact angle measurements of zirconia surface with various treatments. (a) Silicone wheel (SW), (b) sandblast (SB), (c) tribochemical (TC).

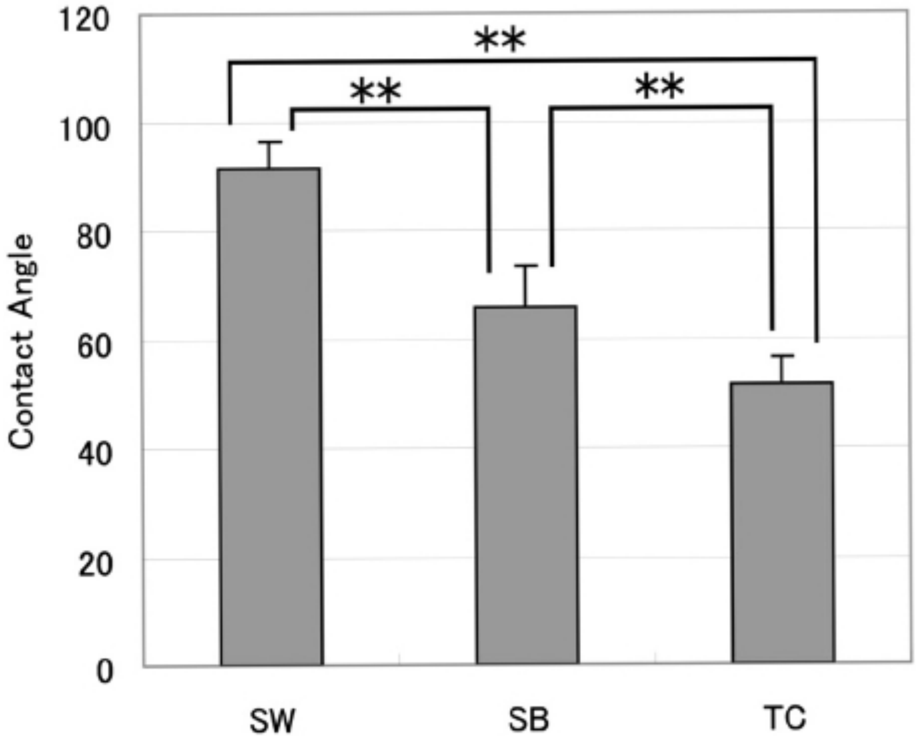

Fig. 7. Contact angle for the treatments.

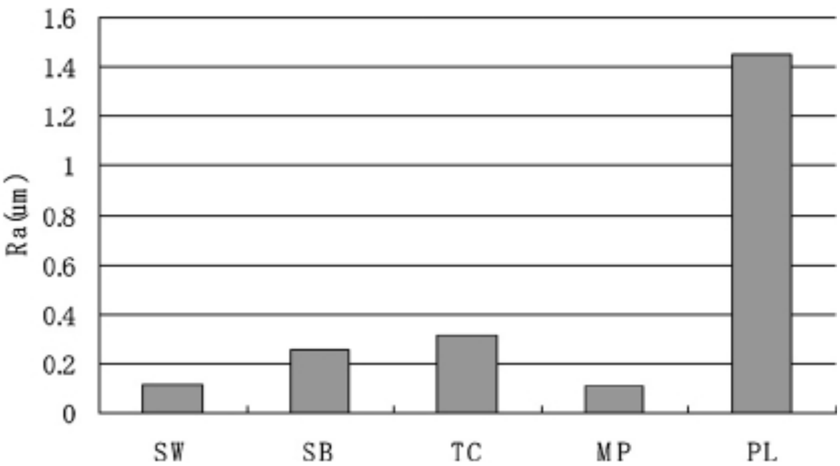

Fig. 8. Surface roughness of zirconia with various treatments.

Application of Fourier transform for analysis of surface topographic properties of dental zirconia

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***Keywords**: dental zirconia, surface roughness, Fourier transform, shear bond strength, resin cement*

Synopsis

The clinical application of dental zirconia has increased. Adhesion on dental zirconia is important in the usage such as the hybrid type abutment to adhesive to titanium cylinder. For the analysis of surface roughness to influence on various material properties [1], conventionally the value of depth directions such as the Ra has been widely used. However, the periodicity (wavelength) of roughness in the horizontal direction may also influence adhesive property. The Fourier transform that can perform frequency analysis was effective for the examination of a complicated roughness curve, composed of multiple waves. Shear bond strength test was conducted in the specimen with four kinds of surface roughness (control, low, high, low and high frequency element). Shear bond strength became strong (14MPa) in the specimen with a short wavelength (high frequency element), and weak (4~5MPa) for a long wavelength (low frequency element). The surface sensitive properties depend not only on the Ra but also on the wavelength. In this study the Fourier transform was effective for various characteristic examinations of surface properties such as the adhesive property and shear bond strength could be better understood by wavelength dependence.

Introduction

Dental zirconia has been used for the application as an internal frame in the beginning [2]. Zirconia begins to be used as dental implant with its good compatibility [3, 4] to both hard tissue [5] and soft tissue [6]. Recently, applied cases have been enlarged, such as the hybrid type abutment to adhesive titanium cylinder, and the titanium base screw retained zirconia crown. In those cases the fewer adhesion of plaque and higher adhesive strength to resin cement are favored [7, 8]. For the analysis of the influence of surface roughness, conventionally the value in the depth directions, such as Ra (arithmetic mean roughness) has been used [9]. However, the periodicity (wavelength) of the roughness in the plane direction may have a larger influence, depending on the surface-sensitive properties. In this study, Fourier transform, which enables frequency analysis, was applied for the analysis of the wavelength of the zirconia surface roughness and used for the detection of the roughness level responsible for the resin cement adhesive strength [10,11].

Materials and methods

1. Specimen:

   Pairs of small and large plate specimens (12x12x5 mm^3, 18x20x10 mm^3) were made from semi-sintered zirconia (Aadva zirconia disk: GC) and the surface was smoothed with abrasive paper (#1500). ALL zirconia specimens were sintered for 4 hours at 1500°C and slowly cooled down to 200°C taking for 10 hours. Specimens shrank approximately 20% by sintering (10x10x4 mm^3, 14x18x8 mm^3).

2. Surface treatments:

   Four different types of surface treatment were done for all the specimens. 1) Untreated as control (CTR), 2) 1mm interval groove added by fine diamond bar as low frequency surface roughness (Low), 3) Sandblast treatments (alumina 50 μm, 2 atm) as high frequency surface roughness (High), 4) Sandblast treatments after 1mm interval groove added as low and high frequency (Low+High) (Fig.1).

3. Adhesion:

   Pairs of plate specimen were bonded after surface roughness and contact angle measurements. Resin cement (BeautiCem SA, SHOFU, Japan) was used as adhesive with and without primer treatment (monobond-plus: Ivoclar Vivadent, Principality of Liechtenstein).

   Analysis:

   1) Surface roughness: The surface roughness was measured using SURFCOM 1400A (Tokyo Seimitu, Japan) (measurement length: 8500 μm, measurement speed: 60 μm/sec, plotting points: 14168 pts.). For the specimen Low and Low+High, roughness was measured in the vertical direction to the groove. 2) Shear bond strength: Large plate specimens were adjusted to a fixed side, and small plate specimens were used for the test piece as a load side. Compression shear bond strength was measured using a universal testing machine INSTRON model-5584 (Instron, USA) with a load cell of 5kN and a crosshead speed of 1.0 mm/min (Fig.2). After both plates were adhered, the jig was set to press down the side of small plate specimen. For the specimens Low and Low+High, shear test was done in the vertical direction to the

groove array (Fig.2 b). 3) Wettability: Contact angle was measured using Drop Muster DMs-200 (Kyowa Interface Science, Japan) (n=10) (Fig.3). For the specimens Low and Low+High, roughness was measured in the vertical direction to the groove (Fig.3 b). 4) Fourier analysis: Software of Visual FFT (free soft) and excel (Microsoft) were used for Fourier transform analysis (Fig.6). When $g(x)$ is the original surface roughness profile in real space, the Fourier transform of $g(x)$, the function $G(f)$, is the frequency spectrum, which is the complex variable consisting of a real part (G_r) and imaginary parts (G_i) (eq.1). The power spectrum $|G(f)|$ is used to express the intensity of each frequency peak (eq.2). Function $g(x)$ is the inverse Fourier transform, which is calculated from the real part (G_r) and imaginary parts (G_i) (eq.3). If $G(f)$ is Fourier transformed again (inverse Fourier transform), the original $g(x)$ is obtained. If part of the frequency peaks in $G(f)$, function $H(f)$, is selected, the wave to the selected frequency is reformed in the roughness profile by inverse Fourier transform (eq.4). After the plotting data numbers for measurement length was adapted to the data numbers of 2^n for the Fast Fourier transform analysis, the wavelength was calculated from length and frequency (Table.1).

$$G(f) = \int_{-\infty}^{\infty} g(x)\, e^{-2\pi i f x}\, dx = G_r(f) + iG_i(f) \tag{1}$$

$$|G(f)| = \sqrt{G_r(f)^2 + G_i(f)^2} \tag{2}$$

$$g(x) = \int_{-\infty}^{\infty} G(f)\, e^{-2\pi i f x}\, dx = \int_{-\infty}^{\infty} (G_r(f) + iG_i(f))\, e^{-2\pi i f x}\, dx \tag{3}$$

$$h(x) = \int_{-\infty}^{\infty} H(f)\, e^{-2\pi i f x}\, dx = \int_{-\infty}^{\infty} (H_r(f) + iH_i(f))\, e^{-2\pi i f x}\, dx \tag{4}$$

5) SEM observation: JSM-6390 (JEOL, Japan) was used for Scanning Electron Microscope (SEM) observation after compression shear bond strength test (Fig.4, 7).

Results

1. Surface roughness

Fig.4 shows the SEM observation of specimen surface. Fig.4a is control, b is sandblast treatments, c is fine diamond bar treatments, and d is fine diamond bar and sandblast treatments. Fig.5 shows the corresponding surface roughness curves of each specimen. Fig.4a is the surface of CTR after sintering with the roughness Ra 0.2 μm as shown in Fig.5a. The scratches formed by mechanical polishing with abrasive paper (#1500) before sintering can be still observed with a slight contrast. Fig.4b reveals the surface the specimen of High with the high frequency roughness element formed by sandblast treatments with the Ra 0.4 μm (Fig.5b). Fig.4c shows the mechanical striation used to be formed by fine diamond bar inside the groove with the Ra 11 μm in the center to right side (Fig.5c). In Low+High (Fig.4d) with the

Ra 13 μm (Fig.5d) the mechanical striation used to be formed by fine diamond bar in the groove before sandblast treatment disappeared and high frequency element by sandblast was observed both on the flat surface and in the groove.

2. Fourier analysis

Fig.6 shows the example of Fourier analysis for the specimen Low+High. Right figures show the real space (surface roughness curves) and left figures show the Fourier space (frequency spectrum). The roughness curve of Low+High (Fig.6a) could be converted into power spectrum composed of the waves with different frequencies (Fig.6b) by the Fourier transform. The largest peak detected in the low-frequency area was the wave with the frequency 0.8 mm^{-1} (Fig.6 c). After inverse Fourier transform, the curve reformed from the wave of the frequency 0.8 mm^{-1} (bold line) was approximately in accordance with the roughness repetition of original roughness curve (dotted line) (Fig.6 d). After the selection of peaks in the low frequency range was expanded up to the frequency 2.4mm^{-1} (Fig.6e), the roughness curve of inverse Fourier transform becomes much closer to the original curve (Fig.6f). The largest peak detected in the high-frequency area was the wave of with the frequency 82 mm^{-1} (Fig.6 g). After inverse Fourier transform, the curve reformed from the wave of the frequency 82mm^{-1} was approximately in accordance with the fine roughness repetition of original roughness curve (Fig.6 h).

Surface characterization formed by each surface treatment was summarized in Table 1 with Ra detected by the surface roughness-measuring instrument and the wavelength λ obtained from Fourier analysis.

3. SEM observation

Fig.7 shows the SEM observation of exfoliated surface with resin cement on zirconia after shear bond strength test. Fig.7a is CTR, b is Low, c is Low+High, d is High, e is the enlargement of c, and f is the enlargement of d. The part with black contrast was the remained resin cement and the bright part was zirconia. The contrast exhibits the atomic number effect of reflected electrons with the darker contrast for the resin cement composed of light atoms and the brighter contrast for zirconia including the heavy atom Zr. The fracture mode of resin cement was mostly interface fracture. In the fracture surface of resin cement, the filler particles of composite resin structure could be observed (Fig.7a, f). The resin cement remained partially in the trough as low frequency roughness (Fig.7 b, c). In the specimen with a high frequency element, cohesion failure was slightly observed near the boundary line of resin cement and zirconia (Fig, 7f).

4. Compression shear bond strength

Fig.8 shows the Ra dependence of shear bond strength (White bar: No Primer, Black bar: Primer). The result of compression shear bond strength test had the largest for Ra=0.4μm (14MPa), and the smallest for Ra=11μm (4~5MPa). Compression shear bond strength was not in the order of Ra. Shear bond strength was strong in the specimen with a short wavelength (high frequency element), and weak in the specimen with a long wavelength (low frequency element). Shear bond strength was decreasing in the order of wavelength (Fig.9). The mean values of No Primer and Primer were evaluated by Non- repeated Measures ANOVA to compare the difference in Ra (Fig.8) and wavelength (Fig.9) (n=4) (*$p < 0.05$, **$p < 0.001$). The difference of the primer was small.

5. Wettability

Fig.10 shows the contact angle in the order of wavelength. Contact angle with the water for the low frequency roughness element (longer wavelength: λ=1600μm) has few changes from CTR (80°). Contact angle became smaller (60°) by the high frequency element (shorter wavelength: λ=12μm). All the experimental results were evaluated by Non- repeated Measures ANOVA (n = 10) (**$p < 0.001$).

Discussion

1. Ra and wavelength effect on surface sensitive properties.

Conventionally, as the method to improve adhesive strength, the addition of surface roughness has been done to expect the increase of surface area and interlocking effect. Ra is the most representative value to express surface roughness and conventionally Ra dependence for surface sensitive properties such as adhesive strength and contact angle has been widely investigated. In this study Ra increased noticeably by forming the large grooves of low frequency in Low, Low + High, while Ra showed a slight increase by forming the high frequency roughness in High (Fig.5). The shear bond strength of resin cement on zirconia was not well understood by Ra dependence (Fig.8). The periodicity (wavelength) of the roughness in the plane direction looked to have a larger influence, which depends on the surface-sensitive properties. The Fourier transform that can perform frequency analysis was effective to examine the complicated wave pattern and extract the important wave to contribute to the surface sensitive properties, shear bond strength in this case (Fig.6). The shear bond strength showed the tendency to become stronger as the wavelength became shorter (Fig.9). Thus, the evaluation by the wavelength was more appropriate than Ra to interpret the dependence phenomena of compression shear bond strength in the present case.

The effect of primer was not so obvious in this study. This may be due to the wide size of adhesion area, which may easily include the defect and affect the fracture strength, and also the combination of the used resin cement and the primer of the different makers. However there seems more effect in the use of primer for the specimen with the high frequency element.

2. Fracture mode of resin cement on zirconia

SEM observation showed that resin cement partially remained in the trough, which was expected to contribute the large interlocking effect (Fig.7 b, c). Almost all the specimens showed an interface fracture, except that cohesion fracture was slightly observed in part in the specimen with the high frequency roughness (Fig.7 f). These suggest that the adhesive by chemical bond on zirconia is still insufficient and has a room for further improvement. High and Low+High with the high frequency showed the higher bond strength than the roughness of the low frequency (Fig.9).

The surface modulation of the wavelength 12μm obtained by Fourier analysis could be approximately recognized in High on zirconia surface (Fig.7d). Those surface modulations were responsible for the increase of bond strength.

Wettability was improved for high frequency (short wavelength) than low frequency (long wavelength) (Fig.10), which is more appropriate to understand by the wavelength dependence than Ra.

Conclusion

Conventionally, Ra has been mainly used for the evaluation of the surface roughness (Fig.11). In the present study, attention was paid to the dependency not only on Ra but also wavelength. The influence of the wavelength may be more effective than the Ra, depending on the surface sensitive properties. The short wavelength of 10~20 microns contributed more efficiently to the improvement of the bond strength than the big roughness. Analysis using the Fourier transform was effective for various characteristic examinations of the surface-relating properties such as the adhesive strength.

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Figure caption

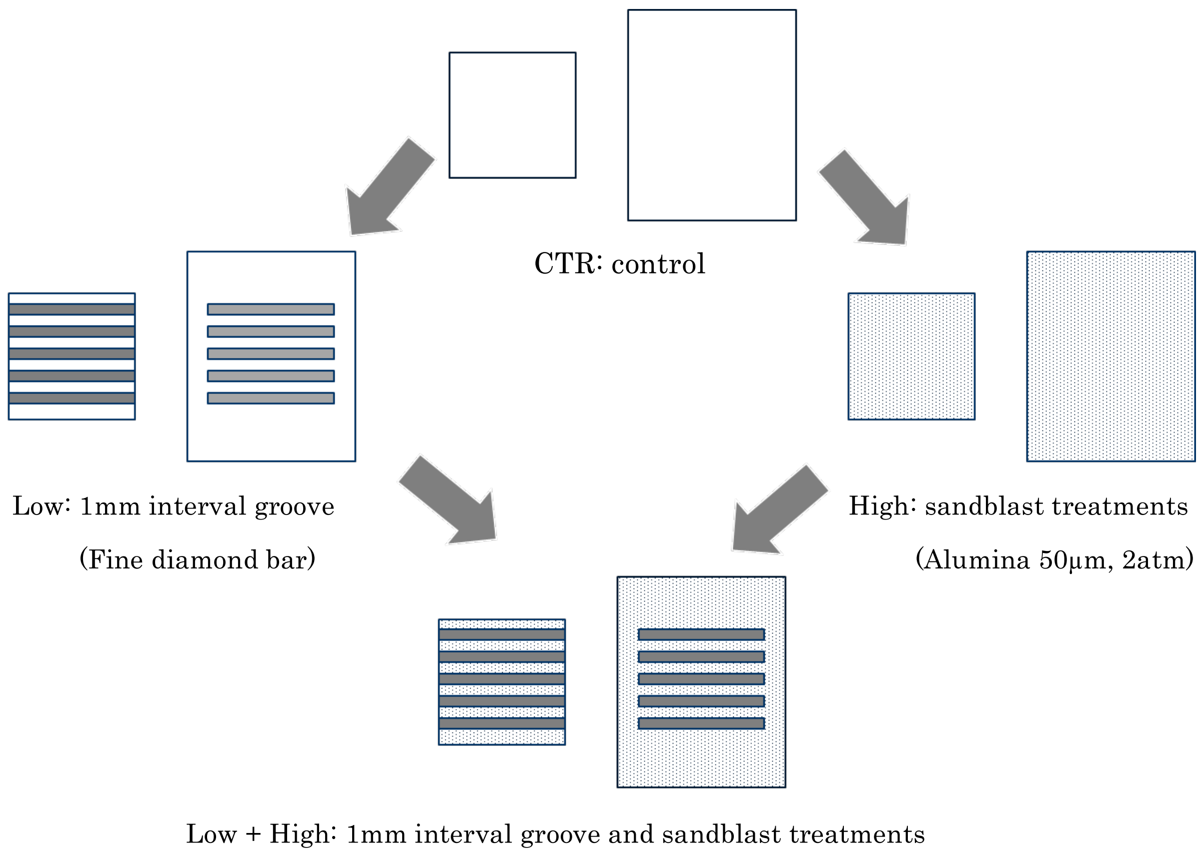


Fig.1 Preparation and procedure of treatments of specimens with surface roughness of the different frequencies (Low, High, Low + High).

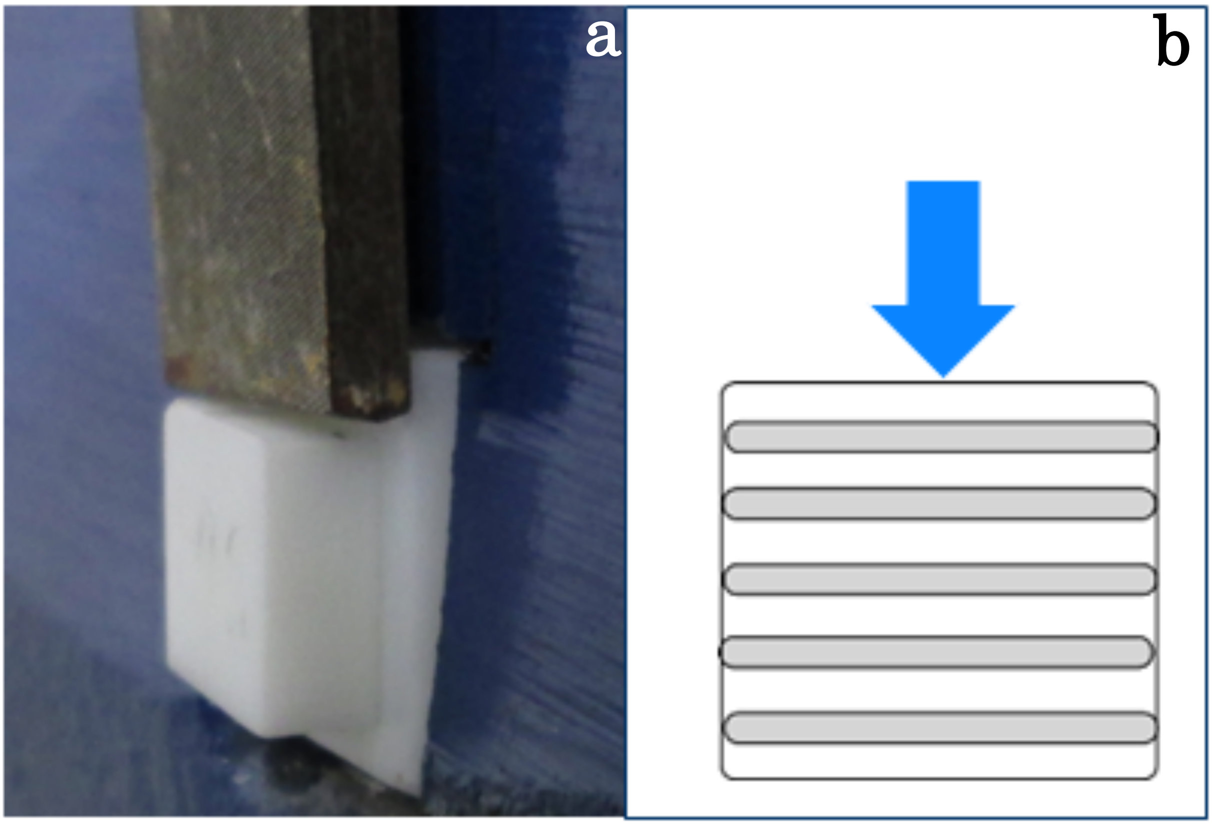


Fig.2 Compression shear bond strength test (a), and the direction of loading on the specimens Low and Low + High (b).

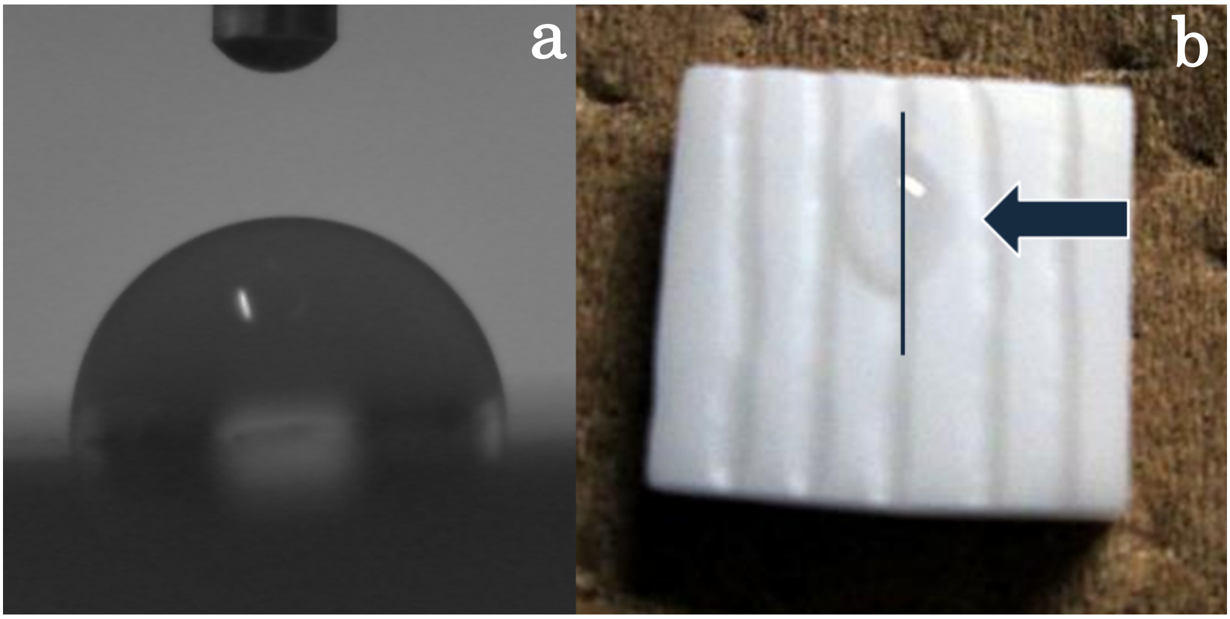


Fig.3 Contact angle measurements (a), and the measurement section for the specimens Low and Low + High (b).

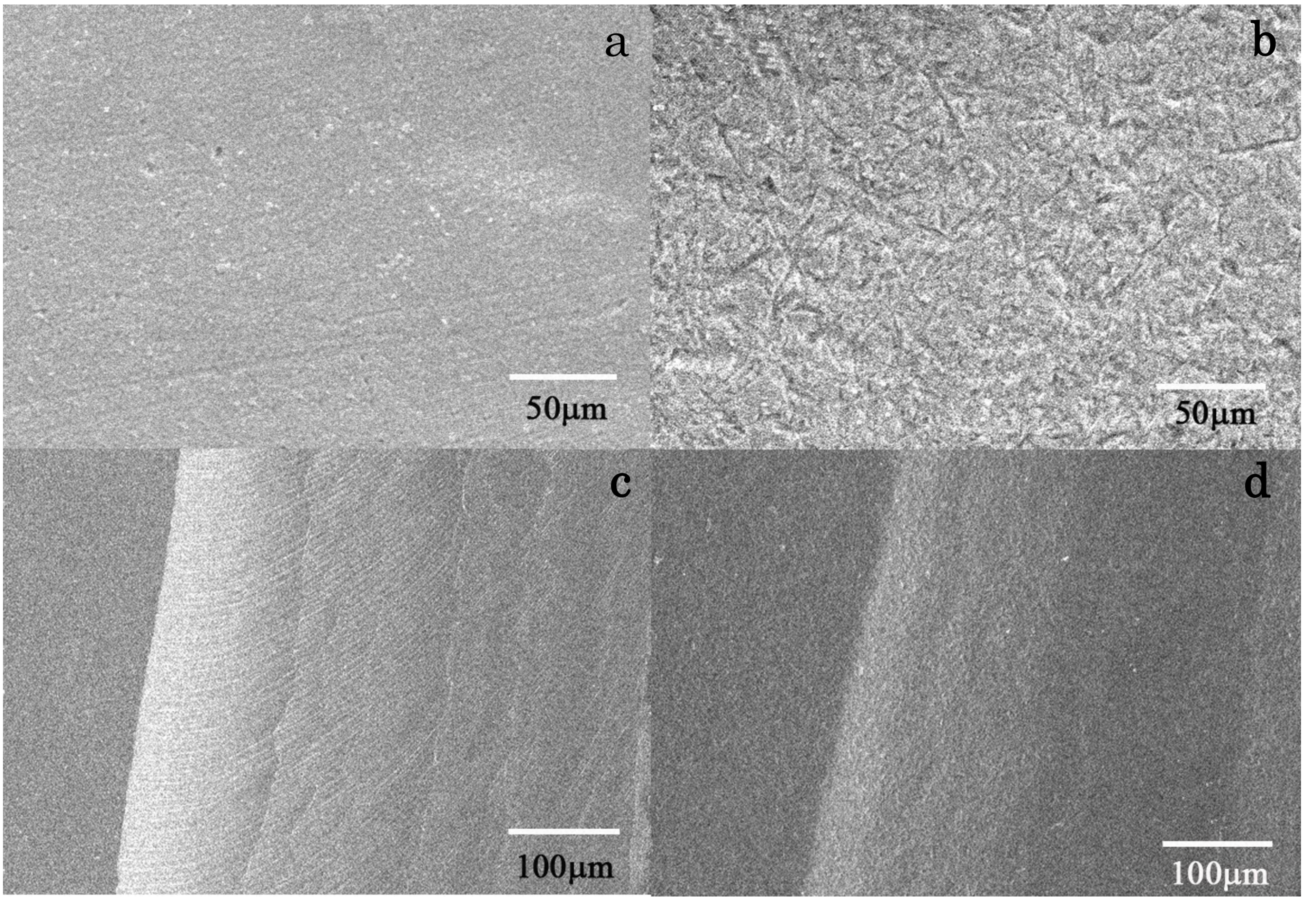


Fig.4 SEM observation of specimen surface a: control, b: sandblast treatments, c: fine diamond bar d: fine diamond bar and sandblast.

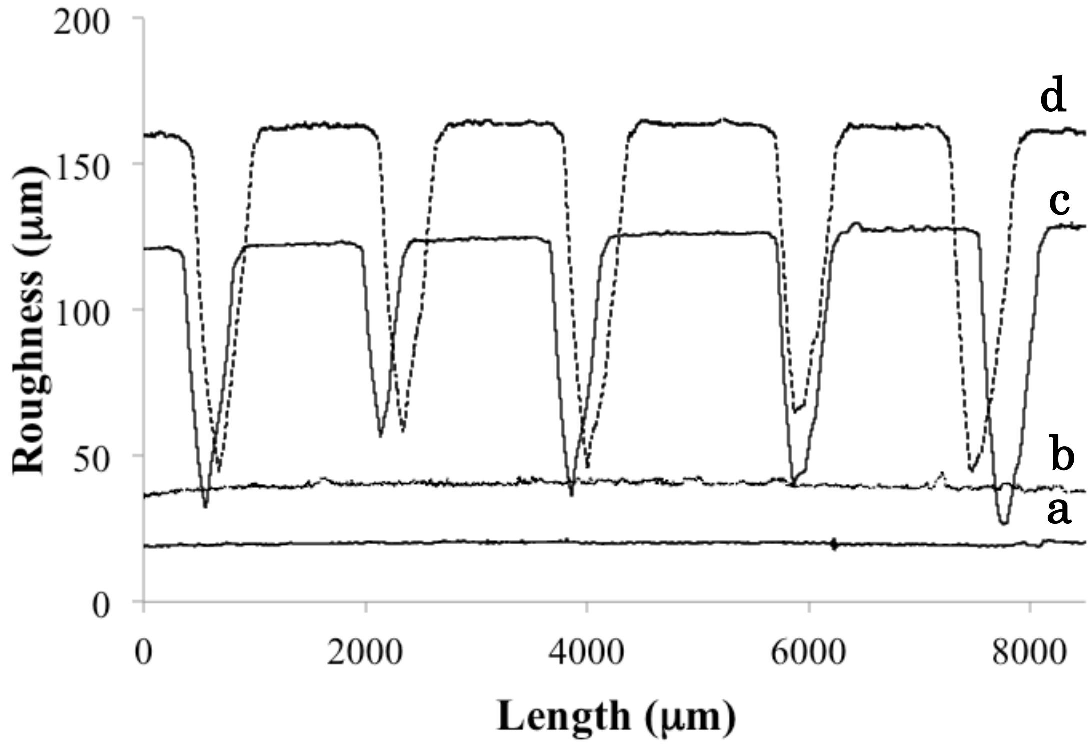
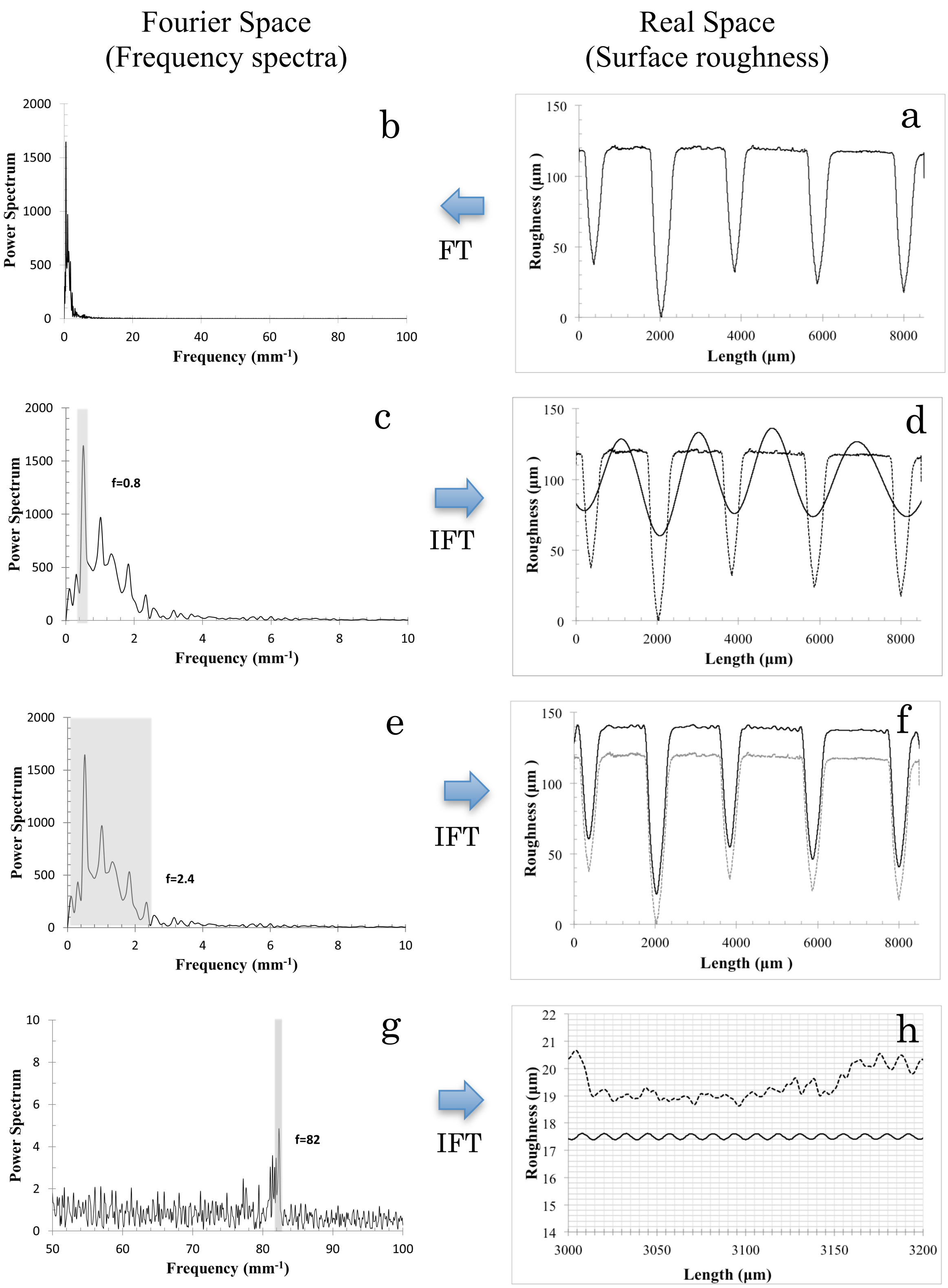


Fig.5 Surface roughness curves of each specimen.

a: CTR (Ra:0.2μm), b: High (0.4μm), c: Low (11μm), d: Low+High (13μm).



Fourier Space
(Frequency spectra)
Real Space
(Surface roughness)
b
Power Spectrum
2000
1500
1000
500
0
0
20
40
60
80
100
Frequency (mm-1)
a
Roughness (µm)
150
100
50
0
0
2000
4000
6000
8000
Length (µm)
FT
c
f=0.8
Power Spectrum
Frequency (mm-1)
0
2
4
6
8
10
d
Roughness (µm)
Length (µm)
IFT
e
f=2.4
Power Spectrum
Frequency (mm-1)
f
Roughness (µm)
Length (µm)
IFT
g
f=82
Power Spectrum
10
8
6
4
2
0
50
60
70
80
90
100
Frequency (mm-1)
h
Roughness (µm)
22
21
20
19
18
17
16
15
14
3000
3050
3100
3150
3200
Length (µm)
IFT

Fig.6 Fourier analysis of the specimen Low+High. Right figures show the real space (surface roughness curves). Left figures show the Fourier space (frequency spectra)

a: Surface roughness profile corresponding to the specimen of Fig.3b and 4b.

b: Frequency spectrum obtained by Fourier transform (FT) of a.

c: Frequency spectrum highlighted with Low-frequency peak at $f=0.8mm^{-1}$.

d: After inverse Fourier transform (IFT) of the highlighted peak in c. The wavelength ($\lambda=1600\mu m$) formed from the selected Low-frequency peak is approximately in accordance with the large roughness repetition of original roughness curve (dotted line).

e: Frequency spectrum highlighted with the extended Low-frequency peaks below $f=2.4mm^{-1}$.

f: After inverse Fourier transform of the highlighted peaks in e. The shape of reformed roughness curve becomes closer to the original curve (dotted line).

g: Frequency spectrum highlighted with High-frequency peak of $f=82mm^{-1}$.

h: After inverse Fourier transform of the highlighted peak in g. The wavelength ($\lambda=12\mu m$) formed from the selected High-frequency peak in g approximately in accordance with the fine roughness repetition of original curve (dotted line).

Table.1 Summary of surface roughness characterization for each specimen: Average values of Ra and wavelength.

	Ra (µm)	**λ (µm)**
CTR	0.2	9800
High	0.4	12
Low	11	1600
Low + High	13	1600+12

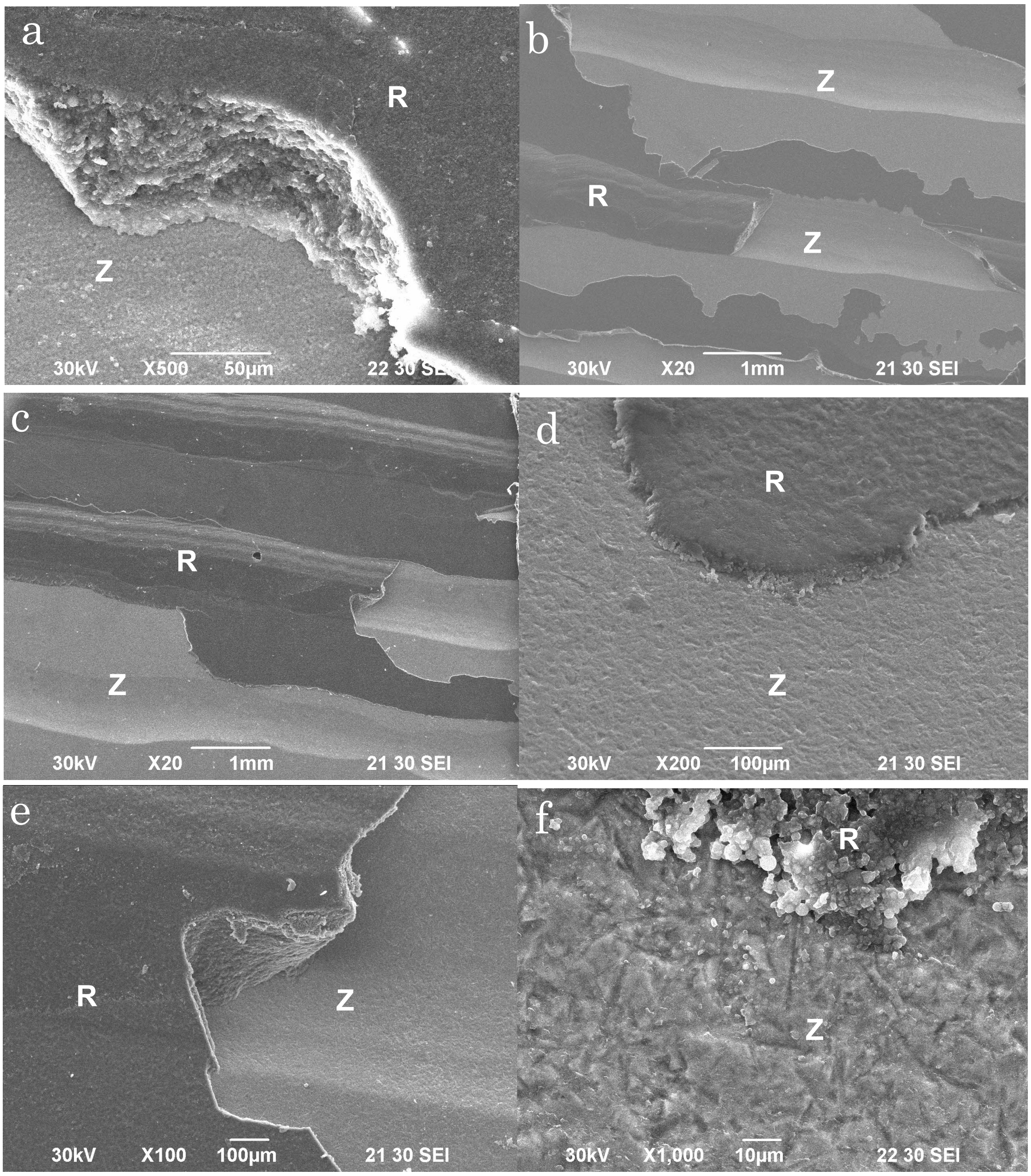


Fig.7 SEM observation of exfoliated surface with resin cement (R) on zirconia (Z) after shear bond strength test. The part with black contrast is the remained resin cement and the bright part is zirconia. a: CTR, b: Low, c: Low + High, d: High, e: Enlargement of c, f: Enlargement of d.

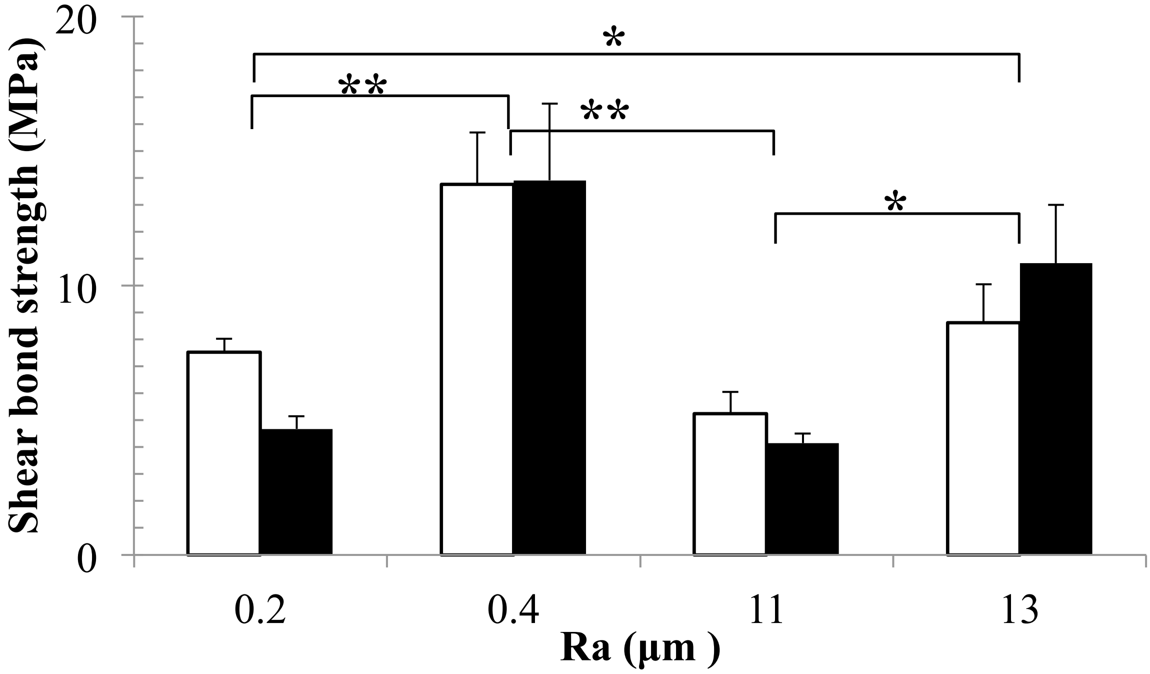


Fig.8 Ra dependence of shear bond strength (White bar: No Primer, Black bar: Primer).

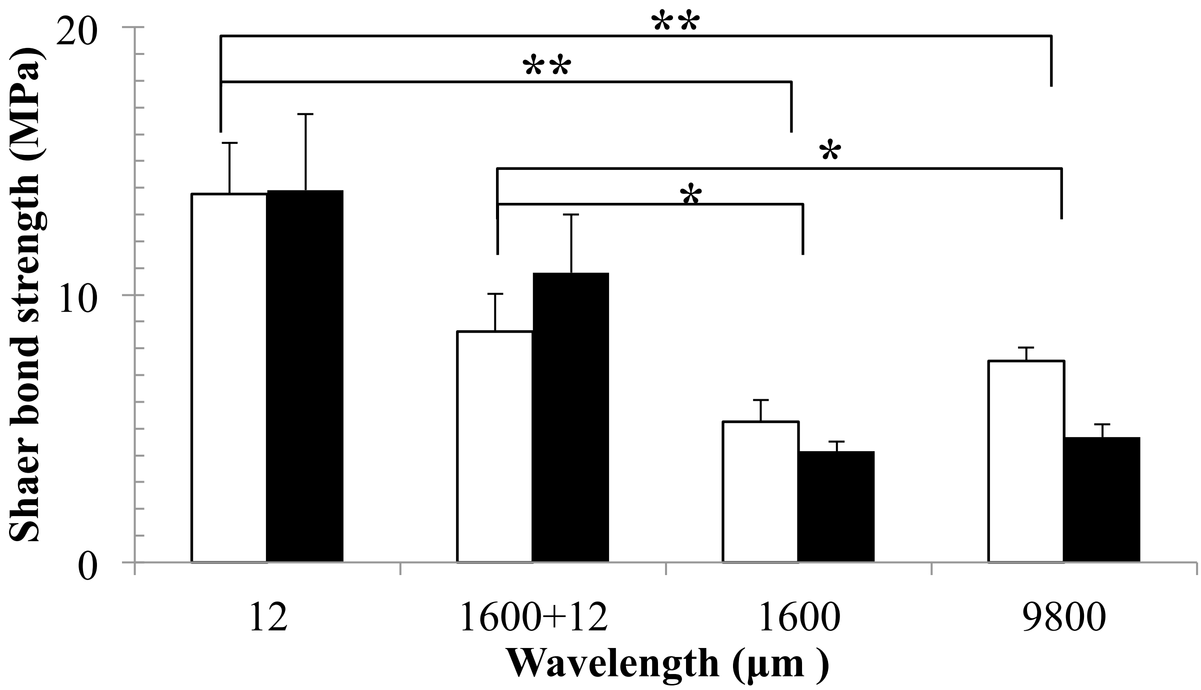


Fig.9 Shear bond strengths in the order of wavelength (White bar: No Primer, Black bar: Primer).

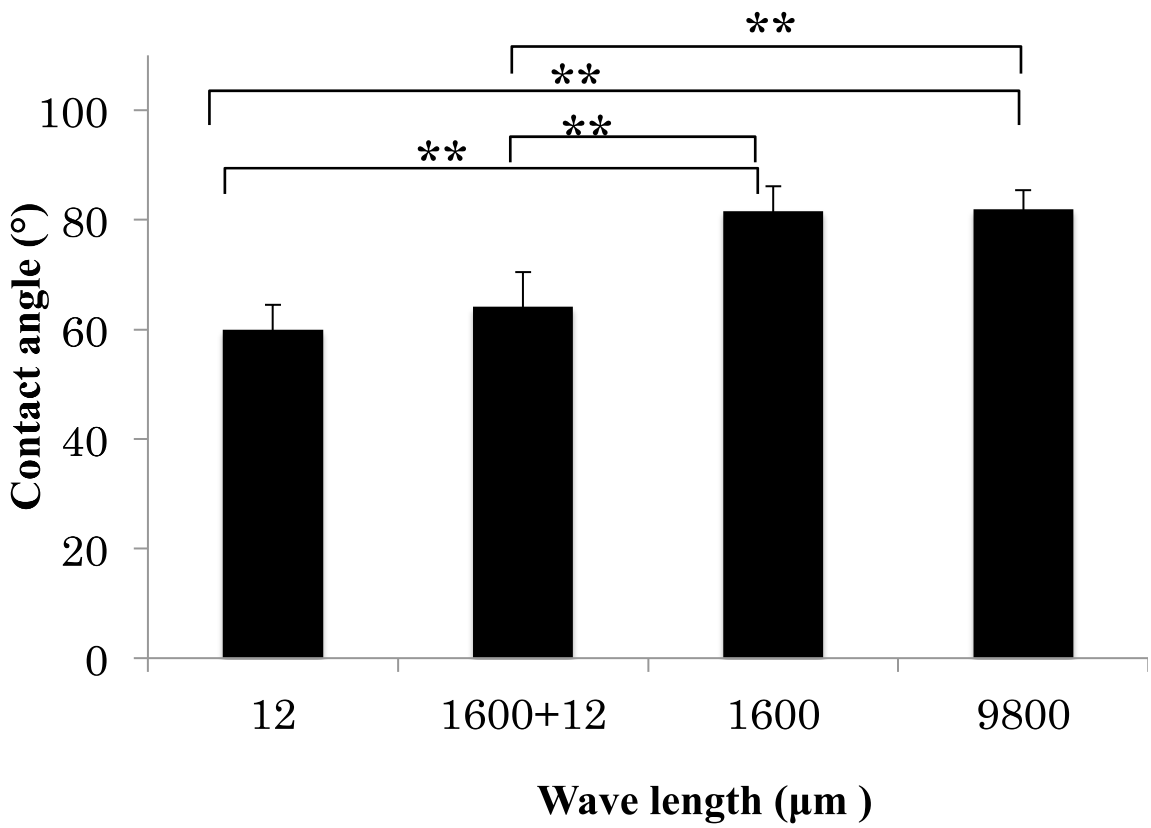


Fig.10 Contact angle in the order of wavelength.

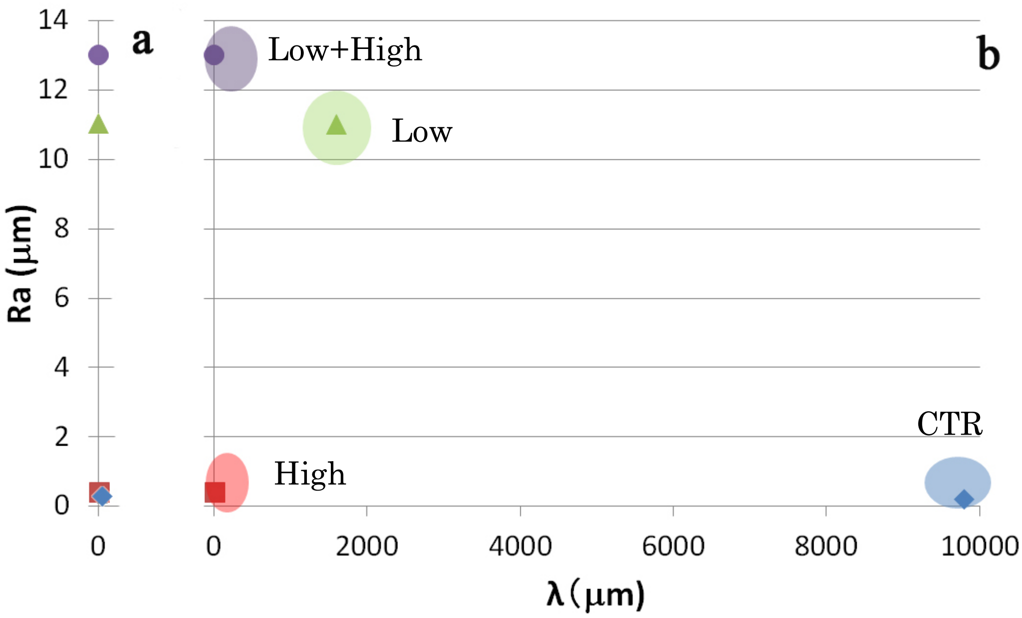


Fig.11 Evaluation conditions of surface roughness properties. a: Ra mono-dependence of surface roughness effect in the conventional researches. b: Ra and wavelength dependence in the present study.