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Influence of hydrolysis degradation of silane coupling agents on mechanical performance of CAD/CAM resin composites: *In silico* multi-scale analysis

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The aim of this study was to build an *in silico* computer-aided design and computer-aided manufacturing (CAD/CAM) resin-composite-block (RCB) model with different silane coupling ratios and to evaluate the physical and mechanical properties of the models, including the elastic modulus, Poisson's ratio, compressive strength, and maximum principal strain. Nanoscale CAD/CAM RCB models were designed by using CAD software that consisted of twelve spherical silica nanofiller particles and a resin matrix. Seven nanoscale models with different silane coupling ratios were prepared with the same filler volume contents. Homogenization analysis was conducted by using voxel-base finite-element analysis software to predict the elastic moduli and Poisson's ratio of the macro CAD/CAM RCB. Localization analysis was used to analyze the maximum principal strain distribution in the hydrolysis layer. *In silico* multi-scale analysis demonstrated that the compressive strength of the CAD/CAM RCB was reduced with a decrease in the silane coupling ratios of the fillers.

Keywords: Computer-aided design and computer-aided manufacturing resin composite block, Restorative material, Finite-element analysis, Multi-scale analysis, Hydrolysis degradation

INTRODUCTION

Since the introduction of computer-aided design/computer-aided manufacturing (CAD/CAM) techniques in dentistry, the demand for restoratives produced by the CAD/CAM technique has been increased steadily[1] because of their promising clinical performance[2,3], esthetic appearance[4], uniform quality, and cost-effectiveness[5]. Among the CAD/CAM restorative materials, CAD/CAM resin composite blocks (RCB) have been selected over CAD/CAM ceramic blocks because of their machinability[6,7], edge toughness[8], and stress-relaxation behavior for implant restorations[9]. The mechanical properties of the CAD/CAM RCB are improved considerably by applying a high-pressure and high-temperature polymerization technique[10] and by incorporating nanofiller particles[11]. However, some mechanical properties, including the flexural strength and elastic modulus, of resin composite materials remain inferior to that of ceramic materials, such as lithium disilicate glass ceramic[12] or yttria-stabilized tetragonal zirconia polycrystals[13].

When fillers are incorporated into the CAD/CAM RCB resin matrix, the filler surfaces are treated by silane coupling agents, which promote adhesion between the inorganic fillers and organic matrices through dual reactivity[14]. The silane mixture does not tend to show a perfect coupling ratio because the organic acid that is added to the silane to promote bonding on the organic matrix side may decrease the bond durability on the filler side[15]. Furthermore, filler-matrices that are formed by the silane layer could fail because of the hydrolysis of silane coupling agents[16], which can occur in watery intraoral environments. Thus, defective filler-matrix interfaces arise because of the reasons described above, and the mechanical properties of the CAD/CAM RCB can be decreased. It is not known how the defective filler-matrix interfaces affect the mechanical properties of the CAD/CAM RCB, because it has not been possible to establish reasonable *in vitro* models with controllable silane coupling ratios thus far.

Instead of *in vitro* models, *in silico* three-dimensional finite-element analysis has been used to predict the properties of resin composite materials, such as resin properties with various filler contents[17] or filler sizes[18]. Yamaguchi *et al*. have confirmed that predicted flexural strengths by *in silico* analysis was significantly correlated to those obtained by *in vitro* tests[19]. By using nanoscale properties of CAD/CAM RCB components, including the mechanical properties of silica fillers and resin matrices, macroproperties, such as the elastic modulus and Poisson's ratio of the CAD/CAM RCB can be predicted by homogenization analysis[18,20]. When a force is added to the CAD/CAM RCB at a macroscale, the strain and stress distribution of the CAD/CAM RCB, including the maximum principal strain (MPS), which is known as the failure criteria of composite materials[19,21] at a certain nanoscale area can be analyzed by localization analysis. By *in silico* multi-scale analysis, which is an *in silico* technique that combines homogenization and localization analysis, the mechanical properties of CAD/CAM RCB under various conditions can be investigated. *In silico* multi-scale analysis has been established to solve nonlinear elastic problems of heterogeneous substance considering the material properties in micro-scale such as composites[22] and recently introduced to

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predict mechanical properties of composites[18], porous ceramics[23], and titanium[24].

The aim of this study was to build *in silico* CAD/CAM RCB models with different silane coupling ratios and to evaluate the physical and mechanical properties of the models, including the elastic modulus, Poisson's ratio, compressive strength, and MPS.

MATERIALS AND METHODS

Nanoscale models with different silane coupling ratios

Nanoscale models of CAD/CAM RCB were designed by using CAD software (Solidworks Simulation 2011, Dassault Systèmes Solidworks, Waltham, MA, USA) that consisted of spherical silica 12 nanofiller particles with a 40-nm diameter and a resin matrix (urethane dimethacrylate: UDMA/triethyleneglycol dimethacrylate: TEGDMA) (90×90×90 nm) by following material composition of the commercially available CAD/CAM RCB: Katana Avencia Block (Kuraray Noritake Dental, Tokyo, Japan)[20] (Fig. 1). Seven nanoscale models with different silane coupling ratios (75.5, 81.7, 87.9, 91.7, 94.4, 98.1, and 100%) were prepared with the same filler volume contents of 55.161% (Fig. 2). Each silane coupling layer was defined as 2.0 nm ensure the minimum thickness (one voxel size: 1.0 nm), that is close to the theoretical silane chain length[25]. The material properties of the silica and UDMA/TEGDMA are summarized in Table 1.

Homogenization analysis

The elastic modulus and Poisson's ratio for the macroscale CAD/CAM RCB were calculated by homogenization analysis in voxel-based finite-element analysis software (VOXELCON2015, Quint, Tokyo, Japan). Each model was isotropically voxelized by 1.0 nm in resolution and the total voxel number was 729,000. The element-by-element method was selected as a matrix solver with an error of 0.0001. The models were analyzed for seven different silane coupling ratios.

Macroscale model for compressive analysis

A macroscale model of the CAD/CAM RCB (3×3×3 mm) was designed by using CAD software (Fig. 1) for *in silico* compressive analysis. The macroscale model was isotropically voxelized by 0.05 mm in resolution and the total voxel number was 216,000.

Compressive analysis

The bottom surface of the macroscale model was fixed and a 6,075 N load was applied on the top center surface of the macroscale model. An *in silico* compressive analysis was conducted by using voxel-based finite-element analysis software with an elastic moduli and Poisson's ratios from the homogenization analysis. Compressive strengths were defined as values when the fracture loads exceeded 6,075 N. The MPS distribution in the macroscale model was observed and normal strains in the x-, y-, and z-axes and shear strains in the yz-, zx-, and xy-planes were recorded at the maximum MPS value.

Localization analysis

The MPS distribution in the nanoscale models where the

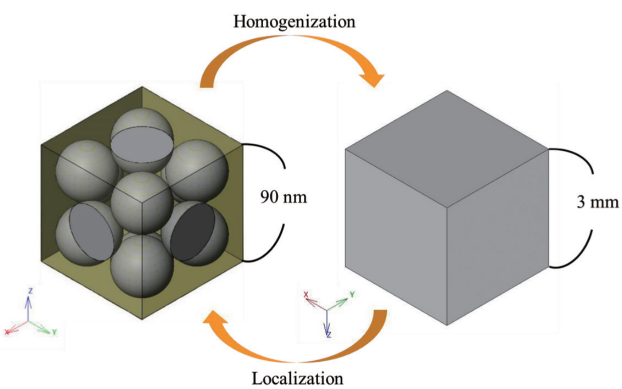

Fig. 1 Nanoscale model of CAD/CAM RCB.
Silica fillers (gray) and resin matrix (transparent yellow).

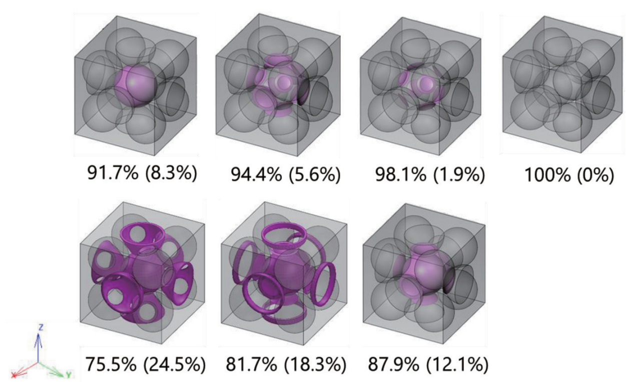

Fig. 2 Hydrolysis layer of silane coupling agents (purple) and resin matrix (transparent gray).
Elastic modulus of the hydrolysis layer was set to 0 GPa and a 2-nm thickness.

Table 1 Material properties of CAD/CAM RCB

	Elastic modulus (GPa)	Poisson's ratio
Silica	72	0.16
UDMA/TEGDMA	2	0.35

maximum MPS values were obtained in the macroscale model was examined by localization analysis. The maximum MPS values at the nanoscale that related to the threshold of fracture initiation were compared.

RESULTS

Elastic modulus and Poisson's ratio

Elastic moduli and Poisson's ratios that were obtained by the homogenization analysis are shown in Figs. 3 and 4, respectively. For a silane coupling ratio below 87.2%, the change in elastic moduli converged, whereas the change in Poisson's ratios showed an opposite trend.

Compressive strength

The *in silico* compressive analyses showed that maximum MPS values were observed at the vertex on the top surface of the CAD/CAM RCB. Normal strains in the x-, y-, and z-axes at the maximum MPS values were 8.89×10^{4}, 8.89×10^{4}, and -2.03×10^{5}, respectively. The shear strains in the yz-, zx-, and xy-planes at the same location were 2.82×10^{4}, -2.82×10^{4}, and -4.16×10^{4}, respectively. The compressive strengths of each silane coupling ratio are shown in Fig. 5. For the silane coupling ratio below 87.2%, the change in compressive strength and elastic moduli converged.

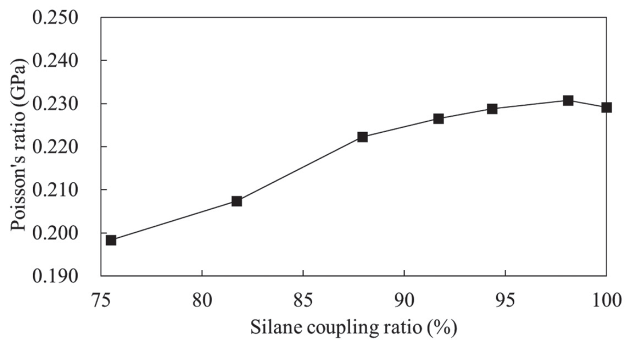

Fig. 4 Poisson's ratios obtained by *in silico* homogenization analysis of nanoscale models of CAD/CAM RCB for each silane coupling ratio.

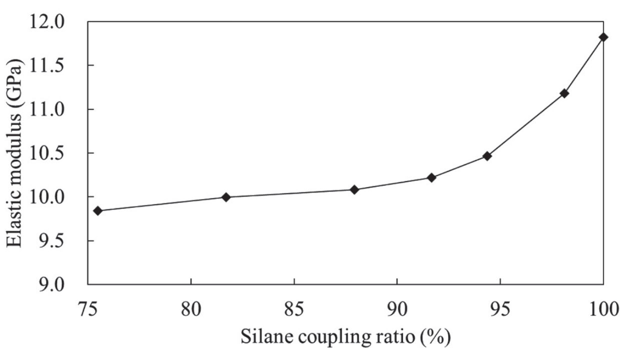

Fig. 3 Elastic moduli obtained by *in silico* homogenization analysis of nanoscale model of CAD/CAM RCB for each silane coupling ratio.

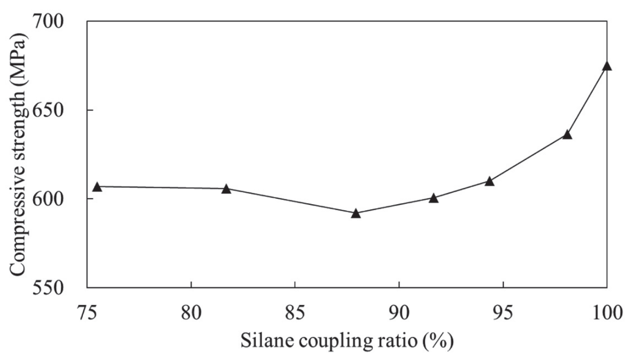

Fig. 5 Predicted compressive strengths of macroscale model of CAD/CAM RCB.

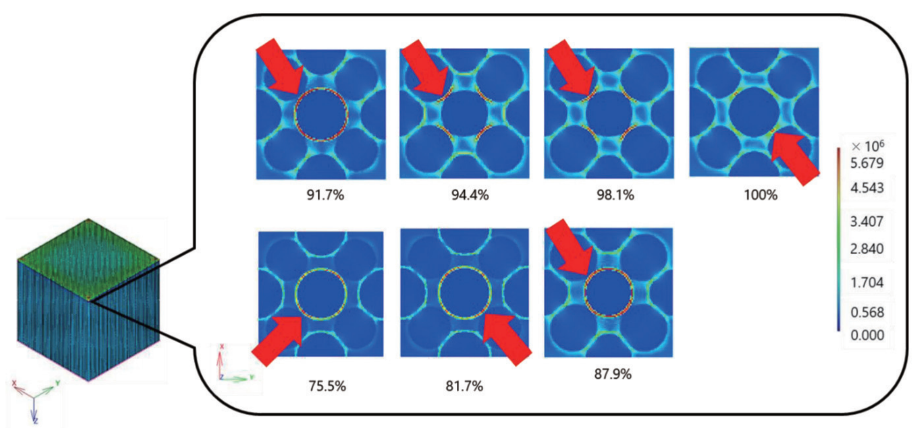

Fig. 6 MPS distribution obtained by *in silico* localization analysis at section of nanoscale model of CAD/CAM RCB.
Each red arrow indicates the location of the maximum observed MPS.

MPS at the nanoscale

The MPS distribution in the nanoscale model for seven different silane coupling ratios is shown in Fig. 6. The maximum MPS values for a 75.5, 81.7, 87.9, 91.7, 94.4, 98.1, and 100% silane coupling were 7.22×10^6, 7.12×10^6, 1.13×10^7, 1.12×10^7, 9.62×10^6, 9.25×10^6, and 5.68×10^6, respectively. All maximum MPS values were observed at a hydrolysis layer that excluded the 100% silane coupling model.

DISCUSSION

We have established an *in silico* multi-scale analysis for CAD/CAM RCB with different silane coupling ratios. The multi-scale analysis could clarify the influence of hydrolysis of the silane coupling agents for CAD/CAM RCB on the mechanical performance.

Hydrolysis of the silane coupling agents was assumed as a 2-nm-thin layer in a resin matrix with no elasticity (0 GPa, that is no bonding condition). Those layers were designed as a complete symmetric model to avoid any mechanical property anisotropy, which could focus only on factors of hydrolysis degradation. The detection of silane-coupling-agent hydrolysis by CAD/CAM RCB by *in vitro* tests remains challenging. The *in silico* model that was established in this study may provide an alternative to *in vitro* tests to investigate the influence of silane-coupling-agent hydrolysis on the mechanical performance of CAD/CAM RCB.

The mean of the elastic modulus of a CAD/CAM RCB model that was based on cryo-electron microscopy images, and assuming perfect silane coupling among the amorphous fillers and resin matrix has been reported as 10.71±1.79 GPa[20]. The elastic modulus for a 100% silane coupling model consists of spherical fillers and resin matrix was 11.82 GPa in this study. This result suggests that the filler shape (spherical or amorphous) does not influence the elastic modulus of the CAD/CAM RCB significantly and may influence the shrinkage-stress/strain kinetics[26,27]. The elastic modulus of the 75.5% silane coupling model decreased to 16.8% compared with that of the 100% silane coupling model. These results support that excessive water uptake may decrease the elastic modulus for the resin composites further[28] compared with the ceramics because of the hydrolytic degradation[16]. The decrease in elastic modulus may induce the debonding of CAD/CAM resin composite crowns by pumping or deformation and margin spread[29].

The Poisson's ratio of each CAD/CAM RCB ranged from 0.198 to 0.229 (difference=0.031, 13.5% reduction). The Poisson's ratios of the four different commercial CAD/CAM RCB have been reported from 0.277 to 0.306 with no statistically significant difference[30], which suggests that the change in Poisson's ratio that was obtained in this study may not cause hydrolytic degradation.

By decreasing the silane coupling ratio, the compressive strength decreased by 10.1%. The relationship between the silane coupling ratio and the compressive strength was non-linear, which suggests that the compressive strength has a potential for improvement by increasing the silane coupling ratio of 94.4%. The larger compressive strength may improve the fatigue resistance of the CAD/CAM resin composite crowns[18]. Silane coupling agent, gamma-methacryloxypropyl trimethoxysilane (γ-MPTS) was used mostly for commercial CAD/CAM RCB and resin composites for filling. By using or developing hydrophobic silane coupling agents[31], the mechanical performance of the CAD/CAM RCB may be improved.

The MPS that was used in this study has been reported as a failure criterion to predict flexural strengths for resin composites[19]. All maximum MPS values that were obtained by localization analysis were observed at a hydrolysis layer that excluded the 100% silane coupling model, which suggests that fracture initiation may occur at the location hydrolysis of the silane coupling agents. For the 87.9% and 91.7% silane coupling models with a spherical thin hydrolysis layer that covered the center filler, the maximum MPS values were larger than those of other models. These results suggest that fracture initiation is related to the silane layer morphology.

Within the limitation of this *in silico* multi-scale analysis, the influence of hydrolysis of the silane coupling agents for CAD/CAM RCB on mechanical performance could be quantified. As a further study, long-term water absorption tests, such as for a month or a year and the establishment of an approach to detect free hydroxyl groups are ongoing to investigate the change in elastic modulus of the CAD/CAM RCB *in vitro*. Additionally, the investigation of hydrolysis degradation in a resin matrix is important to elucidate which materials (silane coupling agents or resin matrix) improve the mechanical performance of the CAD/CAM RCB most. By comparing the *in vitro* compressive strength of the CAD/CAM RCB, a percentage of silane-coupling-agent hydrolysis may be predictable. The percentage is useful to understand the current hydrolysis of silane coupling agents of the test CAD/CAM RCB and to accelerate the development of new CAD/CAM RCB with an excellent mechanical performance.

CONCLUSIONS

The *in silico* multi-scale analysis that was established in this study shows that the compressive strength of the CAD/CAM RCB was reduced when the silane coupling ratios of the fillers decreased. This approach would be useful to accelerate the development of new CAD/CAM RCB with an excellent mechanical performance.

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CONFLICT OF INTEREST

None.

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