Effects of Heat and pH in Silanation Process on Flexural Properties and Hydrolytic Durabilities of Composite Resin after Hot Water Storage

Mansuang ARKSORNNUKIT¹, Hidekazu TAKAHASHI², Norihiro NISHIYAMA³ and Prasit PAVASANT⁴
¹Department of Prosthodontics, Faculty of Dentistry, Chulalongkorn University, Henri-Dunant Road, Bangkok 10330, Thailand
²Advanced Biomaterials, Graduate School, Tokyo Medical and Dental University, Yushima 1-5-45, Bunkyo-ku, Tokyo, 113-8549, Japan
³Department of Dental Material, Nihon University School of Dentistry at Matsudo, 870-1, Sakaecho-Nishi, Matsudo, Chiba 271-8587, Japan
⁴Department of Anatomy, Faculty of Dentistry, Chulalongkorn University, Henri-Dunant Road, Bangkok 10330, Thailand

Corresponding author, E-mail: Mansuang.A@chula.ac.th
Received January 15, 2004/Accepted March 19, 2004

The objectives of this study were to evaluate the effect of heat application after silanation and the pH effect of silanated solution on flexural properties and hydrolytic durability of experimental composites. A spherical-shaped filler was silanated with 0.66 mass% of ϒ-MPTS in 70 vol% ethanol solution. For the heating effect, the filler was heated after silanation for 3 hours at 50°C, 80°C and 110°C. For the effect of pH, ethanol solution with HCl solution of pH 1, 2 and 4 were used. All fillers were mixed to make photopolymerized experimental composite resins. All specimens after immersion in 37°C water for 24 hours were additionally immersed in Soxhlet’s extractor for another 1, 7 and 28 days. A three-point bending test was performed in 37°C water. The heat application of 50°C and 80°C increased flexural strength while heat of 110°C and pH showed no effects on flexural properties at p<0.05.

Key words: ϒ-MPTS, Flexural properties, Hydrolytic durability

INTRODUCTION

The use of composite resin in restorative dentistry has gained popularity. The durability of composite resin placed intraorally should be maintained to ascertain the long term success of the restoration. From previous studies, the degradation of composite is believed to occur from the resin matrix¹⁻³, the degradation of filler⁴⁻⁶ and hydrolytic instability of silane coupling agent at the polymer and filler interface⁷,⁸.

There were several methods used in evaluation of durability: wear⁹,¹⁰, thermocycling, immersion in water¹¹,¹² and solvent¹³, cyclic loading¹¹,¹⁴, biological stimulated deterioration utilizing a specific enzyme¹⁵ and thermal stress in water and ethanol¹⁶. Among these various accelerated aging methods, thermal stress by boiling is considerably suitable to evaluate the durability as shown in previous studies¹⁷.

Several studies have been performed to evaluate the resin matrix and durability of filler particle. Regarding silane coupling agent, there were several studies about the introduction of new silane coupling agents in order to achieve a more hydrolytic durability of the silane coupling agent layer¹⁸⁻²⁰. Nevertheless, ϒ-methacryloyloxypropyltrimethoxysilane (ϒ-MPTS) is still the popular silane coupling agent used in dental restorative composite resin. The silanation process has also been studied to achieve good composite performance. These include the amount, pH and heat²¹,²². Recently, the amount effect of ϒ-MPTS adsorbed on silica surface on durability of composite has been reported. The existence of ϒ-MPTS is a prerequisite to provide hydrolytic durability for composite resins. This is providing that a certain amount of ϒ-MPTS is applied²³. Slightly acidity of the solution in hydrolyzing the silane coupling agent was believed to accelerate the hydrolysis of the methoxy group in the ϒ-MPTS, and to decelerate the condensation amongst the hydrolyzed silane species. The application of heat in drying silane coupling agent priming ceramic before bonding to visible light cured resin resulted in the higher shear bond strength²⁴. There is a lot of information concerning temperature used in treating the filler²⁵⁻³⁰. To date, there is no consensus on the proper temperature used for drying filler.

Therefore, it was the objective of this study to evaluate separately the effect of temperature in drying silanated filler and pH of the silanated solution used in hydrolytic durability of experimental composite.

MATERIAL AND METHODS

Silanation of filler

A spherical-shaped filler (SS15, Osaka Chemical, Osaka, Japan), with a diameter of 1.5 μm, was used...
in this study. Gamma-MPTS (KBM 503, Shin-Etsu Chemical, Tokyo, Japan) was used in silanating the filler. For temperature effect, the filler was silanated with 0.66 mass% of χ-MPTS in an adequate amount of 70 vol% ethanol aqueous solution. The ethanol aqueous solution was prepared by diluting 95% ethanol (Wako Pure Chemical, Osaka, Japan) with deionized water (Elix 3, Japan Millipore, Tokyo, Japan; pH is around 5.5). After the solvent had evaporated at room temperature, the filler was randomly divided into three groups and each was subjected to heating temperature at 50°C, 80°C and 110°C for three hours. After the fillers cooled down to room temperature, they were ready to make composite. For the effect of pH, filler was also silanated with 0.66 mass% of χ-MPTS with 70 vol% ethanol solution with pH equaling 1, 2, and 4 by adjustment with hydrochloric acid (Merck, German) and deionized water. For the control group, the filler was silanated with 0.66 mass% of χ-MPTS using 70 vol% ethanol solution. After silanation, the filler was left to dry at room temperature for an additional 14 days prior to make composite.

**Characteristics of silanated filler**

Silanated filler of each group was investigated to understand the characteristics of silanated filler by a differential scanning calorimeter (DSC). Heat flow of approximately 10 mg of fillers was monitored during heating from 25°C to 300°C using a differential scanning calorimeter (DSC3100, Bruker AXS, Yokohama, Japan) at a heating rate of 10°C/minute. Five measurements were carried out for each filler condition. Measured heat flows were analyzed with one-way ANOVA and Dunnett comparison at p<0.05.

**Composite resin preparation**

The resin matrix of all experimental composite was 70/30 mass% of urethane dimethacrylate (UDMA; Art resin SH-500B, Negami Chemical, Ishikawa, Japan) and triethylene glycol dimethacrylate (TEGDMA; 3G, Shin Nakamura, Wakayama, Japan). Zero point five mass% of camphorquinone (Aldrich Chemical, Milwaukee, Wis) and 1.0 mass% of dimethyliymethacrylate (Wako Pure Chemical, Osaka, Japan) were used as the photoinitiator and reducing agent, respectively. All materials were used as received without any further purification. The filler loading of all experimental composite resins was kept constant at 65 mass%. One hundred and sixty eight specimens, 24 from each composite, were fabricated from seven experimental composite resins. There were T50, T80 and T110 groups for effect of temperature and pH 1, pH 2 and pH 4 groups for effect of pH while the silanated filler using ethanol solution without adjusting pH at room temperature served as the control for both groups.

**Flexural test**

The 2x2x25 mm rectangular specimen was fabricated as suggested in ISO 4049:2000. The specimen was irradiated using a laboratory light-polymerizing unit (Labolight II, GC, Tokyo, Japan) for 3 minutes from each side of the specimen. The specimen was later kept in the 37°C water. After 24 hours storage in the incubator at 37°C, six specimens were randomly selected from each group and tested for baseline value at day 0. The remaining specimens were then placed in the Soxhlet's extractor and subjected to the boiling water condition for additional 1, 7, and 28 days. At the end of each time, six specimens were again randomly selected and tested. All specimens were subjected to a 3-point bending test in 37°C water using a micro material test machine (MMT-250N, Shimadzu, Kyoto, Japan). Flexural strength and flexural modulus were obtained from each test using analyzing software (Trapezium II, Shimadzu, Kyoto, Japan). Each effect was separately analyzed using 2-way ANOVA and all groups were further analyzed with the Dunnett comparison. Statistical significance was considered to be p<0.05.

**SEM observation**

Fracture surfaces of specimens after the flexural test were gold sputter coated and examined by secondary electron imaging using a scanning electron microscope (Hitachi S-4500, Tokyo, Japan).

**RESULT**

Figures 1 and 2 show the flexural strength and flexural modulus of the experiment composites at each storage period. For the temperature effect, statistic analysis showed significant differences of two main factors, the temperature factor and storage period, for flexural strength, while flexural modulus showed significant differences of two main factors and the interaction. The flexural strengths of T50 and T80 were significantly greater than those of the control and T110 group (Fig. 3). However, the effect of water storage on flexural strength did not change like the temperature effect because the interaction was not significant. The flexural modulus of T110 was significantly greater than that of the control (Fig. 4). The flexural modulus showed the maximum value at 1 day storage. Regarding pH effect, there was no significant difference in the main factor, pH, on both flexural strength and flexural modulus; however, significant differences in storage period and interaction were detected. Flexural strength and flexural modulus showed the maximum value after storage.

A broad exothermal peak from 110 to 210°C was observed by DSC. Amounts of exothermal heat were exhibited in Fig. 5. The exothermal heat, associated with the polymerization of the vinyl group for the
Fig. 1 Effect of silanation conditions on flexural strength over storage period.

Fig. 2 Effect of silanation conditions on flexural modulus over storage period.

Fig. 3 Flexural strength of different heating temperature and pH. Bars with an asterisk were significantly different from the control.

Fig. 4 Flexural modulus of different heating temperature and pH. A Bar with an asterisk was significantly different from the control.

Fig. 5 Heat flow of fillers with various silanation condition. Bars with an asterisk were significantly different from the control.

Increasing the silane species adsorbed on the silica surface of the control was approximately 4.9 J/g. The heat flow significantly decreased with heating treatment, while amounts of exothermal heat did not change or increase with acidic solutions.

SEM images of fracture surfaces from all groups except T110 showed that the filler surface was covered with matrix resin. However, the fracture surface of T110 showed exposed filler surface and dimple due to filler drop-out, which demonstrated poor bonding between the filler and matrix (Fig. 6).

DISCUSSION

In this study, a spherical shaped silica was used in order to avoid the interlocking effect from the filler of other shapes. The result of the study suggested that application of heat less than 80°C for drying filler resulted in better flexural strength. The result of this study is in agreement with Nishiyama et al. The utilization of 110°C in drying silanated filler may promote the chemisorption of the silane molecule to the silica surface, the condensation of the silane species, as well as the polymerization of the vinyl group amongst the silane species. Thus the cross-linked multilayer, consisting of a chemisorbed
layer associated with the siloxane bond between the silane species and the silica surface, and a physisorbed layer associated with the hydrogen bond and van der Waals force on the silica surface might be formed. The exothermal heat monitored by DSC decreased with the increase of the silanation process temperature. This decrease suggests that some of the silane species adsorbed on the silica surface underwent polymerization during the heating process for drying. Therefore, heating of the silanated silica at 110°C might cause a decrease in flexural strength, since the probability in the copolymerization between the silane species and matrix resin decreased. This finding was also supported by SEM of the fracture surface of 110°C, which showed obviously poor bonding between the filler and resin matrix.

The effect of temperature used in drying filler on flexural modulus was not strongly affected as in flexural strength. The flexural modulus of all groups showed comparable values even with significant differences as shown in statistic analysis. Stiffness may result from postpolymerization of the resin matrix and the interlocking effect of filler particle in composite.

From the result of this study, there was no effect of pH on hydrolytic durability of composite on both flexural strength and flexural modulus. According to the results of DSC observation, the amounts of exothermal heat were the same among pH 1, pH 4 and control. This finding suggests that the reactivity of the vinyl group of the silane species was not influenced by the differential in the chemical structure and molecular weight of the silane species adsorbed on the silica surface. Nevertheless, the previous study did not elucidate the effect of pH on silanated solution in terms of mechanical properties and hydrolytic stability of composite. However, this result supported the finding of Naviroj et al. that the absorption of γ-MPTS on silica is independent of pH unlike other silane coupling agents. Unlike the temperature effect, the effect of pH, which was demonstrated in different molecular weight moieties in adsorption on silica showed no effect on flexural properties and durability of composite. The significant differences in storage period on both flexural strength and modulus, for which 1 day storage showed greatest value, were due to the postpolymerization of resin matrix which can also be observed on temperature effect, even though they were insignificant.

CONCLUSION

The effects of heat application to the filler and pH on the flexural properties and hydrolytic stability of experimental composites were studied to understand the optimal condition in silanation using γ-MPTS. Within the limitation of this study, it was concluded that heating at 50°C and 80°C increased flexural strength while heat of 110°C and pH showed no effects on flexural properties and durability of composite.

REFERENCES


