Effect of pre-coating with methyl methacrylate containing UV photoinitiators on the bond strength of poly(ether ether ketone)

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This study investigates the effect of pre-coating with methyl methacrylate (MMA) containing ultraviolet (UV) photoinitiators on the bond strength of poly(ether ether ketone) (PEEK). Cylindrical PEEK blocks were irradiated with 365 nm UV light for 5–20 s after they were coated with MMA containing 0.4–3.0 wt% UV photoinitiators: [1-phenyl-1,2-propanedione (PPD)], [diphenyl(2,4,6-trimethylbenzoyl) (TMDPO)], and [phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide (BTMPO)]. Pre-coated PEEKs were bonded to PEEK blocks with a MMA-based adhesive resin. The shear bond strength was measured using a universal testing machine. Secondary electron images were captured to observe failure surfaces. The data were analyzed with one- and two-way ANOVA and Tukey's *post hoc* tests ($p < 0.05$). The highest bond strength (20.7 ± 5.1 MPa) was observed for pre-coating with MMA containing 0.4 wt% BTMPO, for 20 s of UV irradiation. Cohesive failure of the adhesive resin was observed. The use of this pre-coating led to improved bonding performance of PEEK.

Keywords: Poly(ether ether ketone), UV photoinitiator, Shear bond strength, Surface modification

INTRODUCTION

Poly(ether ether ketone) (PEEK) has applications in the dental and medical fields as a type of material that recovers the loss of body functions, owing to its excellent biocompatibility^{1–3}. Recently, several dental prostheses, implants, and medical devices composed of PEEKs have been fabricated by computer-aid design/computer-aided manufacturing (CAD/CAM) and 3-D printing techniques^{4,5}. PEEKs are polymeric materials with excellent mechanical properties, and their elastic modulus is similar to that of bone. Therefore, PEEKs are capable of minimizing the bone resorption associated with the stress shielding property of a rigid system².

PEEK is chemically inert, and hence, possesses poor adhesive properties. To facilitate their widespread use as biomaterials, the adhesive properties of PEEK and its fiber composites need to be improved.

In previous studies^{6–21}, the bond strengths of PEEK and fiber-reinforced PEEKs were investigated after the modification of their surfaces by sandblasting^{6–11}, chemical treatment^{6,7,9,10,12,13}, and plasma^{14–18} and UV^{19–21} irradiation. These studies showed that the bond strengths of PEEK and fiber-reinforced PEEKs increase following their surface modification, and are slightly higher than 10 MPa in dental applications. However, surface modifications in chairside dentistry are limited.

In this study, we particularly focus on the dental curing light system. Ultraviolet (UV) light is used to modify the PEEK surface instead of visible light^{19–21} because the wavelength of UV light is shorter than that of visible light, and thus, the light energy from UV light is higher than that from visible light. Therefore, the

PEEK surface was modified by the UV light energy.

The use of visible light-activated polymers, however, has been extended to dental materials and several presentations are available. All contain diacrylate resin monomers, suitable pigments and visible light initiators which produce the free radicals needed to promote addition polymerization²². We note that a methyl methacrylate (MMA) is used as a solvent for UV photoinitiators because a MMA monomer is a clear and colorless liquid. After the PEEK surface was pre-coated with a MMA monomer containing a UV photoinitiator, the surface was evenly irradiated with UV light at a wavelength of 365 nm. Free radicals can be subsequently produced and causes the polymerization of MMA to form a polymethylmethacrylate (PMMA) film. It is hypothesized that PMMA formed by the polymerization of MMA is strongly bonded to the modified PEEK surface.

The objective of this study is to evaluate the effect of UV initiators, their concentrations, and UV irradiation time on the bond strength of PEEK.

MATERIALS AND METHODS

Specimens

PEEK rods (Ketron 1000 PEEK, Quadrant Polypenco Japan, Tokyo, Japan) with a diameter of 10 mm were cut into cylindrical PEEK blocks with a height of approximately 5 mm using a cutting unit. Half of the blocks were embedded in a thermal curing resin to prepare adherend blocks. The ends of the flat surface of the adherends and cylindrical PEEK blocks were polished with 1000-grit SiC waterproof paper under

running tap water. Both PEEK blocks were cleaned ultrasonically in distilled water for 10 min, and were air-dried completely.

Pretreatment

Considering photoinitiator stability and the wide use of photoinitiators in free radical polymerization for dentistry²³, we focused on the following three photoinitiators; [1-phenyl-1,2-propanedione (PPD) (Tokyo Chemical Industry, Tokyo, Japan)], [diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TMDPO) (Tokyo Chemical Industry)], and [phenyl bis(2,4,6-trimethylbenzoyl) phosphine oxide (BTMPO) (Tokyo Chemical Industry)]. These photoinitiators were dissolved in MMA monomer (FUJIFILM WAKO Pure Chemical, Osaka, Japan) to prepare pre-coating solutions of different concentrations ranging from 0.4 to 3.0 wt%.

The prepared solution was pre-coated on both, the adherend and the cylindrical PEEK block surfaces, with a brush. Subsequently, the surfaces were individually exposed to UV light (EXECURE 4000, HOYA, Japan) of wavelength 365 nm for 20 s.

Absorption peaks for the prepared MMA solutions

A UV-visible programmable spectrophotometer (DU640, Beckman Instruments, CA, USA) with an operational range of 200 to 700 nm was employed to measure the maximum wavelength of the prepared 0.4 wt% solutions.

Fourier transform infrared (FTIR) spectroscopy

The pretreated specimen with 0.4 wt% BTMPO was analyzed using a Fourier transform infrared (FTIR) spectrometer (FTIR-7300, JASCO, Hachioji, Japan) to verify the formation of PMMA. A total of 256 scans were collected at a resolution of 4 cm⁻¹, and the spectrum was obtained in the reflectance mode in the region of 4400 to 400 cm⁻¹.

Bonding procedure

A thin polyethylene terephthalate seal with a circular hole of diameter 6 mm was placed on the pretreated adherend specimen surface to maintain the adhesive area constant. The specimen was bonded to the cylindrical PEEK block using a MMA adhesive resin (Super-Bond C&B, Sun Medical, Shiga, Japan) according to the manufacturer's instructions (*n*=5). After bonding, the specimens were left for 1 h under atmospheric conditions and then stored in distilled water at 37±1°C for 24 h.

Bond strength test

The bonded specimens were stressed in shear compression using a universal testing machine (AE-1000, Shimadzu, Kyoto, Japan) at a crosshead speed of 1.0 mm/min until failure. A total of five specimens were examined under each condition.

Observation of failure surfaces

The secondary electron (SE) imaging mode of an electron beam micro-analyzer (EPMA8710, Shimadzu)

was utilized to observe the failure surface. The failure surfaces were coated with AgPd in a sputter coater before observing them.

Statistical analysis

Data were analyzed with one- and two-way ANOVA (UV photoinitiator versus its concentration and bond strength), and Tukey's *post hoc* test at a pre-set significance level of 0.05.

RESULTS

Spectrum distribution for UV-visible light

Figure 1 displays the UV-visible light absorption spectra of the 0.4 wt% pre-coating solutions. The absorption spectra of the solutions revealed that the maximum absorption occurred in the wavelength region of 300 to 500 nm, with a λ_{max} of 415 nm.

FTIR

The FTIR spectrum of the pretreated specimen is shown in Fig. 2. The peaks are assigned as described elsewhere²⁴. The peak at approximately 3,000 cm⁻¹ is attributed to C-H stretching in CH₃, as is the peak at 1,385 cm⁻¹. The intense peak at 1,732 cm⁻¹ is assigned to C=O double bond stretching, whereas the broad envelope between 1,244 and 1,151 cm⁻¹ is attributed to C-O-C single-bond stretching. The peaks at 1,520, 1,388, and 754 cm⁻¹ are attributed to C=C stretching.

Shear bond strengths

The compressive shear bond strengths of the specimens with different pre-coatings are shown in Fig. 3.

Fig. 1 Spectral distribution of UV-visible light in comparison with the absorption peaks for the prepared 0.4 wt% solutions.

The absorbance maxima were observed at 415 nm in the wavelength region of 300 to 500 nm. In this study, the excitation wavelength of the photoinitiators was selected as approximately 365 nm.

Fig. 2 FTIR spectrum of the specimen pretreated with 0.4 wt% BTMPO. The specimen mainly contains carbonyl groups exhibiting a band at $1,732\text{ cm}^{-1}$, which is attributed to PMMA.

Fig. 3 Compressive shear bond strengths. Bars indicate standard deviation. Single asterisk indicates $p < 0.05$ for specimen comparison. Control: without UV initiators in MMA. UV initiators: PPD, TMDPO, and BTMPO.

Statistically significant differences were found among the specimens pre-coated with 0.4 wt% PPD, TMDPO, BTMPO, and the control. There was no statistically significant difference in the bond strength associated with changes in the concentration of PPD. However, the bond strength of the specimen pre-coated with 0.4 wt% TMDPO was significantly higher than that of the specimen pre-coated with 3.0 wt% TMDPO. Additionally, the bond strength of the specimen pre-coated with 0.4 wt% BTMPO was significantly higher than the bond strengths of the specimens pre-coated with 1.0 and 3.0 wt% BTMPO. The specimens pre-coated with the same concentration of UV photoinitiators exhibited similar bond strengths regardless of the type of UV photoinitiators.

Fig. 4 SE images of the fractured PEEK surfaces. (a) As-polished, (b) Control, (c) 0.4 wt% PPD, (d) 0.4 wt% TMDPO, and (e) 0.4 wt% BTMPO. Polishing streaks were observed in (a), traces of adhesive resin along the polishing streaks were observed in (b), torn resin strips were detected in (c) and (d), no polishing streaks, but cohesive failure, was observed in (e).

Observation of failure surfaces

Because the bond strengths of the specimens pre-coated with the 0.4 wt% UV photoinitiator were higher than those of the other specimens, the PEEK failure surfaces under this condition and the polished PEEK surfaces were observed (Fig. 4). In the control, traces of the adhesive resin were detected along the polishing streaks. On the other hand, in the specimens pre-coated with PPD and TMDPO, torn resin strips were observed at the polishing streaks. However, no adhesive resin was present on the flat surfaces of the polishing streaks. In the specimen pre-coated with BTMPO, no polishing streaks were detected, and cohesive failure of the adhesive resin was observed.

Effect of irradiation time on bond strength

Figure 5 shows the relationship between the UV irradiation time and bond strength for 0.4 wt% PPD and BTMPO. There was no statistically significant difference between the control and the specimen pre-coated with PPD when irradiated for 5 s. However, the bond strength of the specimen pre-coated with BTMPO was significantly higher than the bond strengths of the control and the specimen pre-coated with PPD. In contrast, the bond strengths of specimens pre-coated with UV photoinitiators were significantly higher than

Fig. 5 Relationship between UV light irradiation time and compressive shear bond strengths. Bars indicate standard deviation. Single asterisk indicates $p < 0.05$ for specimen comparison. Control: pretreatment with only MMA (without UV initiators in MMA). 0.4 wt% PPD and 0.4 wt% BTMPO: MMA solutions containing 0.4% UV initiators (*i.e.*, PPD and BTMPO).

the bond strength of the control when irradiated for 20 s. Moreover, the bond strength of the specimen pre-coated with BTMPO was significantly higher than that of the specimen pre-coated with PPD. The specimen pre-coated with 0.4 wt% BTMPO exhibited the highest bond strength for an irradiation time of 20 s.

DISCUSSION

Several studies⁶⁻²¹ have reported many surface treatments for PEEK, such as sandblasting, chemical treatment, and plasma and UV treatments that endow PEEK with adhesive properties. The bond strength of PEEK was significantly enhanced due to these surface treatments. Schmidlin *et al.*⁶ evaluated the shear bond strengths of sandblasted and acid-etched PEEKs as well as luting materials. The bond strengths of sandblasted and acid-etched PEEKs were 13.5 ± 2.4 and 18.2 ± 5.4 MPa, respectively. Thus, the authors concluded that sandblasting and chemical treatment produced highly porous and permeable surfaces. Mechanical coupling could be achieved by their treatments. On the other hand, Huang *et al.*²⁵ reported that the aromatic ring between the two ether links in PEEK was sulfonated upon the treatment of PEEK with concentrated sulfuric acid, which probably resulted in chemical bonding.

Bötel *et al.*²⁶ observed that the bond strengths of PEEK were in the range of 19.6 to 33.8 MPa after sandblasting and Ar/O₂ plasma treatments. Moreover, Shi *et al.*¹⁹ reported that UV treatment effectively modified the chemical structure of a PEEK surface and improved its wettability. Thus, plasma and UV treatments improved the wettability of the PEEK surface and formed specific additional functional groups

on the PEEK surface. The new functional groups that formed on the modified PEEK surface included COO and OH^{27,28}, which were expected to chemically bond with the adhesive resin.

We propose a novel surface treatment of PEEK in order to generate relatively high bond strength. Ikemura *et al.*²³ reported an excitation wavelength of approximately 400 nm for PPD and TMDPO, which is similar to the result obtained in this study. Meanwhile, a shorter wavelength of UV light has higher energy. According to a previous report²⁸, UV light (365 nm) can break the C-O and C=O bonds of PEEK, and the decomposed species can be expected to bond chemically to each other and to undergo polymerization upon exposure to UV light. For the above reasons, under UV light irradiation, the excitation wavelength of the photoinitiators was selected as approximately 365 nm. The UV photoinitiators would produce radicals that facilitate the polymerization of MMA at a UV light excitation wavelength of 365 nm. The FTIR results indicated the presence of PMMA, and thus suggested that a thin PMMA film was formed on the pre-coated PEEK surface.

Incidentally, the most common resins for using esthetic restorative materials in light-curing system are based on dimethacrylate or urethane dimethacrylate oligomers. These oligomers are viscous liquids²⁹. Therefore, it is difficult to dissolve UV initiators in these oligomers. However, MMA, a common monomer used to make complete dentures, is a liquid. UV initiators can easily dissolve in MMA. This is mainly because MMA is used as a solvent for UV initiators.

Based on the results, the mean bond strength increased from 7.3 MPa to high as 20.7 MPa, depending on the pre-coatings. Higher strengths were observed using lower concentrations of UV photoinitiators. According to the Beer-Lambert law for optical transmittance³⁰, a lower concentration results in less absorption, thereby increasing the penetration depth of UV light. Therefore, it was possible to decompose functional groups of the PEEK surface and perform light curing for both, the groups and MMA. Hence, relatively high bond strengths were obtained.

In general, the polymerization rate was proportional to the square root of the initiator concentration, and the polymerization degree was relatively high³¹. The mechanical properties of the polymer that was formed by UV light initiation were excellent at high concentrations of initiators. However, based on the principle of the Beer-Lambert law, a high concentration of initiators is associated with insufficient light penetration at the interface. Thus, any of the functional groups present at the surface of PEEK hardly decomposed. For these reasons, interfacial chemical bonding between the PEEK surface and PMMA polymerized by UV light irradiation is unfavorable. Therefore, the bond strengths associated with high-concentration initiators were not improved.

From the failure observation, wave-like traces of the resin formed by the tearing of the adhesive resin into polishing streaks were observed along the polishing

streaks on the specimens pre-coated with PPD and TMDPO. Both, mechanical and chemical bonds, could occur on these specimens. In contrast, no polishing streaks were observed, and wave-like traces as well as small pieces of the resin were observed on the specimen pre-coated with BTMPO. The fracture pattern indicated the fracture of the resin layer, however, interface failure was not observed. Hence, strong chemical bonds could occur between the surface of PEEK and the resin. The pre-coating of the specimen with BTMPO led to the highest bond strength.

We also investigated the effect of irradiation time on the bond strength with the 0.4 wt% photoinitiator. The behaviors of the bond strengths of the specimens pre-coated with TMDPO and BTMPO were similar, which was attributed to the fact that both photoinitiators contained acylphosphine oxide and possessed similar molecular structures. Acylphosphine oxide has the distinct advantage of absorbing in the near UV-range to undergo a fast photolysis which generates reactive benzoyl and phosphinoly radicals³². Therefore, PPD and BTMPO were selected as the UV photoinitiators and were used to examine the effect of irradiation time on bond strength. The results postulate that longer irradiation times lead to higher bond strengths. Longer irradiation times supply additional light energy to the interface because photon irradiance is defined as the number of photons per unit area per unit time. Moreover, the radicals were rapidly generated. Thereby, they could facilitate an increased decomposition of C-O or C=O bonds in the PEEK polymer chains. Thus, graft polymerization would be expected to occur at the interface. In fact, Kyomoto *et al.*³³ reported the graft polymerization of multifunctional poly(2-methacryloyloxyethyl phosphorylcholine) on the PEEK surface by utilizing a benzophenone (BP) photoinitiator and UV lamp with a wavelength of 350±50 nm. Moreover, Deng *et al.*³⁴ indicated that UV-induced surface graft polymerization and chemical bonding with PMMA enhanced the bond strength. Thus, UV-assisted graft polymerization can be conducted using longer irradiation times, resulting in higher bond strengths.

This study does not estimate the effect of a specific thermal stress on the bond strength. Stawarczyk *et al.*¹³ reported that the bond strengths of PEEK were slightly lower than those achieved after the thermal stress, however, their values were within clinical target ranges and were capable of achieving a sufficient level. Therefore, the bond strengths achieved after the thermal stress would be slightly low.

The pre-coating with MMA containing UV photoinitiators, as mentioned above, was simple in comparison with plasma and laser treatments, and can be introduced in clinical practice. This pre-coating method would contribute to increased bond strengths of PEEK.

CONCLUSIONS

After pre-coating the surfaces of PEEKs with MMA containing UV photoinitiators, they were irradiated with

UV light of wavelength 365 nm. This pretreatment was performed before bonding the PEEKs to PEEK blocks using the MMA-based adhesive resin. The mean bond strength was 20.7±5.1 MPa for pre-coating with MMA containing 0.4 wt% BTMPO, for 20 s of UV irradiation. In addition, cohesive failure of the adhesive resin was observed. Graft polymerization of PEEK could be induced on the PEEK surface. The use of this pre-coating led to relatively better bonding performance of PEEK.

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