

Development of dual-curing type experimental composite resin cement for orthodontic bonding –Effect of additional amount of accelerators on the mechanical properties–

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In this study, a dual-curing type composite resin cement that included a photo-initiator and two accelerators was designed. In particular, special emphasis was made on addressing questions on the effects from different amounts of additional accelerators on the flexural strength of the designed experimental composite resin cement, as well as on the tensile bond strength of the bracket bonded onto the enamel surface by the experimental composite resin cement.

When 0.25 mass% of the *p*-tolydiethanolamine and sodium *p*-toluenesulfinate were added, the maximum flexural strength was obtained for the chemical-cured and dual-cured experimental composite resin cement. The dual-cured experimental composite resin cement's flexural strength value was in the mid-range of the values exhibited from the commercial resin cements. However, the dual-cured experimental composite resin cement exhibited noticeably high tensile bond strength when compared with the results obtained with the commercial resin cements.

Keywords: Resin cement for bracket bonding, Flexural strength, Tensile bond strength of bracket

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INTRODUCTION

The introduction of the acid-etched technique to orthodontic bonding by Buonocore¹⁾, has facilitated the development of many different types of bonding systems^{2,3)} and numerous types of resin cements⁴⁻⁶⁾ that are critical in the correct application of orthodontic forces.

In clinical practice, most orthodontists will activate the orthodontic appliances in the mouth from 15 to 30 minutes after using resin cement to bond the bracket onto the enamel surface. The initial bond strength of the bracket to the enamel surface is, therefore, very important in ensuring the successful application of the direct bonding orthodontic technique.

Currently, a wide variety of orthodontic resin cements are commercially available. The orthodontic resin cements are classified into one of three resin cement types of: 1) chemical-curing, 2) light-curing and 3) dual-curing (combination of chemical and light curing), resin cements. The chemical-curing type 4-methacryloyloxyethyl trimellitate anhydride (4-META)/methyl methacrylate (MMA) resin cement, also known as Super Bond, is widely used by orthodontists since the Super Bond provides noticeably high bond strength for bonding the bracket onto the enamel surface^{7,8)}. However, in practice, the clinician must wait approximately 4-8 minutes for the Super Bond to harden before proceeding with the orthodontic treatment.

In order to directly control the setting time of the resin cement and to obtain high bond strength of the bracket immediately after bonding, clinicians utilize a light-curing type resin cement to bond the bracket to the enamel surface⁹⁻¹¹⁾. However, when the metal

bracket is placed onto the enamel surface, the metal bracket inhibits the transmittance of the visible light that is necessary for initiating the polymerizing reaction of the light-curing type resin cement that exists under the bracket. Thus, drawbacks in the application of light-curing resin cements are: 1) amount of time that is required to cure the resin cement under the metal bracket, and 2) regardless of the curing time that is used, the clinician may never be totally assured of the complete polymerization of the resin under the bracket¹²⁾. Incomplete polymerized areas within the adhesive layer of the resin cement may allow for the diffusion of water that may impair the bond strength in these areas and thus compromise the long-term effectiveness of the adhesive resin cement.

So as to overcome these drawbacks, as well as, to directly control the setting time of the resin cement and to improve the polymerization conversion of the resin cement that exists under the metal bracket, a dual-curing type composite resin cement, designed with additional capabilities, e.g. self-adhesiveness and fluoride release, was developed by adding 4-methacryloyloxy ethyl trimellitic acid (4-MET)¹³⁻¹⁵⁾, Penta(methacryloyloxy-ethyl-oxy)-cyclophosphazene monofluoride (PEM-F)¹⁶⁾ to the base monomer of the experimental resin cement.

In this study, a dual-curing type composite resin cement that consisted of two types of pastes, a photo-initiator or accelerators for a photo and chemical polymerizations, was designed. In particular, special emphasis was placed on addressing questions on the effects from different amounts of additional photo and chemical accelerators on the flexural strength of the designed experimental composite resin cement, and on the tensile bond strength of the bracket bonded onto

the enamel surface by the experimental composite resin cement.

MATERIALS AND METHODS

The designed dual-curing type composite resin cement consisted of two types of pastes. The components and compositions of the base monomer A for paste A and base monomer B for paste B are shown in Table 1. There, *p*-tolylidethanolamine (*p*-TDEA; Tokyo Chemical Industry Co., Tokyo, Japan) and sodium *p*-toluenesulfinate (*p*-TSNa; Tokyo Chemical Industry Co., Tokyo, Japan) were used as accelerators for photo or chemical polymerization. The amount of additional accelerators, *p*-TDEA and *p*-TSNa to base monomer B were 0.125, 0.25, 0.5, 1 and 2.5 mass%, respectively. Furthermore, 0.5 mass% of camphorquinone (CQ; Wako, Osaka, Japan), as a photo initiator, was dissolved in base monomer A.

In addition, a base monomer A without CQ for chemical-curing and a base monomer B with 0.25 mass% of *p*-TDEA only for light-curing were also prepared.

During the preparation of the experiment composite resin cement, colloidal silica (Aerosil 130, Aerosil Nippon Co, Tokyo, Japan) was used as filler. The surface of the colloidal silica was silanated by 6 mass% of γ -methacryloxypropyl trimethoxysilane. After which, 10 g or 8 g of silanated colloidal silica was filled into 10 g of base monomer A and base monomer B, respectively.

A light-curing type composite resin cement (Kurasper[®] F, KF; Kuraray Medical Inc., Osaka, Japan) and a chemical-curing type 4-META/MMA resin cement (Super Bond, SB; Sun Medical, Shiga, Japan) were used as a control.

Measurement of gelation time of base monomer mixture

Equal amounts of base monomer A without CQ and

base monomer B with different amounts of accelerators, *p*-TDEA and *p*-TSNa, were weighted and then mixed at room temperature by using a plastic spatula on a mixing paper for 20 seconds. After mixing, the base monomer mixture was collected in a mixing dish. The surface of the mixed monomer was then covered with poly vinylidene chloride (Saran Wrap[®], Asahi Kasei Corp., Tokyo, Japan). Thereafter, the surface of the mixed base monomer was probed by using an explorer. The gelation times of the base monomer mixtures were measured while varying the amount of additional accelerators. Measurements of the gelation time were repeated six times for each experimental group inside of a dark room.

ESR measurement

The base monomer A without CQ and base monomer B with accelerators, *p*-TDEA and *p*-TSNa were mixed in a 1:1 ratio for 20 seconds. There, the amount of additional accelerators was 0.25 mass%, respectively. Next, the base monomer mixture was inserted into a silica tube for electron spin resonance (ESR) measurement. The ESR spectra of the chemical-cured base monomer mixture during hardening were then observed as a function of time by using an ESR spectrum apparatus (JES FA 300, JEOL, Tokyo, Japan). The measurement conditions were as follows: microwave power of 8 mW; magnetic field of 335.4±5 mT; sweep time of 2 minutes; modulation frequency of 100 kHz; and time constant of 0.03 seconds.

In addition, when the mixture of the base monomer A with 0.5 mass% of CQ and base monomer B with 0.25 mass% of the accelerators was dual-cured through visible-light irradiation by a light curing unit (XL3000, 3M-ESPE, Grafenau, Germany), the ESR spectra of the base monomer mixture were observed as a function of time after visible-light irradiation. There, the mixing of the base monomers A and B, and the measurement of the ESR spectrum of each sample were conducted. The

Table 1 Components and compositions of base monomer A and B for the experimental composite resin cement

Base monomer A	Manufacture	mass%
Bis-GMA	Polysciences Inc., Warrington, USA	6.7
HEMA	Polysciences Inc., Warrington, USA	33.3
4-MET	Dentsply-Sankin, Tokyo, Japan	26.7
CB-1	Shin-Nakamura Chemical, Wakayama, Japan	20.0
PEM-F	Fushimi Pharmaceutical, Marugame, Japan	13.3
Base monomer B		
Bis-GMA	Polysciences Inc., Warrington, USA	64.3
TEGDMA	Wako Pure Chemical Inc, Osaka, Japan	35.7

Bis-GMA: bisphenol A glycidyl dimethacrylate; HEMA: 2-hydroxyethyl methacrylate; 4-MET: 4-methacryloyloxyethyl dihydrogen trimellitate; CB-1: β -methacryloyloxyethyl hydrogen phthalate; PEM-F: Penta(methacryloxy-ethyl-oxy)-cyclophosphazene mono-fluoride; TEGDMA: triethylene glycol dimethacrylate

ESR observations of the dual-cured and chemical-cured base monomer mixtures were performed two times inside of a dark room.

Measurement of flexural strength

The experimental composite resin cement consisting of paste A with 0.5 mass% of CQ and paste B with different amounts of accelerator, *p*-TDEA and *p*-TSNa, were mixed in a 1:1 ratio for 20 seconds. Each paste mixture was then filled into a stainless steel split mold that had been glued onto a glass slide. The split mold was then used to produce a specimen bar, where the experimental composite resin cement had hardened with a width of 4.2 mm, a height of 2.1 mm and a length of 35 mm. A transparent thin film was placed on the top surface of the mixture. Visible-light was then irradiated on the mixture from the transparent film side for 30 seconds, and then irradiated on the mixture from the glass slide side for 30 seconds, respectively, by using a light-curing unit (α -light II, Morita, Tokyo, Japan). After removing the specimens from the split mold, they were immersed in water at 37°C for 1 day. After which, the specimens were polished with a sequence of 600-grit and 1000-grit carbide papers under a stream of water. The width and height of the hardened specimen bars were fixed to 4.0 mm and 2.0 mm, respectively. The specimens were then placed on a three-point bending fixture mounted on a universal testing machine (TG-5KN, Minebea, Kanagawa, Japan). There, the span distance for the three-point bending fixture was 10 mm and a crosshead was placed at the center of the bending fixture. A load was applied to the specimen bar under a crosshead speed of 1 mm/min. Concurrently, the load-deflection curve was recorded on the computer. Using the load-deflection curve, the flexural strength was derived from the maximum load and the elastic modulus was derived from the deflection when the load was 0.4 kN. The maximum deflection was determined from the load-deflection curve where the maximum load was detected.

Furthermore, the flexural strength of the chemical-cured experimental composite resin cement, consisting of paste A without CQ and paste B with different amounts of accelerators, *p*-TDEA and *p*-TSNa, was measured as per the previously discussed methods. The flexural strength of the light-cured experimental composite resin cement consisting of paste A with 0.5 mass% of CQ and paste B with 0.25 mass% of *p*-TDEA only, was also determined.

In addition, the flexural strengths of two commercial resin cements, KF and SB were measured as per the previously discussed methods, after the specimens were prepared, as a control.

The number of specimens for each experimental group was seven. The mean values of flexural strength, elastic modulus, maximum deflection and their standard deviation (SD) were calculated for each experimental group. The results were analyzed by one-way analysis of variance (ANOVA) and Scheffé's multiple comparison tests.

Preparation of the specimens for tensile bond strength test

Fresh, intact, anterior human teeth that were immediately stored in water at 4 °C after extraction were used for the tensile bond strength test. After cutting the root, the labial enamel surface of each anterior tooth was cleaned, rinsed, and dried according to generally accepted procedures. The labial enamel surface was then etched with an etching gel (Xeno Ortho, Dentsply-Sankin, Tokyo, Japan) for 30 seconds, rinsed for 20 seconds, and then dried for 30 seconds.

A metal bracket (Standard number 105-1100, Dentsply-Sankin, Tokyo, Japan) was bonded to the conditioned enamel by applying the dual-curing type experimental composite resin cement. There, the amount of additional accelerators, *p*-TDEA and *p*-TSNa, was 0.25 mass%. Next, visible light was irradiated at a 45° angle to the mesial-gingival corner of the bracket for 5 seconds and then at a 45° angle to the distal-occlusal corner for another 5 seconds by using a light curing unit.

The bonded specimens with a metal bracket adhered to the labial enamel surface by the chemical-cured experimental composite resin cement or light-cured experimental composite resin cement with visible-light irradiation were also prepared using the same methods as previously described. There, when the bracket was bonded to the enamel surface by the light-curing type experimental composite resin cement, visible light was irradiated at a 45° angle to the mesial-gingival corner of the bracket for 30 seconds and then at a 45° angle to the distal-occlusal corner for another 30 seconds.

Furthermore, commercial resin cements, KF or SB were applied to bond the metal bracket to the labial enamel surface, as per the respective resin cements instructions. The bonded specimens were stored in water at 37°C for 1 day.

Measurement of tensile bond strength

After being immersed in water at 37°C for 1 day, the bonded specimens were molded with a self-curing pour resin (Shofu Inc, Kyoto, Japan). Next, an orthodontic wire (0.457×0.558 mm; RMO Inc., Denver, USA) was fastened to the metal bracket by using a ligature wire (0.305 mm; RMO Inc.). The molded specimens were then mounted on a universal testing machine. After hooking the orthodontic wire with a stainless steel device, the orthodontic bracket was vertically pulled against the enamel surface under a crosshead speed of 1mm/min. The tensile bond strength of the orthodontic bracket to the enamel surface was thereby measured.

The number of specimens for each experimental group was 7. The mean value of tensile bond strength and its standard deviation (SD) were calculated for each experimental group. The results were analyzed by one-way analysis of variance (ANOVA) and Scheffé's multiple comparison tests.

RESULTS

Gelation time of the base monomer mixtures for chemical-cured experimental composite resin cement

Figure 1 shows the effects from the amounts of additional accelerators, *p*-TDEA and *p*-TSNa, to the base monomer B on the gelation time when the mixture of base monomers A and B was chemical-cured. In this case, the base monomer A without CQ was utilized.

When the amount of additional accelerators to the base monomer B was increased from 0.125 to 2.5 mass%, the gelation time was reduced from 554.2 to 172.0 seconds.

Figures 2 and 3 show the ESR spectra of the mixture of base monomers A and B when the mixture was chemical-cured or dual-cured. In both case, the amount of accelerators, *p*-TDEA and *p*-TSNa, added to base monomer B was 0.25 mass%.

When the mixture of base monomer A without CQ and base monomer B with the accelerators was chemical-cured, no ESR signals were detected in the ESR spectra, as shown in Fig. 2. In addition, it took 491 seconds for the base monomer mixture to harden into a gel.

In contrast, when the mixture of the base monomer A with 0.5 mass% of CQ and base monomer B with the accelerators was dual-cured through visible-light irradiation, three ESR signals were detected in the

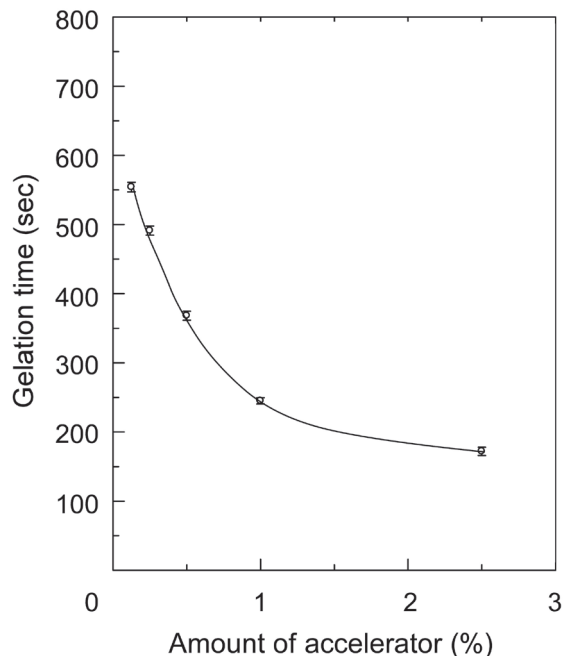


Fig. 1 Effects from different additional amounts of accelerator on the gelation time of the mixture of the base monomer A and B for the chemical-curing type experimental resin cements. The CQ was not added to the base monomer A. The error bar shows SD.

ESR spectra, as shown in Fig. 3. The ESR signals were assigned to the carbon radical, since the *g*-value of the developed ESR signal was 2.0009.

Flexural strength of experimental composite resin cement

Figure 4 shows the effects from different amounts of additional accelerators, *p*-TDEA and *p*-TSNa, on the flexural strength of the experimental composite resin cements. The white circles indicate the flexural strength when the experimental composite resin cement, comprised of paste A with 0.5 mass% of CQ and paste B with accelerators, was dual-cured through visible-light irradiation. The white squares show the flexural strength when the experimental composite resin cement, comprised of paste A without CQ and paste B with accelerators, was chemical-cured.

When the amount of additional accelerators was 0.25 mass%, the chemical-curing type experimental composite resin cement exhibited a maximum flexural strength of 65.3 MPa. However, further increases in the amount of additional accelerators resulted in decreases in the flexural strength.

Conversely, when the experimental composite resin cement was dual-cured, the mean flexural strength significantly increased to above 90.0 MPa. For all additional amounts of accelerators, the dual-cured experimental composite resin cement provided noticeably higher flexural strength than that of the chemical-cured experimental composite resin cement ($p < 0.05$). However, the effects from the amount of additional accelerators on the flexural strength resulted

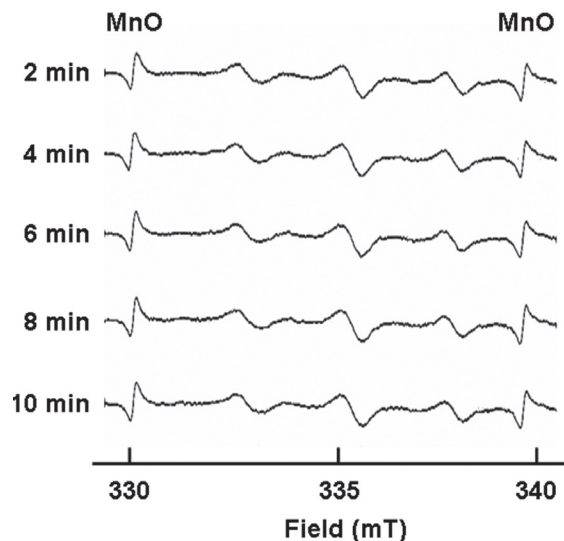


Fig. 2 ESR spectra of chemical-curing type base monomer mixture as a function of curing time. The amount of additional *p*-TDEA and *p*-TSNa used for base monomer B was 0.25 mass%. The CQ was not added to the base monomer A.

in almost the same as that of the chemical-cured experimental composite resin cement. The addition of 0.25 mass% of accelerators also exhibited a maximum flexural strength of 114.6 MPa.

Comparison of the mechanical properties and tensile bond strengths of the experimental composite resin cement with those of the commercial resin cements

Table 2 shows the flexural strengths, elastic moduli and maximum deflections of the experimental composite resin cements and of the commercial resin cements, as well as, the tensile bond strengths of the

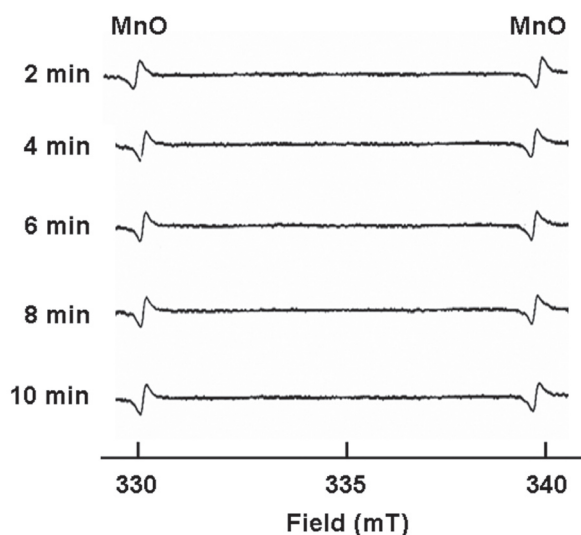


Fig. 3 ESR spectra of dual-curing type base monomer mixture as a function of curing time. The amount of additional *p*-TDEA and *p*-TSNa used for base monomer B was 0.25 mass%. The amount of additional CQ used for base monomer A was 0.5 mass%.

bracket bonded to the enamel by the experimental composite resin cements or by the commercial resin cements. There, when the experimental composite resin cement was dual-cured, paste A with 0.5 mass% of CQ and paste B with 0.25 mass% of *p*-TDEA and *p*-TSNa were utilized. In contrast, when the experimental composite resin cement was chemical-cured, paste A without CQ and paste B with 0.25 mass% of *p*-TDEA

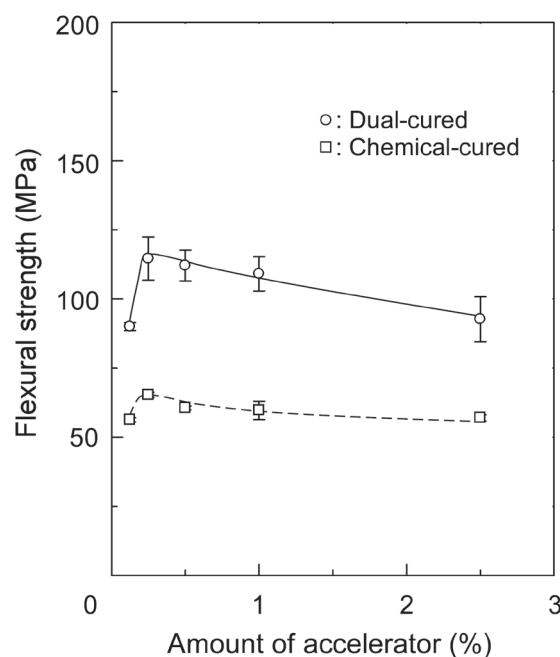


Fig. 4 Effects from different additional amounts of accelerators to base monomer B on the flexural strength of the experimental composite resin cements. The error bar shows SD.

Table 2 The flexural strengths, maximum deflections and elastic moduli of the experimental composite resin cements and the commercial resin cements, as well as the tensile bond strengths of the bracket bonded to the enamel by the experimental composite resin cements and the commercial resin cements

Resin cement	Flexural strength (MPa)	Deflection (mm)	Elastic (GPa)	Tensile bond strength (MPa)
Experimental resin cement				
Dual-cure	114.6 (7.8) ^A	0.20 (0.03) ^A	4.7 (0.3) ^A	7.5 (0.8) ^A
Chemical-cure	65.3 (1.0) ^B	0.31 (0.04) ^B	2.1 (0.2) ^B	4.4 (1.2) ^B
Light-cure	34.3 (3.2) ^C	0.29 (0.05) ^B	1.1 (0.2) ^C	4.1 (0.3) ^B
Commercial resin cement				
KF [Light-curing type]	176.2 (7.2) ^D	0.19 (0.01) ^A	8.3 (0.5) ^D	6.5 (2.1) ^A
SB [Chemical-curing type]	88.0 (1.8) ^E	0.67 (0.07) ^C	1.7 (0.1) ^E	6.1 (2.1) ^A

(): SD

Within the same vertical column: median values with the different superscript letters (A–E) showing a statistical difference ($p < 0.05$).

KF: Kurasper[®] F (Kuraray Medical Inc., Osaka, Japan), SB: Super Bond (Sun Medical, Shiga, Japan)

and *p*-TSNa were utilized. Conversely, when the experimental composite resin cement was light-cured, paste A with 0.5 mass% of CQ and paste B with 0.25 mass% of *p*-TDEA only, were utilized.

The mean flexural strengths of the SB and KF were 88.0 and 176.2 MPa, respectively. The KF resin cement exhibited the highest flexural strength. The flexural strengths of the dual-cured, chemical-cured and light-cured experimental composite resin cements were 114.6, 65.3 and 34.3 MPa, respectively.

The mean elastic moduli of the SB and KF were 1.7 and 8.3 GPa, respectively. The KF exhibited the highest elastic modulus. The elastic moduli of the dual-cured, chemical-cured and light-cured experimental composite resin cements were 4.7, 2.1 and 1.1 GPa, respectively.

The mean maximum deflections of the SB and KF were 0.67 and 0.19 mm, respectively. The SB exhibited the highest maximum deflection. The maximum deflections of the dual-cured, chemical-cured and light-cured experimental composite resin cements were 0.20, 0.31 and 0.29 mm, respectively.

The mean tensile bond strengths of the metal bracket bonded to the enamel surface by the SB and KF were 6.1 and 6.5 MPa, respectively. The tensile bond strengths of the dual-cured, chemical-cured and light-cured experimental composite resin cements were 7.5, 4.4 and 4.1 MPa, respectively. The dual-curing type experimental composite resin cement exhibited the highest tensile bond strength.

DISCUSSION

So as to better understand how the resin cement could better resist fracturing of the resin cement's adhesive layer that bonds the bracket to the enamel surface, it is important to examine the mechanical properties since the functional stresses, e.g. tensile, shear, torque, and peel, are exerted on the bonded bracket^{17,18}.

In this study, in order to increase the bond strength of the metal bracket to the enamel surface by increasing the polymerization conversion of the resin cement under the bracket, a dual-curing type experimental composite resin cement was designed. The effects from different amounts of additional accelerators, *p*-TDEA and *p*-TSNa, on the flexural properties of the dual-curing type experimental composite resin cement were examined. The efficacy of this dual-curing type experimental composite resin cement, developed for direct bonding systems, was then discussed through a comparison with the mechanical properties of the commercial resin cements.

When the mixture of the base monomer A without CQ and base monomer B with accelerators, *p*-TDEA and *p*-TSNa was chemical-cured, the gelation time of the mixture became shorter as the amount of additional accelerators was increased. The gelation time of the mixture was strongly dependent on the amount of additional accelerators. In order to understand the chemical-curing mechanism of the base monomer

mixture, ESR analyses were performed during hardening.

When the mixture of base monomer A with 0.5 mass% of CQ and base monomer B with 0.25 mass% of accelerators was dual-cured through visible-light irradiation, ESR signals, attributed to the carbon radical, were detected. The development of the carbon radical suggests that the dual-curing mechanism of the base monomer mixture is of a radical polymerization. This was possible since the irradiation of visible light resulted in the activation of the CQ.

In contrast, when the mixture of the base monomer A without CQ and base monomer B with 0.25 mass% of accelerators was chemical-cured, no ESR signal was observed. This result suggests that the chemical-curing mechanism of the mixture is not of a radical polymerization. The mixture may have been hardened by anionic polymerization, which could be initiated by the carboxylic acid in the 4-MET, and/or the CB-1 molecule, and the *p*-TSNa, as well as, by the *p*-TDEA¹⁹. In order to understand the chemical-curing mechanism of the base monomer mixture, further research should be conducted in the future.

Next, the experimental composite resin cements were prepared by mixing silanated colloidal silica to the base monomers A and B. The effects from different amounts of additional accelerators on the flexural strength of the experimental composite resin cement were then examined. When the amount of accelerators was 0.25 mass%, the dual-cured and chemical-cured experimental composite resin cements exhibited the maximum flexural strengths. However, further increases in the amount of additional accelerators resulted in decreases in the mean flexural strength. These observed decreases in the flexural strength caused by increasing the amount of additional accelerators was caused by the *p*-TSNa and *p*-TDEA acting as a plasticizer, since both chemicals do not have a functional group in their molecules for polymerization. The flexural strength of the dual-cured experimental composite resin cement was in the mid-range of the values observed with the KF and SB.

As shown in Table 2, we designed three experimental composite resin cements with different types of curing systems. It seemed that the mechanical properties of the experimental composite resin cement were strongly dependent on the type of curing system. The dual-curing type experimental composite resin cement exhibited higher mechanical properties, *i.e.* flexural strength and elastic modulus, than the chemical-curing and light-curing type experimental composite resins. The flexural strength, elastic modulus and maximum deflection of the experimental composite resin cement, in decreasing order were, dual-curing, chemical-curing and light-curing. The observed decreases in the mechanical properties of the chemical-cured and light-cured experimental resin cements, when compared to the dual-cured experimental resin cement, were probably due to decreases in the polymerization conversion of the base monomer.

Further, the commercial composite resin cement, KF, exhibited noticeable higher flexural strength and elastic modulus, when compared with the experimental composite resin cements. The observed higher flexural strength and elastic modulus of the KF than those of the experimental composite resin cements were due to differences in the amount of filler content. In fact, the amount of KF's filler content (78.1 mass% as determined by the Ash method²⁰⁾) is greater than those of the experimental composite resin cements.

Wright and Powers²¹⁾ reported on the reliability requirements for tensile bond strength in clinical applications. They cited a requirement of a maximum force exerted on a bracket of 5.9 MPa. The dual-cured experimental composite resin cement and the commercial KF and SB met this requirement. However, the chemical-cured and light-cured experimental composite resin cements were not able to meet this requirement. Specifically, the light-cured experimental composite resin cement exhibited the lowest tensile bond strength. This drawback was due to 1) the mechanical properties of the light-cured experimental composite resin cement being lower than the other two experimental composite resin cements and 2) the light-cured experimental composite resin cement that existed under the metal bracket could not polymerize completely, since the metal bracket inhibited the transmittance of visible light. In contrast, the dual-curing type experimental composite resin cement provided higher tensile bond strength than that of the light-cured experimental composite resin cement. This result was possible since the dual-cured experimental composite resin cement that existed under the metal bracket could be chemical-cured, even when visible light was directly unable to irradiate the dual-cured experimental composite resin cement that existed under the metal bracket.

The dual-curing type experimental composite resin cement exhibited noticeably high tensile bond strength when compared with the result obtained with the KF, even though the flexural strength of the experimental composite resin cement was lower than that of the KF ($p < 0.05$). Keizer *et al.*¹⁷⁾ reported that the flexural strength of the resin cement was related to the tensile bond strength of the bracket to the enamel. However, we did not observe any correlation between the flexural strength and tensile bond strength when the mechanical properties of the dual-curing type were compared with those of the KF. This observed difference in behaviors was attributed to the degree of polymerization conversion of the resin cement that existed under the metal bracket. Consequently, the light-curing type KF provided noticeably low tensile bond strength when compared with the result obtained with the dual-cured experimental composite resin cement, since the degree of polymerization conversion of the light-cured KF that existed under the metal bracket was lower, due to insufficient amount of visible light reaching the KF to activate the photo polymerization of the KF under the bracket, when

compared with that of the KF that was not hindered by the metal bracket that was directly irradiated by visible light.

The observed enhancement in the tensile bond strength of the metal bracket bonded by the dual-cured experimental composite resin cement than that of the light-curing type KF was probably due to the polymerization conversion of the dual-curing experimental composite resin cement that existed under the metal bracket being greater than that of the light-curing type KF. This was possible since the carboxylic acid in the 4-MET, and/or the CB-1 molecule, the *p*-TSNa, as well as, the *p*-TDEA initiated the anionic polymerization of the base monomer that existed under the metal bracket. These results clearly suggest that the designed dual-curing type experimental composite resin cement would be an advantageous material for use in direct bonding systems for the bonding of the metal bracket to the enamel surface.

In this study, so as to provide additional capabilities to the experimental composite resin cement, 4-MET and PEM-F were utilized in the base monomer A as part of the experimental composite resin cement. In the future, investigation of the self-adhesiveness and fluoride release of the designed experimental composite resin cement should be conducted.

CONCLUSION

Under the conditions of this study, the following conclusions were made:

1. The addition of 0.25 mass% of *p*-TSNa and *p*-TDEA to base monomer B provided maximum flexural strengths after the experimental composite resin cement was chemical-cured or dual-cured.
2. The dual-cured experimental composite resin cement provided noticeably high tensile bond strength when compared with the result obtained with the commercial light-curing type composite resin cement, KF, even though the flexural strength of the experimental composite resin cement was lower than that of the KF.

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