Novel, Multi-purpose, PMMA-type Adhesive Resin with Newly Synthesized Microcapsule of Radical Polymerization Initiators

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Received June 22, 2007/Accepted August 6, 2007

The behavior of microencapsulated polymerization initiators in dental adhesives is unknown. This study investigated the effects of new microencapsulated initiators in novel, multi-purpose, PMMA-type adhesive resin on the bonding performance and polymerization reactivity. Microencapsulated BPO and 1,3,5-trimethylbarbituric acid (TMBA) with PEMA as a shell polymer were quantitatively synthesized at 97–98% yield with 30–54 μm diameter. Adhesive-MC (comprising the synthesized microcapsules) and Adhesive-BR (comprising bare BPO and bare TMBA) were prepared and stored at 5°C, 23°C, and 40°C for two months. MMA monomer was used as a solvent for the microcapsules. At the starting period, there were no significant differences between Adhesive-MC and Adhesive-BR in shear bond strength to enamel or dentin treated with or without surface treatment agent ($p < 0.05$); moreover, their curing times ($t_c = 304$ seconds) were almost the same. After two months' storage at 40°C, Adhesive-BR degraded in bond strength and showed markedly delayed polymerization reactivity as storage period progressed. In direct contrast, it was found that Adhesive-MC still retained its capabilities for adhesion to gold alloy and initiation of radical polymerization ($p < 0.05$).

Keywords: Multi-purpose PMMA-type adhesive resin, Microcapsule, Radical polymerization initiator

INTRODUCTION

It is now well recognized that radical polymerization initiators play an important role in bonding adhesive resins to teeth and dental alloys. Masuhara *et al.*¹⁾ found that methyl methacrylate (MMA) resin initiated by tri-*n*-butylborane (TBB) could adhere to moist ground ivory, which was used as a model adherend for dentin substrate, against high polymerization shrinkage attacked at the bonding interface. This success opened new vistas in the field of adhesive dentistry. Following this discovery by Masuhara *et al.*¹⁾, numerous studies^{2–9)} have since sought to improve and develop advanced radical polymerization initiators.

Since a study by Brederick *et al.*²⁾, much attention has been paid to the use of barbituric acid derivatives to initiate the polymerization of dental resins. To date, three kinds of ternary polymerization initiator systems comprising 5-monosubstituted barbituric acid (5-MSBA) (Fig. 1) have been developed^{6–9)}. An adhesive resin which contained the initiator system comprising 5-MSBA, organic peroxide, aromatic tertiary amine, and adhesive monomers of 4-acryloxyethyltrimellitic acid (4-AET) and its acid anhydride (4-AETA) showed good bonding performance and curing time⁹⁾. The ternary initiator system of 5-MSBA, aromatic sulfinic amide (ASA), and *tert*-butyl peroxy maleic acid (*t*-BPMA) also exhibited good polymerization initiating ability⁹⁾. However, it was anticipated that these bare and unencapsulated polymerization initiators would interact among themselves or with acidic adhesive monomers, thereby

forming charge transfer (CT) complexes^{9–10)} with a problematic stability. To develop multi-purpose adhesive resins, polymerization initiators and adhesive monomers should be able to coexist within the adhesive formulation with good stability.

On the aspect of encapsulation, microcapsule technologies have received considerable recent attention both because of the inherently interesting physical chemistry or polymer science of the microcapsules, and because they were widely applied in various fields such as information recording, cosmetics, paintings, medicine, agriculture, and food¹¹⁾. Moreover, active researches and developments are ongoing to prepare microcapsules that can perform various functions¹²⁾. With regard to the application of microcapsules in adhesive dentistry, the two-liquid type of adhesive has been modified into one-liquid type. In this case, the microencapsulated reactive compound, such as the polymerization initiator, was mixed beforehand with the matrix agent. Subsequently, the microcapsules were broken with an appropriate stimulus. If microcapsules were to be applied in the field of adhesive biomaterials, then microcapsules will have to be prepared using biocompatible materials. Accordingly, therefore, it is necessary to investigate whether microcapsules can be prepared using biocompatible materials.

Although microcapsule technologies have been well investigated in various fields, little attention has been paid to their application in the field of adhesive dentistry. Consequently, the behavior of microencapsulated polymerization initiators formulated in dental adhesives is unknown. In order to develop a

General formula of 5-MSBA

Abbr.	R ₁	R ₂	R ₃	mp (°C)
BBA	-H	-H	-(CH ₂) ₃ CH ₃	200.0-210.0
CEBA		-H	-CH ₂ CH ₃	115.0-117.5
BPBA	-CH ₂ -	-H		156.5-159.0
TMBA	-CH ₃	-CH ₃	-CH ₃	150.5-153.0

Fig. 1 Structure of 5-monosubstituted barbituric acids (5-MSBA) that consist of three kinds of polymerization initiators previously developed⁶⁻⁹. BBA: 5-butylbarbituric acid, CEBA: 1-cyclohexyl-5-ethylbarbituric acid, BPBA: 1-benzyl-5-phenylbarbituric acid. 1,3,5-trimethylbarbituric acid (TMBA) was employed in this study.

multi-purpose, poly(methyl methacrylate) (PMMA)-type adhesive resin with a new material design, our research strategy focused on microencapsulating polymerization initiators in the adhesive formulation.

Therefore, the aims of this study were: (1) to synthesize and characterize newly designed microcapsules (MC-BPO and MC-TMBA) of benzoyl peroxide (BPO) and 1,3,5-trimethylbarbituric acid (TMBA); and (2) to investigate the effects of MC-BPO and MC-TMBA formulated in multi-purpose, PMMA-type adhesive resin on bonding performance and polymerization initiating activity. To further assess their stability performance, these microcapsules were stored at 40°C and a relative humidity of 75% for two months, and then compared against a control adhesive resin comprising bare, non-microencapsulated polymerization initiators (Bare-BPO and Bare-TMBA). The null hypothesis tested was that the new microencapsulated polymerization initiators will serve well the multiple purposes of good bonding performance and polymerization initiating activity, and at the same time offer the novel PMMA-type adhesive resin with good stability after an artificial aging period.

MATERIALS AND METHODS

Preparation of reagents

BPO, used as a core material of microcapsule in this study, was purchased from Kawaguchi Chemical Co. Ltd. (Tokyo, Japan). A barbituric acid, TMBA (mp 150.5–153.0°C) (Fig. 1), used also as a core mate-

rial, was synthesized using a method previously reported^{2,9}. Poly(ethyl methacrylate) (PEMA) (MW = 80000; Negami Chemical Industrial Co., Tokyo, Japan) was used as the microcapsule shell polymer. Two types of calcium carbonate (CC) (Komesho Sekkai Kogyo Co., Ohita, Japan) with different crystal shapes, namely needle and cubic forms, were used as stabilizer. Sodium dodecyl sulfonate (DBS) (Daiichi Kogyo Seiyaku Co. Ltd., Kyoto, Japan) was used as a co-stabilizer. Adhesive monomers of 4-AET and 4-AETA were synthesized by a method previously reported^{13,14}. PEMA, PMMA (Mitsubishi Rayon Co. Ltd., Tokyo, Japan), PMMA-PEMA copolymer (Negami Chemical Industrial Co., Tokyo, Japan), and Si-treated silica fillers (mean particle size: 1.5 μ m), which were prepared by treating with γ -methacryloxypropyl trimethoxysilane (KBM-503, Shin-Etsu Chemical Co. Ltd., Niigata, Japan), were used as components of powdery adhesives.

MMA (Mitsubishi Rayon Co. Ltd., Tokyo, Japan), 2-hydroxyethyl methacrylate (HEMA) (Mitsubishi Rayon Co. Ltd., Tokyo, Japan), and ethylene glycol dimethacrylate (EGDMA) (Shin-nakamura Chemical Co. Ltd., Wakayama, Japan) were used as components of liquid adhesive. Methoxy hydroquinone (MEHQ), butylated hydroxytoluene (=2,6-di-*t*-butyl-4-methylphenol) (BHT), and *N,N*-dihydroxyethyl-*p*-toluidine (DEPT) were purchased from Wako Pure Chemical Industries Ltd. (Tokyo, Japan) and used without further purification.

Synthesis of microcapsules of BPO and TMBA

Figure 2 depicts a schematic illustration of the synthesis of microcapsules (MC-BPO and MC-TMBA) in this study. Table 1 shows the experimental conditions for the synthesis of the microcapsules.

Given amounts of PEMA and BPO (or TMBA) were added to MMA of a given volume. This mixture was kneaded for five minutes at a rotation speed of 16.7 s⁻¹ with Thinky Non-bubbling Kneader (NBK-2, Nihonseiki Kaisha Ltd., Tokyo, Japan) to prepare a primary suspension (solid in oil; S/O), which was in the dispersed phase. This dispersed phase was poured into the continuous water phase, in which given amounts of DBS and CC were added. For the latter, needle form (particle size: 1.00, 2.00, 5.00 μ m) and cubic form (particle size: 0.04, 0.15, 0.80 μ m) of CC were used as stabilizers. This (solid/oil)/water dispersion [(S/O)/W] was irradiated with ultrasound under these conditions: 150 W and 35 kHz for three minutes, and then mixed at a rotation speed of 83.3 s⁻¹ for five minutes with a rotary homogenizer (EM-2, Nihonseiki Kaisha Ltd., Tokyo, Japan). The (S/O)/W dispersion was transferred to a separable flask with an effective volume of 5.0 $\times 10^{-4}$ m³ and four Teflon baffle plates of 1.0 $\times 10^{-2}$ m width. To remove MMA from the solvent, the latter was under

Fig. 2 Schematic illustration of the synthesis of microcapsules (MC-BPO and MC-TMBA) in this study. In the microencapsulation process, PEMA and BPO (or TMBA) were added to MMA to prepare dispersed phase (solid in oil; S/O), and this dispersed phase was poured into a continuous phase. MMA in solvent was removed from this solid-oil-water dispersion [(S/O)/W] under reduced pressure. Two types of calcium carbonate powders were used as stabilizer. Six kinds of microencapsulated BPO or TMBA were quantitatively obtained (97–98% yield).

Table 1 Experimental conditions for microcapsule synthesis

Continuous phase	Deionized water [ml]	300
	Amount of CC [g]	2.7,5.4,8.1
	Concentration [wt%]	0.9,1.8,2.7
Dispersed phase	DBS [g]	2.7×10^{-2}
	PEMA [g]	7.0
	MMA [g]	28.0
	BPO or TMBA [g]	7.0
Hold up		0.1
Stirring speed		5g^{-1}
Drying condition		40°C, 3h, 700 mmHg

Note: CC: calcium carbonate, DBS: sodium dodecyl sulfonate, PEMA: poly(ethy methacrylate), MMA: methyl methacrylate, BPO: benzoyl peroxide, TMBA: 1,3,5-trimethylbarbituric acid

a reduced pressure of 700 mmHg and a rotation speed of 5 s^{-1} using EYELA Unitrap UT-2000 (Tokyo Rikakikai Co. Ltd., Tokyo, Japan) for three hours at 40°C.

Microcapsules were prepared by separation using a centrifugal separator (Type 7700, Kubota, Tokyo, Japan) under these conditions: acceleration of $134.3 \times 10^3\text{ m/s}^2$ at 5°C for one hour. Separated microcapsules were thoroughly washed with ion-exchanged water and freeze-dried for seven days. Next, the freeze-dried microcapsules of a given amount were suspended in $1.0 \times 10^{-4}\text{ m}^3$ of ion-exchanged water, and 1 N hydrochloric acid solution

was added to remove calcium carbonate under magnetic agitation (2 s^{-1}). This suspension was then filtered under reduced pressure, and microcapsules were thoroughly washed with ion-exchanged water and freeze-dried. These freeze-dried microcapsules of a given amount were suspended in n -hexane of $30 \times 10^{-4}\text{ m}^3$ for one hour to remove unmicroencapsulated BPO or TMBA under room temperature and magnetic agitation (2 s^{-1}), and then filtered. After one more washing with n -hexane, microcapsules were dried at room temperature for one hour under a reduced pressure of 350 mmHg, and then dried again at 30°C for one hour under high vacuum of 0.05 Torr.

Through the microencapsulation process, six kinds of microencapsulated BPO (MC-BPO) and TMBA (MC-TMBA) derived from needle and cubic forms of CC were quantitatively obtained.

Characterization of microcapsules

1. SEM observation of microcapsules

Micromorphologies of the whole microcapsule and in a cross-sectioned view were examined using a scanning electron microscopy (SEM) (JSM-6390LA, JEOL Ltd., Tokyo, Japan). All the six kinds of microencapsulated BPO (MC-BPO) and TMBA (MC-TMBA) derived from the needle form (particle size: 1.00, 2.00, 5.00 μm) and cubic form (particle size: 0.04, 0.15, 0.80 μm) of CC were subjected to SEM observation.

To prepare the cross-sectioned specimens, the microcapsules were embedded in epoxy resin. After hardening, the specimens were polished with 600-grit SiC waterproof abrasive paper under running water.

The exposed surfaces of the specimens were washed again with *n*-hexane to remove BPO from the microcapsule before SEM observation. Since similar morphological results of MC-BPO and MC-TMBA were obtained, this paper reports only MC-BPO in the characterization of the microcapsule.

2. Diameter distribution and mean diameter

Diameter distributions and mean diameters of microcapsules were measured from the photographs of about 500 microcapsules taken with an optical microscope. The mean diameter was Sauter mean diameter.

3. Microencapsulation efficiency

Microencapsulation efficiency of BPO was investigated using high performance liquid chromatography (HPLC) (Shimadzu LC-4A, Shimadzu Co. Ltd., Kyoto, Japan) in the following manner. Microcapsules of 10 mg were dissolved in 10 ml of acetone. This solution was filtered through a 0.45- μ m membrane filter and used as a test solution. Standard solutions were prepared to plot the calibration curve by dissolving a given weight of BPO in 10 ml of acetone. Microencapsulation efficiency was estimated by comparing the value obtained for the test solution against the one for calibration curve. Measurement conditions of HPLC were as follows — HPLC system: LC-10AVP, Eluent: CH₃CN/H₂O (70/30, vol%), Flow rate: 0.5 ml/min, Column temperature: 50°C, Detection: UV 210 nm, Injection volume: 5 μ l.

Preparation of adhesive resins

Two experimental powder-liquid, PMMA-type adhesive resins were prepared according to the compositions listed in Table 2. The powder adhesive (Adhesive-MC) was formulated using PMMA, PEMA,

PMMA-PEMA, Si-treated fillers, adhesive monomers of 4-AET and 4-AETA, and MC-BPO and MC-TMBA. Control adhesive resin (Adhesive-BR) comprising non-microencapsulated polymerization initiators (Bare-BPO and Bare-TMBA), which were displaced with MC-BPO and MC-TMBA, were prepared according to a method described in a previous work⁹. The liquid of two powder adhesives was composed of DEPT in MMA monomer. The latter was used as a solvent for PEMA of microcapsules in consideration of biosafety. The liquid was then used to mix with powders of Adhesive-MC and -BR. Prepared adhesive resins were placed in air at 5°C, 23°C, and 40°C (75% relative humidity) for two months, and their bonding performance and curing time were examined.

Shear bond strength measurement

1. Preparation of adherends

Due to the large number of teeth required in this study, freshly extracted bovine incisors were used as substitutes for human specimens¹⁵. Bovine teeth with the root cut off were embedded in epoxy resin, ground with 600-grit SiC abrasive paper under running water until enamel or dentin was visibly exposed, and then air-dried (ground enamel or dentin).

A dental gold alloy (Super Gold Type 4, Shofu Inc., Kyoto, Japan) was cast with a casting machine (Argon Caster, Shofu Inc., Kyoto, Japan), and gold alloy rods (6.0 $\pm$ 0.1 mm in diameter, 3.0 mm in height) were prepared. Commercially pure titanium (CP Ti) was purchased from Daido Steel Co. Ltd. (Nagoya, Aichi, Japan). Subsequently, the adhesive surfaces of SUS 303 rod (5.0 $\pm$ 0.1 mm in diameter,

Table 2 Compositions of experimental PMMA-type adhesive resins

Powdery adhesive	PMMA	PMMA-PEMA	PEMA	SiO ₂ powder	4-AET	4-AETA	BPO	TMBA
Adhesive-MC [g]	40.0	45.0	15.0	15.0	2.3	0.8	MC* 0.63(0.3)	MC* 2.05(1.0)
Adhesive-BR [g]	40.0	45.0	15.0	15.0	2.3	0.8	Bare 0.3	Bare 1.0
	MMA	HEMA	EGDMA	DEPT	MEHQ	BHT		
Liquid adhesive [g]	100.0	5.0	2.0	1.2	0.004	0.3		

Note: PMMA: poly(methyl methacrylate), PMMA-PEMA: copolymer of poly(methyl methacrylate) and poly(ethyl methacrylate), PEMA: poly(ethyl methacrylate), 4-AET: 4-acryloxyethyltrimellitic acid, 4-AETA: 4-acryloxyethyltrimellitic anhydride, SiO₂ powder (=Si-treated silica): particle size 1.5 μ m, BPO: benzoyl peroxide, TMBA: 1,3,5-trimethylbarbituric acid, MMA: methylmethacrylate, HEMA: 2-hydroxyethyl methacrylate, EGDMA: ethyleneglycol dimethacrylate, DEPT: *N,N*-dihydroxyethyl-*p*-toluidine, MEHQ: methoxy hydroquinone, BHT: butylated hydrotoluene, *: Figures in parentheses indicate the amount of BPO or TMBA in microcapsule, where in the content of BPO in MC is 47.9% and the content of TMBA in MC is 48.8%

6.0±0.1 mm in height), gold alloy, and titanium (4.0±0.1 mm in diameter, 6.0±0.1 mm in height) were embedded in epoxy resin, ground flat using 600-grit SiC abrasive paper; and then sandblasted with aluminum oxide (40–50 μm) (Hi-alumina, Shofu Inc., Kyoto, Japan) under a pressure of 5 kgf/cm². Sandblasted SUS rod, gold alloy, and titanium metal were cleaned ultrasonically and dried at room temperature to be used as metal adherends (*i.e.*, sandblasted SUS rod, gold alloy, and titanium metal) in this study.

2. Shear bond testing

The prepared adherends were treated with a surface treatment agent before adhesion. The adhesive surface of metal (*i.e.*, sandblasted SUS rod, titanium, or gold alloy) was treated with Metal Link Primer (Shofu Inc., Kyoto, Japan) — a metal primer for adhesion to precious and non-precious metals. The SUS rod or gold alloy without Metal Link Primer treatment was used as a control.

The adhesive surface of ground enamel or dentin was treated with or without ResiCem Primer (Shofu Inc., Kyoto, Japan) — a self-etching primer for adhesion to enamel and dentin. Adhesive-MC or Adhesive-BR mixed with the adhesive liquid as listed in Table 2 was applied by brush-on technique on the adherends and bonded with: (1) titanium and ground enamel or dentin with or without surface treatment agent; and (2) SUS rod and gold alloy. A load of 200 g was applied on the titanium or SUS rod for a curing time previously determined plus an additional one minute. After 30 minutes, the test specimens ($n=10$) were immersed in distilled water at 37°C for 24 hours. Shear bond strength was measured using a mechanical testing machine (Instron 5543, Instron Co., USA) at a crosshead speed of 1 mm/min.

All tests were conducted at 23±1°C. Fractured surfaces of specimens were examined using a microscope, and failure type (*i.e.*, adhesive failure, cohesive failure, or mixed failure) was recorded. The mean and standard deviation for the load at failure were calculated, and the results subjected to one-way analysis of variance (ANOVA) followed by Newman–Keuls multiple comparison test.

Curing time measurement

The curing times of experimental adhesive resins containing microencapsulated polymerization initiators or bare initiators were measured with a thermograph (DX104-1-1, Yokogawa, Tokyo, Japan) to obtain a thermal curve representing different levels of degradation. The powder of Adhesive-MC or -BR of 5.0 g was added into a silicon cup and 2.5 g of adhesive liquid was poured into this cup. These materials were mixed for 10 seconds using a spatula. Thermocouples were embedded into these materials, and the time (curing time) required for the tempera-

ture to rise to the highest value was measured immediately after mixing both adhesive materials.

The same procedure of curing time measurement was performed again for Adhesive-MC or -BR (*i.e.*, mixing the powder adhesive with adhesive liquid and recording the curing time) after two months' storage at 40°C in air and in relative humidity of 75%.

RESULTS

Synthesis and characterization of microencapsulated BPO and TMBA

Six kinds of newly designed microcapsules (MC-BPO or MC-TMBA) were derived from the needle and cubic forms of calcium carbonate (CC) powder used as stabilizer with sodium dodecyl sulfonate (DBS). BPO or TMBA was used as a core material with PEMA as a wall material, and synthesis was by drying-in-liquid method (Fig. 2).

In the microencapsulation process, PEMA and BPO (or TMBA) were added to MMA to prepare a primary suspension (solid in oil; S/O) (dispersed phase). This dispersed phase was poured into a continuous phase, in which given amounts of DBS and CC were added. This solid-oil-water dispersion was transferred to a separable flask, and MMA in the solvent was removed under reduced pressure (700 mmHg). Freeze-dried microcapsules of a given amount were suspended in *n*-hexane, then dried. Through the microencapsulation process, six kinds of microencapsulated BPO and TMBA were quantitatively obtained from the needle form (particle size: 1.00, 2.00, 5.00 μm) and cubic form (particle size: 0.04, 0.15, 0.80 μm) of CC. For example, the yield based on PEMA was 98% for MC-BPO and 97% for MC-TMBA derived from 0.04- μm cubic-shaped crystals of calcium carbonate, and the content of BPO in MC-BPO was 47.9% and that of TMBA in MC-TMBA was 48.8%.

Figure 3 shows the typical SEM micrographs of whole, BPO-containing microcapsules prepared by adding 5.4 g of CC. Six kinds of microencapsulated BPO derived from the two types of CC powder stabilizer — needle form (particle size: 1.00, 2.00, 5.00 μm) and cubic form (particle size: 0.04, 0.15, 0.80 μm) — were observed. These micrographs showed that the microcapsules synthesized were almost spherical with 30–45 μm diameter — be it derived from needle or cubic form. The surface became rougher in the case of needle shape than in the case of cubic shape and with increase in the size of needle-shaped calcium carbonate. Furthermore, presence of fine pores on the microcapsule surface decreased with decrease in the size of calcium carbonate crystals. From these results, it was suggested that the surface morphology was constituted by traces of calcium carbonate adhering on the microcapsule surface.

1.0 μm -Needle shape crystal

0.04 μm -Cubic shape crystal

2.0 μm -Needle shape crystal

0.15 μm -Cubic shape crystal

5.0 μm -Needle shape crystal

0.80 μm -Cubic shape crystal

Fig. 3 Typical SEM micrographs of the whole microcapsules of BPO that were almost spherical with 30–45 μm diameter. Six kinds of MC-BPO were derived from the needle form (particle size: 1.00, 2.00, 5.00 μm) and cubic form (particle size: 0.04, 0.15, 0.80 μm) of calcium carbonate.

1.0 μm-Needle shape crystal

0.04 μm-Cubic shape crystal

2.0 μm-Needle shape crystal

0.15 μm-Cubic shape crystal

5.0 μm-Needle shape crystal

0.80 μm-Cubic shape crystal

Fig. 4 SEM micrographs of the cross-section microcapsules that corresponded with the microcapsules in Fig. 3. No differences in the inner structure of microcapsules due to the shape and size of calcium carbonate were observed. BPO as core material was found to be well microencapsulated.

Figure 4 shows the SEM micrographs of the cross-sectioned microcapsules that corresponded with the microcapsules in Fig. 3. Traces of BPO crystals could be seen in all the photographs, but no differences in the inner structure of microcapsules due to the shape and size of calcium carbonate crystals were observed. From these results, it was apparent that BPO as a core material was indeed well microencapsulated.

Figure 5 depicts the dependence of mean diameter (dp) on the amount adhered (W) per unit surface area of microcapsule. The amount adhered per unit surface area was calculated by assuming that CC added entirely adhered on the surface of microcap-

Fig. 5 Dependence of mean diameter (dp) on the amount adhered (W) per unit surface area of microcapsule. It was found that the mean diameter strongly depended on the amount adhered per unit surface area and that their dependence behaviors differed according to the shape of calcium carbonate.

sules. From this figure, it was found that the mean diameter strongly depended on the amount adhered per unit surface area and that their dependence behaviors differed according to the shape of CC crystals. As the adhesion layer of CC with smaller particle size might become more minute and the resultant emulsion being more stable, the dependence for cubic-shaped CC might become saturated by a smaller amount and hence smaller than that for needle-shaped CC.

Figure 6 depicts the dependence of microencapsulation efficiency on the concentration of CC. It was found that microencapsulation efficiencies were above 0.9 at all the conditions and were slightly

Fig. 6 Dependence of microencapsulation efficiency on the concentration of calcium carbonate (CC). It was found that microencapsulation efficiencies were above 0.9 at all the conditions and were slightly higher in the case of cubic-shaped CC.

Table 3 Shear bond strengths of experimental adhesive resins and unetched ground enamel or dentin

Adherend	Surface treatment agent	Adhesive	Bond strength (MPa)	A/M/C(%) [§]
Titanium-enamel	No	Adhesive-MC	16.6(6.5) ^a	20/80/0
Titanium-enamel	No	Adhesive-BR	15.7(6.5) ^a	20/80/0
Titanium-enamel	Yes	Adhesive-MC	15.2(4.5) ^a	20/80/0
Titanium-enamel	Yes	Adhesive-BR	15.8(4.8) ^a	20/80/0
Titanium-dentin	No	Adhesive-MC	4.0(2.4) ^b	100/0/0
Titanium-dentin	No	Adhesive-BR	3.8(2.2) ^b	100/0/0
Titanium-dentin	Yes	Adhesive-MC	18.7(6.1) ^a	20/80/0
Titanium-dentin	Yes	Adhesive-BR	17.5(5.8) ^a	20/80/0

Note: $n=10$, Adhesive-MC: adhesive resin comprising microencapsulated polymerization initiators. Adhesive-BR: adhesive resin comprising bare polymerization initiators. Surface-treating agent: Yes: Metal-Link Primer for titanium (CP Ti), ResiCem Primer for ground enamel or ground dentin., No: not treated with these primers. Values are means (standard deviation), Group from the same column that are identified with the same superscript letters are not significantly different ($p>0.05$). § Failure modes (A/M/C): percent of Adhesive failure/Mixed failure/Cohesive failure in adhesive.

higher in the case of cubic-shaped CC. These results might be attributed to the dispersion stability being established by adding CC powder as a stabilizer and becoming higher with cubic-shaped CC than with needle-shaped CC, as shown in Fig. 5.

Shear bond strength measurement and polymerization initiating activity

Based on the characterization of microcapsules (Figs. 3–6), MC-BPO and MC-TMBA derived from 0.04- μm cubic-shaped crystals of calcium carbonate were used to formulate the PMMA-type adhesive resin (Adhesive-MC) in this study. Table 3 presents the shear bond strength results of experimental Adhesive-MC comprising microencapsulated initiators (MC-BPO and MC-TMBA) and those of Adhesive-BR comprising bare initiators (Bare-BPO and Bare-TMBA) between the sandblasted titanium and unetched ground enamel/dentin with or without surface treatment agent.

Statistical analysis (ANOVA) indicated that there were no significant differences between Adhesive-MC and Adhesive-BR in their bond strengths to unetched ground enamel (15.2–16.6 MPa) with or without surface treatment agent ($p < 0.05$). As to unetched ground dentin treated with surface treatment agent, there were no significant differences in bond strength between Adhesive-MC and Adhesive-BR ($p < 0.05$). This was a similar scenario for Adhesive-MC and Adhesive-BR to unetched ground dentin without surface treatment agent. In sharp contrast, between unetched ground dentin treated with surface treatment agent (17.5–18.7 MPa) and that without surface treatment agent (3.8–4.0 MPa), statistically significant differences were observed ($p < 0.05$).

Table 4 represents the shear bond strength

results of Adhesive-MC and Adhesive-BR between the sandblasted SUS rod and sandblasted gold alloy that was treated with Metal Link Primer. Evaluation periods were namely at the start of the storage period, after one month and two months at 5°C, 23°C, and 40°C in a relative humidity of 75%. With regard to the effect of Metal Link Primer treatment on adhesion, bond strengths to the gold alloy treated with Metal Link Primer at the starting period were significantly higher than those without the primer treatment (Control) for both adhesive resins ($p < 0.05$).

Statistical analysis (ANOVA) indicated that the bond strengths of Adhesive-MC to gold alloy maintained [starting: 42.5 (3.7) MPa] after two-month storage period at 5°C [41.8 (4.8) MPa] and 23°C [39.5 (8.1) MPa], and also after one-month storage at 40°C [31.0 (9.8) MPa] ($p < 0.05$). For the aforementioned storage periods and conditions, 100% mixed failure (M) of adhesive resin was observed on the fractured surfaces. On the contrary, the bond strength of Adhesive-BR to gold alloy after two-month storage period at 23°C [12.8 (6.4) MPa] was significantly decreased ($p < 0.05$) with 90% adhesive failure (A). Furthermore, the bond strengths using Adhesive-BR after one and two months of storage at 40°C could not be tested (CNT). While there were no significant differences between Adhesive-MC and Adhesive-BR in bond strength after two-month storage at 5°C and one-month storage 23°C, there were significant differences between both adhesive resins in bond strength after two-month storage at 23°C and 40°C ($p < 0.05$).

Figure 7 presents the thermal curves as obtained with the polymerization of Adhesive-MC and Adhesive-BR at the start of the storage period and after one and two months of storage at 5°C, 23°C, and 40°C in a relative humidity of 75%. At the starting

Table 4 Shear bond strengths of experimental adhesive resins between SUS rod and gold alloy

Storage period of adhesive resins	Adhesive-MC		Adhesive-BR	
	Bond strength (MPa)	A/M/C(%) [§]	Bond strength (MPa)	A/M/C(%) [§]
Control*	7.5(3.5) ^c	100/0/0	7.0(5.3) ^c	100/0/0
Starting	42.5(3.7) ^a	0/100/0	39.8(4.9) ^a	0/100/0
1-month at 5°C	41.0(8.0) ^a	0/100/0	40.3(2.8) ^a	0/100/0
2-month at 5°C	41.8(4.8) ^a	0/100/0	40.1(2.8) ^a	0/100/0
1-month at 23°C	40.7(7.8) ^a	0/100/0	43.8(3.5) ^a	0/100/0
2-month at 23°C	39.5(8.1) ^a	0/100/0	12.8(6.4) ^{b,c}	90/10/0
1-month at 40°C	31.0(9.8) ^{a,b}	0/100/0	CNT	CNT
2-month at 40°C	27.2(7.8) ^b	20/80/0	CNT	CNT

Note: $n=10$, Adhesive-MC: adhesive resin comprising microencapsulated polymerization initiators, Adhesive-BR: adhesive resin comprising bare polymerization initiators. The adhesive surface of SUS rod or gold alloy except Control* was treated with Metal Link Primer. Values are means (standard deviation). Group from the same column that are identified with the same superscript letters are not significantly different ($p > 0.05$). CNT: could not be tested.

§ Failure modes (A/M/C): percent of Adhesive failure/Mixed failure/Cohesive failure in adhesive.

Fig. 7 Thermal curves of Adhesive-MC and Adhesive-BR. The curing times of Adhesive-MC at 40°C were $t_c=304$ s at starting period and $t_c=490$ s after 1 month (1.6 times of starting period). In contrast, Adhesive-BR at 40°C after 1 month showed a delayed curing time of $t_c=1222$ s (4.0 times of starting period).

Fig. 8 Powdery adhesive of Adhesive-BR after 1-month storage at 40°C (75% relative humidity). Adhesive-BR was markedly changed after 1-month storage because of agglomeration (1.42–3.19 mm), which had an adverse effect on handling property, especially brush-on technique for PMMA-type adhesive resin.

period, both mixed powder-liquid adhesives ($P/L=2.0$) showed almost the same curing time ($t_c=304$ seconds). However, after one and two months of storage at 40°C, the curing times for Adhesive-MC were $t_c=490$ seconds and $t_c=970$ seconds respectively. For Adhesive-BR, it was $t_c=1222$ seconds after one-month storage. After two months' storage, curing time could not be measured for Adhesive-BR—in

other words, BPO was substantially deactivated.

The powder property of Adhesive-MC was not significantly changed even after two months' storage at 40°C in terms of good handling property and ease of applying brush-on technique. By contrast, Adhesive-BR was markedly changed after one-month storage at 40°C. This was a result of adhesive resin powder agglomeration, yielding agglomerates which were almost spherical in shape with 1.42–3.19 mm diameter (Fig. 8). Agglomerated Adhesive-BR powder had an adverse effect on handling property, especially in terms of the ease of applying PMMA-type adhesive resin by brush-on technique.

DISCUSSION

A multi-purpose adhesive resin should allow strong and durable adhesion to the various adherends coexisting in the oral environment, such as the dental hard tissues (*i.e.*, enamel and dentin), precious metals (*i.e.*, gold, platinum and gold alloys), non-precious metals, and porcelains and ceramics (*i.e.*, alumina- and zirconia-based ceramics). To design such an adhesive resin, not only super-adhesive monomers that exhibit good chemical interaction with these adherends¹⁶, but also advanced radical polymerization initiators are extremely valuable components in the adhesive formulation. Thus, numerous studies have tirelessly explored and sought for active initiating polymerization initiators^{1,2,9}. However, previous investigations on polymerization initiators have almost exclusively dealt with bare polymerization initiators. It was anticipated that these bare active initiators could interact among themselves or with adhesive monomers, thereby posing a problem to the long-term stability of adhesive resins.

To circumvent these adverse effects of bare polymerization initiators on stability, we proposed to amalgamate microcapsule technology with dental adhesive technology to the end of developing a novel, multi-purpose, PMMA-type adhesive resin. Results of this study that involved a novel dental adhesive comprising microencapsulated polymerization initiators might thus yield important information for the future development of an advanced dental adhesive.

To date, the behavior of microencapsulated reactive compounds in a dental adhesive is unknown. In general, the structure of a microcapsule consists of a core material and a shell (wall) material. In this study, six kinds of newly designed microcapsules (MC-BPO or MC-TMBA) were derived from the needle and cubic forms of calcium carbonate (CC) powder used as stabilizer with sodium dodecyl sulfonate (DBS). BPO or TMBA was used as a core material with PEMA as a wall material, and synthesis was by drying-in-liquid method (Fig. 2). Quantitative yield was 97–98%, and the contents of BPO in MC-BPO

and TMBA in MC-TMBA were 47.9% and 48.8% respectively. From SEM observation, the microcapsules synthesized were almost spherical with 30–45 μm diameter — be it needle or cubic form (Fig. 3). In particular, BPO as a core material was found to be well microencapsulated indeed (Figs. 2–5).

In general, the mean droplet diameter in liquid dispersion decreases with concentration of solid powder and that diameter distribution becomes narrower with decrease in powder particle size^{17–19}. In this study, the effect of the added amount of CC on the mean diameter of microcapsules was investigated. It was found that the mean diameter strongly depended on the amount adhered per unit surface area and that their dependence behaviors differed according to the shape of CC crystals (Fig. 5). Regarding the dependence of microencapsulation efficiency on CC concentration, it was found that microencapsulation efficiencies were above 0.9 at all the conditions and were slightly higher with cubic-shaped CC than with needle-shaped CC (Fig. 6). These results could be attributed to dispersion stability being established by adding CC powder as a stabilizer and becoming higher with cubic-shaped CC than with needle type CC.

To avoid compromised adhesion arising from undesirable salt formation caused by BPO-DEPT redox initiator system, TMBA-BPO-DEPT ternary initiator system⁹ with or without microencapsulation was employed so that acidic adhesive monomers could perform their essential adhesion-promoting functions. The ternary initiator system markedly reduced the adverse effects on both polymerization and adhesion⁹, and at the same time increased the cohesive strength of adhesive layer between the adherends^{9,16,20}. Indeed, co-initiators of 5-mono-substituted barbituric acids (5-MSBA) (Fig. 1), *i.e.*, TMBA, are of remarkable importance for adhesive resin compositions in which acidic adhesive monomers are incorporated. To date, details of the polymerization initiation mechanism of 5-MSBA-BPO-DEPT and 5-MSBA-ASA-*t*-BPMA initiator systems is still unknown. Nonetheless, the initiation behavior of 5-MSBA could be triggered by auto-oxidation of C-H at the 5-position in the barbituric acid ring to form a peroxide of -C-O-O-H in the presence of an inorganic base^{2,9}. The unique 5-MSBA can perform the function of a reducing agent as a nitrogen-containing compound and the function of a 5-positioned C-H active initiator as an acidic cyclic acid. In another aspect of material design, TMBA was deliberately microencapsulated with PEMA. This was because the solubility of PEMA in MMA monomer is higher than that of PMMA, and thus PEMA was selected as a shell polymer in this study.

This study further investigated the effects of novel, PMMA-type adhesive resin — formulated from

newly synthesized microcapsules of BPO (MC-BPO) and TMBA (MC-TMBA) — on multi-purpose adhesion to enamel, dentin, titanium, and gold alloy, together with comparing against control adhesive resin comprising non-microencapsulated polymerization initiators (Bare-BPO and Bare-TMBA). MC-BPO and MC-TMBA derived from 0.04- μm cubic-shaped crystals of calcium carbonate were used. Taking into account that shearing force is applied at the interface between an inlay and the tooth structure by virtue of occlusal mastication force, conventional shear bond strength testing was thus employed in this study. For the bond strengths of adhesive resins to unetched ground enamel with or without surface treatment agent, there were no significant differences between Adhesive-MC and Adhesive-BR ($p < 0.05$) (Table 3). However, there were significant differences in bond strength to ground dentin with and without surface treatment agent ($p < 0.05$).

As for bonding performance to gold alloy (Table 4), it was found that Adhesive-MC maintained its shear bond strength after two months' storage at 5°C and 23°C. After one month's storage at 40°C, shear bond strength decreased to about 73% of the starting bond strength but with no statistically significant difference ($p < 0.05$). Even after two months' storage period at 40°C, adhesive strength remained at about 64% of the starting bond strength. By contrast for Adhesive-BR, bond strength was found to significantly decrease with storage period and to be completely lost after two months' storage at 40°C. These results confirmed that the microcapsules aptly controlled and regulated the function of polymerization activation in Adhesive-MC, thereby providing an adequate supply for the entire test period of two months.

With regard to the surface treatment agents used in this study, ground enamel and dentin were treated with ResiCem Primer, while SUS rod, titanium, and gold alloy used were treated with Metal Link Primer. The bond strengths of Adhesive-MC and Adhesive-BR to dentin treated with ResiCem Primer [MC: 18.7 (6.1); BR: 17.5 (5.8) MPa] were significantly higher (about 4.6 times higher) than those to dentin without surface treatment agent [MC: 4.0 (2.4); BR: 3.8 (2.2) MPa] ($p < 0.05$) (Table 3). It is noteworthy that ResiCem Primer contained 6-methacryloyloxyhexyl phosphonoacetate (6-MHPA)¹⁶ and 4-AET as acidic adhesive monomers. On a separate note, Adhesive-MC and Adhesive-BR strongly adhered to the gold alloy treated with Metal Link Primer [starting: MC: 42.5 (3.7); BR: 39.8 (4.9) MPa], such that significantly higher values (about 5.7 times higher) than those without the primer treatment [Control: MC: 7.5 (3.5); BR: 7.0 (5.3) MPa] ($p < 0.05$) (Table 4) were obtained. It is noteworthy that Metal Link Primer contained both a phosphorus-contain-

ing monomer, *i.e.*, 6-MHPA, and a sulfur-containing monomer, *i.e.*, 10-methacryloyloxydecyl 6,8-dithiooctanate (10-MDDT)²¹⁾, in the formulation. As such, this primer could strongly enhance the adhesion to both precious metals and non-precious metals alike. Furthermore, a recent work²³⁾ found that 6-MHPA in AZ Primer (Shofu Inc., Kyoto, Japan) exhibited strong adhesion to alumina- and zirconia-based all-ceramic prostheses. Thus, 6-MHPA and 10-MDDT are indeed the must-have adhesive monomers for the design of multi-purpose adhesives.

The effect on polymerization initiating activity of newly synthesized microcapsules was further investigated by measuring the curing times of Adhesive-MC and Adhesive-BR (Fig. 7). The curing times of Adhesive-MC at 40°C showed $t_c=304$ seconds at the starting period, $t_c=490$ seconds after one month (1.6 times that of starting period), and $t_c=970$ seconds after two months (3.2 times that of starting period). In sharp contrast, Adhesive-BR showed a severely delayed curing time of $t_c=1222$ seconds after one month at 40°C (4.0 times that of starting period). After two months' storage, the curing time of Adhesive-BR could not be tested (CNT). It must be highlighted that at the starting period, both Adhesive-MC and Adhesive-BR had almost the same curing time ($t_c=304$ seconds). These results thus showed that the PEMA of MC-BPO or MC-TMBA was immediately dissolved by MMA monomer when the powder adhesive was mixed with the adhesive liquid, such that the exposed BPO and TMBA reacted with DEPT in the liquid to initiate the polymerization of Adhesive-MC.

The temperature of half-value period (10 hours, $t_{1/2}$) — defined as the temperature of 50% decomposition of peroxide for 10 hours — of diacyl peroxides is 20–75°C, and that of BPO is about 50°C²³⁾. It was suggested that the curing time of Adhesive-MC was influenced only by the lower $t_{1/2}$ of BPO. However, the delayed curing time of Adhesive-BR was caused not only by the lower $t_{1/2}$ of BPO, but also by the undesirable interaction of bare BPO with bare TMBA, 4-AET and 4-AETA. It is noteworthy that despite the lower $t_{1/2}$ of BPO, Adhesive-MC exhibited good stability even after two months' storage at 40°C in this study. Nonetheless, further investigations on the effect of microencapsulation of BPO on thermal stability should be performed.

The powder property of Adhesive-MC was not significantly changed in terms of good handling property even after two months' storage at 40°C. On the contrary, that of Adhesive-BR was markedly changed after one month's storage at 40°C because of agglomeration (Fig. 8). Agglomerated Adhesive-BR powder had an adverse effect on handling property, especially in terms of mixing and the ease of applying PMMA-type adhesive resin by brush-on technique.

It was thought that the agglomeration of Adhesive-BR powder might be caused by the hygroscopic nature of bare TMBA — which took up water after two months' storage at 40°C in a relative humidity of 70%. Therefore, when the adverse hygroscopic nature of TMBA was masked by the microencapsulation of TMBA with PEMA polymer, Adhesive-MR demonstrated good stability. Further on stability, the curing time behavior and shear bond strength of Adhesive-MC to gold alloy during the two-month storage at 40°C showed a highly negative correlation ($r=-0.861$; $y=-0.02x+45.3$). It was thus apparent that polymerization reactivity influenced the bonding performance of adhesive resins.

Based on these results, it was found that compared to non-microencapsulated initiators, the newly designed microcapsules of BPO and TMBA contributed to good multi-purpose bonding performance and polymerization activity of PMMA-type adhesive resin — with formulation stability — after artificial aging periods. Thus, these findings supported the acceptance of the null hypothesis in this study. Moreover, microcapsules synthesized in this study were found to possess the ability to initiate polymerization even after two months' storage. This was applicable not only on dental materials, but also when used in conjunction with pharmaceutical products and medical biomaterials (such as PMMA-type bone cements) to avoid undesirable interaction of bare reactive compounds. On this note, this basic study should be further pursued and extended to other dental products, such as dental PMMA-type self-cured resins and PMMA-type adhesives for orthodontic brackets, splinting of mobile teeth, metallic denture base, inlay and crown, and alumina- and zirconia-based all-ceramic prostheses.

Although microcapsule technology is rarely explored and applied in the field of adhesive dentistry, recent works^{24,25)} in our research series invented curable compositions comprising microcapsules²⁴⁾ and one-pack medical and dental curable compositions comprising micro- and/or nanocapsules²⁵⁾. All the findings in the present study were gleaned from the research studies for these inventions. In a prior art, bare aromatic diacyl peroxides react with bare aromatic tertiary amines for redox-initiated polymerization, bare aromatic tertiary amines interact with bare acidic adhesive monomers to form salts, and bare polyalkenoic acids react with fluoroaluminosilicate glass as an acid-base reaction to form hardened glass ionomer cements²⁶⁾. Therefore, these reactive components are not able to coexist within a one-pack formulation. In our research efforts to circumvent these adverse effects of bare reactive compounds on stability, we found that microcapsules and/or nanocapsules containing peroxides, aromatic tertiary amines, acidic adhesive monomers,

polyalkenoic acids, or reactive glass fillers were able to coexist within one-pack composition with good stability. These findings suggested that micro- and/or nano-encapsulated polymerization initiators or polyalkenoic acids facilitated the formulation of one-pack curable compositions with good stability, such as one-pack chemically cured adhesive resins or one-pack glass ionomer cements^{24,25}.

It is expected that micro- and/or nanocapsule technologies would open new vistas in the field of adhesive dentistry. To develop the all-encompassing, multi-purpose adhesive resin, research efforts on micro- and/or nanocapsule technologies should continue unabated while in the mean time seeking out active initiating polymerization initiators and super-adhesive monomers.

CONCLUSIONS

This study presented a novel, multi-purpose, PMMA-type adhesive resin based on the amalgamation of dental adhesive technology with microcapsule technology. New microcapsules of polymerization initiators were synthesized, and their bonding performance and polymerization reactivity were investigated. The following findings were obtained:

- (1) Microencapsulated BPO and TMBA with PEMA as a shell polymer were derived from the needle and cubic forms of calcium carbonate. Synthesis was by drying-in-liquid method with 97–98% yield and 30–54 μm diameter.
- (2) The mean diameter of microcapsules strongly depended on the amount of calcium carbonate adhering on the microcapsule surface.
- (3) There were no significant differences between Adhesive-MC and Adhesive-BR in shear bond strength to ground enamel and dentin with or without surface treatment agent ($p < 0.05$).
- (4) Adhesive-MC still retained its capabilities for adhesion to gold alloy and initiation of radical polymerization even after two months' storage at 40°C ($p < 0.05$). In direct contrast, Adhesive-BR degraded in bond strength and showed markedly delayed polymerization reactivity as storage period progressed.
- (5) The new microencapsulated BPO and TMBA enabled PMMA-type adhesive resin to exhibit good multi-purpose bonding performance and polymerization activity with formulation stability.

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