Effect of novel dithiooctanoate monomers, in comparison with various sulfur-containing adhesive monomers, on adhesion to precious metals and alloys

Kunio IKEMURA¹, Katsunori KOJIMA², Takeshi ENDO³ and Yoshinori KADOMA²

¹Department of Research and Development, Shofu Inc., 11 Kamitakamatsu-cho, Fukuine, Higashiyama-ku, Kyoto 605-0983, Japan

²Department of Applied Functional Molecules, Division of Biofunctional Molecules, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan

³Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka 820-8555, Japan

Corresponding author, Kunio IKEMURA; E-mail: k-ikemura@shofu.co.jp

This study investigated the effect of novel dithiooctanoate monomers, in comparison with conventional sulfur-containing monomers, on adhesion to precious metals and alloys. Nine experimental primers containing 5.0 wt% 2-methacryloyloxyethyl 6,8-dithiooctanoate (2-MEDT), 6-methacryloyloxyhexyl 6,8-dithiooctanoate (6-MHDT), 10-methacryloyloxydecyl 6,8-dithiooctanoate (10-MDDT), bis(2-methacryloyloxyethyl) disulfide (BMEDS), bis(5-methacryloyloxyethyl) disulfide (BMPDS), bis(10-methacryloyloxydecyl) disulfide (BMDDS), 6-(4-vinylbenzyl-*n*-propyl) amino-1,3,5-triazine-2,4-dithione (VBATDT), *N*-(4-mercaptophenyl)methacrylamide (MPMA), or 4-methacryloyloxyethoxycarbonylphthalic anhydride (4-META; control) were prepared. After primer pretreatment and bonding using modified MMA-PMMA/BPO-DEPT resin, tensile bond strengths to precious metals and alloys after 2,000 thermal cycles were measured. For bonding to Au or Ag, novel 2-MEDT, 6-MHDT, and 10-MDDT exhibited significantly higher tensile bond strengths than conventional BMEDS, BMPDS, BMDDS, VBATDT, MPMA, and 4-META ($p < 0.05$). For bonding to Au alloy, Ag alloy, and Au-Ag-Pd alloy, all the novel dithiooctanoate monomers showed significantly higher tensile bond strengths than conventional BMEDS, BMPDS, VBATDT, MPMA, and 4-META ($p < 0.05$). It was found that novel dithiooctanoate monomers exhibited excellent bonding to precious metals and alloys when compared with conventional sulfur-containing monomers.

Keywords: Dithiooctanoate monomer, Sulfur-containing adhesive monomer, Precious metal, Dental precious metal alloy

INTRODUCTION

In prosthetic dentistry, resin-veneered prostheses are now frequently used in dental practice¹. The use of metal primer in the fabrication of resin composite-veneered restorations and intraoral repair of fractured ceramic or resin composite veneers has increased substantially, mainly because of the development of adhesion-promoting monomers (adhesive monomers) for dental casting alloys and ceramics². Bonding to non-precious metals and alloys has been progressed considerably³, mainly by the use of metal primers which contain acidic adhesive monomers^{4–8} and the employment of surface modification techniques^{9–11}. In contrast, bonding of acidic adhesive monomers to precious metals and alloys has been characterized by low bond strengths due to the poor water resistance of the adhesive systems¹² or the chemical inertness of precious metals and alloys¹³. To achieve strong adhesion, numerous surface modification methods have been developed—such as heat treatment^{12,14}, electroplating with tin^{15,16}, silica coating^{9,11,17}, ion-coating¹², and the application of liquid Ga-Sn alloy¹⁸.

Over the past decade, relentless efforts to improve the bonding technology of dental adhesives to precious metals and alloys have yielded major advances, notably the development of sulfur-containing adhesive monomers which contain at least one sulfur atom in their structures. Sulfur-containing adhesive monomers boast of two key advantages that are highly desirable: simple application with effective adhesion. These advantages stem from

their ability to form chemical bonds with metal atoms on the surfaces of precious metals^{19,20}, due to the chemical adsorption of organic sulfur compounds on gold surfaces and the formation of monolayer films by a spontaneous assembly of organic thiols^{21,22}. Thereby, numerous sulfur-containing adhesive monomers^{13,23–25} were developed—such as thiophenols, thiophosphoric acids, triazinedithiones, thiols, thiobarbituric acids, sulfides, disulfides, and thiouracil and thirane monomers. Some of these sulfur-containing monomers were already included as an extremely valuable component in the formulations of some commercial metal primers for bonding to dental precious metal alloys. Incidentally, most of sulfur-containing adhesive monomers were developed in Japan, and that most of the studies which pertained to bonding to precious metals and alloys using sulfur-containing monomers were conducted by Japanese researchers. The research and development of sulfur-containing adhesive monomers is still continuing unabated in Japan.

In our quest for more advanced sulfur-containing adhesive monomers, eight kinds of novel acryloyloxyalkyl and methacryloyloxyalkyl 6,8-dithiooctanoates (dithiooctanoate monomers) were previously synthesized²⁶. It was found that novel dithiooctanoate monomers exhibited excellent bonding performances to precious metals and alloys using methyl methacrylate-polymethyl methacrylate/tri-*n*-butylborane oxide (MMA-PMMA/TBBO) as the adhesive resin²⁶. In light of this encouraging result, our research strategy further focused an attractive target which was to compare the

bonding abilities of dithiooctanoate monomers²⁶⁾ to precious metals and alloys against those of conventional sulfur-containing monomers, such as thiophenols²³⁾, disulfides²⁴⁾, and triazinedithiones²⁵⁾.

Therefore, the aim of the present study was to investigate the effect of three kinds of novel dithiooctanoate monomers on adhesion to precious metals and alloys [namely, gold (Au), silver (Ag), platinum (Pt), palladium (Pd), Au alloy, Ag alloy, and Au-Ag-Pd alloy] using a modified MMA-PMMA resin having benzoyl peroxide (BPO)-*N,N*-di(2-hydroxyethyl)-*p*-toluidine (DEPT) as a polymerization initiator system. The obtained bond results were then compared with five kinds of conventional sulfur-containing adhesive monomers (namely, three disulfides, one triazinedithione, and one thiophenol) and one acidic monomer.

MATERIALS AND METHODS

Preparation of adhesive monomers

Figure 1 shows the chemical structures of sulfur-containing adhesive monomers (Figs. 1a–d) and 4-META (Fig. 1e) used in this study. For the dithiooctanoate monomers (Fig. 1a) —namely, 2-methacryloyloxyethyl 6,8-dithiooctanoate (2-MEDT), 6-methacryloyloxyhexyl 6,8-dithiooctanoate (6-MHDT), and 10-methacryloyloxydecyl 6,8-dithiooctanoate (10-MDDT), they were synthesized by an esterification reaction between 6,8-dithiooctanoic acid and 2-hydroxyethyl methacrylate, 2-hydroxyhexyl methacrylate, or 10-hydroxydecyl methacrylate respectively according to the method reported in our previous study²⁶⁾. For the non-cyclic disulfide monomers (Fig. 1b) —namely, bis(2-methacryloyloxyethyl) disulfide (BMEDS), bis(5-methacryloyloxyethyl) disulfide (BMPDS), and bis(10-

Fig. 1 Schematic illustration of the chemical structures of sulfur-containing adhesive monomers and non sulfur-containing monomer used in this study. 2-MEDT: 2-methacryloyloxyethyl 6,8-dithiooctanoate, 6-MHDT: 6-methacryloyloxyhexyl 6,8-dithiooctanoate, 10-MDDT: 10-methacryloyloxydecyl 6,8-dithiooctanoate, BMEDS: Bis(2-methacryloyloxyethyl) disulfide, BMPDS: Bis(5-methacryloyloxyethyl) disulfide, BMDDS: Bis(10-methacryloyloxydecyl) disulfide, VBATDT: 6-(4-(vinylbenzyl)-*n*-propyl)amino-1,3,5-triazine-2,4-dithione, MPMA: *N*-(4-mercaptophenyl)methacrylamide, 4-META: 4-methacryloyloxyethoxycarbonylphthalic anhydride.

methacryloyloxydecyl) disulfide (BMDDS), they were prepared as previously reported²⁴. Similarly, for triazinedithione [6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithione (VBATDT); Fig. 1c]²⁵, thiophenol [*N*-(4-mercaptophenyl)methacrylamide (MPMA); Fig. 1d]²³, and non sulfur-containing monomer [4-methacryloyloxyethoxycarbonylphthalic anhydride (4-META); Fig. 1e]²⁷, they were prepared as previously reported.

Preparation of other reagents

Methyl methacrylate (MMA), polymethyl methacrylate (PMMA), and 2-hydroxyethyl methacrylate (HEMA) were purchased from Mitsubishi Rayon Co. Ltd. (Tokyo, Japan). Poly(ethyl methacrylate) (PEMA) (MW=80,000) and PMMA-PEMA copolymer were purchased from Negami Chemical Industrial Co. (Tokyo, Japan). Ethylene glycol dimethacrylate (EGDMA) was purchased from Shin-Nakamura Chemical Co. Ltd. (Wakayama, Japan). Benzoyl peroxide (BPO) was purchased from Kawaguchi Chemical Co. Ltd. (Tokyo, Japan). Butylated hydroxytoluene (BHT) and *N,N*-di(2-hydroxyethyl)-*p*-toluidine (DEPT) were purchased from Wako Pure Chemical Co. Ltd. (Tokyo, Japan) and used without further purification. Silane-treated silica fillers (mean particle size: 1.5 μ m) were prepared using γ -methacryloyloxypropyltrimethoxysilane (KBM-503; Shin-Etsu Chemical Co. Ltd., Tokyo, Japan).

Preparation of experimental adhesive primers and adhesive resin

Nine kinds of experimental adhesive primers, whereby each primer contained 5.0 wt% of a dithiooctanoate monomer (*i.e.*, 2-MEDT, 6-MHDT, or 10-MDDT), a non-cyclic disulfide monomer (*i.e.*, BMEDS, BMPDS, or BMDDS), or a sulfur-containing monomer (*i.e.*, VBATDT or MPMA) in acetone, were prepared. For comparison purpose, a control primer containing 5.0 wt% of 4-META as a non sulfur-containing monomer was prepared.

For the experimental adhesive resin, it was prepared based on the composition listed in Table 1. The powder was prepared using PMMA, PEMA, PMMA-PEMA copolymer, silane-treated silica fillers, and BPO. The liquid was prepared using MMA, HEMA, EGDMA, DEPT, and BHT. Since silane-treated silica fillers, EGDMA, and HEMA were added to MMA-PMMA resin, the experimental adhesive resin was hence termed as

“modified” MMA-PMMA/BPO-DEPT resin.

Preparation of metal adherends

Four kinds of precious metals [namely, gold (Au), silver (Ag), platinum (Pt), and palladium (Pd)] used as precious metal adherends were purchased from ISHIFUKU Metal Industry Co., Ltd. (Tokyo, Japan). The dental precious metal alloys used in this study were namely, Au alloy (Casting Gold M.C. Type IV, GC Dental Products Corp., Tokyo Japan), Ag alloy (Sunsilver, Sankin Kogyo Co. Ltd., Tokyo, Japan), and Au-Ag-Pd alloy (Castwell M.C., GC Dental Products Corp., Tokyo, Japan). Their compositions were as per those given in a previous report¹⁸.

Tensile bond strength test

The surface of each metal adherend was abrasively finished with alumina sandpapers of 1,000, 2,000, and 4,000 grits. An experimental primer was coated on each metal surface. Each primer-coated metal adherend was ultrasonically cleaned in acetone and allowed to stand overnight in acetone. After which, it was further cleaned ultrasonically in acetone and dried. On each metal adherend surface, the adhesion area was defined using a cellophane tape with a 5-mm perforation. The powder and liquid of modified MMA-PMMA/BPO-DEPT resin were mixed together at a powder/liquid ratio of 2.5/1, and then the resin was chemically cured for 5.5 minutes at 23 $\pm$ 1°C on the adhesion area of each primer-treated metal adherend surface. For bonding durability evaluation, the bonded specimens were subjected to a thermal cycling test of 2,000 cycles between water baths of 4°C and 60°C in alternate one-minute intervals. Tensile bond strength measurements were made on five specimens for each metal with a universal testing machine (Autograph AGS-1000A, Shimadzu Co., Kyoto, Japan) at a crosshead speed of 2.0 mm/min and at 23 $\pm$ 1°C.

Statistical analysis

Fractured surfaces after tensile bond strength testing were not examined in this study. 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 at 5% confidence level.

Table 1 Compositions of the powder and liquid of experimental modified MMA-PMMA/BPO-DEPT resin used in this study

Powder ^φ	(wt%)	Liquid ^φ	(wt%)
polymethyl methacrylate [PMMA]	35.0	methyl methacrylate [MMA]	91.5
poly(ethyl methacrylate) [PEMA]	13.0	2-hydroxyethyl methacrylate	5.0
PMMA-PEMA copolymer	39.0	ethylene glycol dimethacrylate	2.0
Si-treated silica powder	12.3	<i>N,N</i> -di(2-hydroxyethyl)- <i>p</i> -toluidine [DEPT]	1.2
benzoyl peroxide [BPO]	0.7	butylated hydroxytoluene	0.3

^φ Powder/Liquid ratio: 2.5/1.

RESULTS

Tables 2 and 3 respectively present the tensile bond strengths of modified MMA-PMMA/BPO-DEPT resin to precious metals (*i.e.*, Au, Ag, Pt, and Pd) and precious metal alloys (*i.e.*, Au alloy, Ag alloy, and Au-Ag-Pd alloy), using nine experimental primers respectively containing 2-MEDT, 6-MHDT, 10-MDDT, BMEDS, BMPDS, BMDDS, VBATDT, MPMA, or 4-META (control) after 2,000 thermal cycles. It could be seen in Tables 2 and 3 that the control acidic adhesive monomer, 4-META, exhibited either 0 MPa bond strength or poor adhesion to both precious metals and alloys. In sharp contrast, all the three novel dithiooctanoate monomers exhibited significantly higher bond strengths than 4-META ($p<0.05$).

On bonding to Au, significant differences ($p<0.05$) in bond strength were observed between the novel dithiooctanoate monomers (2-MEDT, 6-MHDT, and

10-MDDT) (19.0–20.5 MPa) and the conventional sulfur-containing monomers (BMEDS, BMPDS, BMDDS, VBATDT, and MPMA) (0–6.8 MPa). On bonding to Ag, the dithiooctanoate monomers exhibited significantly higher bond strengths (38.8–43.5 MPa) than the conventional sulfur-containing monomers (0 MPa) ($p<0.05$). On bonding to Pt and Pd, significant differences in bond strength were observed between the dithiooctanoate monomers and BMEDS, VBATDT, and MPMA ($p<0.05$).

On bonding to Au alloy, the bond strengths of 2-MEDT, 6-MHDT, and 10-MDDT were significantly higher than that of conventional sulfur-containing monomers of BMEDS, BMPDS, VBATDT, and MPMA ($p<0.05$). On bonding to Ag alloy and Au-Ag-Pd alloy, the bond strengths of all the novel dithiooctanoate monomers were significantly higher than all the conventional sulfur-containing monomers ($p<0.05$).

Table 2 Effects of dithiooctanoate monomers and conventional sulfur-containing monomers on tensile bond strength (TBS) to precious metals, using modified MMA-PMMA/BPO-DEPT resin, after 2,000 thermal cycles

Sulfur-containing monomer	TBS [mean (standard deviation)] to precious metals			
	Au	Ag	Pt	Pd
2-MEDT	19.2 (4.1) ^a	38.8 (5.5) ^a	33.1 (3.2) ^a	18.9 (3.9) ^a
6-MHDT	19.0 (6.6) ^a	40.1 (6.2) ^a	33.0 (5.2) ^a	30.8 (4.0) ^a
10-MDDT	20.5 (5.6) ^a	43.5 (5.8) ^a	33.6 (4.2) ^a	31.3 (4.3) ^a
BMEDS	0	0	21.8 (1.2) ^b	11.6 (3.3) ^b
BMPDS	6.3 (0.5) ^b	0	34.7 (3.8) ^a	21.1 (3.8) ^a
BMDDS	6.5 (0.8) ^b	0	34.4 (4.2) ^a	21.3 (3.1) ^a
VBATDT	6.8 (2.1) ^b	0	14.6 (2.2) ^c	9.8 (3.2) ^b
MPMA	1.6 (0.8) ^c	0	0.5 (0.2) ^d	6.9 (2.6) ^b
4-META (Control)	0	0	0	2.6 (0.5) ^c

Note: $n=5$.

Adhesive resin used: Modified MMA-PMMA/BPO-DEPT resin.

One thermal cycle: 4°C water for 1 min and 60°C water for 1 min.

Groups from the same column that are identified with the same superscript letter are not significantly different ($p>0.05$).

Table 3 Effects of dithiooctanoate monomers and conventional sulfur-containing monomers on tensile bond strength (TBS) to dental precious metal alloys, using modified MMA-PMMA/BPO-DEPT resin, after 2,000 thermal cycles

Sulfur-containing monomer	TBS [mean (standard deviation)] to dental precious metal alloys		
	Au alloy	Ag alloy	Au-Ag-Pd alloy
2-MEDT	40.4 (6.5) ^a	38.8 (3.5) ^a	39.2 (4.4) ^a
6-MHDT	41.2 (7.8) ^a	30.0 (4.7) ^a	40.2 (6.3) ^a
10-MDDT	45.5 (7.1) ^a	31.2 (4.6) ^a	40.9 (5.6) ^a
BMEDS	23.1 (3.3) ^b	10.4 (2.1) ^b	24.1 (3.8) ^b
BMPDS	28.2 (2.8) ^b	13.7 (3.1) ^b	23.9 (2.6) ^b
BMDDS	36.1 (3.3) ^a	28.3 (3.0) ^b	32.5 (3.5) ^b
VBATDT	25.8 (4.2) ^b	25.2 (3.5) ^c	27.5 (3.2) ^b
MPMA	3.7 (0.3) ^c	21.4 (3.6) ^c	11.3 (2.4) ^c
4-META (Control)	0	10.3 (2.2) ^b	15.5 (2.5) ^c

Note: $n=5$.

Adhesive resin used: Modified MMA-PMMA/BPO-DEPT resin.

One thermal cycle: 4°C water for 1 min and 60°C water for 1 min.

Groups from the same column that are identified with the same superscript letter are not significantly different ($p>0.05$).

DISCUSSION

The use of metal primers for the fabrication of seating cast restorations and fixed dental prostheses has increased substantially²⁸. To develop more advanced metal primers, this study was undertaken to evaluate the bonding performances of three novel dithiooctanoate monomers (namely, 2-MEDT, 6-MHDT, and 10-MDDT)²⁶ on adhesion to seven kinds of precious metals and alloys and then compare their bond performance results against five sulfur-containing monomers. The conventional sulfur-containing monomers selected for comparison in this study were three non-cyclic disulfides (*i.e.*, BMEDS, BMPDS, and BMDDS)²⁴, a triazinedithione (VBATDT)²⁵, and a thiophenol (MPMA)²³. For a non sulfur-containing monomer, the acidic adhesive monomer of 4-META was selected as the control monomer. For luting, a modified MMA-PMMA/BPO-DEPT resin was used. As shown in Fig. 1, the chemical structures of all the sulfur-containing adhesive monomers typically comprised three parts: a polymerizable functional group, a connecting group, and an adhesion-promoting group

containing sulfur atom(s)²⁹. Despite the commonality of possessing the typical three parts in their structures, significant differences ($p < 0.05$) in bond strength were observed for adhesion to Au, Ag, Au alloy, Ag alloy, and Au-Ag-Pd alloy between the three novel dithiooctanoate monomers and the five conventional sulfur-containing monomers.

On the significant differences ($p < 0.05$) in bond strength between the three cyclic disulfide compounds (dithiooctanoate monomers) and the non-cyclic disulfide compounds, it was thought that their bond strengths were attributed to the ability of chemical interaction derived from their structures. For the cyclic disulfide monomers, findings of previous surface-enhanced Raman scattering (SERS) spectroscopy studies^{19,20} showed that organic sulfur compounds were chemically adsorbed onto Au, leading to the formation of monolayer films by a spontaneous assembly of organic thiols on the Au surface. Leveraging on this finding^{19,20}, it was plausible to suggest that the cyclic disulfide group of 6,8-dithiooctanoate moiety underwent the cleavage of the disulfide bonds ($-S-S-$) intermolecularly on the Au surface. The reaction

Fig. 2 Plausible chemical interaction of sulfur-containing adhesive monomers on the Au surface. Both dithiooctanoate monomers and non-cyclic disulfide monomers undergo cleavage of the $-S-S-$ bond, and interacted chemically with Au atoms to form $-S-Au$ on the Au surface.

products were absorbed and interacted immediately with Au atom to form -S-Au bond on the metal surface (Fig. 2)^{28,29}. For the non-cyclic disulfide monomers, their bond strengths to precious metal and alloys decreased in the following order: BMDDS>BMPDS>BMEDS. They might have also undergone similar cleavage of the -S-S-bond, resulting in a chemical interaction with Au atoms to form -S-Au bond on the Au surface (Fig. 2). Although it remained to be elucidated the differences in chemical reaction between cyclic dithiooctanoate monomers and non-cyclic disulfide monomers with Au, it was clearly shown in this study that the bond strength of dithiooctanoate monomers to Au was significantly higher than that of non-cyclic disulfide monomers ($p<0.05$).

On the bond strengths of triazinedithione monomer (VBATDT) and thiophenol monomer (MPMA) to precious metals and alloys, they were found to be significantly lower ($p<0.05$) than the three dithiooctanoate monomers. As per the above argument for non-cyclic disulfide monomers, it was thought that their chemical structures accounted for the host of differences in chemical interaction and polymerization reactivity between dithiooctanoate monomers and VBATDT or MPMA. In particular, the low bond strengths obtained by MPMA were caused by adverse polymerization reactivity with acrylic resin-based adhesives because the thiols acted as so-called chain transfer agents³⁰. For VBATDT, a contradicting result was obtained in a previous study³⁰ which reported that VBATDT was effective for bonding to precious metals. In the case of VBATDT, the influence of its chemical structure on bond strength seemed to be rather ambivalent because of the presence of tautomeric structures such as triazinedithione and triazine-dithiol^{20,25}. In a study by Suzuki *et al.*²⁰ which investigated the tensile bond strength of MMA-PMMA/TBBO resin to Au, it was found that pretreatment with a metal primer which comprised 0.5 wt% of VBATDT yielded 25.7 MPa after 2,000 times of thermal cycling. This value did not agree with the bond strength of VBATDT to Au (6.8 MPa) in this study, although modified MMA-PMMA/BPO-DEPT resin was used instead. These findings seemed to suggest that polymerization initiators had influence on adhesion. However, for the novel dithiooctanoate monomers of 2-MEDT, 6-MHDT, and 10-MDDT, their bond strengths with modified MMA-PMMA/BPO-DEPT resin in this study were comparable with those obtained by eight kinds of novel dithiooctanoate monomers with MMA-PMMA/TBBO resin in our previous study²⁶. The mean tensile bond strength of 10-MDDT to Au was 20.5 MPa, as compared to that of 6.5 MPa by a conventional sulfur-containing monomer BMDDS, and even 0 MPa by 4-META. On the whole, the bond strength values of all tested monomers to precious metals and alloys seemed to be of such a tendency: 10-MDDT>BMDDS>4-META. This trend considerably correlated with the degree of chemical adsorption and reactivity of adhesive monomers on the Au surface. In other words, the bonding performance of an adhesive monomer was dependent on its degree of chemical interaction with Au, which in turn

was dependent on the chemical structure. In the context of this study, 4-META was an acidic compound which rendered it incapable of bonding to precious metals. Consequently, the poor chemical bonding of 4-META with Au atoms caused the bonded specimens to fail during thermal cycling.

In dental prosthetic practices, sandblasting is frequently used as a surface roughening treatment prior to the bonding of resin composites to alloys³¹ or the bonding of metal alloys to enamel³¹. This is because sandblasting increases the surface areas of metals and their mechanical retentive forces, hence increasing the bond strength to metals. However, for intraoral repair of fractured porcelain- or composite-veneers, sandblasting is not a convenient treatment method in the oral environment. In the present study, the mean tensile bond strength of 10-MDDT to Au alloy, without sandblasting treatment, was 45.5 MPa. Therefore, this study showed that 10-MDDT exhibited higher bonding performance than conventional sulfur-containing adhesive monomers even without any prior surface roughening treatment. To preclude the influence of mechanical retentive forces caused by surface irregularities, highly smooth metal surfaces (polished up to 4,000 grit) were used in this study. Apart from showing the difference in bonding durability between dithiooctanoate monomers and conventional sulfur-containing monomers, results obtained in this study also showed that the bonding ability of adhesive monomers to metals could be unbiasedly evaluated using highly smooth metal surfaces after exposure to 2,000 times of thermal cycling.

The appearance of the three novel dithiooctanoate monomers was a yellowish liquid. When compared with conventional sulfur-containing monomers such as thiols, thiophenols, and thiophosphoric acids, the novel dithiooctanoate monomers possess inherent advantages such as absence of bad odor and good stability both in air and in organic solvents (such as acetone and ethanol). These properties are highly desirable improvements over the conventional sulfur-containing monomers for application to commercial products. Indeed, 10-MDDT, which was shown in this study to exhibit superior bonding performance, was already included in the formulation of a commercial primer, Metal Link Primer (M.L. Primer, Shofu Inc., Kyoto, Japan) in 2003. In a recent study by Okuya *et al.*³², it was favorably reported that the highest shear bond strengths of M.L. Primer to Au and high-gold content alloy after 2,000 times of thermal cycling were 33.5 MPa and 33.3 MPa respectively.

Apart from the utilization of 10-MDDT in Metal Link Primer, the newly developed dithiooctanoate adhesive monomers have been patented as “(meth) acrylic ester derivatives” which can provide high and durable adhesion to precious metals and alloys²⁶. The next step forward is to explore the feasibility of combining the newly developed dithiooctanoate monomers with acidic adhesive monomers and examine the effect thereof on adhesion to precious metals, precious metal alloys, and non-precious metal alloys.

CONCLUSIONS

Based on the findings in this study, the following conclusions were drawn.

1. On bonding to Au and Ag, the novel dithiooctanoate monomers of 2-MEDT, 6-MHDT, and 10-MDDT exhibited significantly higher tensile bond strengths than the conventional sulfur-containing monomers (BMEDS, BMPDS, BMDDS, VBATDT, MPMA) and acidic adhesive monomer 4-META ($p < 0.05$).
2. On bonding to Au alloy, Ag alloy, and Au-Ag-Pd alloy, all the three novel dithiooctanoate monomers showed significantly higher tensile bond strengths than the conventional sulfur-containing monomers (except BMDDS) and 4-META ($p < 0.05$).
3. When compared with the conventional sulfur-containing monomers tested in this study, the novel dithiooctanoate monomers exhibited excellent bonding to both precious metals and alloys.

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