Effect on Adhesion of New Polymerization Initiator Systems Comprising 5-Monosubstituted Barbituric Acids, Aromatic Sulfinate Amides, and *tert*-Butyl Peroxymaleic Acid in Dental Adhesive Resin

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ABSTRACT: To develop a multipurpose dental adhesive resin, the effects of polymerization initiator systems comprising 5-monosubstituted barbituric acid (5-MSBA), aromatic sulfinate amide (ASA), and *tert*-butyl peroxymaleic acid (*t*-BPMA) with 4-acryloxyethyltrimellitic acid (4-AET) or its anhydride (4-AETA) on adhesion and curing time were investigated. Tensile bond strength values of a Ni—Cr alloy are affected by the inclusion of *t*-BPMA, and the optimum concentration of *t*-BPMA in a 5-MSBA–ASA–*t*-BPMA-type initiator system was found to be 0.5–2.0 wt %, and it was noteworthy that the correlation between the tensile bond strength and curing time on the *t*-BPMA-concentration showed a highly negative correlation of a benzenesulfinate morphoride (BSMo) series adhesive: $r = -0.957$, and a *p*-toluenesulfinate morphoride (*p*-TSMo) series adhesive: $r = -0.949$. The combination of 1-cyclohexyl-5-ethylbarbiturioc acid (CEBA) with ASA provides a high level of tensile bond strength to the Ni—Cr alloy, and the optimum concentration of CEBA in a CEBA–ASA–*t*-BPMA-type initiator and the bond strength values were found to be 0.75 wt % CEBA: 52.3 MPa (with BSMo), and 1.0 wt % CEBA: 50.9 MPa (with *p*-TSMo), respectively. It was suggested that 5-MSBA, ASA, and *t*-BPMA and their combinations provided the environment where 4-AETA exhibited good bonding performance with increasing wettability to metal without interference of a charge-transfer complex derived from a polymerization initiator system such as benzoyl peroxide (BPO)–amine. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1655–1668, 1999

Key words: polymerization initiator system; 5-monosubstituted barbituric acid; aromatic sulfinate amide; *tert*-butyl peroxymaleic acid; adhesion; dental adhesive resin

INTRODUCTION

In the field of prosthetic dentistry, there is now an increasing demand for the development of a multipurpose dental adhesive that will provide good adhesion to dental alloys as well as to enamel and dentin. Accordingly, there has been a long continuous search to achieve a strong adhesion to these adherents. While acrylic resins used in dentistry have many advantages, that is, quick curing, easy to use, and with an esthetic nature for tooth-colored restoration, it is known that acrylic resins

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provide inadequate adhesion. A fundamental problem with acrylic resins on adhesion is attributable to an internal stress arisen from volume shrinkage during polymerization at the adhesive interface. Endo et al.[1–4] developed several spirocyclic monomers that performed volume expansion during ring-opening polymerization.

To circumvent the shrinkage related to the internal stress during polymerization, it is now recognized that radical polymerization initiator systems play an important role in adhesive resins. Regarding a polymerization initiator system on adhesion, Masuhara et al.[5] developed an adhesive resin designed to facilitate chemical adhesion to collagen, using tri-*n*-butyl borane (TBB) as a catalyst, and suggested that the effective bonding performance of TBB-initiated methyl methacrylate (MMA) to dentin is attributable to the polymerization mechanism initiated from the moist dentin surface with a minimized effect of the volume shrinkage force. However, it is noted that this TBB-initiator system is inflammable and has been restricted within the application to MMA since its development. A redox polymerization initiator of benzoyl peroxide (BPO) with aromatic tertiary amines usually used for dental acrylic resins will provide the following serious disadvantages: (1) The residual reaction product of BPO with the amine in the cured resin can easily change its color by ultraviolet light and thermal change in an oral environment, and (2) also unreacted accelerator and monomer will lead to degraded mechanical strength of the cured resin.[6,7] Also, the amine can react with an acidic group in adhesion-promoting monomers to form a charge-transfer complex (CT complex)[8,9] and ultimately lead to degraded polymerization and insufficient adhesion. To circumvent the affection derived from the reaction product of BPO with amines, Yamauchi[10] developed a polymerization initiator system and reported that an initiator system consisting BPO, aromatic tertiary amines, and *p*-toluenesulfinic acid sodium salt (*p*-TSNa) with an adhesive-promoting monomer of 2-methacryloxyethyl phenyl hydrogen phosphate (phenyl-P) provided good adhesion to dentin. It was suggested that hydrophilic *p*-TSNa will react with the acidic monomer to form a phenyl radical against the CT complex described above. Furthermore, several initiator systems without aromatic tertiary amines have been studied. Bredereck et al.[11] reported that barbituric acid derivatives and halogen compounds with metal ions provided an effective radical-initiating polymerization of acrylic monomers, and this initiator system provides good color stability and good mechanical strength of the polymers. Kadoma et al.[12–15] proposed thiobarbituric acid derivatives (TBAD)/copper acetylacetonate (CuAcAc)[12] as a cold polymerization initiator and TBAD/camphorquinone (CQ),[13] methyl-substituted TBAD/CQ,[14] and 5-(4-vinylbenzyl)-2-thiobarbituric acid/CQ[15] as a visible-light polymerization initiator. Ohta et al.[16,17] investigated the adhesion of a resin to dentin using barbituric acid derivatives/cupric chloride ($CuCl_2$) as initiator systems. Imai et al.[18–20] reported that the bond strength of about 11 MPa obtained with the barbituric acid/$CuCl_2$ system under optimal conditions was comparable to that of 9.3–11.0 MPa reported for TBB-initiated MMA resin on bonding to dentin.

In the course of our development of dental adhesive resins, we previously invented three kinds of radical polymerization initiator systems containing 5-monosubstituted barbituric acid (5-MSBA),[21–23] and previous works in this series have shown that a new adhesion-promoting monomer, 4-acryloxyethyltrimellitic acid (4-AET), exhibited a noteworthy effect on adhesion to dentin.[24,25] While the evaluation of barbituric acid derivatives as polymerization initiators with application to dental adhesive resins is well known, little attention has been paid to evaluate the effect of 5-MSBA in combination with aromatic sulfinate amide (ASA) and *tert*-butyl peroxymaleic acid (*t*-BPMA) on adhesion. In response to the demand described above, it is expected that the combination of these new initiator systems with a new adhesive-promoting monomer will endow adhesive resin with an effective bonding performance.

In this article, we report the investigation of the effect of new radical polymerization initiator systems, mainly of 5-MSBA–ASA–*t*-BPMA-type, together with new adhesion-promoting monomers, 4-acryloxyethyltrimellitate anhydride (4-AETA) and 4-AET, on the adhesion to a dental Ni—Cr alloy and on curing time.

EXPERIMENTAL

Syntheses of ASA

p-*Toluenesulfinate Morphoride* (p-*TSMo*)

To a stirred mixture of *p*-toluenesulfinic acid sodium salt dihydrate (*p*-TSNa, 146 g, 0.82 mol) and 140 g THF, thionyl chloride (238 g, 2.0 mol) was added dropwise for 2 h at 23°C, and was further stirred for 4 h at 70°C, and the solvent was then

removed from the reaction mixture by rotary evaporation. Ethyl ether (500 mL) was added to the residue and precipitated NaCl was filtered off, and the ether solution containing *p*-toluenesulfinic acid chloride (*p*-TSCl) was obtained. The ether solution was added dropwise for 3 h to the stirred solution of morphorine (226 g, 2.6 mol) in 500 mL ethyl ether at 5°C, and the resulting mixture was further stirred at 23°C for 3 h. After the reaction, precipitated chloric acid salt was filtered off, and the resulting reaction mixture was washed with water and dried over magnesium sulfate and concentrated by rotary evaporation. The residual product (130 g) was purified by recrystallization from acetone: yield 80 g (43%), light yellow crystals, and mp 120–123°C. The synthesized *p*-TSMo was identified by ^{1}H-NMR spectra (PMX60SI, JEOL Co., Tokyo, Japan) and elemental analysis.

^{1}H-NMR (ppm) 2.4 (3H, ph-CH_3), 2.9–3.2 (4H, —O—CH_2CH_2—), 3.6–3.8 (4H, —N—CH_2CH_2—), 7.2–7.6 (4H, benzene ring).

ANAL. Calcd for $C_{11}H_{16}NO_2S$: C, 58.68%; H, 6.71%; N, 6.22%. Found: C, 58.23%; H, 6.54%; N, 5.95%.

Benzenesulfinate Morphoride (BSMo)

The title compound was prepared from morphorine and benzenesulfinic acid chloride prepared from benzenesulfinic acid sodium salt dihydrate and thionyl chloride similarly to *p*-TSMo as mentioned above. Purification was carried out by recrystallization from acetone.

Yield 36%; light yellow crystals; mp 73–75°C. ^{1}H-NMR (ppm) 2.9–3.2 (4H, —O—CH_2CH_2—), 3.6–3.8 (4H, —N—CH_2CH_2—), 7.2–7.7 (5H, benzene ring).

ANAL. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85%; H, 6.20%; N, 6.63%. Found: C, 57.17%; H, 6.08%; N, 6.46%.

p-*Toluenesulfinate Amide* (p-*TSA)*

To a stirred mixture of *p*-TSNa (45 g, 0.25 mol) and 300 g methylene chloride, thionyl chloride (65 g, 0.55 mol) was added dropwise for 2 h at 23°C and was further stirred for 3 h at 45°C. Precipitated NaCl was filtered off and a methylene chloride solution containing *p*-TSCl was obtained. Liquid ammonia (17 g, 1.0 mol) was added to methylene chloride frozen at −70°C, the solution containing *p*-TSCl was added dropwise for 3 h to the stirred solution of liquid ammonia at 5°C, and the resulting mixture was further stirred at 23°C for 3 h. Distilled water (500 mL) was added to the reaction mixture and stirred. The ammonia solution was added to the mixture until alkaline. The reaction compound was extracted with 500 mL methylene chloride. The organic phase was washed and dried and concentrated by rotary evaporation. Purification was carried out by recrystallization from acetone.

Yield 14 g (36%); white crystals; mp 100–111°C. ^{1}H-NMR (ppm) 2.3 (3H, —CH_3), 6.1 (3H, ph-CH_3), 6.1 (2H, —NH_3), 7.2–7.7 (4H, benzene ring).

ANAL. Calcd for C_7H_9NOS: C, 54.17%; H, 5.84%; N, 9.02%. Found: C, 54.16%; H, 5.78%; N, 8.84%.

N,N-*Dimethyl*-p-*toluenesulfinate Amide* (p-*TSA-DM)*

The title compound was prepared from dimethylamine (45 g, 1.0 mol) and *p*-TSCl. The latter was prepared from *p*-TSNa (45 g, 0.25 mol) and thionyl chloride (65 g, 0.55 mol), similarly to *p*-TSA as described above. Purification was carried out by recrystallization from acetone, and the title compound (19 g) was obtained.

Yield 41.5%; white crystals; mp 47.5–52.5°C. ^{1}H-NMR (ppm) 2.3 (3H, ph-CH_3), 2.6 {6H, N—$(CH_3)_2$}, 6.1 (3H, —CH_3), 7.2–7.6 (4H, benzene ring).

ANAL. Calcd for $C_9H_{13}NOS$: C, 58.98%; H, 7.15%; N, 7.64%. Found: C, 58.33%; H, 7.11%; N, 7.27%.

The scheme of the syntheses of the aromatic sulfinate amides used in the present study is given in Figure 1.

Preparation of 5-MSBA Organic Peroxides, and Accelerators

5-Butylbarbituric acid (BBA), 1-cyclohexyl-5-ethylbarbituric acid (CEBA), and 1-benzyl-5-phenylbarbituric acid (BPBA) were synthesized by the reaction of malonic acid diethylester derivatives and urea derivatives according to the method previously reported.[11] *BBA:* mp 200–210°C, light brown crystals. *CEBA:* mp 115–117.5°C, white needle crystals. *BPBA:* mp 156.5–159.0°C, white needle crystals. The structural formulas of BBA, CEBA, and BPBA are illustrated in Figure 2. Organic peroxides of *t*-BPMA and BPO were purchased from Nihon Oil and Fat Co. Ltd., Tokyo, Japan and *p,p′*-dichlorobenzoyl peroxide (Cl-BPO) was purchased from Kayaku Akzo Co., Tokyo, Japan and were used without further purification. Accelerators of *N,N*-di(hydroxyethyl)-*p*-toluidine (DEPT), *N,N*-dimethyl-*p*-toluidine (DMPT), and *p*-

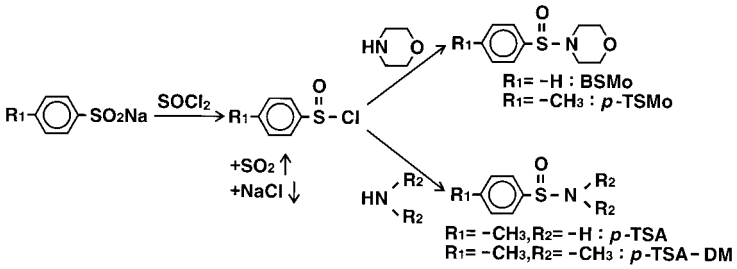


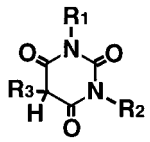
Figure 1 Scheme of the syntheses of ASA used.

toluene-sulfinic acid sodium salts (*p*-TSNa) were reagent grade (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and were used without further purification. Classification of the radical polymerization initiator systems used in the present study are listed in Table I.

Preparation of Urethane Methacrylates

Dimethacryloxyethyl Isophorone Diurethane (IPDI–HEMA)

The title compound was synthesized by the addition of 3-isocyanatemethyl-3,5,5-tri-methyl-cyclohexyl isocyanate = isophorone diisocyanate (IPDI) and 2-hydroxyethyl methacrylate (HEMA) in a 1 : 2 molar ratio, according to the method previously reported.[26] After the reaction, the absorption of $\nu_{N=C=O}$ (2340 cm^{-1}) had disappeared from the IR spectra, and a translucent viscous liquid was quantitatively obtained. *IPDI–HEMA:* $\eta_{23°C}$ 3400–3600 cp [containing 20 wt % ethylene glycol dimethacrylate (EGDMA)], IR spectra (FT-300, Horiba Ltd., Kyoto, Japan; neat, cm^{-1}): 1535, 1635, 1720, UV^{THF} (nm): 233, NCO[27] (%): 0.054, OH value[28] (%): 3.52 (calcd 3.50).



General formula of 5-MSBA

Abbr.	R_1	R_2	R_3	mp (℃)
BBA	-H	-H	$-(CH_2)_3CH_3$	200-210
CEBA		-H	$-CH_2CH_3$	115.0-117.5
BPBA	$-CH_2$ 	-H		156.5-159.0

Figure 2 Structural formulas of 5-MSBA used.

Dimethacryloxypropyl–Methacryloxyethyl Isophorone Diurethane (IPDI–HEMA–GDMA)

The title compound was synthesized by the addition of isophorone diisocyanate and HEMA and 1,2,3-trihydroxypropane (glyceline) dimethacrylate (GDMA) in a 1 : 1 : 1 molar ratio. IPDI was reacted with DGMA to form IPDI–GDMA, and the IPDI–GDMA was then reacted with HEMA. *IPDI–HEMA–GDMA:* $\eta_{23°C}$ 12,000 cp, IR spectra (neat, cm^{-1}): 1530, 1625, 1720, NCO[28] (%): 0.014. The structural formulas of IPDI–HEMA and IPDI–HEMA–GDMA are shown in Figure 3.

Preparation of Adhesion Promoting Monomers and other Reagents

4-AETA and 4-AET as new adhesion-promoting monomers were synthesized according to the

Table I Radical Polymerization Initiator Systems Used

Classification	Polymerization Initiators and Accelerators
5-Monosubstituted barbituric acids (5-MSBA)	BBA, BPBA, CEBA
Aromatic sulfinate amides (ASA)	BSMo, *p*-TSMo, *p*-TSA, *p*-TSA-DM
Aromatic sulfinic acid sodium salts (ASNa)	BSNa, *p*-TSNa
Aromatic amines (AA)	DMPT, DEPT
Organic peroxides (OP)	BPO, *t*-BPMA

BBA: 5-butylbarbituric acid; BPBA: 1-benzyl-5-phenylbarbituric acid; CEBA: 1-cyclohexyl-5-ethylbarbituric acid; BSMo: benzenesulfinate morphoride; *p*-TSMo: *p*-toluenesulfinate morphoride; *p*-TSA: *p*-toluenesulfinate amide; *p*-TSA-DM: *N,N*-dimethyl-*p*-toluenesulfinate amide; BSNa: benzenesulfinic acid sodium salt; *p*-TSNa: *p*-toluenesulfinic acid sodium salt; DMPT: *N,N*-dimethyl-*p*-toluidine; DEPT: *N,N*-di(hydroxyethyl)-*p*-toluidine; BPO: benzoyl peroxide; *t*-BPMA = *tert*-butyl peroxymaleic acid.

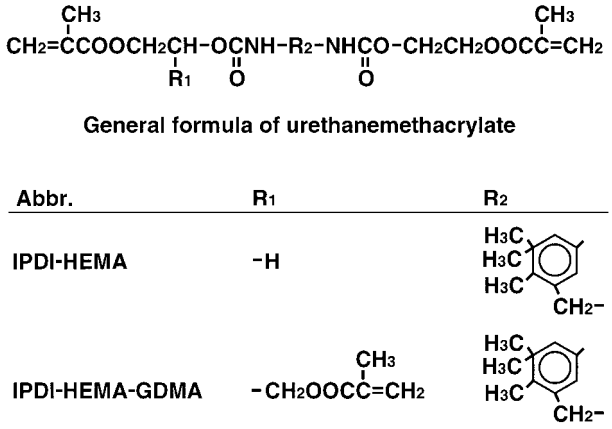


Figure 3 Structural formulas of urethane methacrylates used.

method previously reported.[24,25] The scheme of the syntheses of 4-AETA and 4-AET is given in Figure 4. Di(2-Methacryloxyethyl) acid phosphate (DMEP) was purchased from Johoku Chemical Industry Co. Ltd., Tokyo, Japan and was used without further purification. The 2-hydroxy-3-(*p*-methylphenoxy)propyl methacrylate (Cr–GMA) was synthesized by the addition of *p*-cresol (Cr) and glycidyl methacrylate (GMA) in a 1 : 1 molar ratio: mp 37°C; white crystals. Cross-linking agents of EGDMA and triethylene glycol dimethacrylate (TEGDMA) were purchased from Shin Nakamura Chemical Co. Ltd., Wakayama, Japan. Butylated hydroxytoluene (BHT) was reagent grade (Wako Pure Chemical Industries, Ltd.) and was used without further purification. The silane-treated silica filler (Si filler) was prepared according to the acetic acid method previously reported.[26]

Preparation of Adhesive Resins

Experimental two-component adhesive resins consisting of powder and liquid were prepared according to our patents.[21–23] The adhesive resins were prepared from Si filler, 4-AETA, 4-AET, DMEP, IPDI–HEMA, IPDI–HEMA–GDMA, Cr–GMA, EGDMA, TEGDMA, PEMA, MMA, and BHT, together with the initiator systems described above, as the compositions listed in Tables II–VIII.

Table II Composition of BPO–DEPT–*p*-TSNa-type[a] Adhesive Resins[b] (1)

Contents	Ingredients
Powder A	99.8, 99.6, 99.4, 99.2, 99.0, 98.8, 98.3 wt % Si filler,[c] 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5 wt % *p*-TSNa,[d] 0.2 wt % DEPT[e]
Liquid B	59.8 wt % IPDI–HEMA–GDMA,[f] 35 wt % EGDMA,[g] 5 wt % 4-AETA[h] or DMEP,[i] 0.2 wt % BPO,[j] 800 ppm BHT[k]

[a] Denoted by the same definition as described in Table I.
[b] Ratio of powder/liquid = 3.5/1.0.
[c] Silane-treated filler ($SiO_2/BaSO_4$ = 75/25).
[d,e] Same as footnote a.
[f] Adduct of isophorondiisocyanate and 2-hydroxyethylmethacrylate and 1,2,3-tri-hydroxypropane dimethacrylate in a 1 : 1 : 1 molar ratio.
[g] Ethylene glycol dimethacrylate.
[h] 4-Acryloxyethyltrimellitate anhydride.
[i] Di(2-meth-acryloxyethyl) acid phosphate.
[j] Benzoylperoxide.
[k] Butylated hydroxytoluene.

Measurement of Curing Time

The powder and liquid components of the adhesive resin were mixed at a 3.5 : 1.0 ratio by weight. The mixed slurry (0.45 g) was packed into a small polyethylene container (internal diameter 8 mm and length 16 mm) and then a thermocouple probe connected to a recorder was inserted

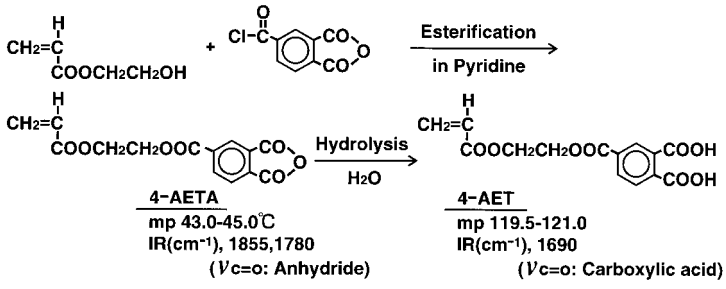


Figure 4 Structural formulas of adhesive-promoting monomers used.

Table III Composition of BPO–DEPT–*p*-TSNa-type[a] Adhesive Resins[b] (2)

Contents	Ingredients
Powder C	99.4 wt % Si filler,[c] 0.4 wt % *p*-TSNa,[d] 0.2 wt % DEPT[e]
Liquid D	59.8 wt % IPDI–HEMA–GDMA,[f] 40, 39, 37, 35, 33, 30 wt % EGDMA,[g] 0, 1, 3, 5, 7, 10 wt % 4-AETA[h] or DMEP,[i] 0.2 wt % BPO,[j] 800 ppm BHT[k]

[a–k] Denoted by the same definition as described in Table II.

into the center of the resin mass, and curing time was determined at 25°C from the time of mixing until the observation of an exothermic peak on the recorder. The measurements were made in triplicate and the mean was calculated.

Measurement of Tensile Bond Strength

Tensile bond testing was carried out in a manner similar to that previously reported.[25] A dental Ni—Cr alloy (Summalloy Nickel, Shofu Inc., Kyoto, Japan) was cast using a casting machine (Argon Caster, Shofu Inc.), and a metal rod (4.5 ± 0.1 mm in diameter, 6.0 ± 0.1 mm in height) and a metal plate (3.0 × 8.0 × 10.0 mm) were prepared. The adhesive surface of the metal rod and plate were flat-ground using 600-grit SiC abrasive paper; sandblasting was then applied. Then, the metal specimens were cleaned ultrasonically for 5 min. After drying the metal, the mixed slurry of the adhesive resin (P/L = 3.5) was applied to the surface of the metal rod and plate, cured, and made to adhere both metals. The experimental adhesive resin cements were cured for 5–7 min at 24 ± 1°C. Thirty minutes after curing of the cement, the test specimens (n = 8–9) were

Table IV Composition of BPBA–BPO–DMPT-type[a] Adhesive Resins[b]

Contents	Ingredients
Powder E	98, 88, 68, 48 wt % Si filler,[c] 0, 10, 30, 50 wt % PEMA,[d] 1.6 wt % 4-AETA,[e] 0.2 wt % BPBA,[f] 0.2 wt % BPO[g]
Liquid F	99.8, 89.8, 69.8, 49.8 wt % IPDI–HEMA–GDMA[h]/TEGDMA[i] (60/40), 0, 10, 30, 50 wt % MMA,[j] 0.2 wt % DMPT,[k] 800 ppm BHT[l]

[a] Denoted by the same definition as described in Table I.
[b,c] Denoted by the same definition as described in Table II.
[d] Poly(ethyl methacrylate).
[e] Same as footnote b,c.
[f,g] Same as footnote a.
[h] Same as footnote b,c.
[i] Triethyleneglycol dimethacrylate.
[j] Methyl methacrylate.
[k] Same as footnote a.
[l] Same as footnote b,c.

Table V Composition of 5-MSBA–ASA–*t*-BPMA-type[a] Adhesive Resins[b] (1)

Contents	Ingredients
Powder G	97.5, 97.25, 97.0, 96.75, 96.5, 96.25, 96.0, 95.5 wt % Si filler,[c] 1.0 wt % CEBA,[d] 1.5 wt % 4-AET,[e] 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0 wt % *t*-BPMA[f]
Liquid H	57.2 wt % IPDI–HEMA,[g] 20 wt % TEGDMA,[h] 20 wt % Cr-GMA,[i] 2.0 wt % ASA[j] (BSMo[k] and *p*-TSMo[l]), 0.75 wt % DEPT,[m] 500 ppm BHT[n]

[a–d] Denoted by the same definitions as described in Tables I–IV.
[e] 4-Acryloxyethyltrimellitic acid.
[f] Same as footnote a–d.
[g] Adduct of isophorone diisocyanate and 2-hydroxyethyl methacrylate in 1 : 2 molar ratio.
[h] Same as footnote a–d.
[i] Adduct of *p*-cresol and glycydilmethacrylate in 1 : 1 molar ratio.
[j–n] Same as footnote a–d.

Table VI Composition of 5-MSBA–ASA–*t*-BPMA-type[a] Adhesive Resins[b] (2)

Contents	Ingredients
Powder I	96.5 wt % Si-filler,[c] 1.0 wt % CEBA,[d] 1.0 wt % *t*-BPMA,[e] 1.5 wt % 4-AET[f]
Liquid J	60.0, 59.0, 58.5, 58.0, 57.5, 57.0, 56.0 wt % IPDI–HEMA[g] (20% EGDMA[h]), 0, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 wt % ASA[i] (BSMo,[i] *p*-TSMo[k]), 19.6 wt % TEGDMA,[l] 19.6 wt % Cr-GMA,[m] 0.75 wt % DEPT,[n] 0.05 wt % BHT[o]

[a–o] Denoted by the same definitions as described in Tables I–V.

Table VII Composition of 5-MSBA–ASA–*t*-BPMA-type[a] Adhesive Resins[b] (3)

Contents	Ingredients
Powder K	97.50, 97.25, 97.00, 96.75, 96.25, 99.60, 95.50 wt % Si filler,[c] 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0 wt % CEBA,[d] 1.5 wt % 4-AET,[e] 1.0 wt % *t*-BPMA[f]
Liquid L	57.2 wt % IPDI–HEMA,[g] 20 wt % TEGDMA,[h] 20 wt % Cr-GMA,[i] 2.0 wt % ASA[j] (BSMo[k] and *p*-TSMo[l]), 0.75 wt % DEPT,[m] 500 ppm BHT[n]

[a–n] Denoted by the same definitions as described in Tables I–IV.

immersed in distilled water at 37 ± 1°C for 24 h and then the tensile bond strength was measured using a mechanical testing machine (Instron 5567, Instron Co.) at a crosshead speed of 1 mm/min. The mean and standard deviation for the load at failure were calculated and the results were subjected to a two-way analysis of variance (ANOVA), followed by the Newman–Keuls multiple comparison test.

RESULTS AND DISCUSSION

Measurement of Tensile Bond Strength and Curing Time

The investigation on both the polymerization initiator systems and the effective adhesion-promoting monomers with their combination is of importance for the development of a multipurpose dental adhesive resin. To make clear the role of the polymerization initiator systems in dental adhesive resin, the effects of new polymerization initiator systems, mainly 5-MSBA–ASA–*p*-BPMA, with the new adhesion monomers of 4-AETA and 4-AET on the tensile bond strength of the experimental adhesive resins to the sandblasted Ni—Cr alloy and curing time were investigated. Data with respect to the experimental adhesive resins listed in Tables II–VIII and mean tensile bond strength, standard deviation, and curing time are given in Figures 5 and 6 and 9–12 and Tables IX and X.

Table VIII Composition of 5-MSBA–ASA–*t*-BPMA-type[a] Adhesive Resins[b] (4)

Contents	Ingredients
Powder M	96.5 wt % Si filler,[c] 1.0 wt % 5-MSBA[d] (BBA,[e] CEBA,[f] BPBA[g]), 1.0 wt % *t*-BPMA,[h] 1.5 wt % 4-AET[i]
Liquid N	56 wt % IPDI–HEMA[j] (20% EGDMA[k]), 3.0 wt % ASA[l] (BSMo,[m] *p*-TSMo,[n] *p*-TSA,[o] *p*-TSA–DM[p]), 20 wt % TEGDMA,[q] 20 wt % Cr-GMA,[r] 0.9 wt % DEPT,[s] 0.1 wt % BHT[t]

[a–t] Denoted by the same definitions as described in Tables I–IV.

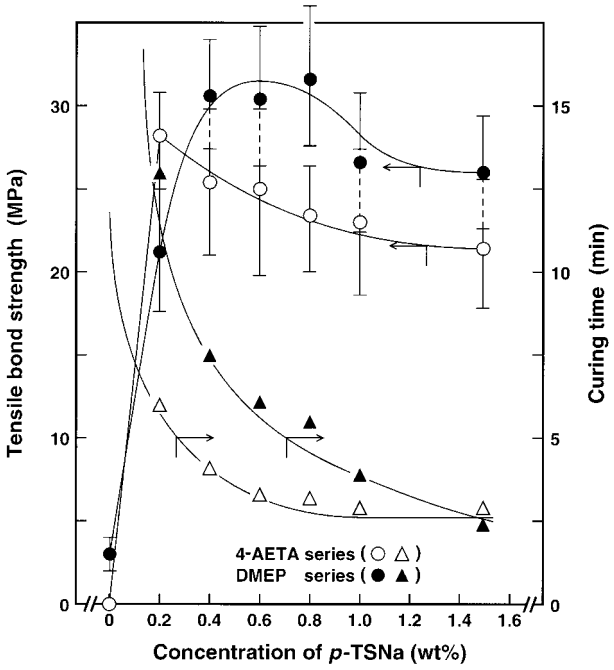


Figure 5 Effect of *p*-TSNa concentration in BPO–DEPT–*p*-TSNa-type polymerization initiator system on adhesion to Ni—Cr alloy and curing time.

Effect of BPO–DEPT–*p*-TSNa-type Initiator System on Adhesion

The effect of the inclusion of *p*-toluenesulfinic acid sodium salt (*p*-TSNa) in the BPO–DEPT–*p*-TSNa-type adhesive resin (Powder A and Liquid B in Table II) on bonding to the Ni—Cr alloy was investigated. Figure 5 illustrates the data on the bonding to the sandblasted Ni—Cr alloy and curing time achieved with the inclusion of 0–1.5 wt % *p*-TSNa, together with the adhesive-promoting

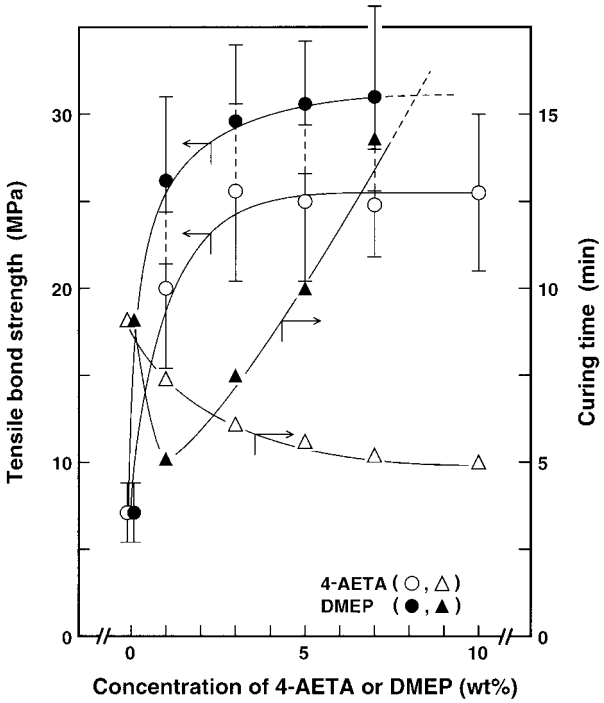


Figure 6 Effects of concentration of adhesive-promoting monomer of 4-AETA or DMEP with BPO–DEPT–*p*-TSNa-type polymerization initiator system on adhesion to Ni—Cr alloy and curing time.

monomer, 5 wt % 4-AETA or 5 wt % DMEP, using Powder A and Liquid B in Table II. As apparent from Figure 5, the tensile bond strengths to the Ni—Cr alloy are significantly affected by the inclusion of *p*-TSNa when these adhesion-promoting monomers were used, and it is indicated that increasing the content of *p*-TSNa results in increased bond strength. Statistical analysis (ANOVA) indicated that with the adhesive resins containing 0.2–1.5 wt % *p*-TSNa there was a significant difference in the bond strength to the metal when compared with the control (0 wt % *p*-TSNa; $P < 0.01$). The optimum *p*-TSNa concentrations were found to be 0.4–0.8 wt % (DMEP series) and 0.2 wt % (4-AETA series), and the corresponding tensile bond strengths were 30.4–31.7 and 28.2 MPa, respectively. The curing time of adhesive resin is also affected by the inclusion of *p*-TSNa, and it is revealed that increasing the content of *p*-TSNa results in a shortened curing time. It is confirmed that where *p*-TSNa was not included the bond strengths are significantly degraded: 0 wt % *p*-TSNa, 0 MPa for the 4-AETA series, and 3.0 MPa for DMEP series, together with a longer curing time (over 60 min). It is noteworthy that the tensile bond strength and curing time show a highly negative correlation for the 4-AETA series adhesive: $r = -0.975$, and the DMET series adhesive: $r = -0.947$.

The effect of the inclusion of 0–10 wt % 4-AETA or DMEP as an adhesion-promoting monomer in the BPO–DEPT–*p*-TSNa-type adhesive resin (Powder C and Liquid D in Table III) on the tensile bond strength and curing time was assessed, and the data are shown in Figure 6. It is apparent that the tensile bond strength to the Ni—Cr alloy is affected by the inclusion of 4-AETA or DMEP, and increasing the content of these monomers results in increased bond strength. The analysis indicated that when the adhesive resin contained 1–10 wt % 4-AETA or 1–7 wt % DMEP there was not a significant difference in the bond strength to metal; however, there was a significant difference when compared with the control (0 wt % adhesion monomer; $P < 0.01$). Particularly, 3–10 wt % 4-AETA and 3–7 wt % DMEP show high values of tensile bond strength of 23.6–25.5 and 29.6–30.7 MPa, respectively. The curing time of the adhesive resin shows that increasing the content of 4-AET resulted in a shortened curing time; however, DMEP content over 5 wt % degraded the curing ability of the adhesive resin. The optimum concentration was revealed to be 3–7 wt % for 4-AETA and 3–5 wt % for DMEP. The correlation between the tensile bond strength and curing time as measured for the 4-AETA series adhesive was $r = -0.798$, and the DMET series adhesive, $r = 0.334$.

Regarding the mechanism of redox polymerization initiated by BPO and aromatic tertiary amine, it is known that a reaction product (**I**) soon comes to equilibrium, and (**I**) decomposes slowly to form a tetra-ammonium salt (**II**) as the rate-determining step (Fig. 7)[6] and will provide some disadvantages: The hardened material has an unacceptable color change derived from the reaction products of BPO with tertiary amine during exposure to ultraviolet light or heat and the mechanical strength is degraded. In the present study, where the BPO–DEPT-type initiator system (0 wt % *p*-TSNa in Fig. 6) was used, the lowest values of the tensile bond strength were measured. It was suggested that where 4-AETA bearing the acid anhydride group was incorporated with the BPO–amine redox initiator, the aromatic acid anhydride (electron acceptor) reacted with the aromatic tertiary amine (electron donor) to form a yellowish CT complex (Fig. 8)[8,9]

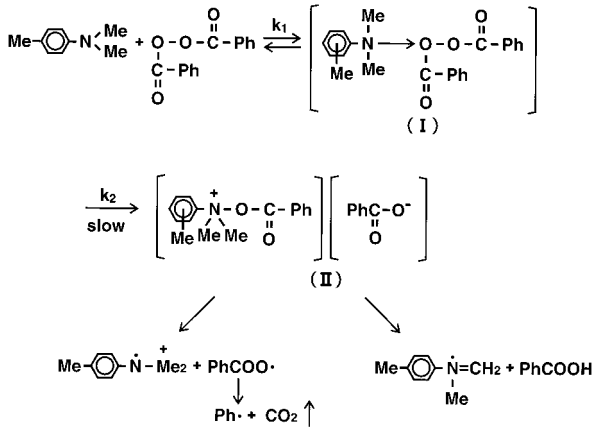


Figure 7 Initiating mechanism of the redox polymerization of BPO with aromatic tertiary amines.

and ultimately led to degraded polymerization and insufficient adhesion.

To circumvent the effect related to the reaction product and the CT complex, Yamauchi[10] reported that BPO–aromatic tertiary amines–*p*-toluenesulfinic acid sodium salt (*p*-TSNa) with a phosphate monomer (phenyl-P) provided good adhesion to dentin. In the present study, the inclusion of *p*-TSNa in the BPO–amine redox system revealed a noteworthy effect on both the tensile bond strength and curing time even when acidic monomers of 4-AETA and DMEP were incorporated, and increasing the content of *p*-TSNa in the BPO–DEPT–*p*-TSNa-type initiator system resulted in increased tensile bond strength and shortened curing time. The effective bond strength showed a tendency similar to the data in a previous article.[10] Regarding the mechanism of radical polymerization of the BPO–DEPT–*p*-TSNa-type initiator system with adhesion-promoting monomers bearing acidic groups, it is expected that aromatic sulfinic acid sodium salt can rapidly react with the acidic groups to form the sodium salt before formation of the CT complex and produces a phenyl radical as illustrated in Figure 8. Therefore, the degradation of the BPO–amine redox polymerization derived from the formation of CT complex is avoided.

Effect of BPBA–BPO–DMPT-type Initiator System on Adhesion

The effect of poly(ethyl methacrylate) (PEMA) as a soft-segment in the powder on bonding to the Ni—Cr alloy was investigated, using the adhesive resin (Powder E and Liquid F in Table IV) comprising the BPBA–BPO–DMPT-type initiator system. Table IX gives the data on bonding to the sandblasted Ni—Cr alloy and curing time achieved with the inclusion of 0, 10, 30, and 50 wt % PEMA as the soft-segment in Powder E and 0, 10, 30, and 50 wt % MMA in Liquid F, together with a primer containing 15 wt % 4-AETA in MMA. It is revealed that increasing the content of PEMA and MMA results in decreased bond strength. The analysis indicated that when the adhesive resin contained 10–30 wt % PEMA and MMA there was no significant difference in the tensile bond strength to the metal when compared with the control (0 wt % PEMA and MMA: 42.0 MPa; $P < 0.01$). However, the optimum content of PEMA and MMA is 10 wt %, and the corresponding bond strength is 48.2 MPa with a cohesive failure (*C*) fractured mode in the adhesive.

The effect of PEMA in the powder, together with BPBA as 5-MSBA, instead of *p*-TSNa, which was found to have a noteworthy effect on the adhesion in the experiment described above, on bonding to the Ni—Cr alloy was investigated. In Table IX, the tensile bond strengths to the Ni—Cr alloy were significantly influenced by the inclusion of PEMA and MMA when the BPBA–BPO–DMPT-type initiator system was used, and it was found that these tensile bond strengths showed significantly higher values than the bonding strength values obtained by the *p*-TSNa–BPO–DEPT-type initiator system described above.

Effect of 5-MSBA–ASA–*t*-BPMA-type Initiator System on Adhesion

The role of *t*-BPMA in the 5-MSBA–BPO–DEPT-type initiator system was investigated. Figure 9 illustrates the effects of the concentration varying from 0 (as control) to 2.0 wt % *t*-BPMA in Powder G (Table V) comprising 1.5 wt % 4-AETA on bond-

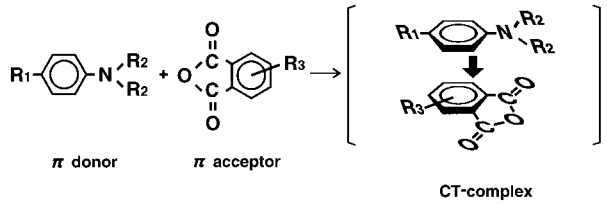


Figure 8 Mechanism of the formation of CT complex of aromatic acid anhydride with aromatic tertiary amines.

Table IX Effect of PEMA[a] in BPBA[b]–BPO–DMPT-type Adhesive Resins[c] on Tensile Bond Strength (MPa) to Ni—Cr alloy[d] using a Primer[e]

Concentration of MMA (wt %)	TBS[f] (10 wt % PEMA)			TBS (30 wt % PEMA)			TBS (50 wt % PEMA)		
	Mean	SD	M[g]	Mean	SD	M	Mean	SD	M
10	48.2 ä	8.3	C[h]	41.2 ä	5.9	C/A	37.4 ä ø	8.5	A
30	40.4 ä ø	8.0	C/A	45.4 ä ø	4.8	C/A	30.3 ø	5.0	A
50	39.1 ä ø	6.0	A[i]	30.2 ø	4.6	A	20.2	3.8	A

n = 8–9. Tensile bond strength of control (0 wt % PEMA and MMA) to the metal: 42.0 ± 8.3 MPa (n = 8) (C/A). Means with small letters (ä, ø) were not significantly different at the level of 0.01.

[a] Poly(ethyl methacrylate).
[b] 1-Benzyl-5-phenylbarbituric acid.
[c] P/L = 3.5/1.0.
[d] Sandblasted.
[e] Containing 15 wt % 4-AETA and 0.5 wt % *p*-chlorobenzoylperoxide in MMA.
[f] Tensile bond strength.
[g] Fractured mode.
[h] Cohesive failure in adhesive.
[i] Adhesive failure.

ing to the Ni—Cr alloy and curing time. As apparent from Figure 9, the tensile bond strengths to the Ni—Cr alloy are affected by the inclusion of *t*-BPMA when Liquid H comprising 2.0 wt % BSMo or *p*-TSMo was used, and it is revealed that increasing the content of *t*-BPMA results in increased bond strength. The analysis indicated that when the adhesive resins containing 0.25–2.0 wt % *t*-BPMA, together with 4-AETA, there was a significant difference in the bond strength to the Ni—Cr alloy when compared with the control (0 wt % *t*-BPMA; $P < 0.01$). It is apparent that high values of the bond strength of 48.2–50.0 MPa (BSMo series) and 45.3–517 MPa (*p*-TSMo series) without the 4-AETA primer are obtainable in the *t*-BPMA concentration range of 0.5–2.0 wt %. The curing time of the adhesive resin is also affected by the inclusion of *t*-BPMA, and it is revealed that increasing the content of *t*-BPMA results in a shortened curing time. It is noteworthy that the correlation between the tensile bond strength and curing time on the *t*-BPMA concentration shows a highly negative correlation: $r = -0.957$ for the BSMo series adhesive and $r = -0.949$ for the *p*-TSMo series adhesive (Fig. 10).

The effect of the concentration varying from 0 (as control) to 4.0 wt % BSMo and *p*-TSMo as ASA in the CEBA–ASA–*t*-BPMA-type initiator system in the adhesive resin (Powder I and Liquid J in Table VI) on bonding to the sandblasted Ni—Cr alloy and curing time was investigated, and the data are illustrated in Figure 11. In Figure 11, the tensile bond strengths are affected by the inclusion of BSMo or *p*-TSMo. The analysis indicated that when the adhesive resin contained 1.0–4.0 wt % BSMo or *p*-TSMo, there was a significant difference in the bond strength to the Ni—Cr alloy when compared with the control (0 wt % ASA; $P < 0.01$). The maximum tensile bond strength values found were 48.7 MPa (1.5 wt % BSMo) and 52.3 MPa

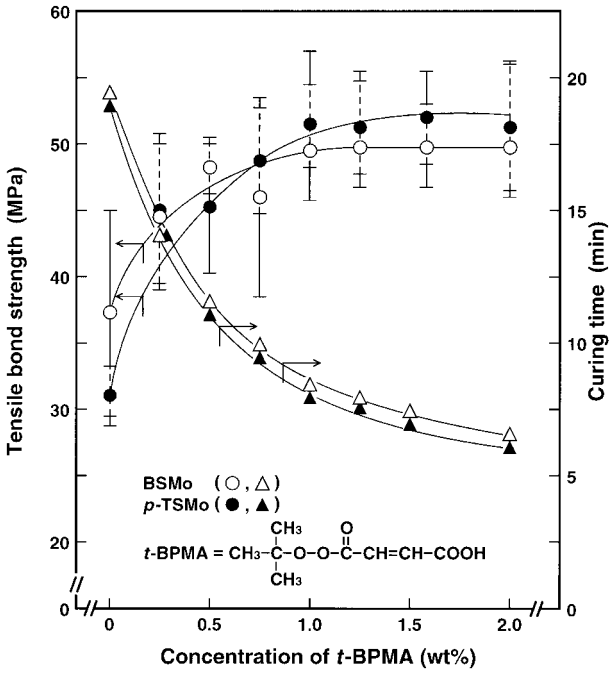


Figure 9 Effects of *t*-BPMA concentration in 5-MSBA–ASA–*t*-BPMA-type polymerization initiator system on adhesion to Ni—Cr alloy and curing time.

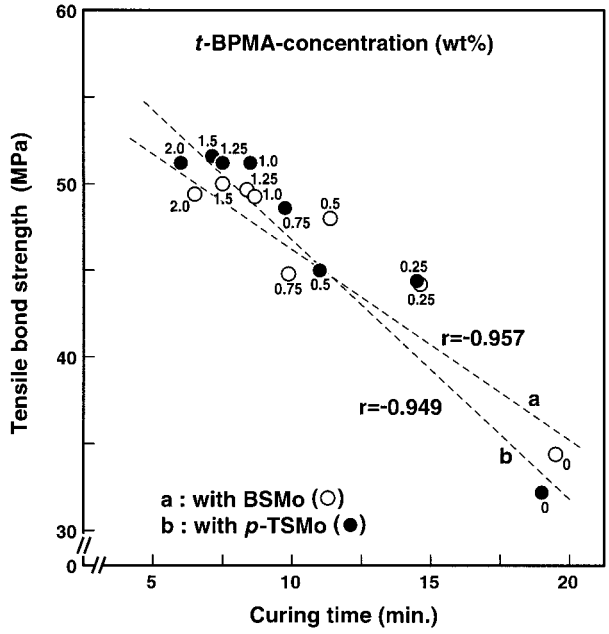


Figure 10 Correlation between tensile bond strength and curing time on *t*-BPMA concentration in 5-MSBA–ASA–*t*-BPMA-type polymerization initiator system. Small letters indicate the *t*-BPMA concentration with (○) BSMo and (●) *p*-TSMo.

(1.0 wt % *p*-TSMo). The curing time of the adhesive resin is slightly affected by the inclusion of BSMo or *p*-TSMo.

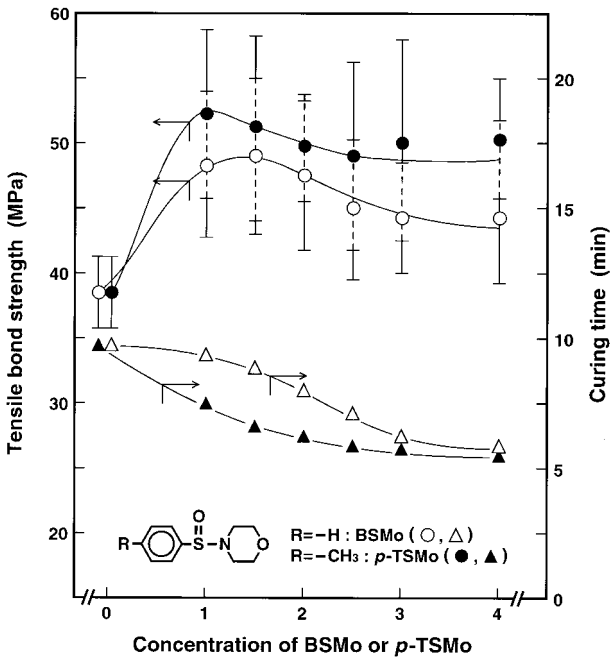


Figure 11 Effects of ASA concentration in 5-MSBA–ASA–*t*-BPMA-type polymerization initiator system on adhesion to Ni—Cr alloy and curing time.

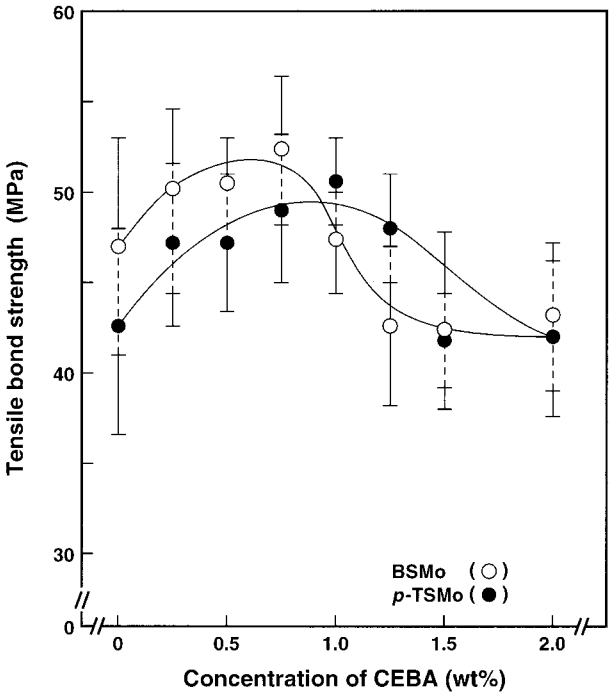


Figure 12 Effects of CEBA concentration in 5-MSBA–ASA–*t*-BPMA-type polymerization initiator system on adhesion to Ni—Cr alloy and curing time.

Figure 12 illustrates the effects of the inclusion of 0–2.0 wt % CEBA with 1.5 wt % 4-AET in the CEBA–ASA–*t*-BPMA-type initiator system (Powder K and Liquid L in Table VII) on bonding to the Ni—Cr alloy and on curing time. In Figure 12, the tensile bond strengths to the Ni—Cr alloy are affected by the inclusion of CEBA when Liquid H containing 2.0 wt % BSMo or *p*-TSMo was used. The analysis indicated that when the adhesive resins contained 0–2.0 wt % 5-MSBA there was no significant difference in the bond strength to the Ni—Cr alloy ($P < 0.01$). However, the optimum CEBA concentration and the corresponding tensile bond strength values are 52.3 MPa (with BSMo) for 0.75 wt % CEBA and 50.9 MPa (with *p*-TSMo) for 1.0 wt % CEBA, respectively.

The effect of the combination of 5-MSBA and ASA in the 5-MSBA–ASA–*t*-BPMA-type initiator system (Powder M and Liquid N in Table VIII) on adhesion was investigated, and the data of bonding to the sandblasted Ni—Cr alloy achieved with the inclusion of 1.0 wt % 5-MSBA in Powder M and 3.0 wt % ASA in Liquid N, together with 1.5 wt % 4-AET in Powder M, are given in Table X. In Table X, it is apparent that the combination of 5-MSBA with ASA increases the bond strength to the metal, and the analysis indicated that there

Table X Effect of 5-MSBA–ASA–*t*-BPMA-type[a] Initiator in Adhesive Resins on Tensile Bond Strength (MPa) to Metal[b]

	BBA[c]			CEBA[d]			BPBA[e]		
ASA[f]	Mean	SD	Max	Mean	SD	Max	Mean	SD	Max
BSMo[g]	45.3 ä	6.4	54.1	48.8 ä	7.1	57.8	42.5 ä ø	5.1	50.3
p-TSMo[h]	35.8 ø	3.5	45.0	40.7 ä ø	6.2	50.6	43.5 ä ø	9.9	58.7
p-TSA[i]	41.3 ä ø	2.4	38.6	38.6 ä ø	5.6	45.6	43.3 ä ø	5.8	52.5
p-TSA–DM[j]	40.9 ä ø	6.5	52.0	44.7 ä	4.8	49.4	41.3 ä ø	4.0	47.3

$n = 9$. Means with small letters (ä, ø) were not significantly different at the level of 0.01.
[a] Denoted by the same definition as described in Table I.
[b] Sandblasted Ni—Cr alloy.
[c–j] Same as footnote a.

was no significant difference in the bond strength to the Ni—Cr alloy, except for the combination of BBA with *p*-TSMo ($P < 0.01$). However, it is revealed that the combination of CEBA with BSMo provides a high value (48.8 MPa) of tensile bond strength to the Ni—Cr alloy. In the combination of CEBA with BSMo or *p*-TSMo, it is revealed that this system provides high values of tensile bond strength to the Ni—Cr alloy, and an optimum concentration of CEBA in the CEBA–ASA–*t*-BPMA-type initiator system and corresponding tensile bond strength values were found to be 0.75 wt % CEBA: 52.3 MPa (with BSMo) and 1.0 wt % CEBA: 50.9 MPa (with *p*-TSMo), respectively. Also, the optimum *t*-BPMA concentration in the 5-MSBA–ASA–*t*-BPMA-type initiator system was found to be 0.5–2.0 wt %. It was noteworthy that the correlation between the tensile bond strength and curing time on the *t*-BPMA-concentration shows a highly negative correlation of the BSMo series adhesive: $r = -0.957$, and the *p*-TSMo series adhesive: $r = -0.949$ (Fig. 10).

Little attention has been paid to evaluating the effect of ASA in combination with 5-MSBA and *t*-BPMA in dental adhesive resin on adhesion. The ASA used were synthesized by the addition reaction of corresponding amides and aromatic sulfinic acid chloride which were synthesized by the addition of aromatic sulfinic acid sodium salt and thionyl chloride. Figure 1 shows the ASA syntheses scheme. The yields of these sulfinate amides were 36–43%. Although *p*-TSNa is insoluble in hydrophobic monomers, the sulfinate amides are soluble in the monomer. The effect on bonding to the Ni—Cr alloy of ASA, instead of *p*-TSNa, which was found to show an effective adhesion in the experiment described above, was investigated. It is apparent that the 5-MSBA–ASA–*t*-BPMA-type initiator system provided significantly improved tensile bond strength to the metal when compared with the BPO–DEPT–*p*-TSNa-type initiator system. It was thought that the *p*-TSNa used in this study will react with both the —COOH group of the adhesive monomer to

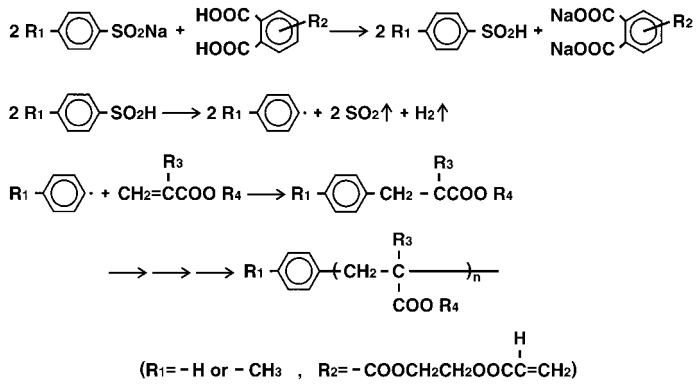


Figure 13 Initiating mechanism of polymerization by the reaction of aromatic sulfinic acid sodium salts with aromatic carboxylic acids.

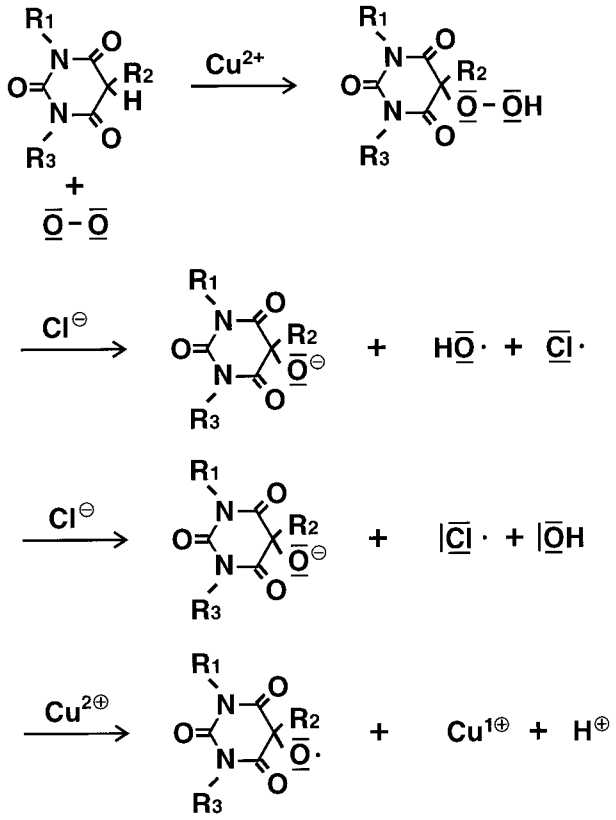


Figure 14 Initiating mechanism of C—H active radical polymerization of 5-MSBA with chloro ion and cupric cation.

form the phenyl radical (Fig. 13). It was suggested that 5-MSBA and *t*-BPMA play an important role in adhesion in the initiator system comprising ASA.

Recently, much attention has been paid to the use of barbituric acid derivatives derived from their high initiating ability. Kadoma and Imai[12–15] proposed several kinds of initiator systems comprising 5-MSBA or TBAD. Imai et al.[18–20] investigated the adhesion to dentin with the barbituric acid/$CuCl_2$ system. With respect to the initiating mechanism of 5-MSBA Bredereck et al.[11] reported that barbituric acid derivatives and halogen compounds with metal ions are effective polymerization initiators of acrylic monomers, and Gross[7] proposed the radical-initiating mechanism of 5-MSBA with the chloro ion (Cl^-) and cupric cation (Cu^{2+}) as redox polymerization (Fig. 14). This initiator system provides good color stability and good mechanical strength of the polymers derived from the mechanism of the polymerization initiator. While the evaluation of barbituric acid derivatives as polymerization initiators with application to dental adhesive resin is well known, little attention has been paid to evaluate the effect of 5-MSBA in combination with ASA and *t*-BPMA on adhesion. While the polymerization mechanism of the 5-MSBA–ASA–*t*-BPMA-type initiator system is unknown at the present stage, it can be expected from the previous work. The behavior of initiation of C—H active 5-MSBA will be similar to the mechanism illustrated in Figure 14 as autooxidation of C—H at the 5-position in barbituric ring in the presence of a DEPT base. It was suggested that the 5-MSBA–ASA–*t*-BPMA-type initiator system can create the preferable environment when adhesive-promoting monomers can have an effective bonding performance to Ni—Cr alloy without interference from polymerization initiator system such as BPO–amine. In view of the above findings, it is concluded that the combination of 5-MSBA, ASA, and *t*-BPMA with an adhesive-promoting monomer can endows adhesive resin with good adhesion.

CONCLUSIONS

In view of the above facts, the most reasonable conclusions to be drawn from the available data are as follows:

1. Increasing the content of *p*-TSNa in the BPO–DEPT–*p*-TSNa-type initiator resulted in increased tensile bond strength and shortened the curing time. The correlation coefficient of the 4-AETA series adhesive was: $r = -0.975$, and of the DMET series adhesive, $r = -0.947$.
2. The optimum concentration of *t*-BPMA in the 5-MSBA–ASA–*t*-BPMA-type initiator was found to be 0.5–2.0 wt %, and the correlation between the tensile bond strength and curing time on the *t*-BPMA-concentration shows a negative correlation for the BSMo series adhesive: $r = -0.957$, and the *p*-TSMo series adhesive: $r = -0.949$.
3. The combination of CEBA with ASA provides a high level of tensile bond strength to the Ni—Cr alloy, and the optimum concentration of CEBA in the CEBA–ASA–*t*-BPMA-type initiator and the bond strength values were found to be 0.75 wt % CEBA: 52.3 MPa (with BSMo), and 1.0 wt % CEBA: 50.9 MPa (with *p*-TSMo), respectively.
4. It was suggested that the 5-MSBA–ASA–*t*-

BPMA-type initiator system could provide a preferable environment when adhesive-promoting monomers will have an effective bonding performance to the Ni—Cr alloy without interference from polymerization initiator system such as BPO–amine.

5. It is concluded that the combination of 5-MSBA, ASA, and *t*-BPMA with an adhesive-promoting monomer can endow adhesive resin with good adhesion.

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