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Properties of Magnetically Attractive Experimental Resin Composites

Susumu HIRANO, Hiromi YASUKAWA, Rie NOMOTO,
Keisuke MORIYAMA and Tadashi HIRASAWA

Department of Dental Engineering, Tsurumi University School of Dental Medicine
2-1-3 Tsurumi, Tsurumi-ku, Yokohama 230, Japan.

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SUS444 stainless steel filled chemically cured resin composites that can attract magnet were fabricated. The filler was treated with various concentrations of silane. The experimental composite was easy to handle and showed a good shelf life. The maximal properties obtained are as follows ; The attraction force to a magnetic attachment was 1/3-1/4 lower than the commercially available magnet-keeper system for dental magnetic attachment. Flexural strength and Knoop hardness of the composite were 76MPa (7.7kgf/mm^2) and 64KHN. These values were lower than the commercially available chemically cured composite used as a reference. Eluted metal from the composite in 1% lactic acid solution for 7days showed 0.7mg/cm^2, but in 0.9%NaCl solution for 7 days, it could not be detected.

Key words: Resin composite, Stainless steel filler, Attraction force to magnet

INTRODUCTION

The use of magnetic attachment in dental applications is becoming more common in Japan. Magnetic attachment is achieved using a pair of a magnet sealed with stainless steel and a keeper made of ferritic stainless steel as the attractive component[1]. The magnet is normally set in the denture, and the keeper is fixed on the root cap. The keeper is incorporated in the root cap made by casting Au alloy or Au-Pd-Ag-Cu alloy.

In the oral environment, the difference in the electrode potentials between the root cap alloy and the keeper causes the keeper to be susceptible to crevice or pitting corrosion if the Cr content in stainless steel has not been made sufficiently passive. Incorporating the keeper in the root cap during casting is an intricate process. If a resin composite that can attract a magnet should be fabricated, it could be directly molded in a root cap with the keeper as a single unit.

For several years authors studied resin composites that could attract magnets[2,3]. A new experimental two-paste type resin composite was developed for this purpose. The present study evaluates the properties of this experimental resin composite.

MATERIALS AND METHODS

Monomer formulation

The monomer formulation of this composite was bisGMA* (2,2-bis[4-(3-methacryloxy-2-

* Polysciences, Inc., Warrinton, USA

hydroxypropoxy)phenyl] propane)/TEGDMA** (triethyleneglycol dimethacrylate)=6/4.

As a catalyst paste, 0.9 wt% BPO (benzoyl peroxide) and 0.01 wt% MHQ (hydroquinone monomethyl ether) of monomer weight were added. The base paste included 1 wt% HEPT (N, N-dihydroxyethyl-p-toluidine).

Filler Treatment

18%Cr-2%Mo stainless steel (SUS444) powder# was used. The powder was sieved and passed through a 625 mesh (<20μm) and used as filler as shown in Fig. 1. The filler was immersed in benzene to dissolve the zinc stearate used as a lubricant, then rinsed in acetone. The filler was then treated using 70% ethyl alcohol solutions with various concentrations of γMPTS (γ-methacryloxypropyltrimethoxysilane)[4]. The concentrations adopted were 1, 1.5 and 3g of γMPTS in 100ml ethyl alcohol solution per 100g of filler. The filler was stirred in 60°C ethyl alcohol solution containing γMPTS for 1h, then oven dried at 120°C for 4h.

Resin composites mixed with 87 wt% stainless steel filler treated with various concentrations of γMPTS both in catalyst and base paste were fabricated (Table 1).

Setting Time

A teflon tube ϕ6×10mm was attached with sticky wax to a teflon plate, and a C-C thermocouple was placed in the center of the tube. Equal weights of catalyst and base paste were mixed for 30s at room temperature, then the mixture was used to fill the container at

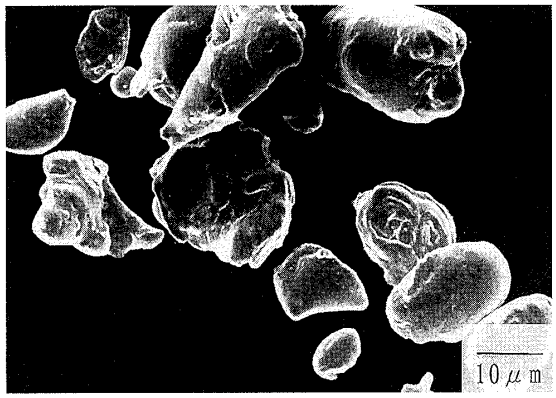


Fig. 1 Stainless steel filler used.

Table 1 Experimental resin composite

	Base paste	Catalyst paste
Monomer	bisGMA/TEGDMA(6/4) 13 wt% BPO 0.9 wt%+MHQ 0.01 wt%	bisGMA/TEGDMA(6/4)13 wt% HEPT 1 wt%
Filler*	18Cr-2Mo stainless steel 87 wt% (625mesh under)	18Cr-2Mo stainless steel 87 wt% (625mesh under)

* Filler was treated with various concentration of γMPTS.

** Shin−Nakamura Chemical Co. Ltd., Wakayama, Japan

Daido Steel Co. Ltd., Tokyo, Japan

37°C. The peak temperature for setting reaction of the composite was measured. The initial setting time was shown as the time from the start of mixing to the peak temperature. Measurements were repeated 5 times.

Flexural strength and Knoop hardness

Five specimens measuring 2×2×30mm were fabricated in a stainless steel mold. A three-point bending test with a span length of 20mm was calculated using an Instron type universal testing machine with a crosshead speed of 1mm/min. The elastic modulus was also calculated from the load measured at the deflection of 0.05mm.

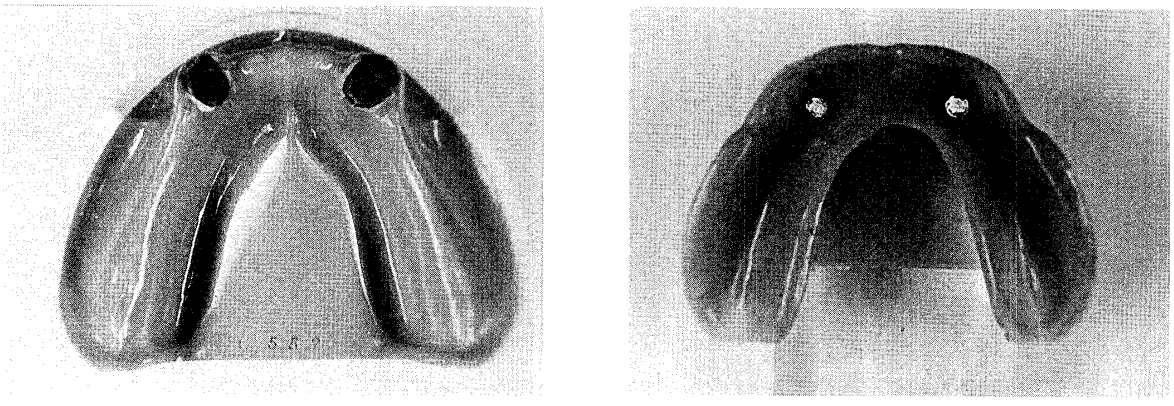
Specimens were polished with #1200 emery paper and the Knoop hardness was measured with a load at 0.987N (100gf) and a holding time of 30s. Three specimens were tested, and five points were measured for each specimen.

Eluted metal

Disks measuring ϕ20×1mm were fabricated in a stainless steel mold and surfaces were finished with #1200 emery paper and stored in a desiccator with silica gel for one week to dry completely. Disks were stored in 1v/v% lactic acid solution or 0.9% NaCl solution of 50ml at 37°C for 7days. Solutions were analyzed by ICP and the amount of eluted metal was estimated. Three specimens were tested under each condition.

Attraction force measurement using a mandibular model

The attraction force of the overlay denture equipped with 2 magnets## (attraction force 8.88N (900gf)×2 attached to the keeper) was measured on a mandibular model. This model was chosen because the bilateral mandibular canine teeth were available as abutments, and both abutments were restored with the composite (Fig. 2). The attraction forces of 2 sets of



(a) (b)

Fig. 2 (a) The model of the mandibular both side of canine tooth as the abutment
(b) The denture corresponded to the model equipped 2 magnets

Hicorex Super4515, J. Morita Corp., Tokyo, Japan.

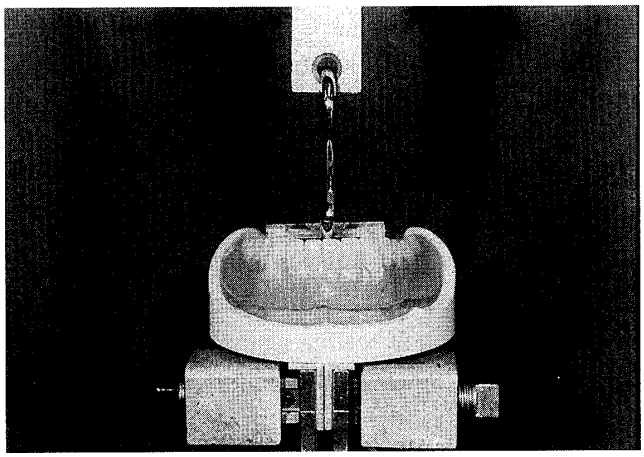


Fig. 3 The attraction force measurement of the denture on the model.

partial dentures were measured using the Instron type universal testing machine at a crosshead speed of 1mm/min (Fig. 3). Measurements were obtained 7 times in each overlay denture.

RESULTS AND DISCUSSION

The experimental two-paste type composite has a good shelf life and is easily handled during restoration. These pastes did not set within 6 months at room temperature, although in a previous report[5] the catalyst paste set within two weeks after fabrication. This may be due to a reaction between solute ferric ion from the filler and the impurities of bisGMA used. The bisGMA used in the present study was higher purity than previous report[6].

The initial setting time of the composite was 3min 20s and the peak temperature which was noted to determine setting time, involved an increase of 2-3°C in each container. For reference, a chemically cured composite@ for core building was also measured. The reference composite showed 2min 18s setting time with a 5-9°C increase in temperature. From these results, the test composite showed a longer setting time and more moderate setting reaction than the reference composite (Table 2).

The measurements of mechanical properties are shown in Table 3. The specific surface area of the stainless steel powder was measured 0.108m^2/g by BET method@@. Maximal mechanical properties were obtained when the filler was treated with 1.5g γMPTS in 70% ethyl alcohol solution per 100g of stainless steel filler. That is, the flexural strength and Knoop hardness values of this composite were 76 MPa (7.7kgf/mm^2) and 64KHN respectively. But those were about 20% lower than the reference composite. The volume fraction of filler in the experimental composite was under 50 vol%, while that of the reference composite was over 60 vol%. The elastic modulus of the experimental composite was equal to that of the reference composite. This was influenced by the large difference of the elastic modulus

@ Coalite, GC Corp., Tokyo, Japan
@@ measured by Flow Sorb II, Shimadzu, Kyoto, Japan

between the stainless steel filler and silica filler.

The properties of the composite with powder reinforced cannot be predicted because factors affecting the properties were many, such as the degree of adhesion bond between filler and matrix, shape of filler, filler content, and types of dispersion (filler was agglomerated, or in contact with each other)[7-9]. In the composite with high filler content the interparticle distance between the filler shortened, therefore the effect of reinforcing was enhanced. The low flexural strength and the hardness of the experimental composite mainly depend upon the weakness of the filler/matrix interface judged on the flexural strength, and also upon lower filler content and larger filler size than the reference composite, although the filler was treated with silane. In general, the low flexural strength of restorative materials causes breakdown at the margins, so an improvement in mechanical properties of the composite is nessesary for clinical application. Especially, the filler size of this composite is larger than that of commercially available composites, and a smaller filler must be used for that reason.

The results of the eluted metal from the composite are shown in Table 4. The elution

Table 2 Setting time of composites

Composite	Setting Time	Temp increased
Exp composite	3min 20s(9s)	2-3°C
Chemical cured composite	2 18 (9)	5-9

( ) : SD

Table 3 Effect of silane treatment to filler on mechanical properties of composite

Silane concenteration (g)*	Flexural strength (MPa)	Elastic modulous (GPa)	KHN
1.0	58.2(3.9)	9.36(0.81)	
1.5	76.0(6.9)	13.67(1.04)	64(12)
3.0	63.1(3.0)	9.22(0.74)	
Chemical cured composite	105.6(2.0)	13.06(0.97)	88(16)

* γMPTS was added in 100ml of 70% ethanol solution to treat 100g of stainless steel.
( ) : SD

Table 4 Eluted metal after immersion in 1% lactic acid and 0.9% sodium cloride solutions

	1v/v% lactic acid solution	0.9%sodium cloride solution
Exp composite	0.70(0.03) mg/cm^2	Not detectable

Immersion period: 7 days, ( ) : SD

Table 5 Attraction force of denture to the magnet for magnetic attachment

Composite	Attraction force(N)	References
Exp composite	4.39(0.24)	Magnet* 8.88N × 2 =17.76N
	4.26(0.53)	
Exp composite #	3.33(0.56)	Magnet** 5.92 N × 2 =11.84 N
Keeper/Magnet #	10.69(0.45)	Magnet** 5.92 N × 2 =11.84 N

* Hicorex Super(4515), ** Magfit 600,
# former reported data, see ref. (3).

test was according to the Japanese approval specification for dental casting Ni-Cr alloy. In 1% lactic acid solution, 90% of metal eluted from the composite was Fe, while Cr comprised about 10%. The total amount of eluted metal was 0.7mg/cm^2. The value is below the value of Japanese approval specifications for dental casting Ni-Cr alloys for Ni (below 1mg/cm^2).

Using 0.9% NaCl solution, there was no significant difference between the solution in which the specimen was immersed and the blank solution. Therefore the composite should be acceptable for clinical applications.

The attraction force measured using the mandibular model was also similar to those reported previously[3] (Table 5). The attraction force decreased by 25% of the magnet-keeper system when the composite was used. When another 2 magnets[$] (attractive force 5.9N (600gf×2)) were used in the mandibular model and keepers were attached, the attraction force obtained was 10.2N (1,033gf), and when composites containing 17Cr-2Mo stainless steel filler were used instead of keepers, the attraction force was 3.3N (337gf)[3]. The attractive force decreased 1/3-1/4 compared to that with the keeper attached. Since electro-magnetic properties cannot be predicted from the simple "law of mixture"[10], the data obtained is considered reasonable. Therefore, in clinical situations, the composite should be applied the over denture for children or some cases to molars, since the composite has less influence on MRI (Magnetic Resonance Image) than the keeper[11].

CONCLUSION

This new experimental composite has a good shelf life and can be easily handled during restoration.

The flexural strength and the Knoop hardness value of this composite were 76MPa (7.7kgf/mm^2) and 64KHN respectively, when the filler was treated with 1.5g γMPTS in 70% ethyl alcohol solution per 100g of stainless steel filler. However, mechanical properties of the composite require improvement for clinical application.

After immersion in 1% lactic acid solution at 37°C for 7 days, the total amount of metal eluted from the composite was 0.7mg/cm^2. This value is below the Japanese approval specifications for dental casting Ni-Cr alloys for Ni (1mg/cm^2).

The attraction force measurement using a mandibular model showed a 25% decrease in attraction force of the magnet/composite system compared to the magnet/keeper system.

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[$] Magfit 600, GC Corp., Tokyo, Japan

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本号掲載論文の和文抄録

歯科用チタン：アメリカにおける研究の推移

中島　裕，岡部　徹

Department of Biomaterials Science, Baylor College of Dentistry

近年，チタンは材料学研究者や臨床医に大きく注目を浴びてきている．アメリカでのチタンの生体材料としての歴史は，1940年にチタンインプラントの動物実験が行われた時から始まる．その後，1959年，口腔内インプラントを作製するにあたりチタン鋳造の必要性をアメリカのBedgerとPlogerがはじめて唱えた．1977年には最初のチタン鋳造による歯科補綴物が作製する試みがなされたと報告されている．過去10年間，IADRおよびAADRにおいてチタンに関連する発表数は毎年増加し続けている．大多数の研究発表は，アメリカからの研究であるが，そのうち半数以上は歯科用インプラントに関連したものである．チタン鋳造や補綴物としての応用に関するアメリカからの報告は，近年増加しているものの，今のところ数が限られている．このレポートは，アメリカにおける歯科用チタンの発展と研究の動向を報告する．

磁石と吸引する試作コンポジットレジンの性質

平野　進，安川宏美，野本理恵，森山圭介，平澤　忠

鶴見大学歯学部歯科理工学教室

SUS 444ステンレス鋼フィラーを含み，磁石と吸着する化学重合型コンポジットレジンを作製した．フィラーには種々の濃度のシラン処理を施した．このコンポジットレジンは操作性がよく，保存安定性に優れていた．もっとも良い性質を示したコンポジットレジンは以下のようであった．市販磁性アタッチメント用の磁石に対する吸引力は磁石附属のキーパシステムのそれの1/3-1/4であった．曲げ強さとヌープ硬さは各々76 MPa (7.7 kgf/mm^2) ならびに64 KHNで，市販の化学重合型コア用コンポジットレジンよりも低い値であった．コンポジットレジンからの溶出金属量は1％乳酸溶液7日間浸漬の結果0.7 mg/cm^{2}で，0.9%NaCl溶液7日間浸漬では検出できなかった．

フィラー形状および粒径が試作光重合型コンポジットレジンの機械的性質に及ぼす影響

宮坂　平

日本歯科大学歯学部歯科理工学教室

平均粒径1.7～21.5 μmの無定形フィラー4種類，平均粒径0.46～31.2 μmの球形フィラー5種類および平均0.04 μmのミクロフィラーのうちから，それぞれ2種類づつを組み合わせて混合した二成分系のハイブリッド型フィラーを用い光重合型コンポジットレジンを試作し，圧縮強さおよび間接引張強さを測定した．この結果，無定形フィラーと球形フィラーを混合すると，組み合わせるフィラーの粒径が小さいほど強度は大きくなる傾向