博 士 論 文

Development of Novel Orthodontic Adhesive for Protecting Teeth at Debonding

（ブラケット撤去時に歯を保護する新規矯正歯科用接着材の開発）

令和3年3月 申請

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Chapter 1

Optical and Chromatic Evaluation of Fluorescent Orthodontic Bonding Materials Doped with a Europium β-diketonate Complex

synopsis

We have the purpose of evaluating fluorescent imaging for orthodontic bonding materials doped with a europium β-diketonate complex. Tris(1 ,3 -diphenyl-1,3 -propanedionato)(1,10-phenanthroline)Eu(III) [Eu(DBM)$_3$Phen]-doped poly(methyl methacrylate) (PMMA) adhesives were prepared by two kinds of radical *in situ* polymerization methods at room temperature benzoyl peroxide/tertiary amine (BPO/amine) redox method, and radical generation by oxygen coordination to partially oxidized tri-n-butyl borane (TBBO) method. However, the photoluminescence of the composites obtained by the latter system was inadequate. The reason for this phenomenon is speculated to be steric hindrance of DBM by TBBO. In contrast, fluorescent Eu(DBM)$_3$Phen/PMMA composites were successfully prepared by the BPO/amine redox method. The transparent and almost colorless appearance of these composites under natural light is favorable for application as an esthetic dental product. Strong emission of Eu^{3+} at 613 nm was observed to gradually increase as the concentration of the complex increased. Based on the results obtained, we can conclude t at this Eu(DBM)$_3$Phen/PMMA adhesive can be used for developing photoluminescent orthodontic bonding materials.

Introduction

Orthodontic treatment using a multibracket appliance that consists of a set of brackets and wires attached to both upper and lower teeth, is one of the most popular and effective method to correct malocclusions. Orthodontic brackets are usually bonded to acid-etched surfaces of teeth (enamel) using methacrylate or dimethacrylate resins. The brackets and the residual bonding materials should be removed at the lowest possible iatrogenic damage to enamel surfaces after completing the active treatment. We have been actively attempting to introduce fluorescent imaging into orthodontic adhesives to minimize such damages, and have had some positive outcomes using different kinds of europium-doped nanophosphors [1–2].

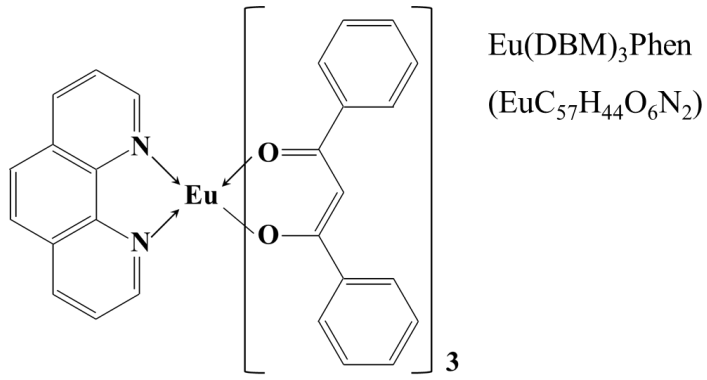
A large number of detailed studies have been performed on lanthanide complexes because of their particular luminescent properties [3–6]. Europium is one of the most useful lanthanides because of its very narrow emission band , large Stokes' shift, and longer decay time.[4,7]. Moreover, the maximum excitation wavelength of europium is in the near UV region that is closest to the visible light region, resulting in relatively limited detrimental effects to patients. Poly(methyl methacrylate) (PMMA) doped with europium β-diketonate complexes has been extensively studied [7–18] because the maximum emission wavelength of these complexes is in the low-loss window region of PMMA[12,15–17].However, to the best of our knowledge, comparatively little research has been performed on acrylic adhesives containing lanthanide complexes.

In this study, we examined europium β-diketonate complex doped PMMA to fabricate fluorescent adhesives as alternative to inorganic nanophosphors.

Materials and Methods

1. Reagents and fabrication of Eu complex doped PMMA composites

Tris(1,3-diphenyl-1,3-propanedionato)(1,10-phenanthroline)Eu(III) [$Eu(DBM)_3Phen$] [purity of 95.0% < ; Tokyo Chemical Industry Co., Ltd., Tokyo, Japan] (Schema 1) was used. $Eu(DBM)_3Phen$/PMMA composite specimens (20×20×1 mm; content of Eu complex: 0, 0.5, 1.0, 1.5, 2.0 wt%) were prepared using a PMMA/methyl methacrylate (MMA)-based autopolymerizing dental resin. Two kinds of initiation systems for radical *in-situ* polymerization of PMMA were employed; one was a benzoyl peroxide (BPO)/tertiary amine (the raw material is not officially released) redox system, and the other utilized radical generation by oxygen coordination to partially oxidized tri-n-butyl borane (TBBO). The MMA liquid from the radical generation method included 4-methacryloxyethyl trimellitate anhydride (4-META) . After the admixtures were left to stand for 10 min at room temperature, all the specimens underwent heating at 60°C overnight.



$Eu(DBM)_3Phen$

($EuC_{57}H_{44}O_6N_2$)

Scheme 1 Molecular Structure of $Eu(DBM)_3Phen$ complex.

2. Characterization

Room-temperature photoluminescence spectra of the $Eu(DBM)_3Phen$/PMMA specimens were measured by a spectrofluorometer (FP-8300, JASCO Co., Tokyo, Japan) under the following conditions: spectral band pass = 5 nm and wavelength scanning speed = 50 nm/min. For colorimetric characterization, an LED light with a C illuminant and a fluorescent tube with a central wavelength of 368 nm (FPL27BLB, Sankyo Denki, Kanagawa, Japan) to provide near-UV illuminant were used. A haze meter (HZ-1, Suga Test Instruments, Tokyo, Japan) was used to measure both the total light transmittance(Tt) and haze employing a C illuminant as a light source. The color coordinates of the specimens were identified in a CIE L*a*b* manner by a dedicated software package (ScopeVIEWER, Spectra Co-op, Tokyo, Japan). The coordinates were also converted to corresponding color values in the color space CIE XYZ, and marked in the CIE color diagram. Furthermore, the CIE 1976 L*a*b* color differences (ΔE^*_{ab}) were also calculated by following formula:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (1)$$

Results

Figure 1 shows emission spectra from the $Eu(DBM)_3Phen$/PMMA specimens (Eu complex content: 2.0 wt%) subjected to 395 nm UV irradiation. In addition to the emission spectra, excitation spectra are also shown for an emission wavelength of 612 nm.

For the specimens polymerized by BPO/amine redox system[$Eu(DBM)_3Phen$/PMMA (BPO/amine)], emission peaks at 579, 591, 613 and 652 nm were observed (Fig. 1, solid line). The strongest emission and absorption peaks were identified at 613 nm and 388 nm, respectively. Moreover, the emission intensity increased with increasing concentration of $Eu(DBM)_3Phen$ (Fig. 2). In contrast, both the emission and excitation spectra of the specimens via the TBBO initiation system [$Eu(DBM)_3Phen$/PMMA (TBBO)] showed two characteristics. First, the emission peaks were very weak. Secondly, no distinctive absorption band in the range of 350–400 nm was detected, although another absorption band (approximately 290–350 nm) was present (Fig. 1, dashed line).

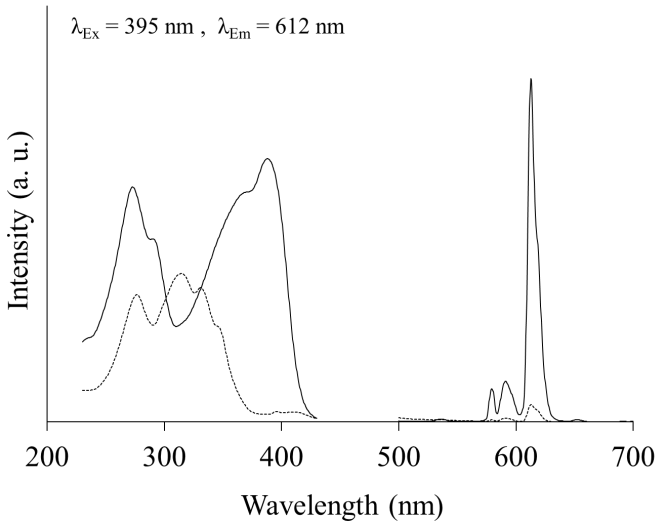


Fig. 1
Excitation and emission spectra of the $Eu(DBM)_3Phen$/PMMA specimens.
solid line: PMMA/MMA-BPO/amine, dashed line: 4-META/MMA-TBB

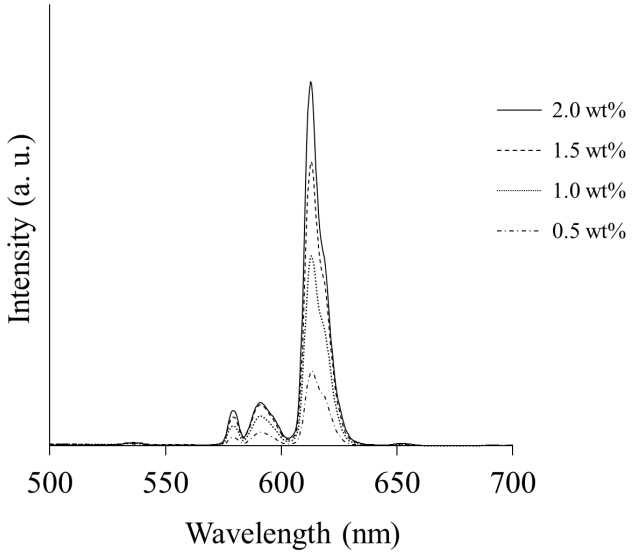


Fig. 2
Excitation and emission spectra of the $Eu(DBM)_3Phen$/PMMA specimens.
solid line: 2.0 wt%, dashed line: 1.5 wt%,
dotted line: 1.0 wt%, dashed-dotted line: 0.5 wt%

Under natural light, all specimens, except for the bright yellow Eu(DBM)3Phen/PMMA (TBBO) were transparent and had increasingly intense pale brown with increasing concentration of the complex (Fig. 3). The $Eu(DBM)_3Phen$/PMMA (BPO/amine) specimens emitted red light when excited by near-UV light (approximately368 nm), and the emission intensity increased with increasing concentration of the complex. As for the $Eu(DBM)_3Phen$/PMMA (TBBO), specimen, almost invisible dim emission was observed even if the content of the complex was 2.0 wt%. The solubility of the $Eu(DBM)_3Phen$ in each solution demonstrated that the complex was hardly soluble in the TBBO liquid, whereas it was quite soluble both in the MMA-BPO liquid and the MMA-4-META liquid (Fig. 4).

Based on the above-mentioned results, subsequent experiments were performed using only the $Eu(DBM)_3Phen$/PMMA (BPO/amine)samples. The total light transmittance and the haze were nearly constant independent of the concentration of the complex (Fig. 5). From the CIE chromaticity diagram (Fig. 6), the photoluminescence colors of the 1.5 and 2.0 wt% specimens were observed to be bright orange-red domain whereas the 0.5 and 1.0 wt% specimens were bluish-red as observed macroscopically (Fig. 6). The colors of all the specimens with different complex concentrations were clearly distinguishable with each other (Table 1).

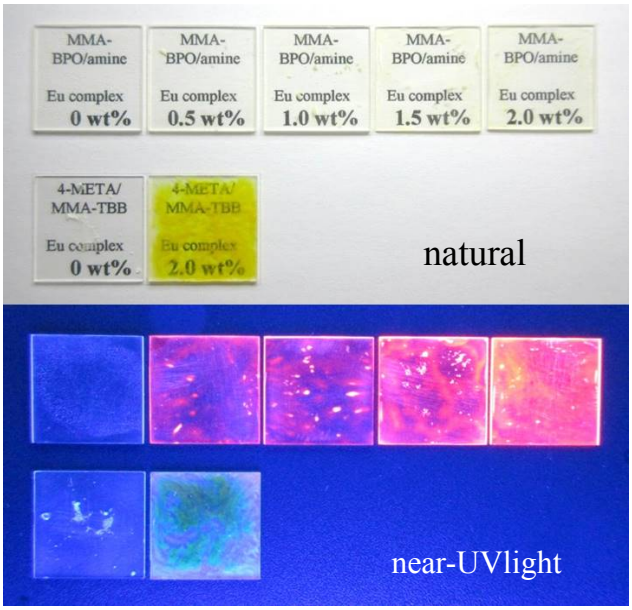


Fig. 3
Macroscopic appearance of the $Eu(DBM)_3Phen$/PMMA specimens.

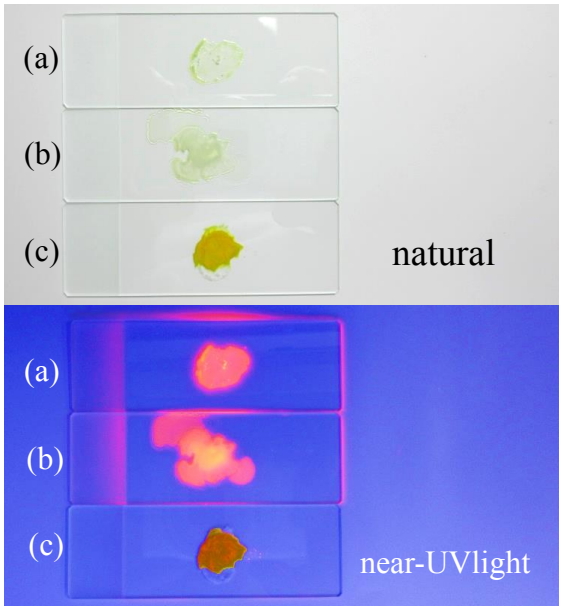


Fig. 4
Solubility and photoluminescence of $Eu(DBM)_3Phen$ in each solutions.
a: BPO-MMA, b: 4-META-MMA, c: TBBO

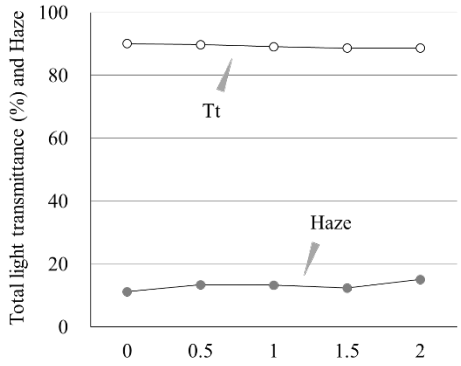


Fig. 5
Total light transmittance and haze of $Eu(DBM)_3Phen$/PMMA specimens.

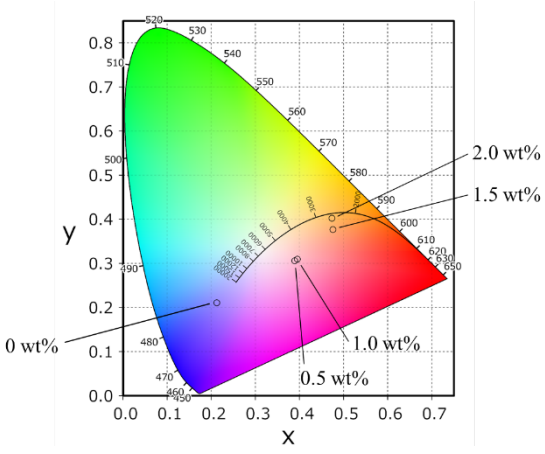


Fig. 6
CIE chromaticity diagram with the color coordinate of $Eu(DBM)_3Phen$/PMMA specimens.

	0.5 wt%	1.0 wt%	1.5 wt%	2.0 wt%
0.5 wt%	---	6.78	44.35	53.41
1.0 wt%	---	---	38.26	52.21
1.5 wt%	---	---	---	18.68
2.0 wt%	---	---	---	---

ΔE* (NBS unit)	0-0.5	Trace
	0.5-1.5	Slight
	1.5-3.0	Noticeable
	3.0-6.0	Appreciable
	6.0-12.0	Much
	12.0 <	Very much

Table 1 CIE 1976 L*a*b* color difference.

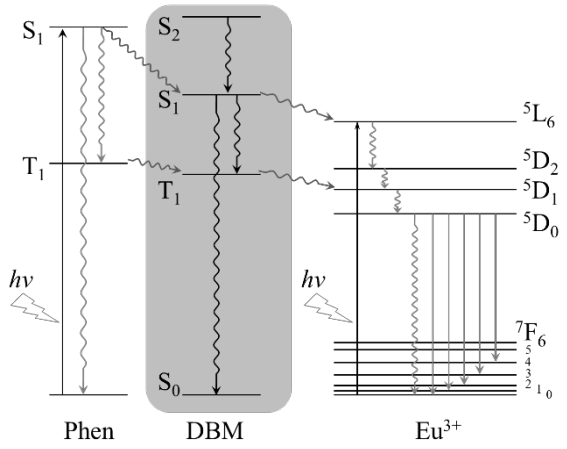
Discussion

Identifying the adhesives in an oral cavity is exceedingly difficult because of the transparency or whitish color of the adhesives currently in use. Additionally, there is no universally approved protocol for safe and complete removal of these adhesives [19]. We are confident that a photoluminescent adhesive is an innovative solution to this problem.

Obtaining lanthanide complex-doped polymers with high quantum yields is challenging endeavor[5]. We aim to establish a $Eu(DBM)_3Phen$/PMMA adhesive by utilizing radical *in-situ* polymerization at room temperature. Although a large number of studies have been performed on $Eu(\beta\text{-diketonate})_3Phen$/PMMA, only a few of these studies used any kind of polymerization [7,10,11,15–17], however, all of these procedures were thermal polymerization at high temperatures and pressures inapplicable to the human body. Milanova et al. [11] mentioned that $Eu(DBM)_3Phen$ and other complexes these authors investigated are unsuitable in the presence of peroxide ; therefore , preparing the matrix by monomer polymerization is not a suitable method. On the contrary, our $Eu(DBM)_3Phen$/PMMA (BPO/amine) exhibited satisfactory excitation and emission spectra (Fig. 1). The emission peaks at 579, 591, 613 and 652 nm are assigned to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_3$ transitions of Eu^{3+} ions, respectively [7,9,10,13,15–17]. Regardless of the positive results described avobe, the $Eu(DBM)_3Phen$/PMMA (TBBO) system could not yield the expected photoluminescence and was bright yellow under natural light. The insolubility of $Eu(DBM)_3Phen$ in TBBO was due to the difference in polarity of these molecules, and therefore the mixture exhibited an intrinsic bright yellow color owing to the d-d transition of the suspending complex. Furthermore, since $Eu(DBM)_3Phen$ emitted a strong red light even if this molecule was dissolved in liquid solutions of MMA-BPO or MMA-4-META (Fig. 4), we speculate that DBM might be sterically hindered by TBBO, and unable to absorb UV light effectively. As for the appearance of the absorption band in the range approximately 290–350 nm, we presume that this band was the result of a conjugative action toward 1,10-phenanthroline (Phen) induced by phthalic-anhydride of 4-META. Therefore, we believe that if by Phen absorbance occurs, the energy transfer cascade from the singlet level of Phen to DBM and then to Eu^{3+} through short-range interactions does not occur owing to steric hindrance by DBM (Scheme 2) [4,5,12,13,20]. Whatever the explanation for this result, further works is still needed to develop a fluorescent 4-META/MMA-TBBO adhesive.

Transparency is one of the most important requirement for orthodontic adhesives. To evaluate the transparency of the $Eu(DBM)_3Phen$/PMMA specimens, we measured total light transmittance (Tt) and haze of the samples. Haze is defined as the proportion of diffuse transmittance to Tt. Here, diffuse light is defined as refracting light that deviates more than 2.5° from the parallel light. Although neither Tt nor haze directly indicate the degree of transparency of the specimens, the obtained results are promising, and the shades of pale brown observed for several concentration of the complex do not affect the application of investigated system as an esthetically pleasing orthodontic adhesive.

The emission color was evaluated by an internationally accepted CIE color coordinate system (Fig. 6). The bluish-red emission for the 0.5 and 1.0 wt% specimens is due to a mixture of weak red emission and the wide range of bluish light from the near-UV illuminant. Additionally, a strong orange-red emission was observed for the 1.5 and 2.0 wt% specimens. Although we are still investigating this proposed system, we can conclude based on the results obtained that the $Eu(DBM)_3Phen$/PMMA is a promising material for application to fluorescent orthodontic adhesives.



Scheme 2
Energy level diagram for explaining inhibition of the cascade energy transfer in the $Eu(DBM)_3Phen$.

Conclusion

Fluorescent adhesive PMMA composites doped with $Eu(DBM)_3Phen$ were successfully prepared by the polymerization via the PMMA/MMA-BPO/amine initiation system at room temperature. The transparent and almost colorless appearance of this composite under natural light is favorable for an application to an orthodontic adhesive. The strong luminescence under near-UV light, especially when the content of the complex was above 1.5 wt%, is promising for safe and complete removal of this adhesive after completing active treatments. The results support our hypothesis that monomer polymerization can be applicable to $Eu(DBM)_3Phen$ even in the presence of peroxide. The reason for the inadequate results from the composites polymerized via the radical generation by TBBO is still unclear, and therefore ,this problem still requires further investigation.

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Short summary

In this study, as a method to reduce the burden on the tooth surface when removing a bracket, we have developed an adhesive that can prevent excessive damage to the enamel by visualizing the adhesive.
However, there are still problems with pain and cracks when removing the bracket.
Therefore, we have also developed a dismantlable adhesive that reduces the force required to remove the bracket from teeth

Chapter 2

Development of dismantlable adhesives using temperature-responsive polymers

Introduction

A bracket used for multi-bracket appliances is firmly adhered to each tooth with an adhesive for orthodontic treatment. When active orthodontic treatment is finished, the appliance is removed from the tooth surface by a mechanical force.

Resin and glass ionomer cements are usually used to adhere orthodontic appliances, such as brackets, to the tooth mainly by mechanical fitting and chemical bonding forces, respectively.[1,2] In addition,some resin cements was added functional monomers, which were developed to promote the bonding resin to tooth substance. The functional monomer has also become essential to the enamel bonding. Especially,4META is one of the acidic functional monomers, and many studies has been investigated about adhesive strength of 4META / MMA-TBB resin.[3-8] 4META / MMA-TBB resin has been commonly used in orthodontic practice because of the strong adhesiveness. However, it requires a strong mechanical force to remove brackets from the tooth surfaces, which causes patients to feel pain, and also form cracks on the tooth surfaces that frequently induce cold water pain.[9-11] It has been reported that the lower anterior teeth are the most painful during removal of brackets, and some patients experience considerable pain. Although reducing the pain during removal of brackets is an urgent issue, an effective solution is still unclear.

Therefore, this problem can be solved by developing an adhesive that softens the adherence and requires a weaker force to remove brackets when needed. We focused on a temperature-responsive polymer gel as the key material. Some polymer gels have a shape memory property, in which they undergo a soft rubber-like state and are restored to a preformed shape by heating, and then become hard again by cooling. [12-14] A stearyl acrylate/acrylic acid and a methyl acrylate/acrylic acid copolymer gels are examples of shape-memory polymer gels with such properties.[12]

In this study, we developed a novel orthodontic adhesive using shape memory polymer gels that can reduce the mechanical force required to remove brackets, and evaluated its mechanical properties.

Materials and Methods

In this study, stearyl acrylate/acrylic acid copolymer gel ([poly(SA-co-AA)]) with swelling-shrink transition temperature of 50 °C and methyl acrylate/acrylic acid copolymer gel([poly(MA-co-AA)]) were used as shape memory polymer gels.

1. Producing temperature-responsive dismantling adhesives

(i) Synthesis of stearyl acrylate/acrylic and methyl acrylate/acrylic acid copolymer gels

Stearyl acrylate (SA, TCI), methyl acrylate (MA, TCI), and acrylic acid (AA, Fuji Film Wako Pure Chemical Industries, Ltd.) were used as the monomers. The monomer ratio was SA (MA): AA = 1: 1 (mol: mol), and the total monomer concentration was 3 mol/L. 1 mol% of methylenebisacrylamide (Fuji Film Wako Pure Chemical Industries, Ltd.) was added to the monomer as a cross-linking agent and 0.1 mol% of α-ketoglutaric acid (Fuji Film Wako Pure Chemical Industries, Ltd.) was added as a radical initiator. The mixture was dissolved in ethanol, poured into a glass mold, and irradiated with ultraviolet rays for 8 h in an argon atmosphere. The synthesized gel was immersed into pure water, which was exchanged three times to remove unreacted raw materials and ethanol to obtain a

copolymerized gel.

(ii) Addition of gel to the adhesive and preparation of test specimens

The obtained gel was frozen at -50 °C and the pressure was reduced to 10 Pa. During the pressure reduction, the temperature was changed every 6 h in the order of -50, -20, -15, and 25 °C, and freeze-dried. Using a crusher bead shocker, samples were encapsulated with metal cones in crushed capsules and coarsely crushed by repeating 2000 rpm 5 times for 2 min. The coarsely pulverized gel was further pulverized in a mortar to obtain a powdered gel. Crushed gels were added to a 4META/MMA-TBB based resin, which is often used in orthodontic treatment, at a concentration of 10%, and specimens (diameter 10 mm, thickness 1.8 mm) were prepared using the brush-on technique. Test specimens of pure 4META/MMA-TBB based resin were also prepared as controls using the same method.

2. Viscoelasticity test

A viscoelasticity test was performed on a 4META/ MMA-TBB resin including poly(SA-co-AA) and poly(MA-co-AA), and controlled with a dynamic viscoelasticity measuring device (Ares-G2 TA Instruments Co., Ltd.). The settings of the oscillation strain and frequency were 0.4% and 5.0 Hz, respectively. The measurement temperature ranged from 10 to 80 °C at a heating rate of 3 °C /min.

Result

The storage modulus of the control (4META/MMA-TBB resin only) gradually decreased with the increase in the temperature, and the decrease rate slightly increased from approximately 45 °C. In contrast, the storage modulus of the 4META/MMA-TBB resin including poly (SA-co-AA), considerably decreased with the increase in temperature compared to that of the control. The storage modulus of the 4META/MMA-TBB resin doped with poly(SA-co-AA) was higher than that of the control in the range from 10 to 20 ° C; however, the storage modulus was equal to the control at 23 °C , 2/3 of the control at 40 °C, and was less than half that of the control above 50 °C. The storage modulus of the 4META/MMA-TBB resin including poly(MA-co-AA) was sufficiently lower than that of the others at all temperatures (Fig. 1).

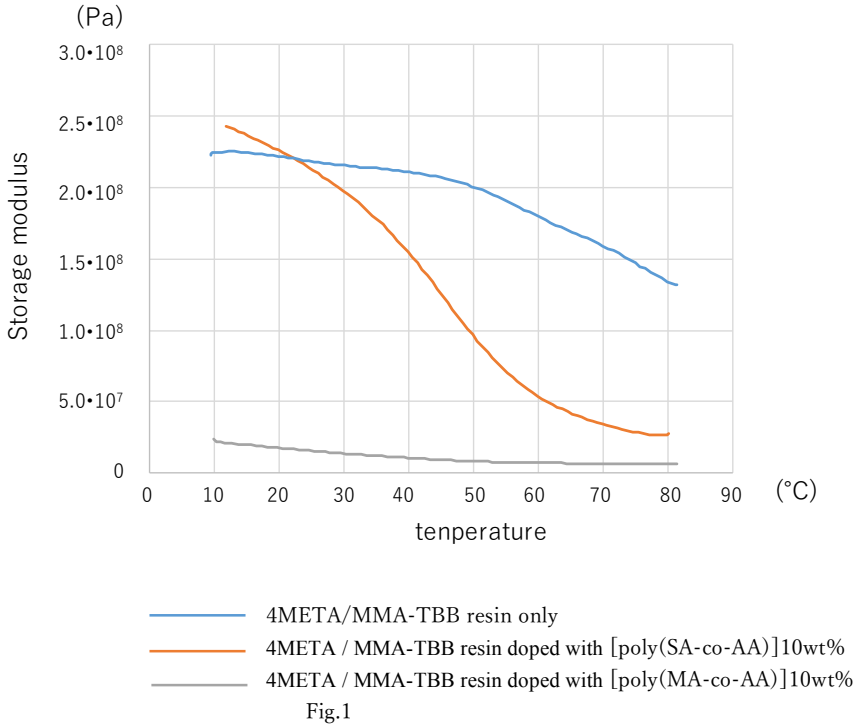

Fig.1

Discussion

In this study, we attempted to fabricate an adhesive that softens and is easily broken by an increase in temperature. If this adhesive is used in orthodontic practice, it is assumed that during the removal of brackets, teeth are also heated. Heating teeth may affect the dental pulp. It has been reported that the pulp organically changes when it is heated 5 °C above body temperature. [15]Based on this, the pulp would be damaged at approximately 42 °C, as the body temperature is approximately 37 °C. However, it has been found that pulp cells recover by returning to body temperature even if they are exposed to a temperature 5 °C higher than the body temperature for 30 min. [16]In addition, it is predicted that the pulp does not reach 42 °C by introducing heat through the enamel and dentin when the adhesive is heated to 42 °C. For these reasons, it is expected that heating the adhesive to 42 °C will not severely affect the pulp. From the viscoelasticity test results, the storage modulus of the 4META /MMA-TBB resin including poly(SA-co-AA) could be considerably reduced with the increase in temperature compared to that of the control sample, and was approximately 2/3 of the control at 42 °C. Chen et al. reported that a force of 7.8 Pa or more for the removal of brackets causes cracks on the enamel surface, and the higher the removing force, the higher the incidence of cracks and the larger the size of cracks. [9] The adhesive strength to enamel surface of the 4META/MMA-TBB resin is approximately 12 Pa, and a reduction of 2/3 in the adhesive strength is assumed to be sufficient to protect teeth from cracks. It can also be expected that reducing the adhesive strength decreases pain when removing brackets on the tooth surface. Although the detachment of brackets from teeth when ingesting something hot is a concern because of the reduced adhesive strength, it is considered that hot food is chewed in various places of the oral cavity, and hot drinks are immediately swallowed. In addition, a gap between the oral and the adhesive temperature occurs because the bracket needs to transfer heat to the adhesive.[17] Therefore, it is expected that eating and drinking does not severely reduce the adhesive strength.

Using high temperatures in the oral cavity may cause discomfort. However, as mentioned above, although the required temperature may be several degrees above the usual oral temperature, it requires time to be transferred. Therefore, it is considered that patients have almost no discomfort during the process of heating the adhesive.

Poly(SA-co-AA) was reported to have a transition temperature of 50 °C, at which physical properties change. In this study, the storage modulus of 4META/MMA-TBB resin, including poly (SA-co-AA), considerably decreased at temperatures below 50 °C. There are two possible reasons for this phenomenon. One is the reaction speed of the obtained poly(SA-co-AA). This gel slowly softens around 50 °C; thus, it is considered that some time may be required for this gel to change its physical properties in response to temperature. The other reason is the heating mechanism with the dynamic viscoelasticity measuring device. This device heats samples only from the bottom. Therefore, there is a time lag for the transmission of the heat to the entire sample.

The storage modulus of the 4META/MMA-TBB resin containing poly(SA-co-AA) and the 4META/MMA-TBB resin were almost the same at 10–20 °C. In contrast, the storage modulus of the 4META/MMA-TBB resin containing poly(MA-co-AA) was sufficiently lower than 4META/MMA-TBB resin only and 4META / MMA-TBB resin containing poly(SA-co-AA). The mechanical properties of these gels were determined according to the carbon chain length of molecules copolymerized with acrylic acid. Therefore, it is suggested that the mechanical strength of poly(SA-co-AA) was sufficient at room temperature, but that of poly(MA-co-AA) was too high even at room temperature. However, in this study, because the specimen was prepared by the brush-on technique in accordance with clinical practice, an error may occur due to the P/L ratio.

In the future, we will prepare copolymer gels with different carbon chain lengths or different copolymers, such as a stearyl acrylate/methyl acid copolymer(poly (SA/MA)), and evaluate changes in the storage modulus. Poly(SA / MA) can change the transition temperature by changing the polymerization ratio of SA and MA. Using these methods, we will seek an appropriate transition temperature for use as an orthodontic adhesive.

After determining the transition temperature, we plan to measure the adhesive strength and the time required for heat to be transferred to the adhesive.

Conclusion

It was suggested that [poly (SA-co-AA)] is effective in developing an adhesive that can be removed with a weak force at the debonding by increasing the temperature of the adhesive.

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