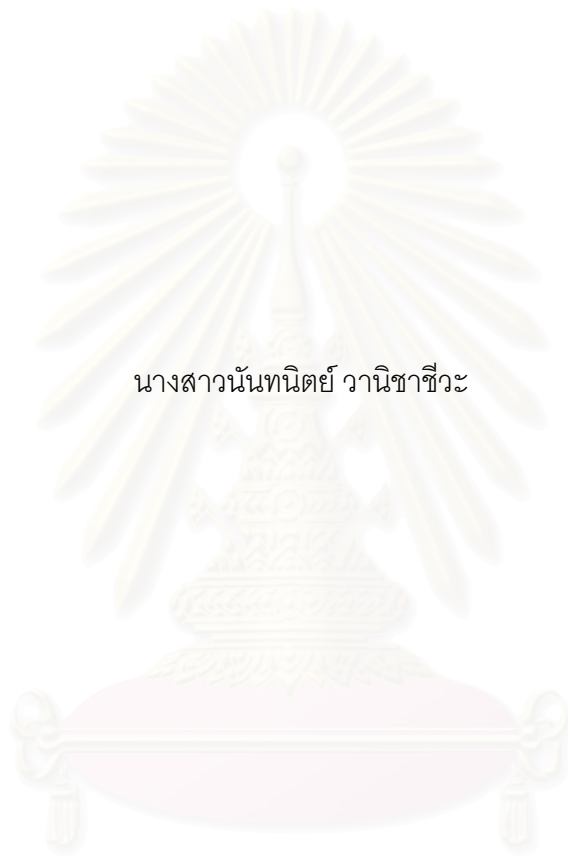


พอลิเมอร์เซชันของโลหะเวซินคอมโพสิตสำหรับทำวัสดุบุรณะฟัน



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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

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ลิขสิทธิ์ของ จุฬาลงกรณ์มหาวิทยาลัย

POLYMERIZATION OF METAL-RESIN COMPOSITE FOR
RESTORATIVE DENTAL MATERIAL

Miss Nantanit Wanichacheva

สถาบันวิทยบริการ

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โลหะ 5 ชนิดได้แก่ โลหะเงิน เซอร์โคเนียม ทองแดง โมลิบดีนัม และ สังกะสี ถูกนำมาทดสอบความสามารถในการเหนียวทำให้เกิดปฏิกิริยาพอลิเมอร์เรซินของ urethane dimethacrylate (UDMA) โมโนเมอร์ โมโนเมอร์ที่มีสารเติมแต่งแตกต่างกัน 4 ชนิดถูกนำมาใช้ในการศึกษาโดยนำมาผสมกับโลหะ จากผลการทดลองพบว่าโลหะเงิน และ เซอร์โคเนียม ไม่สามารถที่จะเหนียวทำให้เกิดปฏิกิริยา พอลิเมอร์เรซินของ UDMA โมโนเมอร์ได้ แม้ว่าจะมีการผสมสารที่ทำให้เกิดการเชื่อมขวางของ (4 – methacryloyl -oxyethyl trimellitate anhydride (4-META) หรือ แรคดิเคิลอินินิเอเตอร์ (benzoyl peroxide, BPO) ก็ตาม ส่วนโลหะทองแดงและโมลิบดีนัมนั้นพบว่ามีความสามารถในการเหนียวทำให้เกิดปฏิกิริยาพอลิเมอร์เรซินได้แม้ว่าจะไม่มีสารเชื่อมขวาง 4-META ผสมอยู่ แต่ไม่สามารถเหนียวทำให้เกิดปฏิกิริยาพอลิเมอร์เรซินได้ถ้าไม่มี แรคดิเคิลอินินิเอเตอร์ (BPO) เป็นส่วนผสม ทั้งนี้ความสามารถดังกล่าวตรงกันข้ามกับการใช้โลหะสังกะสีเหนียวทำให้เกิดปฏิกิริยาพอลิเมอร์เรซินของUDMAโมโนเมอร์แต่ไม่สามารถเหนียวทำให้เกิดปฏิกิริยาพอลิเมอร์เรซินได้ดีถ้าไม่มีสารเชื่อมขวาง 4-META เป็นส่วนผสม

จากการศึกษาขั้นต้นดังกล่าว โลหะโมลิบดีนัมถูกเลือกมาใช้ในการศึกษารายละเอียดของปฏิกิริยาพอลิเมอร์เรซิน ในการศึกษาโลหะโมลิบดีนัมจะถูกทำให้เปียกด้วยน้ำปริมาณเล็กน้อยและนำไปศึกษาผลของการใช้โมโนเมอร์ที่แตกต่างกัน 2 ชนิด คือ bisphenol glycidyl methacrylate (BisGMA) และ UDMA และศึกษาปริมาณ 4-META ที่เติมลงไปในวัสดุ ต่อเวลาในการคงตัว และ degree of conversion (DC) ของวัสดุที่ได้ จากผลการทดลองพบว่าโลหะโมลิบดีนัมสามารถเหนียวให้เกิดการคงตัวของโมโนเมอร์ได้ทั้งชนิด BisGMA และ UDMA และพบว่าการเติม4-METAในปริมาณที่มากขึ้นจะไปหน่วงเวลาของการเกิดปฏิกิริยาพอลิเมอร์เรซิน แต่ในขณะเดียวกันกลับไปเพิ่ม DC ทั้งในวัสดุที่ใช้ BisGMA และ UDMA เป็นโมโนเมอร์ นอกจากนี้ยังพบว่าวัสดุชนิดโมลิบดีนัมเรซินคอมโพสิตนี้มี DC สูงกว่าโลหะเรซินคอมโพสิตชนิดเดิมมาก

ภาควิชา.....	เคมี.....	ลายมือชื่อนิสิต.....
สาขาวิชา.....	เคมี.....	ลายมือชื่ออาจารย์ที่ปรึกษา.....
ปีการศึกษา.....	2543.....	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

NANTANIT WANICHACHEVA: POLYMERIZATION OF METAL-RESIN COMPOSITE FOR RESTORATIVE DENTAL MATERIAL. THESIS ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D., THESIS CO-ADVISOR: PROFESSOR YUKIO MIYAGAWA, D.D.S., Ph.D., 54 pp. ISBN 974-13-0544-3.

Five kinds of metal particles, *i.e.*, Ag, Zr, Cu, Mo and Zn were examined to establish if they could induce the polymerization of urethane dimethacrylate (UDMA) based monomer. Four different monomer compositions were used to combine with metal filler. As-received, Ag and Zr particles could not induce the polymerization of UDMA based monomer either containing coupling reagent (4-methacryloyloxyethyl trimellitate anhydride, 4-META) or radical initiator (benzoyl peroxide, BPO) or without containing of those components. Cu and Mo particles could induce the polymerization of UDMA based monomer even in the absence of 4-META, but they could not have the ability to do so in the absence of BPO. Zn particles could induce the polymerization of UDMA based monomer in the absence of BPO, but they could not have good ability in the absence of 4-META.

From the above observation, molybdenum particles were chosen to study the details of the polymerization phenomena. The mixture of molybdenum particles moistened with a small amount of water and either bisphenol glycidyl methacrylate (Bis-GMA) based monomer or UDMA based monomer containing 4-META and BPO was investigated. The effects of monomer types and 4-META concentrations on the setting time and degree of conversion (DC) were studied. Molybdenum particles could induce the polymerization of both Bis-GMA based monomer and UDMA based monomer. A higher concentration of 4-META retarded the setting time but increased DC in both monomers. This molybdenum-resin composite had much higher DC than the previous metal-resin composites.

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Academic year 2000

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LIST OF ABBREVIATIONS

cm ⁻¹	unit of wavenumber
M.W.	molecular weight
Fig.	Figure
°C	degree celsius
μl	microliter
mg	milligram
mm	millimeter
g	gram (s)
wt	weight
min	minute
sec	second
DC	degree of conversion
UDMA	urethane dimethacrylate
BisGMA	bisphenol glycidyl methacrylate
4-META	4-methacryloyloxyethyl trimellitate anhydride
BPO	benzoyl peroxide
TEDGMA	triethyleneglycol dimethacrylate
EGDMA	ethyleneglycol dimethacrylate
DMPT	<i>N,N</i> -dimethyl- <i>p</i> -toluidine

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CHAPTER I

INTRODUCTION

Dental resin composites were introduced commercially in the mid-1960s for the restoration of anterior teeth. Since their advent, resin composites have undergone significant development, which continues to improve the longevity of resin composite restorations. However, despite vast improvements which have expanded indications for their use present-day resin composites still have shortcomings limiting their application. Inadequate resistance to wear (loss of anatomic form) under masticatory attrition, and marginal leakage due to polymerization shrinkage are often cited as being the main problems of resin composites.

Recently, metal-resin composites have been developed in order to rectify the main deficiencies of dental resin composite. Since the aforementioned problems were dependent on the filler components in the composites [1], metal fillers were used in metal-resin composite instead of the inorganic fillers.

The development of this new restorative materials was originated after the recovery of Ogura and Honda [2]. They found that metal particles could use as the filler and incorporate in the polymerization system of urethane dimethacrylate monomer (UDMA) at room temperature in the presence of the 4-methacryloyloxyethyl trimellitate anhydride (4-META) as coupling reagent, benzoyl peroxide (BPO) as radical initiator, and tertiary amine (DMPT) as accelerator. These phenomena showed that metal particles could be used instead of the inorganic filler in the dental composite system. The further study by Miyagawa *et.al.*[3] showed that several kinds of metal particles, *i.e.* Cu, Zn, Mo, Sn, Co, In, and alloy of silver (Ag/Cu, Ag/Sn, Ag-In) could be involved in the polymerization of resin composites. However, some kinds of metal such as Ag, Al, Cr, Ni, Ti and Zr particles could not induce the polymerization. Another highlight of this research was that DMPT, which may result in less discoloration of the resin matrix, could be eliminated from the components of dental restorative resins. This recovery could state that the activity of metal-particles in polymerization reaction of resin composite were different from inorganic filler. In support of this assumption, the later study of

Wanichacheva *et.al.*[4] reported that zinc-resin composite, in which zinc particle was used as the filler, could eliminate BPO, which is well-known for the cause of the cancer and allergy [5], from the composites system.

There were several studies on the properties as well as degree of conversion (DC) of metal-resin composites in the last 2 years [4,6-10]. The composites using spherical Ag/Sn alloy particles as the filler gave acceptable mechanical and physical properties in the studies of Katkuta *et. al* [6] and Urapepon *et.al.*[7-9]. The DC of metal-resin composites using zinc particles [4] and Ag/Cu alloy particles[10] was reported to be higher than the dental composites using inorganic filler. Since DC was the parameter relating to several physical properties of dental resins, the higher DC could be expected to improve the properties of this material [1,11-12]. All of these studies have suggested that the metals in metal-resin composites could provide the interesting phenomena and involve in the improvement of properties which may rectify the shortcomings of the resin composites.

However, there were no studies that compared the effects of metal types (Cu, Zn, Mo, Ag, Zr) and organic compositions on the setting time of metal-resin composites. As well as, there were no studies that compared the efficiency of bisphenol glycidyl methacrylate (BisGMA monomer) against UDMA monomer in metal-resin composites even though both of them are outstanding as monomer-based in dental composites.

The objectives of this research were:

1. to study the effects of metal types and organic compositions on the polymerization setting time in an attempt to elucidate the polymerization mechanism for future use,
2. to investigate the effects of monomer types (BisGMA and UDMA) and concentrations of coupling reagent (4-META) on the setting phenomena of molybdenum-resin composite, and
3. to investigate the effects of monomer types (BisGMA and UDMA) and concentrations of coupling reagent (4-META) on the degree of conversion of molybdenum-resin composite.

CHAPTER II

LITERATURE REVIEWS

2.1 Resin composites in dentistry

A composite material has been defined as a “three-dimensional combination of at least two chemically different materials with a distinct interface separating the components”[13]. Dental resin composites comprise a blend of hard, inorganic particles bound together by a soft, resin matrix, and generally encompass three main components:

- (1) the resin matrix comprising: (i) a monomer system, (ii) an initiator system for free radical polymerization, and (iii) stabilizers for maximizing the storage stability of the uncured resin composite and the chemical stability of the cured resin composite,
- (2) the coupling agent, usually an organo-silane, that chemically bonds the reinforcing filler to the resin matrix, and
- (3) the inorganic filler consisting of particulates such as glass, quartz, and/or fused silica.

Obviously, the properties and hence the performance of resin composites are dependent upon the three basic components of the material. Some of the properties are mainly related to the filler and the coupling agent, whereas other properties mainly seem from the resin matrix. The first group of properties includes strength, stiffness, abrasion resistance, and coefficient of thermal expansion, while color stability and softening tendency can be found in the second group. A third group of properties may be identified that, to a higher degree, depends on both filler and matrix. Such properties are polymerization shrinkage and water sorption. However, as most properties are derived for all three basic constituents of the material, this classification of properties is not very sharp. For example, mechanical properties are, as stated, highly influenced by the filler and the coupling agent, but also the organic matrix plays a significant role for strength, stiffness, and abrasion resistance.

Judging from the formulation changes which have been reflected in commercial resin composites over the years, the development of these materials has mainly focused on mechanisms of initiation and filler technology, whereas the resin monomer component has remained essentially unchanged. The details of dental monomers will be described in next section.

2.1.1 The monomer system

The resin component of a cured dental resin composite is a polymeric matrix. A polymer is a large molecule built up by repetitive bonding together of many smaller units called monomers. The process by which monomers are joined together and converted into polymers is called *polymerization*. Monomers used in dentistry are generally liquids, and during the process of polymerization they are converted to solids. The degree of which carbon double bonds (C=C) are converted into carbon single bond is known as the *degree of conversion*.

The monomer systems of most present-day resin composites are based on BisGMA, developed some 40 years ago, or derivatives of BisGMA. In the remaining resin composites, urethane monomers or oligomers are used as the basis of the monomer system. Main deficiencies of current resin composites are polymerization shrinkage and insufficient wear resistance under high masticatory forces. Both factors are highly influenced by the monomer system, and considerable efforts are being made around the world to reduce or eliminate these undesirable properties.

(1) BisGMA resins

BisGMA resins was synthesized in 1956 as a new monomer, initiating the era of dental resin composites [14]. It was prepared from bisphenol A and glycidyl methacrylate, in which the later was obtained from the diglycidyl ether of bisphenol A and methacrylic acid (Fig.1). Polymerization of the monomer, which was given the acronym BisGMA, occurs through the carbon-carbon double bonds of the two methacrylate groups.

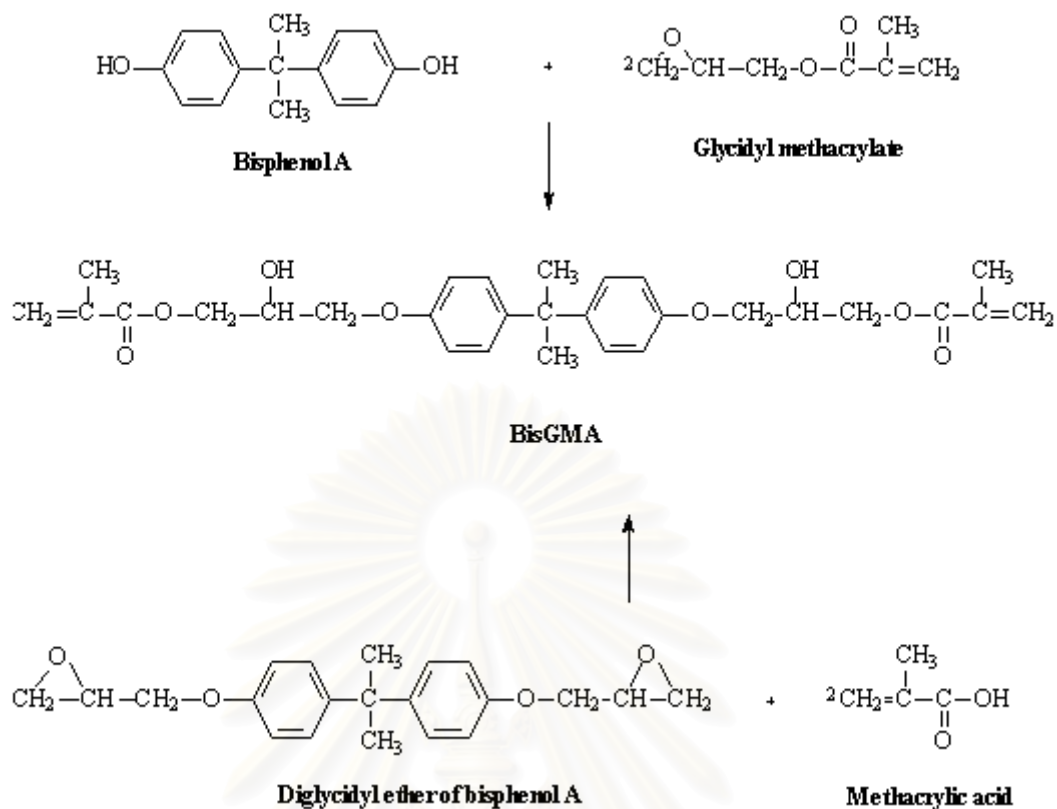


Fig.1. Synthesis of BisGMA either from bisphenol A and glycidyl methacrylate or from the diglycidyl ether of bisphenol A and methacrylic acid.

This bulky, difunctional monomer is superior to methyl methacrylate because of its large molecular size and chemical structure, providing low volatility, low polymerization shrinkage, rapid hardening, and production of strong and stiff resins. The high viscosity of BisGMA is lowered by admixture with dimethacrylate monomers of lower molecular weight to achieve a viscosity suitable for filler incorporation. The monomers most often used as diluents for BisGMA are ethyleneglycol dimethacrylate (EGDMA) and triethyleneglycol dimethacrylate (TEGDMA). (The chemical structures of EGDMA and TEGDMA are shown in Fig.2.) While the viscosity of water is approximately 1 mPa.s (23°C), the viscosity of BisGMA is approximately 1,000,000 mPa.s (23°C) and that of TEGDMA approximately 10 mPa.s (23°C). The lower the viscosity of the monomer mixture, the more filler would be incorporated into the mixture. All other things being equal, an increase in filler content will improve several properties of the polymerized material, e.g. strength, stiffness, and

coefficient of thermal expansion. However, dilution of BisGMA also has negative effects such as increased polymerization shrinkage, as discussed in the following.

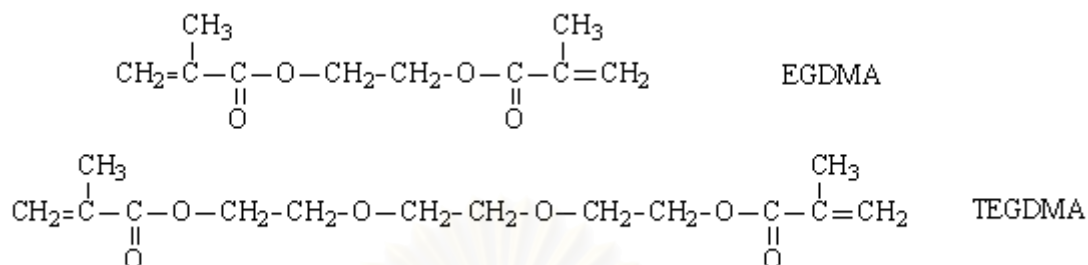


Fig.2. Two dimethacrylate monomers often used as diluents for BisGMA: EGDMA and TEGDMA.

As a consequence of polymerization, resin systems shrink mainly because the formation of a macromolecular chain network from discrete monomer species involves conversion of intermolecular distances of 0.3-0.4 nm into primary, covalent bonds with lengths of about 0.15 nm. The extent of polymerization shrinkage depends, among other things, on the molecular weight and functionality of the monomers. Thus, comparing monomers of the same molecular weight, polymerization shrinkage increases when functionality increases. In addition, comparing monomers of the same functionality, polymerization shrinkage increases when molecular weight decreases. Consequently, dilution of BisGMA increases polymerization shrinkage.

Studies on the formation of homopolymers from dimethacrylates of mono-, di- tri-, and tetraethyleneglycol have shown that the reactivity of the monomers increases with increasing distance between the methacrylate groups. It follows that TEGDMA is more reactive than EGDMA. Due to favorable stereochemistry, long chain, flexible dimethacrylates of oligoethyleneglycols have been found to exhibit relatively high degree of conversion. Compared with the dimethacrylates TEGDMA, the aromatic monomer BisGMA is much more rigid. As a consequence, the degree of conversion in BisGMA and TEGDMA copolymer has been found to decrease with an increasing content of BisGMA. The relative stiffness of BisGMA is related to the bulky, aromatic groups of the central part

of the molecule, causing much larger barriers to rotation about the bonds. Thus, strength, hardness, and certain other mechanical properties are influenced not only by the degree of conversion but also by the nature of the monomeric subunits in the polymer. On the other hand, other properties are determined mainly by the degree of conversion.

Dimethacrylate monomers polymerize to highly crosslinked, three-dimensional networks. As polymerization proceeds, diffusion rates of propagating free radicals and unreacted dimethacrylate molecules are drastically reduced, hampering complete conversion of methacrylate double bonds. Thus, as much as 25 to 50% of the methacrylate groups remain unreacted (Fig.3). Of these 25 to 50% unreacted methacrylate groups, approximately one tenth is present as residual monomer [15].

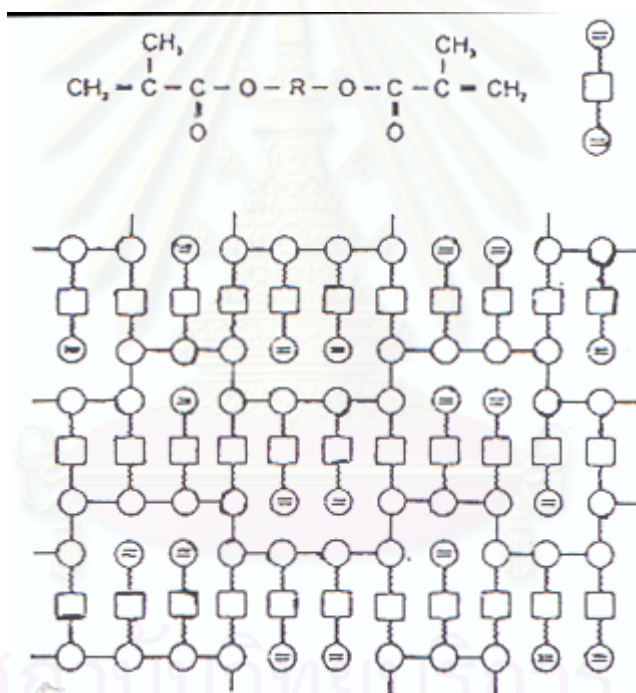


Fig.3 Simplified representation of a three-dimensional dimethacrylate network having 70% conversion of the methacrylate double bonds to crosslinks. (⊖) = unreacted carbon-carbon double bonds; (-) = carbon-carbon single bonds.

The presence of unreacted monomer or unreacted carbon-carbon double bonds has a plasticizing effect on the polymer. Thus, in contrast to resin composites of differing monomer systems, the physical properties of a given system are correlated with the degree of conversion.

Thus, to this day the majority of commercial resin composites contain a monomer system based on BisGMA or variations thereof. This fact may indicate that for several years following the development of BisGMA, other components of resin composites than the monomer system were more in need of optimization. However, recent research in the field of dental monomers has produced several results which may be expected to appear in commercial resin composites in the near future.

(2) UDMA resins

A group of monomers which has found commercial use are the urethane dimethacrylates. The first type of urethane dimethacrylate to appear was synthesized from hydroxyalkyl methacrylates and diisocyanates [16]. These monomers have molecular weights nearly equal to that of BisGMA, but are less viscous. The most commonly used monomer of this type, UDMA, is the reaction product of 2-hydroxyethyl methacrylate and 2,4,4-trimethylhexamethylenediisocyanate (Fig.4.). This monomer has been used alone or in combination with other monomers, e.g., BisGMA and TEGDMA.

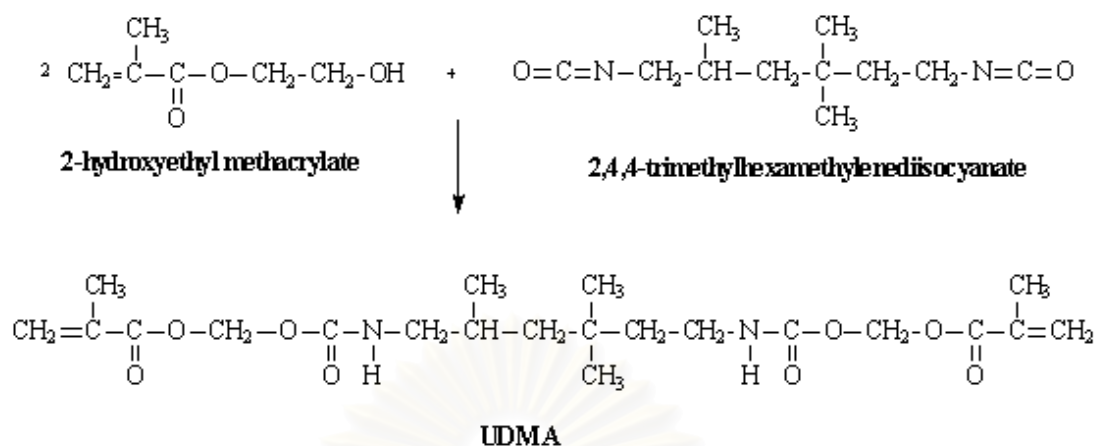


Fig.4. Synthesis of UDMA from 2-hydroxyethyl methacrylate and 2,4,4-trimethylhexamethylene-diisocyanate.

The advantages of UDMA have been reported to be the lower viscosity (approximately 11,000 mPa.s at 23 °C) and a greater flexibility of the urethane linkage, which may improve toughness [17]. However, a general difference between resin composites based on UDMA and conventional BisGMA-based resin composites is very difficult to deduce from existing in vitro and in vivo studies. One reason for this difficulty is that actual differences caused by dissimilar monomer systems are camouflaged by the fact that the materials differ in many other aspects, e.g., type and amount of filler, type and amount of initiators, and quality of silanization of the filler particles, the effect of which may be more determinative for the properties. This, however, does not imply that the choice of monomer system is insignificant. The results of in vitro studies, in which all other components than the monomer system were kept constant, indicate the resin composites based on UDMA will have improved mechanical properties compared with resin composites based on BisGMA [17-20]. Also, there are indications that higher degrees of conversion are obtainable with urethane dimethacrylates as compared with BisGMA:TEGDMA mixtures [17]. All other things being equal, this would result in improved biocompatibility of the resin composite. Fewer pendant methacrylate groups and less residual monomer may be oxidized to formaldehyde or methacrylic acid.

Furthermore, by use of urethane dimethacrylates, the risk of bisphenol A formation is nonexistent.

2.1.2 Adhesive monomers

The polymerization shrinkage of resin composites often leads to marginal gap formation, allowing for the passage of bacteria, fluids, molecules or ions between the restoration and the cavity wall [21]. This microleakage seems to predispose to secondary caries, marginal discoloration, and pulpal damage, reducing the longevity of the restoration [22]. Therefore, the capability of establishing a strong and permanent bond to both enamel and dentin is a highly desirable property of a resin composite. Besides preventing marginal gap formation and its resulting problems, effective adhesion renders the removal of healthy dentin for retentive undercuts unnecessary and extends esthetic treatment options.

In 1955, Buonocore [23] introduced the so-called acid-etch technique enabling resin composites to be bonded to enamel. Resin penetrates microporosities created in the enamel surface by phosphoric acid treatment and, after polymerization, is durably and reliably attached to the enamel by micromechanical retention. There are many instances, however, in which it would be very beneficial to bond to dentin, including the restoration of teeth with deep coronal caries, root caries, and fractures involving dentin. Dentin is fundamentally a much more difficult tissue to bond to than enamel, and the problem of dentin adhesion has been a formidable challenge. Unlike enamel, which is largely inert, dentin is a living tissue composed mostly of hydrophilic calcium phosphate crystals and collagen, with a significant amount of water. In spite of the presence of hydroxyl groups, monomers like BisGMA or UDMA are insufficiently hydrophilic to compete with water for interaction with tooth structures. Consequently, a coupling agent is needed for bonding resin composite to dentin. In short, effective coupling agents contain hydrophilic as well as hydrophobic groups in order to enable them to compete with water for penetration and infiltration into dentin and to copolymerize with dental monomers. Fig.5 shows the structural principle of the bifunctional molecules which have been investigated for use as

coupling agents [24]. Through an intermediate group R, the hydrophobic methacrylate group M is linked to the hydrophilic, reactive group X.

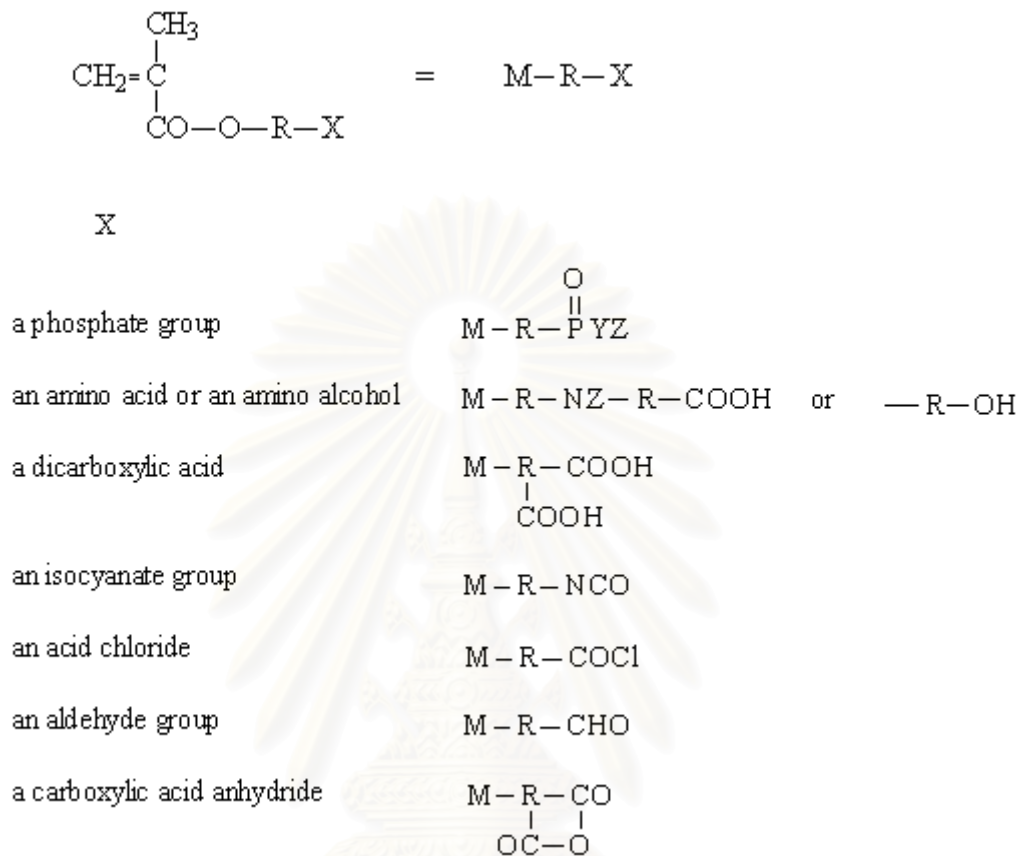


Fig.5. Schematic representations of methacrylate based coupling agents. M = a methacrylate group; R = an intermediate group; X = a group capable of promoting a bond dentin.

Recently, the 4-methacryloyloxyethyl trimellitate anhydride (4-META) is one of the bonding agents which is widely used in dental composites. 4-META has a carboxylic group as chelating agents which should be particularly effective in promoting adsorption and adhesion to cationic tooth surfaces composed of hydroxyapatite. Because of satisfied results in several researches, the dental composites which consisted of 4-META have been capitalized until now. The chemical structure of 4-META is shown in Fig.6.

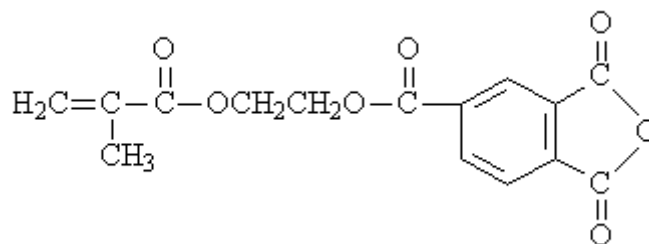


Fig. 6. The chemical structure of 4-META

For nearly 30 years, dentin bonding was believed to be the result of a chemical reaction between the coupling agent and either the inorganic or the organic constituents of dentin. Recently, another mechanism of dentin bonding was recognized, and today dentin bonding is thought to be primarily the result of micromechanical retention due to the formation of a hybrid layer of polymerized resin infiltrated in a subsurface dentin zone [25]. This better understanding of the mechanisms of action in dentin bonding will no doubt lead to improved commercial products extending the longevity of resin composite restorations bonded to dentin. Obtaining such improvements would be greatly facilitated by the concurrent development of resin composites which demonstrate reduced polymerization shrinkage.

2.1.3 Filler

Incorporation of filler particles into a resin matrix significantly improves the properties of the matrix material if the filler particles are well bonded to the matrix. If not, the filler particles can weaken the material. Because of the importance of well-bonded filler particles, it is obvious that the use of a filler coupling agent is extremely important to the success of a composite. Traditional inorganic filler particles are commonly produced by grinding or milling quartz or glasses to produce particles ranging in size from 8 to 25 μm .

2.2 Degree of Conversion

The degree of conversion is a measure of the percentage of consumed carbon double bonds (Fig.7).

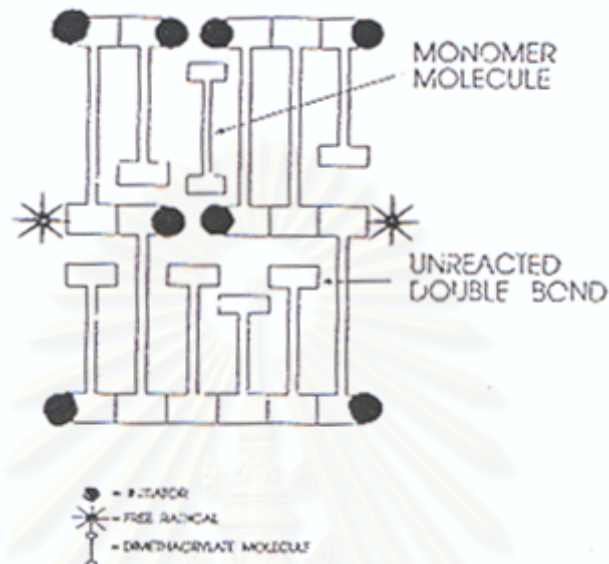


Fig. 7. Degree of conversion reflects the percentage of consumed methacrylate double bonds. [26]

The figure shows that a dimethacrylate monomer molecule can have one or two unreacted groups. If one group has reacted, the molecule is bonded to the polymer network and will not be released from the polymer as the completely unreacted monomer molecule. In other words, a conversion degree of 50% to 60%, which is typical of BisGMA-based composites, implies that 50% to 60% of the methacrylate groups have polymerized. This does not imply that 40% to 50% of the monomer molecules are left in the resin, because one of the two methacrylate groups per dimethacrylate molecule may have reacted and be covalently bonded to the polymer structure. Conversion of the monomer to polymer is dependent on several factors, such as the resin composition, the transmission of light through the material, and the amount of activator initiator and inhibitor that is present. Transmission of light through the material is controlled by absorption and scattering of the light by filler particles and by any tooth structure interposed between the light source and composite.

2.2.1 High – conversion, High – strength monomer systems

As mentioned previously, a large number of methacrylate groups of the dimethacrylate monomers in most resin composites are left unreacted in the crosslinked polymer. As the presence of significant residual unsaturation impairs the physical, mechanical, and chemical properties, new monomer systems with a potential for better conversion have been requested [13]. However, high conversion is not a goal in itself. For instance, increasing the content of TEGDMA in a BisGMA:TEGDMA comonomer will increase conversion, leave hardness unaffected [27], but at the same time make the material very brittle and prone to fracture. Also, the degree of conversion of dimethacrylates may be very high if the distance between the methacrylate groups is long, i.e., the molecular weight is high. However, if the monomer is very flexible and not sufficiently bulky, mechanical properties will be poor. The task, therefore, is to develop high conversion resin system while not impairing mechanical properties.

In an attempt to develop a mechanically stronger and hopefully more wear and fracture resistant resin composite, Peutzfeldt & Asmussen [28] proposed that the degree of crosslinking in the polymer matrix could be increased by the addition of carboxylic anhydride to convert monomer mixtures. It was hypothesized that a cyclic anhydride could react with a hydroxyl group pendant in BisGMA, or with an amino group present in UDMA or methacrylamide. The hydroxyl group of the carboxylic acid formed following ring opening of the cyclic anhydride could then react with a second mole of alcohol or amide and result in a crosslinking of two polymer chains (Fig.8).

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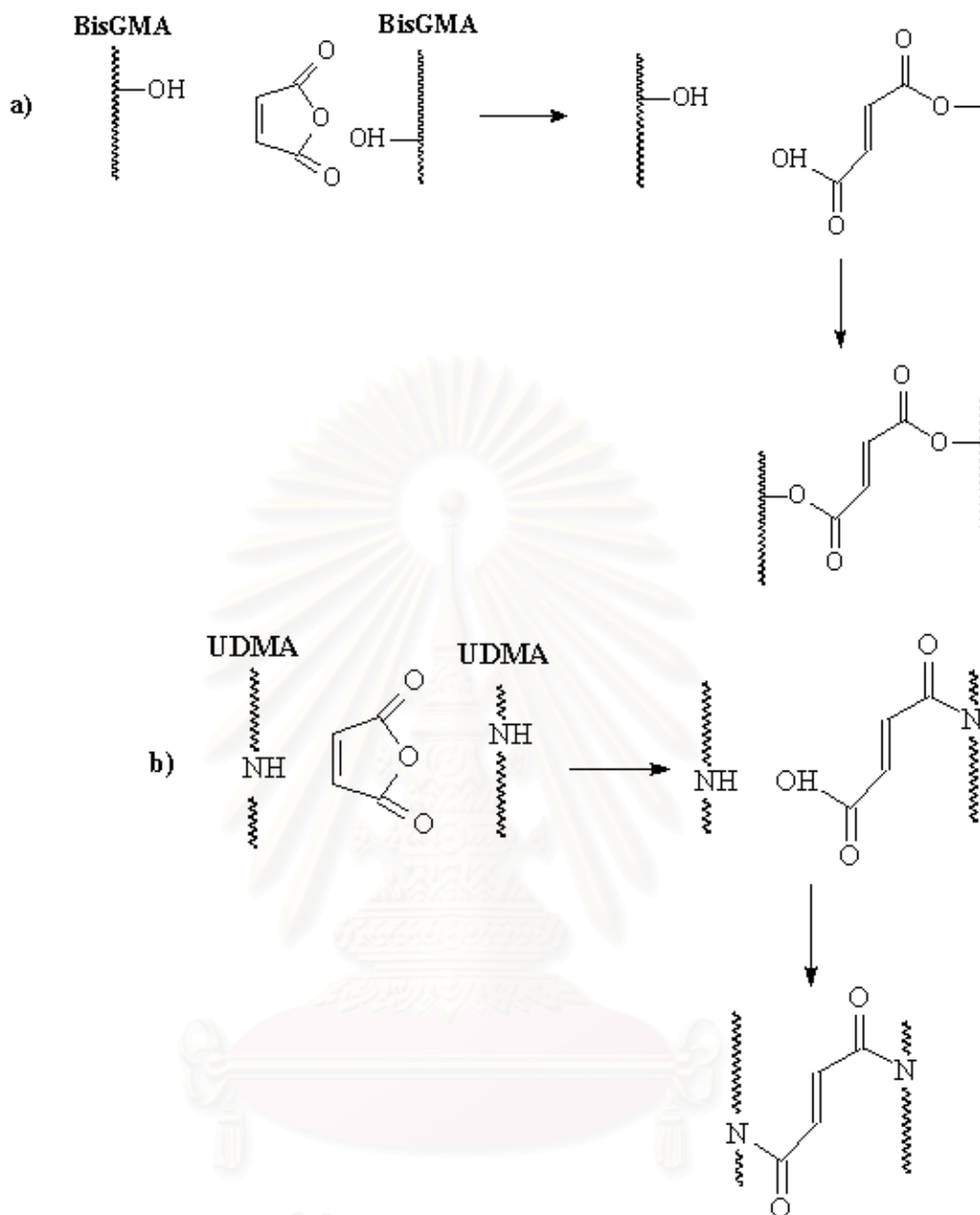


Fig. 8. Hypothesized reaction mechanisms of maleic anhydride with pendant or backbone functional groups in a polymer. (a) Maleic anhydride reacts with two hydroxyl groups stemming from, e.g. BisGMA. A crosslink is formed by ester linkages. (b) Maleic anhydride reacts with two backbone amino groups stemming from, e.g. UDMA. A crosslink is formed by imide linkages. [15]

Theoretically, the second reaction will only take place at elevated temperatures, limiting the use of the anhydride concept to the inlay technique. When testing this hypothesis on experimental resin composites, the addition of cyclic carboxylic anhydrides was found to increase mechanical properties significantly. Most pronounced effects of anhydride addition were measured for resin composites based on UDMA, as compared with materials based on BisGMA and TEGDMA and for materials also containing methacrylamide. Such materials resulted in a 20% increase in strength and stiffness [28]. The results may be interpreted as a corroboration of the crosslinking reaction (b) in Fig.8, but the exact reaction mechanism still needs to be confirmed. Experiments directed to optimize the post-curing conditions of resin composites containing carboxylic anhydrides indicated that a 1-h heat-treatment at 150°C was preferable [29,30].

Several researchers [33-35] found that the addition of crosslinking agents has also affected the mechanical properties of resin composite filling materials. However, it was concluded that the enhancements in mechanical properties were probably reflected by an increased conversion of double bonds rather than a crosslinking of other functional groups.

2.3. Metal-resin composites

Metal resin composites were discovered after Ogura and Honda [2] found that metal particles could be used as the filler in the polymerization of UDMA monomer at room temperature in the presence of 4-META as coupling reagent, benzoyl peroxide (BPO) as radical initiator, and *N,N*-dimethyl-*p*-toluidine (DMPT) as accelerator. These phenomena showed that metal particles could be used instead of the inorganic filler in the dental composite system. This initiation system can be advantageous for metal-resin composite restorative materials. When metal particles and 4-META are involved in the initiation reaction, a stronger bond between metal particles and resin matrix may be expected.

There were several studies about properties of metal-resin composites in the last 2 years. [4,6-10]. The composites using Ag/Sn alloy spherical particles as the filler gave acceptable mechanical and physical properties in the studies of Katkuta *et. al* [6] and Urapepon *et.al.*[7-9]. They have worked to develop metal-resin composite restorative materials using silver alloy particles as filler. In their studies, an ordinary redox initiation system consisting of BPO and tertiary amine was used; therefore, the polymer chain propagation basically would have started independently from the metal surface, and 4-META should have functioned only as a coupling agent between the alloy particles and the resin matrix. Similarly, filler particles including usual inorganic fillers in dental resin composite materials have not been involved in the initiation reaction of the resin matrix.

Katkuta *et. al.* (1999) imitated the study of metal resin composite with the ordinary 2-paste composite system. The amalgam alloy particles (Ag/Sn/Cu alloy) were used as the filler. These particles were treated with 4-META acetone solution, then heated to 80 °C. The treated particles were mixed in 2 different pastes of UDMA/TEGDMA monomer containing either BPO or DMPT. The maximum flexural strength of composites was observed about 61 MPa after 2 different pastes were mixed.

Urapepon *et. al.* (1999) studied the flexural strength of 2-paste composite of Ag/Sn resin composite by using Ag/Sn particles treated with acid and heat. They found that the surface treatment of filler could affect on mechanical properties of metal resin composites. The flexural strength of composites increased when using the atomized particles that treated with acid or acid and heat treatment at 150 °C, but then significantly decreased at the heat treatment temperature increased to 200 °C and 250 °C. The flexural strength of composite that used the atomized particles treated with acid or acid and heat treatment at 150 °C was significantly higher than those of other composites, and exceeded that (about 60 MPa) of the previous composite with no treatment. [7]

Later, Urapepon and Ogura (2000) improved the flexural strength of the Ag/Sn composite by conversion of 2-paste composite system to the powder-liquid system. They found that the flexural strength of the powder-liquid composite was improved to 91.8 MPa, which was higher than that of the 2-paste composite (64.0 MPa) by about 43.0%. This was

achieved when using the condition in preparing metal particles at a 0.1 ratio of 4-META concentration, 30s immersion time and 94% filler content. These results indicate that the powder-liquid system is effective for improving the properties of the metal-resin composites [8].

Recently, Urapepon *et al.*(2000) found that the flexural strength of the irregular particle metal-resin composites was slightly improved when compared with the spherical particle metal-resin composites. The highest flexural strength (97.6 MPa) was obtained from < 20 micrometers particle size at 94% filler content.[9]

In 2000, Miyagawa *et al.* [3] reported that several kinds of metal particles, i.e., Cu, Zn, Mo, Sn, Co, In, and alloy of silver (Ag/Cu, Ag/Sn, Ag/In), could initiate the polymerization of UDMA-based monomer at room temperature in combination with BPO and 4-META in the absence of tertiary amine. However, some kinds of metal such as Ag, Al, Cr, Ni, Ti and Zr particles could not induce the polymerization in this condition. Among the pure metal particles studied, Cu particles apparently showed the highest ability to induce the setting. All the three kinds of silver alloy particles examined (72% Ag/Cu, 73.2% Ag/Sn and 75% Ag/In) also had this ability, although pure silver metal particles could not induce the setting. Furthermore, they could observe the phenomena of copper-resin composite. They found that the presence of 4-META drastically shortened the setting time of the mixture of Cu particles and the monomer containing BPO, while higher concentration of BPO in the monomer significantly shortened the setting time. Moreover, this research found that amine (DMPT), which may cause the discoloration of the dental restorative material, could be eliminated from the components of dental restorative resins.

This recovery stated that the activity of metal-particles in polymerization reaction of resin composite was different from inorganic filler.

In support of this assumption, the later study of Wanichacheva *et.al.*(2000) reported that zinc-resin composite, which zinc particle was used as the filler, could eliminate BPO, which is well-known for the cause of the cancer and allergy [5], from the composites system. The zinc particles moistened with a small amount of water could induce the initiation step of polymerization of UDMA-based monomer containing 4-META

in the absence of BPO and tertiary amine. The concentration of 4-META and BPO influenced the setting phenomenon. Higher concentrations of 4-META up to 6% accelerated the setting reaction, and the presence of BPO generally retarded the setting reaction although its effect was dependent on the 4-META concentration. Moreover, they found that zinc ions could affect the setting phenomenon. The zinc particles mixed with a small amount of 10% ZnSO₄ or 10% acetic acid instead of water could induce the initiation step of polymerization of UDMA-based monomer containing BPO even in the absence of the amine activator and 4-META. However, higher amounts of zinc ions tended to retard the setting reaction in the presence of 4-META [4].

There were several studies about degree of conversion (DC) of metal-resin composites in the last 2 years [4-5].

The DC of metal-resin composites using zinc particles [4] and Ag/Cu alloy particles[10] was reported to be higher than the dental composites using inorganic filler. Since DC was the parameter relating physical properties of dental resins, the higher DC could be expected to improve the properties of this material [1,11,13].

All of these studies have suggested that the metals in metal-resin composites could provide the interesting phenomena and involve in the improvement of properties that may rectify the shortcomings of the resin composites.

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CHAPTER III EXPERIMENTS

3.1 Chemicals and Materials

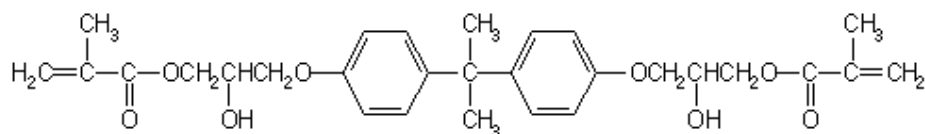
Chemicals and materials used in this study are listed in Table 1 and some of chemical structures were shown in Fig. 9.

Table 1. Materials used in this study

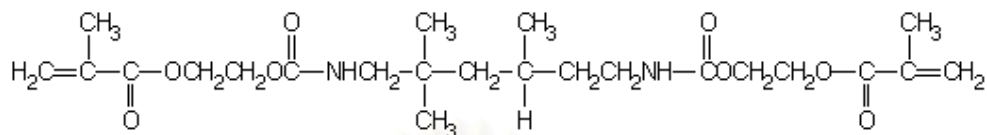
Materials	Abbreviation	Batch No.	Supplier
Zinc particles	Zn	M6P4469	Nacalai Tesque, Kyoto, Japan
Silver particles	Ag	M6A8306	Nacalai Tesque, Kyoto, Japan
Copper particles	Cu	K21185003 603	Nacalai Tesque, Kyoto, Japan
Zirconium particles	Zr	M5R1353	Nacalai Tesque, Kyoto, Japan
Molybdenum particles	Mo	M6 P4469	Nacalai Tesque, Kyoto, Japan
4-(2-Methacryloyloxyethoxycarbonyl) phthalic anhydride	4-META	T 1001	Sun Medical, Osaka, Japan
1,6-Bis(methacryloyloxy-2-ethoxy carbonyl-amino)-2,4,4(2,2,4)-trimethylhexane	UDMA	050186	Negami Kogyo, Negami, Japan
Bisphenol glycidyl methacrylate	Bis-GMA	0901H	Shin Nakamura Kagaku Kogyo, Osaka, Japan
Triethylene glycol dimethacrylate	TEGDMA	FGA01	Shin Nakamura Kagaku Kogyo, Osaka, Japan
Benzoyl peroxide	BPO	M6 K9289	Sanken Kakou, Osaka, Japan

3.2 Instruments and Analytical Methods

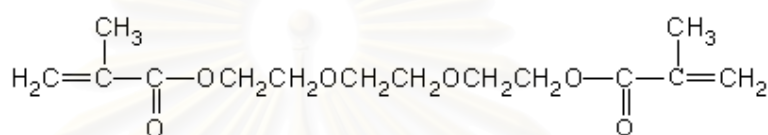
3.2.1 Thermocouple apparatus: An apparatus for determination the setting time using a method described in ISO 4049: 1988 (Dentistry--Resin-based filling materials) [36] is shown in Figure 10.



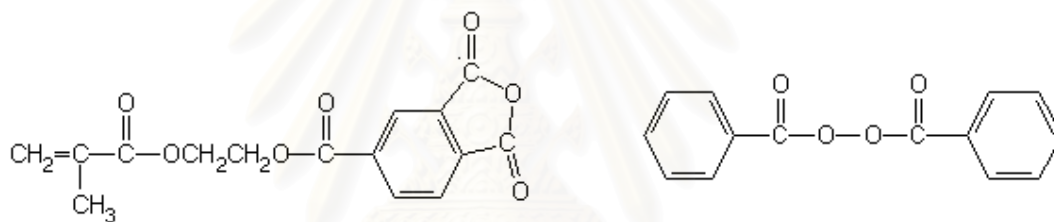
Bisphenol glycidyl methacrylate (Bis-GMA)



Urethane dimethacrylate (UDMA)



Triethylene glycol dimethacrylate (TEGDMA)

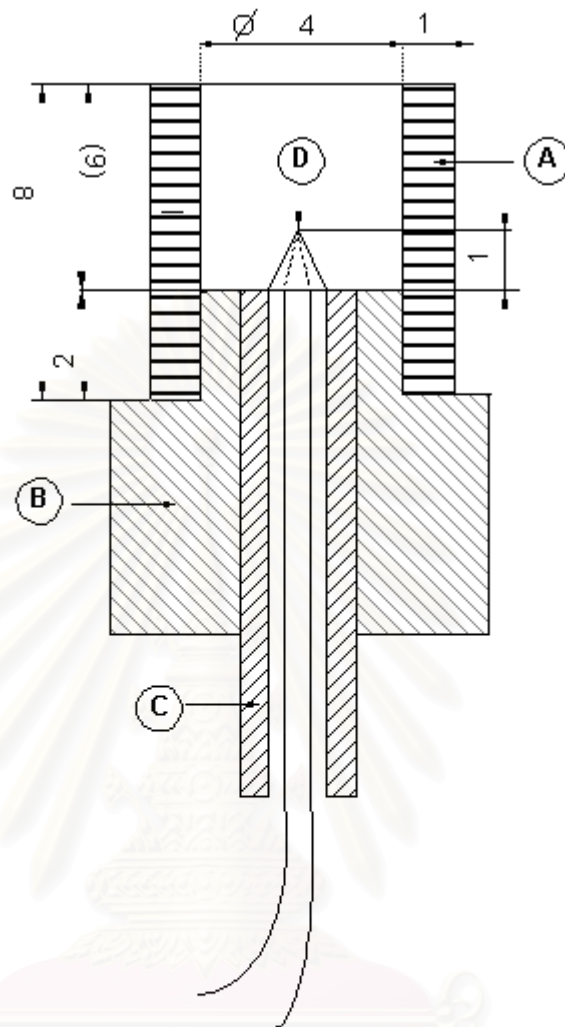


4-methacryloxyethyl trimellitate anhydride (4-META) Benzoyl peroxide (BPO)

Fig. 9. Structure of chemicals used in this study

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Dimensions in millimeters



- (A) Polyethylene
- (B) Polyamide block
- (C) Stainless steel tube
- (D) Thermocouple-cone of solder

NOTE - Dimensional tolerances shall be ± 0.2 mm

Fig. 10. Apparatus for determination of setting times

The apparatus consists of a piece of polyethylene (or similar material) tubing, A, located on a block of polyamide or similar material, B, which has a hole into which is inserted a stainless steel tube, C, containing a stabilized thermocouple D.

The tube A is 8 mm long, 4 mm in internal diameter and has a wall thickness of 1 mm. The locating part of block B is 4 mm in diameter and 2 mm high. When assembled the two components form a specimen well 6 mm high x 4 mm in diameter. In order to facilitate removal of the specimen after testing, the thermocouple D has a conical tip which protrudes 1 mm into the base of the specimen well. The tolerances on the above-mentioned dimensions are ± 0.2 mm.

The thermocouple consists of wires (0.2 ± 0.05) mm in diameter, made of a material (e.g. copper/constantan) capable of registering temperature changes in a specimen of setting material to an accuracy of 0.1°C . The thermocouple is connected to an instrument (e.g. voltmeter or chart recorder) capable of recording the temperature to that accuracy.

Procedure for determination the setting time: Prepare the testing sample and start timing from the moment mixing is begun. Maintain the mould at $(23 \pm 1)^{\circ}\text{C}$ and, 30 s after the start of mixing, place the mixed material in the mould and record the temperature, t_1 of the material. Maintain the apparatus at $(23 \pm 1)^{\circ}\text{C}$ and continuously record the temperature of the material. The temperature change of the specimen was recorded on a chart, and the setting time was determined from the time at the start of mixing until the maximum temperature was reached. A typical recording trace is shown in fig.11.

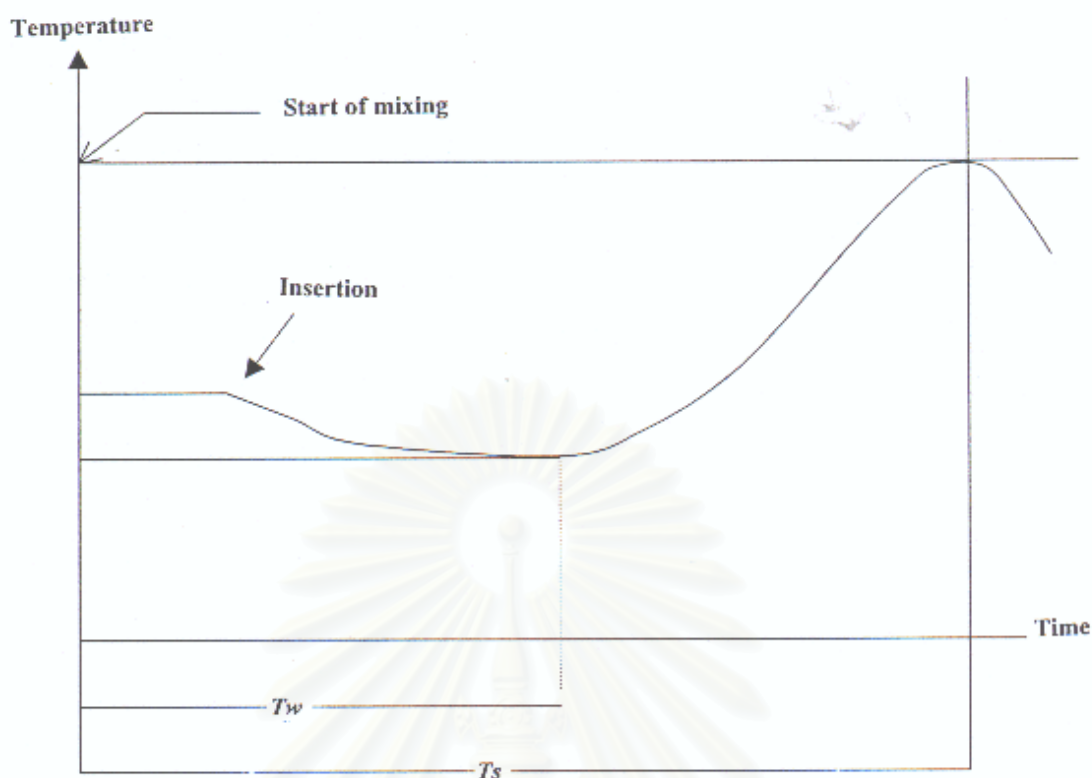


Fig. 11. Method for determining setting time

3.2.2 Fourier Transform Infrared Spectrometer (FT-IR)

The FT-IR spectra were recorded by means of a FT-IR spectrometer (FT/IR – 620, Jasco corp., Tokyo, Japan). Since the set samples used for FT-IR measurement contain 70 mass % of metal, the simple infrared transmission method could not give good spectrum. In order to determine the degree of conversion (DC), the diffuse reflectance (DR) sampling method was used because the solid samples in the form of powders gave mainly diffuse reflection.

Procedure to determine the DC: After having been ground using a mortar, the set samples were dried in a desiccator. Six different experimental monomers and the ground set samples were mixed with ground potassium bromide (KBr) at a ratio of 0.02g:0.48g and 0.07g:0.43g, respectively, for the control of the same amount of organic compositions. Spectra of the monomers and set samples were obtained under vacuum immediately after mixing with KBr using the FT-IR spectrometer. The diffuse reflectance

(DR) technique was used, and Kubelka-Munk function was applied to correct the absorbance for the quantitative analysis. The calculation of DC will be explained in next section.

3.3 METHODS

The experiment was divided into three parts as follows:

- 1) effect of metal types and organic composition on the setting time,
- 2) effect of based-monomer types and 4-META concentrations on the setting time , and
- 3) determination of the degree of conversion using FT-IR measurement.

1) Effect of metal types and organic composition on the setting time.

Four kinds of experimental monomers were prepared by dissolving various compositions of additive monomer in UDMA-based monomer consisting of 75% mass% UDMA and 25% mass% TEGDMA with a trace amount of inhibitor, i.e., UDMA-based monomer with TEGDMA, UDMA-based monomer with TEGDMA and 1% BPO, UDMA-based monomer with TEGDMA and 2% 4-META, UDMA-based monomer with TEGDMA, 1%BPO and 2% 4-META. The polymerization of several kinds of metal (Cu, Zn, Mo, Ag, Zr) was observed. After 0.03 g. of deionized water was added, 0.35 g. of each kind of metal was mixed with 0.15 g. of each of the experimental monomers in a ceramic dish. Twenty mixed samples were observed for the setting phenomena 10 min, 1 hour, 1 day, 1 week and 1 month after the start of mixing.

2) Effect of based-monomer types and 4-META concentrations on the setting time

Eight kinds of experimental monomers were prepared by dissolving various amounts of 4-META in two different types of based monomers, BisGMA-based monomer and UDMA-based monomer. The based-monomer included 1 mass% benzoyl peroxide (BPO) and a trace amount of inhibitor. Four different concentrations of 4-META (0, 1.5, 3 and 4.5 mass%) were examined. After 0.02 g of pure water was added, 0.35 g of molybdenum particles (average particle size: 3 μm , purity: extra pure reagent) was mixed

with 0.15 g of each of the experimental monomers in a ceramic dish. Three replications were made randomly for eight different experimental conditions. The data of the setting time were analyzed using two-way ANOVA for the factors of based-monomer type and 4-META concentration. In addition, the mean values were compared using Duncan's multiple range test following one-way ANOVA, respectively.

3) *Determination of the degree of conversion using FT-IR measurement*

Six different experimental monomers were prepared by dissolving various amounts of 4-META (0, 1.5, 4.5 mass%) in two different types of based monomers, BisGMA-based monomer and UDMA-based monomer. The based-monomer included 1 mass% benzoyl peroxide (BPO) and a trace amount of inhibitor. After 0.02 g of pure water was added, 0.35 g of molybdenum particles (average particle size: 3 μm , purity: extra pure reagent) was mixed with 0.15 g of each of the experimental monomers in a ceramic dish, then the samples were left to set in the ceramic dish. Three different set samples in 0, 1.5 and 4.5 mass% concentrations of 4-META were examined for DC comparing with monomers.

To calculate DC of monomer mixtures based on the non-aromatic monomers (UDMA and TEGDMA), we used the absorption bands at 1717 cm^{-1} of the C=O band as the reference band. On the other hand, we used the absorption bands at 1717 cm^{-1} of the C=O band and 1617 cm^{-1} of the C=C aromatic band as the reference bands for the monomer mixtures based on the aromatic monomers (BisGMA). DC was obtained as follows: From the spectrum of a monomer, the absorbance of the C=C band at 1637 cm^{-1} ($^M A_{\text{db}}$), the absorbance of the C=O band at 1717 cm^{-1} ($^M A_{1717}$), and the absorbance of the C=C band at 1617 cm^{-1} ($^M A_{1617}$) were determined by the area under curve by the base line method. Likewise, from the spectrum of the resulting polymer (set sample), the absorbance $^P A_{\text{db}}$, $^P A_{1717}$, and $^P A_{1617}$ at the same frequencies as the monomer were determined. DC for each reference band was estimated using one of the following equations:

$$\begin{aligned} \text{DC}_{1717}(\%) &= 100 \{1 - (^P A_{\text{db}} / ^M A_{\text{db}}) \times (^M A_{1717} / ^P A_{1717})\} \text{ and} \\ \text{DC}_{1617}(\%) &= 100 \{1 - (^P A_{\text{db}} / ^M A_{\text{db}}) \times (^M A_{1617} / ^P A_{1617})\}. \end{aligned}$$

The mean value of DC_{1717} and DC_{1617} , was used to analyze the data for BisGMA based monomer. All experiments were carried out in triplicate. The DC of the samples was analyzed using two-way ANOVA for the factors of based-monomer type and 4-META concentration. In addition, the mean values were compared using Duncan's multiple range test following one-way ANOVA, respectively.



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CHAPTER IV

RESULTS AND DISCUSSION

The results of the observation of setting phenomena using different metal particles and different monomer composition are shown in Table 2.

Table 2. The setting time of five different metal resin composites after changing organic composition.

Metal filler	Cu	Zn	Mo	Ag	Zr
Organic composition					
UDMA	> 1 month	< 1 day	> 1 month	> 1 month	> 1 month
1%BPO in UDMA	< 10 min	< 1 day	< 1 hour	< 1 week (do not set well)	> 1 month
2% 4-META in UDMA	> 1 month	< 1 hour	> 1 month	> 1 month	> 1 month
1% BPO, 2%4-META in UDMA	< 10 min	< 10 min	< 1 hour	> 1 month	> 1 month

The results showed that copper (Cu) and molybdenum (Mo) particles could induce the polymerization of resin composites containing 1%BPO in UDMA and 1% BPO, 2%4-META in UDMA. However, in the conditions that do not contain BPO initiator (UDMA condition and 2% 4-META in UDMA condition), copper and molybdenum particles could not induce the polymerization of resin composites. Both silver (Ag) and zirconium (Zr) could not induce the polymerization of all conditions in this experiment. Some of these results were agreed with the previous study of Miyagawa *et.al.* [3] which reported that several kinds of metal particles, i.e., copper (Cu), zinc (Zn), molybdenum (Mo), tin (Sn), cobalt (Co), indium

(In), and alloy of silver (Ag/Cu, Ag/Sn, Ag/In) could initiate the polymerization of UDMA-based monomer at room temperature in combination with BPO and 4-META in the absence of tertiary amine. On the contrary, some kinds of metal such as silver (Ag), aluminium (Al), chromium (Cr), nickel (Ni), titanium (Ti) and zirconium (Zr) particles could not induce the polymerization in this condition. However, it was further shown in the present study that pure silver and zirconium could not induce the polymerization of UDMA in every condition. Moreover, it was further shown in the present study that molybdenum (Mo) particles could induce the polymerization of resin composite in the absence of coupling reagent although copper (Cu) particles had been reported for this kind of activity in the previous work [3]. However, the setting of copper-resin composite was too quick to observe for the phenomena and to be used as a restorative material.

Zinc (Zn) particles could give the different activities among other metals. Similar to the previous study [4], zinc could initiate the polymerization of UDMA-based monomer in the absence of peroxides. However, it was further shown in the present study that zinc could not induce the polymerization in the absence of 4-META.

From the observation data in the first part, due to the suitable setting time and the activity to set without coupling reagent, we will select molybdenum particles to study for the effect of based-monomer types (BisGMA and UDMA) and 4-META concentrations on the setting time and degree of conversion of metal resin composite. The results of molybdenum resin composite will be explained in next section.

Effect of based-monomer types and 4-META concentrations on the setting time

The mean values and standard deviations of the setting time for different types of based monomers and 4-META concentrations are shown in Table 3. The mean setting time ranged from 6.58 min (3% 4-META in BisGMA based monomer) to 30.30 min (3% 4-META in UDMA-based monomer).

Table 3. Effect of monomer types and 4-META concentrations on the setting time (min).

Monomer	4-META concentration (%)			
	0	1.5	3	4.5
Bis-GMA	6.58 (0.24)	11.30 (1.73)	11.30 (1.98)	10.28 (1.04)
UDMA	26.79 (1.69)	28.49 (1.42)	30.30 (2.21)	28.88 (2.02)

standard deviation in parentheses

As clearly shown in Fig.12, the addition of 4-META generally retarded the setting reaction for both BisGMA based monomer and UDMA-based monomer.

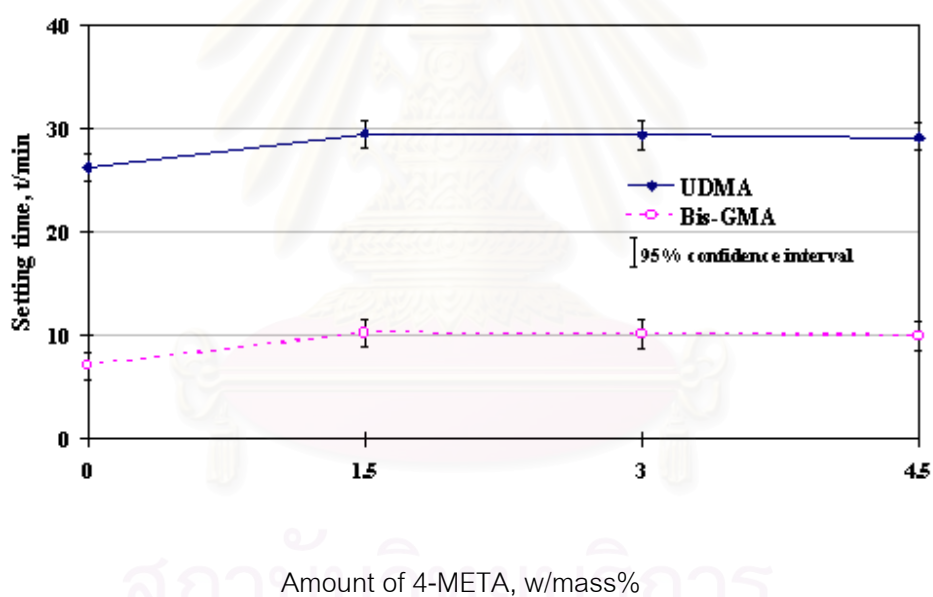


Fig. 12. Effect of monomer types and 4-META concentrations on the setting time (min)

In the condition when 4-META was absent and present, Duncan's multiple range test indicated that the reactivity BisGMA based monomers was greater than UDMA-based monomer. Two-way ANOVA (Table 4) showed that both of the two main factors of these factors influenced the setting time very significantly ($p < 0.01$).

Table 4. Results of two way ANOVA for the setting time : Effect of monomer types and 4-META concentrations

Factors	df	Sum of square	Mean squares	F value	P value
MONOMER	1	2969.89	2969.89	1086.40	0.000
4-META	3	56.66	18.89	6.909	0.002
MONOMER x 4-META	3	17.79	5.93	2.169	0.118
Error	24	65.61	2.73		
Total	31	3109.95			

It is well-known that metal ions such as Fe^{2+} , Cr^{3+} , V^{3+} , Ti^{3+} , Co^{2+} , and Cu^{+} in emulsion or aqueous systems can be used in redox initiation when they are combined with peroxides [37]. The previous studies [3,4,10] reported that after mixing with a small amount of water several kinds of metals, Cu, Zn, Mo, Sn, Co, In and silver alloy particles, could induce polymerization of UDMA monomer in the presence of peroxides (BPO). It was further shown in the present study that molybdenum particles could induce initiation step of polymerization not only of UDMA monomer but also of Bis-GMA monomer. Molybdenum, one of the transition metals, has six valence electrons and free d-orbitals on the center atom. Therefore, molybdenum could act as weak acid bonding with base positions, nitrogen and oxygen atom, on based-monomer and coupling reagent. The proposed of complex formation of molybdenum atom and heteroatoms as ligands is shown in Fig.13.

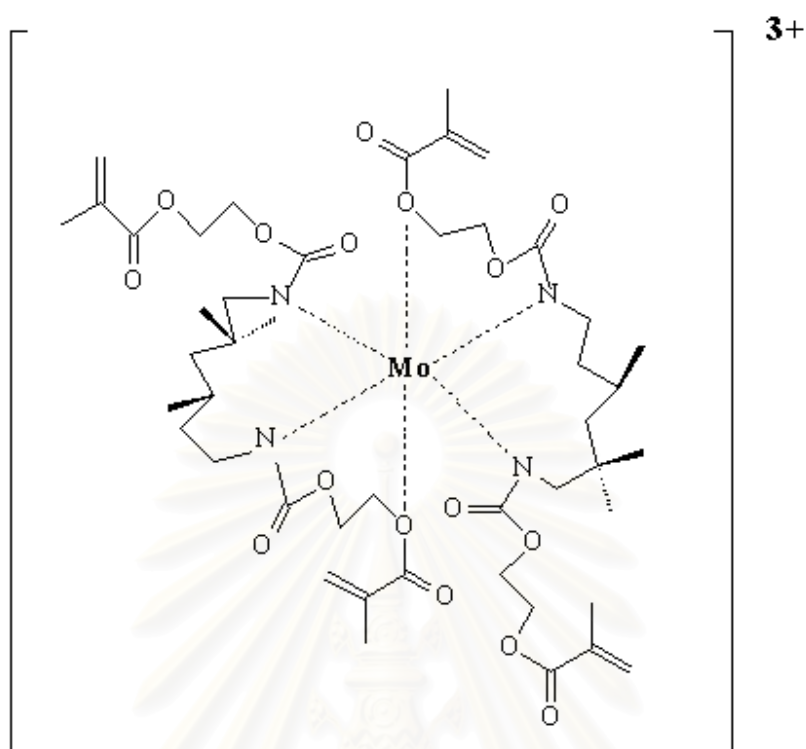


Fig. 13. Proposed hexagonal coordinate covalent bond between organic composition and molybdenum atom.

Moreover, the SEM observation in the previous studies [6-9] showing excellent bond among metal surface, monomer and coupling reagent might be explained by this assumption as well. However, the inducement of molybdenum particles for the initiation reaction in this study also agrees with a previous study [38] that molybdenum compound could initiate the polymerization of 1,7,7-trimethylbicyclo[2.2.1]hept-2-ene. The crosslinking mechanism of UDMA, 4-META with metal has been proposed in Fig.14.

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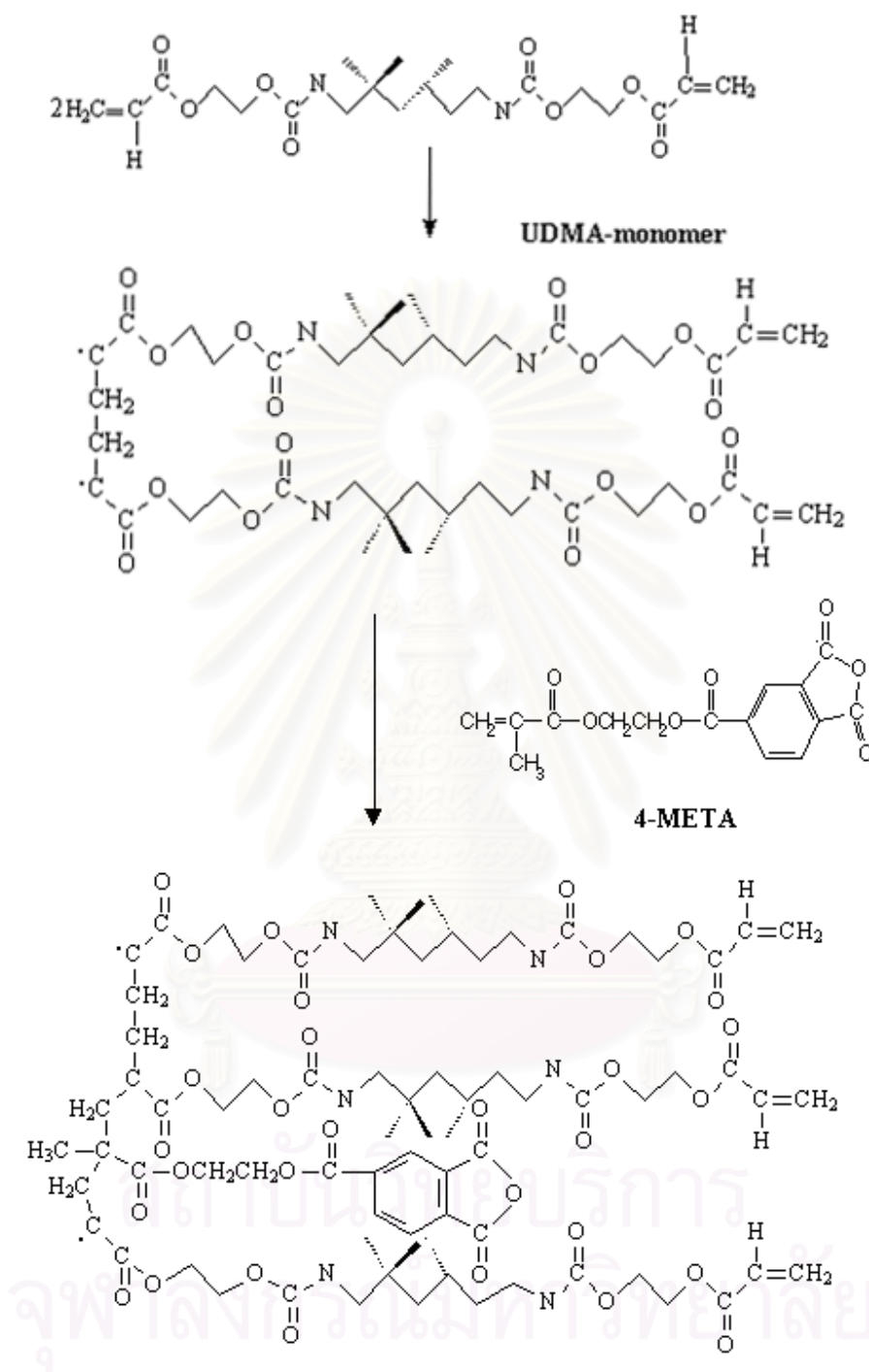


Fig.14. Proposed crosslinking mechanism of UDMA and 4-META

Molybdenum particles could be activated when a small amount of water was added. As aforementioned, water may activate the molybdenum surface to become the electrophilic position with subsequent breaking of BPO to radical. However, a different setting phenomenon was observed after using BisGMA monomer and UDMA monomer. The setting time of materials after mixing with BisGMA monomer were obviously faster than those mixing with UDMA-monomer. Since the monomers which are used in composites have not changed significantly within the last 20 years, and still belong to the class of the so-called high molecular weight dimethacrylates, BisGMA and UDMA monomers. These two monomers exhibit very good physical and chemical properties, very good longevity in the oral cavity, low polymerization shrinkage (approx. 5 to 6 percent by volume), and acceptable biocompatibility. However, there were no studies which investigated the obvious setting time between BisGMA and UDMA monomers when the same amount of metal components in composites was used. The results in this present study confirmed that monomer type of based-monomer played the important role in setting phenomena of metal–resin composite. This different phenomena may be explained by using chemical reactivity of functional groups on the monomers. BisGMA monomer has 2 aromatic rings and 8 atoms of oxygen while UDMA monomer has 2 atoms of nitrogen and 8 atoms of oxygen. The π -electrons on aromatic ring having no steric effect may be more reactive to the free orbitals of molybdenum atom than the lone pair of nitrogen atom on UDMA. Therefore, the reaction time of BisGMA monomer should be faster than that of UDMA monomer.

The effect of 4-META concentration on the setting time is shown in Fig 12. In both based-monomers, the increase of the concentration of 4-META retarded the setting time. In contrast to previous researches in copper-resin composite and zinc–resin composite, the increase of concentration of 4-META reduced the setting time. 4-META, one type of the coupling reagents, is needed for bonding resin composite to dentin and for crosslinking with based-monomer. Peutzfeldt and Asmussen [28] proposed that the degree of crosslinking in polymer matrix could be increased by the increase of carboxylic anhydride to monomer mixture. Thus, the mechanical properties, strength and stiffness of materials could increase

20% when the concentration of anhydride was increased. Since 4-META used in this study has the anhydride functional group which corresponds with the degree of crosslinking, the increase of mechanical properties could be expected even its reactivity retards the setting time.

Determination of the degree of conversion using FT-IR measurement

The mean values and standard deviations of DC are presented in Table 5. The mean DC ranged from 87.1 to 95.9%.

Table 5. Effect of monomer types and 4-META concentrations on the degree of conversion (%)

Monomer	Reference peaks	4-META concentration (%)		
		0	1.5	4.5
Bis-GMA	C=O	90.6 (2.53)	95.9 (0.75)	95.7 (0.65)
	C=C _{aromatic}	89.9 (2.13)	94.2 (1.48)	94.3 (0.74)
UDMA	C=O	87.1 (2.01)	91.0 (1.02)	91.7 (0.65)

standard deviation in parentheses

Figs.15-24 show the FT-IR spectra of the monomer and molybdenum resin composite using in this experiment. Fig.25 shows the FT-IR spectra comparing between the monomer and set sample in 0% 4-META in BisGMA based monomer condition.

As shown in Fig.25 a decrease in the quantity of C=C band absorbance at 1637 cm^{-1} in the set material as compared with the monomer was observed for every combination measured. This demonstrated that the observed settings were caused by the polymerization of the monomers.

Two-way ANOVA (Table 6) showed that both of the two main factors of these factors influenced the setting time very significantly ($p < 0.01$). In the condition where 4-META was not added, Duncan's multiple range test indicated that the DC of BisGMA based

monomer was higher than UDMA-based monomer. In the condition when 4-META was added, each polymer (set sample) was not statistically different among all of them.

Table 6. Results of two way ANOVA for the degree of conversion: Effect of monomer types and 4-META concentrations

Factors	df	Sum of square	Mean squares	F value	P value
MONOMER	1	306.28	306.28	164.69	0.000
4-META	2	72.17	36.08	19.40	0.002
MONOMER x 4-META	2	6.22	3.11	1.67	0.229
Error	12	22.32	1.86		
Total	17	406.99			

The minimization of the polymerization shrinkage and maximization of the degree of conversion (DC) and mechanical properties was the concept of resin composite inlays. Several previous researches [11-12, 28, 33-34] showed that the increase of DC could enhance in mechanical properties of materials rather than the increase of crosslinking agent. Therefore, it should be important to study the DC of this new material. The DC is the degree that carbon double bonds (C=C) are converted into carbon single bonds (C-C). After molybdenum-resin composite was polymerized, C=C bonds such as methacryloyl groups remained in the resin. Since UDMA-based resins used in the present study had no aromatic C=C absorption band that could serve as a good reference band, the absorption band of C=O at 1717cm^{-1} was chosen as the reference band. Even though some researchers [12,39] utilized the absorption band of N-H bond at 3360 or 3373cm^{-1} , it could not be used in this study because it was interfered with the very broad O-H stretching band of the adhesive monomers in this study. However, aromatic C=C absorption band at 1610cm^{-1} and C=O absorption band at 1717cm^{-1} were used as reference band for BisGMA monomer. Table 5 shows that the DC was increased when coupling reagent (4-META) was added. In addition, the results showed that DC of molybdenum-resin composites using

BisGMA monomer is higher than those using UDMA monomer. The highest DC of this was 95.9% in 1.5% 4-META BisGMA condition. This was much higher than the resin composites using inorganic filler (70% DC). Moreover, the DC in molybdenum-resin composite in this study was higher than the DC in zinc-resin composite (77.8-85.0%) and copper-resin composite (49.1-80.1%) in the previous studies. Therefore, these phenomena illustrated that molybdenum-resin composite could be expected for an improvement of mechanical properties of a new material in the near future.



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CHAPTER V

CONCLUSION

Five kinds of metal particles, *i.e.*, Silver, zirconium, copper, molybdenum and zinc were examined to establish if they could induce the polymerization of UDMA-based monomer. Four different monomer compositions were used to combine with metals filler. As-received, silver and zirconium particles could not induce the polymerization of UDMA based monomer either containing coupling reagent (4-META) or radical initiator (BPO) or without containing of those components. Copper and molybdenum particles could induce the polymerization of UDMA based monomer even in the absence of 4-META, but they could not have ability to do so in the absence of BPO. Zinc particles could induce the polymerization of UDMA based monomer in the absence of BPO, but they could not have ability to do that in the absence of 4-META.

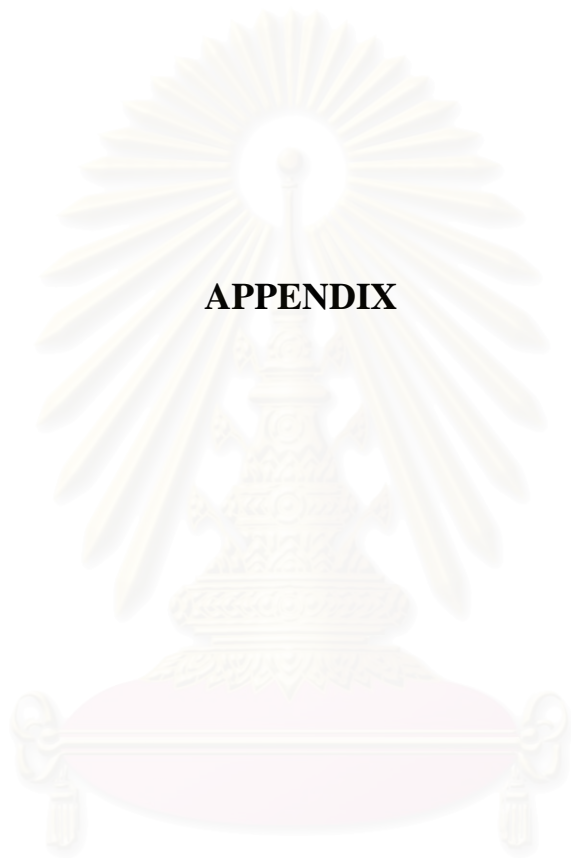
From above observation, molybdenum particles were chosen to study the details of the polymerization phenomena. Molybdenum particles moistened with a small amount of water, coupling reagent (4-META), benzoyl peroxide in both BisGMA based monomer and UDMA based monomer were investigated. The effects of monomer types and 4-META concentrations on the setting time and degree of conversion (DC) were studied. As-received molybdenum particles could induce the polymerization of both BisGMA and UDMA monomer. The type of monomer-based and the concentration of 4-META had influence the setting and the degree of conversion (DC). A higher concentration of 4-META retarded the setting time but increased DC in both monomers. In addition, this molybdenum-resin composite had much higher DC than the previous metal-resin composites.

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APPENDIX

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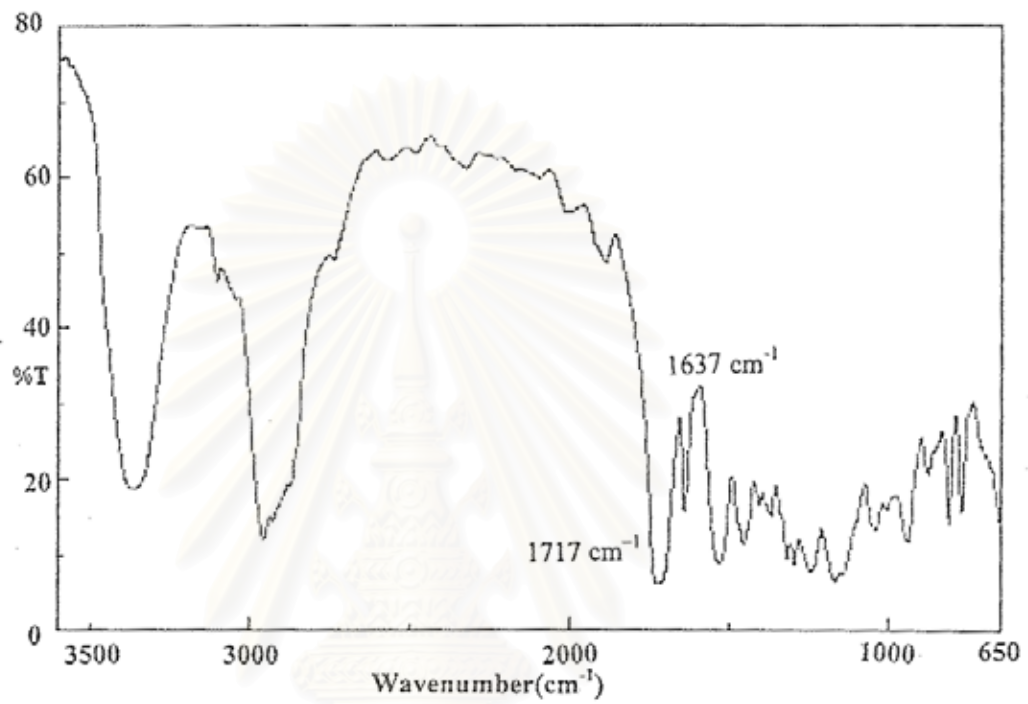


Fig.15. FT-IR spectrum of UDMA monomer containing 1%BPO.

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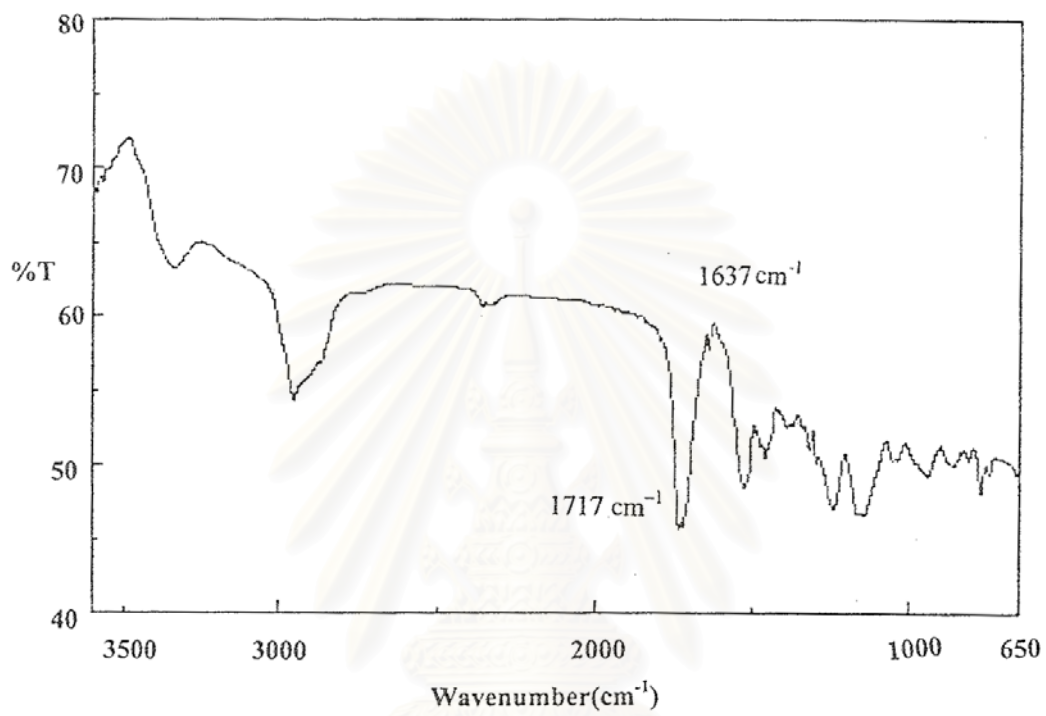


Fig.16. FT-IR spectrum of molybdenum resin composite from UDMA monomer containing 1%BPO.

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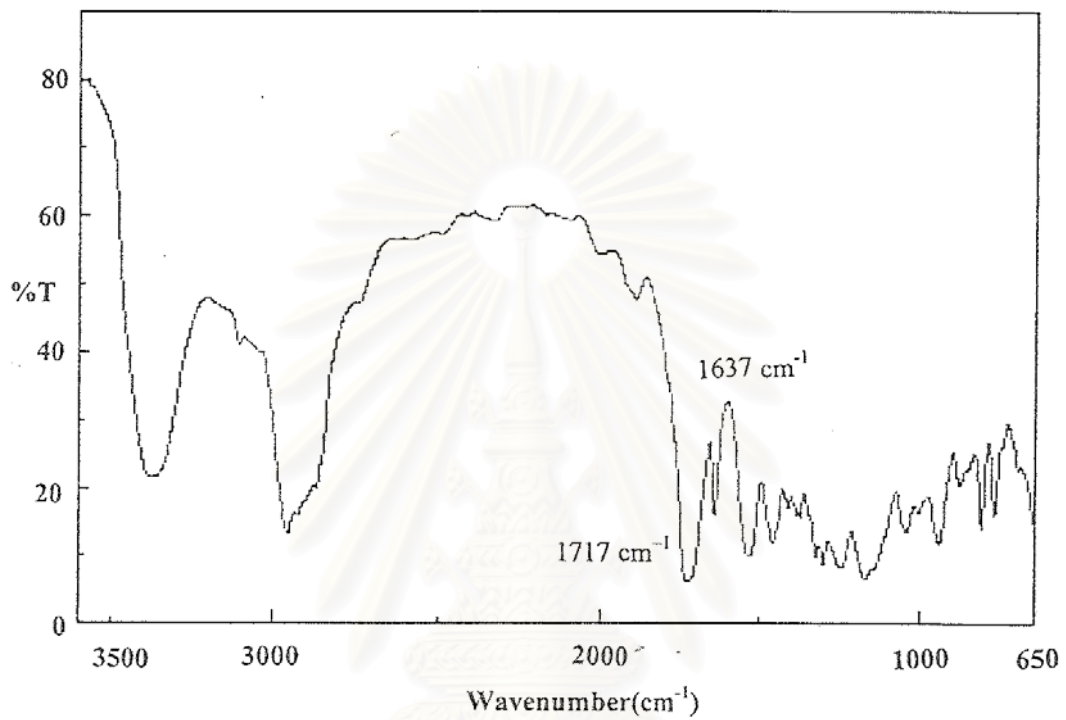


Fig.17. FT-IR spectrum of UDMA monomer containing 1%BPO and 4.5% 4-META

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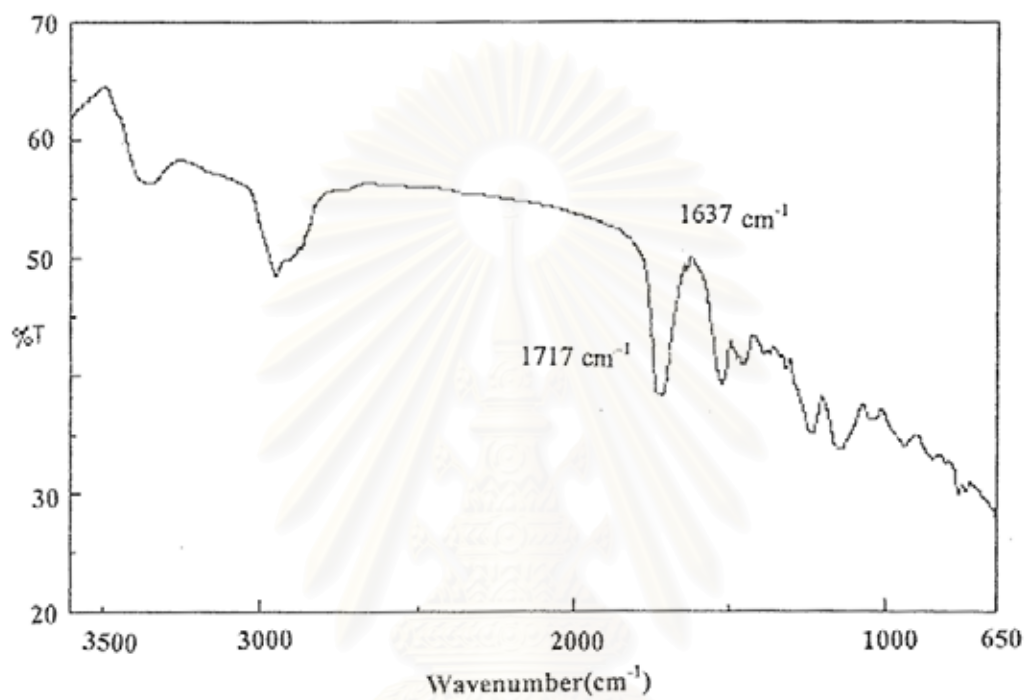


Fig.18. FT-IR spectrum of molybdenum resin composite from UDMA monomer containing 1%BPO and 2% 4-META.

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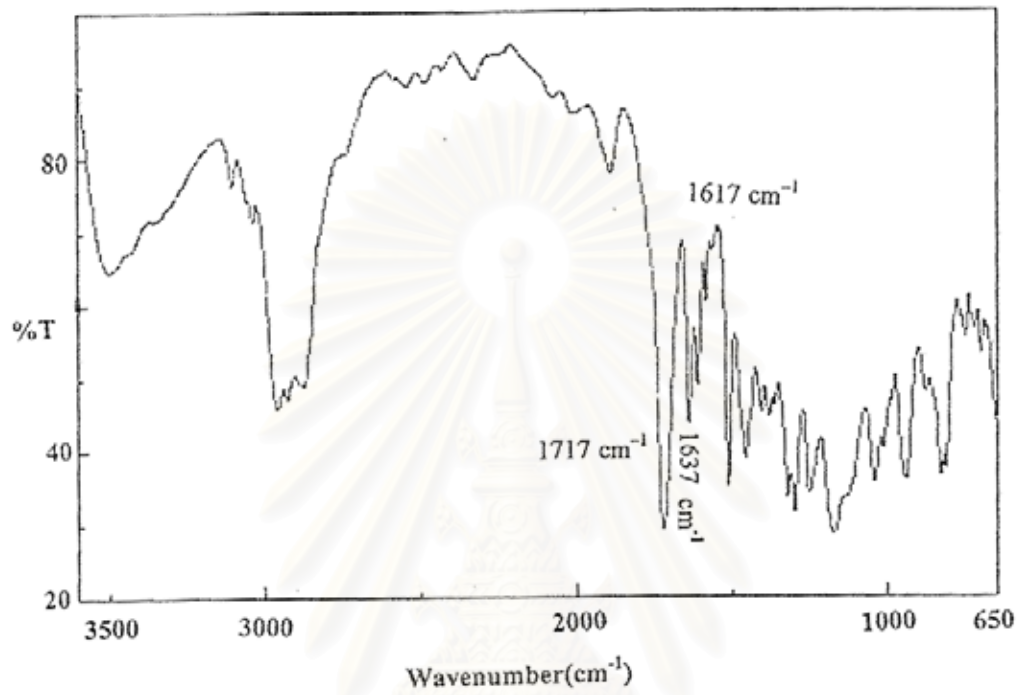


Fig.19. FT-IR spectrum of BisGMA monomer containing 1%BPO.

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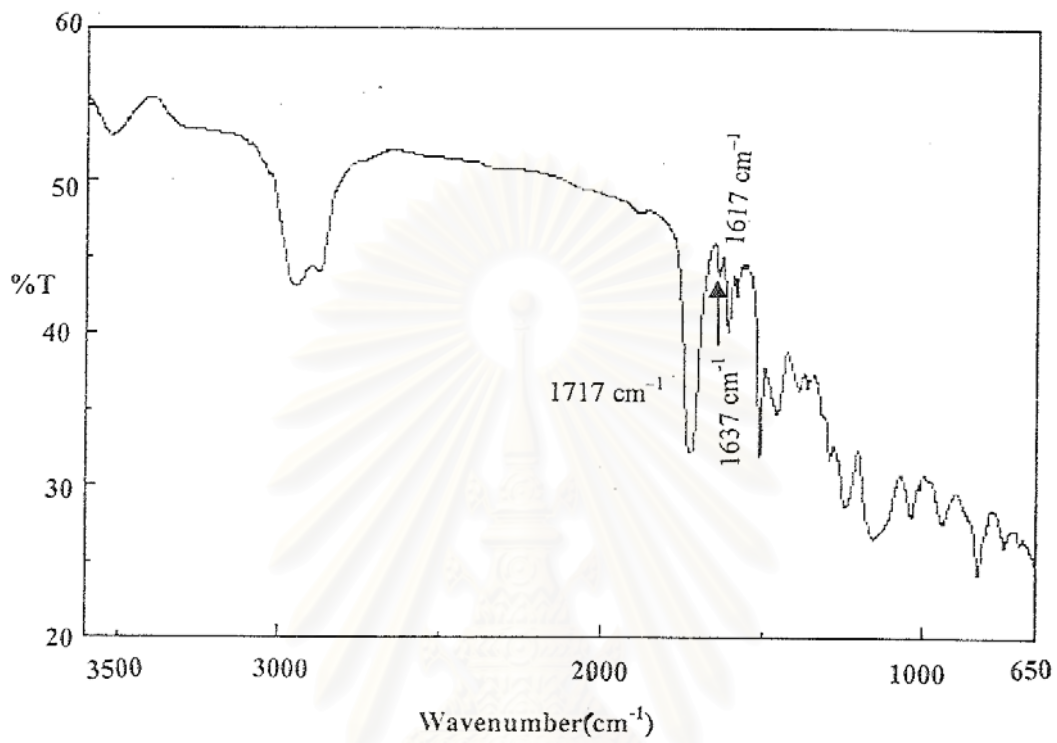


Fig.20. FT-IR spectrum of molybdenum resin composite from BisGMA monomer containing 1%BPO.

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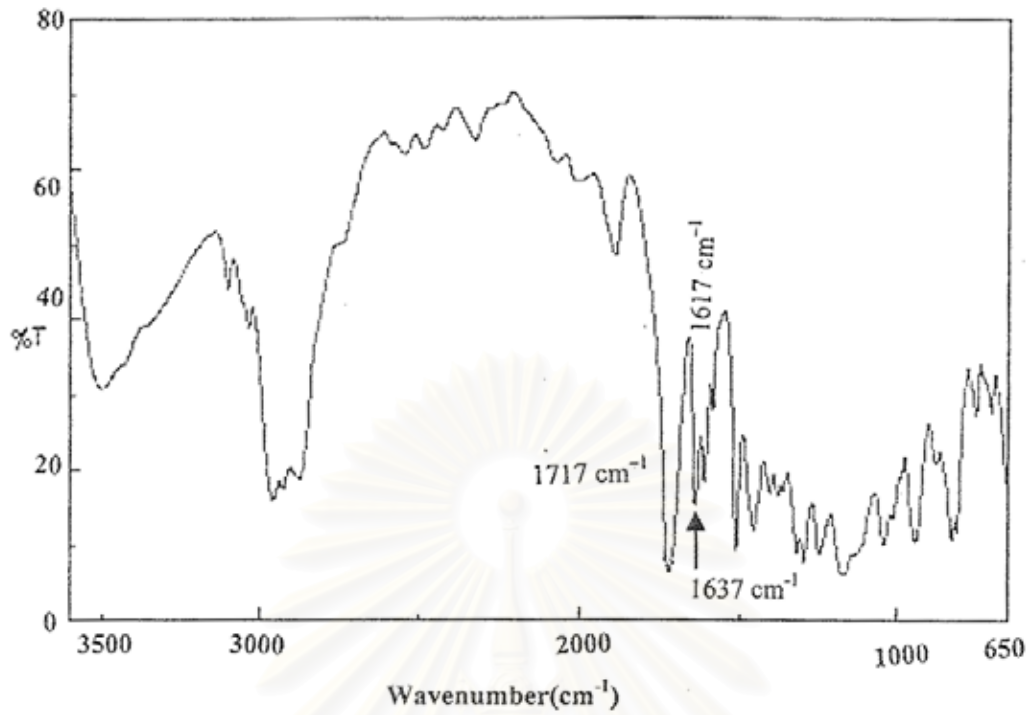


Fig.21. FT-IR spectrum of BisGMA monomer containing 1%BPO and 1.5% 4-META.

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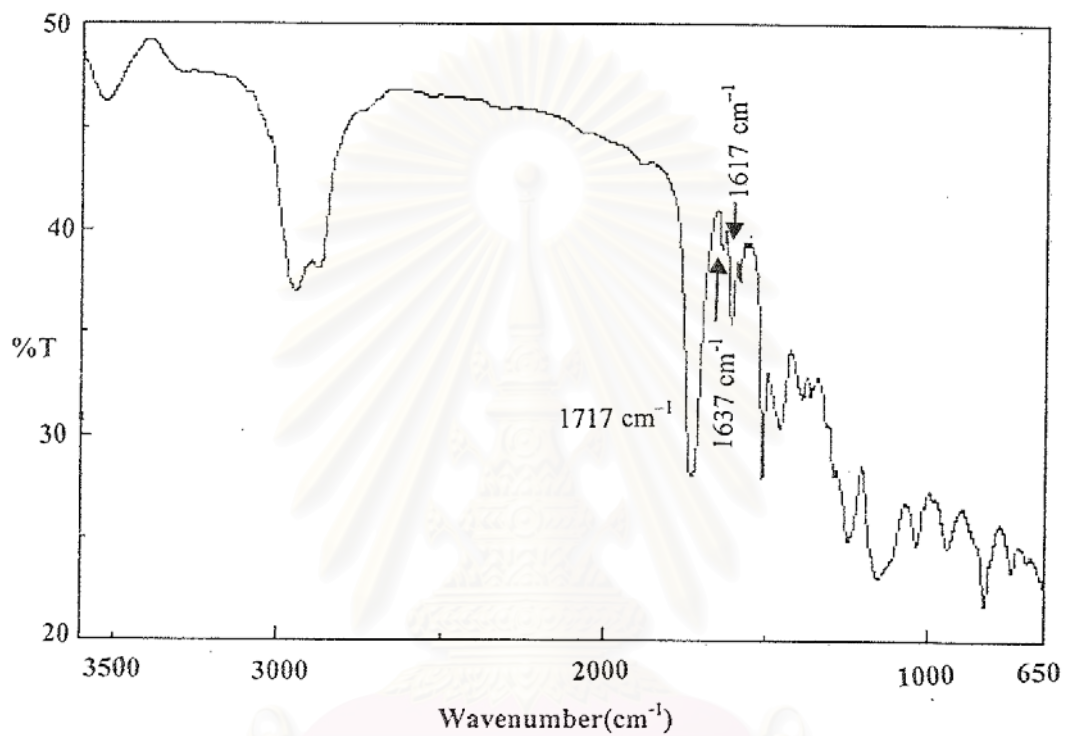


Fig.22. FT-IR spectrum of molybdenum resin composite from BisGMA monomer containing 1%BPO and 1.5% 4-META.

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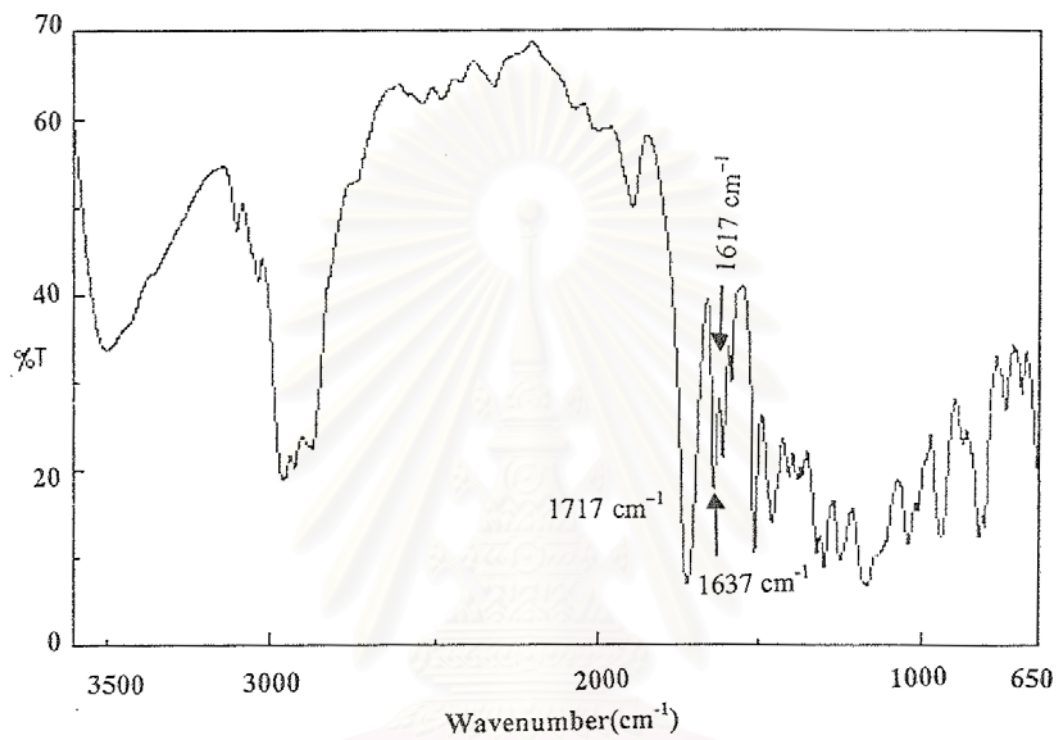


Fig.23. FT-IR spectrum of molybdenum resin composite from BisGMA monomer containing 1%BPO and 4.5% 4-META.

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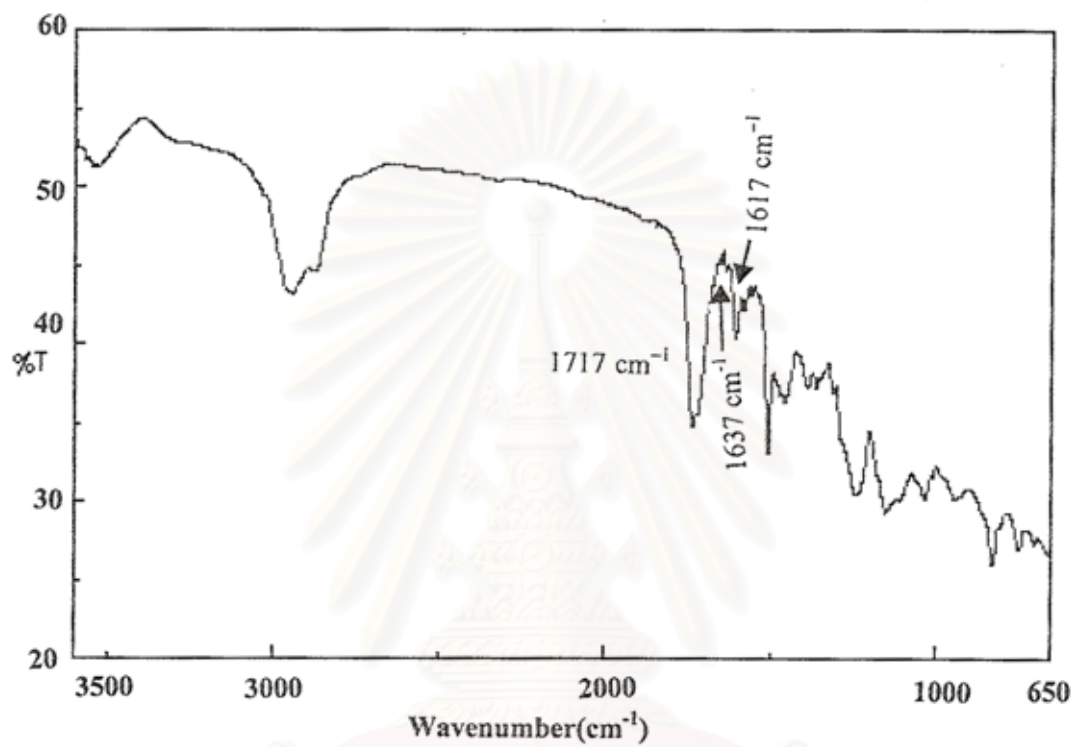


Fig.24. FT-IR spectrum of molybdenum resin composite from BisGMA monomer containing 1%BPO and 4.5% 4-META.

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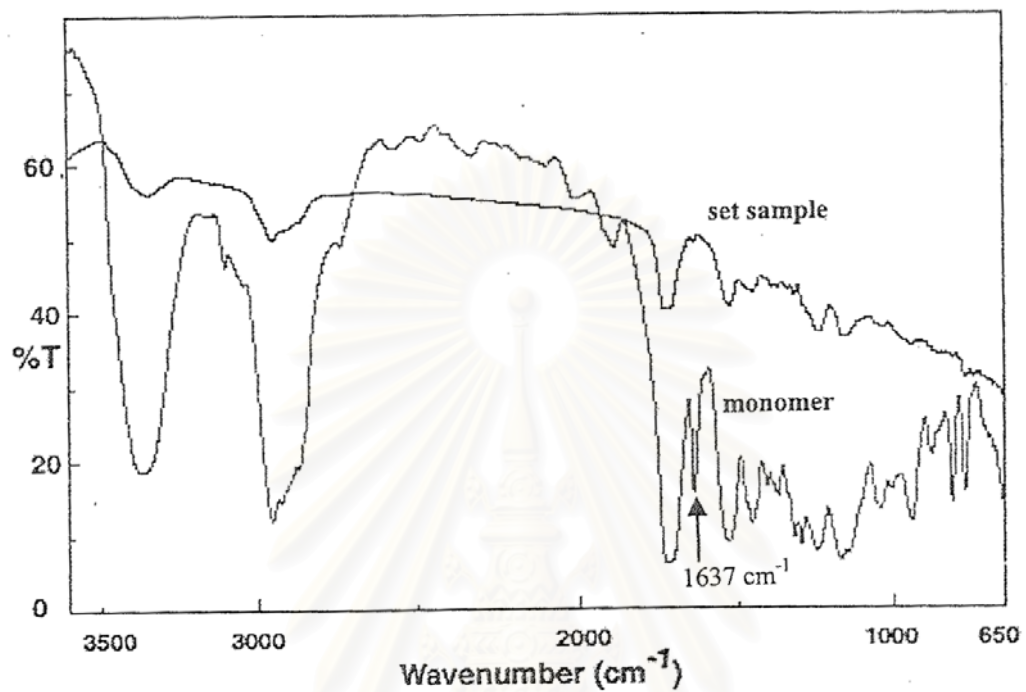


Fig.25. FT-IR spectra comparing between the monomer and set sample in BisGMA monomer containing 1% BPO (0%4-META).

สถาบันวิทยบริการ
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VITA

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