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Heat of polymerization of Dimethacrylate Monomers Investigated by Isothermal DSC Measurement

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Heat of polymerization of Bis-GMA—TEDMA monomer mixtures, corresponding to the conceivable constituents of composite resins, was evaluated from the area of exothermic peak in DSC curves, and also the conversions of polymerization were calculated from the ratio of the heat of polymerization for each monomer mixture to an assumed one at 100% conversion. The effects of composition of monomers and environmental atmosphere on the polymerization were examined. The results suggest that increasing amounts of TEDMA in the monomer mixtures increases the length of the inhibition period for oxygen-inhibited polymerization of dimethacrylate monomers, but decreases the porosity of cured resins.

Key Words: Heat of Polymerization, Composite Resins, DSC.

INTRODUCTION

Methacrylate monomers, such as Bis-GMA and TEDMA, have been used extensively in commercial composite resins. There have been many investigations into the causes of pulp irritation by the residual monomer. Furthermore, the mechanical properties are well correlated with the amount of residual monomer1). Using a method of liquid chromatograph, the amounts of residual Bis-GMA monomer at the setting time were in the range 0.4–1.21% of the original weight of cured resin2). Infrared spectroscopy (IR) has been often used to evaluate the conversion of polymerization of commercial composite resins3),4). However, with IR methods, interference in the critical vinyl absorption region by the filler component makes sample preparation difficult. Isothermal differential scanning calorimetry (DSC) used in this study does not have such a problem. The DSC methods can be adapted to studies on the polymerization and polymer reaction5),6), and can also be used in the study of setting reaction of dental materials7)~9). The purposes of this investigation are to obtain the heat of polymerization and the conversion of Bis-GMA—TEDMA monomer mixtures from DSC curves, and to discuss the effects of composition of monomers and environmental atmosphere on the polymerization and the adaptability of isothermal DSC measurement by comparison with IR measurement.

MATERIALS AND METHODS

The monomers used in this study were Bis-GMA* and TEDMA (triethylene-glycole-dimethacrylate)*. Either BPO (benzoyl-peroxide)** as initiator or DMPT (dimethyl-para-

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* Shin-Nakamura Chemical Industries Ltd., Wakayama, Japan

** Wako Pure Chemical Industries Ltd., Osaka, Japan toluidine)** as accelerator were dissolved in each monomer, and HQME (hydroquinone-monomethyl-ether)* as inhibitor was dissolved in both monomers. The Bis-GMA—TEDMA monomer mixture contained 20%, 30%, 40%, 50%, 60%, 80% and 100% TEDMA by weight. The monomer content of BPO, DMPT and HQME was 1.0%, 0.5% and 0.3% by weight, respectively. The additive-containing monomers were used in combinations that gave setting times between 3 and 10 minutes according to previous results[10)~12)].

Differential scanning calorimeter (DSC)[#] was used in this study. The experiments were conducted under air or argon gas at 23°C, isothermally. The instrument was calibrated using In, Sn, Pb, KNO_3 and $KClO_4$. With DSC measurement, the samples were produced as follows: An amine-containing monomer was mixed with an equal content of a peroxide-containing monomer for 20 seconds. Samples (approximately 10 mg) were then placed in DSC aluminum pans and were quickly transferred within 10 seconds to the sample holder of the instrument. The sample weight was obtained by subtracting the weight of the pan from the final weight after the run. The heat of polymerization was evaluated from the planimeter measurement of the total area of exothermic peak in the DSC curves. A base line for the DSC curve was obtained by a second measurement of the polymerized material under the same condition. At least 5 samples of each monomer were measured in the same manner. Details of the DSC measurement are the same as those described previously[7),9)].

The conversion C was calculated from the ratio of the observed heat of polymerization $\varDelta Q$ for each sample to the assumed one $\varDelta Qt$ at 100% conversion:

$$C = 100 \cdot \varDelta Q / \varDelta Qt \,. \tag{1}$$

The assumed heat of polymerization $\varDelta Qt$ at 100% conversion is derived as follows;

$$\varDelta Qt = \frac{2 \cdot \varDelta Q_0}{100} \left(\frac{100 - X}{Mb} + \frac{X}{Mt} \right), \tag{2}$$

where Mb and Mt are the molecular weights of Bis-GMA (=512) and TEDMA (=286), respectively. X is weight percentage of TEDMA in the Bis-GMA—TEDMA monomer mixture and $\varDelta Q_0$ is the heat of polymerization of methacrylate monomer. A basic assumption of this method is that heat from the reaction for the conversion of a vinyl group to saturated carbon-carbon bond is the same for all methacrylate monomers, and is only proportional to the number of reacted vinyl groups[7)]. The value of $\varDelta Q_0$ used in this study is 13.3 kcal/mole for methyl-methacrylate[13)].

The cured monomer mixtures were mounted in epoxy resins and polished. Cross sections of the samples were observed by a Scanning Electron Microscopy (SEM)[##].

The unreacted methacrylate groups, having C=C bond, were quantitatively analyzed for reaction time by means of infrared spectroscopy (IR)[###] and compared with the results obtained by DSC measurement. Samples were mixed for 20 seconds the same as the pro-

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* Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan

[#] Rigaku Denki Co., Ltd. Standard model, Tokyo, Japan

[##] JOEL JXA-50A, Tokyo, Japan

[###] Hitachi Model 215, Tokyo, Japan

cedure for DSC measurement, then quickly pressed between two KBr crystal plates (ϕ30 mm) and the infrared absorption spectra between 1700 cm^{-1} and 1550 cm^{-1} were measured every minute for the first 15 minutes and several times after that until saturated value. The measurement time to obtain a spectrum was about 10 seconds. The amounts of the unreacted methacrylate groups were evaluated from the ratio of the intensity of C=C stretching bands at arround 1640 cm^{-1} to that of aromatic C..C bands at arround 1600 cm^{-1}. This method is basically the same as the one developed by Ruyter and Györösi[14]. Details of the calibration and the determination of the amounts of C=C are the same as those described previously[10],[15].

RESULTS AND DISCUSSION

Figure 1 shows the change in the DSC curves during the curing for the Bis-GMA—TEDMA monomer mixtures at 23°C under air. The heat of polymerization, conversion, Tp and Te for each monomer mixtures were obtained from these curves, where Tp is the time to the peak of the DSC curve from the start of mixing and Te is the time to 5% of the height of the peak from the start of mixing. Te corresponds to the setting time measured with an oscillating rheometer according to ISO-4049[9]. Obtained values of the heat of polymerization, conversion, Tp and Te are summarized in Table 1, with the comparison of the results under argon gas. Both Tp and Te were retarded with increasing amounts of TEDMA in monomer mixtures, and the times of those polymerized under air were more retarded than those under argon gas. Furthermore, the difference of these times according to the difference of atmosphere increased with increasing amounts of TEDMA in monomer mixtures.

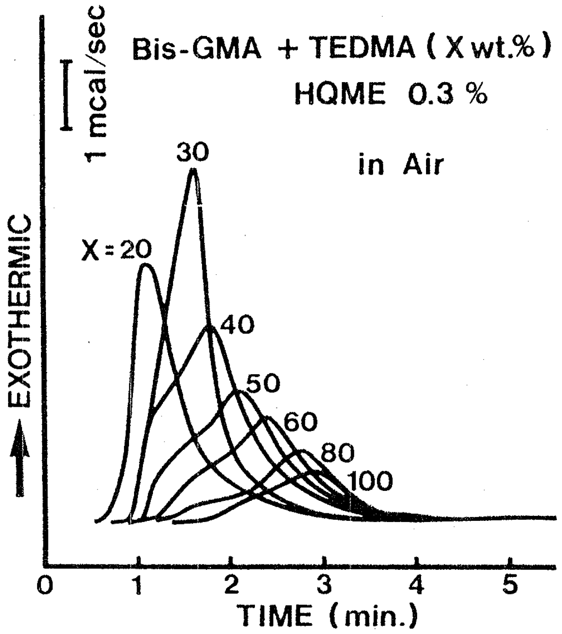

Figure 1 Change in the DSC curves for Bis-GMA—TEDMA monomer mixtures at 23°C under air. DSC range and chart speed were ±16 mcal/sec and 20 mm/min respectively.

Table 1 Results measured with DSC for Bis-GMA—TEDMA monomer mixtures at 23°C under air and argon.

	Amounts of TEDMA (wt.%)	ΔQ (cal/g)		ΔQt (cal/g)	$100 \cdot \Delta Q/\Delta Qt$ (%)		Tp (min)		Te (min)	
air	20	24.60*	1.87**	60.16	40.89	3.11	1.18	0.09	2.52	0.16
	30	32.88	1.35	64.27	51.16	2.10	1.33	0.04	2.78	0.07
	40	24.67	0.96	68.37	36.04	1.40	1.95	0.15	3.75	0.29
	50	18.10	1.60	72.48	24.97	2.21	2.19	0.04	3.72	0.10
	60	19.75	1.44	76.58	25.79	1.88	2.49	0.10	3.98	0.10
	80	11.90	1.43	84.79	14.03	1.69	2.88	0.09	4.33	0.19
	100	8.22	2.04	93.00	8.84	2.19	2.95	0.09	4.21	0.12
argon	20	26.61	2.56	60.16	44.23	4.25	1.26	0.11	2.14	0.19
	30	34.23	5.58	64.27	53.26	8.68	1.23	0.05	2.54	0.36
	40	43.18	1.74	68.37	63.16	2.50	1.79	0.20	3.26	0.18
	50	42.50	7.46	72.48	58.64	10.29	1.85	0.19	3.55	0.24
	60	42.79	5.08	76.58	55.88	6.63	2.11	0.07	3.45	0.30
	80	46.43	0.92	84.79	54.76	1.09	2.36	0.07	3.48	0.10
	100	44.42	3.42	93.00	47.76	3.68	2.53	0.09	3.56	0.14

*; mean **; standard deviation

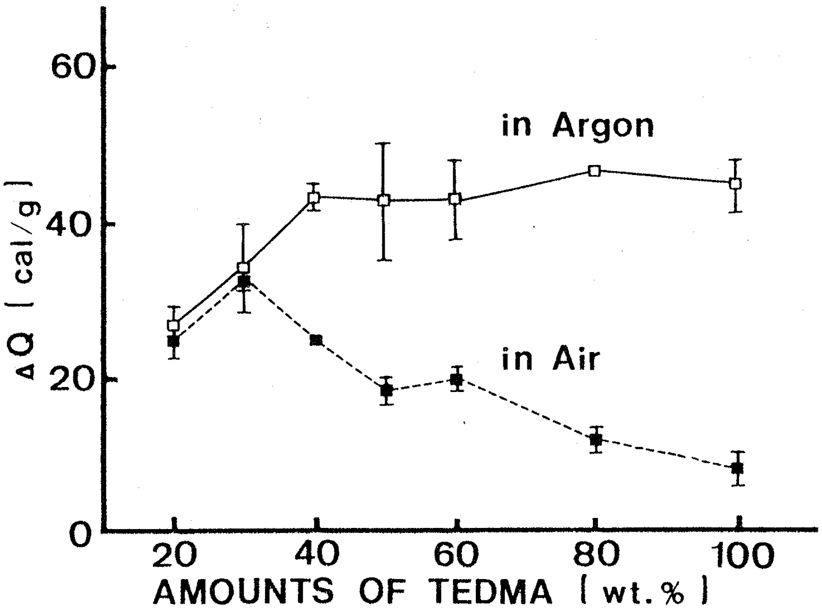

Figure 2 Relationship between heat of polymerization and amounts of TEDMA in Bis-GMA—TEDMA monomer mixtures at 23°C under air and argon gas.

Figure 2 shows the heat of polymerization and Figure 3 shows the conversion summarized in Table 1. In case of polymerization under air, the monomer mixture containing 30% TEDMA by weight showed the highest heat of polymerization and conversion. In the case of polymerization under argon gas, the monomer mixture containing 40% TEDMA

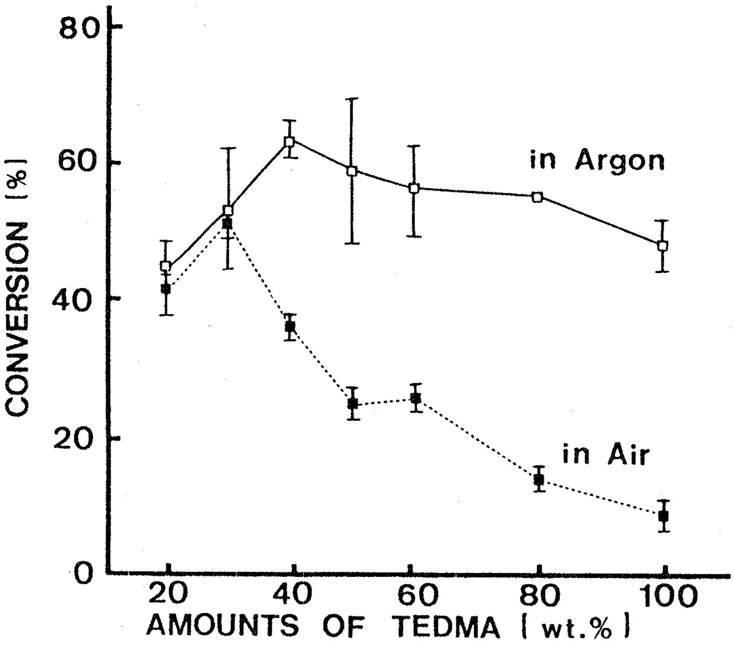

Figure 3 Relationship between conversions and amounts of TEDMA in Bis-GMA—TEDMA monomer mixtures at 23°C under air and argon gas.

by weight showed the highest conversion. These heat of polymerization and conversion under air were lower than those under argon gas. Furthermore, the differences of these according to the difference of environmental atmosphere increased with increasing amounts of TEDMA in monomer mixtures as well as the change of Tp and Te. It is suggested that the length of the inhibition period for oxygen-inhibited polymerization of dimethacrylate monomers increased with increasing amounts of TEDMA in monomer mixtures.

Oxygen itself is well-known as a polymerization inhibitor. The role of oxygen in the mechanism of vinyl polymerization is peroxide formation in preference to polymerization. In the presence of excess oxygen, polymerization is either greatly retarded or entirely prevented[16]. On the other hand, HQME was also dissolved as an inhibitor in the monomers. Phenols such as HQME are known to have little effect on the rate of polymerization in the absence of oxygen. Phenols act simply as antioxidants in the inhibition of vinyl polymerization in the presence of oxygen. The role of phenols in the inhibition of stabilization process is simply to prevent the oxygen from being consumed rapidly and thus to maintain the oxygen concentration at a level high enough to cause inhibition for a longer time[17]. It is apparent that the inhibition observed in this study is dependent on the effects of HQME and atmospheric oxygen. According to Ruyter[3], it is assumed that the rate of oxygen diffusion in a resin liquid decreases with increasing viscosity, and as the viscosity is of the same magnitude, the supply of oxygen to the reactive site; i.e. the radicals, is of the same order of magnitude. Asmussen's investigation[18] showed that the viscosity of Bis-GMA—TEDMA monomer mixtures decreased with increasing amounts of TEDMA in the monomer mixtures. Thus, it can be seen that increasing amounts of TEDMA in the monomer mixtures increased the length of the inhibition period for oxygen-inhibited polymerization of dimethacrylate monomers.

Figure 4 shows the SEM photographs of sections of cured resins containing 20%, 30%, 40% and 50% TEDMA by weight. Pores of about 100 μm or less in diameter were found in 20% and 30% TEDMA by weight, but were extremely rare in 40% and 50% TEDMA by weight. It appears that the pores in cured resin, caused by entrapment of air during mixing, were increased with increasing viscosity of monomer mixtures. As described previously, the viscosity of Bis-GMA—TEDMA monomer mixtures decreased with increasing amounts of TEDMA in the monomer mixtures and increased with decreasing amounts of TEDMA. And it can be seen that polymerization of monomers containing the pores was inhibited by oxygen on the surface and in the pores As seen in Figure 3, in case of polymerization under argon gas, the conversions of the monomer mixtures containing 20% and 30% TEDMA by weight were relatively less than the conversions of the other monomer mixtures; furthermore, the difference of the conversions by the difference of environmental atmosphere was rather small.

Table 2 shows the conversions evaluated from the change in the C=C bonds obtained by IR measurement during polymerization of Bis-GMA—TEDMA monomer mixtures at 23°C. These results correspond to those obtained by DSC measurement under argon gas

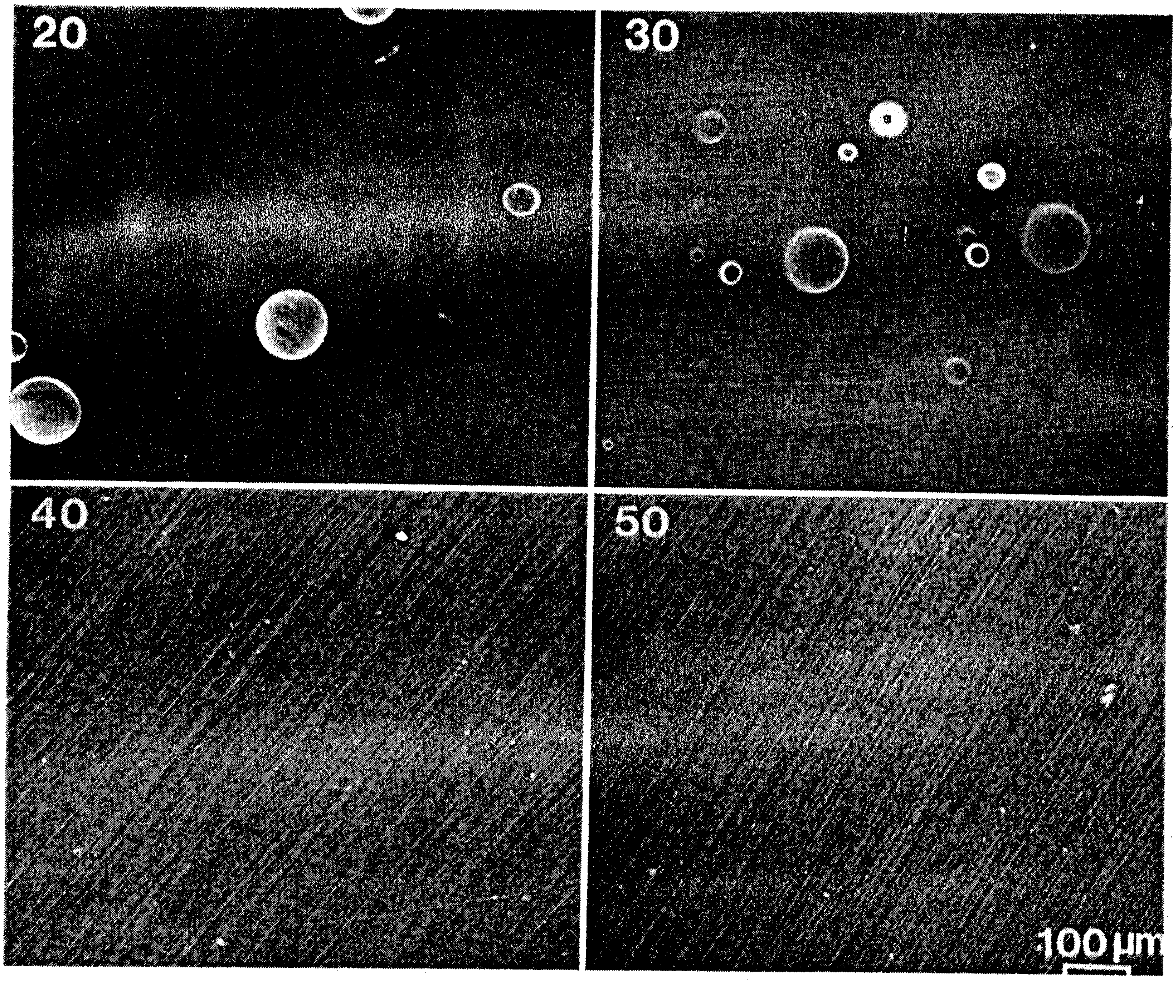

Figure 4 SEM photographs of section of cured resins. Figures stand for amounts of TEDMA in Bis-GMA—TEDMA monomer mixtures.

Table 2 Results measured with IR for Bis-GMA—TEDMA monomer mixtures at 23°C.

Amounts of TEDMA (wt.%)	Conversion (%)					
	5 min		10 min		24 hr	
20	26.3*	6.4**	31.3	2.0	32.3	2.2
30	30.1	6.9	35.1	7.5	37.0	6.3
40	21.4	4.4	45.6	5.8	57.4	1.2
50	40.2	5.3	55.3	8.9	58.1	5.0
60	12.7	6.7	39.9	8.3	66.4	2.4

*; mean **; standard deviation

summarized in Table 1. Except for the conversion of 60% TEDMA by weight after 24 hours from the start of mixing, the conversion obtained by IR was less than the one by DSC. In IR measurement, samples were pressed between KBr crystal plates; so that samples did not come into contact with air and pores were extremely rare. However, samples came into contact with KBr plates having large heat capacity, and the temperature of the samples was not raised by heat of polymerization. Thus, it seems that the rate of polymerization was not accelerated by the rise of temperature and the conversion was less than the one by DSC. Considering the procedures for clinical samples, DSC analysis is more applicable than IR.

In the case of the conversion obtained by IR after 24 hours from the start of mixing, the conversion increased with increasing amounts of TEDMA in the monomer mixtures. This is in agreement with results by Asmussen2),7) and Ruyter et al.15) On the other hand, in the case of conversion obtained by DSC measurement under argon gas, conversion showed the highest in 40% TEDMA by weight, but decreased with more than 40% TEDMA by weight such as Figure 4. As described previously, increasing amounts of TEDMA in the monomer mixtures increased the length of the inhibition period for oxygen-inhibited polymerization. And it seems that the rate of polymerization in DSC measurement was inhibited by diffused oxygen on mixing and impure oxygen in argon gas. Furthermore, in the case of greatly retarded polymerization, the DSC curve is broad and total area of exothermic peak in the curve is difficult to measure precisely. Thus, it should be noted that the DSC method is not always possible in the case of greatly retarded reaction.

CONCLUTIONS

The isothermal DSC measurement used in this study was suitable as a method for determining the conversion of polymerization of dimethacrylate monomers, such as Bis-GMA and TEDMA used in commercial composite resins. It was also found that increasing amounts of TEDMA in monomer mixture increased the length of the inhibition period for oxygen-inhibited polymerization of dimethacrylate monomers, but decreased the porosity of cured resins.

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クロルヘキシジン塩酸塩を配合した抗菌性根管充填用シーラーに関する研究

第1報　ベースとなるシーラーの組成の影響について

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酸化亜鉛ユージノール系のシーラーについて，酸化亜鉛の熱処理やロジンの配合量の違いが，硬化時間と封鎖性に与える影響を検討した。酸化亜鉛とチョウジ油の練和物では，700℃以上で熱処理された酸化亜鉛の粉末を用いた場合，急激に硬化時間が延長した。また処理温度700℃の粉末を用いた場合に封鎖性は最も良くなった。この練和物へのロジン配合率について，5～15%の場合硬化時間は延長したが，配合率が増加するにつれ短縮し，30%で最小値となった。この傾向は硬化機序におけるロジンの影響が大きいことを示唆している。封鎖性は配合率の増加につれ良くなったが，臨床における操作性の点で，過大な粘着性をもつ配合率40%以上のものは実用的ではない。これらより抗菌性を持つシーラーのベースとしての酸化亜鉛ユージノール系シーラーは，700℃で熱処理した酸化亜鉛を含み，ロジンが30%配合されているものが適しているといえる。

X線による高溶卑金属合金鋳造体の非破壊検査

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コバルト・クロム系およびニッケル・クロム系合金は耐食性にすぐれ機械的強度も大きく軽量で，しかも生体組織へのなじみも良好である。さらに精密鋳造成形法についてもほぼ確立され，比較的精度の良い鋳造体が得られるようになってきた。最近では鋳造床のみならずクラウンーブリッジ，メタルボンドポーセレンさらにインプラント用として広く活用されようとしている。しかしこの種の合金には鋳造欠陥が多発するという大きな難点がある。とくに内部鋳造欠陥の発生は鋳造成形物の機械的性質や耐食性を著しく低下させ生物学的にも種々の問題を包含している。そこで鋳造体内部の欠陥の発生機構を解析し，欠陥防止法を究明するために歯科鋳造体専用のX線装置を開発し，その性能を調べるとともにいくつかの実験を行ってみた。すなわち，コバルト・クロム合金（Bionium）およびニッケル・クロム合金（Wiron）で鋳造成形された階段状の test piece を使用した。test piece の厚径は 0.35 mm から 4.55 mm までを 0.35 mm ごとに13段階にしたものである。なお，臨床実験例としてコバルト・クロム合金による鋳造床とクラウン，骨膜下インプラントの下部構造体などの内部欠陥を観察した。

その結果，歯科鋳造体専用X線装置（Bio-X）を用いることによってきわめて鮮明なX線像が得られることが分かった。本法によればブローホールや樹枝状鋳巣のような微細な欠陥まで観察が可能で，とくに管電圧 50, 60 および 70 KVp で90秒間の曝写条件でコバルト・クロム系およびニッケル・クロム系合金鋳造体内部のほとんどの欠陥が観察された。

以上のことから，X線による金属鋳造体の非破壊検査は臨床上非常に有用なものであることが理解できた。とくに鋳造性能のよくない高溶卑金属金鋳造体については臨床応用以前における必須の検査法として採用すべきであろう。

DSC 等温法によるジメタクリレートモノマーの重合発熱の研究

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愛知学院大学歯学部歯科理工学教室

市販コンポジットレジンの主成分である Bis-GMA と TEDMA モノマー混合物の硬化反応を DSC 等温法に

より検討した。重合発熱量はDSC曲線の発熱ピーク面積より求め，重合率は各試料の重合が100%であると仮定した場合の重合発熱量に対する比率から計算した。そして重合反応に与えるモノマー組成および重合雰囲気の影響を検討した。また，赤外分光分析による結果と比較することにより，DSC等温法の適応性についても検討した。その結果，モノマー混合物中のTEDMA含有量が多い程，重合反応におよぼす酸素の抑制作用は大きくなった。一方，TEDMA含有量が少ないと，硬化体内部に気泡が残存し気泡中の酸素による重合抑制が生じた。また臨床操作を考慮すると，DSC法は赤外分光法よりも，コンポジットレジンの硬化反応の研究に適するが，遅い発熱速度の場合は注意を要する。

光重合型コンポジットレジン内の光の分布についての実験的研究とそのモデル化

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歯科修復に用いられるコンポジットレジンの重合に，感光性の開始剤が使用されることが多くなってきている。今回，重合を起こさせる化学反応の機能といった硬化機構や無機質フィラーによる光の散乱についての実験的，理論的研究を行なった。われわれの実験から得られた結果は，古典的なBeer-Lambertの吸収の法則からはあきらかにかけはなれていた。これらの結果から，コンポジットレジンが歯牙窩洞内において重合される場合，均一な硬さを得ることが困難であることが示された。

貴金属修復物の高温における変形機構

（第1報）Au-Pt-Pd合金系の高温のたわみ

安藤進夫，中山正彦，西川良子

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陶材焼成時における鋳造体の変形機構を解明するため，高温たわみ測定装置を試作し，試作合金の鋳造体を用いて高温わたみ量を測定し，合金組成との関係を検討した。高温わたみ量は，支持距離30mmとし，24℃/minで1050℃まで加熱冷却したときの試験片中央部のたわみ量とした。実験に用いた合金は，金80～90wt%，白金0～20wt%，パラジウム0～10wt%の範囲内でそれぞれ5%ずつ変化させた9種の合金である。

高温たわみ量の最も大きい合金組成は，80Au-20Pt合金であり，最も小さい組成は90Au-10Pd合金であった。また高温たわみ量は，パラジウムの含有量が増すと減少する傾向が認められた。

高温たわみ量と変形開始温度には，相関が認められた。