Impact Properties of Acrylic Denture Base Resin Part 3 Impact Properties of Cross-linked Polymers

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The impact properties in acrylic denture base resins cross-linked using 6 diacrylates, such as ethylene glycol dimethacrylate (EDMA) and *p*-divinyl benzene (DVB), were investigated and discussed. In addition, the creep characteristics of these cross-linked resins were examined and related with their impact characteristics. From these results, it was seen that both characteristics deteriorated with an increase in the diacrylate concentration from 2 mol% to 10 mol%. On the other hand, an increase in the repeated number (*n*) of $(-\text{CH}_2-\text{CH}_2-\text{O}-)_n$ promoted a flexibility in the materials which resulted in a higher impact strength and toughness. But, there was no a significant difference in the resilience of these materials.

Key words: Acrylic resin, Cross-linking agent, Impact property

INTRODUCTION

Numerous studies have reported the impact properties of acrylic denture base resins. In these studies, however, all tests have been performed at a higher hitting speed as compared with chewing speed. It is considered that the flexibility of the molecular chain sufficiently affects the impact strength of the materials for the relatively slow hitting speed characteristic of chewing¹⁻⁵⁾.

On the other hand, in clinical use, it is preferable for the denture base to exhibit a high impact resistance against the impact forces associated with chewing⁶⁻⁸⁾. In commercial denture base materials, therefore, several diacrylates have been added to methyl methacrylate for this purpose⁹⁾.

The purpose of this investigation is to examine the impact properties of cross-linked polymers and the creep characteristics of such materials.

MATERIALS AND METHODS

Materials

The materials used in this investigation along with the code, composition of materials, and curing conditions are presented in Table 1. Six diacrylates which contain two polymerizable bonds were used as a cross-linking agent, and benzoyl peroxide (0.5% of base comonomer weight) was incorporated in the base comonomer. The structural formula of materials used are as follows :

Table 1 Composition of materials used and curing conditions

Code	Diacrylate added to MMA ¹⁾	Comonomer (mol%)		PMMA ²⁾ /comonomer ratio	Curing condition
		MMA	Diacrylate		
A	none	100	0	2/1	I
B ₁	EDMA ³⁾	98	2	2/1	II
B ₂		95	5	2/1	II
B ₃		90	10	2/1	II
C ₁	Di-EDMA ⁴⁾	98	2	2/1	II
C ₂		95	5	2/1	II
C ₃		90	10	2/1	II
D ₁	Tri-EDMA ⁵⁾	98	2	2/1	II
D ₂		95	5	2/1	II
D ₃		90	10	2/1	II
E ₁	Tetra-EDMA ⁶⁾	98	2	2/1	II
E ₂		95	5	2/1	II
E ₃		90	10	2/1	II
F ₁	DVB ⁷⁾	98	2	2/1	II
F ₂		95	5	2/1	II
F ₃		90	10	2/1	II
G ₁	BPDMA ⁸⁾	98	2	2/1	II
G ₂		95	5	2/1	II
G ₃		90	10	2/1	II

I : Raising the temperature according to dental curing techniques and keeping it for 1 h at 100°C in an atmosphere of N₂ gas (3 kgf/cm²)

II : Raising the temperature according to dental curing techniques and keeping it for 1.5 h at 100°C in an atmosphere of N₂ gas (3 kgf/cm²)

1) MMA : Methyl methacrylate (1st class reagent)

2) PMMA : Polymethyl methacrylate (Acricon)

3) EDMA : Ethylene glycol dimethacrylate (1st class reagent)

4) Di-EDMA : Di-ethylene glycol dimethacrylate (1st class reagent)

5) Tri-EDMA : Tri-ethylene glycol dimethacrylate (1st class reagent)

6) Tetra-EDMA : Tetra-ethylene glycol dimethacrylate (1st class reagent)

7) DVB : *p*-divinyl benzene (1st class reagent)

8) BPDMA : Bisphenol-A dimethacrylate (1st class reagent)

Methyl methacrylate (MMA)

- $n=1$, Ethylene glycol dimethacrylate (EDMA)
 $n=2$, Di-ethylene glycol dimethacrylate (Di-EDMA)
 $n=3$, Tri-ethylene glycol dimethacrylate (Tri-EDMA)
 $n=4$, Tetra-ethylene glycol dimethacrylate (Tetra-EDMA)

p-divinyl benzene (DVB)

Bisphenol-A dimethacrylate (BPDMA)

All specimens were polymerized in a PTFE mold ($3.1 \times 3.1 \times 60$ mm) according to the curing technique described in previous reports^{11, 12}. After polymerization, the specimens were classified into the following 2 groups.

(1) Specimen stored in a desiccator (23°C) for 1 week after polymerization (for use in the impact test and creep test in air).

(2) Specimen stored in water (37°C) for 3 weeks after polymerization (for use in the impact test in air and the creep test in water).

A V-notch was incised on the smooth surface of each impact test specimen immediately before testing, using a double angle (45°) convex cutter. The depth of each V-notch was 20% of the original specimen thickness. The specimens used in this investigation were 3 mm in thickness, 3 mm in width, and 40 mm in length. The specimen supporting span was 30 mm in length for the impact test and 15 mm in length for the creep test.

Methods

1) Impact test¹⁰⁻¹²

The apparatus used in this investigation was the impact testing machine described in previous reports^{11,12}. All impact tests were carried out in air (at 23°C) with a hitting speed of 13.5 cm/s.

2) Creep test¹³⁻¹⁵

The creep test were performed using a modification of the transverse testing machine described in the Japanese Industrial Standard (JIS T-6051). All creep tests were carried out in air and in water (at 23°C) by adding the static load (3.5 kgf) for 120 min to the center of a specimen, and the creep compliance $J(t)$ was calculated from the resulting creep curve.

3) Measurement of water absorption¹⁶

Seven pillar shaped specimens ($3.0 \times 3.0 \times 58.0$ mm) were accurately weighed and immediately immersed in distilled water for 3 weeks at 37°C. Water absorption was determined by calculating the difference in a specimen's weight before and after immersion in water.

Fig. 1 Variation in impact strength, resilience and toughness with concentration (mol%) of diacrylate for notched specimen (3 mm $\times$ 3 mm $\times$ 60 mm) of cross-linked resins ($l=30$ mm). All specimens were stored in a desiccator (23°C) for 1 week after the polymerization.

●, A; ○, B₁, 2, 3; ×, C₁, 2, 3; △, D₁, 2, 3; □, E₁, 2, 3; ▲, F₁, 2, 3; ■, G₁, 2, 3.

Fig. 2 Variation of water absorption of cross-linked polymer (added 2 mol% diacrylate to base MMA monomer) against cross-linking agents. All specimens were soaked into distilled water (37°C) for 3 weeks after polymerization.

RESULTS AND DISCUSSION

The variation, in the impact strength, resilience and toughness with the concentration of diacrylates is shown in Fig. 1. The impact strength and toughness for group (1) specimens,

Fig. 3 Variation in impact strength, resilience and toughness of cross-linked polymer (added 2 mol% diacrylate to base MMA monomer) against types of cross-linking agents. Solid line shows the specimen tested in air (23°C). Broken line shows the specimen soaked into water (37°C) for 3 weeks after polymerization and the specimen tested in air (23°C).
 ●, $n=1$ (B₁), $n=2$ (C₁), $n=3$ (D₁), $n=4$ (E₁); ■, for dried specimen (A, F₁ and G₁);
 ▲, water absorptive specimen (A, F₁ and G₁).

diminished slightly with an increase in the diacrylate concentration of methyl methacrylate, and they increased with an increase in the repeated number (n) in $(-\text{CH}_2-\text{CH}_2-\text{O}-)_n$ in the EDMA groups. On the other hand, the resilience was constant $\{(4.8 \pm 0.2) \times 10^{-3} \text{ J}\}$, independent of the concentration of the diacrylate.

These results indicate that an increase in the cross-linking reaction has diminished the flowability of polymer, which has resulted in a reduction of impact strength.

The maximum values of the impact strength for the 6 group materials (B to G) were determined for specimens in a diacrylate concentration of 2 mol%. All measurements of water absorption and creep were taken using these specimens.

The water absorption values for the specimens of code numbers A, B₁, C₁, D₁, E₁, F₁, and G₁ are shown in Fig. 2. It is apparent that the water absorption increased with an increase in the repeated number (n) in the $(-\text{CH}_2-\text{CH}_2-\text{O}-)_n$ group in the ethylene glycol dimethacrylate monomer. Figure 3 shows the impact properties for the dry specimens and water absorbed specimens. There was almost no recognizable difference between them. These results indicate that impact properties will be affected significantly by an increase in n , but for speeds seen in chewing, they will not be affected very much by the moisture content

Fig. 4 Variation of creep compliance $J(t)$ with time for specimen stored in desiccator (23°C) for 1 week after polymerization and tested in air (23°C).
 ●, A; ○, B; ×, C; △, D; □, E; ▲, F; ■, G.

Fig. 5 Variation of creep compliance $J(t)$ with time for specimen soaked in water (37°C) for 3 weeks after polymerization and tested in water (23°C).
 ●, A; ○, B; ×, C; △, D; □, E; ▲, F; ■, G.

absorbed into the specimen. Figures 4 and 5 shows how the creep compliance $J(t)$ varies with time from the start of measurement. Since $J(t)$ is defined as the inverse number of the elastic modulus, the increase in values of $J(t)$ means that the flowability of materials is large. From these two figures, it is seen that each material flows considerably with time under a load, and the flowability slightly rises with an increase in n .

This tendency was also observed in the polymer containing benzene rings, and its flowability progressed with an increase in the number of benzene rings in the diacrylates. The

Table 2 Comparison of resilience obtained by impact test (23°C) and 1/J (0.1) obtained by creep test (23°C)

Code	Diacylate added to MMA	Resilience ($\times 10^{-3}$ J)		1/J (0.1) ($\times 10^{10}$ dyn/cm ²)	
		Dried specimen	Wet specimen (tested in air)	Dried specimen	Wet specimen (tested in water)
A	none	4.57 (0.188)	4.55 (0.148)	2.50	2.47
B ₁	EDMA	5.00 (0.200)	4.90 (0.164)	2.57	2.51
C ₁	Di-EDMA	4.88 (0.144)	4.79 (0.247)	2.48	2.36
D ₁	Tri-EDMA	4.73 (0.0968)	4.79 (0.190)	2.29	2.20
E ₁	Tetra-EDMA	4.69 (0.107)	4.66 (0.0991)	2.20	2.14
F ₁	DVB	4.99 (0.118)	5.00 (0.149)	2.34	2.28
G ₁	BPDMA	4.76 (0.0715)	4.76 (0.149)	2.17	2.12

() : SD

individual values for resilience and 1/J(0.1)* are listed in Table 2. It would appear that the values of resilience and 1/J(0.1) for the dried specimens and wet specimens were in good agreement. This result indicates that water absorbed by the specimen does not significantly affect the mechanical properties of the specimen.

In general, it has been reported that in many cases, the benzene rings which exist in the main molecular chains, contribute exceedingly to improvements in hardness and in other mechanical properties of a material. In this investigation, however, the impact properties (impact strength, resilience and toughness) and creep characteristics (creep compliance and flowability) for F₁₋₃) and G₁₋₃) were almost equivalent to those of the EDMA series (B₁₋₃ to E₁₋₃).

CONCLUSIONS

Impact and creep tests on cross-linked polymethyl methacrylate materials were carried out.

(1) The impact strength and toughness of the cross-linked polymer diminished slightly with an increase in the concentration of the individual cross-linking agents.

(2) The increase of n in the $(-\text{CH}_2-\text{CH}_2-\text{O}-)_n$ group slightly improved the impact property of the material.

(3) From the differences in the values of J(0.1) and J(120) in the creep test, it was seen that the flowability of the materials slightly increased. However, in the case of materials that had absorbed water, the values of 1/J(0.1) for the dried specimens and wet specimens were in good agreement.

(4) Though water absorbed into a specimen acts generally as a plasticizer, it is possible that in test speeds seen in chewing, the impact properties of the materials will not be affected by the absorbed water.

* J(0.1) is the creep compliance at 0.1 min from the start of measurement.

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快削性セラミックスの歯科的応用に関する研究（第1報）色彩学的検討

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切削加工が容易な快削性セラミックスの加工性の原理の一つは、へき開性を有する結晶を素材内部に分散させ加工時に発生したクラックが結晶のへき開性により進展を止められる機構を利用したものである。歯科領域においても最近 CAD-CAM による補綴物製作の試みがなされている。本報では、快削性セラミックスの歯科応用についての基礎的研究の一環として、8種類の市販快削性セラミックスと Vita の焼付陶材用 shade guide を用い

て色彩色差計による色彩学的検討を行なった。

その結果、長石陶材系の Vita shade guide に比較して、いずれの快削性セラミックスも強い不透明感を与える白色を呈することが明らかとなった。今後、産業用に開発された快削性セラミックスを改良して歯冠修復材料として利用するためには、母相と分散相からなる微細構造を変化させ照度 (L^*) を大幅に下げる必要があることが示唆された。

アクリル系義歯床用レジンの衝撃特性

— 第3報 — 架橋ポリマーの耐衝撃性

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6種類の架橋剤を用いて、加熱重合したアクリル系義歯床用レジンの耐衝撃性を、試作衝撃試験機（第1報、第2報）を用いて調べた。また、このレジンのクリープ挙動、吸水性を調べ、衝撃特性値（衝撃強さ・レジリエンス・靱性）との関係を検討した。メタクリル酸メチルモノマーに対する各架橋剤濃度（2 mol% から 10 mol% 範囲で）が高くなるにつれて、重合体の衝撃強さ・靱性はわずかに低下する傾向を示したが、レジリエンスに

は変化がみられず、 $(4.8 \pm 0.2) \times 10^{-3} \text{ J}$ の安定した値を示した。エチレングリコールジメタクリレート系 (EDMA, Di-EDMA, Tri-EDMA, Tetra-EDMA) モノマー中の2官能基間の鎖 $(-\text{CH}_2-\text{CH}_2-\text{O}-)_n$ において、反復度数 (n) の増加にしたがって衝撃強さおよび靱性値は幾分上昇する傾向を示した。また、架橋剤濃度 2 mol% の試料間では、反復度数 (n) の増加にともなってクリープコンプライアンス、吸水率は増加した。

人歯牙象牙質およびエナメル質のねじりにおける動的弾性率

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ねじれ自由減衰型粘弾性測定装置をもちいて人歯牙象牙質およびエナメル質の動的弾性率を測定した。

象牙質の弾性率は約 50~100°C において、水分の散逸によると思われるわずかな増加がみられた。損失率は約 75°C 付近にピークが観察された。一方、エナメル質では温度による弾性率および損失率の変化はほとんどなく非常に安定している。60個の歯冠部象牙質試料のずり弾性率の平均は $8.70 \times 10^{10} \text{ dyn/cm}^2$ であった。同一歯牙にお

ける歯冠部象牙質と歯根部象牙質の値に明確な差異はみられなかった。40個のエナメル質試料の値の平均は $3.10 \times 10^{11} \text{ dyn/cm}^2$ であった。エナメル質は象牙質に比べ約 3~5 倍高い弾性率を示し、これは理論値とほぼ一致した。またエナメル質の損失率は象牙質に比べ低い値を示した。

象牙質、エナメル質ともに弾性率の値と歯牙の履歴（性別、年齢、部位）との間に明確な相関はみられなかった。