Early Compressive Strength and Phase-Formation of Dental Amalgam

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The compressive strength of five different amalgams was measured at one hour, six hours, 24 hours, and seven days, and X-ray diffraction analysis was carried out for each amalgam at the same times in order to investigate the early strength characteristics of the amalgams in relation to the formation of different phases. At 24 hours all tested amalgams reached about 90% or more of their seven-day compressive strength, but the increase in the early compressive strength from one hour to 24 hours varied between different amalgams. Two of the five amalgams tested reached about 90% of their seven-day compressive strength at six hours. A significant correlation was found between the ratio of early compressive strength to seven-day compressive strength, and the X-ray diffraction intensity ratio (ratios of one-, six- and 24-hour intensity to seven-day intensity) for the γ₁ phase, indicating that the increases in early compressive strength are mainly dependent upon the formation of γ₁.

Key words: Amalgam, Compressive strength, Intermetallic compound

INTRODUCTION

The early strength of dental amalgam is one of the main factors influencing its risk of the early fracture and thus is of great interest to the dentist. The one-hour compressive strength of dental amalgam is regarded as an essential parameter for evaluating its early strength and is included in the national standards of various countries as well as the International Standard for dental amalgam (ISO 1559). Although one-hour compressive strength is a valid criterion for the standardization of dental amalgam, the changes in the early strength from one hour to 24 hours, especially at several hours after insertion, are also important from a clinical point of view to assess the resistance of the amalgam restoration to possible early fracture.

For conventional low copper amalgams, it has been pointed out by Phillips¹¹ that the increase in the compressive strength is mostly achieved within eight hours of insertion, at which time the amalgam reaches from 70 to 90% of its maximum strength. As for high copper amalgams, the studies of Malhotra et al.²¹ and Duke et al.³¹ consistently indicate that the greatest increase in strength is achieved in the period from one hour to 24 hours and the rate of this increase varies among alloys. In these studies, however, the strength at several hours after mixing was not measured and thus the characteristics of the strength increase from one hour to 24 hours, during which period an amalgam restoration is frequently exposed to the risk of early fracture have not been well described.
The strength of dental amalgam increases with the progress of the reaction between the metal elements of an amalgam alloy and mercury. In conventional low copper amalgmas, two intermetallic compounds, Ag₂Hg₃ (γ₁) and Sn₇₋₈Hg (γ₂) are formed as a result of the reaction, whereas γ₁ and Cu₆Sn₅ (η') are formed in high copper amalgams without or with γ₂ formation. Theoretically these phases are responsible for the increase in strength. It has been shown by the aforementioned study² that high copper amalgams mainly consisting of γ₁ and η' have higher one-hour compressive strengths than conventional low copper amalgams consisting of γ₁ and γ₂. In general, the one-hour compressive strength of unicompositional high copper amalgam is higher than that of admixed high copper amalgam²,³. Although these results indicate that the early compressive strength of dental amalgam varies with different alloys which produce different phases, little is known about how the strength increase is related to the formation of these different phases.

In the present study the compressive strength of five different amalgams was measured at one hour, six hours, 24 hours, and 168 hours (seven days) and X-ray diffraction analysis was carried out for each amalgam at the same times in order to investigate the early strength characteristics of the amalgams in relation to the formation of different phases.

MATERIALS AND METHODS

Five different amalgam alloys were chosen for the present study: one unicompositional high copper alloy, two ad-mixed high copper alloys, one low copper spherical alloy and one low copper lathecut alloy. The name, code and type of each alloy are listed in Table 1.

Each amalgam alloy was mechanically mixed with mercury using an amalgamator* and the mix was used for the preparation of specimens for a compressive test and X-ray diffraction analysis. Alloy-to-mercury ratio, mixing time, and batch number for each alloy are shown in Table 2. 0.6 g of alloy was used for each compressive test specimen and two mixes (1.2 g of alloy) were used for the X-ray diffraction specimens.

Compressive test specimens were prepared following ISO 1559, "Alloys for dental

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Table 1 Product names, codes, and types of amalgam alloys

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Code</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical D¹</td>
<td>SD</td>
<td>High copper, Unicompositional spherical particle</td>
</tr>
<tr>
<td>Dispersalloy²</td>
<td>DP</td>
<td>High copper, Ad-mixed particle</td>
</tr>
<tr>
<td>Cavex³</td>
<td>CV</td>
<td>High copper, Ad-mixed particle</td>
</tr>
<tr>
<td>Luna Alloy⁴</td>
<td>LU</td>
<td>Low copper, Lathe-cut particle</td>
</tr>
<tr>
<td>Hi Atomic M⁵</td>
<td>HA</td>
<td>Low Copper, Spherical particle</td>
</tr>
</tbody>
</table>

¹ Shofu Inc., Kyoto, Japan
² Johnson & Johnson, N.J., U.S.A.
³ Cavex Holland BV, The Netherlands
⁴ GC Corp., Tokyo, Japan
⁵ GC Corp., Tokyo, Japan

* Himix VS II, GC Corp., Tokyo, Japan
amalgam”, and then stored at 37°C for different time periods: one hour, six hours, 24 hours and seven days. A total of 12 specimens were prepared for each alloy and the compressive strength was measured in three of the 12 specimens after each storage period, using a mechanical testing machine**. The procedure of the compressive test also followed ISO 1559. The data were analyzed using two-way analysis of variance and Tukey’s interval for multiple comparison of the means. The ratio of the early compressive strength at one hour, six hours and 24 hours to the seven-day compressive strength was calculated for each amalgam to evaluate the rate of the increase in the early compressive strength.

Specimens for X-ray diffraction analysis were prepared using a special glass plate with a shallow rectangular groove (18×20×0.5 mm). Two amalgam mixes were condensed in the groove, and the surface of the amalgam was flattened and smoothed using a stainless steel blade so that the surfaces of the amalgam and glass plate formed one flat plane. Two specimens were prepared for each alloy and stored at 37°C. X-ray diffraction measurements were carried out for each specimen at the same time periods as the compressive tests, using a diffractometer equipped with a personal computer#. After the diffraction measurement at each time period, the specimen was again stored at 37°C for the next measurement. Each specimen was scanned at 4°/min from 20° to 80° of 2-theta angle with Cu K-alpha radiation at 40 kV and 40 mA. The JCPDS card file and reported 2-theta values4-7) were used to identify the formed phases. The diffraction intensity of each phase was computed and the ratios of one-, six-, and 24-hour intensity to seven-day intensity (diffraction intensity ratio) were calculated.

Multiple regression analysis was used to examine the correlation between the ratio of early compressive strength and the diffraction intensity ratios for three phases: γ₁, γ₂ and η'.

RESULTS

Table 3 shows the mean values of the measured compressive strengths for each amalgam at the different time periods, and Tukey’s interval at $\alpha = 0.05$ for multiple comparison between the mean values. Two-way analysis of variance showed that two factors (alloy and time period) and the interaction of these factors were highly significant, which indicates that not only the compressive strength varies with different alloys and time periods but also the effect of the time period on strength differs between alloys. As indicated by the mean values and Tukey’s interval ($\pm 30.5$ MPa) in Table 3, significant differences in compressive strength were found between the different alloys and the different time periods.

** Universal Testing Machine DSS-5000, Shimizu Seisakusho, Kyoto, Japan.
# Rint 1200 Diffractometer, Rigaku Corp., Tokyo, Japan.
The change of the ratio of the early compressive strength from one hour to 24 hours is illustrated in Fig. 1. Two low copper amalgams, LU and HA, reached about 10% of their seven-day compressive strength at one hour, and then nearly 50% at six hours. One high copper ad-mixed amalgam, DP, attained 27% at one hour and about 50% at six hours. Two high copper amalgams, one unicompositional (SD) and one ad-mixed (CV), had higher ratio of early compressive strength at one hour (approximately 40%) than the other three amalgam, increasing to nearly 90% at six hours. At 24 hours all amalgams reached nearly 90% or more of their seven-day compressive strength.

X-day diffraction analysis revealed that $\gamma_1$ was formed in all tested amalgams at all time periods. The formation of $\gamma_2$ was identified in two amalgams, LU and HA, with three major diffraction peaks of (001), (101) and (200). Although the (200) peak of $\gamma_2$ was identified in two ad-mixed high copper amalgams, DP and CV, the other two major peaks were not found and thus the formation of $\gamma_2$ in these amalgams could not be confirmed. $\eta'$ phase was identified in all high copper amalgams with (202), (220) and (402) peaks.

Table 4 shows the average diffraction intensities of the dominant peaks, diffracted from (411) for $\gamma_1$, (001) for $\gamma_2$ and (202) for $\eta'$, and the average intensity ratios at one, six and 24 hours to the seven-day intensity for each amalgam. Multiple regression analysis was performed with the ratio of early compressive strength as a criterion variable and the
Table 4  Average diffraction intensity (cps) of dominant peak\(^1\) and intensity ratio to seven-day intensity

<table>
<thead>
<tr>
<th>Product</th>
<th>Time (hour)</th>
<th>(\gamma_1) (cps)</th>
<th>Ratio</th>
<th>(\eta') (cps)</th>
<th>Ratio</th>
<th>(\gamma_2) (cps)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD</td>
<td>1</td>
<td>1692</td>
<td>0.74</td>
<td>90</td>
<td>0.92</td>
<td>–</td>
<td>–</td>
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<tr>
<td></td>
<td>6</td>
<td>2211</td>
<td>0.98</td>
<td>91</td>
<td>0.93</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>2387</td>
<td>1.05</td>
<td>93</td>
<td>0.95</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>168</td>
<td>2267</td>
<td>1</td>
<td>98</td>
<td>1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>DP</td>
<td>1</td>
<td>1419</td>
<td>0.65</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2025</td>
<td>0.92</td>
<td>21</td>
<td>0.53</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>2198</td>
<td>1.00</td>
<td>33</td>
<td>0.85</td>
<td>–</td>
<td>–</td>
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<tr>
<td></td>
<td>168</td>
<td>2199</td>
<td>1</td>
<td>39</td>
<td>1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CV</td>
<td>1</td>
<td>1778</td>
<td>0.71</td>
<td>44</td>
<td>0.96</td>
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<td>–</td>
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<tr>
<td></td>
<td>6</td>
<td>2431</td>
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<td>50</td>
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<td>50</td>
<td>0.98</td>
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<tr>
<td></td>
<td>168</td>
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<td>51</td>
<td>1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>LU</td>
<td>1</td>
<td>2797</td>
<td>0.71</td>
<td>–</td>
<td>–</td>
<td>723</td>
<td>0.85</td>
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<tr>
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<td>–</td>
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<td>875</td>
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<tr>
<td></td>
<td>168</td>
<td>3917</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>846</td>
<td>1</td>
</tr>
<tr>
<td>HA</td>
<td>1</td>
<td>1312</td>
<td>0.56</td>
<td>–</td>
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<td>53</td>
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<td>1.00</td>
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<tr>
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<td>168</td>
<td>2339</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>85</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^1\) Dominant peak: (411) for \(\gamma_1\), (202) for \(\eta'\), (001) for \(\gamma_2\)

Diffraction intensity ratios either of 1) \(\gamma_1\) and \(\gamma_2\) for low copper amalgams or 2) \(\gamma_1\) and \(\eta'\) for high copper amalgams as explanatory variables. Multiple regression was significant \((p<0.05)\) for both low copper and high copper amalgams, but the regression coefficients of the diffraction intensity ratios for \(\gamma_2\) and \(\eta'\) were not significant. Only the regression coefficient of the diffraction intensity ratio for \(\gamma_1\) was significant \((p<0.01)\). Single regression analysis was performed with the ratio of early compressive strength as a criterion variable and the diffraction intensity ratio for \(\gamma_1\) as an explanatory variable. These variables were examined using Pearson's coefficient of correlation, revealing a significant correlation between the ratio of early compressive strength and the diffraction intensity ratio \((p<0.01)\). The regression was also significant \((p<0.01)\) by analysis of variance. The relation between these variables and the regression equation is shown in Fig. 2. As shown in the figure, the ratio of compressive strength increased proportionally with the diffraction intensity ratio for \(\gamma_1\).

**DISCUSSION**

In the present study, all tested amalgams reached approximately 90% or more of their seven-day compressive strength at 24 hours, but the increases in the ratio of early compressive...
Fig. 2 Correlation between ratio of early compressive strength and diffraction intensity ratio for $\gamma_1$

strength from one hour to 24 hours varied with different amalgams. This was found by measurement of compressive strength at several time periods; a more detailed evaluation of the increase in the early compressive strength could be achieved by measurement of the strength with more frequent intervals such as every hour or every two hours during the initial 24 hours.

It has been recommended by Phillips\textsuperscript{1,8) that patients should be cautioned not to subject an amalgam restoration to a high degree of biting stress for at least eight hours after insertion. This recommendation seems to be based on results obtained mainly from compressive strength measurements of low copper amalgams at eight hours. The present study showed that two high copper amalgams, SD and CV, reached about 90\% of their seven-day compressive strength at six hours after mixing. This result indicates not only that these two high copper amalgams are more resistant to possible early fracture than the other tested amalgams, but also that these amalgam restorations can be exposed to biting stress earlier than the time recommended by Phillips\textsuperscript{1,8).}

As mentioned before, the increase in the early compressive strength between one hour and 24 hours varied between different amalgams, indicating that the minimum time in which biting stress can be applied differs from one product to the other. Based on this finding, it is recommended that manufacturers provide users with information about early compressive strength at several time periods. In addition, it may be necessary to amend the present amalgam standard to include early compressive strengths at more than one time period.

Among three high copper amalgams, the unicompositional amalgam, SD, and one ad-mixed amalgam, CV, showed almost the same increase in the ratio of early compressive strength from one hour to 24 hours, whereas another ad-mixed amalgam, DP, had a different result from the other two amalgams, as shown in Fig. 1. This suggests that the ratio of increase in early compressive strength is independent from differences in types of amalgam alloys. Phillips\textsuperscript{1) has pointed out that fine particles appear to produce increased early strength and the difference in the strength increase between DP and CV may be due to the
finer particle size claimed by the manufacturer.

An increase in the ratio of early compressive strength over time is theoretically related to the progress of the amalgamation reaction, which can be evaluated by the formation rate of three phases: $\gamma_1$, $\gamma_2$ and $\eta'$. With this in mind, X-ray diffraction analysis was carried out for each amalgam and the diffraction intensity ratios at one hour, six hours and 24 hours to the seven-day intensity were determined for each phase.

For the X-ray diffraction measurements, specimens were prepared by filling the shallow groove of a sample holder with amalgam mixes. Using this procedure, the peak intensities of the formed phases could be measured at different time periods without interfering with the progress of the reaction, and thus the diffraction intensity ratio of amalgamation at a given time period to the seven-day intensity could be directly determined for each specimen. Usually, a powdered specimen is used for this type of analysis, but it was not possible to obtain fine powder from one-hour specimens and prepare a flat surface with it. In addition, the effect of the powdering process on the reaction of an early amalgam is not known. For these reasons, powder was not used for the specimen preparation.

It has been shown by some studies $^{9-11}$ that high copper admixed amalgams produce $\gamma_2$ soon after mixing. Although one of the three major peaks of $\gamma_2$, a (200) peak, was found in both ad-mixed amalgams (DP and CV), the other two major peaks, (001) and (101), were not found, and thus the $\gamma_2$ for these amalgams was not included in the regression analysis. The aforementioned specimen preparation procedure may have interfered with the diffraction of the two major peaks, resulting in their absence.

Multiple and single regression analyses showed a significant linear correlation between the ratio of early compressive strength and the diffraction intensity ratio for $\gamma_1$, as shown in Fig. 2. On the other hand, the correlation between the ratio of early compressive strength and the diffraction intensity ratios for the other two phases, $\gamma_2$ and $\eta'$, was not significant. These results indicate that an increase in early compressive strength is only dependent upon the formation $\gamma_1$. The progress of the amalgamation reaction, however, is related to the formation of all three phases and the other two phases, especially $\eta'$, may also be responsible for an increase in early compressive strength. The result which showed no significant correlation between the ratio of early compressive strength and the diffraction intensity ratios for these phases may be explained by the following reasons.

The amounts of the formed $\eta'$ and $\gamma_2$ are far lower than that of $\gamma_1$,$^{9,10,12,13}$ and thus the effect of these phases on the strength is primarily that of $\gamma_1$. $\gamma_2$ is the weakest of the three phases$^{14,15}$ and may have little effect on the increase in the early strength as observed in these results. However, $\eta'$ may have some effect since this phase is the hardest of the three$^{16}$. This may be demonstrated by the X-ray diffraction data of $\eta'$. As shown in Table 4, neither, the diffraction intensity nor the intensity ratio for $\eta'$ were available at one hour for one ad-mixed high copper amalgam since the (202) peak did not appear at this stage. Although the intensity could have been 0 or several cps, the exact intensity was not measurable because of scattering from the background. For this reason, the one-hour intensity ratio for $\eta'$ of DP amalgam was not included in the regression analysis. When the one-hour intensity ratio (0 cps for DP amalgam) was included in the regression analysis, the correlation became significant ($p < 0.05$). Therefore, it is very probable that $\eta'$ has an effect on the increase in
early compressive strength. In addition, it should be noted that the other two high copper amalgams had more than a 0.9 intensity ratio for $\eta'$ at one hour. This suggests that the effect of $\eta'$ on these amalgams may have already appeared before one hour. A detailed investigation should be conducted to determine the effect of $\eta'$ formation on early strength.

CONCLUSION

In the present study the compressive strength of five different amalgams was measured at one hour, six hours, 24 hours, and seven days after mixing, and the ratios of the early compressive strength at one-, six- and 24 hours to the seven-day compressive strength were obtained. X-ray diffraction analysis was carried out for each amalgam at the same time periods as the compressive strength measurements and the diffraction intensity ratios at one, six and 24 hours to the seven-day intensity (diffraction intensity ratio) were determined for the three formed phases: $\gamma_1$, $\gamma_2$ and $\eta'$.

All tested amalgams reached about 90% or more of their seven-day compressive strength in 24 hours, but the increase in the ratio of early compressive strength from one hour to 24 hours varied with different amalgams. Two of the five tested amalgams reached about 90% of their seven-day compressive strength in six hours, which indicates that these amalgams can be subjected to biting stress sooner than the currently recommended time. A significant correlation was found between the ratio of early compressive strength and the diffraction intensity ratio for $\gamma_1$. This result indicates that an increase in early compressive strength is mainly dependent upon the formation of $\gamma_1$.

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The authors acknowledge Professor Kengo Nakamura of The Nippon Dental University, School of Dentistry at Niigata, for his valuable suggestions.

REFERENCES


歯科用アマルガムの初期圧縮強さと合金相の生成

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歯科用アマルガムの初期強さ特性を合金相の生成と関連づけて調べるために，5種のアマルガムについて1時間後，6時間後，24時間後，および7日の圧縮強さを測定し，同一時間後に各アマルガムのX線回折を行った．試験したアマルガムは，いずれも24時間後に7日の圧縮強さを約90％に達した．他は，それ以上に達した．しかし，1時間後から24時間後までの初期圧縮強さの増加はアマルガムの種類によって異していた．試験した5種のうち，2種のアマルガムは6時間後に7日後の圧縮強さの約90％に達した．7日後の圧縮強さに対する初期圧縮強さの比とγ相の逆折程度比（7日の逆折程度に対する1時間後，6時間後ならびに24時間後の逆折程度の比）の間には有意な相関が認められ，初期圧縮強さの増加は主としてγ相の生成に依存することが示された．

象牙質接着システムにおける接着領域の
平均応力および塑性域の計算モデル

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¹薬剤学研究所

本研究では，象牙質接着システムにおいてコンポジットレジンと重合する接着場所としての接着領域（bonding area）での剪断接着試験による平均応力およびnano-indentation試験で求めた変形挙動を評価することとした．はじめに，接着領域内平均応力は象牙質・接着レジン界面応力によって表わすことができた．さらに，この接着領域ではB/H0（接着領域の厚さ）比がその接着領域の厚さに依存することや塑性域の大きさを示す（b/2a）比（b；塑性域の大きさ，2a；nano-indentation試験での圧痕長さ）が接着領域の弾性率の増加とともに大きくなることを確認に示した．