Compressive Creep and Recovery of Composite Resins with Various Filler Contents in Water

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The compressive creep and the recovery of composites in water were examined. The creep strain of the composites after a 500h test linearly decreased with the increase of their filler content.

Their water sorption during testing decreased with the increase of applied stress on the composites containing low filler contents. In the composites containing high filler contents, the water sorption was almost constant for some stress levels.

The recovery of the composites after testing was significant immediately after testing. From the measurement of the water sorption of the composites, the microcrack or the craze should occur at the filler/matrix interface or in the matrix itself during the creep test, and water could diffuse to the microcrack or the craze after testing in unstressed conditions.

This would explain the increase in the water absorbed in the composites in the recovery period.

Key words: Composite resin, Compressive creep, Recovery

INTRODUCTION

The creep of the dental composite resins should be considered as being one of its most important mechanical properties, especially in the use for posterior restorations as a substitute for dental amalgam. The results of creep tests have been reported, but only few investigations conducted in water have been reported. In the oral environment, the composite resins undergo water sorption, making it important to test these materials in water. In a previous report, the authors estimated the stress of the hygroscopic expansion of a composite resin derived from the results of compressive creep at several compressive stress levels. This estimation was based on the fact that the water sorption of the composite was almost constant under some reduced compressive stress levels because of the low volumetric strain in the high filler content of the composite.

The purpose of this investigation was to confirm the constant water sorption of the composite resins with various filler contents under compressive creep at several stress levels and to measure the recovery after conducting the creep test in composite resins.

MATERIALS AND METHODS

The experimental light cured composite resins were fabricated. The resin matrix was bisGMA/TEGDMA = 6/4 by mol ratio and, as a catalyst, CQ (Camphorquinone) and DMAEMA (2-(Dimethylamino) ethyl Methacrylate) were each added at 0.5 mol%. A spheri-
cal filler (nominal diameter 12μm, density 2.0) of SiO$_2$ with silane treatment ($\gamma$-
-Methacryloxypropyl-trimethoxysilane) was used, and the composite resins containing fillers
of 30%, 50% and 70% by weight were prepared. The composite was injected by a syringe
into a 2 φmm teflon tube, and immediately irradiated for 90s*. Then, the sample was stored
in an oven at 90°C for 24h to polymerize it completely. The sample was cut by a low speed
saw $^5$, and was finally finished at a size of 2φ×10mm. Thereafter, it was stored in a
desiccator with silica gel at 37°C for at least one week.

The compressive creep test was carried out for a period of 500h with the same apparatus
in water at 37°C as previously described$^{10}$. The stresses applied were selected at 0, 1.0, 1.9, 3.
5 and 5.1 kgf/mm² stress levels within which the specimens were not fractured or buckled.
The stress level of 5.1 kgf/mm² almost corresponded to the maximum stress level of normal
occlusion$^{12}$.

The recovery and the water uptake of the specimens were carried out for a period of
500h after completion of the creep test. All the specimens were stored in distilled water at
37°C. Within 15min following the creep test, the longitudinal length of the specimen$^6$ was
measured 5 times, and the mean value was used to calculate the instantaneous recovery. At
a fixed interval, the length of the specimen was measured and the recovery was calculated
over a given period of time. The water uptake of the specimen$^+ during the testing was also
measured within 15min after completion of test, and the weight gain was indicated in terms
of the water sorption. The measurement of water absorbed on the specimen after the creep
test was also carried out at fixed intervals.

Three specimens in each condition were measured and the mean values were assessed.

RESULTS

Compressive creep strain

The creep strain and the recovery of the composites are shown in Table 1.

In unfilled resins, the creep strain at a compressive stress level of 0 kgf/mm², i. e., the
hygroscopic expansion of the unfilled resin, was about 1% expansion after a 500h test. The
creep strain at compressive stresses of 1.0 and 1.9 kgf/mm² were 1.37 and 4.25%, respectively.
However, the specimens of the unfilled resin were all fractured by about 100h at a stress level
of 3.5 kgf/mm².(Fig. 1)

In the composites containing a filler fraction of 0.21 ($V_f=0.21$), the creep strain was
decreased 1.18 and 3.46% at stress levels of 1.0 and 1.9 kgf/mm², respectively, which was an
indication of the reinforcing effect of fillers. These values were about 15-20% lower than
those of the unfilled resin. One of the specimens was buckled at a stress level of 3.5 kgf/mm²;
therefore, the curve of the creep strain with time showed the inflection between 100 and 200h,
Table 1  Creep strain and recovery of the composite resins

<table>
<thead>
<tr>
<th>Filler Content</th>
<th>Compressive Stress(kgf/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>C_{is}</td>
<td>0.34(0.25)</td>
</tr>
<tr>
<td>C_{rs}</td>
<td>+0.94(0.07)</td>
</tr>
<tr>
<td>R_{ir}</td>
<td>0.28(0.28)</td>
</tr>
<tr>
<td>R_{rs}</td>
<td>+1.19(0.15)</td>
</tr>
<tr>
<td>30(21)</td>
<td></td>
</tr>
<tr>
<td>C_{is}</td>
<td>0.50(0.11)</td>
</tr>
<tr>
<td>C_{rs}</td>
<td>+0.99(0.10)</td>
</tr>
<tr>
<td>R_{ir}</td>
<td>0.61(0.40)</td>
</tr>
<tr>
<td>R_{rs}</td>
<td>+1.26(0.13)</td>
</tr>
<tr>
<td>50(38)</td>
<td></td>
</tr>
<tr>
<td>C_{is}</td>
<td>0.09(0.03)</td>
</tr>
<tr>
<td>C_{rs}</td>
<td>+0.70(0.06)</td>
</tr>
<tr>
<td>R_{ir}</td>
<td>0.20(0.13)</td>
</tr>
<tr>
<td>R_{rs}</td>
<td>+0.94(0.20)</td>
</tr>
<tr>
<td>70(59)</td>
<td></td>
</tr>
<tr>
<td>C_{is}</td>
<td>0.44(0.08)</td>
</tr>
<tr>
<td>C_{rs}</td>
<td>+0.34(0.06)</td>
</tr>
<tr>
<td>R_{ir}</td>
<td>0.52(0.09)</td>
</tr>
<tr>
<td>R_{rs}</td>
<td>+0.52(0.01)</td>
</tr>
</tbody>
</table>

unit: %, ( ): S D, and + values mean expansion

C_{is}: instantaneous creep strain
C_{rs}: creep strain after 21 days (500h) creep test
R_{ir}: initial rapid recovery after creep test
R_{rs}: total strain of 20 days after creep test

Fig. 1 Creep curves of unfilled resins under several compressive stress levels.
as shown in Fig. 2.

The creep strain of the composites containing $V_f = 0.38$ largely decreased to 0.59 and 2.1% at stress levels of 1.0 and 1.9 kgf/mm², respectively, which were 40–50% lower values than of the unfilled resin. In particular, a creep strain of 9.42% was recorded at a stress level of 5.1 kgf/mm², however the creep curve did not show the same inflection as that shown in Fig. 3.

The creep strain of the composites containing $V_f = 0.59$ at a stress levels of 1.9 kgf/mm² was 0.91%, which was about 80% lower than that of unfilled resin. In addition a low creep strain of 2.47% was recorded at a stress level of 5.1 kgf/mm². In this composite the compressive creep at a stress level of 1.0 kgf/mm² was not conducted because of the particularly low creep strain that had been obtained.(Fig. 4)

The instantanenous creep strain ($C_{is}$) of the composites with the same filler content increased with an increase of the stress level, but the clear linear regression between the instantaneous strain and the stress level could not be obtained.

Recovery after the creep test

The rate of the initial rapid recovery ($R_{ir}$) as shown in Table 1 increased with the compressive stress, but there was not clearly proportional relation between the $R_{ir}$ and the compressive stress.

The 500h recovery after the creep test ($R_{is}-C_{ts}$) caused the specimens to expand by about 0.2% in hygroscopic expansion at a stress level of 0 kgf/mm².

The specimens which had buckled or became largely deformed showed significant

![Fig. 2 Creep curves of the composites with $V_f = 0.21$ under several compressive stress levels.](image-url)
recovery. The creep strain and recovery curve of the composites containing $V_r=0.21$ at a stress level of 3.5 kgf/mm² are shown in Fig. 5. The black circles of the recovery curve show the measuring points, and the points a, b and c denoted on the recovery curve correspond to the photos of the specimen. The largest recovery containing an initial rapid recovery was
revealed just after completion of the creep test; thereafter, the rate gradually decreased with time. Photo a shows the specimen which buckled extensively after the creep test, but recovered significantly 2 day later (photo b) and became almost straight after 20 days (photo c).

Fig. 5 The creep and the recovery curves of a composite with $V_r = 0.21$ under 3.5kgf/mm$^2$ stress levels. In this figure, a, b and c correspond with the photos of the specimen.
The typical creep strain and recovery curves of the composite \( (V_f=0.38) \) are shown in Fig. 6 under 5.1 kgf/mm\(^2\) stress levels.

![Creep and Recovery Curves](image)

(a) in water

(b) in a dry condition

Table 2  Water sorption of the composite resins

<table>
<thead>
<tr>
<th>Filler Content</th>
<th>0</th>
<th>1.0</th>
<th>1.9</th>
<th>3.5</th>
<th>5.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt% (vol%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3.84(0.12)</td>
<td>3.68(0.04)</td>
<td>3.39(0.17)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( m_{01} )</td>
<td>3.80(0.10)</td>
<td>3.96(0.04)</td>
<td>3.86(0.17)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( m_{41} )</td>
<td>0.04(0.03)</td>
<td>0.28(0.09)</td>
<td>0.46(0.01)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30(21)</td>
<td>3.24(0.05)</td>
<td>3.12(0.11)</td>
<td>3.06(0.10)</td>
<td>3.00(0.10)</td>
<td></td>
</tr>
<tr>
<td>( m_{01} )</td>
<td>3.47(0.04)</td>
<td>3.43(0.06)</td>
<td>3.56(0.19)</td>
<td>3.76(0.05)</td>
<td></td>
</tr>
<tr>
<td>( m_{41} )</td>
<td>0.23(0.04)</td>
<td>0.31(0.05)</td>
<td>0.50(0.09)</td>
<td>0.77(0.08)</td>
<td></td>
</tr>
<tr>
<td>( m_{45} - m_{21} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50(38)</td>
<td>2.23(0.04)</td>
<td>2.18(0.03)</td>
<td>2.10(0.11)</td>
<td>2.12(0.10)</td>
<td>2.40(0.25)</td>
</tr>
<tr>
<td>( m_{01} )</td>
<td>2.50(0.08)</td>
<td>2.41(0.04)</td>
<td>2.44(0.12)</td>
<td>2.58(0.12)</td>
<td>3.23(0.14)</td>
</tr>
<tr>
<td>( m_{41} )</td>
<td>0.28(0.05)</td>
<td>0.23(0.04)</td>
<td>0.34(0.02)</td>
<td>0.47(0.03)</td>
<td>0.83(0.18)</td>
</tr>
<tr>
<td>( m_{45} - m_{21} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70(59)</td>
<td>1.15(0.04)</td>
<td>1.16(0.03)</td>
<td>1.13(0.13)</td>
<td>1.21(0.06)</td>
<td></td>
</tr>
<tr>
<td>( m_{01} )</td>
<td>1.28(0.08)</td>
<td>1.23(0.03)</td>
<td>1.33(0.10)</td>
<td>1.40(0.08)</td>
<td></td>
</tr>
<tr>
<td>( m_{41} )</td>
<td>0.13(0.04)</td>
<td>0.07(0.01)</td>
<td>0.20(0.03)</td>
<td>0.22(0.05)</td>
<td></td>
</tr>
<tr>
<td>( m_{45} - m_{21} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table unit: wt\%, (): SD

\( m_{01} \): water sorption after 21 days (500h) creep test

\( m_{41} \): water sorption after 41 days

\( m_{45} - m_{21} \): water sorption of 20 days after creep test
Fig. 6. The specimen in water after the test (Fig. 6 (a)) was seen to be buckled almost as much as the one in Fig. 5. The recovery curve of a dry specimen was continuously recorded by an electromicrometer in the same manner as for hygroscopic expansion measurement. The creep strain after 500h of a composite resin in water was about 4 times larger than that in the dry condition.

Water absorbed in composites

The water sorption of the composites is shown in Table 2. The water sorption during the creep test was labeled as $m_{21}$. The values of $m_{21}$ were obviously decreased with the increase of compressive stress levels in unfilled resins and for the composites of low volume fractions of filler content.

The measured values of $m_{41-21}$ represented the water sorption during the recovery period.

![Fig. 7](image1.png)

Fig. 7 The water uptake after the creep test of the composite shown in Fig. 5.

![Fig. 8](image2.png)

Fig. 8 The water uptake after the creep test of the composite shown in Fig. 6(a).
and increased with the increase of the compressive stress. The rates of water sorption after the creep test (at 500h) and in the recovery process (from 500–1000h) are shown in Fig. 7 and 8. The rate of absorbed water of the composites in Figs. 7 and 8 were of the same composites as shown in Figs. 5 and 6 (a), respectively. The absorbed water of the specimen rapidly increased during first few days of the recovery process and, thereafter, the rate of absorbed water decreased with time. This process of rapid increase of absorbed water in composites coincided with the period during which the largest recovery of the dimensional change in composites was seen.

**DISCUSSION**

**Creep and recovery**

Linear regressions were obtained on the creep of the composite resins with the same filler contents between the creep strain after 500h and the compressive stress, respectively, except for the specimen showing largest deformation (Fig. 9). The obtained results were also consistent with the results reported previously\(^{10}\). Especially the absorbed water on the composites with \( V_f = 0.59 \), indicated by \( m_21 \) in Table 2, was almost constant within a compressive stress level of 5.1 kgf/mm\(^2\). The linear regression of the composites was obtained as follows;

\[
y = 0.267 - 0.538x
\]

where \( y \) : creep strain after 500h, \( x \) : compressive stress level.

The hygroscopic expansion could be estimated at 0.50 kgf/mm\(^2\), where \( y = 0 \) was applied to the equation. The relative value obtained approximated the results reported previously\(^{10}\).

The relationship between the creep strain after 500h and \( V_f \) at stress levels of 1.0 and 1.

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![Graph showing linear regressions obtained between the strain after 500h and the applied compressive stress level.](image-url)
9 kgf/mm² are shown in Fig. 10. Under these stress levels, inverse linear regressions were obtained between the creep strain and \( V_f \). When the creep strain was zero, \( V_f \) values were 0.75 and 0.72, respectively, and were almost consistent with the maximum value, 74%, derived from the close-packed spherical particles.

The water absorbed in the resin has been known to have a plasticizing effect\(^8\) and to lead to an increase in the creep strain\(^3,4,8,9,11\). In addition, the recovery process, i.e., the period of significant recovery (500-600h in Figs. 6 (a) and 7) was in keeping with the period of the rapid increase in water sorption (Figs. 7 and 8). The water absorbed in the composites could play some role to promote their recovery. However, the residual strain on the composites had been occurred 20 days after the completion of the test. These results were same as those reported by Papadogianis \textit{et al.}\(^3,4\) and Tabata\(^11\).

Water absorbed in the composites

The water absorbed in the composite resins during the creep test, \( m_{a1} \), decreased with the increase of the applied stress except for the composites with \( V_f = 0.59 \). This was dependant upon the decrease in volume of the composites in accordance with the increase of applied stress. In the composites with high filler content, such as \( V_f = 0.59 \), the creep strain was very low at some stress levels due to the reinforcing effect of the filler; therefore, the water absorbed should be almost constant.

For example, the interparticle spacing of the filler in the composites was calculated as shown in Table 3\(^13\). In this case, the filler diameter was 12 \( \mu \)m and the interparticle spacing was 5.6 \( \mu \)m when \( V_f = 0.59 \). Therefore, matrix were present in a form like a thin glue. It seems reasonable to stated that the water absorbed in the composites was almost constant at some stress levels.

The water absorbed after the creep test, \( m_{a1} \), was increased in relation to the applied stress during the creep test with even an increase in absorbed water being shown in such a low stress level as that of 1.0 kgf/mm². The rate of water absorption was significantly
increased immediately after testing, and thereafter this rate gradually decreased. The craze or the microcrack would have occurred at the matrix/filler interface or the matrix itself in the composites during testing. The composites were constantly under the stress during the test, and after the test, when they were unstressed, water could then penetrate into any existing craze or microcrack, and thus the rate of water absorbed would be increased. The example of the craze formation was shown in the creep of acrylic denture consisting of PMMA beads and crosslinked MMA. Due to the heterogeneous composites of the materials, the craze formation occurred in weaker PMMA beads by means of heterogeneous deformation during the creep test.

It should be recognized that the deterioration of the composites was dependant upon the formation of a microcrack or craze in the composites under stress (equivalent to the masticatory stress in the oral environment).

### CONCLUSIONS

The compressive creep and the recovery of composite resins in water were examined. The creep strain of the composites after a 500h test linearly decreased with the increase of filler contents in the composites.

The water sorption of the composites during testing decreased with the increase of the applied stress on the composites containing low filler contents. In the composites containing high filler contents, the strain of the composites was reduced, because of the low volume fraction of the matrix and reinforcing effect of fillers, therefore, the water sorption of the composites was almost constant in some stress levels.

The rate of recovery of the composites after testing was significantly rapid immediately after testing. The water sorption of the composites also increased during the same period of significant recovery. The water sorption of buckled specimens during testing also increased significantly in the same period.

A microcrack or craze could occur at the filler/matrix interface or the matrix itself during the creep test, after which water is diffused to the microcrack or the craze during recovery. The increase in the water absorbed in the composites in the recovery process could be explained by this possibility.
REFERENCES


した試料と合着しない試料を製作した。負荷波形としてサイン波、矩形波、三角波について検討した。PMMA 試料を用いたため、亀裂の発生が観察でき、亀裂発生までの繰り返し応力回数と、試料の破断までの回数を記録した。破断面を観察し、破壊疲労を示す表面性状が観察された。負荷波形としては、測定値の変動係数が小さい三角波形の負荷が望ましいと考えられた。疲労強度はセメント合着により改善され、セメントの種類によりその程度は異なった。しかし、亀裂発生から破壊までに与えられた繰り返し応力の回数はセメントの種類の影響を受けなかった。

歯科修復物の辺縁封鎖性の新しい評価法

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辺縁封鎖性評価のための新しい試験装置を開発した。この試験装置は熱サイクル負荷のための流路と満洩検出のための流路からなっており、両流路は被検修復歯で隔絶される。熱サイクル負荷系にはトレーサーとして使用したローダミン B の冷熱水浴液を循環させており、6 つの電磁弁の開閉で試験片に熱サイクルを与えられる。試験片に熱サイクルを与えながら、検出系を循環する蒸留水中に挿入してくるトレーサー量を定期的に分光光度計で測定した。銀合金インレー修復、アルミウムあるいはグラスアイオノマー充填修復について満洩デークを実験式で解析したところ、満洩挙動をかなりよく説明でき、熱サイクルに対する完全封鎖保持期間として辺縁封鎖性を推定評価できた。

Ni-Ti 合金製造体の機械的性質に及ぼす組成および純度の影響

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Ni-Ti 合金製造体の機械的性質および変態点に及ぼす組成およびチタンの純度の影響について、引張試験および示差走査熱量測定により検討した。鍛造用インゴットの組成は、チタンの原子パーセントで 49.0 から 49.2 % とし、比較的純度の高い 3 種類のチタンを材料として使用した。

その結果、Ni-49.0 Ti はやや脆い性質を示し、Ni-49.2 Ti は低い見かけの耐力および高い伸びを示した。残留ひずみは、チタンの組成が高くなるほど増加した。また、チタンの純度のわずかな低下が、Ni-Ti 合金の機械的性質および変態点に影響を及ぼした。すなわち、変態点が下がることにより、見かけの耐力が高くなり、残留ひずみが小さくなり、伸びが減少した。

フィラー含有量の異なるコンポジットレジンの水中浸漬下における圧縮クリープと回復

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フィラー含有量の異なるコンポジットレジンを作製し、その圧縮クリープと回復について水中浸漬下で研究した。500 時間後のコンポジットレジンのクリープひずみはコンポジットレジン中でフィラー含有量の増加にと
光重合コンポジットレジンの残留モノマー量およびベンダント二重結合量

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コンポジットレジン硬化体から切り出した薄切片の微小部位におけるIRスペクトルを顕微赤外測定装置を組み込んだFTIRを用いて測定し、未反応二重結合量（UBD）を求めた。さらにこの薄切片から残留モノマーを溶出させた後の同一部位でのIRスペクトルをも測定し、ベンダント二重結合量（PDB）を求めた。また、この両二重結合量の差から溶出した二重結合量（EDB）を求め、残留モノマー量を推定した。

UDB, PDB, EDBともに深さ方向に対して著しく変化した。PDBは光照射時間にかかわらず、得られた硬化深さの7〜8割の深さまで、一定の値を示した。この部分におけるコンポジットはより密に架橋されていると推察される。モノマー組成によって異なるが、光重合された硬化体内には25〜40％の二重結合がベンダント二重結合として存在することが示唆される。

ペースト・ペーストタイプ覆層用セメントの熱的性質

深瀬康公, 斉藤仁弘, 掛谷昌宏, 大橋正敬, 西山 貞
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4種市販品、ペースト・ペーストタイプ覆層用セメントおよびヒト象牙質の熱的性質についての測定を行なった、測定はヒト象牙質が基準であるとき、測定結果を用いた検討をした。全てのセメントにおいて熱伝導率は、象牙質と同等か、それ以下の値であった。また、この値から1 mmのセメントの厚さを象牙質の厚さに換算すると、0.97〜2.10 mmに相当し、象牙質よりも熱刺激の遮断性が同等もしくは優れていることが判明した。

生物利用におけるマイクロ波加熱出力のコントロール

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マイクロ波による加熱を利用する際には、得られる温度を知るとともに温度調節のできることが望ましい。そ