Influence of Storage Humidity on Hardness of Light-cured Glass Polyalkenoate Cements

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The influence of storage in various environments on the hardness of four commercial light-cured glass polyalkenoate cements and one conventional glass polyalkenoate cement was investigated. Specimens with or without light exposure were stored for 7 days in different humidity conditions. A hardness tester with a diamond indenter point was used and Vickers hardness numbers under minor load conditions were determined. Non-light-exposed specimens did not increase in hardness in either dry or wet conditions. Light-exposed specimens became harder with time in dry conditions. Light-exposed specimens stored in wet conditions hardened only slightly. To investigate the effects of humidity, some light-exposed specimens stored first in wet conditions were stored another 7 days in dry conditions. They became as hard as those first stored in dry conditions for 7 days. It is concluded that the hardness of these cements corresponds with the humidity of the storage environment.

Key words : Glass polyalkenoate cement, Vickers hardness, Immersion test

INTRODUCTION

The primary setting reactions of conventional glass polyalkenoate cements are an acid-base and a sol-gel reaction^{1–3)}. The mechanical properties of these cements change with time as the reactions continue^{4–8)}. Visible light-cured glass polyalkenoate cements contain light-curing resin systems, generally 2-HEMA and camphorquinone^{9,10)}. Light-curing polymerization is incorporated into the conventional setting system⁹⁾. According to manufacturers, light curing allows quick stabilization of the material, greatly reducing water sensitivity during early setting. Many investigations of mechanical properties of these cements have been carried out with storage in water to simulate conditions in the oral cavity^{5–7,11)}. In recent years, however, glass polyalkenoate cements for fillings have come into wide use in clinical applications. Fillings are located dispersively and encounter different humidities in the oral cavity. In this study, we focused on the influence of storage conditions, especially humidity, on the cement's mechanical properties. The hardnesses of the surfaces under different preparation conditions, namely different light-curing and storage humidity conditions, were determined.

MATERIALS AND METHODS

Table 1 shows the name, manufacturer, lot, mixing time, and exposure time of the investigat-

ed cements. FIIL and VLC are cements for fillings. FLC and VTB are for liner/base. KFA is a conventional non-light-cured glass polyalkenoate cement for fillings.

A cylindrical plastic mold (diameter 7 mm, height 1.5 mm) was placed between a mixing paper and a microscopic glass slide with a transparent polyester film. The mold was filled with mixed cement and then exposed through the polyester film with the visible light curing device*. Non-light-exposed specimens were also prepared.

The specimens were removed from the mold at 3 minutes after the start of mixing. They were stored in shaded light at 36% RH (relative humidity) at 37°C, 100% RH at 37°C, distilled water at 37°C, and 50% RH at 23°C. Non-light-exposed specimens were also stored at 36% RH at 37°C and 100% RH at 37°C. Vickers hardness numbers under a load of 300g were determined with a hardness tester** at periods from 20 minutes to 7 days.

The hardness tester in this study allowed the indentation to be observed through the diamond indenter point while under load. With a conventional hardness tester, the indentation recovers after releasing the load on viscoelastic materials such as resin, thus providing a reading in excess of the true hardness¹²⁾. In contrast, the device used here has many advantages for testing cements, including resin systems: It does not matter whether the material is viscoelastic or not, because the load is not removed; the interface between the indenter and the specimen is clearly distinguished, readily to observe the small indentation on the resin or the ceramic with high light transmittance; the specimen can be continuously tested without breaking because of the small indentation and light load¹³⁾. When the indentation diameter was greater than 300 μm , the load was reduced to 50g or 100g. The averages and standard deviations were obtained from 15 indentations on three specimens of each condition.

Some specimens were placed in different storage conditions after 7 days. Fig. 1 shows a flow chart of the experimental procedure. The specimens stored first at 36% RH at 37°C were subsequently stored in water at 37°C for another 7 days. The specimens stored first at 100% RH and in water at 37°C were then stored at 36% RH at 37°C for 7 more days.

Table 1 Materials used.

Code	Material	Lot. No.		Mixing ratio (g/g)	Mixing time (s)	Exposure time (s)
		Powder	Liquid			
FIIL	Fuji II LC ¹	300724	040821	3.0	20	20
VLC	Vari Glass VLC ²	9211192	921201	3.0	30	40
FLC	Fuji LINING LC ¹	030921	091021	1.4	20	30
VTB	Vitrebond ³	2183 R	227	1.4	15	30
KFA	Ketac-Fil Aplicap ⁴	044/19 #	—	3.0	5 ##	—

¹ GC, Tokyo, Japan

² Caulk, Delaware, USA

³ 3M, MN, USA

⁴ Espe, Seefeld, Germany # Capsule ## Mixing machine

* Translux CL, Kulzer GmbH, Wehrheim, Germany

** Optidur, Göttfert GmbH, Buchen, Germany

Fig. 1 Flow diagram of experimental procedure.
The narrow-lined squares represent dry conditions and the broad-lined squares represent wet conditions.

Hardnesses were then determined, and the student's t-test was used to test for significant differences between means.

RESULTS AND DISCUSSION

When the conventional hardness tester is used with viscoelastic materials, the indentation recovers and becomes smaller after the load is removed. Thus the Brinell hardness that is measured by the depth of indentation, the Knoop hardness that uses a long diagonal line, and the Vickers hardness with a major load are often used to correct for this effect. With the tester used in this study, on the other hand, the hardness is easily observed under a minor load. The diameters of the indentations in this study were 100 to 300 μm . This corresponds to indentation depths of 14 to 43 μm . The real surface hardness can also be determined this way. This surface hardness correlates with degradation in the oral cavity caused by friction against food or an opposing tooth cusp. The Vickers hardness is an appropriate parameter for comparison with other filling materials that are classified with Vickers hardness numbers in many standards. The surface hardness cannot be measured under a major load, but this study's hardness tester may be used to determine the hardness of glass polyalkenoate cement.

Figs. 2, 3 and 4 show the hardness curves over time for 7 days. For VLC, non-light-exposed specimens were not prepared because this cement needs light to set. KFA is a conventional cement, and all specimens were non-light-exposed. Non-light-exposed specimens of FIIL, FLC, and VTB did not quite set in either dry or wet conditions; it is indispens-

able for these cements to be cured by light radiation.

Many reports⁴⁻¹¹⁾ have shown that the increase of hardness on aging indicates a continuation of the reaction after exposure to the curing light. A similar pattern was seen in this study. The specimens in dry conditions, in particular, became harder than those in wet conditions upon continued storage. The hardnesses of these cements were determined by storage condition, *i. e.* humidity. Siliceous gels are precipitated around glass particles during setting in conventional glass polyalkenoate cement^{1,14)}. It has been reported that this difference in mechanical behavior between dry and wet conditions is typical of hydrogels^{15,16)}

Fig. 2 Hardness change curves of filling cements on aging in various storage conditions.

-○- : 36% RH at 37°C, -□- : 50% at RH 23°C, -●- : 100% RH at 37°C, -■- : water at 37°C, -△- : without light exposure at 36% RH at 37°C, -▲- : without light exposure at 100% RH at 37°C.

At seven days (168 h), the specimens which were stored at 36% RH at 37°C were placed in water at 37°C, and the specimens which were stored at 100% RH at 37°C and in water at 37°C were changed to 36% RH at 37°C for another seven days.

Fig. 3 Hardness change curves of liner/base cements on aging in various storage conditions. See Fig. 2 for legend.

To investigate the effect of humidity, some specimens were placed in different storage conditions after 7 days. Table 2 and Figs. 2-4 show the hardness changes during the second

Fig. 4 Hardness change curves of the conventional cement on aging in various storage conditions.
See Fig. 2 for legend.

Table 2 Hardness by change of storage condition (HV, Mean(SD)).

Code	Dry	Water	Change %
FIIL	77.93 (4.39) ^{a,b}	35.67 (2.10) ^c	-54.23
VLC	69.40 (7.77) ^{A,d,e}	29.66 (2.91) ^{f,g}	-57.26
FLC	56.79 (4.43) ⁱ	14.13 (0.64) ^j	-75.12
VTB	69.87 (6.40) ^{A,k}	9.567 (0.620)	-86.31
KFA	120.1 (6.7) ^m	102.2 (7.4) ^{n,o}	-14.90
	Wet	Dry	
FIIL	42.51 (2.59)	80.01 (4.49) ^a	88.21
VLC	31.06 (3.27) ^{f,h}	69.79 (5.16) ^{c,d}	124.7
FLC	16.58 (2.62) ^{B,j}	57.63 (1.99) ⁱ	247.6
VTB	15.38 (2.70) ^{B,i}	66.98 (7.18) ^{C,k}	335.5
KFA	92.61 (8.08) ⁿ	116.5 (4.1) ^{m,o}	25.80
	Water	Dry	
FIIL	32.40 (4.28) ^{D,c}	74.31 (4.47) ^b	129.4
VLC	29.56 (1.15) ^{D,g,h}	61.82 (5.42) ^e	109.1
FLC	10.47 (1.26)	34.02 (1.72) ^F	224.9
VTB	13.96 (1.28) ^{E,i}	53.57 (4.02)	283.7
KFA	13.51 (1.28) ^E	30.22 (4.03) ^F	123.7

Mean values designated with the same superscript letter are not statistically different at $p < 0.05$.

Uppercase letters indicate no difference within conditions per test ; lowercase letters indicate no difference within materials.

Dry : 36% RH at 37°C, Water : in water at 37°C, Wet : 100% RH at 37°C.

7 days. The hardness of the specimens stored first at 100% RH increased in dry conditions. The hardness of the specimens stored first in dry conditions decreased in water. It is concluded that the hardness of these cements is related to the humidity of the storage conditions.

The specimens stored first in water did not harden further, unlike those stored first at 100% RH. Fluoride release from light-cured glass polyalkenoate cement has reported to equal that of conventional cements^{11,17-19}, and uptake of water has been observed^{19,20}. It is reported that the acid-base reaction is delayed after light exposure¹⁰, and the unreacted Al and Na ions dissolve into the water²¹. This dissolution of elements prevented an increase in hardness by further storage in dry conditions. KFA showed the smallest hardness after initial storage in water followed by 36% RH. It is clear that light-cured cements are not as severely influenced by storage in water as are conventional cements.

The water sorption values ($\mu\text{g}/\text{mm}^3$ (SD)) of cements after 7 days were: FIIL (140(8)), VLC (85(4)), FLC (249(9)), and VTB (255(12))²². FLC and VTB exhibited high water sorption. The hardness of these specimens in water was much lower than at 36% RH. It is suspected that these cements in water showed so little hardness that the water was allowed to swell them and act as a plasticizer^{23,24}. Wilson *et al.*⁵) reported that the strength of dental cements as directly related to the ratio of “non-evaporable” to “evaporable” water. This observation is in agreement with their results. We conclude that these light-cured cements show the same behavior with respect to their water content as conventional cements.

Changes in mechanical properties caused by varied water content may take place in the oral cavity, as in the case of a mouth breather. This may hasten the degradation of cements; cement fillings should thus be carefully observed over time in clinical usage.

CONCLUSION

In this study, we determined Vickers hardness numbers of four light-cured glass polyalkenoate cements in various storage conditions. The hardness of the specimens increased with time in dry conditions. The hardness of cements stored in high humidity and in water did not increase. The hardness of cements stored in dry conditions after initial storage in wet conditions increased, but cements stored in water after storage in dry conditions decreased in hardness. It is clear that the hardness of cements is controlled by the humidity of the storage condition. Fillings using these materials, as well as conventional glass polyalkenoate cements, should be carefully observed in clinical usage.

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レジン系仮封材がレジンセメントの歯質接着強さに及ぼす影響

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この研究は、レジン系仮封材がレジンセメントの歯質接着強さに及ぼす影響について、400本の牛歯を用い、4種レジン系仮封材と4種レジンセメントを使用して実験を行ったものである。エナメル質では、いずれのレジン

系仮封材もレジンセメントの歯質接着強さを減少させていなかった。象牙質では、いずれのレジン系仮封材も4-META/MMA-TBB系レジンセメントを除くレジンセメントの歯質接着強さを減少させていた。

光重合型ポリアルケノエートセメントの硬さに及ぼす保存湿度の影響

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4種の市販光重合型ガラスポリアルケノエートセメントと1種の従来型ガラスポリアルケノエートセメントの硬さに及ぼす保存環境の影響を検討した。このため光照射有りまたは無しの試料を異なる湿度の環境下で7日間保存した。ダイヤモンド圧子を通して圧痕を観察できる硬さ試験機を用いて低荷重を負荷した状態でのビッカース硬さを測定した。その結果光照射無しの試料は乾燥と湿潤環境下で硬さは増加しなかった。光照射有りの試料

は乾燥環境下で経時的に硬くなったが、湿潤環境下ではほとんど増加しなかった。湿度の影響をさらに検討するため、最初湿潤環境に保存した試料をさらに続いて7日間乾燥環境に保存した。保存後セメントは乾燥環境に最初7日間保存した試料と同程度まで硬くなった。したがって本セメントの硬さは保存環境の湿度に関係していると考えられる。