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Der Einfluss von Polymerisation, Lagerungsbedingung und Materialzusammensetzung auf die mechanischen Eigenschaften zweier Nano-Hybrid-Komposite

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1. Einleitung

Es liegt im Interesse der Zahnärzte, den Zeitaufwand für die Versorgung einer Kavität mit einer Kompositfüllung möglichst gering zu halten. Dementsprechend ist eine Reduktion der Polymerisationszeit zur Lichthärtung dentaler Komposite stets ein interessantes Thema. Infolge der konsequenten Weiterentwicklungen im Bereich der lichtemittierenden Dioden (LED) konnte die Leistung von LED-Polymerisationslampen der zweiten und dritten Generation deutlich erhöht werden.[A-1] Dies führte dazu, dass kürzlich manche Hersteller von modernen LED-Polymerisationslampen eine ausreichende Polymerisationszeit von 5 Sekunden propagierten, obwohl von vielen Herstellern immer noch eine Polymerisationszeit zwischen 20 und 40 Sekunden empfohlen wird. Basierend auf der physikalischen Berechnung der Strahlungsenergie, wonach eine Reduktion der Strahlungsdauer durch einen Anstieg der Strahlungsintensität kompensiert werden kann, warben die Hersteller damit, dass eine 5-sekündige Polymerisationszeit mit der LED-Polymerisationslampe einer Polymerisationszeit von 40 bis 60 Sekunden mit einer Quarz-Wolfram-Halogen-Lampe entspricht. Auch wenn die Formel zur Berechnung der Strahlungsenergie grundsätzlich gültig ist, so hat sich dennoch gezeigt, dass dieselbe Energiemenge bei einer Polymerisation mit kürzerer Belichtung und höherer Intensität zu reduzierten mechanischen Eigenschaften und geringeren Konversionsraten der Komposite führt.[A-2,3]

Die Qualität der Polymerisation von Kompositen wird üblicherweise vorab in Labortests nach ISO Standards überprüft. Die ISO Norm 4049 erfordert für die Messung der makromechanischen Eigenschaften wie der Biegefestigkeit, dass die 2 mm dicken Prüfkörper von zwei Seiten (oben und unten) polymerisiert werden. Somit stellt sich die Frage, ob diese zweiseitige Lichthärtung gerade bei niedrigeren Polymerisationszeiten zu besseren makromechanischen Eigenschaften führt, als dies unter klinischen Bedingungen, bei denen eine Lichthärtung des Komposits oft nur von einer Seite aus möglich ist, der Fall wäre. Darüber hinaus bleibt zu untersuchen, welchen Einfluss gerade bei kurzen

Polymerisationszeiten eine längere Lagerung, als die von der ISO Norm 4049 vorgeschriebenen 24 Stunden, auf die Materialeigenschaften besitzt.

Verschiedene Studien haben festgestellt, dass die Lagerungsbedingungen die mechanischen Eigenschaften sowohl stärker als auch schwächer beeinflussen können.[B-12-15] Das Ausmaß des Einflusses ist abhängig vom untersuchten Komposit. Während eine Lagerung in Alkohol häufig zu signifikant reduzierten Ergebnissen im Bereich der mechanischen Eigenschaften Biegefestigkeit und Vickershärte führte,[B-15,16] war der Unterschied zwischen einer Lagerungen in Wasser oder künstlichem Speichel nicht signifikant.[B-12,13] Einige Studien haben gezeigt, dass die Dauer der Lagerung einen erheblicheren Einfluss auf die mechanischen Eigenschaften der Komposite besitzt als das Medium der Lagerung.[B-12-14] Für Studien in denen transluzente Komposite und deren Alterung untersucht wurden, war Filtek Supreme XT Translucent (3M ESPE, St. Paul, MN, USA) ein häufig ausgewähltes Material.[B-12,14] Die Ergebnisse dieser Untersuchungen zeigen, dass dieses transluzente Komposit andere charakteristische Eigenschaften aufwies als das Vergleichsmaterial Filtek Supreme XT Body des gleichen Komposit-Systems. So ergab sich für Filtek Supreme XT Translucent eine höhere Volumenschrumpfung und Wasseraufnahme als für das Vergleichsmaterial, was mit großer Wahrscheinlichkeit auf den höheren Anteil der organischen Kompositmatrix von Filtek Supreme XT Translucent zurückzuführen ist.[B-12]

Die Materialzusammensetzung von Kompositen hat eine direkte Auswirkung auf die Transluzenz des Komposites, da sie mit zunehmender Füllstoffmenge abnimmt.[B-5] Die Transluzenz nimmt außerdem ab, wenn die Differenz der Brechungsindizes von organischer Kompositmatrix und anorganischer Füllstoffe ansteigt.[B-3,4] Wird die Materialzusammensetzung variiert, um verschiedene Transluzenzen innerhalb eines Komposit-Systems zu erzielen, so hat dies wiederum Auswirkungen auf die mechanischen Eigenschaften.

Ziel der vorliegenden Arbeit – bestehend aus zwei publizierten Fachartikeln – war es, den Einfluss von Polymerisation, Lagerungsbedingung und Materialzusammensetzung auf die mechanischen Eigenschaften zweier Nano-Hybrid-Komposite zu untersuchen, wofür zwei Komposite des Nano-Hybrid-Komposit-Systems IPS Empress Direct (Ivoclar Vivadent, Schaan, Liechtenstein) ausgewählt wurden. Der erste Fachartikel befasst sich mit dem Dentinkomposit Dentin A3, während die zweite Publikation auf den Untersuchungsergebnissen des transluzenten Komposites Trans Opal beruht. Beide Komposite unterscheiden sich hinsichtlich der Materialzusammensetzung deutlich voneinander, da das transluzente Komposit Präpolymere und hochdisperses Siliziumdioxid anstatt Barium-Aluminium-Fluorosilikatglas und Ytterbiumtrifluorid enthält.

Um den Einfluss von Polymerisationszeit, -art und Lagerungsbedingung quantifizieren zu können, wurden von beiden Kompositen 2x2x16 mm große Prüfkörper hergestellt und mit der LED-Polymerisationslampe Elipar Freelight 2 (3M ESPE, Seefeld, Deutschland; 1261 mW/cm^2) bei vier verschiedenen Polymerisationszeiten (5, 10, 20 und 40 Sekunden) lichtgehärtet. Die Art der Polymerisation erfolgte für beide Komposite beidseitig gemäß der ISO Norm 4049. Für den Dentinkomposit wurde eine zusätzliche Versuchsreihe nur einseitig polymerisiert, um die klinischen Bedingungen zu simulieren. Nach 24-stündiger Lagerung in destilliertem Wasser bei 37°C wurde ein Drittel aller Prüfkörper ausgewertet, während der Rest zunächst 5000 Zyklen in einem Thermowechselbad von 5°C und 55°C bei einer Eintauchzeit von je 30 Sekunden durchlief. Im Anschluss wurden die restlichen zwei Drittel zu gleichen Teilen für vier Wochen bei 37°C in einer Ethanol-Wasser-Mischung (1:1) oder künstlichem Speichel gelagert.

Die Bestimmung der makromechanischen Eigenschaften Biegefestigkeit und Biegemodul erfolgte im 3-Punkt-Biegeversuch. Anschließend wurden die mikromechanischen Eigenschaften Vickershärte, E-Modul und Kriechen in einem Universalhärteversuch (Fischerscope H100C, Helmut Fischer GmbH, Sindelfingen, Deutschland) ermittelt. Zusätzlich wurde die Konversionsrate beider Komposite an der Oberfläche und in 2 mm Tiefe

für die vier verschiedenen Polymerisationszeiten (5, 10, 20 und 40 Sekunden) mit Hilfe eines Fourier-Transformations-Infrarotspektrometers (Nexus, Thermo Nicolet, Madison, WI, USA) bestimmt. Hierfür wurde der nichtpolymerisierte Komposit direkt auf dem Messkristall lichtgehärtet und eine 5-minütige Messung der C=C-Doppelbindungen in Echtzeit durchgeführt. Die statistische Auswertung der Messergebnisse erfolgte unter Verwendung ein- und mehrfaktorieller Varianzanalysen mit einem Tukey HSD Post-hoc-Test (α=0,05) und partieller η^2-Statistik. Darüber hinaus wurde für die Werte der Biegefestigkeit eine Weibull-Analyse erstellt.

Die Materialzusammensetzung zeigte einen erheblichen Einfluss auf die mechanischen Eigenschaften des Komposites, da das Dentinkomposit in allen gemessenen Eigenschaften deutlich höhere Werte erzielte als das transluzente Komposit. Hinsichtlich der Lagerungsbedingung führte Alkohol bei dem gewählten Signifikanzniveau von 5% zu einer signifikanten Verminderung der mechanischen Eigenschaften beider Komposite. Dahingegen hatte die vierwöchige Lagerung in künstlichem Speichel einen positiven Einfluss auf die mikromechanischen Eigenschaften des transluzenten Komposites. Der für den Dentinkomposit zusätzlich untersuchte Einfluss der Art der Polymerisationstechnik ergab, dass die mechanischen Eigenschaften bei simulierten klinischen Bedingungen nur bei hohen Polymerisationszeiten und milden Lagerungsbedingungen (20 oder 40 Sekunden und Lagerung in Wasser; 40 Sekunden und Lagerung in Speichel) vergleichbar mit den Messungen nach ISO Norm 4049 sind. Die Konversionsrate des Dentinkomposites war bei allen Polymerisationszeiten signifikant höher an der Oberfläche als in 2 mm Tiefe. Im Gegensatz dazu zeigte das transluzente Komposit das umgekehrte Verhalten und erreichte für alle Polymerisationszeiten unter 40 Sekunden signifikant höhere Werte in einer Tiefe von 2 mm als an der Oberfläche. Die Materialzuverlässigkeit, ausgedrückt durch den Weibull-Parameter, wurde bei dem Dentinkomposit am stärksten durch die Lagerungsbedingung beeinflusst, wohingegen bei dem transluzenten Komposit die Polymerisationszeit den stärksten Einfluss besaß.

1.1. Zusammenfassung (Deutsch)

Für die vorliegende Arbeit wurde der Einfluss von Polymerisation, Lagerungsbedingung und Materialzusammensetzung auf die makro- und mikromechanischen Eigenschaften sowie die Konversionsrate von zwei Kompositen (Dentin A3 und Trans Opal) des Nano-Hybrid-Komposit-Systems IPS Empress Direct (Ivoclar Vivadent, Schaan, Liechtenstein) untersucht, die sich hinsichtlich ihrer Materialzusammensetzung deutlich voneinander unterscheiden. Die makromechanischen Eigenschaften (Biegefestigkeit und Biegemodul) und die mikromechanischen Eigenschaften (Vickershärte, E-Modul und Kriechen) wurden in Bezug auf die variierenden Parameter Lagerungsbedingung (24 Stunden in destilliertem Wasser, 4 Wochen in künstlichem Speichel und 4 Wochen in Alkohol) und Polymerisationszeit (5, 10, 20 und 40 Sekunden) gemessen. Für den Dentinkomposit wurde zusätzlich noch die Art der Polymerisationstechnik (zweiseitig [ISO 4049 Standard] und einseitig/Oberfläche [simulierte klinische Bedingung]) variiert, während das transluzente Komposit gemäß der ISO Norm polymerisiert wurde. Darüber hinaus wurden in Echtzeit durchgeführte Messungen zur Bestimmung der Konversionsrate an der Oberfläche und in 2 mm Tiefe für die vier verschiedenen Polymerisationszeiten (5, 10, 20 und 40 Sekunden) vorgenommen. Der Einfluss von Lagerungsbedingung und Polymerisation wurde statistisch ausgewertet unter der Verwendung ein- und mehrfaktorieller Varianzanalysen mit einem Tukey HSD Post-hoc-Test (α=0,05), partieller η^2-Statistik und einer Weibull-Analyse.

Die Materialzusammensetzung zeigte den bedeutendsten Einfluss auf die mechanischen Eigenschaften, da das Dentinkomposit in allen gemessenen Eigenschaften deutlich höhere Werte erzielte als das transluzente Komposit. Eine Lagerung in Alkohol führt zu einer signifikanten Verminderung der mechanischen Eigenschaften. Vierwöchige Lagerung in künstlichem Speichel hatte einen positiven Einfluss auf die mikromechanischen Eigenschaften des transluzenten Komposites (Trans Opal). Die Messungen nach ISO Standard sind nur bei hohen Polymerisationszeiten und milden Lagerungsbedingungen (20 oder 40 Sekunden und Lagerung in Wasser; 40 Sekunden und Lagerung in Speichel)

vergleichbar mit den Ergebnissen bei simulierten klinischen Bedingungen. Die Konversionsrate des Dentinkomposites war bei allen Polymerisationszeiten signifikant höher an der Oberfläche als in 2 mm Tiefe. Im Gegensatz dazu zeigte das transluzente Komposit das umgekehrte Verhalten und erreichte für alle Polymerisationszeiten unter 40 Sekunden signifikant höhere Werte in einer Tiefe von 2 mm als an der Oberfläche.

Das transluzente Komposit ist nicht indiziert für okklusale Restaurationen im Seitenzahnbereich. Grundsätzlich sind Polymerisationszeiten von mindestens 20 Sekunden mit modernen Hochleistungspolymerisationslampen zu empfehlen, um adäquate mechanische Eigenschaften zu erzielen.

1.2. Zusammenfassung (Englisch)

The present thesis investigated the influence of polymerization, storage condition and material composition on the macro- and micro-mechanical properties as well as the degree of conversion of two composites (Dentin A3 und Trans Opal) of the nano-hybrid composite system IPS Empress Direct (Ivoclar Vivadent, Schaan, Liechtenstein), which distinctly differ concerning their material composition. The macro-mechanical properties (flexural strength and flexural modulus) and the micro-mechanical properties (Vickers hardness, indentation modulus, and creep) were measured in relation to the varying parameters storage condition (24 hours in distilled water, 4 weeks in artificial saliva, and 4 weeks in alcohol) and polymerization time (5, 10, 20, and 40 seconds). Additionally, the way of the polymerization technique (two-sided [ISO 4049 standard] and one-sided/surface [simulated clinical situations]) was varied for the dentin shade, while the translucent shade was polymerized after the ISO standard. Furthermore, the degree of conversion was also measured for these four polymerization times (5, 10, 20, and 40 seconds) at composite specimen surface and at 2 mm depth. Effects of storage condition and polymerization were statistically analyzed using one- and multiple-way ANOVA with Tukey's HSD post hoc test (α=0.05), partial eta-squared statistic, and Weibull analysis.

The material composition showed the most considerable influence on the mechanical properties, since in all measured properties the dentin shade yielded significantly higher results than the translucent shade. Alcohol storage significantly reduced the mechanical properties. Storage in artificial saliva for 4 weeks produced a positive effect on micro-mechanical properties of the highly translucent RBC (Trans Opal). The ISO standard measurements were similar to those measured by simulating clinical conditions only at high polymerization times and mild storage conditions (20 or 40 seconds and water storage; 40 seconds and storing in saliva). The degree of conversion of the dentin shade was significantly higher on the surface than in a depth of 2 mm for all polymerization times. In contrast to that, the translucent shade showed the reverse behavior and reached significantly higher values in a depth of 2 mm than on the surface for all polymerization times lower than 40 seconds.
The highly translucent RBC is not indicated for restorations involving outer occlusal surfaces. Generally, polymerization times are recommended to be at least 20 seconds to yield favorable mechanical properties with modern high-intensity polymerization units.

1.3. Literaturhinweis

Die Literaturhinweise mit dem vorangestellten Buchstaben A beziehen sich auf das Literaturverzeichnis des ersten Fachartikels *"Resin-based Composite Light-cured Properties Assessed by Laboratory Standards and Simulated Clinical Conditions"* (Kapitel 2.1.), wobei die nachfolgende Zahl der entsprechenden Literaturquelle aus diesem Literaturverzeichnis zugeordnet ist. Demzufolge beziehen sich sämtliche Literaturhinweise mit dem vorangestellten Buchstaben B nach dem gleichen Prinzip auf das Literaturverzeichnis des zweiten Fachartikels *"Effects of aging and irradiation time on the properties of a highly translucent resin-based composite"* (Kapitel 2.2.).

2. Publikationen

2.1. *Resin-based Composite Light-cured Properties Assessed by Laboratory Standards and Simulated Clinical Conditions*

(Operative Dentistry 2013 Mar-Apr; 38(2):159-167 [Epub 2012 Jul 11])

Ilie N, Bauer H, Draenert M, Hickel R. (DOI: 10.2341/12-084-L)

CLINICAL RELEVANCE

The irradiation technique, used to measure mechanical properties of resin-based composites according to international standards, consistently differs from clinically simulated conditions, calling into question whether laboratory findings can be unrestrictedly applied clinically, especially at short polymerization times. The study analyzes whether degree of conversion measurements at short post-polymerization time (five minutes) are able to predict the long-term material behavior.

SUMMARY

The following parameters were varied: 1) irradiation technique: top and bottom polymerization according to the ISO standard, and polymerization from only the top, simulating clinical situations; 2) polymerization time: 5, 10, 20, and 40 seconds; 3) storage conditions: 24 hours in distilled water, thermocycling followed by storage for four weeks in artificial saliva or alcohol. Flexural strength (FS), flexural modulus ($E_{flexural}$), indentation modulus (E), Vickers hardness (HV), and degree of conversion (DC) were measured.

The laboratory results were similar to those measured by mimicking clinical conditions only at high polymerization times and mild storage conditions (20 seconds and 40 seconds and storage for 24 hours in water, and 40 seconds with aging and storing in saliva). Significantly higher DC values were measured on the top than on the bottom of a 2-mm layer for all

polymerization times. Overall, 5-second and 10-second irradiation times induced significantly lower DC values compared to the currently recommended polymerization times of 20 and 40 seconds at both the top and bottom of the samples.

The initial DC differences as a function of irradiation time are leveled at 24 hours of storage but seem to do well in predicting long-term material behavior. A minimum irradiation time of 20 seconds is necessary clinically to achieve the best mechanical properties with modern high-intensity light emitting diode (LED) units.

INTRODUCTION

Dentists' requests for a short chair time to prepare a restoration compel a continual reduction in polymerization time for curing resin-based composites (RBCs). When the first high-intensity visible light plasma arc curing (PAC) units were introduced in 1998, the manufacturer claimed to be able to fulfill these wishes, declaring a 3-second polymerization time as sufficient for an adequate polymerization. The manufacturer also claimed that curing for 3 seconds with a high-intensity PAC unit is equivalent to a 40- or 60-second exposure to a quartz-tungsten-halogen (QTH) light.[1] These statements were based on the radiant energy (dose) concept, calculated as a simple reciprocal relationship between irradiation and irradiation time, suggesting that the irradiation time can be shortened when a curing unit's irradiance is proportionally increased. Though generally valid, the radiant energy concept was put into perspective because, within a given dose, shorter exposure time at higher intensity proved to induce decreased properties (lower degree of cure, polymer cross-linking, and physical properties).[2,3] It was also shown that a polymerization of 3 seconds with the high-intensity PAC unit is too short; thus, multiple 3-second exposures are recommended for a clinically adequate performance.[4]

Due to consistent improvements in light emitting diode (LED) technology, a great increase in output power has been achieved in the second and third generation LED units,[1] again

suggesting a shortening of irradiation time. While 20-second or 40-second irradiation times with modern LED units are still indicated by many manufacturers, some have recently suggested short polymerization times of up to 5 seconds.

Although time-saving, a fast cure with a high level of energy has a number of drawbacks, including increased polymerization shrinkage stress,[5,6] which is generally related to several negative clinical effects, such as less integrity of the restoration-cavity interface,[7] marginal staining, cusp fractures,[8] microleakage,[9] secondary caries, postoperative sensitivity, or pain. Also, a rise in temperature and risk of pulp damage[10] are associated with the use of curing units with very high intensity.

The quality of polymerization in RBCs is preliminarily assessed in laboratory tests. To measure macromechanical properties such as flexural strength, international standards (ISO 4049:2009[11]) require curing 2-mm thick slabs from both sides, top and bottom. This double polymerization might generate good mechanical properties with low polymerization times, which could considerably differ from a clinical situation where curing occurs mainly from the top of a restoration. Additionally, the storage time for standard measurements is generally set at 24 hours, raising the question of the role of aging, especially in connection with low polymerization times.

Our study aimed to analyze the effect of aging on the macromechanical and micromechanical properties of a nano-hybrid RBC by varying the polymerization time, the irradiation technique, and the storage conditions. Furthermore, the variation in degree of cure as a function of polymerization time and position – top or bottom of the samples – is analyzed.

The null hypotheses tested in our study were as follows: 1) the irradiation technique – polymerization from both sides, top and bottom, according to ISO standards, and polymerization only from the top, simulating a clinical situation – would not affect the macromechanical (flexural strength and modulus) and micromechanical properties (Vickers hardness and modulus of elasticity); 2) the above mentioned mechanical properties and the

degree of cure would not be influenced by the irradiation time and measuring location (top or bottom); 3) aging (24 hours in distilled water, thermocycling followed by storage for four weeks in artificial saliva or alcohol) would have no influence on the mechanical properties; and 4) the aging agent – saliva or alcohol solution – would not influence the mechanical properties.

MATERIALS AND METHODS

A nano-hybrid resin-based composite (IPS Empress Direct Dentin, Ivoclar Vivadent, Batch No. M68447, dimethacrylate resin matrix, Ba-Al-Si-glass, YbF_3, and SiO_2/ZrO_2-mixed oxide fillers, 75 wt%, 53 vol%) was analyzed by varying the direction of irradiation (top and bottom or only top), the irradiation time (5, 10, 20, and 40 seconds), the storing conditions (24 hours in distilled water or thermocycling followed by storage for four weeks in an aging medium) and the storage medium for aging (artificial saliva or alcohol). A total of 24 combinations of the above mentioned parameters were studied.

Macromechanical Properties

The flexural strength (FS) and flexural modulus ($E_{flexural}$) were determined in a three-point-bending test (n=15). Therefore, 360 samples were made by compressing the composite material between two glass plates with intermediate polyacetate sheets, separated by a steel mold having an internal dimension of 2 x 2 x 16 mm. Irradiation occurred in two different ways: once on the top and bottom of the specimens, as specified in ISO 4049:2009 standards,[11] and once only on top, simulating a clinical situation. When testing, the load was applied to the top surface of these specimens. The times of the light exposures were 5, 10, 20, and 40 seconds, with three light exposures, overlapping one irradiated section no more than 1 mm of the diameter of the light guide (Elipar Freelight 2, 3M ESPE, Seefeld, Germany) to prevent multiple polymerizations. The irradiance of the curing unit (1241 mW/cm^2) was

measured by means of a calibrated fiber optic spectrally resolving radiometer equipped with an integrating sphere (S2000, Ocean Optics, Dunedin, FL, USA). To assess possible variations in irradiation, a calibrated spectrometer (MARC, Blue-Light analytics inc, Halifax, Canada) was used at the beginning, middle, and end of a sample preparation session.

After removal from the mold, the specimens were ground with silicon carbide sand paper (grit size P 1200/4000 [Leco]) to remove disturbing edges or bulges and stored for 24 hours in distilled water at 37°C. One third of the specimens were subsequently measured and considered as references, the rest were additionally aged (thermocycling for 5000 cycles at 5°C to 55°C) before storage for four weeks at 37°C in artificial saliva or a 1:1 ethanol-water mixture. The samples were loaded until failure in a universal testing machine (Z 2.5, Zwick/Roell, Ulm, Germany) in a three-point bending test device, which was constructed according to the guidelines of NIST No. 4877 with a 12-mm distance between the supports.[12] During testing, the specimens were immersed in distilled water at room temperature. The crosshead speed was 0.5 mm/min. The universal testing machine measured the force during bending as a function of deflection of the beam. The bending modulus was calculated from the slope of the linear part of the force-deflection diagram.

Micromechanical Properties

Fragments (n=12) of the three-point bending test specimens of each group were used to determine the micromechanical properties: Vickers hardness (HV) and indentation modulus (E) according to DIN 50359-1:1997[13] by means of a universal-hardness device (Fischerscope H100C, Fischer, Sindelfingen, Germany). Prior to testing, the samples were polished with a grinding system (EXAKT 400 CS, EXAKT, Norderstedt, Germany) using silicon carbide paper (P 2500 followed by P 4000). Measurements were done on the top (n=6) and the bottom (n=6) of the slabs (10 measurements per sample per side). The test procedure was carried out with controlled force; the test load increased and decreased with a constant speed between 0.4

mN and 500 mN. The load and the penetration depth of the indenter were continuously measured during the load-unload-hysteresis. The universal hardness is defined as the test force divided by the apparent area of the indentation under the applied test force. From a multiplicity of measurements, a conversion factor between universal hardness and Vickers hardness was calculated and implemented in the software, such that the measurement results were indicated in the more familiar HV units. The indentation modulus E was calculated from the slope of the tangent of indentation depth-curve at maximum force.

Degree of Cure

The degree of cure (DC) was analyzed by considering two different sample geometries: one 2-mm high increment measured in a white Teflon mold measuring 2 mm in height and 3 mm in diameter and a thin 100-µm composite film. The samples were cured for 5, 10, 20, and 40 seconds by applying the curing unit directly on the sample's surface (n=5). Measurements were made in real time (five minutes, 2 spectra/s, 4 cm^{-1} resolution) with a Fourier transform infrared (FTIR) spectrometer with an attenuated total reflectance (ATR) accessory (Nexus, Thermo Nicolet, Madison, WI, USA) by applying the nonpolymerized composite paste directly on the diamond ATR crystal. The spectra were recorded in this way at the bottom of the samples.

DC was calculated as the variation in peak height ratio of the absorbance intensities of methacrylate carbon double bond peak at 1634 cm^{-1} and that of internal standard peak at 1608 cm^{-1} (aromatic carbon double bond) during polymerization, in relation to the uncured material.

$$DC_{Peak}\% = \left[1 - \frac{(1634cm^{-1}/1608cm^{-1})_{Peak\ height\ after\ curing}}{(1634cm^{-1}/1608cm^{-1})_{Peak\ height\ before\ curing}}\right] * 100$$

Statistical Analysis

The Kolmogorov-Smirnoff test was applied to verify that the data were normally distributed. The results were compared using one- and multiple-way analysis of variance (ANOVA) and Tukey honestly significant difference (HSD) post hoc-test (α=0.05). A multivariate analysis (general linear model with partial eta-squared statistics) assessed the effect of storage, irradiation time, and irradiation mode (ISO/clinical) on the considered properties. An independent t-test additionally analyzed the differences in mechanical properties as a function of irradiation technique (SPSS, version 19.0, SPSS Inc, Chicago, IL, USA). An additional Weibull analysis was performed for the flexural strength data.

A common empirical expression for the cumulative probability of failure P at applied stress is the Weibull model:

$$P_f(\sigma_c) = 1 - exp\left[-\left(\frac{\sigma_c}{\sigma_0}\right)^m\right]$$

where σ_c is the measured strength, m is the Weibull modulus and σ_0 is the characteristic strength, which is defined as the uniform stress at which the probability of failure is 0.63. The double logarithm of this expression gives:

$$\ln\ln\frac{1}{1-P} = m\ln\sigma_c - m\ln\sigma_0$$

By plotting ln ln(1/(1-P)) vs ln sigma, a straight line results with the upward gradient *m*.

RESULTS

Post-hoc multiple pairwise comparisons with Tukey HSD test (p<0.05) showed a decrease in the parameters measured in the flexural strength test (FS, $E_{flexural}$, Figure 1; Table 1) after aging, with a considerable decrease in the properties after storing the samples in alcohol. Preparing the samples by mimicking clinical conditions weakened the properties for almost all polymerization times and storage conditions compared to the groups prepared according to the international standard (p<0.05). Only a high polymerization time and a mild storage

condition (20 seconds and 40 seconds with 24-hour water storage, and 40 seconds with aging and saliva storage) were able to equalize these differences.

Irrespective of irradiation time and storage, the difference between the micromechanical properties measured on the top and bottom of the samples was not statistically significant in the samples polymerized from both sides but was significantly lower at the bottom of the samples polymerized only from the top (Table 2).

As for the degree of cure, significantly higher values were measured for all polymerization times on the top of the samples, simulated by the use of a thin composite film, as in a depth of 2 mm ($p<0.05$) (Figure 2; Table 3). For both conditions, 5-second and 10-second irradiation times induced significantly lower DC values compared to the currently recommended polymerization times of 20 seconds or 40 seconds.

The storage proved to have the greatest influence on all measured mechanical properties (Table 4), exercising the strongest effect on the material's reliability, expressed by the Weibull modulus, m. The effect of irradiation time was greater than the effect of irradiation technique with regard to the parameters measured in the flexural test; both effects were comparable with regard to the micromechanical properties.

The modulus of elasticity measured in both methods – the flexural test and the universal hardness test – correlated well (Pearson correlation coefficient = 0.8). There was also a good correlation between the micromechanical properties (E-HV = 0.97) and macromechanical properties (FS-$E_{flexural}$ = 0.81).

DISCUSSION

Laboratory experiments try to simulate clinical conditions as accurately as possible to obtain information that is directly applicable in daily practice. Therefore, our study compared two irradiation techniques – top and bottom, according to the ISO standard, and only top, to simulate clinical situations. The mechanical properties were assessed on a macroscopic scale,

by determining the strength and the resistance the materials opposed to deformation (modulus of elasticity), and on a microscopic scale (hardness and modulus of elasticity) by means of a dynamic measuring principle, simultaneously recording the load and the corresponding penetration depth of the indenter.[13] With maximum indentation depth in the range of 7-15 µm, the measurements performed at microscopic scale reflect the material properties and not the properties of the individual material components (filler and filler agglomerates or matrix and matrix-reach areas). As for the degree of cure, the measurements were done at the same depth as the measurement of micromechanical properties, by simulating the top and bottom of clinically relevant 2-mm-thick increments, allowing thus a direct comparison among the measured parameters.

The results demonstrated that when samples were stored for 24 hours, the irradiation technique significantly affected the mechanical properties at short irradiation times (5 seconds and 10 seconds), lowering FS and $E_{flexural}$ in simulated clinical conditions when compared to the ISO standard, but showed similar results for both polymerization techniques at high irradiation times (20 seconds and 40 seconds). These results support the recommended irradiation time of at least 20 seconds, as indicated by the manufacturer and also often used in ISO 4049:2009,[11] for both *in vitro* and *in vivo* use. Within the above mentioned curing and storage conditions – irradiation of at least 20 seconds and storage for 24 hours in distilled water – the results of the ISO-irradiation can be directly applied clinically, since both tested irradiation techniques produced not only similar macromechanical properties (FS, $E_{flexural}$) but also similar micromechanical properties (HV, E). After aging and storing in artificial saliva, a polymerization time of 40 seconds is necessary to ensure statistically similar properties between the ISO and the clinically simulated irradiation, whereas storing in alcohol never produced comparable results (40 seconds). These results put in perspective whether the mechanical properties measured according to the current standards are able to reflect the long-term behavior of an RBC filling and confirm the lack of correlation between the clinical

behavior of restorative materials and laboratory results.[14] This statement should not, however, diminish the meaning of preliminary laboratory tests and standardized methods, since an initial selection of materials with adequate properties is of particular importance.[15]

The study also showed that the most sensitive parameter to all of the above mentioned influences (Table 4, highest eta-squared values) was the Weibull modulus *m*, that means the reliability of the tested material, being lower in the samples cured by simulating a clinical situation compared to the groups polymerized according to the ISO standards, for all storage conditions. Furthermore, the material reliability was lowered with aging and with increased aggressiveness of the storage agent. Furthermore, not only curing time and irradiation condition but also the storage conditions and, thus, the softening effect due to aging and storage in saliva or alcohol were more strongly reflected in the reliability determined at a macroscopic scale (Weibull parameter *m*) than in the micromechanical properties E and HV. These observations highlight the importance of performing macromechanical tests with a higher number of samples to allow performance of a Weibull statistical analysis for acquiring sensitive and reliable observation on a material's behavior.

The surface of a restoration was simulated in our study by a 100-µm RBC layer used to assess the evolution of degree of cure as a function of irradiation time in real time. The measurements were done at the bottom of the film to avoid the influence of the oxygen-inhibition layer, which was shown to be less than 20 µm thick.[16] The micromechanical properties were also measured after the oxygen-inhibition layer was eliminated by grinding and polishing; thus, both tests were recorded at similar depth. Differences in DC between the 0.1-mm and 2-mm depths were statistically significant for all irradiation times. The postpolymerization, however, seems to have leveled these differences for longer irradiation times (20 seconds, 40 seconds), as reflected in the mechanical properties (top-bottom) measured 24 hours after storage in water. However, aging again emphasizes the importance of assessing the initial degree of cure since, especially after aging and storage in alcohol

solution, the difference in micromechanical properties between the top and bottom of the samples cured from only one side became evident at all polymerization times. Similar trends were found also for the flexural strength, when both irradiation techniques were compared. Since softening tests in solvents such as ethanol and water are well-established methods of assessing the cross-link density of a polymer network,[17,18] the aging and storage in ethanol performed in this study can be taken as an indicator of the effect of reduced polymerization time as well as attenuated light at the bottom of the specimens. The softening effect of solvents was shown to be generally stronger in a more linear polymer structure than in a highly cross-linked polymer,[19] emphasizing the negative effect of short curing time on the measured mechanical properties. This statement is also consolidated by the measured degree of cure.

The results of the present study also validate the literature indicating that the minimum radiant energies necessary to properly cure RBCs are 16.8 J/cm^2 for a 1-mm increment[20] and 24 J/cm^2 for 2-mm increments.[21] Under the study conditions (light intensity 1241 mW/cm^2, polymerization time 5, 10, 20, and 40 seconds; 2-mm increments), this minimum irradiation was reached only for polymerization times of 20 seconds and 40 seconds.

The statements of the study are limited by having analyzed only one RBC. Though we randomly chose a modern nano-hybrid RBC with moderate mechanical properties,[22] the large diversity of RBCs, which contain complex fillers, organic matrices, and initiator systems, make it difficult to generalize the results but gives at least a reference note for the complex impact of polymerization on material behavior.

CONCLUSIONS

All tested null hypotheses are rejected. The properties measured according to ISO standards were similar to those measured by mimicking clinical conditions only at high polymerization times and mild storage conditions (20 seconds and 40 seconds with 24-hour water storage,

and 40 seconds with aging and storing in saliva). The initial (5-minute) differences in DC measurements as a function of irradiation time are leveled at 24 hours of storage but seem to be a good indicator of the long-term material behavior.

A minimum irradiation time of 20 seconds is clinically necessary to achieve the best mechanical properties, also when modern high-intensity LED units are used.

CONFLICT OF INTEREST

The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service and/or company that is presented in this article.

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TABLES

Table 1: Flexural strength (FS) and modulus of elasticity in flexural test ($E_{flexural}$) are detailed in mean values and standard deviations (in parentheses). Superscript letters indicate statistically homogeneous subgroups within a column (Tukey's HSD test, α=0.05). A t-test analysed differences between the way of curing the samples – ISO or clinical – for each irradiation time. The Weibull parameter *m* is indicated.

Storage	Time	FS [MPa]		*p*	Weibull, *m*		$E_{flexural}$ [GPa]		*p*
	[s]	ISO	Clinical		ISO	Clinical	ISO	Clinical	
24 h water	5	118.7 ^{de} (9.3)	98.0 ^{FG} (9.8)	< 0.001	4.09	2.81	4.7 ^{c} (0.7)	3.4 ^{C} (0.6)	< 0.001
	10	129.7 ^{e} (11.9)	110.6 ^{GH} (12.3)	< 0.001	4.28	3.23	5.6 ^{d} (0.6)	4.1 ^{D} (0.7)	< 0.001
	20	132.1 ^{e} (13.7)	128.5 ^{I} (14.5)	0.491	4.00	3.14	5.3 ^{cd} (0.9)	5.3 ^{EF} (0.7)	0.843
	40	133.1 ^{e} (15.3)	122.8 ^{HI} (8.4)	0.051	4.12	3.37	5.2 ^{cd} (0.8)	5.4 ^{F} (0.6)	0.349
Thermocycling + 4 w saliva	5	105.9 ^{d} (15.8)	78.4 ^{DE} (8.9)	< 0.001	2.48	2.79	5.2 ^{cd} (0.6)	4.1 ^{D} (0.3)	< 0.001
	10	106.8 ^{d} (16.0)	90.4 ^{EF} (17.8)	0.012	2.22	2.08	5.2 ^{cd} (0.6)	4.7 ^{E} (0.4)	0.048
	20	113.4 ^{d} (13.0)	103.0 ^{FG} (10.8)	0.017	3.38	3.20	5.5 ^{d} (0.4)	5.3 ^{EF} (0.3)	0.036
	40	112.8 ^{d} (16.6)	106.7 ^{G} (14.5)	0.277	2.31	2.91	5.6 ^{d} (0.5)	5.7 ^{F} (0.4)	0.828
Thermocycling + 4 w alcohol	5	53.1 ^{a} (8.9)	17.3 ^{A} (5.8)	< 0.001	1.95	0.94	2.5 ^{a} (0.2)	1.6 ^{A} (0.3)	< 0.001
	10	62.0 ^{ab} (9.2)	33.0 ^{B} (12.8)	< 0.001	2.32	0.80	2.7 ^{ab} (0.4)	2.3 ^{B} (0.3)	0.006
	20	76.3 ^{bc} (9.3)	51.4 ^{C} (10.6)	< 0.001	2.65	1.59	3.2 ^{ab} (0.4)	2.4 ^{B} (0.3)	< 0.001
	40	77.1 ^{c} (7.8)	69.0 ^{D} (13.2)	0.040	3.30	1.77	3.2 ^{b} (0.2)	3.2 ^{C} (0.4)	0.829

Table 2: Micro-mechanical properties – modulus of elasticity E and Vickers hardness (HV) – are detailed in mean values and standard deviations (in parentheses). Superscript letters indicate statistically homogeneous subgroups within a column and * indicate statistically homogeneous subgroups within a line. (Tukey's HSD test, α=0.05). For the ISO way of cure, no statistical differences between top and bottom were measured.

Storage	Time [s]	E [GPa]			HV [N/mm²]		
		ISO	Clinical Top	Clinical Bottom	ISO	Clinical Top	Clinical Bottom
24 h water	5	12.4 ^{e*} (0.5)	12.4 ^{E*} (0.4)	6.8 ^{b} (2.1)	66.6 ^{e*} (4.5)	67.5 ^{E*} (4.9)	28.3 ^{a} (13.1)
	10	13.1 ^{g} (0.3)	12.4 ^{E} (1.6)	11.8 ^{ef} (0.8)	73.5 ^{g*} (1.7)	71.7 ^{F*} (6.5)	63.3 ^{g} (6.8)
	20	13.1 ^{g*} (0.3)	13.0 ^{FG*} (1.2)	12.4 ^{fg} (0.3)	74.8 ^{g*} (2.6)	76.0 ^{G*} (6.1)	67.2 ^{g} (2.8)
	40	13.6 ^{d} (0.3)	13.3 ^{G} (0.5)	12.8 ^{g} (0.3)	76.6 ^{h} (2.3)	75.0 ^{G} (3.4)	72.0 ^{h} (2.4)
Thermocycling + 4 w saliva	5	12.6 ^{ef} (0.4)	11.4 ^{D*} (0.6)	8.1 ^{c**} (0.9)	68.5 ^{f} (2.2)	58.4 ^{D*} (4.1)	33.8 ^{bc**} (6.8)
	10	13.0 ^{g} (0.4)	12.4 ^{E*} (0.4)	9.8 ^{d**} (1.0)	70.2 ^{f} (4.8)	65.5 ^{E*} (4.1)	44.3 ^{E**} (8.9)
	20	12.9 ^{g} (0.4)	13.0 ^{FG*} (0.3)	11.2 ^{e**} (0.4)	69.2 ^{f} (3.5)	72.4 ^{F*} (1.8)	58.0 ^{f**} (3.8)
	40	13.1 ^{g} (0.4)	12.6 ^{EF*} (0.5)	11.3 ^{e**} (0.6)	73.3 ^{g} (2.1)	67.4 ^{E*} (4.5)	57.0 ^{f**} (6.1)
Thermocycling + 4 w alcohol	5	7.1 ^{a*} (0.4)	7.2 ^{A*} (0.4)	5.9 ^{a} (0.3)	38.5 ^{a*} (2.3)	37.9 ^{A*} (4.1)	31.6 ^{ab} (2.9)
	10	7.6 ^{b*} (0.3)	8.0 ^{B*} (0.5)	6.9 ^{b} (0.3)	41.5 ^{b*} (3.0)	43.9 ^{B*} (2.4)	37.0 ^{cd} (2.3)
	20	8.4 ^{c*} (0.3)	8.5 ^{C*} (0.4)	7.1 ^{b} (0.4)	48.2 ^{c*} (1.6)	48.7 ^{C*} (2.5)	40.5 ^{de} (2.4)
	40	9.3 ^{d*} (0.5)	8.3 ^{BC*} (0.5)	7.3 ^{b} (0.3)	52.7 ^{d*} (2.7)	45.8 ^{B*} (3.7)	40.4 ^{de} (2.9)

Table 3: Degree of cure (DC) at 0.1 mm and 2 mm are detailed in mean values and standard deviations (in parentheses). Superscript letters indicate statistically homogeneous subgroups within a column (Tukey's HSD test, α=0.05). A t-test analyzed differences between the DC at 0.1 and 2 mm for each irradiation time.

Time [s]	**$DC_{0.1mm}$ [%]**	**DC_{2mm} [%]**	***p***
5	45.3 ^{a} (3.5)	38.6 ^{A} (2.8)	< 0.001
10	46.5 ^{a} (3.0)	41.8 ^{B} (2.3)	< 0.001
20	48.7 ^{b} (2.4)	43.9 ^{C} (1.5)	< 0.001
40	49.6 ^{b} (4.2)	45.0 ^{C} (2.7)	0.005

Table 4: Influence of storage, irradiation time and way of curing on flexural strength (FS), modulus of elasticity in flexural test ($E_{flexural}$) and Weibull parameter *m*, Vickers Hardness (HV), and modulus of elasticity (E), as well as degree of cure (DC). The higher the partial eta-squared values the higher is the influence of the selected variables on the measured properties.

Parameters	**FS**	**$E_{flexural}$**	***m***	**HV**	**E**	**DC**
Storage	.842	.829	.973	.825	.889	
Irradiation time	.402	.409	.776	.531	.483	.292
ISO/clinical	.342	.221	.901	.534	.490	.313

FIGURES

Figure 1: Variation of flexural strength with irradiation time and irradiation technique after: (a) water storage for 24h; (b) thermo cycling followed by storage in saliva for 4 weeks; (c) thermocycling followed by storage in alcohol for 4 weeks

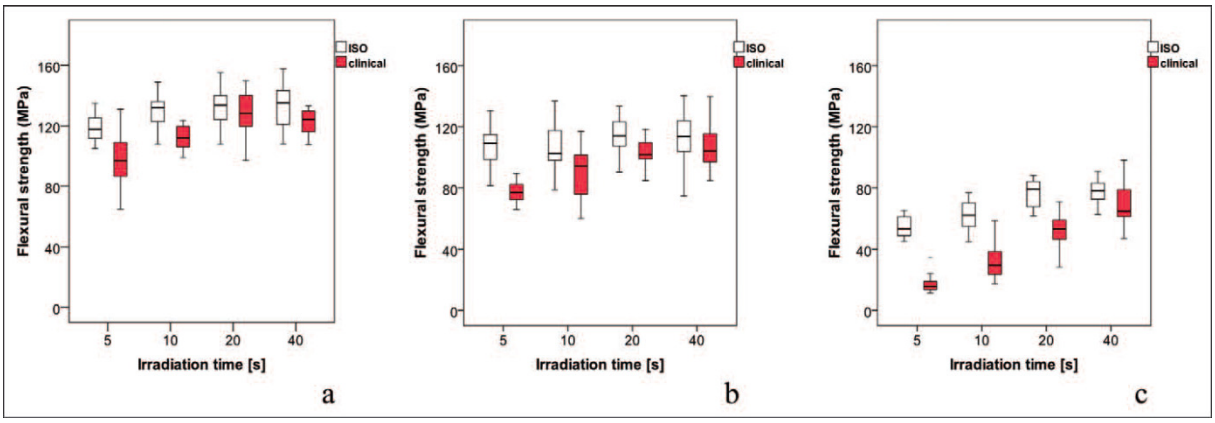
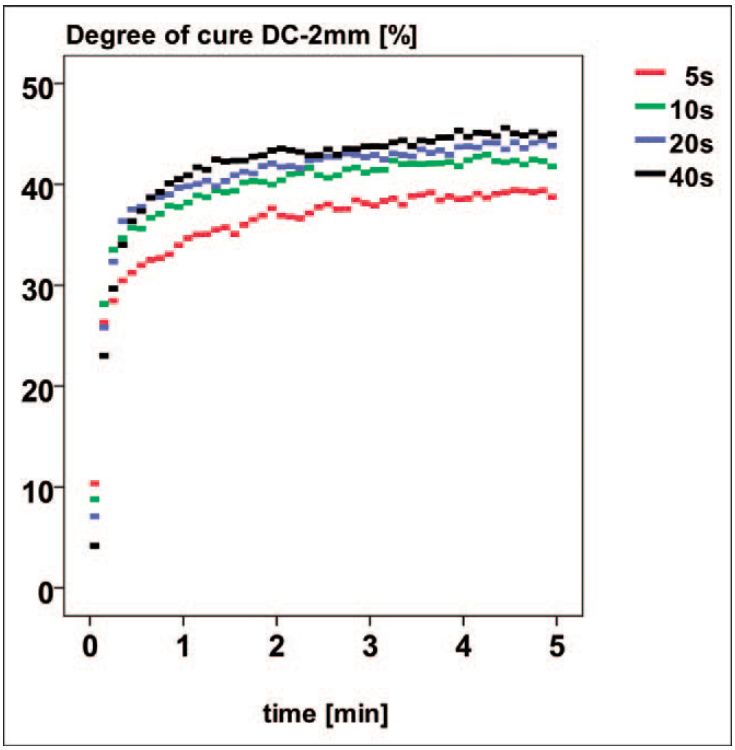


Figure 2: Degree of cure measured at 2-mm depth in real-time for 5 minutes, as function of polymerization time (mean values, n=6).



2.2. *Effects of aging and irradiation time on the properties of a highly translucent resin-based composite*

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ABSTRACT

This study investigated the effects of aging and irradiation time on the macro- and micro-mechanical properties of a highly translucent nanohybrid composite (IPS Empress Direct, Trans Opal shade, Ivoclar Vivadent). Flexural strength, flexural modulus, indentation modulus, Vickers hardness, and creep were measured after being irradiated with different durations (5, 10, 20, and 40 s) and aged under different conditions (24 h at 37°C in water; 5,000 times of thermocycling between 5°C and 55°C followed by 4-week storage in artificial saliva or alcohol). Rate of cure was also measured for these four irradiation times at composite specimen surface and at 2 mm depth.

Effects of aging and irradiation time were statistically analyzed using one-way ANOVA with Tukey's HSD *post hoc* test (α=0.05), partial eta-squared statistic, and Weibull analysis. Alcohol aging significantly reduced the mechanical properties. Aging in saliva produced a positive effect on micro-mechanical properties. Irradiation time should be at least 20 s to yield favorable mechanical properties.

INTRODUCTION

Nowadays, direct resin-based composites (RBCs) provide dental practitioners with esthetic restorations whose appearance and properties parallel those of natural teeth. For optimal clinical outcome, the selected RBC should match the shade and translucency of the

surrounding natural teeth. A prerequisite to achieving optimal esthetics is to understand the optical and mechanical properties of both the natural teeth and the selected RBC.

Translucency is an intermediate state between complete opacity and complete transparency. Amongst the plethora of commercially available RBCs, translucency varied significantly within each brand according to shade designation; and for the same shade designation, translucency varied across the different brands[1)]. For the same brand and shade designation, the translucency of flowable RBC differed significantly from that of universal RBC[2)]. Both investigations have shown that the translucency of a RBC is influenced by its material composition.

Studies found that numerous factors affect the translucency of RBCs: refractive index mismatch, filler amount, and resin layer thickness. Translucency decreased as the difference in refractive indices between organic resin matrix and inorganic filler increased[3,4)]. Translucency also decreased when filler amount increased[5)]. As resin layer thickness diminished, translucency increased exponentially regardless of resin shade[6)]. In a multi-layer composite restoration, translucency was influenced by layer thickness and the proportion of dentin shade thickness to translucent shade thickness[7)].

Aside from material composition and inherent optical properties, external factors such as aging and storage medium also affect the translucency of RBCs. Accelerated aging[8)] and environmental exposure such as daylight exposure[9)] decreased translucency, and so did storage/immersion in media such as salivary esterase[10)], water[9)], and whisky[11)]. A study found that translucent shades were more susceptible to discoloration than enamel shades[11)].

Apart from exerting adverse influence on the optical properties of RBCs, aging also affected the mechanical properties of RBCs[12–15)]. Storage media such as water and artificial saliva produced the same effect on the physical properties (such as flexural strength and Vickers hardness) of RBCs[12,13)], but alcohol resulted in more inferior performance[15,16)]. Some studies showed that storage duration had a more pronounced effect on the mechanical properties of

RBCs than storage medium[12–14)]. Two reasons accounted for the different results among RBCs when they were subjected to the same storage condition: their chemical composition and structure. RBCs with a low resin matrix content showed low water sorption and high flexural strength and flexural modulus after storage in water or artificial saliva[12)]. Similarly, the chemical bonding between resin matrix and filler particles wielded a significant influence on the mechanical properties of RBCs after aging[15)].

For studies on materials aging of translucent RBCs, the Translucent shade of Filtek Supreme XT (Filtek Supreme XT Translucent, 3M ESPE, St. Paul, MN, USA) seemed to be a popular material of choice[12,14)]. A quick survey of these studies revealed that different shades of Filtek Supreme XT yielded different performance characteristics. In one study, it was reported that the water content of Filtek Supreme XT Translucent continued to increase throughout the 12-month water storage, whereas water uptake of the Body shade (Filtek Supreme XT Body) increased up to 3 months and then reached equilibrium[14)]. Filtek Supreme XT Translucent had a higher resin matrix content than Filtek Supreme XT Body, which might thus account for its higher volumetric shrinkage and water uptake[12)].

Limited cure depth is a drawback of light-activated composites[4)]. The rate of cure of RBCs is affected by their shade and translucency, because these optical properties interfere with light transmission. For example, Filtek Supreme XT Translucent showed a higher rate of cure than the Dentin and Enamel shades[17)]. Other factors that affect the rate of cure of RBCs include the type of light curing unit used (with different light intensity outputs and spectral distributions[18–21)]), irradiation time[21)], and distance from the curing light tip[19)].

Generally, translucent shades of direct esthetic composites were less examined for their mechanical properties than for their optical properties. Therefore, the aim of this study was to investigate the effects of aging and irradiation time on the mechanical properties of a highly translucent RBC. Macro-mechanical properties examined were flexural strength and flexural

modulus; micro-mechanical properties examined were Vickers hardness, indentation modulus, and creep. The influence of irradiation time on the rate of cure was also examined.

Three research hypotheses were tested in this study: (1) Aging by storage would not influence the mechanical properties of highly translucent RBC; (2) Irradiation time range between 5 and 40 s would not influence the mechanical properties of highly translucent RBC; (3) Rate of cure would not differ between the top and bottom surfaces of highly translucent RBC.

MATERIALS AND METHODS

The highly translucent RBC selected for this study was a nanohybrid composite of 45% translucency, IPS Empress Direct (Trans Opal shade, Ivoclar Vivadent, Schaan, Liechtenstein; Batch No. M62836). Its composition included dimethacrylate resin matrix, prepolymer and highly dispersed silicon dioxide.

Preparation of RBC specimens for mechanical properties testing

Composite material was filled into a steel mold with internal dimensions of 16×2×2 mm. Top and bottom surfaces of filled steel mold were covered with polyacetate sheets and pressed with glass plates. Irradiation was performed using a LED curing light (Elipar^{TM} Freelight 2, 3M ESPE, Seefeld, Germany; 1261 mW/cm^2) from the top and bottom of the specimens, as specified in ISO/DIN 4049:2009 standards[22)]. Irradiation times were 5, 10, 20, and 40 s with three light exposures each per side. Each light exposure overlapped one irradiated section no more than 1 mm of the diameter of the light guide to prevent multiple polymerization.

After removal from the mold, a total of 180 specimens were ground with 4000-grit silicon carbide papers (Leco, Mönchengladbach, Germany) to remove any flash and excess. All specimens were then stored in 37°C distilled water for 24 h. Fifteen specimens per irradiation time were used as control. The remaining specimens (n=30 per irradiation time) were additionally aged by thermocycling for 5,000 times between 5 and 55°C with a 30-s dwell

time each, and then stored for 4 weeks at 37°C in artificial saliva (*n*=15 per irradiation time) or in a 1:1 alcohol-water mixture (*n*=15 per irradiation time).

Evaluation of macro-mechanical properties

Flexural strength and flexural modulus were determined using a three-point-bending test (*n*=15 per irradiation time per storage condition). Test was carried out using a universal testing machine (Z 2.5, Zwick Roell, Ulm, Germany) with a three-point bend fixture, which had a span length of 12 mm between the supports and which was constructed according to the guidelines of NIST No. 4877[23)].

During the test, specimens were immersed in distilled water at room temperature. Specimens were loaded at a crosshead speed of 0.5 mm/min until failure occurred. The universal testing machine measured the force during bending as a function of beam deflection. Flexural modulus was calculated from the slope of the linear part of the force-deflection curve.

Evaluation of micro-mechanical properties

Among the three-point bending test specimens, six fragments for each irradiation time and storage condition were randomly selected for Vickers hardness (HV), indentation modulus (E), and creep tests. These micro-mechanical properties were measured using a microhardness measuring system (Fischerscope H100C, Helmut Fischer GmbH, Sindelfingen, Germany) as prescribed in German standard DIN 50359-1:1997-10[24)]. Measurements were done on the top surfaces of fragment slabs (10 measurements per slab; 60 measurements for each irradiation time and storage condition).

Prior to testing, specimens were ground sequentially on 2500- and 4000-grit silicon carbide papers (Hermes, Hamburg, Germany) in a grinding system (EXAKT 400CS plate grinder equipped with AW 110 controller, EXAKT, Norderstedt, Germany). Test was performed by applying controlled force, with the test load increasing and decreasing at a constant speed

between 0.4 and 500 mN. Load and penetration depth of the indenter were continuously measured during the loading-unloading hysteresis.

Universal hardness (HU) is defined as the test force divided by the apparent area of the indentation under the applied test force. From a multiplicity of measurements, a conversion factor between HU and HV was derived and implemented in the software, so that measurement results were presented in the more familiar HV units.

Indentation modulus, which matches a material's modulus of elasticity, was determined from the slope of the tangent of the unloading curve at maximum load.

To measure creep, a constant load was applied for 5 s. Indentation creep was determined from the change in indentation depth whilst the applied load was maintained constant for 5 s.

For specimens stored in artificial saliva and alcohol, their fractured surfaces after three-point bending test were inspected and photographed using Fischerscope H100C at 40× magnification.

Rate of cure measurement

Rate of cure (RC) was examined using two different specimen geometries: one 2-mm-high increment measured in a white Teflon mold of 2 mm height and 3 mm diameter *versus* a 0.1-mm-thick composite film. Specimens were cured for 5, 10, 20, and 40 s by applying the light curing unit directly on specimen surface (n=6).

Using a Fourier transform infrared spectrometer with an attenuated total reflectance accessory (Nexus, Thermo Nicolet, Madison, USA), measurements were made in real-time (5-min measurement time, 2 spectra/s, 4 cm^{-1} resolution). By placing the non-polymerized composite paste directly on the diamond attenuated total reflectance crystal, spectra at the bottom of both 0.1-mm-thick and 2-mm-thick specimens were thus recorded.

RC was calculated as the variation in peak height ratio of the absorbance intensities of methacrylate carbon double bond peak at 1634 cm^{-1} before curing and after 5, 10, 20, or 40 s of curing:

$$RC\ (\%) = [1-[(1634cm^{-1})_{\text{Peak height after curing}}/(1634cm^{-1})_{\text{Peak height before curing}}]]\times 100$$

Statistical analysis

Results were statistically compared using one-way ANOVA and Tukey's HSD *post hoc* test (α=0.05). A multivariate analysis (general linear model with partial eta-squared statistics) tested the effects of irradiation time and storage condition on the macro- and micro-mechanical properties (SPSS Inc., Chicago, IL, USA; Version 18.0). Weibull analysis was additionally performed for flexural strength data.

RESULTS

Effects on macro-mechanical properties

Table 1 presents the effects of irradiation time and storage condition on the macro-mechanical properties of highly translucent RBC, namely, flexural strength and flexural modulus. Among the three storage conditions, control specimens stored in water for 24 h showed the highest flexural strengths for all irradiation times — especially when irradiated for 20 and 40 s. For each irradiation time, flexural strength significantly decreased after aging, with a more pronounced decrease after alcohol aging.

Figure 1 shows the surfaces of aged specimens obtained after three-point bending test. The flaw patterns observed well correlated with the flexural strength results. For all specimens aged in alcohol or irradiated for only 5 s, they exhibited similar flaws. The shorter the irradiation time, the larger the flaws.

For specimens aged for 24 h in water or 4 weeks in saliva, their Weibull modulus *m* values were pronouncedly lower at 5-s irradiation time compared to being irradiated for 10 s or

longer (Fig. 2). For specimens aged for 4 weeks in alcohol, they showed lower *m* values than the other storage conditions at 10-, 20-, and 40-s irradiation times.

For specimens aged for 24 h in water or 4 weeks in saliva, they exhibited their highest flexural modulus values when irradiated for 20 or 40 s (Table 1). Aging in alcohol resulted in the lowest flexural modulus value among the three storage conditions for each irradiation time.

Effects on micro-mechanical properties

Table 2 presents the effects of irradiation time and storage condition on the micro-mechanical properties of highly translucent RBC. When aged in saliva and irradiated for 20 s or longer, RBC specimens showed significantly improved values for indentation modulus, Vickers hardness, and creep than the control specimens aged for 24 h in water, which in turn showed significantly higher values than those aged in alcohol. When irradiation time was reduced to less than 20 s, the values of indentation modulus and Vickers hardness also decreased across all the three storage conditions. For creep, storage in alcohol led to inferior results at all irradiation times.

Effects on rate of cure

Table 3 shows the rates of cure at top surface (simulated by 0.1-mm-thick RBC film) and bottom surface (2 mm depth) for all irradiation times. At each irradiation time (except 40 s), significantly higher rates of cure were observed at the bottom surface than at the top surface. When irradiation time was 40 s, both the top and bottom surfaces yielded their highest rates of cure, which were not significantly different from each other. Figure 3 shows that as irradiation time decreased, the rate of cure decreased at both top and bottom surfaces.

Effects of irradiation time and storage condition on mechanical properties

Table 4 presents the effects of storage condition and irradiation time on macro- and micro-mechanical properties. Storage condition was found to have a stronger influence on macro-mechanical properties, whereas irradiation time had a greater influence on micro-mechanical properties.

DISCUSSION

Effects of material composition

The RBC examined in this study, IPS Empress Direct of Trans Opal shade, was distinctly unique from the IPS Empress Direct range of products. Apart from having the highest degree of translucency (45%), it boasted of a different chemical composition[25)]. Typically, ytterbium trifluoride and aluminosilicate glass are used to make dental restorative materials radiopaque[25–27)]. Radiopacity of dental materials is important because it permits tooth-colored restorative materials to be differentiated from the natural tooth or caries on X-rays. However, a high level of radiopacity and translucency cannot be achieved at the same time. In IPS Empress Direct of Trans Opal shade, highly dispersed silicon dioxide and an organic prepolymer were used instead of a high ratio of barium-aluminum-fluorosilicate glass and ytterbium trifluoride.

For IPS Empress Direct of Trans Opal shade, silicon dioxide was not considered as inorganic filler. As a result, the amounts of dimethacrylates in the monomer matrix (17 wt%) and inorganic filler particles (60.5 wt%, 45 vol%) were lower than the other shades of IPS Empress Direct products (21 wt%, 75–79 wt% or 52–59 vol% respectively)[25)]. Translucency increases as filler amount decreases[5)]. The lowest amount of inorganic filler particles in Trans Opal shade thus logically accounted for its highest degree of translucency amongst the wide range of shades and various levels of translucency offered by IPS Empress Direct products.

Changes in material composition and optical properties affect the mechanical properties of RBCs. Our previous study showed that the mechanical properties of IPS Empress Direct Trans Opal were lower than those of Dentin shade[28]. It was also shown that IPS Empress Direct Trans Opal had below-average macro-mechanical properties when compared to other nanohybrid RBCs; its mechanical properties were more comparable to those of microfilled RBCs, flowable RBCs and compomers[29,30].

The clinical indication for Trans Opal shade is limited to esthetic anterior restorations to create the effects of opalescence and translucency in natural enamel. Three-point bending test in this study revealed that the flexural strength of Trans Opal shade was less than 80 MPa, which is the minimum flexural strength limit of ISO 4049 for restorative materials claimed suitable for restorations involving outer occlusal surfaces[22]. Weibull analysis based on flexural strengths provides important information about the reliability of dental materials[31]. The steeper the slope of a straight line, the higher the gradient, the higher is the reliability of the material. In the present study, RBC specimens aged in alcohol demonstrated reduced reliability irrespective of irradiation time (Fig. 2). In contrast, specimens aged in water or saliva showed sharply reduced reliability only when irradiation time was 5 s.

Effects of storage medium

It has been recommended that highly translucent resins be used between the dentin and enamel to achieve satisfactory esthetic outcome that mimics natural teeth[32]. In clinical settings, it might not be feasible to comply with this recommendation because of space constraints at the incisal edge.

In some cases, translucent RBCs are used for the final layer, which means they are constantly exposed to saliva. It has been reported that saliva increased the surface hardness of restorative filling materials[33]. In the present study, aging in artificial saliva also resulted in improved micro-mechanical properties, such as Vickers hardness, as compared to 24-h storage in water.

In contrast, aging in alcohol resulted in inferior mechanical properties. Compared to other liquids, alcohol could more easily — and fully — penetrate the resin matrix. This resulted in the elution of residual, unreacted monomers and a concomitant decrease in flexural strength[34]. Surface observation revealed that monomer elution also resulted in severe surface flaws (Fig. 1). On the other hand, flawed specimens were caused by a decrease in the rate of cure, which in turn led to increased elution of unreacted monomers[35].

Effects of irradiation time

In the present study, the manufacturer-recommended time to light-cure a 2-mm increment with a light intensity of at least 1000 mW/cm^2 was 10 s. The light curing unit used in this study had an intensity of 1261 mW/cm^2. Therefore, a 10-s irradiation time was presumably sufficient. However, results obtained for macro- and micro-mechanical properties and rate of cure (Tables 1–3) showed that irradiation for 20 s or more led to significantly better performance. The results of this study agreed with those of Rueggeberg *et al.*[21], in that the use of manufacturer-recommended irradiation times produced lower flexural strength and scraped composite thickness than did prolonged irradiation times.

Resin layer thickness versus rate of cure

At depths of 3.5–5.5 mm, it was reported that the micorhardness values of light-cured translucent RBCs were about 80% of the surface values[20]. As the clinical indication of translucent RBCs is for anterior restorations to mimic the optical properties of natural teeth, as opposed to restoring deep cavities in posterior teeth, a resin layer thickness greater than 2 mm is rarely used. Therefore in this study, rate of cure was investigated only for the top surface and at 2-mm depth.

Irrespective of irradiation time, rate of cure at 2-mm depth was higher than on the top surface. This could be because an oxygen inhibition layer was present on the top surface, which was

produced when RBC was polymerized in air. Shawkat *et al.*[36] showed that a decrease in composite viscosity brought about by an increase in diluent monomer content in the composite matrix led to an increase in oxygen inhibition layer thickness. However, the oxygen inhibition layer thickness of RBCs ranged between 4 and 40 μm. Nonetheless, this phenomenon of increased hardness at intermediate subsurface depths compared with the hardness at small depths was discussed in numerous studies, such as one by Asmussen and Peutzfeldt[37].

Several reasons were cited for the increasing degree of cure at subsurface depths. They included proximity to the source of heat in polymerization unit or the shrinkage of unbonded light-cured RBC towards the center[38]. The latter served as a preferred explanation for RBCs, which had a reduced filler content and higher shrinkage than universal RBCs[39].

Research hypotheses: acceptance or rejection

The three research hypotheses of this study asserted that storage condition and irradiation time would not influence the mechanical properties of highly translucent RBC and that rate of cure at 2 mm depth would not differ from that on the top surface of RBC. These hypotheses were rejected based on the findings of this study.

CONCLUSION

Within the limitations of the present study, the following conclusions were drawn:

1. Alcohol aging significantly reduced the mechanical properties of highly translucent RBC.
2. Aging in artificial saliva for 4 weeks produced a positive effect on micro-mechanical properties.
3. Irradiation time was recommended to be at least 20 s to yield favorable mechanical properties.

4. Highly translucent RBC was not indicated for restorations involving outer occlusal surfaces.

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TABLES

Table 1: Effects of irradiation time and storage condition on macro-mechanical properties

	Time [s]	Storage condition		
		24 h water	**4 w saliva**	**4 w alcohol**
Flexural modulus [GPa]	**5**	2.2 ^{C} (0.3)	2.8 ^{D,E} (0.2)	1.4 ^{A} (0.1)
	10	2.6 ^{D} (0.3)	2.9 ^{D,E} (0.2)	1.6 ^{A,B} (0.2)
	20	3.1 ^{E,F} (0.4)	3.5 ^{G} (0.3)	1.8 ^{B} (0.2)
	40	3.3 ^{F,G} (0.4)	3.2 ^{F} (0.3)	1.7 ^{A,B} (0.2)
Flexural strength [MPa]	**5**	54.9 ^{C} (8.2)	37.6 ^{B} (7.4)	21.3 ^{A} (2.7)
	10	71.9 ^{D} (5.2)	58.7 ^{C} (5.0)	31.5 ^{B} (3.2)
	20	75.8 ^{D,E} (6.0)	58.1 ^{C} (4.5)	36.9 ^{B} (4.6)
	40	78.1 ^{E} (6.2)	60.6 ^{C} (4.2)	35.6 ^{B} (4.0)
Weibull, *m*	**5**	2.1	1.5	2.2
	10	4.0	3.6	3.0
	20	4.1	4.0	2.5
	40	4.2	4.6	2.7

Flexural modulus and flexural strength values are listed as mean values and standard deviations (in parentheses). Same superscript letters indicate no statistically significant differences (Tukey's HSD test, α=0.05).

Table 2: Effects of irradiation time and storage condition on micro-mechanical properties

	Time	Storage condition		
	[s]	24 h water	4 w saliva	4 w alcohol
E [GPa]	**5**	4.4 ^{A} (1.1)	5.4 ^{D} (0.4)	4.4 ^{A} (0.2)
	10	5.2 ^{C,D} (0.6)	5.8 ^{E} (0.5)	4.7 ^{A,B} (0.2)
	20	6.7 ^{F} (0.7)	7.1 ^{G} (0.3)	5.1 ^{C} (0.2)
	40	6.1 ^{E} (0.5)	7.1 ^{G} (0.6)	5.0 ^{B,C} (0.3)
HV [N/mm^2]	**5**	25.7 ^{A} (9.5)	30.9 ^{B,C,D} (2.8)	28.9 ^{B} (2.7)
	10	29.6 ^{B,C} (5.4)	33.2 ^{D,E} (3.7)	30.0 ^{B,C} (2.2)
	20	40.7 ^{G} (5.8)	44.0 ^{H} (4.0)	35.2 ^{E,F} (2.1)
	40	36.7 ^{F} (4.4)	44.5 ^{H} (6.1)	32.0 ^{C,D} (2.8)
Creep [%]	**5**	4.74 ^{E} (0.22)	4.61 ^{C,D} (0.22)	5.10 ^{F} (0.27)
	10	4.74 ^{E} (0.23)	4.53 ^{B,C} (0.26)	5.07 ^{F} (0.24)
	20	4.53 ^{B,C} (0.25)	4.43 ^{A,B} (0.23)	4.72 ^{D,E} (0.16)
	40	4.70 ^{D,E} (0.19)	4.38 ^{A} (0.22)	5.00 ^{F} (0.24)

Modulus of elasticity (E), Vickers hardness (HV), and creep values are listed as mean values and standard deviations (in parentheses). Same superscript letters indicate no statistically significant differences (Tukey's HSD test, α=0.05).

Table 3: Rates of cure at 0.1-mm and 2-mm depths

Time [s]	**$RC_{0.1mm}$ [%]**	**RC_{2mm} [%]**
5	29.5 ^{A} (2.3)	34.2 ^{B} (1.5)
10	35.2 ^{B} (4.5)	39.1 ^{C} (2.1)
20	39.3 ^{C} (3.3)	44.8 ^{D} (1.7)
40	43.2 ^{D} (4.1)	45.1 ^{D} (2.2)

Rates of cure (RC) at 0.1-mm and 2-mm depths are listed as mean values and standard deviations (in parentheses). Same superscript letters indicate no statistically significant differences (Tukey's HSD test, α=0.05).

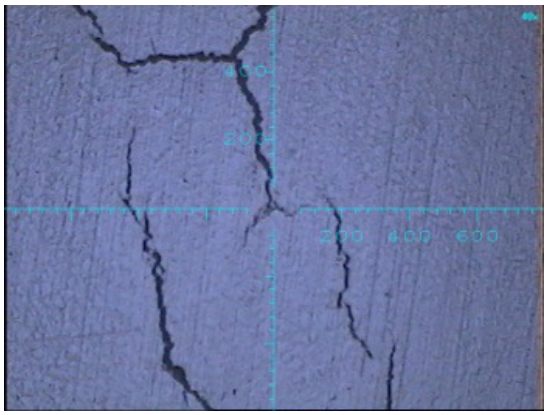
Table 4: Effects of storage condition and irradiation time on mechanical properties

Parameters	**Flexural modulus**	**Flexural strength**	**Weibull**	**E**	**HV**	**Creep**
Storage condition	.905	.865	.195	.356	.269	.164
Irradiation time	.050	.119	.606	.471	.528	.318

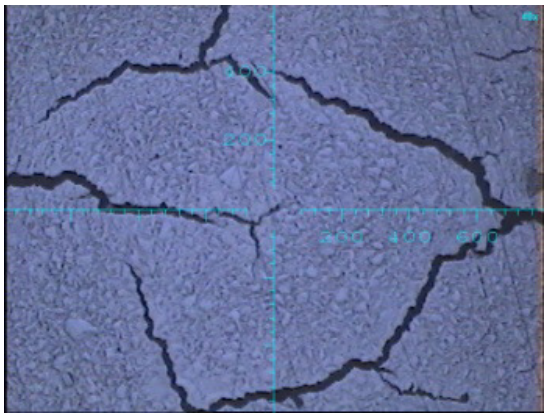
Effects of storage condition and irradiation time on macro- and micro-mechanical properties and Weibull modulus *m*. The higher the partial eta-squared values, the higher is the influence of the variable on the measured property.

FIGURES

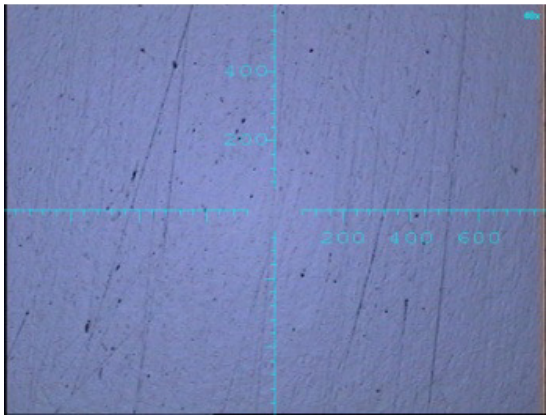
Figure 1: Surfaces of fractured specimens after three-point bending test, according to irradiation time and storage medium (40× magnification).



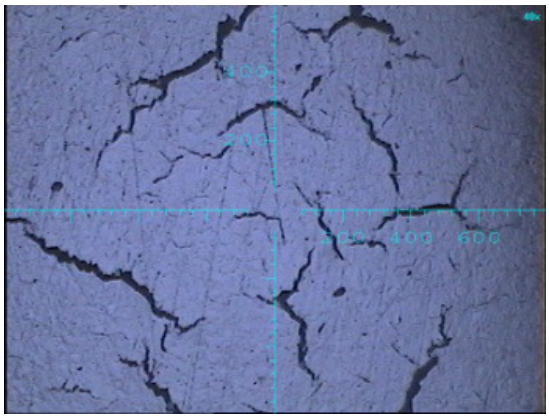
5 s – saliva



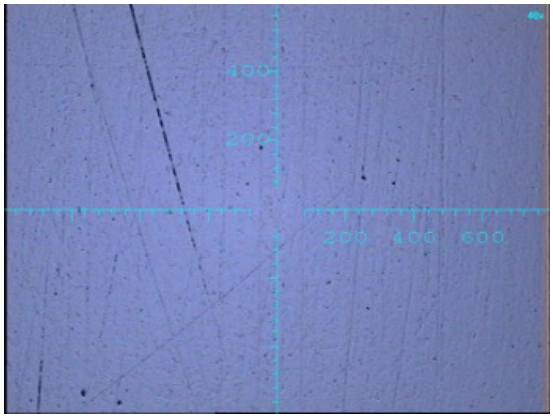
5 s – alcohol



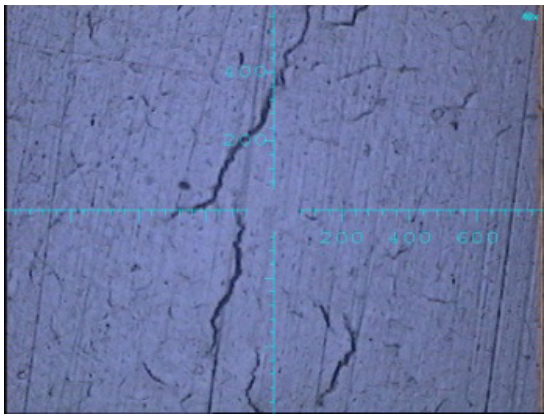
10 s – saliva



10 s – alcohol



40 s – saliva



40 s – alcohol

Figure 2: Weibull analysis of the flexural strengths exhibited under these storage conditions: (a) 24 h in water; (b) 4 weeks in saliva; (c) 4 weeks in alcohol.

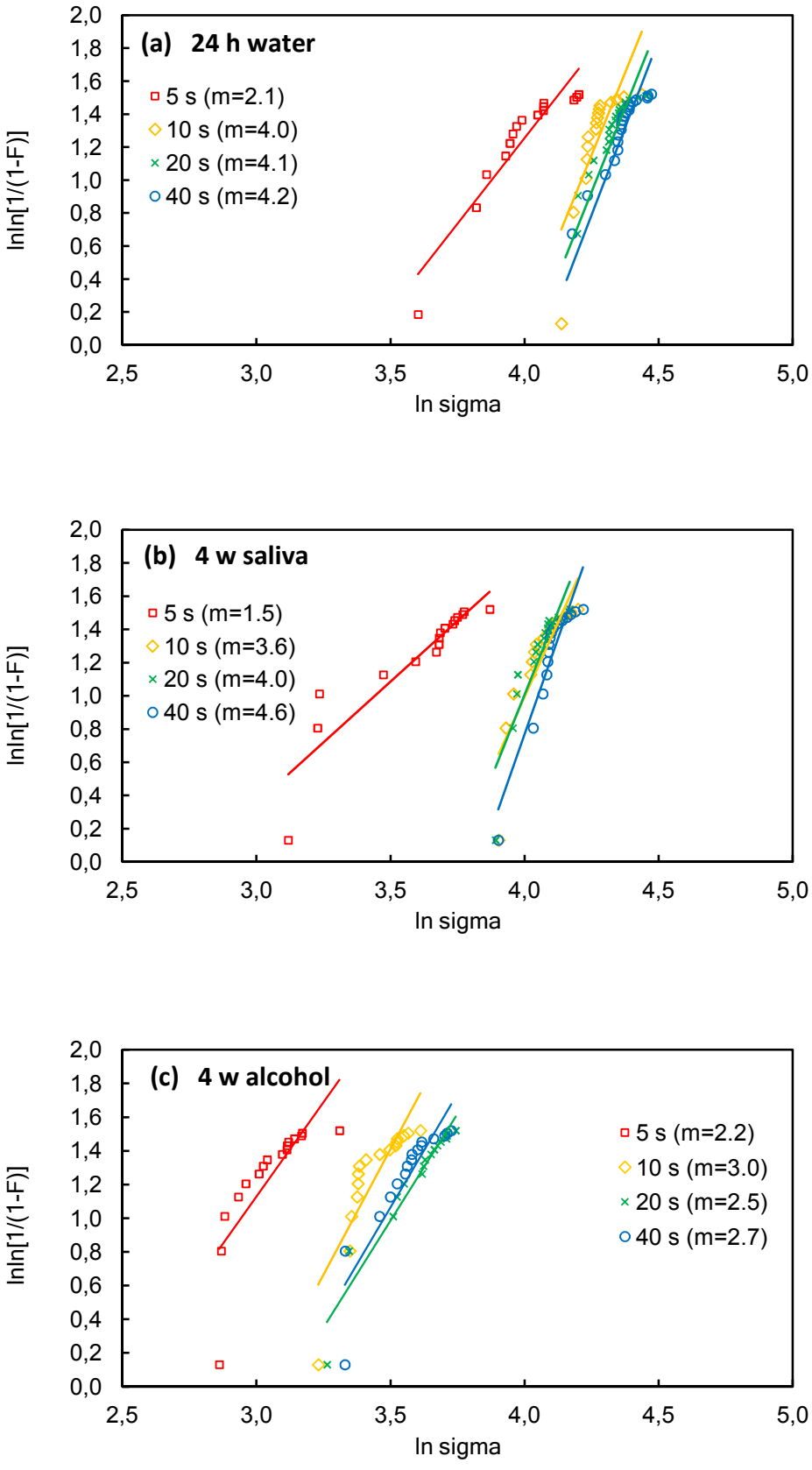


Figure 3: Variation of rate of cure within 5 min after curing according to irradiation time (mean value of 6 measurements per irradiation time): (a) 0.1 mm; (b) 2 mm.