

Werkstoffwissenschaftliche Untersuchung eines gefüllten, matrixmodifizierten zahnärztlichen Komposits

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Abkürzungsverzeichnis

ANOVA	Varianzanalyse (ANalysis Of VAriance)
AFM	Addition Fragmentation Monomers
AUDMA	Aromatic Urethane DiMethAcrylate
ATR-FTIR	Fourier-Transformations-Infrarotspektrometermit attenuated total reflection Fasersonde
Bis-EMA	Bisphenol A EthoxylatedDiMethAcrylate
Bis-GMA	Bisphenol A GlycidylMethAcrylate
CAS-No	Chemical Abstract Service Number (Unique identifier number)
CEJ	Cemento-Enamel Junction
DADMA	Dimer-Acid-Derived DiMethAcrylate
DC	Degree of Cure (Aushärtungsgrad)
DDDMA	1,12-Dodecanediol DiMethAcrylate
DEJ	Dentino-Enamel Junction (Dentin-Schmelz-Grenzschicht)
DoC	Depth of Cure
EGDMA	Ethylene Glycol DiMethAcrylate
FB-B	Filtek Bulk in einem Schritt gefüllt Harz-basiertenKomposite
FB-I	Filtek Bulk inkrementell gefüllt Harz-basiertenKomposite
FEA	Finite Element Analysis
FS-I	Filtek Supreme inkrementell gefüllt Harz-basiertenKomposite
HEMA	Hydroxyethyl MethAcrylate
HPLC	High Performance Liquid Chromatography (Hochleistungs- Flüssigkeitschromatographie)
LED	Light Emitting Diode
LoD	Limit of Detection
LoQ	Limit of Quantification
μCT	Röntgenmikrotomographie
Mw	Molecular Weight
RBC	Resin Based Composite (Harz-basierten Komposite)
REM	Rasterelektronenmikroskop

RP-LC	Reversed-Phase Liquid Chromatography
RT	Retention Time
TEGDMA	TriEthyleneGlycol DiMethAcrylate
UDMA	Urethane DiMethAcrylate
UV	Ultraviolet radiation

1. Deutsche Zusammenfassung

1.1 Einleitung

Deutliche Verbesserungen in der restaurativen Zahnheilkunde wurden durch die Einführung von Harz-basierten Kompositen erreicht, die wegen ihres ästhetischen Aussehens und der Möglichkeit der Erhaltung von mehr Zahnhartsubstanz bei der Kavitätenpräparation gegenüber anderen Ersatzwerkstoffen Vorteile aufweisen (Fusayama 1990). Eigenschaften und klinisches Verhalten dieser Komposite hängen überwiegend von ihrer Zusammensetzung ab. Sie sind ein komplexes Gemisch aus chemisch unterschiedlichen Komponenten, hauptsächlich einer organischen Matrix, anorganischen Füllstoffen, einem Initiator und einem Haftvermittler (Alshali et al. 2015; Hickey et al. 2016).

Trotz der weit verbreiteten Verwendung von Harz-basierten Kompositen in der Zahnmedizin haben diese aber auch weiterhin verschiedene Nachteile. Ein Hauptmangel der photopolymerisierten Komposite ist das Risiko einer unzureichenden Umwandlung von Monomeren und eine mangelnde Aushärtungstiefe (Lindberg, Peutzfeldt, und van Dijken 2005). Es hat sich gezeigt, dass die unzureichende Polymerisation die mechanischen und physikalischen Eigenschaften von Harz-basierten Kompositen verschlechtert (Sgarbi et al. 2017). Darüber hinaus wirkt sich das Auslösen unpolymerisierter monomerer Komponenten negativ auf die Biokompatibilität aus (Kovarik und Ergle 1993). Zusätzlich wird die Polymerisation dieser Komposite von einer volumetrischen Schrumpfung begleitet (Davidson, De Gee, und Feilzer 1984). Die Schrumpfung erzeugt Spannungen und Dehnungen an den Komposit- und Kavitätenwänden sowie an der Grenzfläche zwischen diesen, wodurch die Randintegrität der Restauration beeinträchtigt werden könnte (van Dijken und Pallesen 2014). In tiefen Kavitäten wird eine inkrementelle Schichttechnik mit einer Inkrementdicke von bis zu 2 mm empfohlen, um die Folgen der Polymerisationsschrumpfung zu verringern (Abbas et al. 2003; Kovarik und Ergle 1993).

In den letzten Jahrzehnten wurden deutliche Verbesserungen der Eigenschaften von Harz-basierten Kompositen erreicht (Dukić, Delija, und Dukić 2011) vor allem durch entscheidende Modifikationen ihrer Matrix, der Füllstoffe sowie der Initiatorsysteme (Kawaguchi, Fukushima, und Horibe 1989; Peutzfeldt 1997). Ihre fortwährende Weiterentwicklung mün-

dete in die Einführung von Kompositen mit unterschiedlichen Füllstoffen (Cramer, Stansbury, und Bowman 2011; van Dijken und Pallesen 2014; Zorzin et al. 2015). Gefüllte Komposite wurden eingeführt, um die Sensitivität gegenüber der aufwändigen Füllungs-technik und dem erhöhten Zeitaufwand der inkrementellen Schichttechnik zu reduzieren. Als eine neuere Entwicklung wurden Matrixmodifikationen konventioneller Harz-basierter Komposite vorgestellt, um eine Reduktion der Schrumpfung gefüllter Komposite unter Beibehaltung des Füllstoffgehalts zu erzielen. Dies sollte das Einsetzen, Anpassen und Aushärten von Restaurationen mit einer einzigen Schicht des Materials in Kavitäten von bis zu 5 mm Tiefe, also ohne Schichttechnik und ohne verlängerte Aushärtezeit, ermöglichen (Halvorson, Erickson, und Davidson 2002; Hickey et al. 2016; N Ilie, Bucuta, und Draenert 2013).

Obwohl mehrere Studien zur Analyse von gefüllten Kompositen durchgeführt wurden (Alshali et al. 2015; Nicoleta Ilie et al. 2014; Lempel et al. 2016; Orłowski et al. 2015), fehlen in der Literatur weiterhin hinreichende Daten, um diejenigen Komposite zu bewerten, die auf der Technologie der Matrixmodifikation basieren. Zur Bewertung neu eingeführter Harz-basierter Komposite sind verschiedene Parameter zu analysieren. Der Umwandlungsgrad (DC) wird zur Beurteilung des Ausmaßes der Polymerisationsreaktion verwendet (Braga, Ballester, und Ferracane 2005). Weiterhin ist es erforderlich, die ausgelösten Restmonomere zu identifizieren und zu quantifizieren (Lempel et al. 2014). Die Bewertung der Aushärtungstiefe ist wesentlich, um die ordnungsgemäße klinische Anwendung der Fülltechnik in einem Schritt zu gewährleisten (Frauscher und Ilie 2012; Halvorson, Erickson, und Davidson 2002). Darüber hinaus sind die In-vitro-Bewertung der Polymerisationsschrumpfung und des Mikroleckage ebenfalls wichtig, um die marginale Integrität der Restauration zu gewährleisten (Kamalak und Kamalak 2018; Van Meerbeek et al. 2003).

Dementsprechend war es das Ziel dieser Studie, ein gefülltes Komposit zu bewerten, das auf der Matrixmodifikation eines konventionellen nanogefüllten Komposits basierte. Untersucht wurden der Umwandlungsgrad (DC in %), Monomer-Auswaschung, Polymerisationsschrumpfung und Mikroleckage bei verschiedenen Schichttechniken und Aushärtungszeiten. Zusätzlich wurde der Füllstoffgehalt untersucht. Als Kontrolle wurde ein konventionelles Harz-basiertes Komposit mit dem gleichen Füllstoffsystem verwendet.

1.2 Material und Methoden

Es wurden ein gefülltes Komposit (Filtek Bulk Fill Restorative, 3M OralCare, St. Paul, MN, USA; Kurzbezeichnung: FB) und ein konventionelles nanogefülltes Komposit (Filtek Supreme XTE, 3M OralCare, St. Paul, MN, USA; Kurzbezeichnung: FS; Kontrolle) verwendet, die beide das gleiche Füllstoffsystem haben, sich aber in der Matrixzusammensetzung unterscheiden (gemäß Herstellerangaben).

Zylindrische Proben (Durchmesser: 4 mm, Höhe: 5 mm) wurden aus beiden Materialien unter Verwendung einer Teflon-Splitform mit unterschiedlichen Schichttechniken und Aushärtezeiten vorbereitet. Die Proben wurden präpariert und entsprechend der Schichttechnik in drei verschiedene Gruppen unterteilt: Filtek Supreme inkrementell gefüllt (FS-I), Filtek Bulk inkrementell gefüllt (FB-I) und Filtek Bulk in einem Schrittgefüllt (FB-B). Jede Gruppe wurde weiter in 3 Untergruppen entsprechend der Aushärungszeit in 20-Sekunden-, 30-Sekunden- und 40-Sekunden-Gruppen unterteilt. Dabei wurde das inkrementell gefüllte Komposit in 3 Schichten (2 + 2 + 1) mm gefüllt und jede Schicht einzeln ausgehärtet.

Der Umwandlungsgrad (Anzahl Probekörper: n=6) wurde für jede Versuchsbedingung am Boden der Proben unter Verwendung eines Fourier-Transformations-Infrarotspektrometers mit attenuated total reflection Fasersonde (ATR-FTIR) (PerkinElmer Universal ATR, PerkinElmer, USA) nach 24 Stunden, 7 Tagen und 30 Tagen trockener Lagerung bei 37 °C in einem Inkubator (VWR® Digital Mini Incubator, USA) gemessen.

Die Monomer-Auswaschung (n=6) wurde für jede Versuchsbedingung gemessen, die Proben wurden wie oben beschrieben präpariert und sofort nach dem Aushärten in 1 ml 75%-iges Ethanol (HPLC-Qualität) (Ethanol HPLC Grade, Fisher Chemical, USA) getaucht. Die Konzentrationen von HEMA-, Bis-GMA-, UDMA- und TEGDMA-Monomeren wurden unter Verwendung von Hochleistungs-Flüssigkeitschromatographie (HPLC) (Agilent 1260 series, Agilent Technologies Inc., CA, USA) nach 24 Stunden, 7 Tagen und 30 Tagen trockener Lagerung bei 37 °C in einem Inkubator gemessen.

Das Füllstoffsystem wurde für die beiden verschiedenen Harz-basierten Komposite untersucht. Die kalzinierten Proben jedes Materials wurden gereinigt, getrocknet, in einem Sputtergerät (SCANCOAT six, Edwards Vacuum Germany, Unterschleißheim) mit einer

Gold/Platin-Sputterschicht versehen und dann im Rasterelektronenmikroskop (REM, Philips XL30, FEI Comp, Eindhoven, NL) untersucht.

Die Aushärtungstiefe wurde den Verhältnissen der unteren/oberen Härtezahl zugeordnet. Die Oberflächenmikrohärte wurde an drei verschiedenen Punkten auf der Ober- und Unterseite jeder Probe mit einem Vickers-Mikrohärteprüfgerät (model 422A/423A, Innovatest, Maastricht, Niederland) gemessen, das mit einem analogen Okular (40-fache Vergrößerung) mit Mikrometerablesung zur Messung der Eindruckdiagonalen ausgestattet war. Das Eindruckgewicht betrug 1.000 Gramm mit einer Verweilzeit von 10 Sekunden. Der Mittelwert der 3 Messungen wurde berechnet und das Verhältnis unten/oben wurde ermittelt.

Für die Polymerisationsschrumpfung wurden 30 Proben von FB-5 mm, FB-2 mm und FS-2 mm unter Verwendung von Teflonformen vorbereitet. Jede Probe wurde zunächst mit einem μ CT (Skyscan 1174™, Skyscan, Kontich, Belgien) gescannt, dann 20 Sekunden lang ausgehärtet, gefolgt von 10 Sekunden, dann weitere 10 Sekunden, wobei zwischen den einzelnen Aushärtungszeiten erneut gescannt wurde. Die Daten wurden mit einem interaktiven medizinischen 3D-Bildverarbeitungssystem (Mimics Innovation Suite 22.0, Materialise GmbH, Gilching) rekonstruiert und analysiert. Durch den Vergleich des Volumens vor und nach der Aushärtung konnte der Prozentsatz der Polymerisationsschrumpfung unter Anwendung der folgenden Gleichung berechnet werden:

$$PS \% = ((V - V^0) / V^0) \times 100,$$

wobei PS=Polymerisationsschrumpfung, V=Volumen nach Aushärtung, V^0 =Volumen vor Aushärtung.

Für die Bestimmung des Mikroleackage wurden 90 kürzlich extrahierte menschliche Molaren gesammelt. Die Molaren wurden aufgrund zahnmedizinischer Indikationen extrahiert. Die Wurzelspitze jedes Zahnes wurde mit einem fließfähigen Komposit versiegelt, die Wurzeln wurden mit einem wasserfesten Nagellack (ROCHE-POSAY, L'Oreal, Deutschland) lackiert und dann in Harzblöcke eingebettet. Die Okklusalfächen wurden abgeflacht. In jedem Zahn wurde mit Hilfe einer Bohrmaschine (Kavo Dental GmbH, Germany) und eines Positioniertisches (milling-machine model-F1, DeguDent/Degussa, Frankfurt, Deutschland) eine standardisierte okklusale zylindrische Kavität (5 mm tief) präpariert. Nach den Ätz- und Bonding-Schritten wurden die Materialien gruppenweise gefüllt: (FB-B /FB-I/ FS-I) und für 20, 30 und 40 Sekunden ausgehärtet. Nach 5.000

Thermozyklen bei Temperaturen von 5 und 55 °C (Thermocycler THE-1100, SD Mechatronik GmbH, Deutschland) wurden die Zähne 24 Stunden lang in frisch präpariertem 1%-igem Methylenblau-Farbstoff (Certistain, Merck, Darmstadt, Deutschland) gelagert, dann geschnitten (EXAKT 300 DIAMOND BAND SAW, EXAKT, Deutschland) und unter einem Stereomikroskop (Wild Heerbrugg transmitted-light stand EB, Leica microsystem, Deutschland) auf Farbstoffpenetration untersucht. Die Bewertung der Farbstoffpenetration wurde wie folgt durchgeführt: 0 bedeutet keine Farbstoffpenetration, 1 bedeutet Farbstoffpenetration nur entlang des Zahnschmelzes, ohne die Dentin-Schmelz-Grenzschicht (DEJ) zu passieren, 2 bedeutet Farbstoffpenetration über die DEJ hinaus, ohne den Pulpalboden zu erreichen, 3 bedeutet Farbstoffpenetration in den Pulpaboden und 4 bedeutet Farbstoffpenetration in das Pulpahorn.

Numerische Daten wurden unter Verwendung von Kolmogorov-Smirnov- und Shapiro-Wilk-Tests auf Normalität untersucht. Parametrische Daten wurden durch Mittel- und Standardabweichungswerte (SD) dargestellt. Eine multifaktorielle ANOVA mit gemischtem Modell wurde verwendet, um die Wirkung verschiedener getesteter Variablen und ihre Wechselwirkung zu untersuchen. Wiederholte ANOVA-Messungen, gefolgt von mehreren paarweisen Vergleichen unter Verwendung der Bonferroni-Korrektur, wurden verwendet, um die Auswirkung von Lagerzeiten zu analysieren, während eine Einweg-ANOVA, gefolgt von Tukeys Post-Hoc-Test, zur Analyse der Auswirkungen anderer Variablen (Schichttechniken und Aushärtezeiten) verwendet wurde.

Nichtparametrische Daten wurden als Median- und Bereichswerte dargestellt und unter Verwendung des Kruskal-Wallis-Tests gefolgt vom Mann-Whitney-U-Test für paarweise Mehrfachvergleiche analysiert. Das Signifikanzniveau wurde für alle Tests auf $P \leq 0,05$ eingestellt. Die statistische Analyse wurde mit IBM® SPSS® Statistics Version 25 für Windows (SPSS, IBM Corporation, NY, USA) durchgeführt.

1.3 Ergebnisse

Für die Ergebnisse des DC wurde kein signifikanter Unterschied zwischen (FB-B: $39,1 \pm 6,4$ %) und (FS-I: $38,9 \pm 3,7$ %) gefunden, während der Wert für FB-I mit $46,6 \pm 5,0$ % signifikant höher war. Bei FB hat sich mit zunehmender Aushärtungszeit die DC% signifikant erhöht.

Die Verlängerung der Aushärtungszeit hat jedoch keinen signifikanten Einfluss auf die Gesamtabgabe der Monomere gezeigt. Die Gesamtmonomer-Auswaschung war für FS mit $9,8 \pm 1,2$ $\mu\text{g}/\text{mg}$ signifikant größer als bei FB-B ($5,1 \pm 1,8$ $\mu\text{g}/\text{mg}$). Die Abgabemenge und -rate variierten signifikant zwischen verschiedenen Monomeren. HEMA war das am höchsten ausgewaschene Monomer. Die Gesamtabgabe von HEMA war bei FS mit $34,5 \pm 10,1$ $\mu\text{g}/\text{mg}$ signifikant höher als bei FB-B ($14,6 \pm 2,1$ $\mu\text{g}/\text{mg}$), und die Auswaschung nahm mit der Lagerzeit signifikant zu. Die UDMA-Abgabe zeigte keinen signifikanten Unterschied bei den verschiedenen Materialien. Ausgewaschenes TEGDMA wurde nicht nachgewiesen. Bis-GMA zeigte jedoch eine signifikant höhere Auswaschung aus FB-B ($1,6 \pm 0,4$ $\mu\text{g}/\text{mg}$) als aus FB-I ($1,3 \pm 0,3$ $\mu\text{g}/\text{mg}$).

Unter Verwendung des REM wurde FB dadurch charakterisiert, dass es Cluster mit 3 verschiedenen Füllstoffgrößen (5,0; 2,0 und 0,5 μm) aufwies, während FS zusätzlich zu den submikroskopischen Füllstoffen eine homogenere Verteilung (2,0 und 0,5 μm) aufwies. Die Ergebnisse der Aushärtungstiefe in der vorliegenden Studie zeigten, dass das Härte-Boden/Oberseiten-Verhältnis der beiden getesteten Materialien in allen Gruppen einen Mindestwert von 0,9 erfüllen konnte. Die Polymerisationsschrumpfung lag zwischen -1,4 % (FB-5mm-20Sek.) und -1,9 % (FS-2mm-40Sek.). Es wurden keine signifikanten Unterschiede in der Polymerisationsschrumpfung und im Mikroleckage zwischen verschiedenen Packungstechniken und unterschiedlichen Aushärtungszeiten der beiden Verbundwerkstoffe gefunden.

1.4 Diskussion

Die Polymerisationseffizienz, Aushärtungstiefe und Polymerisationsschrumpfung von Harz-basierten Kompositen hängen hauptsächlich von der Matrixkonfiguration, dem Füllstoffgehalt und den Polymerisationsbedingungen ab (Leprince et al. 2013). Der Hersteller stellte fest, dass Filtek Bulk Fill-Komposite durch Matrixmodifikation von Filtek

Supreme XTE hergestellt wurde, während das Füllstoffsystem unmodifiziert blieb. Die Polymerisationsbedingungen in der aktuellen Studie, einschließlich Temperatur, Form, Bestrahlungsmethode und Farbton der Komposite, wurden standardisiert. Es wird daher angenommen, dass die Unterschiede in den Ergebnissen zwischen den beiden Kompositmaterialien auf die unterschiedliche Chemie der Harzmatrix zurückzuführen ist. Die Unterschiede in der Größe und Ballung oder Anordnung der Füllstoffe, die in dieser Studie gezeigt wurden, könnten sich jedoch auf die Lichtdurchdringung und die Aushärtungseffizienz im Verlauf der Polymerisation auswirken.

DC ist zeit- und temperaturabhängig, daher wurde sie über drei verschiedene Lagerzeiten gemessen und die Proben wurden bei konstanter Temperatur (orale Temperatur von 37 °C) gelagert (Par et al. 2014). Niedrige DC-Werte können auf das Vorkommen einiger Monomere wie TEGDMA zurückzuführen sein, dessen Struktur einige Kohlenstoff-Doppelbindungen (C=C) aufweist, eine auf jeder Seite. Es kann jedoch nur mit einer davon reagieren. In einem solchen Fall ist das Monomer von einer Seite an das Polymernetzwerk gebunden und kann daher nicht ausgewaschen werden. Darüber hinaus können während einer Polymerisationsreaktionen neue Kohlenstoffdoppelbindungen gebildet werden, was zu falsch niedrigen DC-Werten führen kann (Durner et al. 2012). FB-B und FS-I haben vergleichbare DC-Werte aufgrund der Tatsache, dass FB ein innovatives Monomer mit hohem Molekulargewicht (AUDMA) enthält, das eine geringere Konzentration von Doppelbindungen pro Gewichtseinheit aufweist, woraus höhere DC-Werte resultieren können (Lempel et al. 2014). Ein signifikanter Anstieg von DC mit längerer Lagerzeit wird der kontinuierlichen Reaktion von eingeschlossenen Restmonomeren zugeschrieben (Schneider et al. 2006), insbesondere TEGDMA (Sgarbi et al. 2017). Monomere mit kleinem Molekulargewicht konnten in beträchtlich höheren Mengen ausgewaschen werden als größere Monomere (Lempel et al. 2016; Tanaka et al. 1991). TEGDMA-Monomer hat zwar ein geringeres Molekulargewicht als Bis-GMA und UDMA, zeigte aber keine Auswaschung. Dies könnte auf die niedrige Viskosität und hohe Reaktivität des TEGDMA-Moleküls zurückzuführen sein, wodurch es stärker an der Reaktion beteiligt war und sich an die Polymerkette anlagerte (Manojlovic et al. 2011; Polydorou et al. 2007). Darüber hinaus besitzt TEGDMA eine hohe Hydrophilie, was seine Affinität zu Ethanol (organisches Lösungsmittel), und folglich seine Diffusion in die Lösung, ver-

ringert. HEMA dagegen ist ein Monomer mit einem niedrigen Molekulargewicht und inhärenter Flexibilität, was zu einer hohen Freisetzung führt (Rothmund et al. 2017). HEMA ist kein Bestandteil der Matrixmonomere, es wird jedoch in großen Mengen als Abbauprodukt von UDMA abgegeben (Michelsen et al. 2007) oder während der Polymerisationsreaktionen gebildet (Durner et al. 2012).

Das Erreichen eines Mikrohärtte-Verhältnisses von 0,9 unten/oben deutete auf eine ausreichende Polymerisation in jeder Probe hin (Bouschlicher, Rueggeberg, und Wilson 2004), trotz der Kavitätenfüllung von 5 mm in einem Schritt beim FB-Komposit. Dies könnte darauf zurückzuführen sein, dass FB, wie vom Hersteller berichtet, eine höhere Transluzenz vor der Aushärtung aufweist, was ein stärkeres Eindringen des Aushärtungslichts in die tiefe Schicht ohne Abschwächung ermöglicht. Außerdem zeigten REM-Aufnahmen eine höhere Größe und Anhäufung der Füllstoffe in FB, was die Lichtdurchdringung verbessert und somit die Aushärtungstiefe erhöht (Nicoleta Ilie und Stark 2014, 2015).

Der nicht signifikante Unterschied in der Polymerisationsschrumpfung und des Mikroleakage konnte durch das Vorhandensein eines innovativen Spannungsentlastungsmechanismus und großer Monomere in der FB erklärt werden. Die Integration eines Additionsfragmentierungsmoleküls (AFM), das sich während der Polymerisationsreaktion spaltet, könnte einen Mechanismus zum Spannungsabbau während der Polymerisation bieten (Bowman und Kloxin 2012).

1.5 Schlussfolgerungen

Die Anwendung der Matrixmodifizierungstechnologie und die Einführung neuartiger Monomere in Harz-basierten Kompositen ohne Modifizierung des Füllstoffsystems ermöglichte die Füllung der Kavitäten in einer einzigen Schicht bis zu einer Tiefe von 5 mm, wobei eine tolerierbare Polymerisationsschrumpfung und eine akzeptable Polymerisationseffizienz ähnlich wie bei konventionellen Kompositen erreicht wurde.

1.6 Zusammenfassung

Zielsetzung: Ziel dieser Studie war es, ein gefülltes Komposit zu bewerten, das auf der Matrixmodifikation eines konventionellen nanogefüllten Komposits basierte. Untersucht wurden der Umwandlungsgrad (DC in %), Monomer-Auswaschung, Polymerisations-schrumpfung und Mikroleckage bei verschiedenen Schichttechniken und Aushärtungszeiten. Zusätzlich wurde der Füllstoffgehalt untersucht. Als Kontrolle wurde ein konventionelles Harz-basiertes Komposit mit dem gleichen Füllstoffsystem verwendet. **Materialien und Methoden:** Es wurden ein gefülltes Komposit (Filtek Bulk Fill Restorative, 3M OralCare, St. Paul, MN, USA; Kurzbezeichnung: FB) und ein konventionelles nanogefülltes Komposit (Filtek Supreme XTE, 3M OralCare, St. Paul, MN, USA; Kurzbezeichnung: FS; Kontrolle). Zylindrische Proben wurden mit unterschiedlichen Schichttechniken und Aushärtungszeiten hergestellt. Der Umwandlungsgrad wurde unter Verwendung eines Fourier-Transformations-Infrarotspektrometers mit attenuated total reflection Fasersonde (ATR-FTIR) gemessen. Die Monomerelution wurde unter Verwendung von Hochleistungs flüssigkeits-chromatographie (HPLC) gemessen. Das Füllstoffsystem wurde für die beiden verschiedenen Harz-basierten Komposite im Rasterelektronenmikroskop (REM) untersucht. Die Aushärtungstiefe wurde den Verhältnissen der unteren/oberen Härtezahl zugeordnet. Zur Polymerisationsschrumpfung wurde jede Probe unter Verwendung von Mikrocomputertomographie (μ CT) gescannt. Die Daten wurden mit der Mimics-Software verarbeitet. Für die Bestimmung des Mikroleakage wurden 90 Zähne geschnitten und unter einem Stereomikroskop auf Farbstoffpenetration untersucht. **Ergebnisse:** Kein signifikanter Unterschied in DC% über verschiedene Lagerperioden zwischen B-Bulk und S-Inkremental. Eine höhere Monomerelution wurde signifikant aus (FS) als aus (FB) nachgewiesen. Die Elutionsmenge und -rate variierten signifikant über Lagerzeiten und zwischen verschiedenen Monomeren. REM-Bilder zeigten Unterschiede in der Größe der Füllstoffe und der Agglomeration zwischen beiden Materialien. Die Ergebnisse zeigten auch keine signifikanten Unterschiede in der Polymerisationsschrumpfung und im Mikroleakage zwischen verschiedenen Packungstechniken und unterschiedlichen Aushärtungszeiten der beiden Verbundwerkstoffe gefunden. **Schlussfolgerung:** Matrixmodifizierte Bulk-Fill-Verbundwerkstoffe konnten in einer Masse von

bis zu 5 mm mit einer Polymerisationseffizienz ähnlich wie bei herkömmlichen Verbundwerkstoffen verpackt und gehärtet werden.

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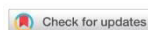
2. Veröffentlichung

2.1. The polymerization efficiency of a bulk-fill composite based on matrix-modification technology

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Research Article



The polymerization efficiency of a bulk-fill composite based on matrix-modification technology

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 Investigation: Elshazly TM. Methodology:
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ABSTRACT

Objectives: To evaluate the polymerization efficiency of a matrix-modified bulk-fill composite, and compare it to a conventional composite which has a similar filler system. The degree of conversion (DC%) and monomer elution were measured over different storage periods. Additionally, fillers' content was examined.

Materials and Methods: Cylindrical specimens were prepared, in bulk and incrementally, from Filtek Bulk Fill (B) and Filtek Supreme XTE (S) composites using a Teflon mold, for each test ($n = 6$). Using attenuated total reflection method of Fourier transformation infrared spectroscopy, DC% was measured after 24 hours, 7 days, and 30 days. Using high-performance liquid chromatography, elution of hydroxyethyl methacrylate, triethylene glycol dimethacrylate, urethane dimethacrylate, and bisphenol-A glycidyl dimethacrylate was measured after 24 hours, 7 days and 30 days. Filler content was examined by scanning electron microscopy (SEM). Data were analyzed using 2-way mixed-model analysis of variance ($\alpha = 0.05$).

Results: There was no significant difference in DC% over different storage periods between B-bulk and S-incremental. Higher monomer elution was detected significantly from S than B. The elution quantity and rate varied significantly over storage periods and between different monomers. SEM images showed differences in fillers' sizes and agglomeration between both materials.

Conclusions: Matrix-modified bulk-fill composites could be packed and cured in bulk with polymerization efficiency similar to conventional composites.

Keywords: Degree of conversion; Dental restoration; Monomer elution; Smart polymer; SEM

INTRODUCTION

Incomplete polymerization of resin-based composites, due to light scattering, yields a resin with a low degree of conversion (DC%), and poor mechanical and physical properties [1]. Moreover, the unpolymerized residual monomers which elute into the oral cavity and the pulp chamber are causing several biocompatibility side effects, including cytotoxicity and mutagenicity [2]. To avoid such risks, incremental placement, with controlled layer thickness, is recommended with separate curing of each increment, however, clinically, such technique is sensitive and time-consuming [3].

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As an effort to introduce resin composites that can be filled in bulk, modifications in monomer chemistry, initiation system, and filler content, as well as developing novel polymerization strategies were investigated [4]. Innovative formulations of resin monomer systems have been evaluated, such as derivatives of urethane dimethacrylate (UDMA) developed by incorporating aromatic or aliphatic groups. Aromatic urethane dimethacrylate (AUDMA) has a high molecular weight, which improves the mechanical properties and reduces the polymerization shrinkage, and water sorption [5-8]. Furthermore, a new pattern of crosslinked polymers called covalent adaptable networks (CANs) has been explored. They have reversible covalent bonds whose reversibility could be triggered by light, temperature, or another external stimulus. They have the ability to adjust their internal structure through either reversible bond exchange mechanisms or reversible addition/condensation polymerization reactions. Any of these mechanisms enable the material to essentially re-equilibrate at its new structure [9]. Addition-fragmentation monomer (AFM) was incorporated in CANs. Upon light curing, subsequent bond exchange within AFM occurs, leading to enhanced photo-induced plasticity, and hence introducing new technology to reduce the polymerization-associated stresses [10]. In literature, in spite of the presence of several studies assessing the bulk-fill resin composites [11-15], there is a lack of data focusing on studying the impact of these novel resin modifications on polymerization efficiency.

The polymerization efficiency of light-activated resin composites can be assessed by measuring the DC% [16]. One of the common ways of measuring DC% is using spectrometers, such as Raman spectrometer and Fourier infrared spectrometer; however, this technique is time and temperature-dependent [17]. The attenuated total reflection method of Fourier transformation infrared spectroscopy is a well-accepted widely used non-destructive method to evaluate DC% of dental materials [14,18-22]. Furthermore, polymerization efficiency could be assessed indirectly by quantification of the unreacted residual monomers. For the quantitative measurement of monomer elution, high-performance liquid chromatography (HPLC) is widely used [23].

The aim of this study was to evaluate the polymerization efficiency of a matrix-modified bulk-fill composite (Filtek Bulk Fill) and compare it to a conventional resin composite (Filtek Supreme XTE), which has nearly the same filler system according to the data provided by the manufacturer. DC% and elution of four monomers were measured over 3 different storage periods (24 hours, 7 days, and 30 days). In addition, the fillers were examined for both materials after calcination by scanning electron microscopy (SEM).

MATERIALS AND METHODS

Specimen preparation

A bulk-fill composite Filtek Bulk Fill (B) (shade: A2) (3M ESPE, St. Paul, MN, USA) and a conventional resin composite Filtek Supreme XTE (S) (shade: A2 body) (3M ESPE) were utilized (Table 1). Cylindrical specimens (diameter: 3 mm, height: 5 mm) were made from both materials using a Teflon mold. A total sample size of 38 specimens was used in this study, 18 specimens for DC% and 18 for monomer elution tests, where the number of specimens in each experimental group equal to six ($n = 6$). For SEM examination, additional 2 specimens were prepared, one from each material. A power analysis was designed to have adequate power to apply a two-sided statistical test of the research hypothesis (null hypothesis) that there is no difference between different tested materials on packing in bulk or incremental.

Matrix-modification of a dental composite

Table 1. Materials used in the study, their lot number and composition

Composite	Lot No.	Composition*
Filtek Bulk Fill posterior restorative (Shade: A2)	N701975	Fillers: non-agglomerated nanosilica of 20 nm size filler and agglomerated zirconia/silica nanocluster with the size of 5–20 nm. The fillers loading is 76.5 wt% (58.5% by volume). Organic matrix: Bis-GMA (1–10 wt%), UDMA (10–20 wt%), TEGDMA (<1 wt.%), bis-EMA6 (1–10 wt%), in addition to, AFM, AUDMA, and DDDMA.
Filtek Supreme XTE Universal (Shade: A2 body)	N862133	Fillers: non-agglomerated nanosilica of 20 nm size filler and agglomerated zirconia/silica nanocluster with the size of 5–20 nm. The fillers loading is 78.5 wt% (63.3% by volume). Organic matrix: Bis-GMA (5–10 wt%), UDMA (5–10 wt%), TEGDMA (5–10 wt%), Bis-EMA6 (1%–10%), and PEGDMA resins.

wt%, percentage by weight; Bis-GMA, bisphenol-A glycidyl dimethacrylate; UDMA, urethane dimethacrylate; TEGDMA, triethylene glycol dimethacrylate; Bis-EMA6, bisphenol A polyethylene glycol diether dimethacrylate; AFM, addition-fragmentation monomer; AUDMA, aromatic urethane dimethacrylate; DDDMA, 1,12-dodecane dimethacrylate; PEGDMA, polyethylene glycol dimethacrylate.

*According to data provided by the manufacturer (3M ESPE, St. Paul, MN, USA).

According to the results of Sgabri *et al.* [1] and Rothmund *et al.* [11], effect size (f) was found to be 9.81. By adopting an alpha (α) level of 0.05 and a beta (β) level of 0.20 (Power = 80%); the predicted sample size (n) was found to be a total of 6 samples, 2 samples per group. Sample size calculation was performed using G*Power (version 3.1.9.4). Filtek Bulk Fill composite was packed in bulk (5 mm one time) (BB group) and incrementally (increments: 2 mm + 2 mm + 1 mm) (BI group), while Filtek Supreme was packed incrementally (increments: 2 mm + 2 mm + 1 mm) (SI group). A celluloid strip was placed on a glass slide under the lower surface of the mold before packing of the materials and another one on the top side after the packing of the last increment and before curing. Specimens were light-cured for 30 sec per each increment (following the manufacturer instructions) using a light-curing device 3M Elipar DeepCure-S (3M ESPE), which produces blue light (430–480) nm wavelength and with an output intensity of 1470 mW/cm². The light guide tip has a 10 mm diameter and was placed perpendicularly and directly on the celluloid strip covering the top surface of the specimen. The light intensity was periodically checked (every 3 irradiations) by a built-in radiometer.

Measurement of DC%

For measuring DC%, specimens were stored immediately after preparation. To keep them dry, they were stored in light-proof glass vials with silica gel orange (2–3 mm) with an indicator (Perform, Carl Roth, Karlsruhe, Germany). They were preserved at 37°C in a VWR digital mini incubator (VWR; Radnor, PA, USA). Specimens were taken for measurement after 24 hours, 7 days and 30 days and stored back in the incubator in-between. Measurements were done using Fourier-transform infrared spectrometer (FTIR) (PerkinElmer Universal ATR, PerkinElmer, Waltham, MA, USA) coupled to a sampling accessory that has an attached Frontier Universal Diamond/ZnSe ATR crystal with a single reflection top-plate and pressure arm. Before starting the measurement, a background spectrum was measured. Five unpolymerized specimens were also measured. The measurement of each polymerized specimen was performed at the bottom surface of the specimen. Each specimen was suitably pressed against the ATR crystal by the aid of the pressure arm to maintain good contact between the specimen and the ATR crystal. The FTIR spectrometer was operated under the following conditions: 4000–500 cm⁻¹ wave number, 4 cm⁻¹ resolution, and 30 scans. Plot wave number versus absorption peak intensity was digitally recorded using a spectrum software (PerkinElmer Spectrum 10; PerkinElmer). The spectra were then transferred to data sheets Excel 2007 (Microsoft, Redmond, WA, USA). DC% was measured by calculating the ratio of the absorbance intensities (Abs) of the aliphatic C=C peak at wave number 1,638 cm⁻¹ and that of the aromatic C=C (internal standard) at 1,608 cm⁻¹ of the uncured and cured specimens. In the case of Filtek Bulk Fill composite, the aromatic C=C peak at wave number 1600 cm⁻¹ was used as an internal

standard due to the lack of the aromatic C=C peak at 1,609 cm⁻¹. DC% was calculated according to the following equation:

$$DC\% = \left(1 - \frac{\left(\frac{\text{Abs aliphatic}}{\text{Abs aromatic}} \right)_{\text{cured}}}{\left(\frac{\text{Abs aliphatic}}{\text{Abs aromatic}} \right)_{\text{uncured}}} \right) \times 100$$

Monomer elution

For measuring monomer elution, each prepared specimen was weighted by a standard level analytical balance that has readability down to 0.1 mg and capacity up to 220 g (Mettler-Toledo, Giessen, Germany). The mean mass of Filtek Bulk Fill specimens was 13.6 mg, and the mean mass of Filtek Supreme XTE specimens was 13.1 mg. Each specimen was then immersed in 1 mL of 75% ethanol/water solution (Ethanol HPLC Grade; Sigma-Aldrich, Steinheim, Germany) in a glass vial and stored in darkness at room temperature. HPLC measurements were performed after 24 hours, 7 days, and 30 days after immersion, respectively. After each interval, the whole solution was taken up for analysis, following that the samples were air-dried with a very mild stream of air and then immersed in 1 mL of fresh 75% ethanol/water solution and then stored back in darkness at room temperature. Quantitative analysis was performed by HPLC device (Agilent 1260 series, Agilent, Santa Clara, CA, USA) equipped with a stationary phase: column C18 (Zorbax Eclipse; Agilent) having 100 mm length, 4.6 mm inner diameter and with a particle size of 3.5 μm. The mobile phase was a mixture of water and acetonitrile (HPLC Grade; Sigma-Aldrich); (H₂O:CH₃CN): (30%:70%) (Isocratic: constant ratio all over the cycle). The flow rate was 1 mL/min and the injector volume was 10 μL. The column temperature was maintained at 40°C. The initial conditions were re-established and held for 5 minutes to ensure minimal carry-over between injections. Ultraviolet detection was performed at 205 nm for monitoring the elution of hydroxyethyl methacrylate (HEMA), bisphenol-A glycidyl dimethacrylate (Bis-GMA), UDMA, and triethylene glycol dimethacrylate (TEGDMA) by a multi-wavelength detector. Data acquisition was completed using Chromeleon software (Dionex, Sunnyvale, CA, USA). Before measurement, the standard solutions were diluted with 75% ethanol/water solution to produce the final calibration solutions: 2.5, 5, 10, 20, 40, and 80 μg/mL. The peak area for each monomer was determined and plotted versus concentration using linear regression analysis (calibration curves). The regression equations of the calibration curves, the linear correlation coefficient (R²), the retention times (RT), the limit of detection (LoD), and the limit of quantification (LoQ) of each investigated monomer are shown in (Table 2). The compounds were identified by comparison of their retention times with those of the reference compounds under the same HPLC conditions. The calculation of the eluted monomers was done after consideration of the mean mass of the specimen of each material to be expressed in the unit μg/mg.

Table 2. The regression equations of the calibration curves, the linear correlation coefficient (R²), the limit of detection (LoD) in μg/mL, the limit of quantification (LoQ) in μg/mL, and the retention times (RT) in min of the investigated monomers at 205 nm

Analytes	Regression equation	R ²	LoD	LoQ	RT
Bis-GMA	y = 45.303x + 21.281	0.9993	4.0651	12.3186	2.322 min
UDMA	y = 20.068x + 18.182	0.9991	4.2875	12.9926	2.023 min
TEGDMA	y = 34.476x + 18.226	0.9997	2.6043	7.8918	1.655 min
HEMA	y = 4.172x + 3.241	0.9980	7.0335	21.3136	1.102 min

R², linear correlation coefficient; LoD, limit of detection; LoQ, limit of quantification; RT, retention time; Bis-GMA, bisphenol-A glycidyl dimethacrylate; UDMA, urethane dimethacrylate; TEGDMA, triethylene glycol dimethacrylate; HEMA, hydroxyethyl methacrylate.

SEM

In order to study the filler content, specimens were calcinated by heating them in dry conditions for one hour at 600°C in a muffle Heraeus Thermicon P furnace (Heraeus Instruments, Hanau, Germany). Calcinated specimens were then cleaned using ethanol solution in an ultrasound bath for 10 minutes and then dried by air. After drying, the specimens were sputter-coated with Gold/Platinum by an ion-sputter instrument (SCD 030, Balzer, Liechtenstein) for 1 minute, and then examined using SEM (Philips XL 30 CP, Philips, Eindhoven, The Netherlands) operated at 10 kV.

Statistical analysis

Two-way mixed model analysis of variance (ANOVA) was used to study the effect of packing techniques of different materials and storage periods, as well as their interaction. Repeated measures ANOVA followed by multiple pairwise comparisons utilizing Bonferroni correction was used to analyze the effect of storage periods, while one-way ANOVA followed by Tukey's post hoc test was used for analyzing the effect of packing techniques ($\alpha = 0.05$, IBM SPSS Statistics for Windows, Version 20.0. IBM Corp, Armonk, NY, USA).

RESULTS

Statistical analysis of DC% results revealed that, after 24 hours and 7 days storage periods, Filtek Bulk Fill-packed incrementally (BI group) had no significant difference in DC%, $50\% \pm 3\%$, $57\% \pm 3\%$, compared to Filtek Bulk Fill composite-packed in bulk (BB group), $48\% \pm 3\%$, $52\% \pm 2\%$, respectively. No significant difference was found in DC% between BB and Filtek Supreme-packed incrementally (SI group) over the different storage periods. For BB, DC% did not increase significantly with increasing storage period (Table 3).

Statistical analysis of monomer elution results revealed that Filtek Supreme composite had significantly higher elution than Filtek Bulk Fill composite packed either in bulk or incrementally. Regarding the difference in elution between different types of monomers, HEMA had the highest mean elution value followed by UDMA then Bis-GMA, while TEGDMA was not quantified. After 30 days, no elution was detected from all groups except for HEMA from BI ($2.8 \pm 0.8 \mu\text{g}/\text{mg}$) and SI ($13.5 \pm 1.6 \mu\text{g}/\text{mg}$) (Table 4).

Unlike the data provided by the manufacturer, that both materials have the same filler system, differences were found in fillers' size and agglomeration between them. Filtek Bulk Fill composite was characterized by having clusters composed of three distinguished filler sizes ($5 \mu\text{m}$, $2 \mu\text{m}$, and $0.5 \mu\text{m}$), while Filtek Supreme composite had a more homogenous distribution ($2 \mu\text{m}$ and $0.5 \mu\text{m}$) in addition to sub-microscopic fillers fill the inter-spaces (Figures 1 and 2).

Table 3. Mean \pm standard deviation (SD) values of degree of conversion (DC%) for different packing techniques and storage periods

Storage period	DC%			p-value
	Packing technique			
	Filtek Bulk Fill-Bulk (BB group)	Filtek Bulk Fill-Incremental (BI group)	Filtek Supreme-Incremental (SI group)	
24 hr	48 ± 3^{ab}	50 ± 3^{ab}	42 ± 4^{ab}	0.015*
7 days	52 ± 2^{ab}	57 ± 3^{ab}	49 ± 2^{ab}	0.013*
30 days	53 ± 3^{ab}	65 ± 5^{ab}	57 ± 5^{ab}	0.037*
p-value	0.067ns	< 0.001*	< 0.001*	

The values are mean \pm SD.

SD, standard deviation; DC%, degree of conversion.

Different uppercase and lowercase superscript letters indicate a statistically significant difference within the same horizontal row and vertical column respectively; *, significant ($p \leq 0.05$); ns, non-significant ($p > 0.05$).

Matrix-modification of a dental composite

Table 4. Mean \pm standard deviation (SD) values of monomer elution ($\mu\text{g}/\text{mg}$) for different packing techniques and storage periods

Monomer	Storage period	Filtek Bulk Fill-Bulk (BB group)	Filtek Bulk Fill-Incremental (BI group)	Supreme-Incremental (SI group)
HEMA	24 hr	12.7 \pm 1.3 ^{Aa}	9.9 \pm 1.8 ^{Aa}	13.8 \pm 1.8 ^{Aa}
	7 days	1.2 \pm 1.0 ^{Bb}	3.4 \pm 1.5 ^{ABab}	7.4 \pm 2.6 ^{Aa}
	30 days	n\	2.8 \pm 0.8 ^{Bb}	13.5 \pm 1.6 ^{Aa}
TEGDMA	24 hr	n\	n\	n\
	7 days	n\	n\	n\
	30 days	n\	n\	n\
UDMA	24 hr	2.6 \pm 0.4 ^{Ba}	2.5 \pm 0.4 ^{Ba}	4.5 \pm 0.6 ^{Aa}
	7 days	2.3 \pm 0.3 ^{Aa}	1.7 \pm 0.4 ^{ABb}	n\
	30 days	n\	n\	n\
Bis-GMA	24 hr	1.1 \pm 0.1 ^{Ba}	1.1 \pm 0.2 ^{Ba}	2.9 \pm 0.4 ^{Aa}
	7 days	n\	n\	n\
	30 days	n\	n\	n\

The values are mean \pm SD.

SD, standard deviation; n\, not detected; HEMA, hydroxyethyl methacrylate; TEGDMA, triethylene glycol dimethacrylate; UDMA, urethane dimethacrylate; Bis-GMA, bisphenol-A glycidyl dimethacrylate.

Different uppercase and lowercase superscript letters indicate a statistically significant difference within the same horizontal row and vertical column respectively in the same monomer.

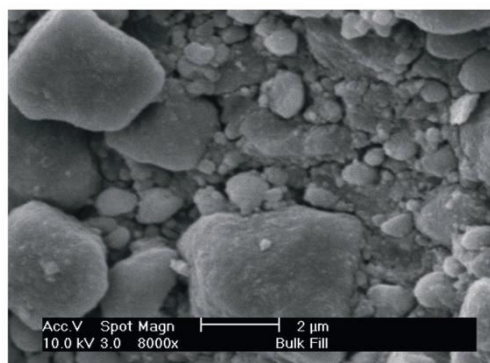


Figure 1. SEM photomicrograph ($\times 8,000$) of Filtek Bulk Fill demonstrating clusters of three distinguished filler sizes (5 μm , 2 μm , and 0.5 μm) in addition to the smaller sub-microscopic fillers.

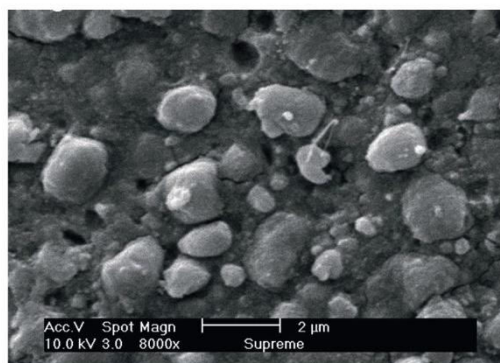


Figure 2. SEM photomicrograph ($\times 8,000$) of Filtek Supreme demonstrating homogenous filler sizes (2 μm and 0.5 μm) in addition to small sub-microscopic sizes.

DISCUSSION

The polymerization efficiency of resin composites depends mainly on matrix formulation, filler content, and polymerization conditions [24]. Filtek Bulk Fill composite was chosen in the current study to evaluate the polymerization efficiency of bulk-fill composites based on matrix modification technology. The manufacturer claimed that Filtek Bulk Fill was produced by matrix-modification of Filtek Supreme XTE with keeping the same filler system unmodified. The polymerization conditions, including temperature, mold, irradiation protocol, and shade of the material were standardized in this study. Hence, the difference in the test results between both materials assumed to be attributed to the difference in the chemistry of the resin matrix.

However, the differences in fillers' size and agglomeration, found in this study, should be considered which might have an impact on light penetration and curing efficiency. Besides, there is a slight difference in the filler volume percentage disclosed by the manufacturer (**Table 1**). Filtek Bulk Fill has a filler volume percentage of 58.5%, while Filtek Supreme has 63.3%. Moreover, no information was disclosed by the manufacturer about the initiator/accelerator content. All of these factors could have an influence on the polymerization process and hence might affect DC% and monomer elution results.

Specimens of DC% test were stored with silica particles in order to ensure dryness and to prevent water adsorption onto specimens; since moisture acts as a source of noise in FTIR measurements on using the mid-IR [18]. DC% is time and temperature-dependent; that's why it was measured over three different storage periods and the specimens were kept stored on a constant temperature (normal mouth temperature) 37°C [17]. DC% after 24 hours was $48 \pm 3\%$ for Filtek Bulk-Bulk (BB) after 30 seconds of curing time. Lempel *et al.* [15] reported that DC% of Filtek Bulk Fill-Bulk was $32 \pm 7\%$ at a depth of 4 mm after 20 seconds of light curing. The disagreement of the results might be referred to as the difference in curing time.

DC is generally reported in the range of 35% to 78% [1,25]. Nonetheless, free monomers represent only 10% of unconverted double bonds. Hence, relatively low DC % is not always related to large numbers of unreacted monomers or unconverted double bonds [26]. However, low DC% can be attributed to the structure of some monomers, like TEGDMA, which have a couple of carbon double bonds (C=C), one on each side and it may react only with one of them. In such a case, the monomer is bonded to the polymer network from one side only and cannot be eluted. Moreover, during the termination of some polymerization reactions, new C=C bonds may be formed, which can give false lower DC% [21]. Additionally, celluloid strips used to prevent the formation of the oxygen-inhibited layer are not fully effective, as this layer is only prevented in an oxygen-free atmosphere [27].

Both BB and SI groups had comparable DC%, which is in agreement with Zorzin *et al.* [20] and Li *et al.* [16]. This could be explained by the fact that Filtek Bulk contains innovative high molecular weight monomer, AUDMA, which has a fewer concentration of double bonds per unit of weight which permits attaining higher DC% values [28].

A significant increase in DC% values was recorded with longer storage, which complies with the findings of Schneider *et al.* [29], who demonstrated that an increase in DC% could still be observed up to one month and they attributed this to the continuous reaction of entrapped residual monomers. Sgarbi *et al.* [1] reported that a larger quantity of TEGDMA is considered

to be the main contributor to post-curing polymerization. This could explain why there was no significant difference in DC% values with a longer storage period of BB group (TEGDMA content is about 1 wt.%); meanwhile, DC% in SI group (TEGDMA content is about 5 wt.%) increased on storage for up to one week (**Table 1**). This was also in harmony with a study by Alshali *et al.* [18], who reported an insignificant difference between immediate and 24 hours DC% of Filtek Bulk composite when it was packed in bulk.

Another explanation of the significant post-cure increase of DC% was reported by Anseth *et al.* [30], who assumed that the free space generated microscopically during the polymerization of monomers needs a harmonious movement of the crosslinked polymer network to be manifested macroscopically as volumetric shrinkage. Otherwise, a temporary excess of internal free space is created within the bulk, which effectively provides more space for the mobility of free radicals. Therefore, higher DC% could be achieved with time till equilibrium. According to the manufacturer data, Filtek Bulk Fill composite was incorporated with AFMs, which provide a mechanism for rapid re-equilibration upon curing to overcome the polymerization shrinkage. That may also explain the insignificant difference in DC% with storage in the case of BB. However, in the case of BI, the oxygen-inhibited layer in-between the increments might contain excess trapped unreacted monomers which contribute to the post-cure polymerization.

Quantification of eluted residual monomers is a crucial indicator of the polymerization efficiency and the biocompatibility of the material [31]. Monomers of high molecular weight, such as Bis-GMA and UDMA decompose in the gas chromatograph, and thus just the products of their decomposition are detectable. On the contrary, HPLC has the capability of detecting leached monomers such as Bis-GMA and UDMA, as well as TEGDMA and HEMA [28,32]. The United States Food and Drug Administration (USFDA) has recommended 75% ethanol/water as a food and oral simulating liquid [33]. Contamination during testing procedures may result in false-positive detection of compounds, so great care was taken in order to avoid any contamination. The use of plastic containers or instruments, as well as disposable gloves, was avoided since they could probably release leachable compounds. Therefore, glass vials and metal instruments were used in the current study [34].

The results of the current study revealed that the quantity and rate of elution varied significantly between different monomers. The monomers eluted in variable quantities in the descending following order: HEMA, UDMA, and Bis-GMA, while TEGDMA was not quantified.

Lempel *et al.* [15] and Tanaka *et al.* [35] reported that monomers with small molecular weight could be extracted in considerably higher quantities than monomers with larger molecular weight. Although TEGDMA has a lower molecular weight than Bis-GMA and UDMA, however, it showed no elution. Polydorou *et al.* [36], as well as Manojlovic *et al.* [32], stated that the low viscosity and high reactivity of TEGDMA made it more involved in the reaction and became attached to the polymer chain. In addition, TEGDMA has high hydrophilicity, which decreases its affinity to organic solvents like ethanol and consequently decreases its diffusion into the solution.

HEMA, on the other hand, is a water-soluble monomer, having a low molecular weight, as well as inherent flexibility, which leads to a high amount of release [11]. On the opposite, Bis-GMA was eluted in lesser amounts due to its high molecular weight and high viscosity. Furthermore, UDMA has a lower molecular weight than Bis-GMA. Therefore, its release is faster and larger at certain time intervals [28].

Although HEMA was not listed in manufacturers' data as one of the components of the organic matrix, it was detected and eluted in significantly high amounts. This was in agreement with previous studies on dental composite resins [21,32,37,38] in which HEMA was eluted into organic solution and saliva, despite it is not a component of their matrix. These findings support the postulation that the HEMA monomer could elute as a degradation product of UDMA [38]. Another postulation [21] stated that HEMA is formed during the polymerization process by chemical reactions or rearrangements in the complex matrix of a composite.

The amount of solvent sorption into the structure of the polymer and the ability to swell and widen the space between the polymer chains are influenced by the degree of conversion, the density of crosslinking between the chains, the affinity of the polymeric network to the solvent and the compliance of the coupling between the resin and the filler [12]. Sideridou *et al.* [39] demonstrated that water sorption of the following homo-polymers was arranged in a descending way in the following order: Poly-TEGDMA, poly-Bis-GMA, and poly-UDMA. The higher water sorption of poly-TEGDMA could be attributed to the flexibility of their polymeric network that allows higher swelling by water. Meanwhile, the high water sorption of poly-Bis-GMA is attributed to the presence of hydroxyl groups. The hydrogen bonds between water and urethane groups of poly-UDMA are weaker. Therefore, it shows less water sorption. Accordingly, it could be clear why higher elution was significantly detected from Filtek Supreme than Filtek Bulk. Since, polymerized Filtek Supreme contains a larger quantity of poly-TEGDMA and poly-Bis-GMA than Filtek Bulk Fill, based on the composition of the matrix of each of them provided by the manufacturer.

According to SEM images, differences in fillers' size and agglomeration could also lead to a difference in the distribution of the matrix in each material, which might also be a reason leads to the difference in monomer elution. Increasing the filler particle size and agglomeration is a method to improve the light penetration, thus increasing the depth of cure, which was observed in Filtek Bulk Fill.

Further studies regarding quantification of the polymerization shrinkage are suggested. In addition, Michelsen *et al.* [40] reported that more than 30 different chemical substances released from dental resin-based composites into different storage media, including residual unreacted monomers, oligomers, polymerization catalysts, initiators, stabilizers, biodegradation products, and polymerization products, as well as, impurities, and metal ions. Hence, it is worth mentioning that the quantitative analysis by HPLC of elution of selected unreacted HEMA, Bis-GMA, TEGDMA, and UDMA would not provide an absolute measure of the quality of released components; and it is a limitation of this study. Therefore, full monomer elution analysis is recommended.

CONCLUSIONS

According to the findings in this study, matrix-modified bulk-fill resin composite could be packed and cured in a single 5 mm thick layer with acceptable polymerization efficiency similar to conventional composites.

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2.2. Evaluation of two resin composites having different matrix composition

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Article

Evaluation of Two Resin Composites Having Different Matrix Compositions

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Abstract: This study compared two resin composites with similar filler systems and different matrix compositions. The depth of cure (DoC), polymerization shrinkage, and marginal leakage were evaluated. A Filtek Bulk Fill resin composite (FB) and a Filtek Supreme resin composite (FS) were used. For the DoC and polymerization shrinkage, cylindrical specimens with different thicknesses were prepared. The DoC was attributed to the bottom/top ratios of Vickers microhardness numbers. For polymerization shrinkage, each specimen was firstly scanned using micro-computed tomography (μ CT) then cured for 20 s, then for 10 s, and then for 10 s, and they were rescanned between each curing time. Data were processed using the Mimics software. For marginal leakage, standardized 5 mm cavities were prepared in 90 molars. After etching and bonding, materials were packed according to groups: FB-bulk, FB-incremental, and FS-incremental, which were cured for 20, 30, and 40 s, respectively. After thermo-cycling, teeth were stored in 1% methylene blue dye for 24 h and then sectioned and observed for dye penetration. The results showed insignificant differences in the shrinkage and leakage between the different packing techniques and curing times of both materials. In conclusion, the introduction of a novel matrix into resin composite composition enabled bulk-filling in one layer up to 5 mm deep while keeping a tolerable polymerization shrinkage.

Keywords: smart polymers; polymerization shrinkage; bulk-fill resin composite; microleakage

1. Introduction

Polymerization reactions of most resin composites involve the rupture of the covalent aliphatic double bonds C=C in the reacting monomers and formation of single covalent bonds C-C. This is mostly accompanied by the shrinkage and reduction of the intermolecular distances by 0.3–0.4 nm between polymer chains [1]. The shrinkage induces stresses and strains in the resin composite and cavity walls, as well as the interface between them [2]. If the adhesion quality is not adequate, adhesive failure and microleakage may occur. Consequently, problems like recurrent caries, discoloration, sensitivity, and pulpal irritation may occur [3,4].

Numerous efforts have been exerted to introduce a material that could be clinically applied with a fast time-saving simple technique instead of the 2 mm incremental layering technique. Modifications in monomers' chemistry, initiation system, and/or fillers have led to the introduction of bulk-fill resin composites [2,5–8]. The technology of bulk-fill resin composites is based on a huge dental industry that has experienced new types of monomers, such as expanding monomers [9] and ring-opening monomers [10], as well as innovative mechanisms of polymerization reactions [11]. Furthermore, the incorporation of high molecular weight monomers has become popular [12]. Additionally, the incorporation of stress-reducing modulators into the resin backbone of a resin

composite could result in the slower development of the modulus of elasticity. Hence, these modulators allow for more time for stress reduction without decreasing the rate of conversion [11,13,14].

An ideal bulk-fill resin composite would be one that could be packed into a deep cavity with a high configuration factor design while still attaining a high degree of conversion throughout the whole restoration and exhibiting very little polymerization shrinkage stresses [15]. In order to evaluate the depth of cure (DoC), Asmussen [16] reported a direct correlation between material's hardness and the curing of the resin composite. The ISO 4049 method has not been found to accurately estimate the DoC for bulk fill materials when it has been compared to the values of the DoC determined by hardness testers [17]. According to a well-accepted definition, the DoC is the adequate thickness of a layer of resin composites, where the hardness at the bottom of it is equal to at least 80% of the maximum hardness at the top of it [12].

Polymerization shrinkage could be indirectly estimated in terms of volumetric/linear shrinkage and cuspal deflections, or it could be indirectly estimated by marginal leakage evaluation. Several methods have been used to determine polymerization shrinkage, and micro-computed tomography (μ CT) is one of them [18,19]. Three-dimensional μ CT is a cone-beam tomography that produces high-resolution images of up to a few micrometers. It is a non-destructive method that is extensively used in the investigation of bone-density [20] and in the assessment of mineral content in dental studies [21]. Furthermore, μ CT data could be used for polymerization shrinkage evaluation, either by the assessment of volumetric changes and micro-gap analysis or by the calculations of the shrinkage vector through tracing particles before and after polymerization [18,22,23].

Marginal microleakage measurements are valuable as pre-clinical screening tests [24]. The use of organic dyes as tracers is one of the oldest and most common in vitro techniques. A number of dyes, different in particle size and affinity to substrates, are used. The type of dye used is known to significantly influence microleakage results [25]. One of the most common dyes is methylene blue dye [26].

3M OralCare has introduced a bulk-fill resin composite (Filtek Bulk Fill) that has the same filler system but is different from conventional resin composites (Filtek supreme XTE) in that it has a novel matrix, as claimed by the manufacturer. This study was designed to compare both resin composites and to evaluate how far the introduction of a novel matrix composition only, without the modification of the filler system, allowed for bulk-filling of a resin composite in one layer in a cavity up to 5 mm deep while keeping a tolerable polymerization shrinkage. The comparison was done via the assessment of the depth of cure, polymerization shrinkage, and marginal leakage with different packing techniques and curing times. The depth of cure was attributed to the bottom/top ratios of Vickers microhardness numbers, polymerization shrinkage was measured using μ CT scanning combined with mimics software, and marginal leakage was semi-quantitatively assessed by a methylene dye penetration test.

2. Materials and Methods

2.1. Materials

The Filtek Bulk Fill (FB) bulk-fill resin composite (shade: A2; 3M OralCare, St. Paul, MN, USA) and the Filtek Supreme XTE (FS) conventional resin composite (shade: A2 Body; 3M OralCare, St. Paul, MN, USA) were utilized. These two resin composites have nearly the same filler system, but they have different polymeric matrixes (Table 1).

Table 1. Materials used in the study, their lot number, and composition.

Material	Lot No.	Composition ¹
Filtek Bulk Fill posterior restorative Shade: A2	N701975	Fillers: non-agglomerated nanosilica of 20 nm filler size and agglomerated zirconia/silica nanocluster with a size of 5–20 nm. The filler loading was 76.5 wt% (58.5% by volume). Organic matrix: Bisphenol-A glycidyl dimethacrylate (Bis-GMA) (1–10 wt%), urethane dimethacrylate (UDMA) (10–20 wt%), triethylene glycol dimethacrylate (TEGDMA) (<1 wt%), bisphenol A polyethylene glycol diether dimethacrylate (Bis-EMA)-6 (1–10 wt%), in addition to addition–fragmentation monomer (AFM), aromatic urethane dimethacrylate (AUDMA), and 1,12-dodecane dimethacrylate (DDDMA).
Filtek Supreme XTE Universal Shade: A2 body	N862133	Fillers: non-agglomerated nanosilica of 20 nm filler size and agglomerated zirconia/silica nanocluster with the size of 5–20 nm. The filler loading was 78.5 wt% (63.3% by volume). Organic matrix: Bis-GMA (5–10 wt%), UDMA (5–10 wt%), TEGDMA (5–10 wt%), Bis-EMA6 (1–10%), and polyethylene glycol dimethacrylate (PEGDMA) resins.

¹ According to data provided by the manufacturer (3M OralCare, St. Paul, MN, USA).

2.2. Methods

2.2.1. Depth of Cure (DoC)

A total of 90 specimens were prepared, with $n = 10$ for each experimental condition. Specimens were grouped based on the material packing technique (type of resin composite and thickness of increments) and the time of curing. In the Filtek Supreme-incremental (FS-I) group, a Filtek Supreme resin composite was applied in an incremental pattern to achieve a final thickness of 5 mm (2 + 2 + 1 mm). In the Filtek Bulk-incremental (FB-I) group, a Filtek Bulk fill resin composite was applied in an incremental pattern to achieve a final thickness of 5 mm (2 + 2 + 1 mm). Finally, in the Filtek Bulk-bulk (FB-B) group, a Filtek Bulk fill resin composite was applied in a bulk pattern with a thickness 5 mm. Each group was subdivided into 3 sub-groups according to the curing time per increment—20, 30, or 40 s.

The material was packed in a Teflon split-mold (4 mm diameter and 5 mm depth). The mold was placed on a glass slide, and a celluloid matrix was placed in between. After the packing of the resin composite, another celluloid strip was placed on the top surface and gently pressed using another glass slide to extrude the excess material. The specimens were light cured using an LED curing device (Elipar DeepCure-S, 3M OralCare, St. Paul, MN, USA), which produces blue light with a wavelength of 430–480 nm and an output intensity of 1470 mW/cm², and its 10 mm diameter light guide tip was directly placed on top of the celluloid strip covering the specimen's surface. The light intensity was checked every 3 samples with a built-in radiometer to ensure consistent light output throughout the study. The resin composite material was packed and cured according to the previously mentioned specimens' grouping. The excess material was removed, and the specimens were polished from top and bottom with 1200-grit silicon carbide grinding paper (CarbiMet 2 Abrasive Discs, Buehler, Lake Bluff, IL, USA). The dimensions of the specimens were checked by a digital caliper (CONNEX, Dettingen, Germany).

The surface microhardness of the top and bottom surfaces of the specimens was measured with a Vickers microhardness tester (model 422A/423A, Innovatest, Maastricht, Nederland) equipped with an analogue eyepiece (40X magnification) with micrometer reading to determine the indent diagonals. The applied load was 1000 g force with a dwell time of 10 s. The average of three measurements was taken for every surface. The DoC was attributed to the bottom/top hardness number ratios.

2.2.2. Polymerization Shrinkage

A total of 30 cylindrical specimens were prepared, 10 specimens per each packing technique ($n = 10$). The material was packed in Teflon split molds (4 mm diameter) with different thicknesses: FB-B = 5 mm, FB-I = 2 mm, and FS-I = 2 mm. After packing the material and before curing, each specimen was scanned using μ CT (Skyscan 1174, Skyscan, Kontich, Belgium) at a resolution of $7.7 \mu\text{m}$, a beam current of $800 \mu\text{A}$, an accelerating voltage of 50 kVp, and an exposure time of 22 s, with no filters and with a rotation of 360° at a 0.5° rotation step. The average of the total number of slices was 1022, with an average scanning time nearly equal to one hour. No curing of the material during scanning was secured since the inner compartment of the equipment was totally dark. After scanning, the specimen was cured for 20 s, as done with the DoC specimens. The specimen was rescanned after curing. Then, the specimen was cured for an extra 10 s to achieve a total curing time of 30 s, and then it was rescanned. Lastly, the specimen was cured for an extra 10 s to achieve a total curing time of 40 s, and it was rescanned using the same parameters each time. The 2D data were exported as DICOM files into a 3D interactive medical image processing system (Mimics 9.0, Materialise, Leuven, Belgium). Mimics offers extended visualization and segmentation functions based on image radio-opacity thresholding. A 3D object of each specimen could be automatically created by growing a threshold region on the entire stack of scans. In addition, the superimposition of the specimen's 3D object before and after curing could be achieved using the 3-matic tools (Figure 1). Optimal radio-opacity threshold determination was a highly-sensitive step during the determination and analysis of the 3D objects; therefore, a sensitivity test was performed to determine the best parameters for defining the correct volume of the specimens. The 3D properties of the object provided information about the volume of the specimen in μm^3 . The volume of the specimen was checked experimentally. Each specimen was a reference to itself, and the polymerization shrinkage calculation was based on the original pre-curing volume of each specimen individually. By comparing the volume before and after curing, the percentage of the polymerization shrinkage could be calculated by applying the following equation:

$$PS \% = \left((V - V^\circ) / V^\circ \right) \times 100$$

where PS is polymerization shrinkage, V is the volume after curing, and V° is the volume before curing.

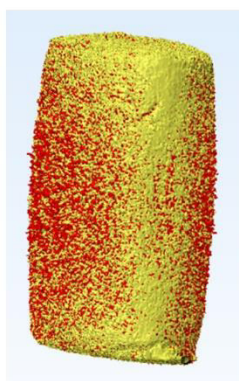


Figure 1. Superimposition of 3D objects created by growing a threshold region on the entire stack of scans of Filtek Bulk Fill resin composite specimen (5 mm) before curing (yellow) and after 20 s curing (red). The 3D properties of the object provided information about the volume of the specimen in μm^3 . By comparing the volume before and after curing, the percentage of the polymerization shrinkage could be calculated.

2.2.3. Marginal Leakage

A total of 90 recently extracted sound human wisdom molars, which were extracted for orthodontic or surgical purposes, were collected from the dental school of the university hospital Bonn. They were cleaned from soft tissue debris by using a manual scaler and then stored until usage in 0.5% chloramine solution at 4 °C until testing for a maximum of two months. The root apices were sealed with a resin composite, and the roots were double coated with a water-proof nail varnish; then, they were embedded in a cold-curing resin blocks (Technovit 4004, Kulzer, Hanau, Germany) up to directly below the cemento–enamel junction for the easier handling of the teeth. The occlusal surfaces of all the samples were flattened by the aid of a water-cooled diamond disc (Komet, Brasseler, Lemgo, Germany). Each tooth block was mounted on the surveying table of a drilling/milling machine (F1 model milling-machine, DeguDent/Degussa, Frankfurt, Germany) that was equipped with Kavo K9 handpiece (Kavo Dental, Biberach, Germany). The handpiece of the drilling machine was only used for a vertical movement depth of up to 5 mm and a rotation speed of 25,000 rpm in presence of copious water spray. A new drill was used for every 5 cavity preparations. One standardized cylindrical occlusal cavity, 5 mm deep, was prepared in each tooth (Figure 2) with a cylindrical 3 mm diameter carbide drill (Carbide tipped jobber drill, Garant, Hoffmann, Munich, Germany). The dimensions of the cavity were determined by the size of the drill, and the machine settings and were verified using a periodontal probe. Teeth with pulp exposure upon cavitation were discarded.

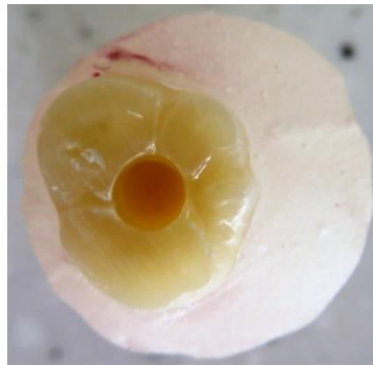


Figure 2. Standardized occlusal cavity with a 5 mm depth in an upper sound molar embedded in a cold-curing resin block up to directly below the cemento–enamel junction after the sealing of the roots by 2 layers of water-proof nail varnish.

The teeth were blindly divided into 9 experimental groups: 3 main groups according to packing technique: FB-B, in which the resin composite was packed in single layer of 5 mm, and FB-I and FS-I, in which the resin composite was incrementally packed in the 5 mm cavity (2 + 2 + 1 mm) and each layer was cured individually. Each main group was subdivided into three different curing time groups (20, 30, and 40 s). Ten teeth were used for each experimental condition ($n = 10$). The enamel margins were etched with a 36% phosphoric acid gel (Scotchbond Universal Etchant Etching Gel, 3M OralCare, St. Paul, MN, USA) for 30 s (manufacturer’s instructions). The cavity was then washed with copious air/water spray for 30 s and then it was gently dried with an oil-free air. A bonding agent (Scotchbond Universal adhesive, 3M OralCare, St. Paul, MN, USA) was applied to the cavity with gentle agitation followed by 5 s of the gentle application of an oil-free air and then 10 s of light-curing (following the manufacturer’s instructions). Light-curing was achieved by using the same LED curing device of the μ CT test.

After the packing and curing of the resin composite according to the previously mentioned specimens’ grouping, the surfaces of the restorations were finished and polished using ascending

grits (Soflex, 3M OralCare, St. Paul, MN, USA). Prepared specimens for microleakage testing were subjected to cycles of thermal fluctuations for the simulation of artificial aging using a thermocycler (Thermocycler THE-1100, SD Mechatronik, Germany) from 55 (± 1) to 5 (± 1) °C, with a dwell time of 30 s and a transfer time between each water bath of 10 s—for 5000 cycles. After the completion of thermo-cycling, the teeth were dried and double coated with a waterproof nail varnish along the whole surfaces except for 1 mm around the margins of the restoration. Then, the teeth were immersed in freshly prepared 1.0% methylene blue dye (Certistain, Merck, Darmstadt, Germany) for 24 h. The teeth were then rinsed thoroughly with running water and sectioned buccolingually along their long axes into two sections using an automated water-cooled diamond saw (EXAKT 300 CP Band System, Norderstedt, Germany). The specimens were examined for marginal leakage and dye penetration by using stereomicroscope (Wild Heerbrugg transmitted-light stand EB, Leica microsystem, Wetzlar and Mannheim, Germany) at a magnification of 15X (Figure 3). The scoring of dye penetration was done for marginal leakage (Figure 4) as follows:

- ❖ 0 = No dye penetration.
- ❖ 1 = Dye penetration is only along enamel and does not pass the dentino–enamel junction (DEJ).
- ❖ 2 = Penetration of the dye beyond the dentino–enamel junction but not reaching the pulpal floor.
- ❖ 3 = Penetration of the dye to the pulpal floor.
- ❖ 4 = Penetration of the dye to the pulp horn.

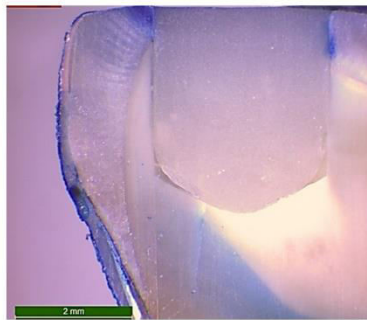


Figure 3. Microphotograph at 15X magnification of a longitudinal section of a restored standardized cavity in a sound molar after 5000 cycles of thermo-cycling and immersion in freshly prepared 1.0% methylene blue dye for 24 h in order to examine the marginal leakage by evaluation of the grade of dye penetration.

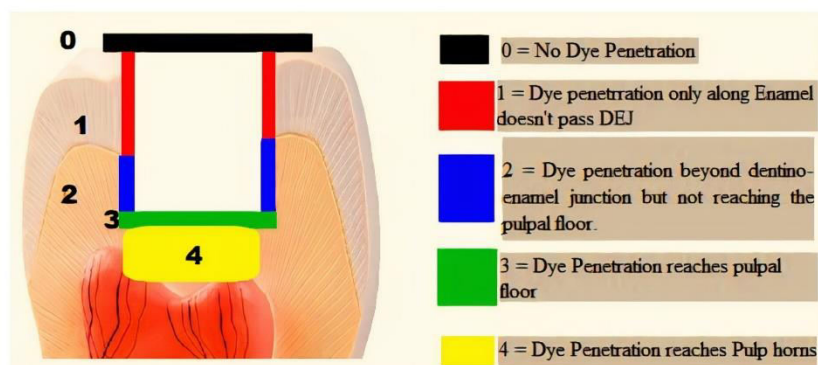


Figure 4. Schematic diagram representing the used scoring system of marginal leakage.

2.2.4. Statistical Analysis

The power analysis was designed to have adequate power to apply a two-sided statistical test of the research hypothesis (null hypothesis) that there was no difference between different tested materials. According to Lima et al. [27], Kamalak et al. [19], and Orłowski et al. [28], effect size (f) was found to be 9.81. By adopting an alpha (α) level of 0.05 and a beta (β) level of 0.20 (power = 80%); the predicted sample size (n) was found to be a total of 4 samples per group. Sample size calculation was performed using G*Power version 3.1.9.4.

Statistical analysis was performed with IBM SPSS (IBM Company, Endicott, New York, USA) Statistics Version 25 for Windows. Regarding the depth of cure and polymerization shrinkage tests, the data were normally distributed, and a two-way ANOVA was used to analyze the effects of curing time, the packing technique, and their interactions. Marginal leakage data are presented as median and range values, and the effect of curing time was analyzed using Friedman's test followed by multiple pairwise comparisons utilizing Wilcoxon signed-rank test with the Bonferroni correction. The effect of the packing technique was analyzed using the Kruskal–Wallis test followed by multiple pairwise comparisons utilizing the Mann–Whitney U test with the Bonferroni correction. The significance level was set at $p \leq 0.05$ for all tests.

3. Results

The results of the DoC in the present study revealed that the hardness bottom/top ratio of both tested materials in all groups fulfilled a minimum value of 0.9. The polymerization shrinkage value range was between -1.4% (FB-bulk—cured for 20 s) and -1.9% (FS-incremental—cured for 40 s). Regarding marginal leakage, (FS-I) and (FB-I) packing techniques at a 40 s curing time were the only groups among the different groups, which recorded a marginal leakage score 4, while the FB-B packing technique group at 20 and 40 s curing times were the only groups that recorded a score of 0. No significant difference was found in polymerization shrinkage and marginal leakage values between the different packing techniques and curing times of both tested resin composite materials.

Means and standard deviations (SD) for the bottom/top ratios' Vickers hardness numbers (depth of cure) for different curing times and packing techniques are presented in Table 2. Mean and standard deviation values for polymerization shrinkage are presented in Table 3. Median and range values for marginal leakage scores for different packing techniques and curing times are presented in Table 4. The percentage (%) of marginal leakage scores for different curing times and packing techniques are presented in Figure 5.

Table 2. Mean \pm standard deviation (SD) values of the bottom/top ratios' Vickers hardness numbers (depth of cure) for different curing times and packing techniques.

Packing Techniques	Curing Time (Means \pm SD)			p-Value
	20 s	30 s	40 s	
Filtek Supreme-Incremental (FS-I)	0.99 \pm 0.17 ^{Aa}	0.96 \pm 0.01 ^{Ba}	0.94 \pm 0.02 ^{Ba}	0.002 *
Filtek Bulk-Incremental (FB-I)	0.97 \pm 0.04 ^{Aa}	0.96 \pm 0.02 ^{Aa}	0.98 \pm 0.03 ^{Aa}	0.676 ^{ns}
Filtek Bulk-Bulk (FB-B)	0.90 \pm 0.02 ^{Bb}	0.99 \pm 0.04 ^{Aa}	0.98 \pm 0.03 ^{ABa}	0.003 *
p-value	<0.001 *	0.054 ^{ns}	0.111 ^{ns}	

Different upper and lowercase superscript letters indicate statistically significant difference within the same row or column, respectively *; significant ($p \leq 0.05$) ^{ns}; non-significant ($p > 0.05$).

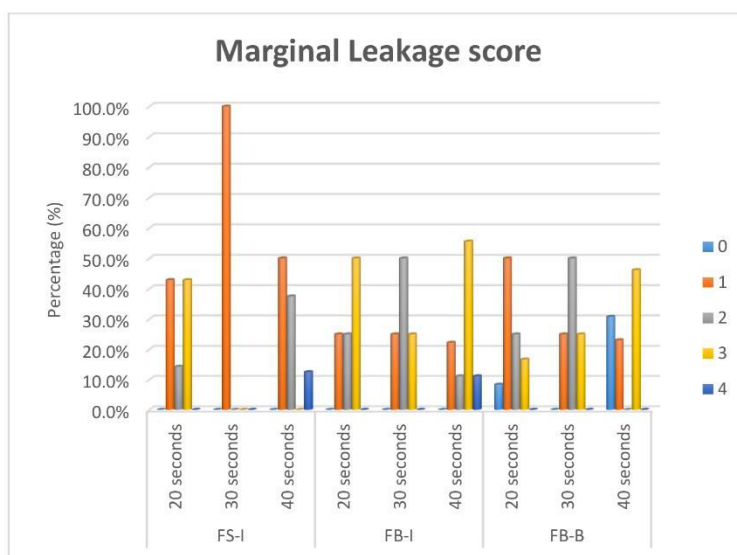
Table 3. Mean \pm SD values of polymerization shrinkage for different packing techniques and curing times.

Packing Technique	Curing Time	Mean	St. Deviation
Filtek Supreme-Incremental (FS-I)	20 s	-1.9%	0.2
	30 s	-2.0%	0.3
	40 s	-1.9%	0.3
Filtek Bulk-Incremental (FB-I)	20 s	-1.6%	0.3
	30 s	-1.7%	0.4
	40 s	-1.7%	0.4
Filtek Bulk-Bulk (FB-B)	20 s	-1.4%	0.3
	30 s	-1.5%	0.3
	40 s	-1.5%	0.4

Table 4. Median (range) values of marginal leakage for different curing times and packing techniques.

Packing Technique	Curing Time			p-Value
	20 s	30 s	40 s	
Filtek Supreme-Incremental (FS-I)	2.0 (2.0)	1.0 (0.0)	1.6 (3.0)	0.72 ^{ns}
Filtek Bulk Fill-Incremental (FB-I)	2.3 (2.0)	2.0 (2.0)	2.7 (3.0)	0.84 ^{ns}
Filtek Bulk Fill-Bulk (FB-B)	1.4 (3.0)	2.0 (2.0)	1.4 (3.0)	0.82 ^{ns}
p-value	0.21 ^{ns}	0.05 *	0.19 ^{ns}	

*; significant ($p \leq 0.05$)^{ns}; non-significant ($p > 0.05$).

**Figure 5.** Bar chart showing the percentage (%) of marginal leakage scores for different curing times and packing techniques of Filtek Bulk-bulk (FB-B), Filtek Bulk-incremental (FB-I), and Filtek Supreme-incremental (FS-I).

4. Discussion

The DoC is a cornerstone in evaluating any newly introduced resin composite [29]. Based on ISO standards, the acceptable restoration's DoC is its thickness when the hardness at its bottom surface is at least 80% of the hardness at its top surface [12,30,31]. However, some authors [11,29] have criticized this method because the size of the micro-indenter is considerably larger than the distance between neighboring fillers of resin composites. However, it is still a well-accepted method in the literature, especially when the hardness number is measured at more than one location on the surface and the mean is taken afterwards [12,31–34].

The Vickers microhardness tester is one of the most commonly used microhardness testers. It has the advantage of assurance of a constant value for the hardness number over a wide range of test load [35]. In the current study, a high load was used (1000 gm) because it could produce a larger impression and therefore made it easier to measure the indentation diagonal [36]. In addition, some studies of microhardness on a wide range of loads have demonstrated that the results are not constant at very low loads [37].

The results of the DoC in the present study revealed that the hardness ratio of all tested materials fulfilled a minimum value of 0.9 bottom/top ratio. This indicated an adequate polymerization throughout the whole specimen in spite of the 5 mm bulk-filling of the FB resin composite. This could be explained by the fact that FB has more pre-curing translucency and the greater penetration of curing light into the deep layer without attenuation due to the conducting adjustment of the refractive indices of the matrix/filler, as reported by the manufacturer. This is in a good agreement with studies by Alshali et al. [38] and Alrahlah et al. [34], who used a Vickers hardness tester to evaluate the DoC of different types of bulk-fill resin composites including FB. They reported that FB attained a sufficient bottom/top hardness ratio. However, Alrahlah et al. [34] reported a maximum depth of cure for FB of only 4.14 mm. This difference could be attributed to the different types of mold used in the study (stainless steel mold).

The FB-B group showed a significantly lower DoC with a 20 s curing time, as compared to the FB-I and FS-I groups, reflecting the requirement of higher amount of radiant exposure to attain an equal bottom/top ratio at a 5 mm depth [39]. A similar study by Lempel et al. [40] reported that the extended curing time of FB significantly increased the DoC, especially at the bottom surface, which consequently increased hardness. An interesting finding revealed by the current study was that the DoC of FS-I at 20 s was significantly higher than with 30 and 40 s curing times ($20 > 30 = 40$). Leprince et al. [29] reported that 40 s of irradiation resulted in a greater mobility of unreacted monomers, leading to more polymerization and, consequently, a higher hardness at the surface of the material, which means a lower bottom/top ratio.

A digital non-destructive full analysis of pre-cured and post-cured material can be performed in three dimensions with sufficient opacity by using μ CT [18,19,22]. The μ CT technique, combined with Mimics software employed in this study, resulted in the successful detection of the specimens and the accurate calculation of their volumes, which were checked experimentally. It was observed that the threshold range was little bit different from Filtek Supreme specimens and Filtek Bulk Fill specimens, which could be referred to the slight difference in filler content percentage (Table 1) [22]. Each specimen was a reference to itself, so the slight difference in volume resulting during the preparation of different specimens could be ignored.

The results of this study showed an insignificant difference in polymerization shrinkage between tested materials despite the difference in the packing techniques and curing times. That could be explained by the presence of an innovative stress-relieving mechanism. The incorporation of a novel monomer called the addition-fragmentation molecule (AFM), which cleaves during the polymerization reaction, could provide a mechanism of stress relief while maintaining the physical properties of the polymer [14]. In addition, the Filtek Bulk Fill resin composite contained modified, high molecular weight aromatic urethane dimethacrylate (AUDMA) monomers. These monomers have a lower concentration of double bonds that consequently increase the degree of conversion while maintaining

a reduced polymerization shrinkage [41,42]. Despite the insignificant differences in the measured shrinkage, however, there was still an apparent and expected decreasing trend from FS-I to FB-I to FB-B.

The polymerization shrinkage values reported in this study were in agreement with many studies that have reported the polymerization shrinkage of the resin composite in the range of 1.2%–2.7% [19,43–45]. Junior et al. [45] reported that the polymerization shrinkage of the incrementally placed Filtek Supreme was $1.2 \pm 1.0\%$, and the slight difference could have been caused by the difference in the layer thickness used in their study (≈ 1.3 mm). Kamalak et al. [19] evaluated the volumetric shrinkage of the flowable Filtek Ultimate (Supreme) and flowable Filtek Bulk Fill using μ CT Skyscan 1172 and the CTAn software. They reported an insignificant difference between Filtek Supreme and Filtek Bulk Fill resin composites with values of 2.1 ± 0.8 and 2.0 ± 0.5 , respectively. Kim et al. [46] measured the polymerization shrinkage using positron sensitive photo detector (PSPD) equipment, and seven different flowable resin composite resins were tested in their study. They reported that the flowable Filtek Supreme demonstrated a shrinkage value of $2.2 \pm 0.7\%$. The difference in these reported values compared to the current study could be attributed to the use of flowable resin composites in their study [2,47]. On the other hand, the results of the current study were different from a study by Sampaio et al. [23], who reported a $5.5 \pm 1.8\%$ polymerization shrinkage of the flowable Filtek Bulk by using the μ CT of different types of resin composites.

The main aim of in vitro marginal leakage tests was to predict the clinical behavior of the restoration. The use of the dye penetration test remained the most popular for in vitro microleakage evaluations, qualitatively or semi-quantitatively [24,25]. Methylene blue dye was used as a tracer in the current study. Different storage periods of the samples in the dye were reported, but 24 h was the most common period [28], and this was the choice in the present study. Nevertheless, it was stated in a review [48] that the storage period in methylene blue dye seems to have no influence on microleakage scores.

In the current study, an occlusal cavity with a cylindrical design was chosen. Several cavity designs have been used in other studies—either class V or occlusal cavities, including cylindrical, rectangular, and wedge-shaped preparations. However, the dentinal tubules in a cylindrically shaped cavity are almost aligned with the walls of the preparation compared to wedge-shaped class V preparation [49]. Moreover, in the class V cavity design, the occurrence of prismless enamel at the gingival margins is frequent. There is a limitation of resin penetration into prismless enamel, which may not provide an effective barrier to dye penetration and may affect results [50]. In addition, the use of a parallelometer ensured the attainment of standardized cavities during the study [51].

Clinically, restorations are exposed to the long-term accumulation of temperature fluctuations, which could lead to marginal deterioration. In an attempt to simulate the clinical situation, specimens were exposed to thermo-cycling from $55 (\pm 1)$ to $5 (\pm 1)$ °C for 5000 cycles [52]. Therefore, the application of thermal cycling during testing is expected to provide a better prediction of in vivo performance [24,53,54].

The results of marginal leakage evaluation revealed an insignificant difference in marginal leakage scores for the bulk resin composite compared to the conventional one, in spite of the difference in packing techniques. This could have been due to the approximately similar filler loadings, as well as the incorporation of stress modulator and high molecular weight monomers in the bulk-fill resin composite matrix (Table 1). The current results also revealed insignificant differences in marginal leakage between different curing times with different packing techniques. This is not in harmony with the understanding of the polymerization reaction kinetics of most resin composites in which a longer curing time leads to the greater formation of free radicals, which means a higher rate of chain growth and higher conversion of double bonds—both of which involve volumetric shrinkage [10,55,56]. However, this conflict could be explained by the presence of stress relieving mechanism in FB, as mentioned before.

These results contradict those of a study done by Kim et al. [46], who reported less microleakage for flowable FB than for flowable FS. They attributed their results to the presence of a bisphenol A polyethylene glycol diether dimethacrylate (Bis-EMA) monomer in FB that usually exhibits a higher

degree of conversion and a lower amount of polymerization shrinkage than the typical bisphenol-A glycidyl dimethacrylate/triethylene glycol dimethacrylate (Bis-GMA/TEGDMA) combination contained in the flowable FS. Zorzini et al. [6] also found that the flowable FB showed less shrinkage than the flowable FS, and they attributed that to presence of a larger amount of TEGDMA in FS (5–10 wt%) than in FB (<1 wt%), which reduced the viscosity of resin composites and hence increased polymerization shrinkage.

In an agreement with Furness et al. [15], it was obvious that dye penetration into the bonded interface had random different behaviors among different materials. In addition, there was a notable gap formation at the pulpal floor of all restorations. Additionally, the observation of dye rush into the dentinal tubules in many sections may be attributed to the position of the micro-gap formation along the interface. If such a formation occurs between the restoration and the hybrid layer, a localized pooling of the dye may be expected, since the tubules remain sealed. However, if the micro-gap occurs between the hybrid layer and the underlying dentine, dye penetration would be expected.

The present study had the limitations of measuring the volumetric polymerization shrinkage of free unbonded resin composite specimens. In addition, the semi-quantitative evaluation of marginal leakage can only act as a precursor to in vivo studies. Furthermore, although methylene blue dye is a commonly used tracer, it has a small particle size and as such may lead to an overestimation of the relevance of its infiltration [26] and give higher microleakage scores than other microscopic evaluations [57]. Further studies are recommended regarding the directions of shrinkage and the correlation between the degree of conversion and the polymerization shrinkage. Clinical studies are suggested.

5. Conclusions

The introduction of a novel matrix into a resin composite, without the modification of the filler system, enabled the bulk-filling in one layer up to 5 mm deep while keeping a tolerable polymerization shrinkage.

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Abbreviations: Bis-GMA: Bisphenol-A glycidyl dimethacrylate, UDMA: Urethane dimethacrylate, TEGDMA: Triethylene glycol dimethacrylate, Bis-EMA6: Bisphenol A polyethylene glycol diether dimethacrylate, AFM: Addition-fragmentation monomer, AUDMA: Aromatic urethane dimethacrylate, DDDMA: 1,12-dodecane dimethacrylate, PEGDMA: Polyethylene glycol dimethacrylate, wt%: % by weight.

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