Storage Temperature Effect on Degree of Polymerization and Surface Hardness of Bulk-Fill Composite Resin

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Abstract

The objective of the study was to evaluate the effect of storage temperature on degree of polymerization and surface hardness of bulk-fill composite resin by storing it for 24 h at three different temperatures before testing: at 5°C, at 25°C, and at 35°C. Thirty-six specimens of composite resin were placed into a Fourier transform infrared spectrometer to analyze degree of polymerization; another 24 specimens of resin were tested for hardness using a hardness tester.

By analyzing results with a one-way ANOVA and LSD post hoc test, we determined that temperature did not significantly affect degree of polymerization, but hardness significantly differed between treatments when compared using a Vicker's hardness number (VHN). The highest mean VHN occurred at 35°C (VHN = 53.86 ± 0.79), followed by 25°C (VHN = 51.94 ± 0.41), and the lowest at 5°C (VHN = 49.22 ± 0.57). Therefore, elevating the storage temperature of bulk-fill composite resin before use may not affect degree of polymerization but will increase surface hardness.

Introduction

Composite resins are widely used in dental practices to re-establish form, function, and aesthetics of teeth and thus, have become an integral part of the modern, esthetic dentistry.[1,2,3] Composite resins have undergone several improvements since they were introduced in 1962.[4] Recently, there have been significant improvements in dental resins (particularly in bulk-fill composite types), which have reduced the time and effort required to apply them.[5] These new types of bulk-fill resins can be cured or polymerized into a single, 4-mm-thick layer, which is considerably more preferable than the technique required for applying traditional resins, which require incremental applications that have to be cured layer by layer in ≤2-mm thicknesses.[6,7] Layer-by-layer application is more time-consuming and creates gaps between resin layers, which results in weaker bonds and contamination between layers.[6,7,8] Other advantages of bulk-fill composite resins are that they adequately polymerize and transmit more light.[6,7,9]

Polymerization is defined as a chemical reaction that converts monomers into a polymer chain structure.[11] Inadequate polymerization can result in resin shrinkage after polymerization and a reduction in resistance to wear.[10] More complete polymerization would maximize the physical, mechanical, and biocompatibility benefits of composite resins.[6] However, not all monomers in composite resins can be converted to polymers during polymerization, which results in unsaturated free monomers (unreacted monomers) in the final product. The amount of unconvertable monomers in the initial product affects its degree of polymerization.[12] The extent to which a monomer is polymerized is determined by the number (or percentage) of double carbon bonds (C=C) that it possesses, which are then converted during polymerization

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to a single carbon bond (C-C) needed to build a polymer chain.[12,13] A lower degree of polymerization means that fewer monomers become bound to the polymer. Furthermore, a lower degree of polymerization in dental restoration results in inferior mechanical properties, greater discoloration and degradation, poorer wear resistance, and lower color stability.[7] In contrast, a higher degree of polymerization improves the physical and mechanical properties of a composite resin.[14,15] An important mechanical property is surface hardness, defined as the material's resistance to permanent penetration or indentation. This property is used to evaluate wear resistance, particularly where a surface encounters large amounts of masticatory forces, such as in posterior stress-bearing areas; polishability; and abrasive effects on antagonist teeth.[8,11,16,17]

Composite resins should be capable of being stored for long periods (i.e., possess a long shelf life) without compromising their physical and mechanical properties.[14] Shelf life is specified by resin manufacturers as the time period during which the material remains suitable for use.[18] Dentists store composite resins in refrigerators to prolong their shelf lives, usually at temperatures ranging from 2°C to 5°C.[19] Such cooled composite resins are often immediately used after being taken from a refrigerator.[14] However, a dental resin should be removed an hour or more before its planned use to allow it reach room temperature due to anticipating alteration the properties of polymerized composite resin.[20,21] In addition, several dentists also increase the temperature of composite resins to improve their malleability, which reduces the viscosity of the material. Lower viscosity of a composite resin enables an easier application, improves marginal adaptation to cavity walls, and reduces microleakages.[12,20,21]

Several studies have reported that storage temperature may affect the polymerization reaction of composite resins restoration.[3] One study examined the mechanical properties of composite resins stored in a 37–40 ºC oven to simulate high temperatures associated with exposure to direct sunlight or storage under ambient conditions in warm climates or during warm seasons.[14,22] However, it is not entirely clear how warm storage temperatures affect the characteristics of composite resins (e.g., their degree of polymerization and surface hardness). Therefore, the aim of this study was to analyze the degree of polymerization and surface hardness of composite resins stored under various temperature regimes: in a refrigerator, at ambient room temperature, and in a warming oven.

Materials and methods

Thirty-six specimens of bulk-fill composite resin (Tetric® N Ceram, Ivoclar Vivadent, Schaan, Liechtenstein) were tested for degree of polymerization (18 samples were not polymerized for initial absorbance and 18 sample were polymerized and tested for absorbance, each divided into three treatments of six samples each). Twenty-four specimens of composite resin were tested for hardness (three treatments each of eight samples each). All test specimens were fabricated into cylinders 5 mm in diameter and 4 mm in height, following the manufacturer's instructions and the International Standards Organization 4049 specifications for split resin molds. All specimens had been approved for ethical clearance (038/KEPKG-FKGULM/EC/IX/2017) before testing.

The bulk-fill resins specimens were subjected to three storage conditions for a 24-h period: Treatment I (refrigerated at 5°C), Treatment II (maintained at an ambient room temperature of 25°C), and Treatment III (kept in a warmed oven at 35°C). After 24 h, the composite resin samples were removed from storage and immediately inserted into a resin mold before its storage (treatment) temperature changed appreciably. A Mylar strip was applied to the top of each specimen. Then each specimen was polymerized by positioning the tip of an LED light (intensity 850 mw/cm^2) in contact with the Mylar strip for 20 s. (This irradiation method was based on the manufacturer's instructions). After being polymerized, the specimens were stored for 24 h in a saline-filled container on an incubator before being test.[7,24]

The degree of polymerization test
Eighteen specimens were used to test for initial absorbance characteristics by inserting the stored composite resin immediately into mold after removing them from storage, but not polymerizing them. The 18 other specimens were tested for absorbance characteristics after polymerizing them in molds. To measure degree

of polymerization, each specimen was placed into a Fourier transform infrared spectrometer (FTIR) that had been equipped with an attenuated total reflectance (ATR) Diamond Accessory (Bruker Alpha). FTIR was used to test degree of polymerization composite specimens not polymerized, whereas the polymerized composite specimens were tested for absorbance characteristics after polymerization. The obtained absorbance values were recorded at wavelengths of 500–4000 cm^{-1}.[4]

The obtained absorbance data were converted to percentages of unreacted carbon double bonds in the resin. The percentage of unreacted carbon-carbon bonds (C=C) were determined by comparing the ratio of absorbance intensity of aliphatic (C=C) bonds (peak = 1637 cm^{-1}) against a baseline by using software or peaks of internal reference aromatic C=C (peak heights at 1608 cm^{-1}) both before and after polymerization of the specimens.[4,11] The degree of polymerization (%DP) was established by subtracting the percentage of double carbon bonds from 100%, according to the formula:

$$\%DP = \left\{ 1 - \frac{Abs\ (1637\ cm^{-1}/1608\ cm^{-1})\ polymerized}{Abs\ (1637\ cm^{-1}/1608\ cm^{-1})\ unpolymerized} \right\} \times 100 \quad (1)$$

wherein Abs 1637 cm^{-1} is aliphatic C=C absorbance at 1637 cm^{-1} and Abs 1608 cm^{-1} is aromatic C=C absorbance at 1608 cm^{-1}.

The surface hardness test

The specimens of composite resin stored in the incubator for 24 h were removed and immediately tested for hardness. Hardness was tested using the Vickers hardness (VH) test in a hardness-testing machine [Micro Vickers Hardness Tester (Buehler® Micro Hardness Tester, USA)]. The VH Tester is equipped with a Vickers diamond, which has a pyramidal diamond microindentor of 136° (where the two diagonals of the indentation left in the surface of the material are measured). The top of each surface of the specimen was divided into four equal quadrants. One indentation was made in each quadrant by the hardness-testing machine, which applied pressure at 300 gf for 15 s to each test point (one indentation per quadrant). Mean hardness values for the four test points (per specimen) were calculated for each surface, based on the Vicker's hardness number

(VHN).[7,11] VHN was calculated based on the formula:

$$VHN = \frac{1.854}{\left(\frac{d1+d2}{2}\right)^2} F \quad (2)$$

Where in F was the load applied (gf), d was the mean length of the diagonals (m), and 1.854 was a constant. All test data for degree of polymerization and hardness were statistically analyzed with one-way Analysis of Variance (ANOVA) using a confidence interval of 95%, followed by a post hoc LSD test.

Results

Degree of polymerization (DP) test

We found that the highest mean value for degree of polymerization (38.17%) occurred in the bulk-fill composite resin treatment stored at 35ºC, whereas the lowest mean value (36.67%) occurred in the 5ºC storage treatment (Table 1). However, the one-way ANOVA showed that there was no significantly different (P = 0.454) among all tested group, storage temperature was not related to degree of polymerization for bulk-fill composite resin (Table 1).

Treatment Group	%DP mean ± SD	P
Temperature 5ºC	36.67 ± 0.82	0.454
Temperature 25ºC	37.17 ± 2.48	
Temperature 35ºC	38.17 ± 2.40	

One-way ANOVA
Not significant (P > 0.05)

Table 1. Degree of polymerization (DP) relative to temperature for bulk-fill composite resin.

Vicker's hardness (VH) test

The measured surface hardness values are listed in Table 3. Along with the elevating temperature 5°C (VHN = 49.22 ± 0.57), 25°C (VHN = 51.94 ± 0.41) and 35°C (VHN = 53.86 ± 0.79) showed that VHN also increased and was significantly different (P = 0.000) from one to another among temperature storage treatment, with the hardest composite resins created under the highest temperatures (Table 2).

Treatment group	Mean ± SD (VHN)	P
Temperature 5ºC	49.22 ± 0.57[A]	0.000*
Temperature 25ºC	51.94 ± 0.79[B]	0.000*
Temperature 35ºC	53.86 ± 0.41[C]	0.000*

Means with the different uppercase superscript letters were significantly different from one another at P < 0.05.
*Significant (P < 0.05).

Table 2. Vicker's hardness number (VHN) relative to storage temperature for all tested groups.

Discussion

We found that storage temperatures from 5°C to 35°C exhibited a slight increase in degree of polymerization (DP), even though the differences were not statistically different. Several researchers have found that high storage temperatures accelerate the photo-polymerization reaction so that much more monomers are converted to polymers, causing an increase in thermal energy of molecules at the subatomic scale, which in turn might improve molecular mobility.[15,25] Our finding is in line with Lohbauer (2009) and Tauböck (2015), both of whom recorded no significant differences in DP resin composites preheated at 68°C, 54°C, or stored at room temperature.[19,26] However, Tauböck (2015) did not store their composite resins at a constant temperature before increasing the temperature to insert them into a mold for testing (to simulate a clinical scenario).[19] There is a time delay between removing resin from a heating device, dispensing it, inserting it into a prepared teeth, contouring it, and subsequently light-curing it, and so a decline in composite temperature during handling might have prevented a sufficient intensification in the polymerization reaction and enhancement in monomer conversion in their tests.[27] Previous studies have shown that resin temperature declines during the 40 s interval from removing a resin from storage to prepared teeth.[28] Furthermore, composite resins cured at different temperatures have been reported to exhibit similar polymer network crosslinking, determined from measurements of their glass transition temperatures.[18,28]

The degree of polymerization and other properties may also vary among resin brands and shades.[28] Factors such as irradiation time, light source, power density, wavelength of the light source, tip size of light guide, light distance, and composition may all influence DP.[11] The minimum DP for composite resins has not yet been established for clinically acceptable restoration.[7] Collares (2014) stated that DP values should be at least 55% for restoring teeth. In our study, DP ranged from 36% to 39%. This difference could be related to the variations in the method of measurement, specimen thickness, or irradiation intensity.[13]

The larger the atomic size and weight, the slower the speed of the atomic vibration amplitude and the slower the polymerization reaction rate. The matrix resin of bulk to fill Tetric® N Ceram is a mixture of bisphenol A diglycidyl ether dimethacrylate (Bis-GMA) and urethane dimethacrylate (UDMA), but its composition is dominated by Bis-GMA, which is comprised of larger and heavier molecules than other matrix resins.[24] Bis-GMA is assumed the most viscous monomer currently available, due to the strong hydrogen bonding of its hydroxyl groups (-OH) on its carbon backbone and the existence of aromatic rings in its structure.[13,29] The monomer UDMA in Tetric® N Ceram is a viscous monomer, but the viscosity of UDMA is much lower and more flexible than Bis-GMA due to the weak hydrogen bond of its amine group relative to its hydroxyl groups.[14] That is why the DP of Bis-GMA varied from 32.7% to 78.50% from previous study; lower DP values at higher Bis-GMA ratios can be attributed to higher viscosity. Therefore, increasing the concentration of Bis-GMA can lower the mobility of monomers in the polymerizing bulk.[13,30] Tetric® N Ceram also contains of germanium-based photoinitiator Ivocerin, which is characterized by more intensive light absorption in the visible range and higher photoreactivity than the photosensitizer camphorquinone.[8,19,31,32]

In our study, elevating storage temperatures from 5°C to 35°C resulted in significant increases in VHN values (from 49.2 to 53.9). These VHN values were not much different than those found by Leprince (2014) (47.7), Jafarzadeh-Kashi (2015) (53.0), and Dionysopoulos (2016) (42.8) for bulk-fill composite resins.[33,34,35] Some authors believe that a VHN exceeding 50 VHN is ideal for composite resins.[11] However, many other factors are known to affect VHN scores: the intensity of light used, curing time, incubation time, distribution of filler particle shapes, size and densities, type of monomers and their

compositions, degree of polymer crosslinking, and type of photoinitiators used.[11] Preheating and precooling composite resins after storage could affect VHN, but the affect mainly depends on the type of composite resin used, depth of curing, the intensity and type of light unit used for curing.[36] Pre-heated composite resins exhibit increased monomer mobility and vibration due to the higher thermal energy of preheated resins, which leads to a lower viscosity than composite resins at room temperature and enhanced mobility of growing chain moieties in the resin material. As a result, DP increases while surface microhardness declines (microhardness indirectly expresses viscosity).[9,14,37] These studies support Awliya (2007), who stated that composite resin stored at low temperatures result in low VHN values.[35] Another study stated that composite resin preheated to 3°C warmer than body temperature (40ºC) flowed better and was significantly harder than composite resins inserted into teeth at room temperature.[38,39] Preheating resin can be clinically beneficial, due to a superior marginal adaptation.[26]

In our study, DP values did not align with VHNs, which agreed with another study that found there was no correlation between the DP and VHN. We found no significant increase for DP with increasing storage temperature, but there were significant increases in VHN with temperature. Although VHN can correlate well with DP for some composite resins based on temperature, VHN cannot be used to predict DP when different composite resins are being compared mainly because all resins are composed a different mixture of monomers; thus, each type of resin has its specific relationship between DP and its mechanical properties.[7,35]

Conclusions

Elevating the storage temperature of bulk-fill composite resin among 5°C (refrigerated condition), 25°C (typical ambient room temperature) and 35°C (air temperature in hot climates) did not significantly affect composite resin's degree of polymerization, but it did significantly increased surface hardness.

Declaration of Interest

The authors report no conflict of interest.

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