Original Article

Micro-Hardness, Degree of Conversion and Elemental Composition of Two Resin

A Comparison of Degree of Conversion, Microhardness and Surface Characterization of Two Commercially Available Composite Materials: An in Vitro Study

Amna Mehwish Ikram[1], Faisal Moeen[1], Muhammad Talal Khan[1]
Muhammad Humza Bin Saeed[2]

ABSTRACT

Objective: To compare the micro-hardness, degree of conversion and elemental composition of two resin based composites available in the market.

Study Design: Comparative study.

Place and Duration of Study: This study was conducted at the Department of Dental Materials, Islamic International Dental College, Islamabad for 06 months from January 2018 to June 2018.

Materials and Methods: 40 disc shaped specimens of two light cured composite filling materials Filtek^{TM}Z250 XT and Filtek^{TM}Z250 were irradiated for 20s and 40s. The degree of conversion, micro-hardness, surface characterization and compositional elemental analysis wererecorded and compared.

Results: The degree of conversion (DC) of Filtek^{TM}Z250-XT was found to be greater thanFiltek^{TM}Z250 composite material yielding a higher mean degree of conversion at 20s and 40s ($p < 0.05$).It was also found that the ultrastructure and size of filler particles of the two composites varied significantly from each other resulting in a statistically significant difference in Vickers hardness micro-hardness (MH) ($p < 0.05$).

Conclusion: The DC and MH of the Filtek^{TM}Z250 composite was found to be lower than the Filtek^{TM}Z250 XT composite. Additionally, with variations in values compared to those acquired from literature it appears that the Z250 composite acquired is a counterfeit. It is recommended that clinicians should purchase original products from authorized dealers and should remain aware of other commercially available counterfeit dental products.

Key Words: Degree of conversion, micro-hardness, scanning electron microscopy, energy dispersive X-ray analyzer, composite resin, FTIR, Vickers hardness

Citation of articles: Ikram AM, Moeen F, Khan MT, Saeed MHB. A Comparison of Degree of Conversion, Microhardness and Surface Characterization of Two Commercially Available Composite Materials: An in Vitro Study. Med Forum 2019;30(8):132-137.

INTRODUCTION

Resin based composite materials gained immense popularity among dental practitioners towards the end of the twentieth century. Over the past couple of decades, with an increasing trend of minimal invasive dentistry, the use of composites both as anterior as well as posterior restorative materials has increased tremendously[1].

1. Department of Dental Materials, Islamic International Dental College, Islamabad.
2. Department of Dental Community Dentistry, Islamic International Dental College, Islamabad.

Correspondence: Faisal Moeen, Department of Dental Materials, Islamic International Dental College, Islamabad.
Contact No: 0334-5298939
Email: faisalmoeen_is@gmail.com

Received: June, 2019
Accepted: July, 2019
Printed: August, 2019

Studies have shown that the longevity and quality of resin-based restorations are improving over time and they are being utilized as a substitutes for silver based amalgam restorations in posterior teeth[2].

Dental composites comprise of four main components; inorganic filler particles, an initiator-accelerator system, an organic polymer matrix and a coupling agent. In order to aid handling and improve mechanical properties, fillers are introduced to the polymeric part of the composite. The most common composites are currently being filled with silicate particles based on oxides of the elements Strontium (Sr), Zinc (Zn), Zirconium (Zr), Barium (Ba), and Aluminium (Al)[2]. It is generally believed that greater the amount of filler load both in weight and volume and higher the conversion of the monomers into such a densely packed polymeric network, better shall be the physical properties such as strength and hardness[3].

The degree of conversion (DC) is defined as the extent to which monomers react to form polymers or as the ratio of C=C double bonds that are converted into C–C single bonds[4]. Fourier Transformation Infrared (FTIR) spectroscopy is one of the most commonly used, powerful and reliable direct methods to detect the C=C stretching vibrations before and after the curing of resin materials[5, 6]. The degree of conversion may play an imperative role in determining the ultimate success of the restoration as the extent of cure may exert not only an effect on the physical and mechanical properties of the resin system but also solubility, dimensional stability, color change, and biocompatibility. The degree of conversion in Bis-GMA-based restorative resins has been analyzed with infrared spectroscopy by a large number of researchers and has been shown to range between 50 to 80%[7].

The Vickers hardness test is effective for measuring the surface hardness of brittle materials. Gajewski et al. suggested that even though different polymers have different reaction kinetics, there exists an almost definitive link between the degree of conversion and the physical properties of composites especially hardness[8].

With the possible existence of widespread sale and utilization of dental composite resins in the Pakistani market, it has become extremely important to verify any compositional changes of suspect materials and the possible effects these variations might have on the physical and mechanical properties of these products. Clinical reports have been issued in regards to the inferior handling properties of recently available Filtek™Z250 micro-hybrid composites. In order to substantiate such a claim, this in-vitro study was undertaken to compare the degree of conversion, micro-hardness, ultrastructure and elemental analysis of Filtek™ Z250 and Filtek™ Z250-XT restorative composite resins. The aim of this study was therefore to identify any possible difference in the DC, MH, ultra structure and elemental composition between the Filtek™Z250 and Filtek™Z250-XT composite resin.

MATERIALS AND METHODS

This experimental study was carried out over a period of six months. The study included two main types of light-cured composite restorative materials; a micro-hybrid composite (ESPE 3M Filtek™Z250) and a Nano-composite (ESPE 3M Filtek™ Z250 XT) that were randomly collected from a number of suppliers from the twin cities of Rawalpindi and Islamabad. A total of 40 disc-shaped specimens (20 specimens of Filtek™Z250 and 20 of Filtek™Z250 XT) were prepared. The specimens were prepared using a metallic mould with a central orifice of 6 mm diameter and a thickness of 2 mm.

Sample preparation and material testing were performed at IRCBM, COMSATS Lahore and at SCME NUST, Islamabad. The main difference between the two materials is related to the fillers incorporated by manufacturers, which are different in size and concentration.

These 20 specimens for each composite material were further subdivided into two groups of 10 specimens each, based on the curing time (20s and 40s). All 40 specimens (before and after curing) were submitted for Fourier transformation infrared spectroscopy(FTIR) for evaluation of the percentage of unreacted carbon to carbon double bonds (C=C) in resin-based composites. All disc-shaped specimens were then submitted for evaluation of Vickers micro-hardness using an ISO standardized hardness tester.

The samples were also submitted for surface characterization and compositional analysis for SEM and EDX.FTIR ATR mode spectra of the uncured and cured specimens of each resin composite were recorded by Fourier transformation infrared spectrometer (Nicolet 6700 FT-IT, Thermo Scientific). For ATR, samples were in direct contact with the ATR diamond crystal. All spectra were collected within the spectral range of 4000-400cm^{-1}. The spectra were measured at 8cm^{-1} resolution accumulating a total of 128 numbers of scans. After collecting spectra of the uncured specimen, the specimen was cured at 20s and 40s using LED light whose tip was in close contact to the mould while curing. The specimens were then stored dry in a sample bottle covered with aluminium foil at room temperature for a few days, after which, Vickers hardness was evaluated with a micro-hardness tester (Wolpert Micro-Hardness Tester 401/402MVD).A load of 50g was applied to the resin disks for 30 seconds, and the scores were recorded in hardness Vickers (HV). The test was performed for every restorative composite resin, and the procedure was divided into 1 indentation for each resin disk.

The surfaces were also slightly etched with a solution of 0.8%(wt./vol) H_3PO_4 for 10 seconds to obtain a clearer image during SEM observation, after which the specimens were oven dried for 1hour at 37-degree centigrade. The samples were then placed on aluminium stubs with conductive tape, sputter coated with gold for 90 seconds and observed under SEM (Vega LMU from TESCAN Brno, Czech Republic) with backscattered electron and secondary electron signals at four different magnifications (1000x, 10000x, 25000x). The compositional analysis was performed using Inca X-Act EDS detector from Oxford Instruments, Oxford UK, which was attached to SEM. Elemental composition of coated samples was determined by performing a line scan throughout the coated thickness.

All data was entered and analysed using SPSS v 23.0. Mean and standard deviation was described for quantitative data, such as micro-hardness and degree of conversion values. The MH and DC values for all samples were tabulated. All data was tested for normality. Statistical comparisons were made between the DC and MH values at 20 s and 40 s between Filtek™ Z250 and Filtek™ Z250-XT. Independent samples T test was used to compare normal data, while the Mann-Whitney U test was applied to compare data not distributed normally. An arbitrary value of 0.05 was considered to be significant**.**

RESULTS

The degree of conversion of Filtek™Z250-XT was found to be significantly different from Filtek™Z250 composite resin, yielding a higher degree of conversion at 20s (p = 0.052) and 40s (p = 0.001), as shown in table 1. The curing mean values of Z250-XT were 92.90 ± 14.85cm^{-1} and 112.80 ± 18.37cm^{-1}, while those for Filtek™Z250 were 77.60 ± 17.87cm-1 and 84.90 ± 8.72cm^{-1} respectively, indicating a much lower degree of conversion in comparison (Table 1).

Figure No.1: Filtek™Z250 utilized in the study

Figure No.2: Metallic Mould.

Table No.1: Analysis of Degree of Conversion for Filtek Z250 and Filtek Z250 XT

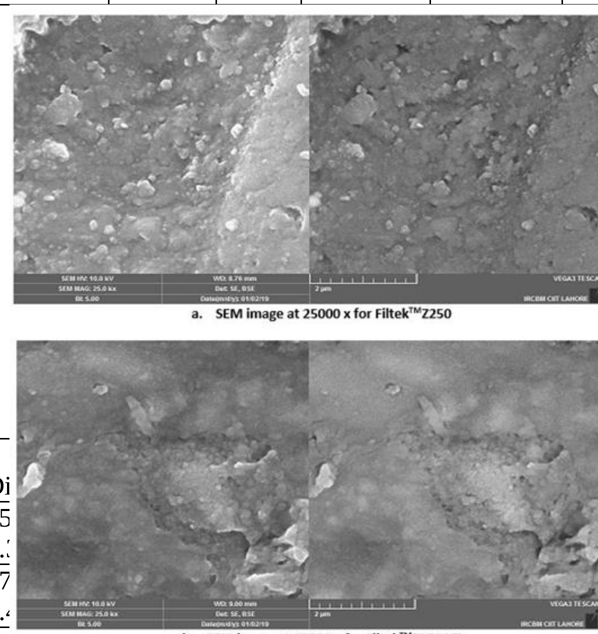
		Filtek Z250	Filtek Z250 XT	Di
Degree of Conversion	20 Minutes	77.60±17.87	92.90±14.85	15 7.:
	40 Minutes	84.90 ± 8.72	112.80±18.37	27 6.4

On analysing the difference in micro-hardness between the two groups, Filtek™Z250-XT was found to have significantly higher micro-hardness values at both 20 and 40 seconds (Table 2).The mean recorded for micro-hardness of Filtek™Z250-XT at 20s and 40s curing time was 65.58 ± 10.36KgF and 93.04 ± 14.52KgF respectively. Whereas, Filtek™Z250 presented with statistically lower micro-hardness mean values recorded at 20s and 40s curing time i.e. 13.03 ± 3.49KgF and 15.20 ± 4.91KgF respectively (Table 2).

Scanning electron microscope (SEM) observation with backscattered electron and secondary electron provided an adequate contrast between the resin matrix and fillers. The shape and size of filler particles were different amongst the composites. The filler particles size and shape was more uniform and dense in Filtek™Z250-XT (nano-composite), whereas the particles size and shape in Filtek™Z250 (micro hybrid) composite were not as dense as in Filtek™Z250. Filtek™Z250 showed both micro and nano sized filler particles and the inter filler distance was greater as compared to Filtek™Z250-XT (Figure 3). Whereas, Filtek™Z250-XT contained nano sized fillers distribution with little inter-filler distance. The images were taken at 1000x, 10000x, 25000x and 50000x magnification.

Table No.2: Analysis of Microhardness for Filtek Z250 and Filtek Z250 XT

		Filtek Z250	Filtek Z250 XT	Mean Difference	P Value
Micro hardness (KgF)	20 Minutes	13.03 ± 3.49	65.58± 10.36	52.55 ± 3.46	< 0.001
	40 Minutes	15.20 ± 4.91	93.04± 14.52	77.84 ± 4.85	< 0.001



a. SEM image at 25000 x for Filtek™Z250

b. SEM image at 25000 x for Filtek™Z250 XT

Figure No. 4: SEM Images for Filtek™Z-250 and Filtek™Z-250 XT at 25000x Magnification

Electron dispersive X-ray analysis (EDX) showed the chemical compositions of the restorative composite resins including the elements with relative values expressed in weight percentage. Similar elements such as carbon(C), oxygen (O), silicon Si and zirconium(Zr) were detected; however, the concentration was different in both composite resins. The filler contents showed interesting differences in elemental composition and concentration. Silicon(Si) and zirconium(Zr) seemed to be a common filler component. Silicon(Si) was present in a greater amount in Filtek™Z250-XT. Zirconium(Zr) filler content was higher in Filtek™Z250 (micro-hybrid) in comparison to Filtek™Z250-XT. The higher concentration of zirconium(Zr) particle in Filtek™Z250 could be due to the presence of micro size particles. However, some selected areas in Filtek™Z250 showed a lack of zirconium (Zr) content that might indicate the lower non-uniform distribution of zirconium(Zr) particles throughout the material. The EDX analysis of the Filtek™Z250-XT composite resin showed the presence of carbon (C), oxygen O, silicon(Si), zirconium(Zr) , and sodium(Na) (Figure 3).

Therefore, the results showed that the Filtek™Z250-XT composite resin presented significantly superior DC and MH values when compared to the Filtek™Z250 composite resin. The comparison revealed that most filler particles are of irregular shape with increased inter-particle distance and non-uniform distribution of filler particles in Filtek™Z250 composite resin and hence decreased filler load, which indicate low DC and MH values.

DISCUSSION

The Filtek™Z250 is being sold in the Pakistani market owing to its low price in comparison to other composites. Filtek™Z250 showed inferior properties comparative to the other tested composite. The findings suggest that even though this composite has a similar packaging and therefore not easily discernible as a counterfeit product, the compositions of the resin, filler and quality are significantly different.

Literature suggests that hardness values that exceed 50 (VHN) are ideal for composite resins. Comparing the hardness values of Filtek™Z250 obtained in this study with literature values, it was concluded that the this material currently available in the market is not ideal and the values for its VHN were below 50 (VHN)[3, 10,11].According to literature, the VHN values of commercially available authentic Filtek™Z250 are higher as compared to the Filtek™Z250 tested in this study[12]. Thus, it was concluded from this study that Filtek™Z250 utilized in this study was similar in packaging to the original Filtek™Z250 but its characterization revealed that this material was counterfeit.SEM images revealed that the counterfeit Filtek™Z250 samples have irregular particles with particle size of 0.01-3.5 µm and original Filtek™Z250-XT contains spherical shaped filler particle materials of size 20–25 nm. Comparatively, Filtek™Z250-XT yielded higher mean values for Vickers hardness and contained a higher filler load in comparison to the Filtek™Z250 composite resin. These results suggest that the hardness of the counterfeit composite resin (Filtek™Z250) could possibly have been enhanced by increasing the filler load concentration as this would result in improved packing of fillers in the polymer matrix.

Previous literature shows that the intensity of light decreases as it passes through the bulk of the restorative material, which in turn reduces the polymerization potential by reduction of the light intensity passing through[13,14]. Major factors associated with light attenuation include absorption and scattering within the material[15], and reflection from the surface of the restoration[16]. These factors are dependent on the composition of the material, predominantly the filler content, type, size and the shape of the particles[17, 18]. This study showed the micro-hybrid composite resin to have lower mean hardness values. This could be attributable to the diameter of the fillers causing light attenuation. Consequently, the composite with the lesser diameter fillers (Filtek™Z250-XT) showed the highest Vickers mean hardness values. Hardness values are also used as an indication of the depth of cure or degree of polymerization. Comparable studies showed that if hardness ratio is below 80%, it could indicate poor polymerization in the test sample. Taking the micro hardness values into consideration, it could be suggested that the Filtek™Z250 used in this study may not have been adequately polymerized. However, the values of DC obtained in this study showed the degree of polymerization within the acceptable range, suggesting adequate polymerization had taken place. These results indicate that this dental composite resin has adequate curing efficiency, which is not reflected by their hardness values.

The DC for Filtek™Z250-XT was significantly higher than Filtek™Z250 at both 20 seconds and 40 seconds. Both micro-hybrid (Filtek™Z250) and nano-hybrid composites (Filtek™Z250-XT) were used with a consistent thickness of 2mm. The findings also showed that composites cured using the LED light curing unit at 40s had a higher degree of conversion compared to those cured at 20s. Giorgi et al suggested that the irradiation time may affect the degree of conversion (DC)[19]. Literature also confirms that longer irradiation times produce a higher DC. Both composite resins in the current study reached an acceptable DC through irradiation at 20s and 40s using LED curing light. The higher degree of conversion observed in Filtek™Z250-XT and adequate DC observed in Filtek™Z250 composite resins can be explained by the presence of UDMA. UDMA based resins have proven to be more reactive than bisGMA-based resins[20]. The higher conversion level in Filtek™Z250-XT could also be related to the partial substitution of the relatively stiff, hydrogen-bonded bisGMA molecules due to longer and more flexible bisGMA molecules. For Filtek™Z250, the lower aliphatic: aromatic ratio could be an additional possible reason[21]. In this study, as both

Filtek™Z250 and Filtek™Z250-XT composite resins have the same polymeric matrix, the difference could rather be attributed to the filler particle size. Furthermore, the DC is said to be increased upon decreasing the distance of the light curing tip, using the fiber optic light guide tip and upon increasing the time of irradiation[22-24].

The distributions of filler particles seen in the SEM-images may indicate a larger inter-particle distance in Filtek™Z250 than in Filtek™Z250-XT. Energy Dispersive X-ray analyser (EDX)results indicate the presence of carbon(C), oxygen(O), silicon(Si) and zirconium(Zr) in Filtek™Z250 (micro-hybrid). The elements carbon(C), oxygen O and zirconiumZr are present in relatively higher concentrations and silicon(Si) is found in relatively lower concentrations in comparison to literature values. Contrary to literature which indicates the presence of sodium(Na) contents in Filtek™ Z250, this study presented an absence of sodium(Na) . Rogelio investigated light cure restorative composite resins which had recently been improved. The EDX results for Filtek™ Z250 indicated the presence of carbon(C), oxygen(O) , sodium(Na), silicon Si, and zirconium(Zr) in concentrations of 37.69, 33.21, 0.17, 19.77 and 9.16 respectively[25]. On the contrary, our study shows the presence of carbon(C), oxygen(O), silicon(Si) and zirconium(Zr) in concentrations of 50.41, 37.21, 12.37 and 14.28 respectively in our sample of Filtek™Z250. This could indicate why the material currently available in the market may not be up to standard as well as it does not meet the clinical demands in terms of mechanical properties. Filler morphology and inter-particle spacing which is dependent on filler load volume and size has proven to be another key factor affecting the wear resistance of composites. The shorter the distance between the particles, the better the matrix will be protected against wear and scratch. From this study it is evident thatFiltek™Z250 had a lower microhardness value owing to greater inter-filler distance in comparison to Filtek™Z250-XT.

This study compared two different composite materialswithout any prior bias, out of which one turned out to be counterfeit based after investigations. Future studies should focus on testing multiple counterfeit composites with tested products of the same filler type.

CONCLUSION

The present study suggests that Filtek™Z250-XT has superior properties, in comparison to Filtek™Z250. The Filtek™Z250 used in this study was a counterfeit product that had a packaging exactly similar to the original company-manufactured product. However, the production was not done under standardized conditions and hence the micro hardness, degree of conversion and the elemental composition were significantly compromised. It is recommended that dentists should remain aware of commercially available counterfeit dental products since these are highly likely to show poor performance in the patients.

Author's Contribution:

Concept & Design of Study:	Amna Mehwish Ikram
Drafting:	Faisal Moeen, Muhammad Talal Khan
Data Analysis:	Muhammad Humza Bin Saeed
Revisiting Critically:	Amna Mehwish Ikram
Final Approval of version:	Amna Mehwish Ikram

Conflict of Interest: The study has no conflict of interest to declare by any author.

REFERENCES

1. Lang B, Jaarda M, WANG RF. Filler particle size and composite resin classification systems. J Oral Rehabilitation 1992;19(6):569-84.
2. Faltermeier A, Rosentritt M, Faltermeier R, Reicheneder C, Müßig D. Influence of filler level on the bond strength of orthodontic adhesives. The Angle Orthodontist 2007;77(3):494-8.
3. Uhl A, Sigusch BW, Jandt KD. Second generation LEDs for the polymerization of oral biomaterials. Dental Materials 2004;20(1):80-7.
4. Yoshida K, Greener E. Effects of two amine reducing agents on the degree of conversion and physical properties of an unfilled light-cured resin. Dental Materials 1993;9(4):246-51.
5. DeWald J, Ferracane J. A comparison of four modes of evaluating depth of cure of light-activated composites. J Dental Research 1987;66(3):727-30.
6. Imazato S, McCabe J, Tarumi H, Ehara A, Ebisu S. Degree of conversion of composites measured by DTA and FTIR. Dental Materials 2001;17(2):178-83.
7. Ferracane J, Mitchem J, Condon J, Todd R. Wear and marginal breakdown of composites with various degrees of cure. J Dental Research 1997;76(8):1508-16.
8. Gajewski VE, Pfeifer CS, Fróes-Salgado NR, Boaro LC, Braga RR. Monomers used in resin composites: degree of conversion, mechanical properties and water sorption/solubility. Brazilian Dental J 2012;23(5):508-14.
9. Sabatini C. Comparative study of surface microhardness of methacrylate-based composite resins polymerized with light-emitting diodes and halogen. Eur J Dentis 2013;7(3):327.
10. Catelan A, de Araújo LSN, da Silveira BCM, Kawano Y, Ambrosano GMB, Marchi GM, et al. Impact of the distance of light curing on the degree of conversion and microhardness of a composite

resin. Acta Odontologica Scandinavica 2015;73(4):298-301.
11. Neumann MG, Miranda Jr WG, Schmitt CC, Rueggeberg FA, Correa ICJJod. Molar extinction coefficients and the photon absorption efficiency of dental photoinitiators and light curing units 2005;33(6):525-32.
12. Lodhi T, Strydom. Influence of shade on curing hardness of two nanocomposites 2014;5:227-32.
13. Dunn WJ, Bush ACJTJotADA. A comparison of polymerization by light-emitting diode and halogen-based light-curing units 2002;133(3): 335-41.
14. Rueggeberg F, Craig RJJoDR. Correlation of parameters used to estimate monomer conversion in a light-cured composite 1988;67(6):932-7.
15. Yearn J. Factors affecting cure of visible light activated composites. Int Dental J 1985;35(3):218-25.
16. Watts D, Amer O, Combe EJDM. Surface hardness development in light-cured composites 1987;3(5):265-9.
17. Abuelenain DA, Neel EAA, Al-Dharrab A. Surface and mechanical properties of different dental composites. Aust J Dent 2015;2(2):1-5.
18. Galvão MR, Caldas SGFR, Bagnato VS, de Souza Rastelli AN, de Andrade MF. Evaluation of degree of conversion and hardness of dental composites photo-activated with different light guide tips. Eur J Dentis 2013;7(1):86.
19. Caldas Giorgi MC, Theobaldo J, Nunes Leite Lima DA, Marchi GM, Ambrosano GM, Baggio Aguiar FH. Influence of successive light-activation on degree of conversion and knoop hardness of the first layered composite increment. Acta Odontologica Scandinavica 2015;73(2):126-31.
20. Lovell LG, Lu H, Elliott JE, Stansbury JW, Bowman CNJDM. The effect of cure rate on the mechanical properties of dental resins 2001;17(6):504-11.
21. Emami N, Söderholm K-JM, Berglund LA. Effect of light power density variations on bulk curing properties of dental composites. J Dentis 2003;31(3):189-96.
22. Mills R, Jandt K, Ashworth SJBdj. Restorative Dentistry: Dental composite depth of cure with halogen and blue light emitting diode Technol 1999;186(8):388.
23. Obici AC, Sinhoreti MAC, Correr-Sobrinho L, Góes MFd, Consani SJJoAOS. Evaluation of mechanical properties of Z250 composite resin light-cured by different methods 2005;13(4):393-8.
24. Uhl A, Mills RW, Jandt KDJB. Photoinitiator dependent composite depth of cure and Knoop hardness with halogen and LED light curing units 2003;24(10):1787-95.
25. Par M, Marovic D, Skenderovic H, Gamulin O, Klaric E, Tarle ZJCoi. Light transmittance and polymerization kinetics of amorphous calcium phosphate composites 2017;21(4):1173-82.