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Synthesis and Characterization of New Composite for Dental Restoration Application - An *In-vitro* Study

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Abstract. To be used as a restorative dental material, bis(phenol)-a-glycidyl-dimethacrylate composite resin cemented with zirconia and silicon was created. By comparing the relative intensities of the aromatic C=C stretching vibration at 1636 cm1 and the methacrylate C=O stretching Raman mode (1714.0 cm1) on top and bottom surfaces, the degree of conversion was estimated using the FTIR approach. Thermogravimetric analysis (TGA) investigation revealed that the thermal stability of the composite increased with longer curing times, while conversion increased up to 30 sec before declining. To investigate the impact of irradiation duration on the mechanical properties of the composites, microhardness and compressive strength of the composite resin were assessed and associated with the level of conversion. Studies on surface morphology demonstrated that zirconia and silica were dispersed fairly and uniformly. The created composite can be used as an alternative to the dental composites that are already available on the market.

Keywords: composite materials, FTIR, hardness, compressive strength

Introduction

Dental composite resins are typically made of Bis-GMA monomers or an analogue of Bis-GMA, fillers like zirconia and silica and in the majority of modern uses, a photoinitiator. In order to achieve specific physical qualities, such as flowability, di-methacrylates are frequently used. By creating special concentrations of each constituent, physical attributes can be further tailored. A significant flaw with dental composite resins is their insufficient polymerization (O'Brien, 2002). The degree of conversion DC, which is the proportion of double bonds reduced during the polymerization process, can be used to analyse this among other methods. Un-reacted monomers from incomplete polymerization leach off the substance in a moist environment. Poor physical characteristics, increased solubility in the oral environment with the release of components such as formaldehyde and methacrylic acid and increased microleakage are issues linked to insufficient polymerization. All of these issues could lead to pulp irritation or recurring decay (Sideridou *et al.*, 2003; Malucelli *et al.*, 1996).

Several photopolymerization approaches have been proposed in an effort to increase DC and decrease polymerization shrinkage. To fulfil various clinical needs, dental composites offer one or more polymerization modes (light, chemical or dual) (Musanje and Darvell, 2003; Peutzfeldt, 1997; Atmadja and Bryant, 1990). The most common application of lightpolymerized composites in clinical practice is the employment of high intensity light to photopolymerize monomers or oligomers into polymers, which results in the transformation of a viscous paste into a final solid product (Chinelatti *et al.*, 2006).

Different methods can be used to directly or indirectly measure the degree of monomer conversion in resin composites. The direct techniques include electron paramagnetic resonance (EPR), differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FTIR), laser Raman spectroscopy (RAMAN), nuclear magnetic resonance (NMR) micro-imaging and fourier transform infrared spectroscopy (FTIR) and differential thermal analysis (DTA). The most used method among these is FTIR, which uses the action of visible light at various depths to compare the DC of the resin composite before and after curing.

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The indirect techniques include surface hardness testing, ocular inspection, scraping and dye uptake (Sobrinho *et al*., 2000). Because surface hardness testing was found to be a reliable predictor of DC, it has been employed in numerous research. It is possible to assess surface hardness either along the specimen's side, which will show a progressive change in the depth of cure, or on the upper and lower surfaces of disc-shaped specimens with a specified thickness (Han *et al*., 2005). The latter is employed to gauge relative hardness, which is also thought to be a reliable predictor of DC (Soares *et al*., 2004).

By determining the Knoop micro-hardness (Oréfice *et al*., 2003) evaluated the effects of one halogen and two LED curing units on the depth of cure of a conventional hybrid and two translucent resin composites. According to the study's findings, LED LCUs were able to attain at least comparable cure depths to those of halogen units in a shorter amount of time. In contrast to two LED curing units, halogen LCU was shown to yield greater Knoop hardness values for conventional hybrid composite. LED curing light cure efficiency varied depending on the material.

When employing a variety of light curing sources, Obici *et al*. (2006) used the FTIR approach to compare the DC of Z250 resin composite at various depths. Plasma arc (PAC) light, a blue LED, and four different QTH exposure situations were used for photo-activation.

Even with all the advantages of the dental materials that are now on the market and studies showing the durability of dental restorations made of different materials (Gariani *et al*., 2023; Verne *et al*., 2002; Hassal and Mellor, 2001), there is always room for improvement. Early dental materials contained a ceramic oxide filler like silica or alumina, but more recent generations of materials have been developed with nanparticles to make composites with great strength that are comparable to the tooth structure (Pereira *et al*., 2005).

The purpose of this study is to prepare biomaterial used as dental restorative materials with a novel filler combination (nanoparticles) and to examine how LED laser irradiation affects the following properties of microfilled and microhybrid composite resin restorations: (1) degree of conversion; (2) compressive strength; (3) thermal stability; and (4) microhardness (Yadav *et al*., 2022).

The most often utilized light-polymerized composite in clinical practice is typically made utilizing high-intensity light to photopolymerize monomers or oligomers into polymers, which results in a change from a fluid paste to a final solid product (Fugolin *et al*., 2020; Musanje and Darvell, 2003; Peutzfeldt, 1997).

Material and Methods

The following substances/chemicals were utilized to create the composite. Sigma Aldrich Co. Ltd. in Germany supplied the bisphenol A glycerolate dimethacrylate (bisGMA). Merck provided the acetone while Aldrich Co. Ltd. in Germany provided the trimethoxy[3-(methylamino) propyl silane and camphorquinone (CQ). Sigma Aldrich Co. Ltd., Germany, 2-(Dimethylamino)ethyl methacrylate. Quaid-e-Azam University in Islamabad, Pakistan's Department of Nanotechnology generously donated silica and zirconia nanoparticles.

Composite preparation. In a petri plate, 4.5 g of Bis-GMA and 1.5 g of acetone were combined to create the polymer matrix. The right amounts of inorganic filler may be incorporated using this ratio, it was discovered. Trimethoxy[3-(methylamino)propyl]silane, an organofunctional silane coupling agent, was used to first treat an equal amount of 7.345 g of each silica and zirconia nanoparticles (100 nm). Composite restorations would not perform as well without this organo-functional silane that promotes adhesion.

The inorganic filler was manually added to the monomer solution and spread out and progressively mixed until a clearly homogeneous mixture was achieved. The homogenous paste of fillers and the monomer solution was then mixed with 0.105 g of photo-initiator CQ and 0.209 g of co-initiator DMAEMA. For later use, composite pastes were stored in a dark area covered with black paper.

LED curing. Woodpecker, LED.B, China, LED light with a wavelength of 470 nm was used to light cure samples, which were formed as discs with dimensions of roughly 5 mm in diameter and 2 mm in height. To observe the impact of light curing on sample depth, discs were cured from one side. Samples were cured for a total of 10, 20, 30 and 40 sec, respectively.

FTIR analysis. Fourier transform infrared spectra of the composites were recorded on a FT-IR (Thermo Nicolet Avatar 320 spectrophotometer USA) using attenuated total reflection (ATR) technique to determine degree of conversion (DC). Calculation is based on the measurements of the net peak area of the C=C bonds and aromatic C=C bonds. In order to measure the degree of conversion, infrared spectra of the composites were captured using an FT-IR (Thermo Nicolet Avatar 320 spectrophotometer USA) (DC). Based on measurements of the aromatic C=C bonds' net peak area, calculations are made.

A distinctive infrared absorption peak for the aliphatic (H2C=C(CH3)C=O) group is located about 1714.0/cm. The aromatic C=C peak at 1636/cm, whose strength is unaffected by the polymerization reaction, is caused by the aromatic bonds of the benzene rings in the monomer molecules. The ratio of the cured material's net absorbance peak area to its uncured counterpart tells us how many double bonds were transformed.

Morphological analysis. On emery paper with a 1000 grit, samples were ground. They were conductively coated with gold via sputter coating. Scanning Electron Microscopy (SEM) (Quanta 200 s, FEI, Holland) was used to examine the surface morphology of the coated composite samples at a 1 kV accelerating voltage.

Thermal analysis. On a thermogravimetric analyser (METTLER TELEDO TGA/ASDA 851e) with a temperature range of 30-800°C at a scanning rate of 10°C/min and a dry nitrogen purge at a flow rate of 80 mL/min, the thermal stability of samples was investigated.

Microhardness measurement. To see the microindent on the microhardness tester, samples were first flattened by fine grinding (1000 grit emery paper). Vickers microhardness Indentec, ZHV 1-M/2007 (Germany) equipment was used to measure the indentations at the microscopic level. Microvicker's hardness tester was used to measure the samples' hardness at a 1 Kg load and a 10 sec dwell duration. On 10 specimen discs, the hardness was assessed at three randomly chosen locations on each specimen and the mean value was derived.

Compressive strength measurement. Samples that measured 9 mm in height and 12.5 mm in diameter were manufactured, then dried for four distinct time periods 10, 20, 30 and 40 sec from both the top and bottom. Utilizing UTM, compressive strength was calculated (TINIUS OLSEN, WILLOW GROVE, PA., USA).

Results and Discussion

The proportion of reacted C=C bonds is used to define the degree of conversion of methacrylic resin composites. This ratio has a significant impact on the resin composite's mechanical, solubility, dimensional stability, colour changes and biocompatibility qualities (Stewart, 2013). As a result, the level of conversion is crucial in deciding the final outcome of a light-activated dental repair (Shortall *et al*., 2012).

FT-IR Analysis. The FTIR method is a common analytical instrument for determining the degree of conversion (DC). The ratio of the cured material's net absorbance peak area to its uncured counterpart tells us how many double bonds were transformed. The following formula was used to determine the degree of conversion for samples from groups C1, C2, C3 and C4 that were cured for 10, 20, 30 and 40 sec using an LED laser.

$$\mathrm{DC\%} = \left[1 - \frac{\left[\dfrac{R_{ac}2}{R_{ac}1} \right] \times A_{ac}}{\left[\dfrac{R_{bc}2}{R_{bc}1} \right] \times A_{bc}} \right] \times 100\%$$

where:

DC = Degree of conversion; $R_{ac}1$ = Region 1 of peak (after curing); $R_{ac}2$ = Region 2 of peak (after curing); $R_{bc}1$ = Region 1 of peak (before curing); $R_{bc}2$ = Region 2 of peak (before curing); A_{ac} = Peak area (after curing); A_{bc} = Peak area (before curing).

Three spectra are shown in Fig. 1(a-c) and they are, respectively which known as the uncured composite resin (spectrum a), cured composite top surface (spectrum b) and cured composite bottom surface (spectrum c). Generally speaking, BISGMA-based composites exhibit an aromatic band at about 1636/cm, making them suitable for use as internal standards and comparisons with ($H_2C=C(CH_3)C=O$). As a function of exposure duration, it can be shown from FTIR spectra that the cured composite exhibits predictable variations in the relative intensities between the peaks at 1714.0/cm carbonyl peak C=O stretching mode and C=C absorption band. As anticipated, a decrease in peak intensity at 1714.5/cm was seen on both surfaces as exposure time was increased. Figs. 2 and 3 show the composite resin's calculated degree of conversion (DC). On the top and bottom surfaces of the specimen C1 that was cured by LED laser irradiation for 10 s, the DC values were 58% and 49%, respectively.

According to the identical Figs. 2 and 3, the degree of conversion (DC) for the composite resin specimens C2 (curing time 20 sec) was 67 and 50% on the top and bottom surfaces, respectively and for 30 sec of irradiation, the values were determined to be 91 and 82%. The observed variations in DC between the top and bottom are likely caused by the samples' thickness. The more layers present, the more challenging it is for light to penetrate deeper layers of composite resin and start the polymerization activity.

The curing time on the degree of conversion of the composite resins C1, C2, C3 and C4 are shown in Figs. 2 and 3 under a constant ambient condition. The degree of conversion (DC) of the composite resins rises as curing time increases before falling after 30 sec. This rise in degree of conversion can be attributed to the fact that a highly crosslinked polymer is produced as the curing time increases due to the production of numerous growth centers. The deterioration of crosslinked polymer by excessive LED light irradiation may be the cause of the drop in DC after 30 sec.

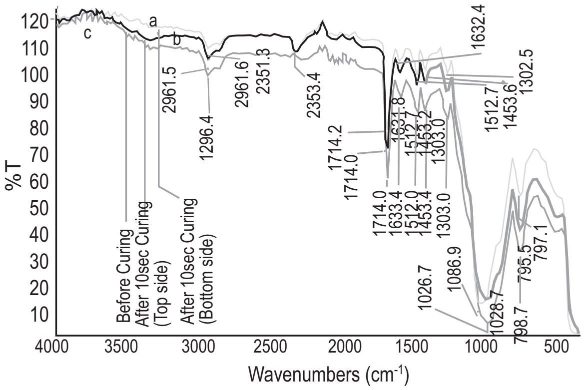

Fig. 1. Degree of conversion of discs cured from top side.

Vickers microhardness measurement. Hardness, which governs how much a material deforms, is widely acknowledged as a significant attribute and a useful benchmark for comparison with tooth structure. Restorative materials' polymerization or maturation condition can be used to explain changes in this property.

The microhardness and compressive strength of the composite materials were examined in order to determine how the length of the LED laser irradiation duration affected their mechanical characteristics.

Figure 4 displays the composite resin's hardness as determined by the Vickers Method[24].

The HV results from testing samples with known levels of monomer conversion as determined by FTIR are shown in Fig. 4. From the findings, it was found that the hardness rises as LED irradiation time increases.

Compressive strength. It is well recognized that only when nanofillers are uniformly spread throughout the matrix can composites attain the highest gains in their final properties. Figure 5 summarizes and displays the compressive strengths of the composite samples that

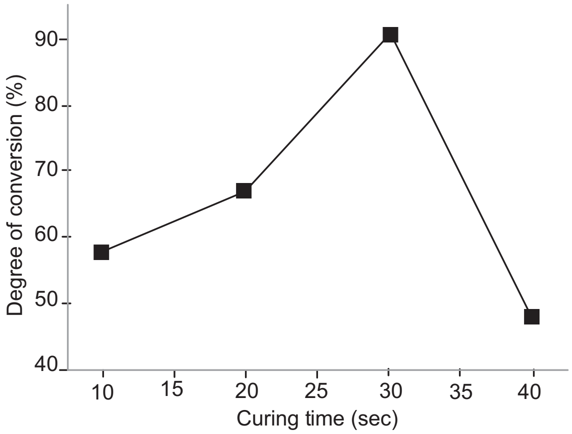

Fig. 2. Degree of conversion of discs cured from top side.

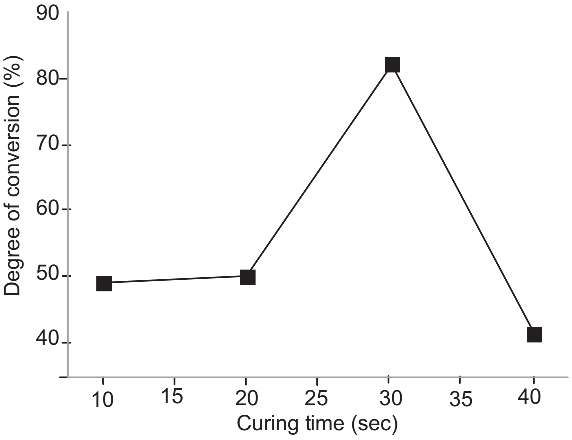

Fig. 3. Degree of conversion of discs cured from bottom side.

were subjected to curing conditions for 10, 20, 30 and 40 sec.

Microhardness and compressive strength were shown to rise with curing time up to 30 sec before decreasing, which is consistent with how long DC was exposed to radiation. According to other studies, the main cause of this is an improvement in photopolymerization efficiency (Giorgi and Paulillo, 2009).

Morphological analysis. To look at the filler dispersion in the composites, SEM observation was done. At the same magnifications. Figures 6, 7, 8 and 9, display the SEM micrograph of each substance. From SEM micrographs, several surface characteristics and appearances might be observed. SEM micrographs showed that the silica/zirconia composites' surface polymerization curing was nearly homogeneous (Jang *et al.*, 2015).

Thermal stability. Figure 10 shows and contrasts Thermogravimetric Analysis (TGA) curves of composite resin cured at various curing times. The results show that as the curing time rose, the thermal degradation changed to a high temperature area. This rise was ascribed to the fact that crosslinking density increased as cure time increases. Zirconia/silica reinforced

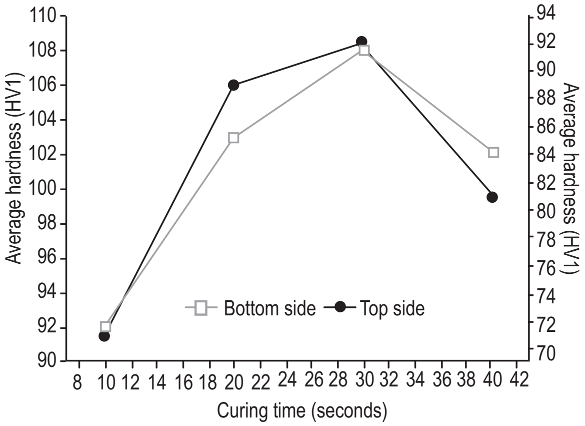

Fig. 4. Microvicker's hardness comparison chart.

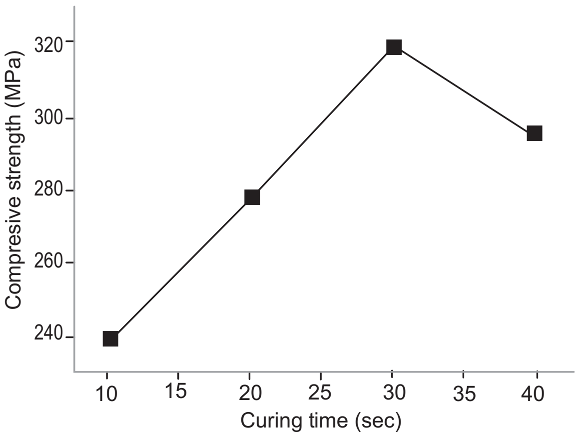

Fig. 5. Compressive strength versus LED light irradiation time.

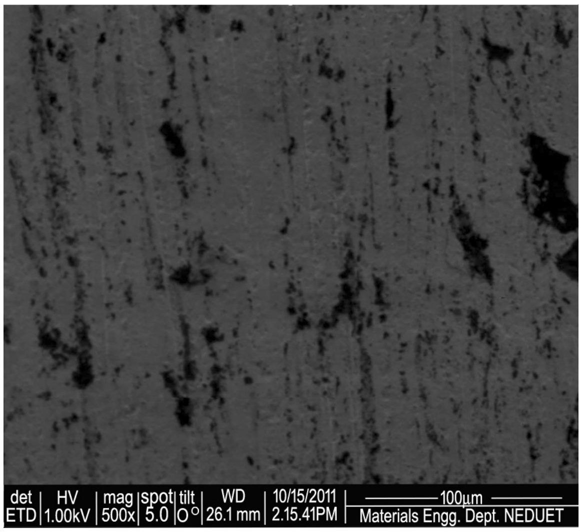

Fig. 6. SEM micrograph of dental composite resin disc cured for 10 sec.

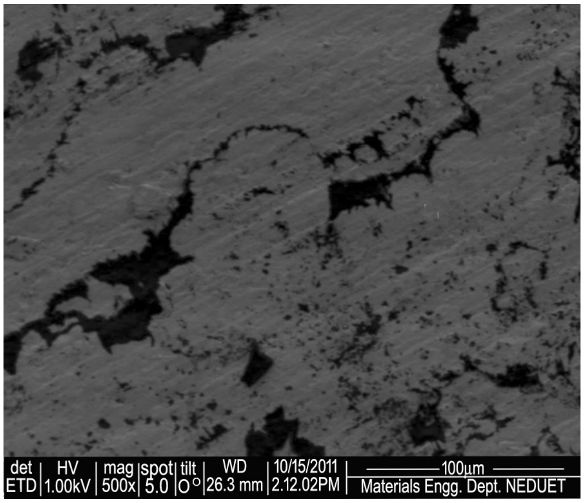

Fig. 7. SEM micrograph of dental composite resin disc cured for 20 sec.

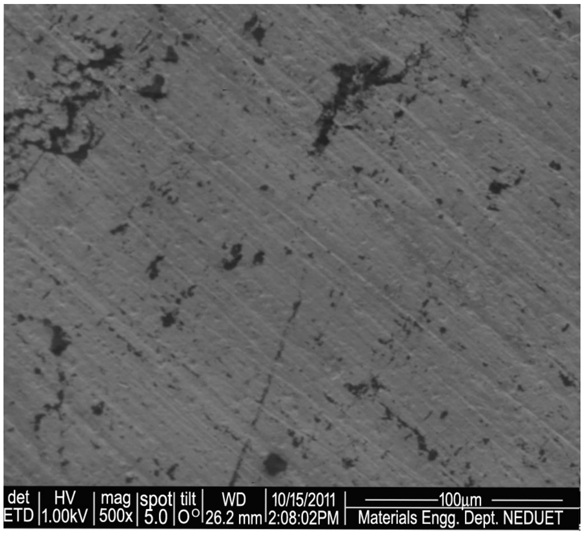

Fig. 8. SEM micrograph of dental composite resin disc cured for 30 sec.

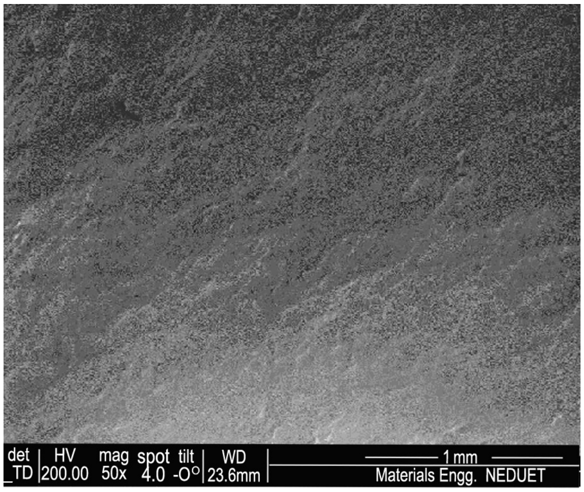

Fig. 9. SEM micrograph of dental composite resin disc cured for 40 sec.

bis(phenol)-A-glycidyl-dimethacrylate composite resin's improved thermal stability has also been attributed to a filler effect that acts as reinforcement between the BISGMA and the zirconia/silica surface. The highly crosslinking polymer and nano-filler can operate as a heat barrier, which improves the composites' overall thermal stability, as seen from the TGA curves.

Conclusion

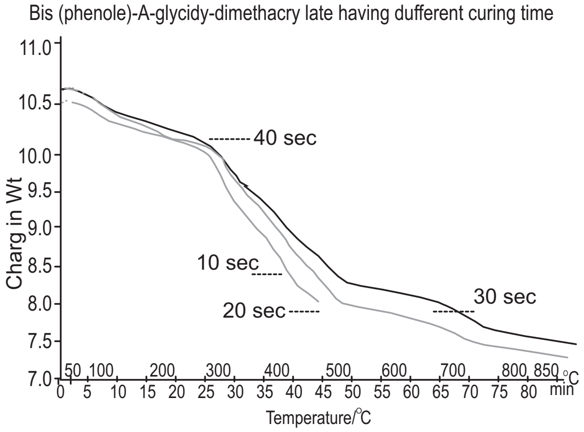

Fig. 10. TGA curves of samples at different cured time.

Using organosilane-treated zirconia and silica as a reinforcing filler added to a polymer matrix based on bisphenol A glycerolate dimethacrylate (bisGMA) monomer solution in acetone, a new dental composite to be used as restorative material was created. The composite was then cured by irradiating it with LED laser light. The results of this investigation shown that the degree of conversion (DC) of the composite resins, as determined by the FTIR technique, increased with longer curing times up to 30 sec before decreasing. According to one theory, this rise may be the result of more crosslinking sites, which would produce a polymer that is strongly crosslinked. The mechanical properties of the resin composites also improved with increasing irradiation time and correlated well with the degree of conversion. SEM results show homogeneous polymerization on the surface of silica/zirconia composites.

Conflict of Interest. The authors declare that they have no conflict of interest.

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