Contents lists available at ScienceDirect



Journal of the Mechanical Behavior of Biomedical Materials

journal homepage: www.elsevier.com/locate/jmbbm

Tribological behavior and wear mechanisms of dental resin composites with different polymeric matrices

Vladja Torno, Paulo Soares

Mechanical Engineering, Polytechnic School, Pontificia Universidade Católica do Paraná, Curitiba - Brazil

ARTICLE INFO	A B S T R A C T
<i>Keywords:</i> Dental resin composites Mechanical properties Wear Crosslinking density Polymeric matrices	The aim of this study was to investigate the effect of different polymeric matrices and their crosslink density on the mechanical and tribological properties of three commercially available dental resin composites, including Filtek Z250XT, Charisma Classic, and Venus Diamond One. The mechanical properties of the composites were investigated by instrumented indentation. The results showed that the polymeric matrix composition has a significant effect on the hardness and elastic modulus of the resins. Wear resistance was investigated by recip- rocating ball-on-plane tests in artificial saliva. Results show that the TCD-based resin composite has higher crosslinking density resulting in a more wear-resistant material. There was also a strong correlation between wear resistance and the mechanical properties of the resin composites when comparing similar fillers. These findings suggest that the wear resistance of resin composites can be improved by increasing their crosslinking density and enhancing their mechanical properties. The study provides insights into the design and development of more wear-resistant resin composites for dental applications.

1. Introduction

Resin based composites (RBC) are a common restorative material used in dentistry for posterior tooth restorations mainly due to an increased demand for better esthetics and to mimic natural teeth (Zafar et al., 2020). They are usually composed of a polymeric matrix, inorganic filler particles, and various other components such as coupling agents and photoinitiators. While dental composites have many advantages, including their esthetic appeal, bonding strength, and versatility, they are also subject to wear over time. Several factors can contribute to the resin composite wear, including.

- (i) Load-bearing capacity: Dental composites may wear due to repeated stress caused by biting and chewing. This wear can occur both on the surface and within the composite material;
- (ii) Abrasion: Abrasive forces can cause wear on the surface of dental composites. This can occur due to the consumption of hard foods, bruxism (teeth grinding), or the use of abrasive toothpaste;
- (iii) Chemical degradation: The chemical composition of dental composites can be affected by exposure to acids in food and drinks or by the presence of bacteria in the oral cavity. This can

cause degradation of the composite material and wear over time (Tsujimoto et al., 2018; Turssi et al., 2003).

Several studies have investigated the wear of dental composites and have found that wear rates vary depending on the composition of the composite material, the size and shape of the restoration, and the type and severity of the forces applied to the restoration (Dionysopoulos and Gerasimidou, 2021; Han et al., 2014; Tsujimoto et al., 2018; Turssi et al., 2003). Some researchers have suggested that nanofilled composites may exhibit less wear than traditional microfilled or hybrid composites (Alzraikat et al., 2018; Liu et al., 2021).

Tribological resistance of dental resin composites refers to the resistance to wear, friction, and degradation during sliding or contact between the resin and opposing surfaces. The polymeric components in dental resin composites play a crucial role in determining the tribological resistance of the material, as they determine the mechanical properties of the material (La Rosa et al., 2022).

Wear resistance is an important property of dental composites because dental restorations are constantly subjected to various mechanical stresses, including occlusal forces, abrasive wear, and cyclic fatigue (Han et al., 2014; Turssi et al., 2003). If a restoration is unable to withstand these stresses, it can lead to failure of the restoration, fracture

* Corresponding author. *E-mail addresses:* tornovladja@gmail.com (V. Torno), pa.soares@pucpr.br (P. Soares).

https://doi.org/10.1016/j.jmbbm.2023.105962

Received 2 May 2023; Received in revised form 4 June 2023; Accepted 6 June 2023 Available online 28 June 2023 1751-6161/© 2023 Published by Elsevier Ltd.

V. Torno and P. Soares

or wear of the opposing tooth, or even the need for additional treatment.

In particular, the wear of dental composites can occur through several mechanisms, such as abrasive wear, attrition, and fatigue wear, which can lead to surface roughness, loss of surface gloss, and microcracking, as well as the release of debris and monomers. This can in turn lead to secondary caries, inflammation, or allergic reactions in the oral environment, which can affect the long-term success of the restoration (Han et al., 2014).

BIS-GMA, UDMA, and TEGDMA are all polymeric matrices that are most commonly used in dental restorative materials (Pratap et al., 2019). Each of these polymers has different properties, which can affect their mechanical and tribological properties. TCD (tricyclodecane dimethanol dimethacrylate) is a relatively new polymeric matrix that has been developed as an alternative to Bis-GMA and UDMA to avoid problems related to polymerization stress contraction (Ilie and Hickel, 2011; Marchesi et al., 2010). During polymerization, the monomers react with each other to form a cross-linked polymer network, which provides mechanical strength and stability to the material. Different monomers have different functional groups, molecular weights, and reactivity ratios that influence the degree of conversion and crosslinking density (Aminoroava et al., 2021). The degree of crosslinking and the density of the network are important factors that determine the wear resistance of the composite. A high degree of crosslinking and a dense polymer network result in a stronger and more durable material, which is more resistant to wear and deformation (Barszczewska-Rybarek, 2019a; Emami and Söderholm, 2005; Marchesi et al., 2010).

Therefore, dental composites with good wear resistance can improve the longevity and durability of restorations, reduce the need for additional treatment or replacement, and enhance patient satisfaction. This is especially important for posterior restorations, where the restoration is exposed to high occlusal forces and the wear resistance of the material is critical to maintaining the functional integrity of the tooth. The choice of the resin composite based on its polymeric matrix can have a significant impact on the mechanical and tribological properties of dental restorative materials.

Thus, this work aimed to investigate the effect of different polymeric matrices and their crosslink density on the mechanical and tribological properties of three different commercial resin composites.

2. Experimental details

2.1. Specimens preparation

Three commercially available dental resin composites with different polymeric matrix compositions were used (Table 1), including Filtek Z250, Charisma Classic, and Venus Diamond One. A total of 15 specimens were prepared for each type of resin composite. A metallic mold (a ring with a hole of diameter 10 mm and depth 2 mm) was placed on a piece of acetate strip. The mold was carefully filled with a slight excess of resin composite (with care taken to minimize entrapped air) and covered with a second acetate strip and compressed with a thin glass slide to obtain a flat surface after light curing.

A light-curing unit (Radii-cal, SDI) was used to cure the composites. The output light intensity was 1200 mW/cm² and the spectral range was 410–500 nm. The upper surfaces were cured for 40 s. The hardened samples were removed from the mold and their test surfaces were wetpolished with 1200-grit SiC papers and a CeO₂ slurry to remove the resin-rich layer and obtain a standard surface finish for the test.

2.2. Crosslinking density

The degree of polymer crosslinking was obtained by measurements of the glass transition temperature and degradation temperature through differential scanning calorimetry (DSC). Specimens of the resin composites prepared in the same way as described before, but with 2 mm deep and 4 mm in diameter, were used for this test. The glass transition temperature (Tg) and degradation temperature (Td) values of specimens from each resin composite were determined using a differential scanning calorimeter (DSC; Netzsch Pegasus) in a sealed aluminum pan at a heating rate of 10 K/min, from 30 to 350 °C. The Tg values were determined from the onset of the heat capacity change and the degradation temperature from the onset of the endothermic peak.

2.3. Mechanical and tribological properties

The mechanical properties of the dental composites were investigated by instrumented indentation. All the tests were performed using the commercially available dynamic ultra-micro hardness tester (DUH-211s, Shimadzu) with a Berkovich diamond tip calibrated using amorphous silica as a standard. Five indentations with one loading/unloading cycle were made on the top of each specimen with a 5-µm spacing between indentations. The maximum applied load was 400 mN and the holding time at the maximum load step was 5 s. The hardness and elastic modulus were determined by the Oliver and Pharr's method (Oliver and Pharr, 1992).

The wear behavior was measured at room temperature by using a ball-on-plate reciprocating tribometer (Anton-Paar). The tests were carried out using an alumina ball (Al₂O₃) as a counter-body. The friction coefficient and wear rate were measured at a normal load of 20 N, a linear speed of 1.0 cm/s, a track length of 2 mm, and a total sliding distance of 50 m. The tests were done with the samples immersed in artificial saliva (KCl - 150 mmol/L, Ca(NO₃)₂.H₂O - 1.5 mmol/L, Na₂HPO₄.2H₂O - 0.9 mmol/L, H₂NC(CH₂OH)₃-0.1 mol/L, and NaF - 0.05 µg/L, with pH of 7.0).

The tracks' profile was obtained using a Taylor-Robson profilometer (Taylor-surf) attached to the tribometer, and the wear rate (W, mm³/N. m) was calculated using values collected at three different points in the track, according to ASTM D7755-11. The wear rate of samples was calculated according to the formula: $W=(S \cdot l)/(F \cdot L)$, where *S* is the cross-sectional area of the wear track (mm²), *l* is the length of the wear track (mm), *F* is the applied load (N), *L* is the sliding distance (m) (Ayerdi et al., 2021). In addition, wear tracks were analyzed by scanning

Table	1
-------	---

Dental resin composites were used in this study.

1		2			
Resin composite	Туре	Matrix ^a	Filler	%wt/%vol filler	Manufacturer (Lot)
Charisma CLASSIC (A2)	Micro- hybrid	Bis-GMA	Barium-aluminum-fluoride glass (Microglass) – 0.7 to 2 μm Pyrogenic SiO2 – 10 to 70 nm	78/61	Kulzer (K010734)
Filtek Z250XT (A2)	Micro- hybrid	Bis-GMA, UDMA, Bis-EMA, PEGDMA, TEGDMA	ZrO2/SiO2 clusters (0.1–10 μm). Non-agglomerated SiO2 (20 nm)	82/68	3 M ESPE (1909200648)
Venus Diamond ONE	Nano- hybrid	TCD-DI-HEA, UDMA	Barium-aluminum-fluoride glass - 5 nm–20 µm	81/64	Kulzer (K010021)

^a Bis-GMA (Bisphenol A diglycidyl ether dimethacrylate). Bis-EMA (Bisphenol A polyethylene glycol diether dimethacrylate) UDMA (urethane dimethacrylate). TEGDMA (triethyleneglycol dimethacrylate)TCD-DI-HEA: 2-propenoic acid; (octahydro-4,7-methano-1H-indene-5-diyl) bis(methyleneiminocarbonyloxy-2,1-ethanediyl) ester.

electron microscopy (Vega3, Tescan) for the identification of tribo-mechanisms.

2.4. Statistical analysis

Statistical analysis for nanoindentation and wear rate measurements was made using ANOVA and post hoc Tukey's test at P < 0.05 level.

3. Results and discussion

3.1. Scanning electron microscopy

The polished surface morphologies of the resin composites are shown in Fig. 1. Images were obtained using backscattering electron (BSE). There is a bimodal size distribution of filler particles in all the polymeric matrices, with large irregular particles and smaller rounded agglomerates. Resin composites from Kulzer (Classic and One) were characterized by the presence of some large barium glass particles ($\geq 20 \ \mu m$).

3.2. Cross-linking density

The DSC curves are shown in Fig. 2 and the thermal events (Tg and thermal degradation) for the groups are summarized in Table 2. From the data of Table 2, the Venus Diamond One with the TCD matrix presented the best thermal stability (higher Tg and degradation temperature). The Charisma Classic resin composite, with BIS-GMA matrix, presented the lowest value for Tg, but higher degradation temperature than Filtek Z250XT.

Crosslinking density refers to the number of chemical bonds formed between the polymer chains in the resin, which can affect the mechanical and tribological properties of the material. The higher the crosslinking density, the more rigid and durable the material will be, and the better it will resist wear. When resin composites are cured, the monomers in the resin mix together and form chemical bonds, creating a polymer network. The degree of crosslinking between the polymer chains can be influenced by the curing conditions, such as the intensity and duration of the light source used to polymerize the resin. Studies have shown that increasing the crosslinking density of polymers can lead to increased wear resistance (McKellop et al., 1999; Muratoglu et al., 2001). This is because the higher crosslinking density makes the material more resistant to deformation and fracture, which helps to maintain its shape and integrity during use.

The glass transition temperature (Tg) of a dental resin composite is also related to its crosslinking density (Soh and Yap, 2004). Tg is the temperature at which a material transitions from a glassy state to a



Fig. 2. DSC curves for the studied resin composites.

Table 2
Thermal events (Tg and thermal degradation) for the resin composites.

	Venus Diamond One	Charisma Classic	Filtek Z250XT
Tg (°C) Td (°C)	$\begin{array}{c} 193.6 \pm 1.6 \\ 293.4 \pm 1.3 \end{array}$	$\begin{array}{c} 158.3 \pm 1.4 \\ 294.9 \pm 1.8 \end{array}$	$\begin{array}{c} 181.8 \pm 1.3 \\ 249.4 \pm 0.9 \end{array}$

rubbery state, and it is a measure of the mobility of the polymer chains within the material. In general, materials with higher crosslinking density tend to have higher Tg values, indicating that the polymer chains are more tightly packed and less mobile.

Differential scanning calorimetry (DSC) is a commonly used technique to measure the Tg of dental resin composites. DSC measures the heat flow associated with the glass transition of a material as a function of temperature. The relationship between crosslinking density and Tg is complex and depends on several factors such as the size and shape of the polymer chains, the presence of fillers or other additives, and the curing conditions. In general, increasing the crosslinking density of a dental resin composite will tend to increase its Tg. This is because the chemical bonds formed between the polymer chains in a highly crosslinked resin constrain the motion of the chains and increase the energy required to transition from a glassy to a rubbery state (Stutz et al., 1990). The degradation temperature of a dental resin composite can also be related



a) Charisma Classic

b) Venus Diamond One

c) Filtek Z250XT

Fig. 1. SEM images of resin composites. Magnification 3,000×. BSE signal.

to its crosslinking density. Degradation temperature refers to the temperature at which a material begins to break down or decompose due to thermal stresses.

Dental resin composites with higher crosslinking density tend to have higher degradation temperatures, indicating that the resin has a more rigid and stable network of polymer chains. This rigid network is less likely to break down or degrade under thermal stresses, leading to a higher degradation temperature. However, it is important to note that the relationship between crosslinking density and degradation temperature is not always straightforward and can be influenced by other factors such as the matrix chemical composition and the type and amount of fillers in the resin composite. Results presented in Fig. 2 and Table 1 show that although Filtek Z250XT has a larger amount of filler particles, the organic matrix is composed of other monomers besides BIS-GMA. Degradation temperature refers to the temperature at which a polymer begins to break down and lose its mechanical properties.

3.3. Nanoindentation

The nanoindentation mean values hardness, H_{IT} (Fig. 3) is 0.59 GPa for Charisma Classic, 0.71 GPa for Venus Diamond One, and 0.97 for Filtek Z250XT. Young's modulus is 12.7 GPa for Charisma Classic, 15.8 GPa for Diamond One, and 16.1 for Filtek Z250XT (Table 3). Statistical analysis of nanoindentation hardness values showed that the average values are significantly different (p < 0.05) between the resin composites. The same ANOVA procedure performed on the Young's modulus data showed no statistically significant difference between Venus Diamond One and Filtek Z250XT, and both are more rigid than Charisma Classic, with higher elastic modulus. Fig. 4 shows the typical load-displacement curves of the resin composites. It shows clearly that the h_{max} (maximum indentation depth) decreases gradually with the increasing filler content.

BIS-GMA (bisphenol A glycidyl methacrylate) is a commonly used matrix in dental composites. It is known for its good mechanical properties, such as high flexural strength and modulus, making it suitable for dental restorations. However, it is also relatively brittle, which can make it prone to cracking or fracturing under stress. UDMA (urethane dimethacrylate) is another commonly used matrix in dental restorative materials. It has a higher degree of crosslinking compared to BIS-GMA, which can improve its mechanical properties and resistance to wear. UDMA also has good flexural strength and modulus, but it is less brittle than BIS-GMA (Aminoroaya et al., 2021). TEGDMA (triethylene glycol dimethacrylate) is a low-viscosity matrix that is often used as a diluent or co-monomer in dental composites. It can improve the handling properties of the material and reduce its viscosity, making it easier to place and shape. However, TEGDMA is known to be more susceptible to water sorption and degradation, which can affect its long-term mechanical and tribological properties (Pfeifer et al., 2009). TCD-DI-HEA

Table 3

Mean values of hardness, elastic modulus, H/E ratio, and wear rate.

	H _{IT} (GPa)	E _{IT} (GPa)	H/E	Wear rate * E–5 (mm ³ /N.m)
Charisma Classic	$\begin{array}{c} \textbf{0.596} \pm \\ \textbf{0.026} \end{array}$	$\begin{array}{c} 12.73 \pm \\ 0.31 \end{array}$	$\begin{array}{c}\textbf{0.219} \pm \\ \textbf{0.026} \end{array}$	1.63224
Venus Diamond	$0.709~\pm$	15.85 \pm	$0.261~\pm$	0.49913
One	0.049	0.46	0.018	
Filtek Z250XT	$0.967~\pm$	16.11 \pm	$0.355~\pm$	1.06918
	0.025	0.25	0.009	



Fig. 4. Representative nanoindentation curves, showing the load-unload cycle for each resin composite.

has been shown to have excellent mechanical properties with high flexural strength (Graf and Ilie, 2022). TCD is also more resistant to degradation from water and oral fluids compared to other polymeric matrices (Putzeys et al., 2019).

Filler and polymeric matrices can have a significant effect on the hardness and elastic modulus of resin composites. Higher filler content can contribute to higher hardness and elastic modulus as the filler particles increase the overall stiffness of the composite (Aminoroaya et al., 2021; Masouras et al., 2008a). The size and shape of filler particles can also impact the mechanical properties of resin composites. For example, smaller particle sizes can result in a smoother surface and increased hardness. The shape of the particles can also impact the packing density of the filler, which can affect the composite's strength and modulus (Masouras et al., 2008b).



Fig. 3. Average values of hardness (H_{TT}) and elastic modulus (E_{TT}) measured by instrumented indentation. Asterisks (*, **, ***) indicate that the difference of the means is significant at the 0.05 level.

When comparing the hardness and elastic modulus of Filtek Z250 and Charisma Classic, it is important to consider the filler content, size, and shape, as well as the polymeric matrix and curing process used for each material. Filtek Z250 is known for having a higher filler content and smaller particle size, which may contribute to its higher hardness and elastic modulus compared to Charisma Classic. Charisma Classic and Venus Diamond One have that same filler particle composition, however, the fraction of particles for Classic is lower than for the Diamond One. This difference clearly influences the hardness and elastic modulus. Besides, it shows that nanohybrid resin presents higher values of H_{TT} and E_{TT} than micro-hybrid resin. It also shows that BIS-GMA-based resin has lower mechanical properties than TCD-based resin.

Microhybrid and nanohybrid resin composites differ in their filler size and composition, which can affect their mechanical properties as measured by nanoindentation. Microhybrid resin composites have larger filler particles, typically ranging from 0.4 to 1.5 µm in size, while nanohybrid resin composites have smaller filler particles, typically ranging from 20 to 75 nm in size. Nanohybrid resin composites also use a higher percentage of nanofillers. The smaller size and higher surface area of nanofillers can contribute to increased strength and stiffness of the composite. Comparing both micro-hybrid resins, it is shown that the amount and composition of filler particles directly affect the mechanical properties. Filtek Z250XT has higher values of hardness, which suggest that the content of the zirconium particles is important. Work conducted by dos Reis et al. (2013) revealed a positive correlation between the amount of zirconium particles present in the composite material and its hardness. Compared to other commonly used fillers based on glass compounds (which typically exhibit a hardness of around 3-4 GPa) (Kim et al., 2002), zirconium particles displayed a hardness of 17 GPa.

3.4. Tribological properties

Fig. 5 presents the friction coefficient measured in an artificial saliva environment. The behavior is similar for all RBCs up to 30 m sliding, with an increase in COF with sliding distance. There is a running-in regime up to 5 m, where there is an accommodation of the ball into the surface. Then a steep increase becomes stationary at 25 m. The COF is higher for the Z250XT, with an average value of 0.35–0.40. COF for Classic and One is lower than for Z250 and is around 0.30. However, from 30 m on, the RBC One presents a COF oscillation, characteristic of a stick-and-slip phenomenon. The stick-slip phenomenon occurs when the COF curve is characterized by the occurrence of alternating periods of high frictional resistance (stick phase) followed by sudden slip events,



during which the surfaces move relative to each other with very little resistance. It occurs when the tribofilm between the two surfaces sticks to the ball and detaches from the sample, leading to sudden slip events and the observed stick-slip behavior.

Journal of the Mechanical Behavior of Biomedical Materials 144 (2023) 105962

Fig. 6a shows representative groove profiles obtained in the center of the wear tracks for each RBC. Charisma Classic presents the largest wear groove, and consequently the highest wear rate, while the Diamond One, presents the lowest wear rate (Fig. 6b).

The wear rate is a measure of the amount of material removed from a surface due to sliding or abrasive contact with another surface and is usually correlated to the H/E, or hardness-to-modulus ratio, which is a measure of a material's resistance to indentation and deformation. Usually, materials with higher H/E ratios tend to exhibit lower wear rates (Leyland and Matthews, 2000). This is because materials with higher H/E ratios are generally more resistant to deformation and can better resist plastic deformation and surface damage, leading to reduced wear. However, the relationship between H/E and wear rate is not always straightforward and can depend on many factors, including the type of wear (e.g., adhesive, abrasive, or erosive), the contact conditions (e.g., sliding speed and load), and the material properties of both the wear surface and the counter surface (Pieniak and Gauda, 2020). This relation works partially for the resin composites studied, as seen in Table 3.

Both resin composites Filtek Z250XT and Venus Diamond One have similar volumetric concentrations of fillers but differ in composition. While the Venus Diamond One has Barium-aluminum fluoride glass, the Filtek Z250XT has Zirconia and Silica as filler particles. The filler content, composition, and size play significant roles in determining the mechanical and tribological properties of resin composites. When comparing filler compositions, Barium–Aluminum glass fillers provide a good balance of mechanical properties, including strength, modulus, wear resistance, and offer improved esthetics due to their translucency. Silica fillers provide high strength, hardness, and wear resistance. Silica fillers offer excellent stability and compatibility with the resin matrix. However, Zirconia fillers exhibit exceptional strength, hardness, and wear resistance. They are known for their high fracture toughness and resistance to crack propagation (Aminoroaya et al., 2021; Hong et al., 2020).

When comparing the resins with the same filler particles composition, the higher H/E for the resin Diamond One results in a lower wear rate. But this relation does not work if we compare the resins Diamond One and Z250XT. In this case, what controls the wear rate is the hardness of the polymeric matrix, and the ability to retain filler particles. In the case of the Diamond One resin composite, the TCD polymeric matrix has greater thermal stability, and consequently, higher mechanical resistance than Bis-GMA, as shown by the DSC results. This indicates that the crosslinking density of dental resin composites is directly related to wear resistance. Also, when the surface wears out due to friction with the sphere, there is the removal of the filler particles, and the filler particles of Z250XT, based on zirconia and silica, are harder than glass particles in the Diamond One resin, which favor the abrasive wear as a third body (Azmy et al., 2022). Moreover, if the filler hardness is too high compared to the resin matrix, it can also increase the wear of resin composites by creating stress concentration and interfacial debonding (Osiewicz et al., 2022). Since the Diamond One resin particles have lower hardness, they break down more easily, forming a tribofilm as seen in the SEM images (Fig. 7). This tribofilm detaches from the wear groove, generating the oscillations observed in the COF curves.

In the SEM images in Fig. 7, it is possible to see more grooves and less tribofilm formation on the Z250XT resin (Fig. 7 f, i). This means that there is more wear on the surface as observed by the wear surfaces on SEM images (Fig. 7g–i), and a significant number of fractured particles can be observed in the wear grooves. Fig. 7f shows less tribofilm formed for Filtek Z250XT resin when compared to Classic and One.

Fig. 5. COF of the resin composite tests against $\mathrm{Al}_2\mathrm{O}_3$ ball, as a function of sliding distance.

Crosslinking plays a crucial role in determining the mechanical and tribological properties of dental resin composites. By altering the



Fig. 6. (a) Representative wear grooves measured by profilometry; (b) wear rate (mm³/N.m).

crosslinking density and using different polymeric matrices, such as Bis-GMA, TEGDMA, and the newly developed TCD, it is possible to influence various characteristics of dental composites.

Crosslinking of the polymer chains in dental resin composites leads to the formation of a three-dimensional network structure. This network structure enhances the material's strength and stiffness by providing intermolecular connections that resist deformation and distribute applied forces more effectively. As a result, the composite becomes less prone to fracture and deformation under mechanical loads. Crosslinking also promotes the formation of a tough and ductile matrix in dental resin composites. The interconnected polymer chains can absorb and dissipate energy more efficiently, preventing crack propagation and enhancing the material's fracture resistance (Cook and Johannson, 1987). This also improves the wear resistance due to the formation of a more durable and resilient network structure. The crosslinks help to distribute and dissipate mechanical stresses, reducing the likelihood of material fatigue, wear, and surface degradation. As a result, the composite can withstand repetitive occlusal forces and abrasive wear from food particles without significant damage.

The specific effects of crosslinking with different polymeric matrices, such as Bis-GMA, TEGDMA, and TCD, can vary. These matrices have different molecular structures and reactivity, leading to variations in crosslinking density and resulting properties. For instance, Bis-GMA is a commonly used polymeric matrix in dental composites. It provides high strength and rigidity but can be relatively brittle. Crosslinking with Bis-GMA improves mechanical properties but may result in increased stiffness and reduced toughness. TEGDMA is another widely used matrix. It imparts flexibility and toughness to the composite. Crosslinking with TEGDMA can enhance wear resistance and toughness while maintaining a certain level of flexibility. TCD-urethane is a newly developed matrix that offers improved mechanical properties and biocompatibility. It can be tailored to achieve a specific crosslinking density, leading to enhanced wear resistance, strength, and durability.

When comparing the crosslinking of Bis-GMA and TCD, it's important to consider their polymeric chains and the types of bonds involved in the crosslinking process. Bis-GMA is a dimethacrylate monomer that consists of two methacrylate groups connected by a bisphenol A backbone. The presence of the bisphenol A structure provides rigidity to the polymeric chain. Bis-GMA undergoes crosslinking through a free radical polymerization mechanism. When exposed to a curing agent, typically a photoinitiator or a chemical initiator, the methacrylate groups of Bis-GMA react with each other, forming covalent bonds known as a methacrylate or acrylic. These bonds link the polymer chains together, creating a three-dimensional network (Barszczewska-Rybarek, 2019). TCD is a cycloaliphatic di(meth)acrylate monomer that contains multiple methacrylate groups. The TCD-urethane monomer has a rigid backbone that reduces the packing density which results in lower shrinkage of the polymer matrix during the curing process. The TCD-urethane crosslinker also has side chains that contribute to the

elasticity of the resulting polymer network. This elasticity helps reduce shrinkage stress during light curing, as the side chains can compensate for some of the stress (Utterodt et al., 2016). TCD can undergo crosslinking through both free radical and cationic polymerization mechanisms. In free radical polymerization, the methacrylate groups of TCD react with each other to form methacrylate or acrylic bonds, similar to Bis-GMA. In cationic polymerization, TCD can also participate in the formation of cationic bonds, which are generated by the reaction of epoxy groups present in TCD with a cationic initiator. These cationic bonds contribute to the crosslinking network. In terms of polymeric chains, Bis-GMA consists of a bisphenol A backbone with two methacrylate groups, while TCD is a cycloaliphatic di(meth)acrylate with multiple methacrylate groups. This structural difference influences the flexibility and rigidity of the resulting crosslinked networks. Bis-GMA, with its rigidity, provides strength and stiffness to the crosslinked network but can be relatively brittle. On the other hand, TCD offers greater flexibility and toughness, potentially enhancing the impact resistance and durability of the composite. The presence of cationic bonds in TCD allows for alternative crosslinking mechanisms, providing versatility in the formulation and processing of dental composites.

In summary, our results highlight the importance of understanding the effect of the polymeric matrix and filler particles on wear resistance, which will help clinicians to choose the most appropriate resin composite to ensure optimal performance and esthetics of the restorations.

4. Conclusions

The hardness, modulus, and crosslinking density of the polymer matrix affect the tribological resistance of the composite. A higher hardness and modulus result in a higher resistance to wear and deformation. The cross-linking density of the matrix determines the stability of the resin, and a higher crosslinking density results in a more stable and wear-resistant material. In addition, the type of filler particles can also affect the tribological resistance of dental resin composites. In terms of tribological properties, both micro-hybrid and nanohybrid fillers can provide good wear resistance for dental composites, but their specific performance can depend on factors such as the composition of the filler particles, the matrix material, and the conditions of use. It was observed that the removed filler particles during the reciprocating wear favor the abrasive wear, acting as a third body that accelerates the composite wear. Thus, the choice of resin and filler compositions can depend on the specific needs of the clinical situation, including the esthetic requirements and the functional demands of the restoration.

CRediT authorship contribution statement

Vladja Torno: Writing – original draft, Validation, Methodology, Formal analysis, Data curation, Conceptualization. Paulo Soares: Writing – review & editing, Writing – original draft, Validation,



Fig. 7. SEM images of the wear grooves produced by reciprocating tribological tests on the studied resin composites. Fig. 7 a, d, g – Charisma Classic, Fig. 7 b, e, h – Venus Diamond One, Fig. 7 c, f, I – Filtek Z250XT.

Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was partially funded by CNPq (Grant 311610/2021-8).

References

- Alzraikat, H., Burrow, M.F., Maghaireh, G.A., Taha, N.A., 2018. Nanofilled resin composite properties and clinical performance: a review. Operat. Dent. 43 (4), E173–E190.
- Aminoroaya, A., Neisiany, R.E., Khorasani, S.N., Panahi, P., Das, O., Madry, H., Cucchiarini, M., Ramakrishna, S., 2021. A review of dental composites: challenges, chemistry aspects, filler influences, and future insights. In: Composites Part B: Engineering, vol. 216. Elsevier Ltd.
- Ayerdi, J.J., Aginagalde, A., Llavori, I., Bonse, J., Spaltmann, D., Zabala, A., 2021. Ballon-flat linear reciprocating tests: critical assessment of wear volume determination methods and suggested improvements for ASTM D7755 standard. Wear 470–471.

V. Torno and P. Soares

- Azmy, E., Al-Kholy, M.R.Z., Fattouh, M., Kenawi, L.M.M., Helal, M.A., 2022. Impact of nanoparticles additions on the strength of dental composite resin. Int. J. Biomater. 2022.
- Barszczewska-Rybarek, I.M., 2019. A guide through the dental dimethacrylate polymer network structural characterization and interpretation of physico-mechanical properties. Materials 12 (Issue 24). MDPI AG.
- Cook, W.D., Johannson, M., 1987. The influence of postcuring on the fracture properties of photo-cured dimethacrylate based dental composite resin. J. Biomed. Mater. Res. 21 (8), 979–989.
- Dionysopoulos, D., Gerasimidou, O., 2021. Wear of contemporary dental composite resin restorations: a literature review. Restorative Dentistry & Endodontics 46 (2).
- dos Reis, A.C., de Castro, D.T., Schiavon, M.A., da Silva, L.J., Agnelli, J.A.M., 2013. Microstructure and mechanical properties of composite resins subjected to accelerated artificial aging. Braz. Dent. J. 24 (6), 599–604.
- Emami, N., Söderholm, K.J.M., 2005. Dynamic mechanical thermal analysis of two lightcured dental composites. Dent. Mater. 21 (10), 977–983.
- Graf, N., Ilie, N., 2022. Long-term mechanical stability and light transmission characteristics of one shade resin-based composites. J. Dent. 116.
- Han, J.M., Zhang, H., Choe, H.S., Lin, H., Zheng, G., Hong, G., 2014. Abrasive wear and surface roughness of contemporary dental composite resin. Dent. Mater. J. 33 (6), 725–732.
- Hong, G., Yang, J., Jin, X., Wu, T., Dai, S., Xie, H., Chen, C., 2020. Mechanical properties of nanohybrid resin composites containing various mass fractions of modified zirconia particles. Int. J. Nanomed. 15, 9891–9907.
- Ilie, N., Hickel, R., 2011. Resin composite restorative materials. Aust. Dent. J. 56 (Suppl. 1), 59–66.
- Kim, K.-H., Ong, J.L., Okuno, O., 2002. The effect of filler loading and morphology on the mechanical properties of contemporary composites. J. Prosthet. Dent 87 (6), 642–649.
- La Rosa, G.R.M., Generali, L., Bugea, C., Ounsi, H.F., Benyőcs, G., Neelakantan, P., Pedullà, E., 2022. Application of tribology concept in dental composites field: a scoping review. J. Funct. Biomater. 13 (Issue 4). MDPI.
- Leyland, A., Matthews, A., 2000. On the significance of the H/E ratio in wear control: a nanocomposite coating approach to optimised tribological behaviour. Wear 246 (1–2), 1–11.
- Liu, J., Zhang, H., Sun, H., Liu, Y., Liu, W., Su, B., Li, S., 2021. The development of filler morphology in dental resin composites: a review. Materials 14 (Issue 19). MDPI.
- Marchesi, G., Breschi, L., Antoniolli, F., Di Lenarda, R., Ferracane, J., Cadenaro, M., 2010. Contraction stress of low-shrinkage composite materials assessed with different testing systems. Dent. Mater. 26 (10), 947–953.
- Masouras, K., Akhtar, R., Watts, D.C., Silikas, N., 2008a. Effect of filler size and shape on local nanoindentation modulus of resin-composites. J. Mater. Sci. Mater. Med. 19 (12), 3561–3566.
- Masouras, K., Silikas, N., Watts, D.C., 2008b. Correlation of filler content and elastic properties of resin-composites. Dent. Mater. 24 (7), 932–939.

- McKellop, H., Shen, F.W., Lu, B., Campbell, P., Salovey, R., 1999. Development of an extremely wear-resistant ultra high molecular weight polyethylene for total hip replacements. J. Orthop. Res. 17 (2), 157–167.
- Muratoglu, O.K., Bragdon, C.R., O'Connor, D.O., Jasty, M., Harris, W.H., 2001. A novel method of cross-linking ultra-high-molecular-weight polyethylene to improve wear, reduce oxidation, and retain mechanical properties: recipient of the 1999 HAP Paul award. J. Arthroplasty 16 (2), 149–160.
- Oliver, W.C., Pharr, G.M., 1992. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. J. Mater. Res. 7 (6), 1564–1583.
- Osiewicz, M.A., Werner, A., Roeters, F.J.M., Kleverlaan, C.J., 2022. Wear of bulk-fill resin composites. Dent. Mater. 38 (3), 549–553.
- Pfeifer, C.S., Silva, L.R., Kawano, Y., Braga, R.R., 2009. Bis-GMA co-polymerizations: influence on conversion, flexural properties, fracture toughness and susceptibility to ethanol degradation of experimental composites. Dent. Mater. 25 (9), 1136–1141.
- Pieniak, D., Gauda, K., 2020. Indentation hardness and tribological wear in conditions of sliding friction of the surface layer of composites based on methacrylate resins with ceramic nanofiller. Advances in Science and Technology Research Journal 14 (2), 112–119.
- Pratap, B., Gupta, R.K., Bhardwaj, B., Nag, M., 2019. Resin based restorative dental materials: characteristics and future perspectives. In: Japanese Dental Science Review, vol. 55. Elsevier Ltd, pp. 126–138. Issue 1.
- Putzeys, E., Nys, S. De, Cokic, S.M., Duca, R.C., Vanoirbeek, J., Godderis, L., Meerbeek, B. Van, Van Landuyt, K.L., 2019. Long-term elution of monomers from resin-based dental composites. Dent. Mater. 35 (3), 477–485.
- Soh, M.S., Yap, A.U.J., 2004. Influence of curing modes on crosslink density in polymer structures. J. Dent. 32 (4), 321–326.
- Stutz, H., Illers, K.-H., Mertes, J., 1990. A generalized theory for the glass transition temperature of crosslinked and uncrosslinked polymers. J. Polym. Sci. B Polym. Phys. 28 (9), 1483–1498.
- Tsujimoto, A., Barkmeier, W.W., Fischer, N.G., Nojiri, K., Nagura, Y., Takamizawa, T., Latta, M.A., Miazaki, M., 2018. Wear of resin composites: current insights into underlying mechanisms, evaluation methods and influential factors. In: Japanese Dental Science Review, vol. 54. Elsevier Ltd, pp. 76–87. Issue 2.
- Turssi, C.P., De Moraes Purquerio, B., Serra, M.C., 2003. Wear of dental resin composites: insights into underlying processes and assessment methods - a review. In: Journal of Biomedical Materials Research - Part B Applied Biomaterials, vol. 65. John Wiley and Sons Inc, pp. 280–285. Issue 2.
- Utterodt, A., Reischl, K., Schönhof, N., Eck, M., Hiersekorn, C., Schneider, J., 2016. Polymerizable Dental Components with Improved usage Properties, Methods for Adjusting the usage Properties of Polymerizable Dental Composites, and Dental Composites Optimized According to Said Methods (Patent No. US9326918B2). U.S. Patent and Trademark Office.
- Zafar, M.S., Amin, F., Fareed, M.A., Ghabbani, H., Riaz, S., Khurshid, Z., Kumar, N., 2020. Biomimetic aspects of restorative dentistry biomaterials. In: Biomimetics, vol. 5. MDPI AG, pp. 1–42, 3.