# Comparative evaluation of Knoop hardness and depth of cure of ORMOCER based resin composites

# Avaliação comparativa de dureza Knoop e profundidade de polimerização de compósitos odontológicos à base de ORMOCER

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## Abstract

*The purpose of this study was to evaluate the Knoop hardness and the depth of cure of Ormocer based composites and to compare them with traditional Bis-GMA or derivatives based composites. Four composite were selected: Two Ormocer based (Definite and Admira), a hybrid (Z250) and a microfilled (A110). Cylindrical specimens with 3mm in diameter for 5mm in height were prepared in a metallic mould and photoactived according the manufacturer's instructions with the curing light unit XL2500 (3M/ESPE). After, they were stored for 24 hours at 37∞C. Knoop hardness measures were obtained with Micro hardness tester HMV (Shimadzu-Japan), with a load of 50g for 15s. Five specimens were made for each resin composite and three Knoop hardness measurements were obtained on surface, 1mm, 2mm, 3mm and 4mm depths. The results were submitted to ANOVA and Tukey's test at 5% level. According to the results, at all depths, Z250 was harder than the others composites. The composites Definite, Admira and A110 had no statistical differences in KHN until the depth of 2mm, after A110 showed decrease in hardness values. Generally, for all tested materials the deeper layers showed lower Knoop hardness values than those of the surface. Compared with hardness surface, statistically significant reductions in KHN occurred at depths of 2mm for Z250 and A110 and 3mm for Definite and Admira. It could be concluded that ORMOCER based materials showed intermediated hardness values and satisfactory depth of cure, when compared to the conventional composites.*

## Uniterms

*Composite resins, hardness; dental restoration, permanent*

## Introduction

Dental resin composites were introduced in the mid-1960s for the restoration of anterior teeth[2]. Since their advent, they have undergone significant development to improve the longevity of the restorations. Nowadays, resin composites are commonly used to aesthetically restore anterior and posterior teeth.

The formulation of light cured resin composites generally comprises three main components: inorganic filler particles, organic resin matrix and a couple agent that chemically bonds the reinforcing filler to the resin matrix [2, 21, 23].

The filler particles are most commonly produced by grinding or milling quartz, glasses (average particle size of 0.7-1.5µm), or silica particles of colloidal size, which are referred as microfillers (average particle size of 0.005-0.04µm) [2]. The filler content, size, and distribution have an important influence on physical and mechanical properties of the resin composites [8, 12, 18]. Besides, hardness pattern and depth of cure are directly affected by the inorganic loading [8, 12, 15, 18, 26].

Resin matrix also has an important influence on the properties of composite materials [3, 4, 7, 8, 21, 23]. It has been suggested that the mechanical properties of resinous materials are associated with the quantity of double bonds remaining in polymer after polymerization, however the monomer molecules per se may also play a role[3, 21, 23] .

The monomer system of most present day resin composites is based on Bis-GMA, developed by Bowen[6] in 1956. It was prepared from Bisphenol A and glycidyl metacrylate and later also from dyglicidyl ether of bisphenol A and metacrylic acid [21, 23]. Even today, the monomer system of most resin composites is based on Bis-GMA or derivatives, such Bis-EMA.

Bis-GMA is a difunctional monomer with large molecular size and a compelx chemical structure, with high molecular weight [21, 23]. It is extremely viscous at room temperature and needs diluent monomers to attain high filler levels and produce pastes of clinically usable consistencies [21, 23]. The monomers most often used as diluents for BisGMA are UEDMA and TEGDMA. They increase the degree of conversion and reduce the viscosity, but also increase the polymerization shrinkage and bioco mpatibility problems [2, 4, 23].

In addition to these classical composite filling materials, a new type of organic-inorganic hybrid dental materials, known as ORMOCERs, have been developed. This technology launched on the market in 1998 (Definite, Degussa AG, Hanau, Germany). In addition to dental application, ORMOCERs are widely used in modern industry [14, 24].

ORMOCER means organically modified ceramics, and it was formed as follows: starting from an alkoxy silane functionalized with a polymerizable group, hydrolysis and condensation led to an oligomeric Si-O-Si-nano-sturcture [21] . These oligomers replace the conventional monomers in composite. In a second step, a three dimensional network is formed by polymerization of the functional groups[21]. ORMOCERs are characterized by this novel inorganic-organic copolymers in the formulation that allows the modification of mechanical parameters over a wide range. The aim of this monomer system was to reduce the polymerization shrinkage, what allows improving marginal adaptation [21]. Best biocompatibility will be achieved if no diluent monomer, such TEGDMA, is needed to reduce the viscosity of the correspondent condensate [21].

The properties, and hence the performance of resin composites, are dependent upon the three basic components of the material (filler particles, resin matrix and the couple agent) [2, 20, 23]. The degree of conversion is mainly related to the resin matrix [12] while the surface hardness and mechanical properties depend mainly of the fillers, with a secondary role played by the resin matrix [3, 4,9]. The purpose of this research was to evaluate the Knoop hardness and depth of cure for ORMOCER based composites and compare them with traditional Bis-GMA or derivatives based composites.

## Material and Method

Four commercially resin composites were used. The list of composites used, the manufacturers, the composition, classification, and the batch numbers are given in Picture 1.

The samples were prepared in a metallic brass containing a cavity with 3mm in diameter and 5mm in height, longitudinally split up in to equal parts, in order to facilitate sample removal after polymerization. Each resin composite was inserted into the cavity in a single portion, exceeding a small amount from the margin of the cavity. The material was adapted by compression of polyester matrix under a glass slab, with static load of 1kg, to remove the excessive material. After the glass slab removal the specimens were light cured for 40s for A110, Admira and Definite and for 20s for Z250, using a XL2500 curing unit (3M/ESPE St.Paul, MN, USA) with 600mW/cm$^2$. Five specimens were prepared for each composite resin.

After polymerization, the specimens were removed from the metallic mold and stored at 37ºC for 24h on dry environment [18]. The specimens were placed in vertical position and included in acrylic resin (Vipi Flash, Dental Vipi, Pirassununga, SP, Brazil). Next, the specimens were ground and polished to the center, using 100, 200, 320, 400, 600, and 1000 grit sandpaper (Norton S.A., São Paulo, SP, Brazil) on an automated polisher (APL-4, Arotec, Cotia, SP, Brazil) and polished using diamond paste containing of 6µm, 3µm, 1µm, and 0.25µm.

Knoop hardness values were measured across the section of the composite resin, using a Microhardness Tester HMV 2000 (Shimadzu, Tokyo, Japan) at automatic procedure with a load of 50g applied for 15s [25]. Three measurement positions (A, B, and C) were made, each with five indentations

(from P1 to P5) from the top to the bottom of the specimen section, giving a total of fifteen measurements for each specimen. The indentation layout is show in Figure 1. The values obtained in micrometers were converted to Knoop Hardness Number (KHN), by indenter software. The results were submitted to ANOVA and means compared by Tukey´s test at the 5% significance level.

**Picture 1 - Description of used composites**

| Composite | Manufacturer | Batch number | Classification (filler %v) | Composition |
|---|---|---|---|---|
| Z250 | 3M Dental Products, St. Paul MN, USA | 0FH | Small particles (60%v) | Bis-EMA, UDMA, TEGDMA, zirconie silica sintetic filler (0,6μm) |
| A110 | 3M Dental Products, St. Paul MN, USA | 0AM | Microfilled (40%v) | Bis-GMA, TEGDMA, alumine oxide, silane, organic filler and silica(0,04μm) |
| Definite | Degussa, Hüls, Germany | 2994703 | Hybrid (56%v) | ORMOCER, bario glass and silica (1-1,5μm) |
| Admira | Voco, Cuxhaven, Germany | 04357 | Small particles (58%v) | ORMOCER, alifatic and aromatic dymethacrylate, glass ceramic filler (0,6μm) |

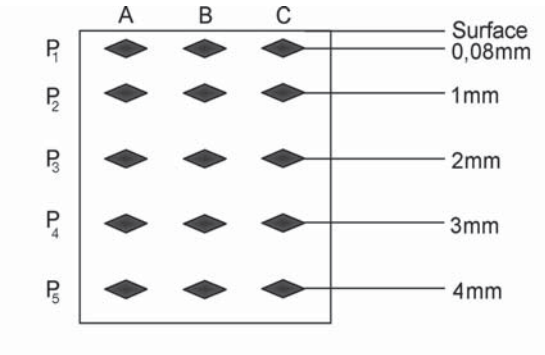


**FIGURE 1** – Schematic representation of the indentation diagram.

## RESULTS

Table 1 shows the means Knoop hardness and standard deviation for the four evaluated resin composites at different depths.

Until the depth of 3mm, Z250 was harder than the other composites. Definite, Admira, and A110 composites had no statistical differences in KHN until the depth of 2mm, after that A110 showed decrease in hardness values. Each material showed a decrease in hardness with increasing depth. For all tested materials, the deeper layers showed lower Knoop hardness values in relation to the surface. Compared with hardness surface, statistically significant reductions in KHN occurred at depths of 2mm for Z250 and A110 and 3mm for Definite and Admira. At the depth of 4mm, the Z250, Definite e Admira resin composites showed similar hardness. The A110 resin composite does not allow the hardness evaluation because it was not polymerized.

**Table 1 - Means Knoop hardness and standard deviation for the four evaluated resin composites at different depths**

| Material | Surface | 1mm | 2mm | 3mm | 4mm |
|---|---|---|---|---|---|
| Z250 | 80.86 ± 3.24 a A | 77.42 ± 2.77 a A | 73.27 ± 2.60 a A | 58.23 ± 3.31 a B | 29.51 ± 2.51 a C |
| Definite | 52.71 ± 6.71 b A | 53.85 ± 5.44 b A | 49.13 ± 4.35 b A | 44.77 ± 3.32 b A | 31.01 ± 2.42 a B |
| Admira | 52.91 ± 3.21 b A | 50.69 ± 1.92 b A | 50.63 ± 1.30 b A | 43.22 ± 2.77 b A | 26.22 ± 2.30 a B |
| A110 | 47.25 ± 3.01 b A | 50.99 ± 2.86 b A | 47.64 ± 2.23 b A | 28.66 ± 3.48 c B | 00.00 ± 0.00 b C |

Means following for different minuscule letters in the column and capital letters in the line differs statistically among themselves for the Tukey's Test at level of 5%.

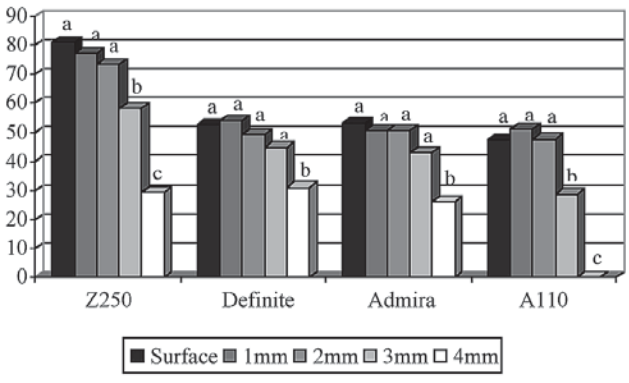


**FIGURE 2** – Graphic representation of the hardness values decreasing as a function of the depth. – Different letters show statistical differences between the groups in the same bars bloc.

## Discussion

Composite hardness results from the interaction of multiple factors associated with the resin matrix and the filler particles. Final hardness depends on both the composition and the degree of polymerization of the resin matrix [2, 3, 4, 9, 20, 23]. Hardness has often been used as an index of the ability of a material to resist abrasion or wear [2]. However, abrasion is a complex mechanism that involves several factors and because of this hardness a limited predictor of abrasion resistance. The hardness test is included in numerous American Dental Association (ADA) specifications for dental materials in order to determine the resistance to indentation of the material. The properties related to hardness are strength and proportional limit [3, 8, 9].

In this study, the mean values of KHN ranged from 47,25 to 80,86. These results are in agreement with the study of resin composites reported by Chung & Greener[9] (1990). In this study, it could be noticed that the composition has a strong effect on the surface hardness of the material.

The filler plays an important role in the properties of the composite[8]. Positive correlation has been established between hardness and the inorganic filler content of dental restorative composite[18]. There is a correlation between the volume fraction of filler and Knoop hardness number, but the kind, size, and distribution have also to be considered [8, 9, 18].

Considering the evaluated composites, Z250 showed the highest KHN values. These results were related to the presence of 60%v inorganic fillers (rounded zirconia/silica fillers - size range from 0,01 to 3,5µm). It certainly has defined the highest KHN [22]. Although Definite and Admira have inorganic content as high as Z250, the KHN was lower than Z250. This could be explained by the differences in composition, size, and distribution of these particles. Definite and Admira fillers (bario-glass and ceramic-glass, respectively) are glasses with lower hardness degree than zirconia fillers, validating the statement that filler particles play the major role on the hardness values. The microfilled composite A110, regardless the depth, showed the lowest hardness values, as expected, considering that the filler particles were based on silica and organic compounds [12].

General differences among resin composites based on different monomer systems are very difficult to deduce from in vitro and in vivo studies [2]. One reason is that the actual difference caused by dissimilar monomer systems is camouflaged by the fact that the materials differ in many other aspects, e.g., type and amount of fillers and initiators, besides the silanization of the filler particles. The effect of these may be more determinative for the properties than the nature of the copolymer. This, however, does not imply that the choice of monomer system is not significant [4, 23].

ORMOCER based restorative systems might be currently considered the most promising development involving modern dental filling materials with plastic contouring properties. The main advantage of these systems would be the combination of hardness (high amount of inorganic network structures) and flexibility (nature and amount of organic crosslinking)[24]. An interpenetrating network of inorganic-organic copolymers characterizes the matrix of ORMOCER based materials[21]. The filler particles are incorporated into this cross-linked inorganic and organic network matrix as with proven composite technology and it is manipulated by dentists like a conventional composite[20]. This work used the composites Admira and Definite, which have similar structures. Both composites presented statistically similar hardness values acceptable for posterior use, but the KHN means were lower than the Z250 means. These values are in agreement with the ones found by Manhart et al. [20] (2000).

In spite of the lower hardness number, ORMOCER based materials have other advantages, as higher wear resistance, when compared with other composites [17, 20, 21]. This is a very favorable characteristic for a restorative material. Other characteristics, such as flexural strength and fracture toughness, have intermediate values considering other composites[1, 19, 20]. However, Chen et al.[7] (2001) observed that ORMOCER based composite shows high contraction stress because of its more rigid matrix with high molecular weight monomers. These features may allow less contraction stress compensation by flow in high amount of residual rigid contraction stress, resulting in poorly adapted restorations.

The hardness test has also been employed for indirect evaluation of the degree of conversion, since an increased conversion rate of carbon double bonds is associated with higher hardness values (KHN)[3, 13]. However, correlation between degree of

conversion and hardness exists only when the same composite is compared in multiple situations[13]. To compare different composites, the absolute hardness number could not be used to predict the degree of conversion.

The degree of conversion of monomer system can be directly correlated with the composition of monomers and oligomers used in the material, the quantity of inhibitor, and photo-initiator; besides it also depends on the light energy available to activate the polymerization reaction[3, 5, 25, 26]. Chung[8] (1990) found that it ranged from 43,5 to 78,5%, depending on the composition of the monomer system. An adequate degree of conversion is very important since the residual monomer or diluents in composite system may affect the mechanical properties, color stability, and biocompatibility. The degree of conversion may play an important role in the success of the restoration[8].

In this study, the Knoop hardness test was applied at different depths to indirectly evaluate the degree of conversion and depth of cure, there is a good correlation between these parameters[10, 11, 13]. There is a current debate concerning the exact cure depth to be considered for a given exposure time. In this study, it was considered the hardness means that does not statistically differ from the surface values.

The depth of cure is limited by and dependent on several variables such as material, exposure time, composite color, quality and intensity of light, and location of light source[25, 26]. In this study, the only variable is the material; all the other parameters were standardized not to have any influence on the results. The top region gives higher values when compared to the bottom region, being also in agreement with other studies[5, 12, 16]. The explanation for this is based on the dynamics of the polymerization process of the composite: the polymerization only occurs where the light reaches the catalyst and react with them. This means that the surface layers mostly exposed to light irradiation cure more efficiently than those deeper in body of the material because there is a loss of light energy by scratching as the light crosses the material body.

According to Figure 2 and Table 1, significant reductions can be seen at 2mm depth for A110 and Z250, and at 3mm depth for Definite and Admira composites. As mentioned before, this reduction is directly related to the light intensity, which reaches the composite at the different depths. Moreover, the photoactivation was done with the same light source (XL 2500) and the same intensity (600mW/cm$^2$), what means that the reduction on the conversion degree at different depths for each composite is related to the composition and the light penetration on the material body.

ORMOCER based materials showed higher depth of cure than the Bis-GMA/Bis-EMA based materials. According to Kanka.[16] (1985), the light scattering is related to the transmission coefficient of each composite. Transmission coefficient depends on the composite color, opacity, and refraction index of each component (the light scattering can be increased by the increase of the difference between the refraction index of the fillers and that of the matrix). The scattering is responsible for the light intensity decrease in deeper layers of the restoration, reducing the depth of cure[16]. This way, it could be suggested that the refraction index of ORMOCER monomer system is closer to the refraction index of the fillers than the Bis-GMA/Bis-EMA monomer system is. This closer refraction index is associated with the presence of inorganic component (Si) on the ORMOCER matrix.

The reduction in conversion degree could also been identified in microfilled composites, like A110, because the microfillers (silica) promote higher light scattering than other fillers[16, 26]. It could also be noticed that A110 samples showed no polymerization at 4mm depth). Considering the results of this study, the composite increments should not be lengthier than 3mm for Definite and Admira, and 2mm for A110 and Z250 to adequately ensure cured restorations in all depths.

This way, depending on the intended use, resin composites of different mechanical properties may be desirable. Resin composites may be designed to fulfill the specific indications for use: the higher chewing stress regions require the higher hardness composites with higher wear strength. In addition, considering primary teeth lower hardness composites may be suitable because of the physiological wear of those teeth. Therefore, it was observed that ORMOCER based composites may be an acceptable option for restorative procedure at anterior and posterior teeth.

## Conclusion

1) For each composite resin, hardness decreased with increasing depth.
2) Z250 composite showed the highest KHN.

3) Definite, Admira, and A110 composites had no statistical differences in hardness values up to the depth of 2mm.
4) The composites Definite and Admira had no statistical differences considering hardness and depth of polymerization, but KHN was lower than Z250´s.
5) Composites resins have different surface hardness depending on composition.

## Resumo

O objetivo do estudo foi avaliar a dureza Knoop e a profundidade de polimerização de compósitos contendo ORMOCER e compará-los àqueles tradicionais a base de Bis-GMA ou derivados. Foram selecionados dois compósitos contendo ORMOCER (Admira e Definite), um híbrido (Z250) e um microparticulado (A110). Corpos-de-prova cilíndricos (3mm de diâmetro X 5mm de altura) foram confeccionados em uma matriz bipartida e polimerizados de acordo com as instruções do fabricante em aparelho XL2500 (3M/ESPE). As amostras foram armazenadas por 24h a 37∞C. As medidas de microdureza Knoop foram obtidas com aparelho Micro Hardness Tester HMV (Shimadzu- Japão) utilizando carga de 50g durante 15s. Foram confeccionados 5 corpos-de-prova, nos quais 3 penetrações foram efetuadas nas regiões de superfície, 1mm, 2mm, 3mm e 4mm abaixo da mesma. Os resultados foram submetidos à análise de variância e Teste de Tukey (5%). Pôde-se observar que, para todas as profundidades o compósito Z250 apresentou dureza superior em relação aos demais. A dureza dos compósitos Definite, Admira e A110 não diferiu estatisticamente até a profundidade de 2mm, após a qual A110 mostrou redução nos valores de dureza. De uma maneira geral, todos os materiais mostraram diminuição da dureza com o aumento da profundidade. Comparando com valores de dureza superficial, reduções significativas ocorreram nas profundidades de 2mm para Z250 e A110 e 3mm para Definite e Admira. Conclui-se que os compósitos a base de ORMOCER apresentaram valores de dureza intermediários e profundidade de polimerização satisfatória quando comparados aos valores obtidos pelos compósitos convencionais.

## Unitermos

Resinas compostas, dureza; restauração dentária permanente

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