ORIGINAL ARTICLE

SURFACE MICROHARDNESS OF MICROHYBRID AND NANOCOMPOSITE AFTER STORAGE IN MOUTH WASHES

Sadia Manzoor[1], Zartashia Arooj[2], Mohammad Abi Waqas[3], Nadia Irshad[2], Asfia Saeed[2], Aeeza Malik[2], Zenab Sarfaraz[2], Malik Saleem Shaukat[2]

Margala Institute of Health Sciences Rawalpindi, [2]University of Health Sciences, Lahore, [3]Multan Medical & Dental College, Multan-Pakistan

Background: Dental composites are aesthetic direct restorative material. However, the effect of mouthwashes on the durability of the material is controversial. This study evaluated and compared the influence of mouthwash composition on the surface hardness of nanofilled (Z350XT) and microhybrid (P60) resin composites. **Methods:** Comparative in-vitro study was conducted over 6 months at Multan Medical & Dental College. Sixty-four disc-shape specimens of each {nanofilled (Z350XT) and microhybrid (P60)} resin composite were prepared and stored in distilled water at 37°C for 24 hours. The baseline microhardness reading (T_o) was recorded by Vickers micro-hardness tester. Samples were then randomly divided into four groups (n=16) and stored in Listerine Cool Mint, Colgate Plax, Clinica and distilled water (control). The hardness test was repeated after 12 hours and 24 hours of storage. **Results:** Nanocomposite (Z350XT) had statistically ($p<0.01$) higher surface hardness. A significant reduction ($p\leq0.05$) in microhardness was observed after immersion of samples in mouthwashes. The reduction in surface hardness was dependent on the immersion time and composition of mouthwashes. Listerine Cool Mint (alcohol-based mouthwash) had greatest degradation effect. **Conclusion:** Mouth rinses negatively impacted the surface microhardness of the tested resin-based materials. Alcohol-based mouthwashes had greater potential for reducing microhardness. Microhybrid composite appears to be a more suitable material for restoring teeth in patients accustomed to using regular mouthwashes.

Keywords: Resin composites; Mouthwashes; Microhardness; Microhybrid composite; Hardness test

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INTRODUCTION

Dental composites are increasingly used as direct restorative materials due to their desirable aesthetic and mechanical properties.[1] They are primarily composed of organic polymer matrix, inorganic fillers and coupling agents.[2] Evidenced based studies have shown that saliva, food and chemicals found in dental plaque, beverages and oral hygiene products can cause hydrolytic degradation of resin matrix, which may affect physico-mechanical properties of the material. Thus, resulting in decreased surface hardness and increased surface wear of material.[2,3]

Hardness is often related to the long-term stability of the composite material.[1] The morphology, size and volume of the fillers have a direct impact on the hardness and clinical performance of the material.[4] Recently, nanocomposites have been introduced in an endeavour to provide superior mechanical and optical properties compared to hybrid composite materials.[1] It has been proposed that the smaller filler particles have less inter-particle space, which provides better protection against hydrolysis of matrix and therefore, reduces 'plucking out' of fillers.[1] However, controversial data is available regarding properties of nanofilled rein composites. Poggio *et al*. reported that nanocomposites had a higher surface microhardness than hybrid composites after conditioning with acidic beverages.[5] On contrary, Jassa *et al*. reported significantly higher Vickers Hardness values for the microhybrid resin compared to nanofilled composites.[6]

Mouthwashes are often used to prevent caries, periodontal diseases and to reduce halitosis.[7] They are readily available as over-the-counter products, consisting of water, antimicrobial agents, preservative and alcohol.[8] Varying the concentration of these constituents can affect the pH of the mouthwash, which in turn affects the degradation rate and surface properties of dental composites.[9,10] Studies have confirmed that alcohol in mouth rinses has a detrimental effect on the surface properties of dental composites. However, little information is available on the effect of alcohol-free mouthwashes on the surface properties of composites. It has been hypothesized that alcohol-free mouthwashes would have little effect on the surface properties of resin-based materials. Additionally, a smaller filler size and higher filler loading of nanocomposites would make the material resistant to softening. Therefore, the study was designed to assess and compare the impact of alcohol-containing and alcohol-free mouth rinses on the microhardness of two resin-based composites; with a different filler particle system, that are microhybrid (Filtek™ P60, 3M ESPE, St. Paul, MN, U.S.A.) and nanocomposite (Filtek™ Z350XT, 3M ESPE, St. Paul, MN, U.S.A.). In addition, the influence of the immersion time on the surface hardness was evaluated.

MATERIAL AND METHODS

A comparative in-vitro study was conducted over 6 months at the Department of Science of Dental Materials, Multan Medical & Dental College, Pakistan. Authorization to conduct research was obtained from the institution's Board of Advance Studies and Research. Two commercial resin-based composites with a different filler particle system, which are microhybrid (P60) and nanocomposite (Z350XT) were used (Table-1). A total of 128 samples (n=64 for each material) of dimension 6×2 mm were prepared by inserting the composite material as a single increment into prefabricated brass split mold placed on a transparent matrix strip and glass slide. The material in the mold was covered with a celluloid strip and pressed flat with another glass slide. The material was light cured using LED light source (LED.B Model: ICR18650 Woodpecker, Guilin, China) from each top and bottom surface with an irradiance of 1000 mW/cm^2 for 20 sec on each side. The prepared samples were polished using 1200 grit silicon carbide sheet and automatic polishing machine (Metkon GRIPO 2V Grinder her, Turkey). Then, the samples were washed and conditioned in distilled water at 37 °C for 24 hours.[10] Baseline micro-hardness measurements (T_o) were recorded using a Vickers micro-hardness tester (Wolpert, 401MVD, EQPT 0002, Germany) using a 200g load with 10 sec dwell time. Each sample was indented at three different points, and average readings were calculated. Samples of each material were then divided into four groups (n=16) based on immersion solution (Figure-1). The samples were stored at 37 °C in an incubator, in individual plastic containers containing 20 ml of the storage solution. Samples from each group were subdivided into two subgroups based on storage time (Figure-1). Samples were rinsed with distilled water for 120 sec and blotted dried prior to testing. The samples from group A (n=8) were subjected to a hardness test after 12 hours of incubation (T_1). This simulated daily mouthwash uses for 2 min over a period of one year whereas samples in group B were subjected to a hardness test after 24 hours (T_2) of immersion, simulating 4min daily use of mouthwash for a period of 1 year.[10] Data was analysed through SPSS version 22 and microhardness values were expressed as mean and SD**.** Independent t-test was applied to compare the microhardness of materials and for the evaluating the effect of immersion time. Analysis of variance (ANOVA) with post hoc Tukey's was applied for inter-group comparison of the surface microhardness of each material based on immersion solution and p-value $\leq$0.05 was considered as significant.

RESULTS

The mean baseline Vickers hardness values for microhybrid (P60) and nanocomposites (Z350XT) before immersion were 88.73±3.86 and 80.16±3.34 respectively. The microhybrid (P60) had a statistically ($p\leq$0.001) higher surface hardness than the nanocomposite (Z350XT). A significant reduction in the micro-hardness values for each sample of tested materials was observed after immersion (Table-2). The null hypothesis was therefore rejected. Independent t-test showed a statistically significant difference in microhardness values between the subgroups except for samples immersed in distilled water (Table-3). Pairwise comparison showed that samples immersed in Listerine Cool Mint exhibited the greatest reduction in surface hardness among all groups.

The analysis of variance showed a significant interaction ($p\leq$0.001) between the variables "composite resins", "immersion times" and "solutions". Inter-group comparison of group A revealed that each sample had significantly lower microhardness values after storage in mouthwashes compared to samples stored in distilled water (control), with exception of samples stored in Colgate Plax (alcohol free- fluoride containing). However, upon continuous immersion in Colgate Plax for 24 hours (group-B), a significant reduction in surface hardness was noted for nanocomposites (Table-4).

Figure 1: Sample distribution of fabricated composite specimens

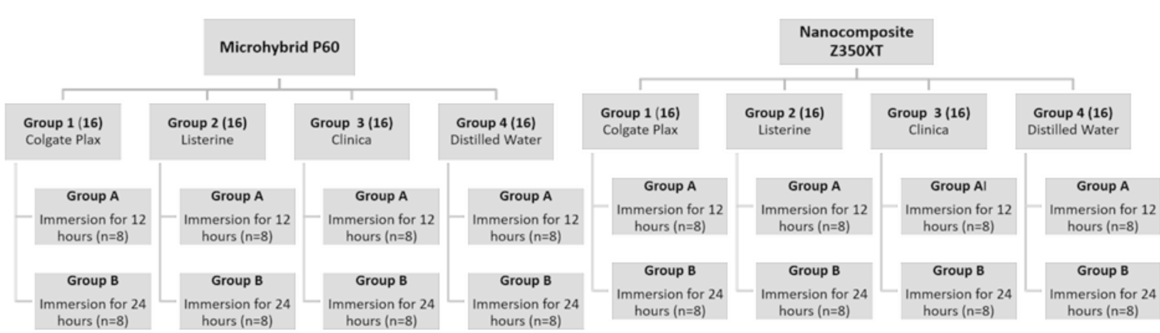

Table-1: Composite Resins and Mouth Rinses tested in the study

Composite Type/Name	Manufacturer	Fillers and Filler Volume	Monomers*
Nano-composite Filtek ™ Z350 XT	3M ESPE, St. Paul, MN, USA	Combination of 0.004-0.02um non-agglomerated zirconia/silica particles and agglomerated 0.60–1.40 um clusters. **Filler volume: 57%**	Bis-GMA, UDMA TEGDMA, PEGDMA, Bis-EMA
Micro-hybrid Filtek™ P60		Combination of 0.19-3.3 um of zirconia/silica particles **Filler volume: 61%**	BisGMA, UDMA, BisEMA
Mouth Rinses	**Manufacturer**	**Composition**	**pH**
Listerine® Cool Mint Alcohol based mouthwash	Johnson and Johnson	Eucalyptol 0.092%, Menthol 0.042%, Methyl salicylate0.060%, Thymol 0.064% Water, Alcohol (21.6%), Sorbitol, Benzoic Acid, Sodium Saccharin, Sodium Benzoate, Flavour	4.9
Colgate Plax Alcohol Free Fluoride containing mouthwash	Colgate-Palmolive Company	Water, Glycerin, Propylene glycol, Sorbitol, Poloxamer, Cetylpyridinium Chloride 0.05%, Potassium sorbate, Sodium fluoride (2ppm), Sodium saccharin, Menthol	6.8
Clinica Chlorhexidine based mouthwash	Platinum Pharmaceutical	Chlorhexidine Gluconate	5.5

BisGMA : Bisphenol A-glycidyl methacrylate, UDMA: Urethane Dimethacrylate, TEGDMA: Triethylene glycol dimethacrylate, Bis-EMA Bisphenol A ethoxylate dimethacrylate, PEGDMA: poly (ethylene glycol) dimethacrylate

Table-2: Comparison of microhardness of composite materials at different time intervals

Composites	Before Immersion	Mouthwashes							
		Colgate Plax		Listerine Cool Mint		Clinica		Distilled Water	
	T_0 (Control)	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2
Microhybrid (P60)	88.73±3.86	81.50±3.23	78.30±3.02	68.20±0.88	59.79±1.14	75.76±3.04	69.98±1.43	85.83±3.02	83.92±3.12
Mean Reduction	-	7.23	10.43	20.53	28.94	12.97	18.75	2.9	4.81
Nanocomposites (Z350XT)	80.16±3.34	72.31±3.24	68.22±3.02	56.79±0.78	45.71±1.86	66.26±2.79	58.73±2.02	78.03±3.13	75.13±2.60
Mean Reduction	-	7.85	11.94	23.37	34.45	13.9	21.43	2.13	5.03
Ind.Sample t-test	6.7157	5.682	6.675	27.444	18.255	6.512	12.857	5.073	6.122
p-value	≤0.001	≤0.001	≤0.001	≤0.001	≤0.001	≤0.001	≤0.001	≤0.001	≤0.001

Table-3: Inter group comparison of microhardness of Microhybrid (P60) and Nanocomposites (Z350XT) at different time intervals

Groups	Materials	Group A (T_1)	Group B (T_2)	Mean Reduction	Ind.Sample t-test	p-value
Colgate Plax	Microhybrid (P60)	81.50±3.23	78.30±3.02	3.20	2.686	0.012
	Nanocomposites (Z350XT)	72.31±3.24	68.22±3.02	4.09	2.612	0.021
Listerine Cool Mint	Microhybrid (P60)	68.20±0.88	59.79±1.14	8.41	16.517	≤0.001
	Nanocomposites (Z350XT)	56.79±0.78	45.71±1.86	11.08	15.538	≤0.001
Clinica	Microhybrid (P60)	75.76±3.04	69.98±1.43	5.78	4.866	≤0.001
	Nanocomposites (Z350XT)	66.26±2.79	58.73±2.02	7.53	6.183	≤0.001
Distilled Water	Microhybrid (P60)	85.83±3.02	83.92±3.12	1.91	1.244	0.23
	Nanocomposites (Z350XT)	78.03±3.13	75.13±2.60	2.90	2.016	0.06

Table 4: Comparison of Vickers microhardness for Microhybrid (P60) and nanocomposites (Z350XT) after storing in different solutions at 12hours and 24hours

Material	Time	Immersion media	Comparing media	Sig.	Time	Immersion media	Comparing media	Sig.
Microhybrid	12hrs	Colgate Plax	Listerine Cool Mint	.001	24hrs	Colgate Plax	Listerine	.000
							Clinica	.011
		Listerine Cool Mint	Colgate Plax	001		Listerine Cool Mint	Colgate Plax	.000
			Clinica	.038			Clinica	.003
			Distilled water	.000			Distilled water	.000
		Clinica	Listerine	.038		Clinica	Colgate Plax	.011
			Distilled water	.008			Listerine	.003
							Distilled water	.000
		Distilled water	Listerine Cool Mint	.000		Distilled water	Listerine	.000
			Clinica	.008			Clinica	.000
Nanocomposites	12hrs	Colgate Plax	Listerine Cool Mint	.001	24hrs	Colgate Plax	Listerine	.000
							Clinica	.006
							Distilled water	.033
		Listerine Cool Mint	Colgate Plax	.001		Listerine Cool Mint	Colgate Plax	.000
			Clinica	.013			Clinica	.001
			distilled water	.000			distilled water	.000
		Clinica	Listerine Cool Mint	.013		Clinica	Colgate Plax	.006
			distilled water	.003			Listerine	.001
							distilled water	.000
		distilled water	Listerine Cool Mint	.000		distilled water	Colgate Plax	.033
			Clinica	.003			Listerine Cool Mint	.000
							Clinica	.000

DISCUSSION

Hardness determines the resistance of material to indentation and abrasion and therefore, is often related to strength and rigidity of material.[9] Frequent use of mouthwashes results in chemical softening of the resin-based restorative materials, which ultimately affects its performance and long-term stability.[11] This *in-vitro* study was designed to assess and compare the effect of different mouthwashes on the surface microhardness of microhybrid and nanocomposite. Microhybrid composite (P60) showed higher baseline hardness value than nanocomposite (Filtek Supreme Z350XT). This was reflected by the comparison of the filler particle size and filler loading of tested dental composites.

A greater reduction in microhardness was noted for the nanocomposite after immersion in treatment solutions, indicating greater susceptibility to the material to chemical degradation. These results may be related to the amount and types of monomers used in nanocomposites, since water sorption decreases in the following order: TEGDMA >Bis-GMA >UDMA.[12] Additionally, the presence of lower filler content of nanocomposites might further explain the difference. In present study, a direct correlation between contact time and surface softening of composite material was observed. This result is in agreement with the findings of Casanova Obando *et al*. who evaluated surface roughness and weight reduction of nanohybrid material after immersion in mouth rinses. They observed that the contact time has a significant impact on the degradation of composites.[13]

Rajasekhar *et al.* found that alcohol-free mouth rinses did not affect the microhardness of micro-hybrid composites.[14] However, in the present study, the surface hardness of resin-based materials was reduced after storage in mouthwashes. These results contradict the popular opinion that alcohol-free mouthwashes are safe for dental composites. The results of present study suggests also suggest that alcohol is not only responsible for the degradation of polymer matrix, but other constituents such as solvents, fluoride and acids present in mouthwashes can cause erosion of restorative materials.[15] Novak et al. also showed that the surface of composite materials was affected by both types of mouth rinses (ethanol-based and ethanol-free).[16] Similarly, Goyal *et al* observed a significant reduction in microhardness of microhybrid and nanocomposites after storage in Colgate Plax.[17]

The intergroup comparison showed that samples immersed in Colgate Plax (alcohol-free mouthwash contacting fluoride) had highest microhardness values, followed by Clinica (chlorhexidine) and Listerine Cool Mint, while distilled water had minimal effect on Vickers hardness. This can be attributed to the acidic nature and alcohol content of Listerine, which causes increased biodegradation of composite material. The results were consistent with previous studies showing that mouthwashes containing alcohol have the greatest effect on the mechanical properties of composite materials.[8] Ethanol causes catalytic degradation of the ester group of Bis-GMA and UDMA-based polymers, resulting in leaching out of components.[15] Koshhar *et al*. compared microhardness of hybrid composite material after conditioning with five commercial mouthwashes. He reported lowest reduction in the microhardness values for samples stored in Proflo (fluoride-based mouthwash). This was followed by Rexidin (chlorhexidine-based) and Listerine.[8] Das and Sowmya also reported greater Vickers' hardness for nanocomposites samples immersed in fluoride-containing mouth rinses compared to samples immersed in fluoride-free mouthwashes.[15] In another study, Moraes *et al*., showed a significant reduction in the microhardness of nanocomposite (Z350 XT) after 12 hours of immersion in a chlorhexidine mouthwash. [18]

It would be pertinent to emphasise that this study was strictly limited to the surface hardness of the composites material and other parameters describing long-term durability of the material were not evaluated. However, the negative impact of alcohol-free mouthwashes on the surface properties of microhybrid and nanocomposites was established in this study. In the future, studies evaluating wear in terms of weight changes and recording of microscopic images of the composite surface should be conducted to support the degradation claim. In addition, in-vivo studies evaluating influence of saliva, temperature and pH variation due to the dietary habit's patients should be carried out.

CONCLUSION

Mouth rinses negatively impacted the surface microhardness of the tested resin-based materials. The effect depended on the type of mouthwashes, exposure time and the composition of the composite resin. Alcohol-based mouthwash had a higher potential for reducing the surface microhardness. Micro hybrid appears to be a more suitable material for tooth restoration in patients who are accustomed to regular mouthwashes

AUTHORS' CONTRIBUTION

MAW: Has agreed to help in data collection, recording analysis and interpretation of data. SM: Has contribution in conceiving and designing the study, and has written or critically reviewed the manuscript. ZA: Has agreed to be responsible for accuracy of results and integrity of the research. Has approved the final version. NI: Has agreed to help in data entry, data analysis, literature search, write-up, gave final approval. AS: Has agreed to help in data collection, Contribution in study design. AM, ZS: Has agreed to help in data entry, data analysis, literature search, write-up, gave final approval. MSS: Has agreed to help in data entry, data analysis, literature search, write-up, gave final approval.

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Address for Correspondence:
Mohammad Abi Waqas, Multan Medical & Dental College, Multan-Pakistan
Email: abi_vaqas@hotmail.com