Influences of Polymeric Magnetic Encapsulated Nanoparticles on the Adhesive Layer for Composite Materials Used for Class I Dental Fillings

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The main properties of dental adhesives should be good marginal adaptation, high retention strength and the possibility of not negatively influencing clinical sustainability. Dental adhesives are continuously improving to increase their retention to dental structures by increasing penetration in these structures, as it was shownin the in-vitro tests requiring imaging and qualitative analysis to allow the evaluation of experimental samples as well as the development of new materials. The main objective of this study is the qualitative and quantitative analysis of the layer of modified dental adhesives with ferrous nanoparticles encapsulated in a SiO_2 *membrane located between the surface of the dental preparation and the surface of the photopolymerizable composite filling. For qualitative and quantitative analysis of the samples, technologies such as SEM, optical microscopy and EDX were used.*

Keywords: dental adhesives, nanoparticles, SEM, EDX, optical microscopy

The development of adhesive techniques in dental medicine has increased the requirements of aesthetic dentistry as well as increasing the number of minimally invasive restorations made on dental surfaces [1].

Contemporary dentistry has been revolutionized by the appearance of dental adhesives, through it, other research directions have emerged for their improvement: the development of methacrylate-based composites, the development of hydrophilic resins and the modification of acid-engraved dental surfaces. Surfaces of dental adhesives are susceptible to biodegradation. This biodegradation includes the interaction of bacterial enzymes, endogenous enzymes and dental biofilm. Acidity and hydrophilicity of resins increase the degree of degradation of the adhesive at its interface, and modified forms of dentin and enamel can affect the adhesion of the adhesive to enamel or dentin [2].

Composite resins have surpassed amalgam and have become the most used materials for dental restorations made by direct technique. Adhesive composite restorations are threatened by secondary caries, the degradation of the adhesive layer present at the interface between the tooth and by the various defective restorationmaterials, which will then be infested by fluids, bacteria and secondary bacterial products, leading ultimately to the failure of the composite filling. Therefore the durability over time of the connections between dentin and adhesives become an issue [3].

Thus, considering the fact that the main reason for the loss of a composite restoration by bacterial colonization and the appearance of secondary caries was generated by the microfissures at the edge of the restoration, the researchers developed the first dental dhesive material that has self-healing properties with antibacterial and remineralizing action. It has increased dental adhesion qualities, but its most important property is the self-healing of fractures at the adhesive interface layer [4].

Dental adhesives have been modified over time to alleviate the deficiencies they have acquired since the first generations, with methacrylamides being added to their component, the main purpose of which is to increase the resistance to hydrolytic and enzymatic degradations occurring at the interface of the adhesive [5].

In the formula of theadhesives components, lysine has been incorporated, which has resulted in good *p*H modulation outcomes, the effect of this modification can improve the durability of composite dental restorations [6].

Previous studies show that the thickness of the adhesive layer at the interface between the tooth and the restoration material is between 0.02 mm and 0.3 mm [7-9].

The presence of resin tags and the thickness of the hybrid layer do not greatly influence adhesion.[10, 11]The strength of adhesion may vary depending on the action time of the acid on the dental surface. At the same time, the surface of the hybrid layer changes, and the long time action of the acid on the surface of the tooth can influence the adhesion in a negative way [12].

Stress at the dentine-adhesive interface may be influenced by the type of adhesive used, with increased stress levels for self-etch adhesives compared to etch-and-rinses and self-etch-primer, both adhesive systems presenting partial demineralized dentin [13].

Dental adhesives have been evaluated over the years using imaging technologies such as optical coherence tomography (OCT), scanning electron microscopy, Raman microspectroscopy and electron paramagnetic resonance spectroscopy [14-20].

Experimental part

In this study, 15 teeth were used, that had Class I Black cavities. The materials used in this study were: phosphoric acid for tooth demineralisation, Evetric Bond (Ivoclar) dental adhesive, Brilliant Flow (Coltene) photo-polymerizable composite flow and multicore-shell Fe_3O_4-SiO_2 magnetic nanoparticles (fig.1).

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Fig.1 Materials used in this study and magnetic nanoparticles samples

After preparing the cavities on the surface of the teeth, they were restored using the adhesive technique. Demineralisation of dental surfaces was done with phosphoric acid for 15 s for dentin and 30 s for the enamel.

The acid was washed with water for 20 s and the surface wasdried with air. After demineralization, the dental adhesive doped with nanoparticles was applied by brushing onto the prepared surface of the cavity (fig.2).

Fig.2. Nanoparticles mixing procedure with dental adhesive

For 5 teeth the adhesive was applied by brush, and for the other 10teeth after brushing the adhesive, a magnetic field was applied to the entire teeth circumference as follows: for 5 teeth the magnetic field was applied for 2 min, and for the other 5 the magnetic field was applied for 5 min (fig.3).

Fig.3. Adhesive application on dental surface in magnetic field for 2 and 5 min

After applying the adhesive, it was photopolimerized with the blue light lamp for 40 s, resulting in anaesthetic filling with slightly colored edges due to the nanomagnetic particles (fig.4).

Fig.4. Aspect of filling after photopolymerization of composite material

Using a Vibrating Sample Magnetometer ADE Technologies VSM 880 we measured at room temperature the magnetization properties in the field range 0 - 1000 kA/m.The magnetic particles have superparamagnetic behaviour with 71 emu/g saturation magnetization, 6.4emu/g remnant magnetization and 4.4 kA/m coercive field.

Further, all 15 samples were sectioned and analysed with the help of FEI Inspect S scanning electron microscope (SEM), optical microscope andEnergy Dispersive X-ray analysis(EDX). The scanning electrone microscope has the following characteristics: tungsten filament mounted in the tetrode cannery assembly with a resolution of 3.0 nm on standard specimen with gold particles separated on a carbon substrate. Focus domain is between 3 and 99 mm with a magnification from 6x to >1.000.000x.

SEM analyzes generated images at 200x magnification in which the dental adhesive layer was observed between the two interfaces of the composite resin and the surface of the tooth structure.

Samples showing the adhesive loaded with magnetic nanoparticles that was applied to the tooth surface by conventional technique were analyzed using SEM, resulting in images at a 200x magnification. EDX quantitative analysis is showing internal components (fig.5).

The interfaces in which the dental adhesive loaded with magnetic nanoparticles was applied in the magnetic field for 2 and 5 min were also analyzed, generating high resolution images at the same magnification. The internal components diagram was also created (figs. 6, 7).

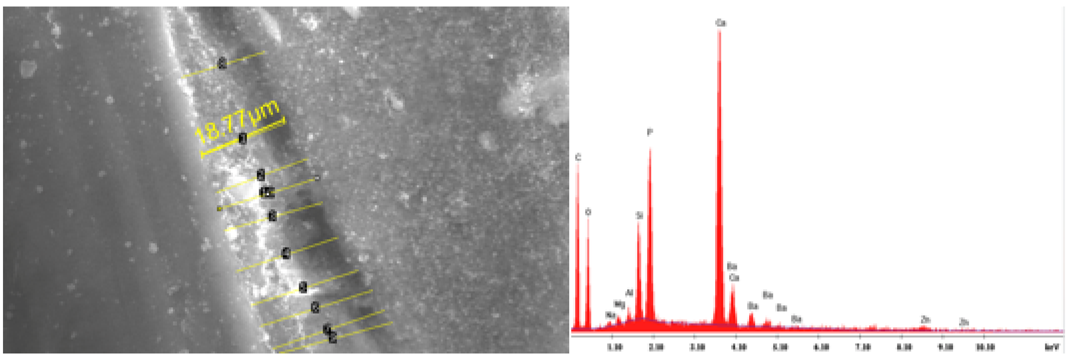

Fig.5. SEM and EDX analisys for the probes with adhesive reinforced with nanoparticles applied on teeth without magnetic field

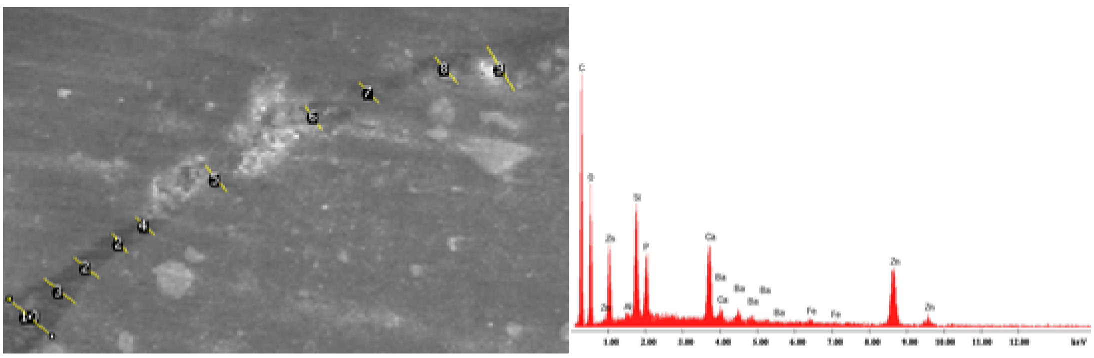

Fig.6. SEM and EDX analisys for the probes with adhesive reinforced with nanoparticles applied on teeth with magnetic field for 2 min

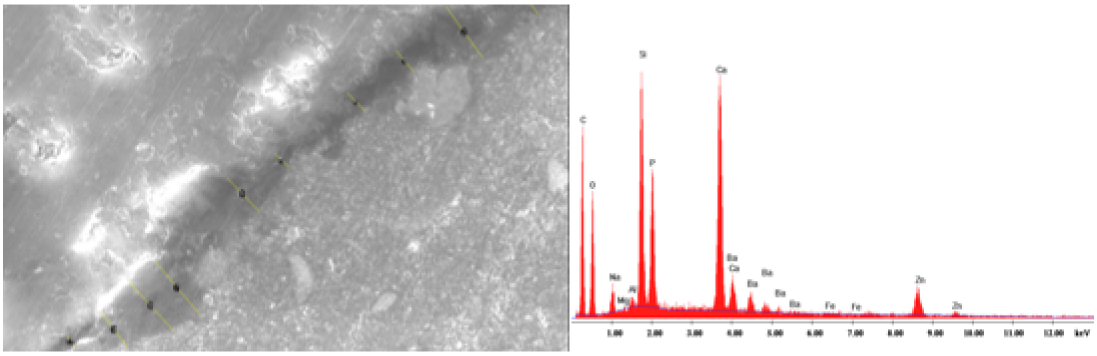

Fig.7. SEM and EDX analisys for the probes with adhesive reinforced with nanoparticles applied on teeth with magnetic field for 5 min

All the samples were analyzed with A377 optical microscope. The microscope has a magnification range between 20X and 800X and an CMOS aquisition sensor of 2MPX. The focus is between 0 mm and 40 mm and the connection with the computer is made with USB 2.0 port. Luminosity on sample probes is adjusted manually with 10 LED lights (figs. 8-10).

Fig.8. Optical microscope analisys for the probes with adhesive reinforced with nanoparticles applied on teeth without magnetic field

Fig.9. Optical microscopy measurements for the samples that presented dental adhesive with magnetic nanoparticles applied in magnetic field for 2 min

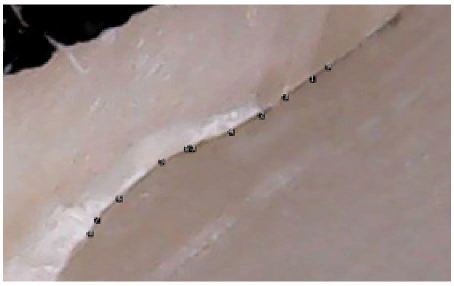

Fig.10. Optical microscopy measurements for the samples that presented dental adhesive with magnetic nanoparticles applied in magnetic field for 5 min

Results and discussions

After recording images using SEM and optical microscopy, they were imported and analyzed using ImageJ software (Wayne Rasband, National Institutes of Health, USA). As a result of the measurements made on the samples where the dental adhesive was loaded with nanoparticles and applied to the surface of the teeth without magnetic field, have resulted thicknesses of the adhesive layer ranging from 10 to 25 microns (table 1).

For adhesives loaded with magnetic nanoparticles and applied in magnetic field for 2 min, the measurements generated adhesive layer sizes between 14 - 36 microns (table 2).

For adhesives loaded with magnetic nanoparticles and applied in the magnetic field for 5 min, the measurements generated adhesive layer sizes between 2-12 microns.

Based on the analysis performed with optical microscopy, the thickness of adhesive layer for samples loaded with magnetic nanoparticles and applied to non-magnetic dental surfaces were between 16-29 microns (table 4).

Table 1

SEM ANALISYS FOR DENTAL ADHESIVE LAYER THICKNESS OF THE SAMPLES REINFORCED WITH NANOPARTICLES APPLIED WITHOUT MAGNETIC FIELD

Nr.Crt.	Area	Mean	Min	Max	Angle	Length (microns)
1	3.463	162.128	77.494	255.000	21.077	**18.774**
2	3.763	179.148	95.330	253.286	19.895	**20.377**
3	3.929	167.167	74.141	255.000	15.811	**21.431**
4	4.129	145.630	73.935	249.820	18.435	**22.505**
5	4.329	172.034	95.448	255.000	18.015	**23.602**
6	4.529	142.062	86.200	224.110	17.632	**24.701**
7	4.562	135.541	79.549	231.866	18.834	**24.872**
8	3.330	152.661	97.337	229.965	16.975	**18.126**
9	4.729	130.432	0.000	193.536	15.219	**25.720**
10	3.963	177.888	111.652	255.000	17.210	**21.587**

Nr. Crt	Area	Mean	Min	Max	Angle	Length (microns)
1	23.443	92.648	83.187	113.333	-53.130	**14.598**
2	29.836	98.373	86.590	112.333	-41.987	**19.318**
3	38.361	93.172	83.308	118.333	-39.806	**24.175**
4	23.443	95.261	83.556	119.000	-48.814	**14.468**
5	31.967	116.135	100.551	139.000	-51.340	**20.064**
6	27.705	126.778	101.444	154.111	-59.036	**17.545**
7	27.705	101.435	88.914	113.444	-45.000	**17.893**
8	31.967	118.346	98.787	153.789	-50.711	**20.828**
9	49.016	129.149	101.000	156.560	-61.189	**32.234**
10	55.410	99.278	83.400	124.000	-41.820	**36.532**

Table 2
SEM ANALISYS FOR DENTAL ADHESIVE LAYER THICKNESS OF THE SAMPLES REINFORCED WITH NANOPARTICLES APPLIED WITH MAGNETIC FIELD FOR 2 min

Nr. Crt.	Area	Mean	Min	Max	Angle	Length (microns)
1	0.619	122.850	112	139	-51.340	**6.247**
2	1.095	119.220	100.447	142.939	-53.936	**11.104**
3	0.466	115.242	100.667	146.000	-49.268	**4.635**
4	0.428	116.631	106.748	152.000	-45.000	**4.277**
5	0.343	118.397	109.016	141.000	-43.831	**3.381**
6	0.771	119.431	101.214	138.598	-45.507	**7.796**
7	1.190	142.553	122.947	186.000	-49.248	**12.106**
8	1.161	154.936	123.563	245.098	-47.344	**11.806**
9	0.752	170.840	141.629	238.320	-52.836	**7.590**
10	0.276	151.699	126.921	203.439	-52.306	**2.712**

Table 3
SEM ANALISYS FOR DENTAL ADHESIVE LAYER THICKNESS OF THE SAMPLES REINFORCED WITH NANOPARTICLES APPLIED WITH MAGNETIC FIELD FOR 5 min

Nr. Crt.	Area	Mean	Min	Max	Angle	Length (mm)
1	2.190E-4	134.630	99.000	186.333	90.000	0.025
2	1.643E-4	139.864	124.333	162.556	26.565	0.016
3	1.643E-4	142.389	114.667	172.222	45.000	0.017
4	2.190E-4	170.414	145.222	195.333	45.000	0.021
5	2.190E-4	163.145	149.444	190.556	45.000	0.023
6	2.190E-4	162.987	141.704	191.370	90.000	0.025
7	2.190E-4	165.417	145.481	197.667	108.435	0.023
8	2.738E-4	145.456	125.852	179.667	63.435	0.029
9	2.190E-4	174.583	125.667	209.000	90.000	0.022
10	2.190E-4	140.630	126.889	164.741	56.310	0.025

Table 4
OPTICAL MICROSCOPY ANALYSIS FOR DENTAL SAMPLES WITH ADHESIVE REINFORCED WITH NANOPARTICLES APPLIED ON TEETH SURFACE WITHOUT MAGNETIC FIELD

Nr. Crt.	Area	Mean	Min	Max	Angle	Length (mm)
1	2.377E-4	95.037	69.000	121.000	45.000	0.022
2	1.783E-4	127.444	102.296	149.370	26.565	0.015
3	1.783E-4	165.333	152.333	177.000	90.000	0.015
4	1.783E-4	131.688	111.556	151.259	45.000	0.018
5	1.783E-4	131.130	129.444	133.778	45.000	0.013
6	2.377E-4	119.463	114.815	125.889	0.000	0.021
7	1.783E-4	133.907	127.667	139.333	0.000	0.014
8	2.971E-4	101.619	93.880	110.667	56.310	0.029
9	2.971E-4	90.217	68.056	133.778	63.435	0.033
10	2.377E-4	114.065	104.037	133.444	18.435	0.023

Table 5
OPTICAL MICROSCOPY ANALYSIS FOR DENTAL SAMPLES WITH ADHESIVE REINFORCED WITH NANOPARTICLES APPLIED ON TEETH SURFACE WITH MAGNETIC FIELD FOR 2 min

Nr. Crt.	Area	Mean	Min	Max	Angle	Length (mm)
1	1.095E-4	103.861	99.278	108.444	-45	0.010
2	1.095E-4	89.389	78.333	100.444	-90	0.007
3	1.095E-4	115.528	113.667	117.389	0	0.007
4	1.095E-4	114.833	107.333	122.333	-45	0.008
5	5.476E-5	142.111	142.111	142.111	0	0.003
6	1.095E-4	154.315	151.963	156.667	-45	0.008
7	1.095E-4	143.444	140.778	146.111	0	0.005
8	1.095E-4	153.690	143.824	163.556	0	0.006
9	1.095E-4	119.583	118.944	120.222	0	0.004
10	1.095E-4	119.954	108.519	131.389	-90	0.008

Table 6
OPTICAL MICROSCOPY ANALYSIS FOR DENTAL SAMPLES WITH ADHESIVE REINFORCED WITH NANOPARTICLES APPLIED ON TEETH SURFACE WITH MAGNETIC FIELD FOR 5 min

For samples using a magnetic field for 2 min, the analyzes generated thicknesses of adhesive layer between 13-33 microns (table 5).

For samples using a magnetic field for 5 min, the analyzes generated adhesive layer thicknesses between 3 - 10 microns (table 6).

EDX semi quantitative analysis for samples with adhesive reinforced with nanoparticles applied on teeth without magnetic field has highlighted the presence of C (49.74 %), O (23.43 %), Na (0.46 %), Mg (0.4 %), Al (0.39 %), Si (3.07 %), P (6.61 %), Ca (12.7 %), Ba (2.23 %) and Zn (0.97 %).

EDX semi quantitative analysis for probes where we used magnetic field for 2 min has highlighted the presence of C (59.46 %), O (23.21 %), Al (0.15 %), Si (3.42 %), P (2.01 %), Ca (2.57 %), Ba (1.24 %), Fe (0.36 %) and Zn (0.97 %).

EDX semi quantitative analysis for samples where we used magnetic field for 5 min has highlighted the presence of C (59.46 %), O (23.21 %), Al (0.15 %), Si (3.42 %), P (2.01 %), Ca (2.57 %), Ba (1.24 %), Fe (0.36 %) and Zn (7.58 %).

Measurements made using scanning electron microscopeand optical microscopy generated results that fall within the same intervals.

Conclusions

The use of magnetic nanoparticles after incorporation into dental adhesives, can reduce the thickness of the adhesive layer by 30% by applying a magnetic field on the tooth surface for 2 min and by 86.5 % for applying the same magnetic field for 5 min compared to the application of dental adhesives by conventional techniques.

Further studies are needed for adhesion strength evaluations.

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