STUDIU COMPARATIV IN VITRO AL REZISTENȚEI MECANICE LA FORȚA DE COMPRESIUNE ȘI TRACȚIUNE ÎNTRE ADEZIVII DE GENERAȚIA a IV-a ȘI ADEZIVII UNIVERSALI

COMPARATIVE IN VITRO STUDY OF MECHANICAL RESISTANCE TO COMPRESSIVE AND TENSILE FORCE BETWEEN 4th GENERATION ADHESIVES AND UNIVERSAL ADHESIVES

ȘTEFAN GEORGE CĂLINOIU[1], CORNELIA BÎCLEȘANU[1], ANAMARIA FLORESCU[1]*, CĂTĂLIN CONSTANTIN DUMITRU[1], MIHAI EFTIMIE[2], ANTON FICAI[2]

[1] Faculty of Dental Medicine, University „Titu Maiorescu", Bucharest, Romania

[2] Department of Science and Engineering of Oxide Materials and Nanomaterials, Faculty of Chemical Engineering and Biotechnology, National University of Science and Technology POLITEHNICA Bucharest, Gh. Polizu 1-7; Bucharest, Romania

[3.] Academy of Romanian Scientists, Ilfov st 2, Bucharest, Romania

The aim of this study is to compare the mechanical strength in compression, tension and FTIR microscopy of 2 types of dental adhesives: 4th generation, considered the "gold standard" and the latest generation adhesives called universal adhesives.

In the dental community, I have noticed that opinions regarding the two adhesives are divided. More comfortable and younger doctors prefer universal adhesive because it gives them easier and faster working times. And the experienced doctors who used the 4th generation adhesive claim that after using the universal adhesive they returned to the "gold standard".

We compared the two adhesives regarding the adhesion they achieve through compressive forces and tensile forces. The compression was carried out with the help of a press and on blocks of Gradia Direct Posterior filling material, which after the first test, the blocks were reformed with the help of the 2 adhesives and retested. After the traction that was performed on extracted teeth on which fillings were made similar to clinical situations, the detachment area was studied under the FTIR microscope.

In tests, All-Bond 3® Bisco adhesive had higher bond strength and compressive strength than CLEARFIL™ Universal Bond Quick Kuraray. Following the tensile tests, the values obtained showed a higher adhesion to the 4th generation adhesive. Also, the interface area where debonding occurred showed that the 4th generation adhesive is superior in terms of adhesion to dental tissues.

Scopul acestui studiu este de a compara rezistența mecanică la compresiune, tracțiune și microscopie FTIR a 2 tipuri de adezivi dentari: generația a 4-a, considerați „standardul de aur" și adezivii de ultimă generație denumiți adezivii universali.

În breasla stomatologilor am observat că părerile privind cei doi adezivi sunt împărțite. Medicii mai comozi și tineri preferă adezivul universal pentru că le oferă timpi de lucru mai simpli și mai rapizi. Iar medicii cu experiență ce au folosit adezivul de generația a 4-a, susțin că ulterior folosirii adezivului universal au revenit la "standardul de aur".

Am comparat cei doi adezivi privind adeziunea pe care aceștia o realizează prin forțe de compresiune și forțe de tracțiune. Compresiunea s-a realizat cu ajutorul unei prese și pe blocuri din material de umplutură Gradia Direct Posterior, care ulterior primei testări blocurile au fost reformate cu ajutorul celor 2 adezivi și retestate. Ulterior tracțiunii care s-a efectuat pe dinți extrași pe care s-au realizat obturații similar situațiilor clinice, zona de desprindere a fost studiată la microscopul FTIR.

În urma testelor efectuate, adezivul All-Bond 3® Bisco a avut o putere de adeziune și rezistență la compresiune mai mare decât adezivul universal CLEARFIL™ Universal Bond Quick Kuraray. În urma testelor de tracțiune, valorile obținute au arătat o adeziune mai mare adezivului de generația a 4-a. De asemenea, zona de interfață unde s-a produs dezlipirea a arătat că adezivul de generația a 4-a este superior privind adeziunea față de țesuturile dentare.

Keywords: *universal, 4th generation adhesives. compressive, tensile, adhesion*

1.Introduction

For a successful restoration, it is essential to have a strong bond between the dental tissues and the adhesive restorative material, which must show predictability, esthetics, strength and satisfactory marginal adaptation. The ability of clinicians to create adhesion between restorative materials and tooth structure with minimally invasive interventions is a significant achievement in modern dentistry.

However, obtaining a high-quality adhesion remains a daunting task even for the most experienced clinicians who are faced with such a large market offer that the choice of materials is difficult. In contemporary dentistry, the success of cosmetic restorative materials largely depends on the use of specific materials such as dental adhesives, resin composites, compomers, hybrid ionomers and glass ionomers [1].

* Autor corespondent/*Corresponding author*,
E-mail: florescu.anamaria@yahoo.com

Dental adhesion, in the context of minimally invasive therapy, was inaugurated in 1955 by Buonocore. Since then, technological advances have led to a constant evolution of adhesion strategies. This led to the development of techniques ranging from no etching to full etching (4th and 5th generation) and later to the emergence of self-etching adhesive systems (6th, 7th- and 8th generation) [2]. Research has focused on increasing adhesion strength. The initial generation of adhesive measured between 1-3 MPa, steadily increasing especially until the fourth generation where it reached an impressive performance of 17-30 MPa. It is noteworthy that this threshold was not significantly exceeded by universal adhesives in a single application step [3].

In the 1980s and 1990s, the fourth generation of adhesives was introduced. This special generation of adhesives completely eliminates the smear-layer and is associated with the total acid etching technique. It involves the use in three separate stages, the demineralizing acid, followed by a primer and finally, the adhesive resin, each product packaged separately and applied in a sequential manner [4]. When used properly, 4th generation adhesives show a high level of effectiveness. It is the most versatile of all adhesive generations, which is why it is widely recognized as the gold standard in adhesion, serving as the standard against which all newer adhesive generations are compared.

However, the three-step application process require more working time [5]. In the age of digitalization, this is a big impediment, that's why the research focused on the association of the demineralizer with the primer (2 bottles) and then the demineralizer, the primer and the adhesive resin in one bottle.

Universal or multifunctional adhesives are monocomponent and can be used as adhesives with demineralization and rinsing (ER), self-etching adhesives (SE), as well as with total or selective demineralization, as the clinical situation requires [1]. Universal adhesives contain monomers with mild to moderate acidity (phosphoric acid, carboxylic acid, etc.) in lower concentrations compared to classic monomers, non-acidic monomers, catalysts for polymerization and an appropriate selection of solvents [6]. The monomer, with moderate acidity and the ability to form water-insoluble salts in dentin, contained in most universal dentin adhesives is 10-MDP (10-methacryloyloxydecyl dihydrogen phosphate). This is considered to be the best solution for achieving adhesion at the dentine level [7].

Clinical and scientific data on universal adhesives demonstrate that they are hydrophilic and degrade faster. In addition, due to the inclusion of 3 components in one container, these systems must have a larger amount of solvent (usually alcohol or water), which limits the depth of infiltration of the resin into the tooth and can create voids. Additionally, the pH must be acidic because the demineralizer is part of this liquid and has been shown to react negatively with composite initiator systems [8].

Recently, Meng et al. postulated that following the demineralization step with phosphoric acid, the released Calcium ions can bind to 10-MDP from the composition of the adhesives, forming stable 10-MDP-Ca bonds that increase adhesion and reduce the risk of marginal infiltrations [9]. Also, the absence of the HEMA (hydroxyethyl methacrylate) component in the 4th generation adhesive helps with less shrinkage and less water absorption which increases marginal adhesion and reduces the occurrence of secondary caries.

Adhesive failures are those that occur between the adhesive and the tooth surface. Cohesive failures can occur within the tooth or in the restorative material. Adhesive failures are often a mixture of adhesive and cohesive failures. The percentages of adhesive failure types can be measured using a scale that specifies the amount (in percent) of the restorative material remaining on the tooth after detachment [10].

The resistance of adhesives subjected to functional masticatory forces as well as parafunctions has been tested and researched in the specialized literature, but for universal adhesives, the last to appear on the market, there are not concluding studies and, in particular, comparative studies with the considered generation the gold standard.

In vitro measurements of traction and compression force as well as adhesion force are important in characterizing the bonding potential of new adhesives and materials for crown restoration. The first purpose of adhesion testing is to measure the tensile strength of an area with created adhesion. The second objective is to observe a possible location of an adhesion failure. On this basis, we carried out this study, the purpose of which was to compare, through mechanical compression and traction tests, the resistance and adhesion force to the dental tissue of a 4th generation adhesive and the latest generation of adhesives.

On this basis, we carried out this study, the purpose of which was to compare, through mechanical compression and traction tests, the resistance and adhesion force to the dental tissue of a 4th generation adhesive, considered the "gold standard" (ALL- BOND 3® from BISCO Dental) and the latest generation of adhesives, also known as universal adhesives (CLEARFIL™ Universal Bond Quick from Kuraray). The composite restorative material used was GRADIA® DIRECT Posterior.

Table 1

Composition of the 2 adhesives used in this study / *Compoziția celor 2 adezivi folosiți în studiu*

All Bond 3 – Bisco [14]	Clearfil Universal Bond – Kuraray [19]
Does not contain HEMA - $C_6H_{10}O_3$. The absence of HEMA helps better adhesion because the adhesive layer reduces water absorption. ALL-BOND 3 consists of strongly cross-linked monomers and is a hydrophobic adhesive for increased adhesion durability. Contains MDP.	Bisphenol A diglycidylmethacrylate – BisGMA 10-25% Ethanol 10-25% 2-hydroxyethyl methacrylate 2.5-10% HEMA 10-Methacryloyloxydecyl dihydrogen phosphate 10-MDP Hydrophilic amide monomers Colloidal silica Silane coupling agent Sodium fluoride dl-Camphorquinone Water

2. Materials and methods

The exact composition of the 2 adhesives used in this study is not public, but the information found is presented below. The notable difference between the two adhesives is the absence of HEMA in the 4th generation adhesive, and the presence of a larger amount of solvents in the 7th generation universal adhesive (Table 1).

2.1.Mechanical resistance to compression

Bond strength testing is usually performed in tension or shear using a universal screw or servo-hydraulic testing machine [11]. The restorative material is pulled perpendicular to the enamel substrate. The two modes of tensile adhesion testing include the inverted truncated cone test and the microtensile test [12, 13].

The study was performed on 20 tablet blocks made of Gradia® Direct Posterior composite cast as uniformly as possible in cylindrical molds with a diameter of 15 mm and a thickness of at least 2 mm (Figure 1).

The composite material application protocol designed by the manufacturers was followed with some adaptations, as our study was not performed on dental substrates (Table 2) [14].

The composite tablets were divided into 2 equal batches, hereafter referred to as Batch 1 and 2. The volume of a tablet with a diameter of 15 mm and a height of 2 mm was calculated and the value of 367.56 mm^3 was obtained. Considering that the manufacturer gives us the density of the Gradia® Direct Posterior composite as 1.9 g/cm^3, by calculation we obtained the ideal weight of a correctly molded tablet as well as homogeneity and thickness as 0.698 g [15]. By weighing and measuring the thickness we ensured that each tablet was cast evenly.

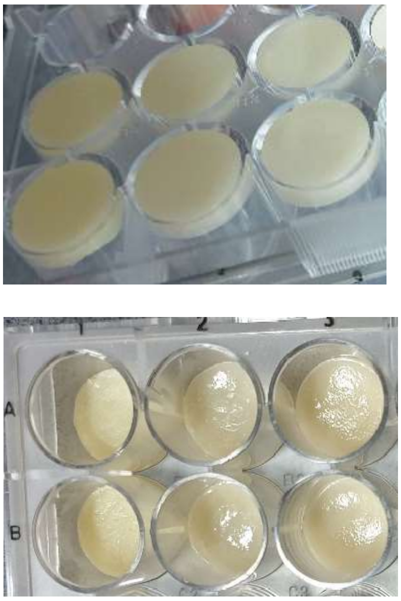


Fig.1- Initial pills from GRADIA® DIRECT Posterior
Pastilele inițiale din GRADIA® DIRECT Posterior

Table 2

Composition and protocol recommended by the manufacturer of GRADIA® DIRECT Posterior and adapted according to the composition of the composite material */ Protocolul recomandat de producătorul de GRADIA® DIRECT și adaptat conform compoziției materialului compozit*

Restorative material	
GRADIA® DIRECT Posterior	Consisting of 2 parts: A. Matrix: urethanedimethacrylate (UDMA) and camphorquinone dymethacrylate B. Filling: fluoro-alumino-silicate in the form of silicon glass powder. 1. Choose any shade of material. 2. The mold requires degreasing, cleaning, drying and preparation for tablet casting. 3. The photo-polymerizable material will be applied in stages, until a thickness of 2 mm is reached. 4. The material condenses very well to be homogeneous and without air gaps. 5. Uniformization of the material on the surface before photo-polymerization. 6. Staged photo-polymerization using a light intensity of 1200mW/cm^2, for 30 seconds. 7. Repeat step 3 until the 2 mm thickness of the pill is reached.

Fig. 2 **-** Steps in the process of grinding and measuring tablets */ Etapele procesului de măcinare și măsurare a tabletelor*

The tablets were ground manually to a uniform thickness of 2mm and weighed to check that the casting was free of air voids or missing substance (Figure 2).

Standard composite tablets were tested in a hydraulic press for mechanical compressive strength [16]. This test was performed on all 20 tablets from batches 1 and 2, and is hereafter referred to as the initial tablet test or test I.

Pascal's law is the foundation of the working principle of hydraulic presses and is based on and consists in the generation of large forces through the high pressure of a liquid medium. The device used works with a force application speed of 2 mm/s and a pressing force of 0.5 Mpa/s constant until the sample fails. The tested tablet is made of a very hard material and will fail during the test when the compressive strength limit is reached. The result is displayed on the press gauge [17].

After testing, the tablets were broken into several pieces. Tablets broken into up to four parts were restored to their original tablet form by bonding using All Bond 3 3-time adhesive and Clearfil universal adhesive. Two batches were obtained with glued pellets following the initial post-test fractures. They reached their original shape of 15 mm diameter and 2 mm thickness as follows:

Batch 1, after initial testing became Batch A - 10 tablets of GRADIA composite material were subsequently bonded with Bisco's All Bond 3 adhesive;

Batch 2, after initial testing became Batch B – 10 tablets of GRADIA composite material were subsequently bonded with Kuraray's CLEARFIL adhesive.

The working protocols of the Clearfil and All Bond 3 adhesives were followed and adapted for the purpose of bonding the composite material. The procedures and working times recommended by the manufacturer (Table 3) were followed to reform the tablets following their breakage during the initial testing [18, 14]. Thus, following the re-filling of the pills, 2 batches A and B of 10 pills each were formed according to the table below (Table 4).

For the tablets that after testing broke into more than 5 fragments, a small amount of the initially used composite was also used (Figure 3).

The pills formed after cementation were again tested for compressive strength in the same press. In what follows, this 2nd test is referred to as test II or the test of reconstituted tablets - Batches A and B.

Table 3

Working protocol for adhesives / *Protocolul pentru adezivi*

Adhesive	Application protocol
Universal Clearfil Bond Quick	It will be applied with the applicator brush, through a rubbing movement on both walls to be cemented. Waiting time is not necessary. It is necessary that the surfaces are degreased and dry. It dries easily. The 2-4 fragments to be cemented are intimately brought together and the pill is reformed. It is photo-polymerized for 30 seconds
All-Bond 3 in 3 steps	1. Demineralization step used for dental tissues 15 seconds and rinse. 2. Remove excess water using a cotton ball or suction, the surface remains slightly damp. 3. Equally mix drops of All-Bond 3® Bisco components A and B, in a 1:1 ratio. 4. Using a brush, mix the adhesive for 5 seconds. 5. Apply 1-2 layers on all surfaces to be cemented for 5-10 seconds. 6. Arrange the cemented fragments intimately in such a way as to reform the pill. 6. Dry thoroughly for at least 10 seconds. If the surface appears shiny, continue, otherwise repeat step 5. 7. Photo-polymerization 30 sec.

Table 4

Study groups / *Loturile studiului*

	Batch A	Batch B
Filler of the original pill	GRADIA® DIRECT Posterior	GRADIA® DIRECT Posterior
Pills reconstructed with the adhesive	All Bond 3, Bisco Adhesive in 3 steps	Clearfil Universal Bond Quick, Kuraray Noritake Dental Inc. Adhesive in one step

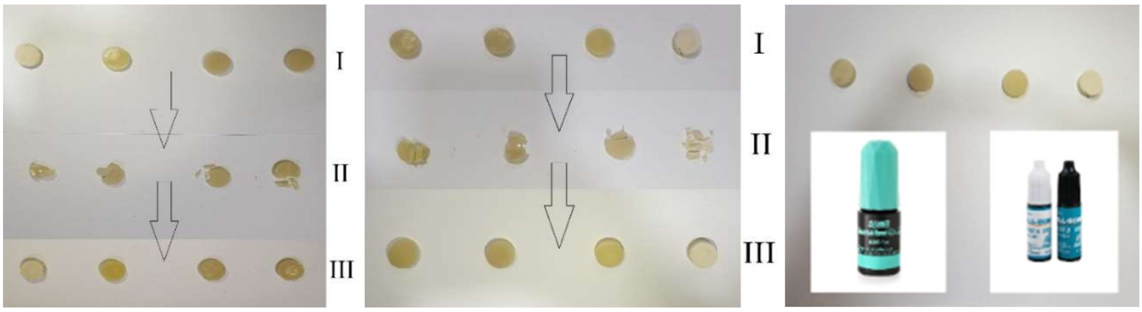


Fig. 3 - The stages of tablet reformation / *Etapele reformării tabletelor:*
I - The initial pill; II – The tablet after the initial test; III – Restoring tablets using Clearfil Universal Quick Bond and All-Bond 3 adhesives
I – Tableta inițială; II – Tableta după testul inițial; III-Refacerea tabletelor cu ajutorul adezivilor Clearfil Universal Quick Bond și All-Bond 3

2.2Traction force

The study was performed on two batches of 20 extracted teeth on which fillings were made with All-Bond 3 and Clearfil Universal Bond Quick adhesives.

Cavities were made on the vestibular or oral surface on molars and premolars, with equal weight in the two groups. The preparations were 2 mm deep on the molars to interest both enamel and dentin. In order to achieve an equal retention surface, before making the cavity, the future cavity was delimited on the enamel, with dimensions of 5 mm mesio-distal and 3 mm from the package to the occlusal edge. The cavity walls were divergent, made non-retentively with the help of an diamond bur with a special rhomboid shape, which had favorable dimensions for our cavity and offered the same angle of convergence of the walls (Figure 4).

Thus, the cavities will have a truncated pyramid shape with the large base representing the access point of the dental bur, and the small base corresponding to the deep wall of the cavity. The deep wall of the cavity is represented by dentin and the walls of the cavity are represented by enamel. We have schematically represented this pyramid trunk to also calculate the area of the contact surface for the adhesive.

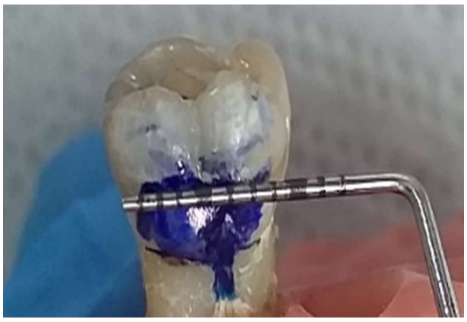


Fig. 4 - The shape of the entry in cavity 3x5 mm - as access to the dental tissue where it was penetrated a bur for a depth of 2 mm / *Trasarea viitoarei cavități pentru a obține suprafețe de adeziune*

After milling, contact surfaces were obtained where the adhesive was applied: the small base represented by dentin of 9.9911 mm^2, and a lateral area represented by enamel of the cavity of 41.96 mm^2. The tubule being embedded in the cavity filling mass with the grip on the large surface of the pyramid trunk. The total adhesion area was 51.9507 mm^2. Following the measurements of the obtained cavities, the teeth that had a deviation of less than 5% of the obtained contact surfaces were chosen.

The adhesive application protocol made by the manufacturers was respected both in terms of stages and operating times (Table 3).

The ALL-BOND 3 3-time adhesive and the CLEARFIL universal adhesive were used and 2 batches of 20 teeth each were formed:

- Batch 1: ALL-BOND 3 adhesive;
- Batch 2: CLEARFIL universal adhesive.

In the obturation material, tubes from Orthometric, used in orthodontics, similar to tubes, were applied, which will facilitate the next stage of traction (Figure 5).

Fig. 5 - Applying the small tubes in the filling material
Aplicarea tubușoarelor în materialul de obturație

After obtaining the two batches of teeth, they were prepared by embedding in a DEVE-produced, rigid, two-component transparent SG 1452 epoxy resin of the highest hardness. The teeth were mechanically cleaned of some dental debris and placed in different molds, corresponding to each batch, into which the resin was poured. The teeth were placed in the mold so that the fillings were outside the resin (Figure 6).

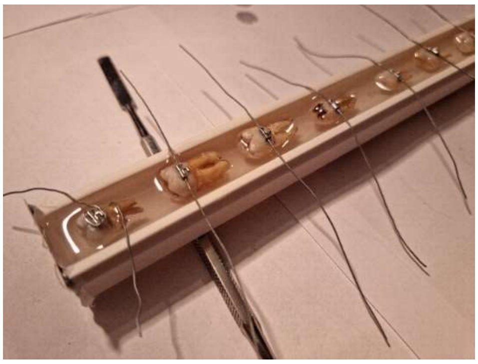


Fig. 6 - Pouring the resin into the 2 dies and rigidly fixing the teeth / *Turnarea rășinii în cele 2 matrici și fixarea rigidă a dinților*

The testing of the two batches was carried out by attaching a wire from Dentaurum with a diameter of 0.6 mm with a very low stretch coefficient, 1800-2000 N/mm^2, which makes it rigid. Due to the structural rigidity of all components subject to tensile force, we anticipate that the fillings will pull out. Pulling out represents the mode of failure by which the attachment element comes off brutally - in the studied case the obturation, without developing full resistance of the base element - the tooth, the failure occurring at the obturation-tooth interface, by fracturing the adhesives [20].

The device with which the 1000N Matest measurements were performed complies with EN 6892-1, EN7050-1, EN 10002, EN 10080, EN 50081-1, EN 15630-1, EN 15630-3 standards and offer results in measure unit Newton (N). The device used works with a force application speed of 0.25 mm/s and a traction force of 5 Mpa/s constant until the sample fails.

After all the samples were subjected to tension, they fractured at the level of the adhesive, at the level of the fracture, adhesive could be observed both on the tooth and on the obturation only for the samples made with All Bond 3 -Bisco.

2.3.FTIR microscopy

After the samples were analyzed macroscopically and Fourier transform infrared spectroscopy and microscopy using a Thermo FTIR Nicolet iN10 MX microscope; the maps were recorded in reflexion mode over the wavenumber range of 675–4000 cm^{-1}, with a resolution of 4 cm^{-1}.

3.Results

3.1.Compressive strength results

Testing I, initial, was performed on batches 1 and 2. The unit of measurement displayed on the press gauge was in kgf/cm^2 and later converted to Mpa. The initial results obtained in testing I were entered in a table (Table 5).

The results obtained after the initial testing were graphically represented in Figure 7.

Table 5

The results obtained in the initial testing for batches 1 and 2 / *Rezultatele obținute la testarea inițială pentru loturile 1 și 2*

The compressive strength values obtained in the laboratory after the Initial Testing [MPa]											
Samples	1	2	3	4	5	6	7	8	9	10	**Medi**
Batches 1	57	54	59	56	55	57	60	53	61	58	57
Batches 2	47	51	50	47	46	51	47	45	46	50	48

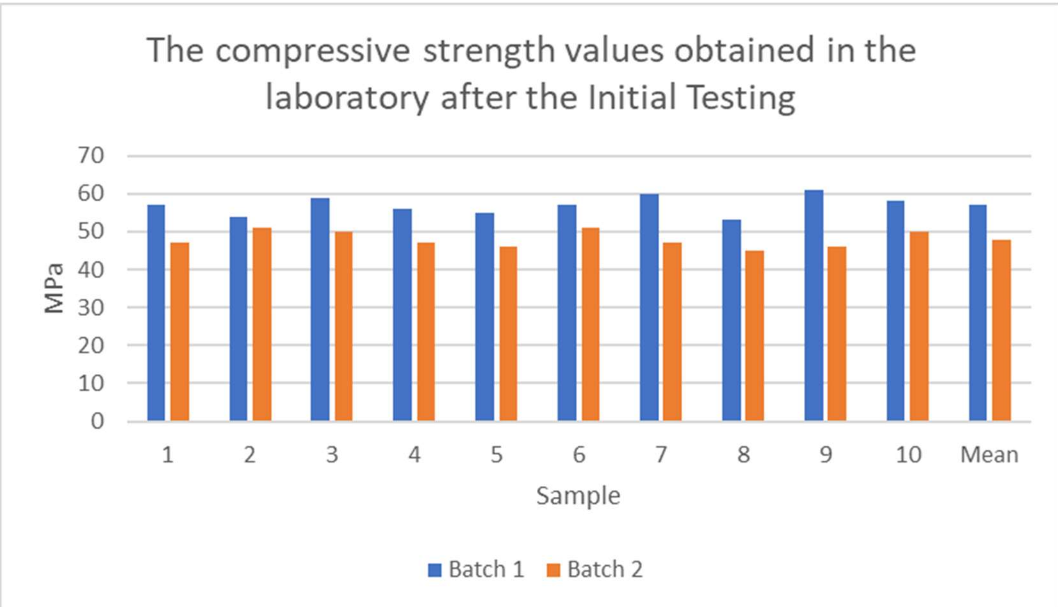


Fig. 7 - Compressive strength values obtained from I - initial testing [MPa] / *Valorile rezistenței la compresiune obținute din I - încercarea inițială [MPa*

Table 6

Estimation of coefficients standard deviation, mean and confidence interval for the mean
Estimarea abaterii standard a coeficienților, a mediei și a intervalului de încredere pentru medie

Value								
					95% confidence interval			
	N	Mean	Standard deviation	Standard error	Inferior bonding	Superior bonding	Minimum	Maximum
1&2	10	56.90	2.767	0.875	54.92	58.88	53	61
Total	20	52.40	5.305	1.186	49.92	54.88	45	51

Table 7

Anova test comparing the means of the 2 groups /*Testul Anova comparand mediile celor două grupuri*

ANOVA					
Value					
	Sum of squares	df	Mean squared	F	Sig.
Between groups	405.000	1	405.000	56.163	0.000
Within groups	129.800	18	7.211		
Total	534.800	19			

Table 8

Centralization of the results obtained in Testing II / *Centralizarea rezultatelor obținute în Testarea II*

Compressive strength values obtained from Test II [MPa]											
Batches	1	2	3	4	5	6	7	8	9	10	**Mean**
Batch A Gradia Direct Posterior composite resin with All Bond 3 adhesive	57	56	55	57	55	58	54	58	56	55	56.1
Batch B Gradia Direct Posterior Composite Resin with Clearfil Universal Quick Bond Adhesive	52	49	50	53	52	51	50	54	52	49	51.2

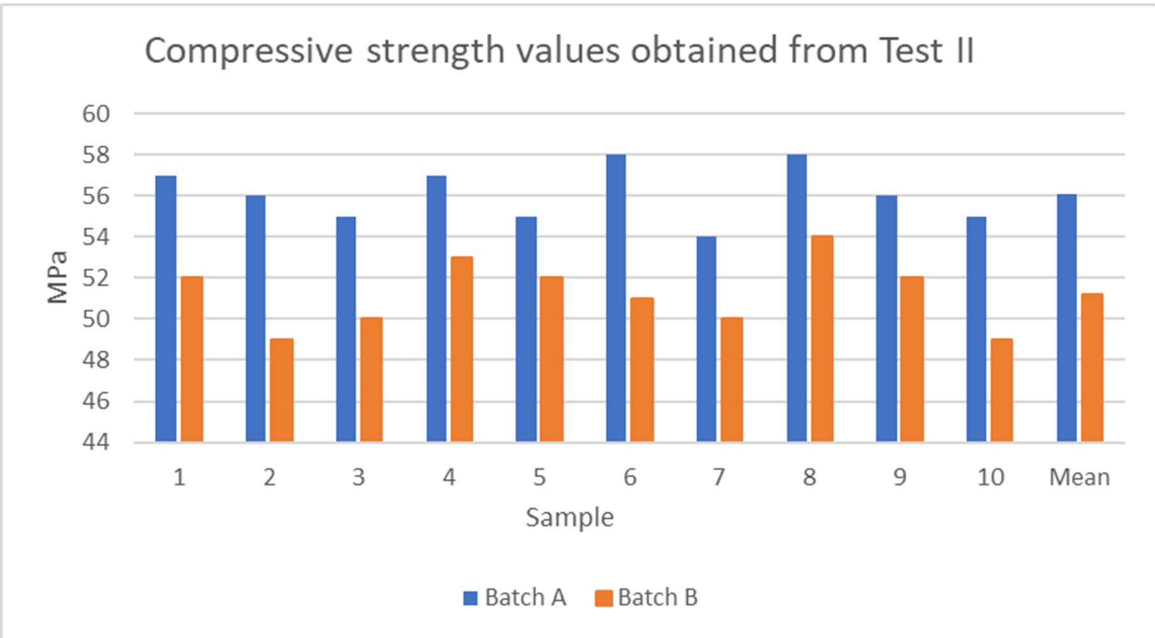


Fig. 8 - Compressive strength values of test II- of the reformed tablets after the initial test [MPa] (batch A and B)
Valorile rezistenței la compresiune ale testului II- ale tabletelor reformate după testul inițial [MPa] (loturile A și B)

To evaluate the statistical correlation, the data were analyzed in SPSS version 21, and the mean, standard error and standard deviation were calculated. The comparative analyzes were made with the Anova and Turkey tests (p<0.05) (Table 6, Table 7).

Since the standard error is not large it is inferred that the mean obtained with the current study cannot vary drastically under similar test conditions with other samples.

The probability is less than 0.05 so there are significant differences between the compressive strength values of the tested composite and ormocer.

Following testing II, performed on the reconstructed tablets from batches A and B, the results obtained were entered in the following table, after the conversion of the unit of measurement (Table 8).

To highlight the performance differences between Clearfil Universal Quick Bond and All-Bond 3® Bisco, a graph was made in which both adhesives appear in parallel (Figure 8)

The statistical analysis of the data obtained in testing II consisted in determining the linear regression, the standard deviation and the Anova and Turkey tests for comparing the means between them. (p<0.05) (Table 9, Table 10).

Because the standard error is not large it is inferred that the mean obtained with the current study cannot vary drastically under similar test conditions with other samples.

The comparative calculation of the average values of the batches between them shows that there are no significant differences.

3.2.Tensile strength results

As a result of testing carried out on both batches, the maximum values of the tensile force before the moment of fracture are centralized in the following table (Table 11):

Table 9

Estimation of linear regression coefficients, mean and confidence interval for the mean
Estimarea coeficienților de regresie liniară, medie și interval de încredere pentru medie

Value	N	Mean	Standard deviation	Standard error	95% Confidence interval		Minimum	Maximum
					Inferior bonding	Superior bonding		
A	10	51.20	1.924	0.860	48.81	53.59	49	54
B	10	42.00	2.449	1.095	38.96	45.04	39	45
Total	20	48.80	5.367	1.200	46.29	51.31	39	58

Table 10

Tukey's test comparison between batches / *Comparația testului lui Tukey între loturi*

Multiple Comparisons						
Dependent variable:	value					
Tukey HSD						
(I) lot		Difference from the mean (I-J)	Standard error	Sig.	95% Confidence interval	
					Inferior bonding	Superior bonding
A	2	9.200*	1.249	0.000	5.63	12.77
	3	-4.000*	1.249	0.026	-7.57	-0.43
	4	4.400*	1.249	0.014	0.83	7.97
B	1	-9.200*	1.249	0.000	-12.77	-5.63
	3	-13.200*	1.249	0.000	-16.77	-9.63
	4	-4.800*	1.249	0.007	-8.37	-1.23
*. The mean difference is significant at the level 0.05.						

Table 11

Values obtained (N) after testing the samples / *Valori obţinute (N) în urma testării probelor*

Values obtained (N) after testing samples/51.9507 mm^2		
	Batch 1 – Gen 4th	Batch 2 - universal
1	112.16	51.11
2	110.43	55.23
3	101.41	51.24
4	115.53	69.58
5	100.7	65.31
6	102.79	61.89
7	135.6	54.4
8	108.86	61.5
9	112.54	52.18
10	115.18	59.84
11	106.47	54.71
12	100.89	52.98
13	113.91	56.44
14	98.71	49.12
15	118.02	51.35
16	106.9	67.55
17	111.93	54.62
18	107.22	58.92
19	103.51	51.85
20	102.11	53.61
Mean	109.2435	56.6715

The values in the table are for standard created cavities that have a contact surface of 51.95mm^2. One can see the big differences between those two generations of adhesive, in all samples the values of the adhesive in 3 steps have considerable higher pull-out tensile force (almost double) compared to the generation of universal adhesive.

Also, in the graph below one can see the clear differences resulting in a better adhesion of the adhesive in 3 steps.

Adhesion failure was determined according to a score used by Bishara SE, Trulove TS (1990).

Score 0 = No glue left on tube
Score 1= <25% of adhesive remaining on tube
Score 2 = 25% of adhesive remaining on tube
Score 3 = 50% of adhesive remaining on tube
Score 4 = 75% of adhesive remaining on tube
Score 5 = 100% of adhesive remaining on tube [21].

Failures can occur at the tooth structures (structural failure), between the adhesive and the substrate (adhesive failure), or within the adhesive (cohesive failure) [22]. Regarding the adhesion failure, the results of our study show that: for the samples from batch 1 – All Bond 3 -Bisco equal parts (similar to score 3) of the adhesive remained on the tooth and on the obturation material, and the samples from batch 2 – Clearfill Universal Bond Quick whole the adhesive remained on the composite obturation material, suggesting poor adhesion at the tooth interface (similar to score 5). The study conducted by Bishara SE, Trulove TS obtained results similar to our research, the seventh generation adhesive used obtained, according to the score, the lowest resistance. In contrast, the 3th generation adhesive scored optimally for any adhesion where the adhesion achieved was equally achieved at both the tooth tissue interface and the adhesive interface. However, the batch where the 3 steps adhesive was used, although achieving good adhesion, yielded within the adhesive, revealing cohesive failure.

3.3.FTIR microscopy assessments

The macroscopically evaluation of the interface surfaces where the detachment occurred, suggested that both the tooth tissue left on the bracket and the adhesive/filler left on the tooth after the pull-out. The assessment was made based on the area occupied by the dental tissue remaining on the bracket or the adhesive area remaining on the tooth. The purpose of a good adhesive is to remain on both surfaces of the interface to provide good adhesion to both the tooth tissue and the filling material.

Thus, the samples that presented the best adhesion from a macroscopic point of view were samples 1 and 4 from batch 1 and samples 8 and 14 from batch 2 were analyzed by FTIR in order to better assess the detaching mechanism.

Fig. 9 reveals the FTIR spectra of the sample 1 (using All-Bond 3 as adhesive) and sample 8 (using Clearfill Universal as adhesive). Based on the two spectra, it can observe a very good similarity which means that the major components are similar. In this case, regardless the sample, for all the FTIR maps we will consider the same peaks. The peak from ~1200cm^{-1} is belonging to the silicate which is present ion these dental materials; the peaks from around 1630 and 1737cm^{-1} can be considered to belongs to the double bonds from the urethane resins while the bands from around 2875 and 2925cm^{-1} can be assigned to the symmetric and anti-symmetric stretching of the methyl and methylene groups.

In all the cases, the spectra reveal the specific peaks of the used dental material which means that the used adhesive adhered well on the surface and after the mechanical testing, the failure occurring within the material and not at the interface by detaching the bracket from the surface of the tooth (regardless if the detachment is a consequence of a bad adherence on the metallic bracket or ion the tooth). Looking on all the maps, regardless the wavelength we select, the maps are quite similar which means that the interface between the bracket and the tooth is homogeneous. Moreover, even on the surface of the metallic components, the presence of the adhesive can be easily identified even in FTIR microscopy, being in good agreements with the visual observation of the surfaces. In the case of sample 14, the failure occurs not at the interface but a part of the teeth was broken and remained attached to the bracket (right side of the image). In this case, because of the absorption of the hydroxyapatite or collagen, differences appeared Figure 10

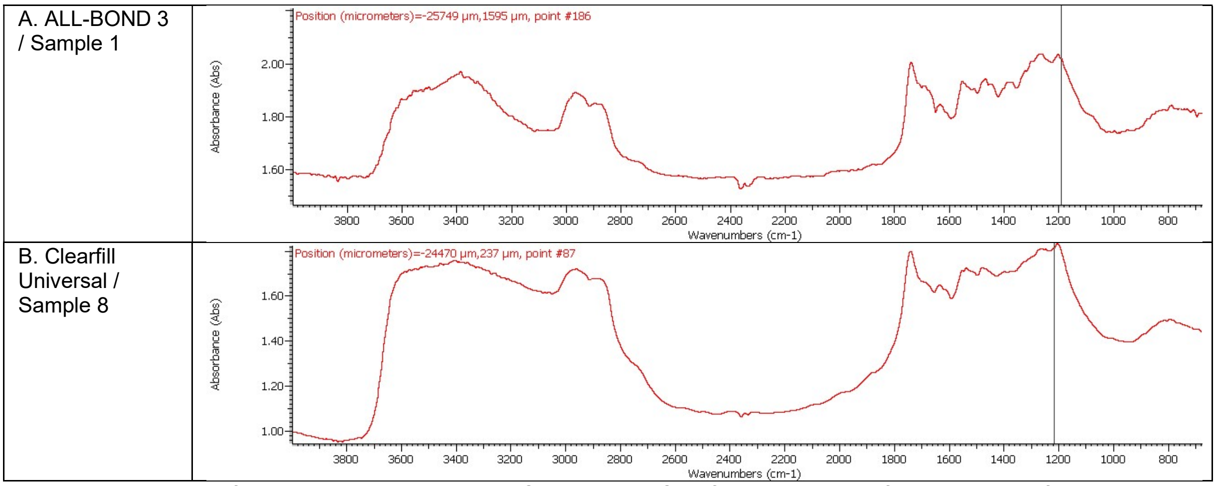
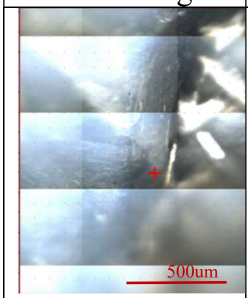
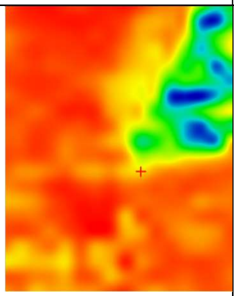
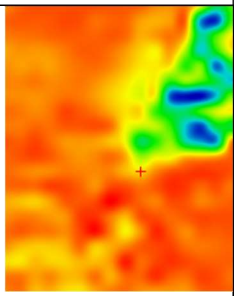
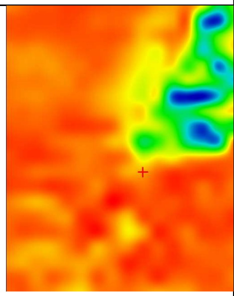
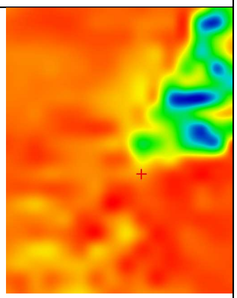


Fig. 9 - FTIR spectra of the dental materials A. ALL-BOND 3 and B. Clearfill Universal used for the bonding of the metallic bracket on the teeth / *Spectrele FTIR ale materialelor dentare A. ALL-BOND 3 şi B. Clearfill Universal utilizat pentru lipirea bracket-ului metalic pe dinţi*

Sample #1				
Video image	1193cm^{-1}	1637 cm^{-1}	1737cm^{-1}	2875cm^{-1}
				

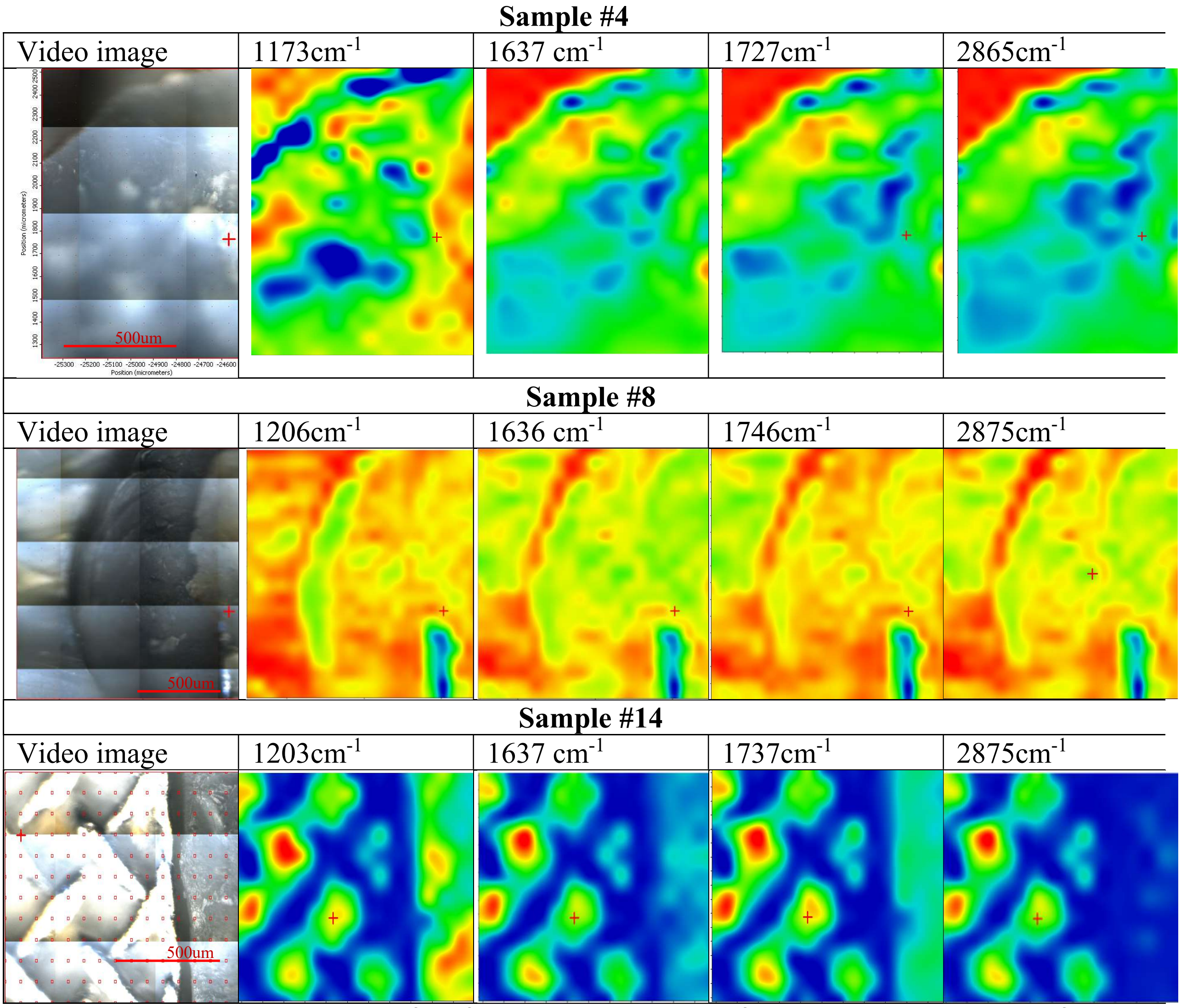


Fig. 10 - FTIR maps recorded on the bracket surface after the mechanical evaluations for the samples 1, 4, 8 and 14 at the following specific wavelength: ~1200; 1630; 1730 and 2875cm^{-1}. / *Hărți FTIR înregistrate pe suprafața bracketului după evaluările mecanice pentru probele 1, 4, 8 și 14 la următoarea lungime de undă specifică: ~1200; 1630; 1730 și 2875cm^{-1}*

4. Discussions

Measuring the strength of dental adhesion (a key factor in determining the long-term durability of restorations) to compressive and tensile forces is a frequently used method for assessing the longevity of restorations. The ideal adhesive system would be one that is hydrophilic like dentin which has a high water content, but then becomes completely hydrophobic after polymerization to stop water absorption and hydrolysis. Unfortunately, no such adhesive currently exists so the best choice would be to switch from hydrophilic to hydrophobic while moving from the tooth tissues to the interface with the restorative material. This is basically the strategy used by 4th generation adhesive systems which involve the placement of hydrophilic primers which are then overlaid with hydrophobic resins [23, 24].

Our study compares the strength of dental adhesion between 2 generations of adhesives, the 4th generation (All-Bond 3® Bisco) and Clearfill Universal Bond Quick, the generation of universal adhesives.

4.1. The compressive strength of the samples

The literature does not establish an optimal bond strength margin for universal adhesives. Previous reports on the strength of universal adhesive range from 5 to 22 MPa [25].

The 4th generation adhesive tested in the study by Söderholm KJ. et al. performed better than the 7th generation adhesives. Even inexperienced clinicians had better results with 4th generation adhesives than with 7th generation adhesives. Dentin adhesion was stronger than enamel adhesion [26]. Adhesives with demineralizer, primer, and bonding agent coupled in a single container are associated with lower values of in vitro adhesive bond strength and lower in vivo longevity of restorations [27].

Regarding the influence of the adhesive strategy used on the performance of the universal adhesives, no differences related to the application technique (ER or SE mode) were detected. This is also in accordance with a recent systematic review which concluded that adhesion to dentin and the occurrence of microinfiltrations do not depend on the application technique [4,44,28]. However, it appears that this trend cannot be fully extrapolated to the clinic, as there are clinical studies and reviews that have reported lower retention rates in the application of SE adhesives [29].

The study carried out by Alsaadawi A. et al., which comparatively determines the magnitude of the adhesion force of several universal adhesives, shows that the choice of the application strategy is important and can determine the increase in adhesive performance. The results of the study thus indicate that CLEARFIL™ Universal Bond Quick Kuraray universal adhesive, when used with the demineralization and rinsing strategy, provides effective adhesive strength to primary enamel (15.82 ± 0.88) [30]. Another study, however, which compares three universal adhesives (G2-Bond Universal (GC), Clearfil SE Bond (Kuraray) and Scotchbond Universal Plus (3M ESPE)) and evaluates shear bond strength in different storage modes and etching them, showed that thermal cycling and choice of adhesive system significantly affected shear strength. Of the three adhesives, G2-Bond Universal had the highest bond strength even after one year in the oral environment and Clearfil SE Bond bond was average. The study concluded that G2-Bond Universal without HEMA is the most effective universal adhesive for clinical practices, especially when applied in self-etch mode [31].

In 2018, the authors of another study, which verified the importance of the demineralization step in the application protocol of universal adhesives, reached the same conclusion, that the results obtained were superior for universal adhesives to which the previous acid demineralization step was added. Thus, we can conclude that adding the steps used in the 3-steps adhesive technique improves the performance of any adhesive [32; 33]. The acid etching step remains the gold standard for the protocol for applying universal adhesives to primary enamel. However, the authors believe that the etching time with phosphoric acid applied 15 vs. 30s showed no significant effect on the initial microtensile strength of universal adhesives to primary enamel [34]. Other studies reported that Clearfil had excellent resistance to shear forces [30; 35; 6].

The value of the average compressive strength of the samples where the All-Bond 3® Bisco adhesive was used is 56 MPa in batch A. It is found that the mechanical compressive strength is close to that of the initially cast material batch 1 - 57 MPa. This highlights the superior cementing qualities of the 4th generation All-Bond 3 adhesive.

After testing the samples cemented with adhesives, the fracture lines obtained did not coincide with those obtained after the first test, so the two adhesives used have high adhesion power on the composite materials.

The use of All-Bond 3® Bisco adhesive in batch A resulted in a maximum strength value of 58 MPa, and in batch B where CLEARFIL™ Universal Bond Quick Kuraray adhesive was used, the maximum strength obtained was 54 MPa. After using the 2 different adhesives on the same GRADIA® DIRECT Posterior composite material, better results were obtained with the All-Bond 3® Bisco adhesive, the average values obtained being approximately 9% higher. The average values calculated indicate a better compressive strength of the pills cemented with All-Bond 3® Bisco adhesive.

4.2.Discussion of tensile strength of specimens

ALL-BOND 3® - BISCO Dental adhesive achieved clearly superior results, yielding at an average tensile strength of 109.24 N, while CLEARFIL™ Universal Bond Quick Kuraray adhesive yielded at an average tensile strength of 56.67 N. Percentage-wise, the results showed that the 3-steps adhesive is 92.76% better.

The breaking occurred at the level of the adhesive, both the filling part of the composite material and the dental tissue being unaffected. In batch 1, where All-Bond 3 adhesive was used in 3 steps for the adhesion of the tubules, there is still adhesive remaining on the dental surface and in batch 2, where Clearfil universal adhesive was used, there were no traces of adhesive left on the dental tissue, this being found completely on the loosened filler material. In conclusion, the adhesion was balanced regarding the interface dental tissue – adhesive and adhesive – obturation material for the 3-steps adhesive, which is reflected in the superior results obtained. It can also be noted the importance of demineralization in the stages of the 4th generation of adhesives, which creates a better bond at the level of the dental tissue and adhesive interface.

The minimum value obtained for the 4th generation All-Bond 3® Bisco adhesive of 98.71 N is superior to the maximum value of 69.58 N for the 7th generation CLEARFIL™ Universal Bond Quick Kuraray adhesive.

Clearfil Universal Bond Quick, whose characteristic is application and zero waiting time, appeared from the desire of clinicians to reduce the number of steps to apply adhesives as well as the waiting time. But as not everything fast is good, a reduced application time did not manage to maintain the adhesion strength at the same parameters. That is why compliance with the manufacturer's instructions is vital, especially since the application time could influence the removal of the *smear layer* and/or the infiltration of the resin monomers into the dentin [36].

Comparing the shear bond strength between universal adhesives and 7th generation adhesives in their study, Mishra A et al. showed this to be significantly different and higher (8.7%) for universal adhesives (p = 0.017) [37].

Dallel I et al. conducted a study related to the impact of different adhesive systems and reached similar results to this study. Their study compared generations 4,5,7 of traction adhesives on orthodontic tubules and concluded that generation 4 and 5 had a similar (p=0.7) but higher bond strength than generation 7 adhesives (p=0.0002). The application of shear forces lower than 15 MPa on the 7th generation adhesives led to the almost complete elimination of tubules. Whereas, applying the same force on generation 5 adhesives produced 66.7% removal and on generation 4, only 40% of brackets were removed. Regarding adhesion efficiency, the findings coincided with our study; a score of 0 was most common in generation 4 adhesives, and 3 was most common in generation 7 [38]. Similar results to our study were obtained by Powers JM, Tate WH, who demonstrated that the current generation of adhesives is considered superior to subsequent generations up to the generation of universal adhesives in terms of tensile strength [10].

In the tensile strength study by De Munck J. et al. the results obtained are better for 3-phase adhesives compared to universal ones. The values obtained after measuring the tensile strength vary between 15.5 MPa (for universal adhesives) and 59.6 MPa (for 3-time adhesives), differences that are comparable to the results obtained in our study [39].

According to the manufacturer Kuraray, of 5 universal adhesives tested, CLEARFIL™ Universal Bond Quick achieved the best tensile strength results, which is why we decided to use it in our tests [33]. The results are contradictory to the study published in August 2020 by Cetin AR, Dinc H., where Clearfill Bond Universal achieved lower tensile strength results than Allbond Universal, Single Bond Universal, Tetric N-Bond Universal [40].

In the conclusions of the study by Cardoso GC, et al., immediate and 6-month adhesion is similar and comparable for universal adhesives with the gold standard, but regarding enamel adhesion, for high performance it is selective acid demineralization or a 4th generation adhesive, in 3 steps [41].

4.3.Discussion of FTIR analysis

Analysis of FTIR spectra of sample 1 (using All-Bond 3 as adhesive) and sample 8 (using Clearfill Universal as adhesive). Based on the two spectra, a very good similarity can be observed, which means that the major components are similar. The peak at approximately 1200cm^{-1} belongs to silicate; the peaks at 1630 and 1737cm^{-1} can be considered as belonging to the double bonds in the resins while the bands at 2875 and 2925cm^{-1} can be attributed to the symmetric and anti-symmetric stretching of the methyl and methylene groups. The absence of the HEMA group in the 4th generation adhesive and the presence of solvents in greater numbers and quantities in the universal adhesive account for the higher solubility and shrinkage of the universal adhesive, which leads to weaker adhesion both immediately and in the long term.

5.Conclusions

The paper is mainly focused on the comparative assessments of the two composite adhesives: All-Bond 3® Bisco (4th generation) adhesive and CLEARFIL™ Universal Bond Quick Kuraray (7th generation) adhesive. Regarding the compression test results, the All-Bond 3® Bisco adhesive had significantly higher bond strength and compressive strength than the universal adhesives (CLEARFIL™ Universal Bond Quick Kuraray). The tensile tests performed showed the fact that the 4th generation adhesive has a significantly higher resistance to debonding in compression compared to the universal adhesive. In conclusion, the All-Bond 3® Bisco adhesive of the 4th generation, using the technique in 3 operating steps, showed significantly higher tensile and compressive strength than universal adhesives (CLEARFIL™ Universal Bond Quick Kuraray). Laboratory tests, however, do not necessarily translate into good clinical performance. Therefore, in order to gain a proper understanding of the performance of adhesives, it is important to associate laboratory research results with clinical evaluations.

REFERENCES

[1] **E. Sofan, A. Sofan, G. Palaia, G. Tenore,U. Romeo, and G. Migliau**, Classification review of dental adhesive systems: from the IV generation to the universal type*,* Ann Stomatol (Roma), Jan-Mar 2017, p. 1–17.

[2] **D. Dionysopoulos, I.O. Gerasimidou, C. Papadopoulos**, *Current modifications of dental adhesive systems for composite resin restorations: a review in literature,* Journal of Adhesion Science and Technology, 2022, p. 453-468.

[3] **G. Freedman***, Dental Adhesives: Past, Present, And Future - Oral Health,* 2019, p. 36-39.

[4] **A.S. Ganesh**, *Comparative evaluation of shear bond strength between fifth, sixth, seventh, and eighth generation bonding agents: An In Vitro study,* Indian J Dent Res, Sep-Oct 2020, **31**(5), pag. 752-757.

[5] **N. Toshniwal, N. Singh, V. Dhanjani, N. Mote and S. Mani,** *Self etching system v/s conventional bonding: Advantages, disadvantages,* International Journal of Applied Dental Sciences 2019, **5**(3), 379-383.

[6] **D. Papadogiannis** and others, *Universal Adhesives: Setting Characteristics and Reactivity with Dentin,* Materials 2019, **12**, p. 1720.

[7] **E. Carrilho** and others, *10-MDP Based Dental Adhesives: Adhesive Interface Characterization and Adhesive Stability-A Systematic Review,* Materials 2019, **12**, 790.

[8] **J. De Munck, K. Van Landuyt, M. Peumans,** *A critical review of the durability of adhesion to tooth tissue: methods and results,* J Dent Res, 2005, **84,** 118-132.

[9] **Y. Meng, F. Huang, S. Wang, M. Li, Y. Lu, D. Pei, A. Li,** *Bonding Performance of Universal Adhesives Applied to Nano-Hydroxyapatite Desensitized Dentin Using Etch-and-Rinse or Self-Etch Mode,* Materials (Basel), 22 Aug 2021, p. 14 - 16.

[10] **W.H. Tate, C. You, J.M. Powers,** *Bond strength of compomers to human enamel,* Oper Dent, 2000, **25**(4), 283-291.

[11] ***R.G.*** **Craig, J.M. Powers,** *Restorative dental materials, 11th edn. Mosby, St. Louis***,** 2002.

[12] **M.M. Barakat, J.M. Powers,** *In vitro bond strength of cements to treated teeth,* Aust Dent J , 1986, **31**(6), 415-419.

[13] **D.H. Pashley, R.M. Carvalho, H. Sano, M. Nakajima, M. Yoshiyama, Y. Shono, C.A. Fernandes, F. Tay,** *The microtensile bond test: a review,* J Adhes Dent, 1999, **1**(4), 299-309.

[14] Bisco**,** *AllBond 3, Instructions for Use,* 2018.

[15] Inc, GC America, Gradia Direct (Shades: A1, A2, A3, A3.5, AO3, BW, and CV).

[16] **M. Budescu, P. Mihai, N. Ţăranu, I. Lungu, O.M. Banu, I.O. Toma***, Determinarea curbei caracteristice complete a betonului la compresiune,* 2015, Revista Română de Materiale / Romanian Journal of Materials, **45** (1), 43 – 54.

[17] **C. Hodanbosi.** Pascal's Principle and Hydraulics, 2018, www.grc.nasa.gov.

[18] Dental, Kuraray, *Brochure how to use Clearfil Universal Bond Quick.* 2018.

[19] B. Kuraray, *Safety Data Sheet acc. to OSHA HCS for Clearfil Universal,* 2017, version 2.

[20] **I. Dumitru, N. Faur.** *Elemente de calcul și aplicații în rezistența materialelor, 1997.*

[21] **S.E. Bishara, T.S. Truvole,** *Comparisons of different debonding techniques for ceramic brackets: An in vitro study Part I Background and methods,* Am J Orthod Dentofacial Orthop, 1990, **98**, 145–53.

[22] Dental Adhesion and Bonding Systems, https://www.biomimeticstudyclub.com/blog/adhesion-and-bonding-systems*,* 2022.

[23] **R.B. Ermis, M. Ugurlu, M.H. Ahmed, B. Van Meerbeek**, *Universal Adhesives Benefit from an Extra Hydrophobic Adhesive Layer When Light Cured Beforehan,* J Adhes Dent, 2019, **21**(2), 179-188.

[24] **M.H. Ahmed, J. De Munck, K. Van Landuyt, M. Peumans, K. Yoshihara, B. Van Meerbeek**, *Do universal adhesives benefit from an extra bonding layer?,* J Adhes Dent, 2019, **21**(2), 117–132.

[25] **A. Kensche** and others, *Shear bond strength of different types of adhesive systems to dentin and enamel of deciduous teeth in vitro,* Clin. Oral Investig, 2016, 20, 831–840.

[26] **K.J.** ***Söderholm, M. Guelmann, E. Bimstein,*** *Shear bond strength of one 4th and two 7th generation bonding agents when used by operators with different bonding experience,* J Adhes Dent, 2005, **7**(1), 57-64.

[27] **M.A. Munoz, Sezinando A, I. Luque-Martinez, A.L. Szesz, A. Reis, A.D. Loguercio, N.H. Bombaeda, J. Perdigao**, *Influence of a hydrophobic resin coating on the bonding efficacy of three of universal adhesives,* 42, s.l.: J Dent, 2014, pg. 595–602.

[28] **H. Chen** and others**,** *Comparison of bond strength of universal adhesives using different etching modes: A systematic review and meta-analysis,* Dent Mater J, 2022, **41**, 1–10.

[29] **K.S. Ma, L.T. Wang, M.B. Blatz,** *Efficacy of adhesive strategies for restorative dentistry: A systematic review and network metaanalysis of double-blind randomized controlled trials over 12 months of follow-up,* J. Prosthodont, 2023, **67**, 35–44.

[30] **A. Alsaadawi**, *Shear Bond Strength and Fluoride Release of a Universal Adhesive: An In-Vitro Study on Primary Teeth, Materials 2023,* **16**, 2573.

[31] **S. Brkanovic,** *Comparison of Different Universal Adhesive Systems on Dentin Bond Strength,* Materials, 2023, 16, 1530.

[32] **H. Pouyanfar, E.S.Tabaii, S. Aghazadeh, S.P. Nobari, M.M. Imani**, *Microtensile Bond Strength of Composite to Enamel Using Universal Adhesive with/without Acid Etching Compared To Etch and Rinse and Self-Etch Bonding Agents,* J Med Sci, 2018, **6**(11), 2186–2192.

[33] **W.L. Rosa, E. Piva, A.F. Silva,** *Bond strength of universal adhesives: A systematic review and meta-analysis,* J Dent, 2015, **43**(7), 765-76.

[34] **D. Hamdy, S. Amend, S. Lücker**, *Effect of conditioning on microtensile bond strength of universal adhesives to primary enamel,* Oral prophylaxe Kinderzahnheilkd, 2023, **45**, 20–22.

[35] **T. Nikaido**, *Fluoride-Releasing Self-Etch Adhesives Create Thick ABRZ at the Interface,* Biomed Res Int, 2021.

[36] **P. Saikaew, M. Matsumoto, A. Chowdhury, R.M. Carvalho, H. Sano**, *Does shortened application time affect long-term bond strength of universal adhesives to dentin?*, Oper Dent, 2018, **43**, 549-558.

[37] **A. Mishra, M. Koul, V.K. Upadhyay**, *A Comparative Evaluation of Shear Bond Strength of Seventh- and Eighth-generation Self-etch Dentin Bonding Agents in Primary Teeth: An In Vitro Study,* Int J Clin Pediatr Dent, 2020, **13**(3), 225–229.

[38] **I.** ***Dallel, S. Lahwar, A.M. Jerbi, S. Tobji, A. Kassab****,* *Impact of adhesive system generation and light curing units on orthodontic bonding: in vitro study,* International Orthodontics, 2019, **17**(4), 799-805.

[39] **J. De Munck, B. Van Meerbeek, I. Satoshi, M. Vargas, Y. Yoshida, S. Armstrong, P. Lambrechts, G. Vanherle***, Microtensile bond strengths of one- and two-step self-etch adhesives to bur-cut enamel and dentin,* Am J Dent, 2003, **16**(6), 414-420.

[40] **A.R. Cetin, H. Dinc,** *Effects of artificial aging on the bond strengths of universal dental adhesives,* Niger J Clin Pract, 2020, **23**(8), 1148-1154.

[41] **G.C. Cardoso, L. Nakanishi, C.P. Isolan, P.D.S. Jardim, R.R. Moraes***, Bond Stability of Universal Adhesives Applied To Dentin Using Etch-And-Rinse or Self-Etch Strategies,* Braz Dent J., 2019, **30**(5), 467-475.

[42] **J.M. Powers, K.L. O'Keefe, C. Kaaden, L.M. Pinzon**, *Correlation of inverted cone tensile and microtensile bond strengths,* 2001, Trans Soc Biomater, **24**.

[43] Tokuyama Dental, Report, Technical, *Estelite Posterior.*

[44] **A. Scribante, M. Bollardi, M. Chiesa, C. Poggio, M. Colombo**, *Flexural Properties and Elastic Modulus of Different Esthetic Restorative Materials: Evaluation after Exposure to Acidic Drink,* Biomed Res Int, 4 Feb 2019.

[45] **B. Shea,** *Taking a look at strength and costs of leading bonding agents,* Dental Products Report, 2020.

****