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Mechanical properties of Self- adhesive Resin Cement incorporated with Nano-structured Hydroxyapatite

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ABSTRACT

Objective: This study was to evaluate the effect of incorporation of different concentrationsof synthesizedNano-structured Hydroxyapatite particles (nHAp) on the mechanical properties of Self- Adhesive Resin Cement (SARC).

Methods: Nanohydroxyapatite was prepared by sol-gel method. The nHAp was prepared at four different concentrations (0 ,2, 4 and 6%) wt, nHAP was added to a Self –adhesive dual resin cement (Unicem Aplicap/3M, ESPE, USA) and it was assessed by X-ray diffraction (XRD), Transmission electron microscope (TEM), and pH analysis.Self-Adhesive Resin Cement with nHAp were tested for their Flexural strength (FS), microhardness (VHN) and Degree of conversion (DC).

Results: The characterization results revealed that, nHAp formed in small particles with accumulation have the particles size range between 20-80nm. The incorporation of 4%wt nHAp revealed significant highest mean flexural strength (69.4±10.16 MPa for light cured)**,** micro-hardness means (168±1.23 for chemical mode) and (173.9±5.1 for light cured) andthe incorporation Self Adhesive Resin Cementwith nHAp improved (DC) for all tested groups.

Conclusion: incorporation of Self-Adhesive Resin Cement with nHApenhanced the mechanical properties and might be prospect filler for Self-Adhesive Resin Cement.

Keyword: Self –adhesive resin cement, Hydroxyapatite, Flexural strength, Microhardness, Degree of conversion.

1. INTRODUCTION

The clinical satisfaction of an indirect restoration depends on the luting materials toattain an optimum link between the prepared tooth and restoration. The restorations impair the light that passes through and get to the luting material,various factors affecting on the light intensity such as reflecting ,scattering, and absorbing properties of the ceramic or indirect resin [(1)]which can affect the degree ofconversion (DC).Thus,manytroubles aregenerated by an insufficient degree of conversion, such as inadequate physical and mechanical properties of the resin luting cement and therefore increasing caries prevalence [(2)], which can affect the durability of the restoration. In an attempt to overcome the light attenuation advocated by the indirect restoration, self-adhesive dual polymerization resin luting cement (SARC) were introduced, the dual technique represents the combination of auto-and light polymerization components, which can promote their polymerization in the absence of light .The clinical performance of SARCs depend on ideal polymerization to reveal clinically acceptablemechanical properties . in some clinical situations, such as in dark zones at the optical region and during the cementation of indirect restorations, light attenuation results in a low degree of conversion and jeopardize mechanical properties [(3)], so the self –curing mode of such product is usually less active than the light-activated mode [(4)].

Vast efforts have been made to refine physical and mechanical properties of theadhesive material by enhancing the adhesive with addition of nanoparticles as fillerto prolong restoration longevity. The nHAp have been used in the formulation of restorative composite systems [(5)], adhesives [(6)] and root canal sealers [(7)], with the purpose of enhancingphysical and mechanical properties.

Various methods were conducted for preparation of HAp such as spray pyrolysis, combustion synthesis, sol-gel synthesis, solid-state reactions, chemical precipitation, micro-emulsion and microwave synthesis. Thesol-gel technique is the popular method used to obtain Nano-sized nHAp of high purity. This study was conducted to synthesize nanoparticles Hydroxyapatite using sol-gel method and evaluate morphology, crystalline structure.

SARC has certain limitation in mechanical properties, so many studies were conducted to add nHAp in order to improve of mechanical properties of many materials [5,6,7] .In this study the addition of different concentrations of nHAp to SARC in order to improve mechanical properties of SARC.

2. MATERIALS AND METHODS

Materials

Dual -cure, self –adhesive resin Cement (Rely X Unicem) was used in this study. The material composition, manufacture and batch number were listed in (Table 1).

Table 1: Material used in current study

Material/Trade name	Composition	Manufacture	Bach number
Dual-cured, self – adhesive resin cement/Rely X Unicom.	Powder: Alkaline(basic) glass fillers, silica, calcium hydroxide, Slanted filler, Initiator components and pigments, Liquid: Methacrylate monomer containing phosphoric acid group, Methacrylate monomer, initiator components and Stabilize	3M ESPE, St Paul, MN, USA	55144

Preparation of Hydroxyapatite by sol-gel method

To prepare Hydroxyapatite from chicken egg shell, only white eggs were selected to avoid unwanted color creation. Egg casting were removed for internal crust then cover was lifted lining of the peel and then wash away the chaff very well to be sure to remove the cover lining. The shellswere crushed in mortar casserole to convert into granular form. It was placed into oven 900 C for an hour which converted the material to snow-white powder ,due to the fact that eggshells consist of material calcium carbonate $CaCO_3$ and when heating lead lysis to subjects of carbon dioxide and calcium oxide(CO_2,CaO) and slow addition of 0.6 M H_3PO_4 (Phosphoric acid) to the aqueous(molar ratio) suspension of CaO under constant mixing and formation of(HA) .The creation was cooled to room(22±3) C ,filter using suppression Buchner with washing several times with distilled water and placed in an oven at a temperature of 110 C in order for drying and sterilization.[8]

Dual-cure, self-adhesive resin cement (SARC) incorporated with Nano-Hydroxyapatite particles (nHAp)

To prepare (SARC) with nanohydroxyapatite the following procedure was followed: This type of SAR Ccement (Rely X) is delivered in acapsule,which contain a certain cover at the one end of capsule. The cover was removed and the whole powder of eachcapsule was collected and weighed on a piece of aluminum foil using electrical sensitive balance of 0.0001 accuracy (AZZOTA, USA). TheHydroxyapatite particle was weighed according to the percentage needed (Table 2). The powder wasput in the mortar and nHAp was added gradually; the mixing procedure continued until all the nHAp powder particles were fully incorporated into SARC powder. The mixed powder was divided equally into ten parts and included into original capsules. The mixing methods was performed under safe-light condition using 10 capsules for each weighing. synthesis Hydroxyapatite (HAp) was used in the study in four different concentrations(0,2,4%and 6%) wt.

Table 2: The original weight of the capsules powder (mg) and the concentrations of added hydroxyapatite particles

The original weight of one capsule	The weight of 10 capsules powder	Concentration of HAP	The HAp was weighed for each capsule	The HAp was weighed for 10 capsules
0.230mg	2.3mg	HA 0% HA 2% HA 4% HA 6%	 0.0046 0.0092 0.0138	 0.046 0.092 0.138

Characterization of SARC modified with nHAp:

1.X-Ray Diffraction (XRD) analysis

Standard disc (10mm diameter × 2mm height) were prepared for each SARC and SARC with (2%) wtnHAp, then were analyzed with X-ray diffraction (6000 Shimadzu, Japan) usingCuKa radiation with wavelength (1.54060A) voltage 50.0 Kv current :35.0 mA. All samples were evaluated in the 2θ angle range 10-80 at a scanning speed of 8.0º /min and a step size of 0.02º and step time of 0.15 s.

2.Trasmission electron microscope (TEM)

The morphology of the SARC and SARC withnHAp were evaluated by the use transmission electron microscopy (TEM; Philips CM10, Holand) for this purpose, the samples were prepared by dispersing a little amount of SARC and SARC modified with nHAp powder on acertain film supported by copper grids.

The pH analysis

standard discs (6 mm in diameter and 2mm in thickness) were prepared, 5 specimens for each concentration. The discs were placed in tightly sealed plastic flasks containing 10 ml of distilled water (pH 6.4), and stored at 37°C. Measurement of pH was performed with a pH meter (Weilheim, Germany) at constant room temperature (25°C). The pH was determined after good stirring of the solution for 5s, then insertion of pH electrode in every sample, and measuring on the pH value. Evaluation were performed at period of 24 hours,7,14 and 28 days. The electrode of the pH device was cleaned and calibrated after every reading.

Mechanical properties

Specimen grouping

Forty specimens were investigatedfor each testingatfour different concentrations (0%,2%,4% and 6%) wt. n=5 for each concentration and for each mode of activation.

Mixing of Self-adhesive resin cement incorporated with Hydroxyapatite

SARC incorporated with nHAp at four different concentrations (0%,2%,4% and6%)wt. Was mixed according to the manufacturer's instructions, the capsule was activated with capsule activator for 2s then mixing the capsules using amalgamator device (Silamat, Vivadent, Austria) about 15s, the capsule was handled with Capsule applier.

Curing of the specimens

In the whole testing procedure, the specimens were photo-polymerized by Light Emitted Diode light –curing unit (LED,Guilin wood pecker medical instrument Co., Ltd, Germany) with light intensity output of 1600 mW/cm^2.

Flexural strength (FS)

The test procedure was carried out according to ISO 4049:2000. Forty specimens with dimensions of (2mm width ×2mm height ×25mm length) were prepared usingrectangular stainless-steel splitmold. Themold was mounted on the top of metal plate covered with celluloid strip. The SARC incorporated with nHAp at different concentrations was mixed according to the manufacturer's instructions and placed into the mold. Asecond celluloid strip was placed on the top material and covered with a glass plate. Pressure was applied to express excess material. Move the glass slide about 6mm according to the diameter of light unit device to allow exit window of the external energy source to reach the material. Irradiate that section of the specimen with light cured for 20s recommended by manufactures. Move the exit window to the section next to that previously cured and irradiate for the appropriate time. Continue this procedure until the entire length of the specimen. The mold was turn over and remove the metal plate and repeat the irradiation procedure on the other side of the specimen. Remove the specimens from the mold and carefully remove any flash by gently abrading it with 600 grit abrasive paper, store in distilled water at 37°C for 24 hours. Before the start of testing, the specimens should visually inspected and any specimen having surface defects and/or air inclusion shall be discarded.

For assessment of chemical activation, the same clinical procedure as above wasfollowed exceptwithout light curing. Five specimens were prepared (foreach mode and for each concentration). The flexural strength test was performed using a Universal testing machine (Sans Testing Machine Co., Ltd Shenzhen, China) so each specimen was subjected to athree-point bend. The device which crapsthe bar of cement on 2 supports (20 mm apart), and positioned whichthe width of the bar was in the same direction as the applied force. A cross-headwas placed at the center of the bar loaded, a crosshead speed of 0.5 mm/min and the maximum load was recorded. Flexural strength was calculated in MPa using the following equation: FS =3FL/2WH2[(10)].

F is the load measure applied to the specimens at the point of fracture is the distance between the supports. W is the average width of the specimens, and H is the average thickness of the specimens.

Microhardness test:

Forty specimens with dimensions (8mm diameter ×0.5mm height) were prepared using cylindrical plastic molds. The mold wasputting on glass slides covered with celluloid strip. The SARC incorporated with nHAp at different concentrations was mixed according to the manufacturer's instructions and placed into the mold. The mold was covered with secondcelluloid matrix and cover with glass slide. Pressure was applied to express excess material. Irradiate the specimen for 20s as recommended by manufactures. The light-curing guidance tip with a diameter of 6mm was placed centered and in direct contact with the second Mylar strip. After photo-polymerization, the cylindrical specimens were removed from the molds and the excess material was removed and polished with silicon carbide papers 600 grit paper .The preparation of the specimens that related to the chemical curing mode same as the method above just without light curing .The whole specimens were stored dry in tightly sealed, light-proof containers at 37 °C for 24 hours. Five specimens were prepared (for each mode and for each concentration)-Then each specimen positioned centrally beneath the Vickers microhardness tester(OTTO WOLPERT, Germany) to calculate the Vickers hardness number (VHN).A diamond indenter with a 0.5kg load and a dwell time of 30 seconds was used, four indention were carried out on each surface of specimens and the mean value was calculated and determined as VHN. The diagonal shape can be seen in indentation surface (Fig.1). The Vickers hardness number for each specimen was calculated according to the following equation:

$$VHN = \frac{1.8544 * L}{D^2}$$

Where L = applied load (kg), and D = mean diagonal length (mm).
Where the Vickers hardness number (VHN) has units of kg/mm^2.

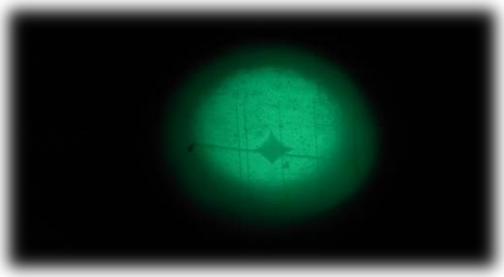

Figure 1: The shape of the diagonal

Degree of conversion (DC)

Forty specimens with dimension (5mm diameter ×2mm height) were prepared using plastic molds. Eachmold was placed on glass slides covered with celluloid strip. The SARCincorporated with nHAp was mixed in accordance with the manufacturers' instruction. Fill mold with material, the mold filled with material was covered with separate celluloid stripand glass slide and pressed with figure pressure to remove the excess. Thespecimen was light cured for 20sas per manufacturer's instructions. The specimens were left undisturbed for 5min to allow polymerization reaction to complete.The whole procedure took place at room temperature (23±1) C.

The chemically cured specimens were prepared in the similar manner as mentioned above but light source was not used, so the specimens were placed into dry and dark container for 5min, Light and chemically cured specimens were stored in dry condition for 24h before testing. The specimens were transferred to the FTIR device.

A FTIR Spectrophotometer used was operated(ALPHA Bruker ,Germany) operated under the following conditions' spectra of the unpolymerized and polymerized SARC were obtained using 24 scans at 4 cm–1 in the absorbance mode and wavelength ranging from 500-3500 cm^{-1} , a little amount of unpolymerized luting cement was also scanned and its spectrum was used as unpolymerized reference .

The degree of conversion was calculated using standard methods that assessed the changes in the ratios of aliphatic C=C bond ($1638cm^{-1}$) tothe aromatic C-C($1608\ cm^{-1}$) in the uncured and cured stateaccording to the equation [11]

$$DC\% = 1 - \left[\frac{1638\,cm^{-1}/1608\,cm^{-1}\ peak\ area\ (after\ curing)}{1638\,cm^{-1}/1608\,cm^{-1}\ peak\ area\ (before\ curing)}\right] \times 100$$

Measurement of DC%value for each groupwas repeatedfivetimes (for each mode and for each concentration) and the mean was reported as the degree of conversion.

Statistical analysis

Data were presented as mean and standard deviation values. One-way analysistest (ANOVA) has been used to study the effect of nHAp concentrations. Duncan's multiple range test was preformed and demonstrated that there is a significant difference between the tested group, Paired-Sample T test was preformed to reveal if there was significant difference between chemical and light mode. Statistical analysis was performed with IBM SPSS, Version 24.

3. RESULTS

nHAp characteristic results

XRD analysis

The XRD patterns of SARC specimens and SARC-modified with nHAp are shown in (Fig.2,3) respectively. The SARC sample (Fig.2) does not reveal any strong or sharp peaks in the XDR patterns, while in the XRD patterns of SARC with nHAp(Fig.3.a) a distinct peak related to the crystalline apatite structure were seen between 30-40 º was match with that of HA(JCPDS 9-432)º(Fig 3.b).These obtained results associated well with those described previously researchers [12].

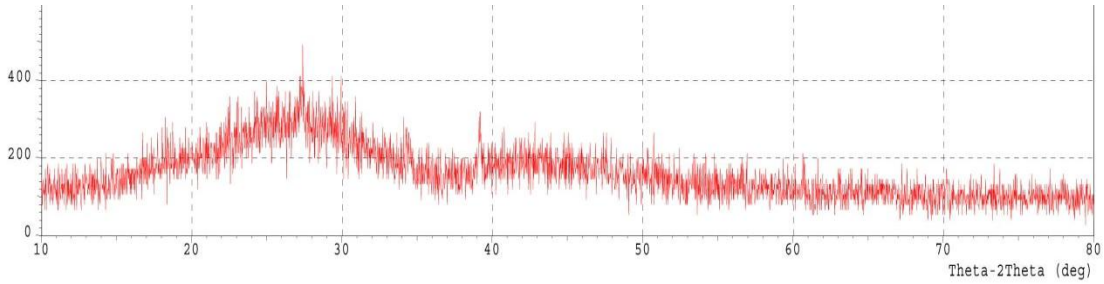

Figure 2: XDR pattern of SARC specimens

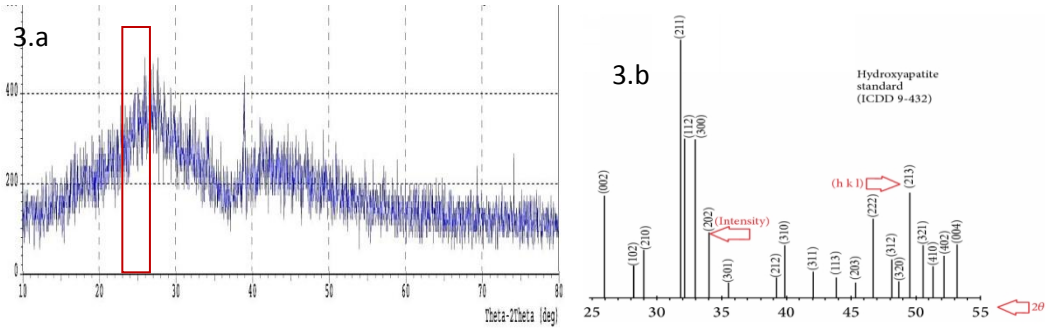

Figure 3: XDR pattern of SARC incorporated with 2% HAp(3.a).The standard XRD peaks of hydroxyapatite (based on ICDD 9–432)(3.b).

FTIR analysis

(Figure 4) represented the IR spectra of the SARC with nHAp .

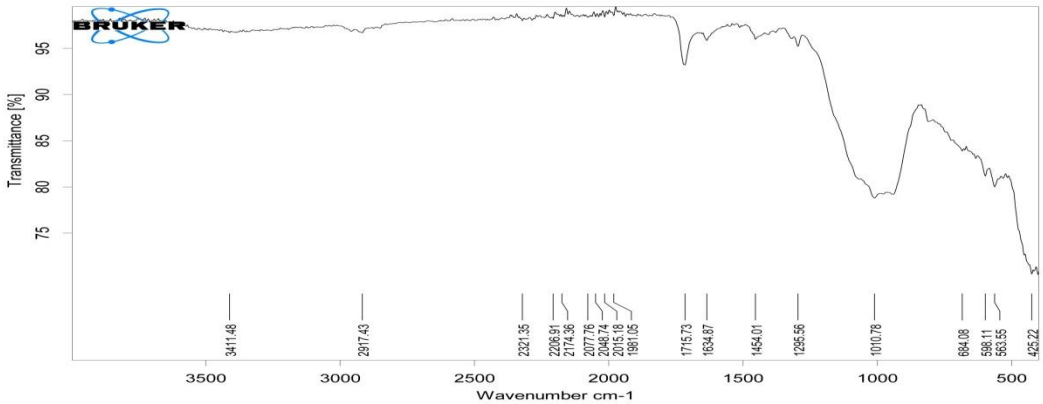

Figure 4: FTIR spectra for the SARC incorporated with nHAp

TEM observation

The TEM micrograph pattern of SARC and SARC with HAp are shown in (Fig.5,6) respectively.The crystalline size of SARC powder was range between 1-6 µm,while the crystalline size of HAp was range between 20-80 nm

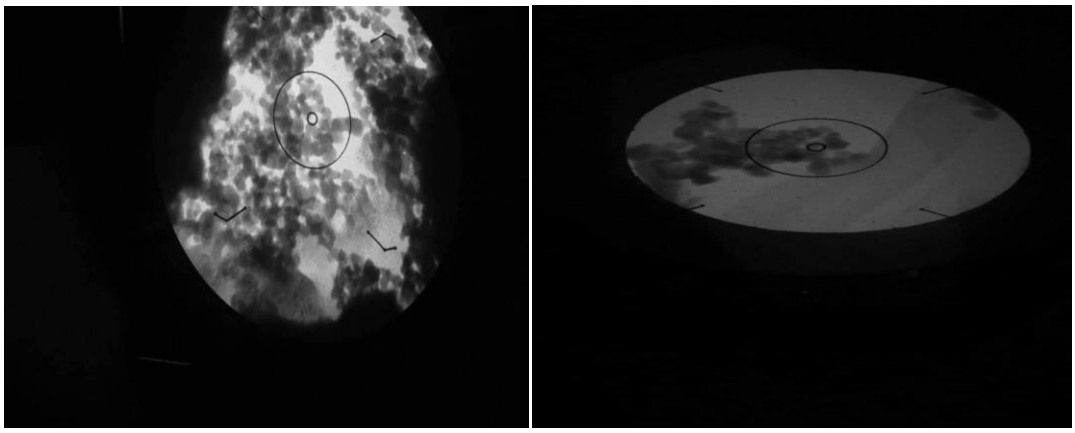

Figure 5: TEM photomicrograph of SARC, Figure(6): TEM photomicrograph of SARC the particles size range between 1-6 µm.with 2%nHAp, the particles size range between 20-80µm.

pH analysis

The means of the pH value SARC and SARC with HAp at different concentrations are presented in(Fig.7) There is an increase in pH value of SARC modified with HAp .SARC gives pH(6.60) after 24 hrs. immersion period and reached (6.8) after 28 days,while the modified SARC gave pH starting with(6.60) and reached(7.1) after 28 days period for different concentration of HAp.

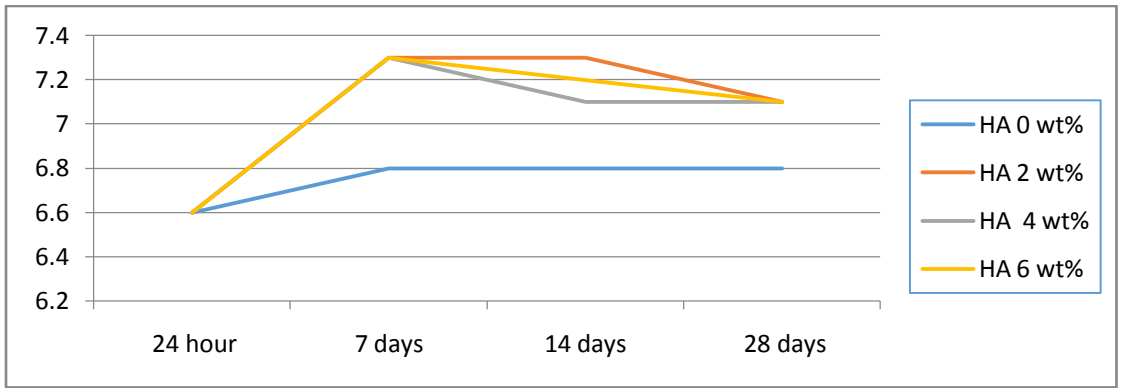

Figure 7: pH profiles of SARC incorporated with different concentrations of nHAp at different periods

Mechanical testing results

Flexural strength

The mean and standard deviation (SD)for different tested parameter atdifferentNano-hydroxyapatite concentrations were presented in (Table 3).

The Flexural strength mean values (Chemical cured), there was no statically significant difference between flexural strength mean values 2%wt and 4%wt HAp(30.6,30.6) respectivelyandflexural strength mean values of 0%wt HAp(31.99).The increase in percentage of HA to 6%wt led to decrease in the flexural strength mean value(17.8). The flexural strength mean values (light mode) were increased as the percentage of HA increased ,the flexural strength mean values 4 %w nHAp group revealed the highest mean statistically significant flexural strength values (69.4±10.16) followed by 2%wt nHApgroup(65.25),where there was no statistically significant difference than 4%wt nHAp group.. The increase in percentage of HA to 6%wt led to decrease in the flexural strength mean value (51.58±1.31). Paired-Sample T reveal there are highly statistically difference between chemical and light mode in all concentrations, flexural strength value for light mode is better than flexural strength value for chemical mode.

Table 3: Mean and standard deviation (SD)For different Nano-hydroxyapatite for different tested

Concentration Of nHAp	Flexural strength				Microhardness				Degree of conversion			
	Chemical cured		Light cured		Chemical cured		Light cured		Chemical cured		Light cured	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
0%	31.99^{Aa}	0.54	52.33^{Ab}	4.81	136.6^{Aa}	3.05	147.8^{Ab}	2.11	32^{Aa}	1.58	87^{Aa}	0.7
2%	30.6^{Aa}	2.5	65.25^{Bb}	2.49	142.7^{Ba}	1.94	149.8^{Ab}	0.82	87^{Ba}	0.89	93^{Ba}	0.7
4%	30.6^{Aa}	2.03	69.4^{Bb}	10.16	154.9^{Ca}	6.63	162^{Ba}	4.73	93^{Ca}	0.7	93^{Ba}	1.2
6%	17.8^{Ba}	0.61	51.58^{Ab}	1.31	168.28^{Da}	1.23	173^{Ca}	5.1	93^{Ca}	1.2	93^{Ba}	1.2

Different capital letter indicate statistical difference in same Column ($p \leq 0.05$).
Different small letter indicates statistical difference in same raw ($p \leq 0.05$).

The microhardness mean values (Chemical cured), the 6 %wtnHAp group revealed the highest mean statistically significant microhardness values(168.28),followed by 4%wtnHAp group(154.9),2%wtnHAp group (142.7) ,and finally the lowest mean values for 0 wt% group(136).The microhardness mean values (Light cured), the 6%wtnHAp group revealed the highest mean statistically significant microhardness values(173),followed by 4%wtnHAp group(162),2%wt HAp group (149.8) ,and finally the lowest mean values for 0 %wt group(147.8). Paired-Sample T reveal there are highly statistically difference between chemical and light mode in all concentrations. Microhardness value for light mode is better than flexural strength value for chemical mode.

The SARC incorporated with nanohydroxyapatite improved DC. The degree of conversion means values (Chemical cured), the 4 wt% and 6wt% HAp group revealed the highest mean statistically significant degree of conversion values (93), followed by 2%wt nHApgroup (87), and finally the lowest mean values for 0%wtgroup (32). The degree of conversion means values (Light cured), there was no statistically significant difference between(0% ,2%,4% and 6%)wt. Paired-Sample T reveal there are highly statistically difference between chemical and light mode in (0%)wt , while there was no statistically significant difference between chemical and light cured in (2%,4 % and 6%)wt nHAp.

4. DISCUSSION

Flexural strength

The Flexural strength was determined the durability and are cement's ability to resist high mastication forces,flexural strength is more important than compressive and tensile strength because the indirect restoration ismore susceptible to bending force than to other types of stress, the flexural strength calculate the tension and compression together simulating the clinical condition [(13)].

The current study revealed that there was significant difference of flexural strength value between chemical and light mode at concentration(0,2,4 and 6%)wt , the incorporation of nHAp has no role on flexural strength value(chemical mode) of modified SARC ,this may be related to role of manufacture of addition of chemical initiator which has negative effect on the mechanical properties of the SARC, the inhomogeneous action between the chemical initiator and inhibitors has adverse effect on the mechanical properties of SARC.The elements responsible for the chemical activation in dual-cured resin cements are not able to compensate the total absence of light and polymerize the cement completely. Resin cements were less effective when not activated by light[(14)]in addition, the polymeric structure formed after the curing process is another important factor in obtaining better mechanical properties, and it may vary according to the composition determined by the manufacturer, this confirm our result that the flexural strength value of modified SARC is more obvious in light mode than in chemical mode.The incorporation of HA concentration at (2,4%)wt for light mode improve the value of flexural strength this may be related, the average particle size of SARC filler <9.5µm [(15)],the particles size of HA nanoparticles (20-80nm) are

comparatively smaller than the particles of SARC ,the nHAp incorporate between the SARC particles creating packing effect [16].

The decrease of flexural strength by increasing the percentage of HA nanoparticles may be due to the refractive index of HA which has high scattering effect [16].

Microhardness

Hardness is considered as one of the most important physical properties to assess the ability of the material to resist a permanent indentation.

HA is the main component of tooth structure; the HA were added to numerous material due to their biocompatible and similar composition to apatite in human dental [17]. The incorporation of HA to certain material can result in improving mechanical properties including the fracture resistance [18].

According to the result of this study a significant difference between SARC and SARC modified with nHAP group, the hardness value will be increased as increased the percentage of HA nanoparticles for both mode (chemical and light mode), this finding may be related that HA reinforced the bond between the filler and matrix. The results obtained in this study were in full agreement with ,Domingo *et al*.,2001 they found that the incorporation of HA with dental composite improve the mechanical properties(Hardness)., Arcis*et al.*,2002[20] they found that the incorporation of a large amount of HA into light cured monomer increase the young modulus and surface hardness, this large amount of HA is considered as reinforcing filler ,Rasheed and Raghad ,2006 they found the addition of different concentration of Hydroxyapatite was enhanced the diametral tensile strength and microhardness of glass ionomer cement . Barandehfard et al.,2016 [12]theyfound that the incorporation of 5 and 8% of HA nanoparticles to the GIC after storage in distilled water 37 C for 1 and 7 days the microhardness were increased.

Degree of conversion (DC):

In this study, Fourier transform infrared spectroscopy (FTIR)was used as analytic equipment for measuring DC.DC is considered as one of quantitative method to assess the durable dentin bonding, so suboptimal DC might reduce interfacial strength and interface instability [22].

The spectrum of material provided information about the composition of material and identified formation of new copolymer [23], therefore FTIR wasused in this study to assess DC of modified SARC firstly and to identify if nHAp has a role in chemical reaction and formation of another compound or just as additive secondly.

The DC(%) of modified SARC was determined from the ratio of the absorbance intensities of aliphatic C=C (peak at 1638cm^{-1})against the internal reference aromatic C-C(peak at 1608cm^{-1})before and after to curing [11].According to this study, the IR analysis for modified SARC(Fig 4 explain as :The band that appear at 470,509 and 600cm^{-1} related to the phosphate bending vibration [24] .Peak reveal at 800,1000 and1100 cm^{-1} which ascribe to Si-O-C, Si-O-Si and Si-OH linkage. These absorptions are related to the presence of Silica as one of the fillers and possibly Vinyl –silane, used as coating of the filler.

The infrared absorption revealed 650,900,650,1000, and1300 $cm^{-1}$and the interval between 1510,1580,1620, 1638and1716 cm^{-1}, these are related to the symmetric and asymmetric stretching of the ester carbonyl double linkage of the vinyl monomer and stretching and bending of the C=C and C-H link of the aromatic ring [25].

The band at 1420cm^{-1} was related to carbonate ions (CO_3^{-2}) incorporated with hydroxyl ions (OH^-)[26]. The bands reveal at 634 and 3571cm^{-1} infirm the presence of bending and stretching hydroxyl ion vibration respectively [3].

This type of SARC has suboptimal DC due to change in viscosity during the auto polymerization reaction which reduce the ability of the radical to migrate and continue the conversion reaction[27]so the presence of oxygen in voids interrupted during mixing could retard polymerization [28],other causes is attribute to the suboptimal concentration of inhibitors added to the material [4],inhibitors are added to SARC in order to increase working time for manipulating the material and /or promote the self-life[4] the inhibitor has a role in reducing the curing rate[30].According to the result of this study the incorporation of nHAp lead to improve DC of modified SARC especially the Chemical cure,the HAp has a role in elevating the pH (Fig.7) and led improving the DC of SARC.

Zang and Wang (2012)[22] revealed that the incorporation of small amount of HA could lead to elevate the (pH) and significant improvement DC.

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