

Synthesis and characterization of new compo glass dental fillings using Nano Calcium Fluoride

Abstract

It was known that fillers play an important role in restorative composite filling. In the present work new composite resins were synthesized including M1-M10 and N1-N4 with various constituents' ratios of glass fillers. Nano CaF_2 particles were replaced the normal sized powders studied in our previous work. Physical characterization of glass fillers the Nano compo glass filling including shrinkage strain, depth of cure, degree of conversion and thermal expansion coefficient were studied and showed an increasing of the above properties, thermal expansion was found to varies between 2.28-36.4. Water absorption and water solubility decreased in comparison with standard values. Mechanical properties of the compo glass studied which include flexural strength was found around 95-135 MPa while the diametric strength (DTS) showed a value of 46-60 MPa especially on using 10% Nano CaF_2 .

Keywords: compo glass, dental filling, Nano Calcium Fluoride

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Introduction

The influence of Nano particle and surface area are important on the properties of the Nano composites. The interphase development and the resulting Nano composite properties have been shown to be greatly affected by Nano particle such as size, shape, aspect ratio, concentration and surface chemistry. Many experimental studies have been performed to understand the employment of particle morphology (size, shape, and aspect ratio) on Nano composite properties. Mechanical properties, such as strength and modulus, have generally increased with decreasing particle size in polymer Nano composites,¹ and direct comparisons between micron-scale and Nano scale particles showed improved mechanical properties in Nano composites when compared with the same filler loading.² Much work has focused upon varying the glass components to reduce shrinkage and improve the mechanical properties and also to prevent bacterial microleakage.³ Shahin et al.,⁴ have used Nano silver within filler to increase the physical property of composite as well as anti bacterial action. Nano gold and Nanosilver composites exhibited higher micro hardness in comparison to non-modified resin composites higher Diametric Tensile Strength.⁵ Many researchers have studied composite compositions on their properties. These effects includes Filler effects,⁶ effects of coupling agent used⁷ and monomer effects⁸ TiO_2 has been used as filler to improve mechanical properties of composites⁹ which showed improvements of micro hardness and flexural strength. Monika et al.,¹⁰ have investigate the mechanical properties on addition 0.5-5%wt CaF_2 of composite and found that addition of 0.5-1.0% will increase the tensile strength. In our study we used Nano CaF_2 to improve the mechanical properties of the composite resin and the depth of curve while the micro leakage of fluoride ion as Caries-prevention Fillers will be our next work.

Experimental

All glass components were Annular, CaF_2 preparation and characterization was presented in our previously published work.^{11,12}

Compoglass synthesis

The glass containing six component (SiO_2 , Al_2O_3 , CaF_2 , AlPO_4 ,

AlF_3 , and NaF). The weight ratio between $\text{Al}_2\text{O}_3/\text{SiO}_2$ change between (0.516 to 0.86). Two method of preparation were used in glass synthesis, the first group A: slowly cooling (N1, N2, N3, and N4). The second group B: melt-quench route (M1 ... M10). Each batch (50g) of different compositions belonging to two types was prepared by weighing out the components required according to the pre-planned formula (Table 1). The powders were mixed by subjected to vibratory milling and homogenization for 30min, the resulting mixture as-milled powders were sieved and particles within size $<75\mu\text{m}$ were isolated. The selected particles were placed into a recrystallized alumina crucible and placed in an electric furnace. The glass melting operation consisted of several stages which include preparation of batch, melting, conditioning, quenching and followed by powder production by ball milling.

Glass synthesized by slowly cooling route (Group A)

The homogenized batch was transferred into a recrystallized alumina crucible and placed at the centre of a raising furnace. Using ivoclar bivalent program at P500 the range of temperature 1200°C Germany. The melting process was initiated at a heating rate of 10°C/min from room temperature to temperature of furnace reached to around 1200°C. When the furnace temperature reached the fusion temperature (1150-1200°C), batch was subjected to melt homogenization for 60min. slowly cooled (the temperature was decreased to room temperature) at a rate of 25°C/min let cool down to room temperature.

Glass synthesized by melt quench route (Group B)

The second method to synthesized glass, the homogenized batch was transferred into a recrystallized alumina crucible and placed at the centre of a raising furnace using MIHM- VOGT P6/B GERMANY to 1200°C. The furnace temperature was set according to the fusion temperature of batch mix. The melting process was initiated at a heating rate of 5°C/min from room temperature to temperature of furnace reached to around 500°C after which a heating rate was increased to 10°C/min. When the furnace temperature reached the fusion temperature (1150-1200°C), batch was subjected to melt homogenization for 60min. The raising heat was quickly moved down.

The raising hearth was quickly moved down and the resulting glass melt was poured directly into a water container to produce granular glass frit. Resultant glass frits were collected and dried, and then it was ground manually by using agate mortar and pestle. Subsequently dry ball milling using (RETSCH. PM 100 Germany) was performed using zirconium balls with diameter cm for 90min. The resulted powder was passed through a sieve to retrieve a powder with mean particle size of <25µm Sieve shakers SCL-SD8-12 Iran and sieve mesh 500 for

sieving powder to get particles <25µm. Table 1 shows the privileges of the results of the studied samples physical and mechanical properties. The order of the samples is in the following order: M2... N4, M1. In our analysis of the Nano, we have chosen the first three samples of the composites, because they proved to be the best with regard to the physical and mechanical properties. In this paper materials used and following the same vein composites and method of preparation as well as the method of measurement used.¹⁰

Table 1 General composition of Calcium fluoroaluminosilicate glasses (in W%)

Sample	SiO ₂	Al ₂ O ₃	CaF ₂	Al ₂ PO ₄	AlF ₃	NaF	SiO ₂ /Al ₂ O ₃	Fusion temperature (°C)
M1, N1	22	18		22	15	23	0.8181	1200
M2, N2	22	19	10W%	39	13	7	0.8636	1200
M3, N3*	29	16.6	34.2	9.9	5.3	5	0.5742	1200
M4, N4	35	25	20	8	6	6	0.7142	1200
M5	39.52	23.6	13.65	3.62	9.7	9.91	0.5971	1200
M6	24.3	27.5	14	19.1	15.1		1.1361	1200
M7	33.9	17.5	8	15	10	15.6	0.5162	1200
M8	56.5	33.5				10	0.592	1200
M9	48.9	29.1	15			7	0.5905	1200
M10	36.3	22	12	9	14.3	6.4	0.59	1200

Results and discussion

The discussion is divided into two parts. The first part, Related to the treatment of the CaF₂NPs. The second part addresses the Nano composites physical and mechanical properties due to filler incorporation

Synthesis of Nano composites dental material

Surface modification of CaF₂NPs

As mentioned earlier in our previous paper¹⁰ CaF₂NPs having specific surface area about 25m²/g. The theoretical loading of silane was calculated to be ~1.5wt.% for CaF₂NPs grafted with γMPT assuming that all silane provided during the reaction formed covalent bonds with silanol groups on the particle surface. After treatment of the CaF₂NPs surface by γMPT, the surface was investigated by FTIR spectroscopy and TGA. Figure 1 shows the FTIR spectra of the chemical structure of CaF₂NPs. The CaF₂NPs exhibited strong absorption peaks at around 1460 and 1650cm⁻¹ assigned to the =CH stretching vibrations and C=O bending vibrations, respectively. At 1121cm⁻¹ absorption peak is assigned to Si-O, weak absorption peaks at around 1720cm⁻¹ due to the stretching vibration of ester carbonyl group, a medium band at 2928cm⁻¹ related to the CH₂- of the coupling agent and weak but visible absorption peaks at 3130cm⁻¹ are assigned to the -OH. Also the theoretical value for silane density on the surface was calculated from TGA data Figure 2. Table 2 shows the mass loss for CaF₂NPs about 1.4%. This value is in good correlation with TGA results for CaF₂NP. Results obtained for silane loading of CaF₂NPs are relatively low.

Sample preparation

To determine the weight percent of filler (Wt%= weight fraction of filler (100%). Volume percent of filler could then be calculated based on filler weight percent, filler density and composite density, according to following equation

$$\text{Vol}\% = \left(\frac{\rho_C}{\rho_F} \right) \times \text{Wt}\%$$

Where Vol% volume fraction of filler *100%, C and F are density of the composite and filler, respectively. The respective series of composites, namely M1, M10, and N4, The total filler included the CaF₂NPs 76% wg% (~58% vol), for each composites three ratio of Nano filler loading 5%, 10% and 15% Vol, The CaF₂NPs mass ratio was determined by weight.

Characterization of Nano composite

Physical properties

Shrinkage strain and rate of shrinkage

Figure 3 shows the typical shrinkage strain curves for the M10 tested Nano composites 5%, 10% and 15% %Vol, respectively. It clearly shows the ratio 10%vol has low shrinkage. The result of shrinkage strain for Nano composites were shown in Figure 4 & Table 3.

Depth of curve

Figure 5 & Table 4 show the depth of curve for tested Nano composites according to ISO 4049:2000, it varies between 3.2mm for M1, 5% Nano and 3.4mm for M10, 10% Nano.

Degree of conversion (DC)

Conversion values obtained from the FTIR results as shown in Table 5 & Figure 6. The degree of conversion for all Nano composites varies between 57.8 and 81.2 for M1, 5% Nano and M1, 15% Nano respectively. All values of Nano composites are nearly lower than M1 composites.

Thermal expansion coefficient

Linear coefficients of thermal expansion CTE were calculated for temperature ranges 0 to 60°C as show in Table 6. Less CTE obtained in the ratio 15% for all nanocomposites tested 42.28, 36.47 and 36.40 for M1, M10 and N4 respectively (Figure 7) (Figure 8).

Water sorption and water solubility

Table 7 shows the mean water sorption and water solubility for each three Nano composites, illustrated in Figure 9 for water sorption and Figure 10 for water solubility.

Density

(Table 8) (Figure 11)

Mechanical properties

Flexural strength and flexural modulus

Table 9 shows the means and standard deviations of flexural strength and elastic modulus. Under the conditions of 40 sec light irradiation at a power density of 500mW/cm², results of flexural strength and elastic modulus ranged from 90.5 to 135.1MPa and from 4.7 to 7.6GPa, respectively (Figure 12) (Figure 13).

Diametrical tensile strength (DTS)

Mean values and standard deviation of the DTS of the tested materials are shown in Figure 14 & Table 10. The values varied from 46MPa to 60MPa.

Dental restorative materials should mimic as much as possible the physical behavior of the tooth and approximate the mechanical properties of enamel and dentin. Thus, any differences in properties may be attributed to the different Nano composite formulations evaluated. Besides irradiation temperature, host temperature and environment, the irradiation regime, light intensity and exposure duration, intrinsic factors such as monomer system, concentration of the catalyst, amount of filler, filler type, size and coupling agent used have been shown to affect the curve of Nano composites reins. Light intensity of 500mW/cm² for 40seconds has been chosen based on the recommendation by manufacturers for most commercial materials to ensure maximum cure. This study was specifically designed to compare and to evaluate the recent Nano composites, using Nano technology in composites fabrication, which is claimed to have superior mechanical properties than the commonly used hybrid and the mono-filled composites. The improvement of Nano filled composite used comes from its fabrication property where its filler particle size ranges from (0.005-0.01 microns). These very small

particles will not interact with the visible light and as a result will not cause scattering which leads in modulus of elasticity, depth of curve and esthetics Shrinkage.

The results of depth of curve showed that, a significant difference was found between the three tested composites ratio, where the 10%vol of Nano composite recorded the best depth of curve followed by Nano filled composite then 5%. Utilization of Nanotechnology is very clear in terms of reducing the CTE decreased from $50 \times 10^{-6} \text{ } ^\circ\text{C}$ to $36 \times 10^{-6} \text{ } ^\circ\text{C}$ in the ratio of 15% and this is a good indicator and a new relationship with the proportion of Nano and CTE for Nano composite. International Organization for Standardization (ISO) specification 4049 for polymer-based restoratives classifies dental polymer classified restorative materials into two different types. The first type is type I which is the material claimed by the manufactures to be appropriate for restoration involving occlusal surfaces. The second type is type II which includes all other polymer-based filling materials. The lowest value of flexural strength required for type I is 80MPa and 50MPa for type II {ISO, 2000}. In this study all materials investigated showed higher mean flexural strength values than ones recommended by the ISO suggesting that these materials can be used as direct restorative materials.

The diametric tensile strength is a property which is suited only for testing brittle material. For this reason, the tensile strength of these materials may be considered to have more clinical relevance than the compressive strength. So Compressive strengths of various composites are about the same, but DTS of some Nano filled composites may be lower than the other Nano filled or hybrid composites. The DTS mean values of the composites tested in the present study are in the DTS range of dental composites, 30-55MPa.¹³ Results of the present study showed that, some Nano filled composites may have lower DTS than the other composite resins (Table 5). The results (in MPa) obtained in this study is similar to the average previously recorded as 38.69 for Palfique Estelite, 44.6MPa for Esthet X and 44.42MPa for Supreme. Mota et al,¹⁴ determined the diametric tensile strength results ranged from 49.24MPa (± 7.10 , Grandio enamel) to 36.08 (± 8.71 , 4 Seasons dentin),¹⁴ and ERL4221 Epoxy resin 28MPa M50 42MPa G60 47MPa Commercial methacrylate Composite 50MPa.¹⁵ However, in our study results are different because large particle size showed lower values of DTS. This could be due to a very high filler contents or large filler particle size that may interfere with light penetration during polymerization and influences the DTS of the material. The Overall results obtained from the present study were in accordance with the previous studies mentioned before^{1,11,12,17,18} and ADA No27 Resinbased Filling Material1993.

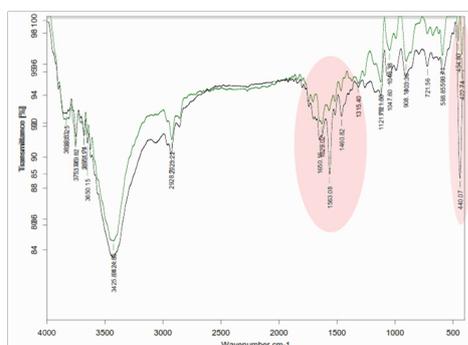


Figure 1 FTIR spectra of the untreated and treated CaF2NPS.

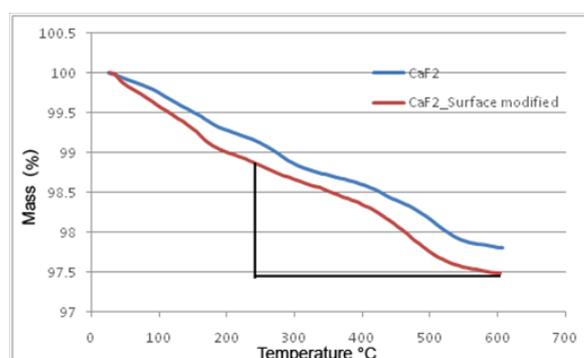


Figure 2 TGA of the untreated and treated CaF2NPS.

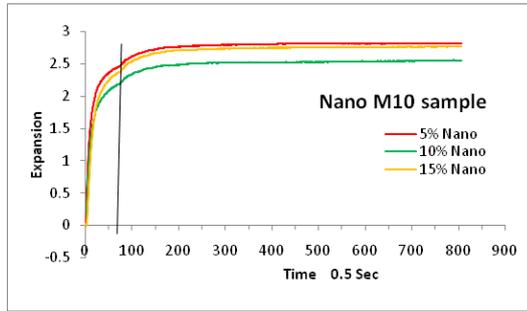


Figure 3 Shrinkage curve and rate of polymerization for M10 Nano composite tested.

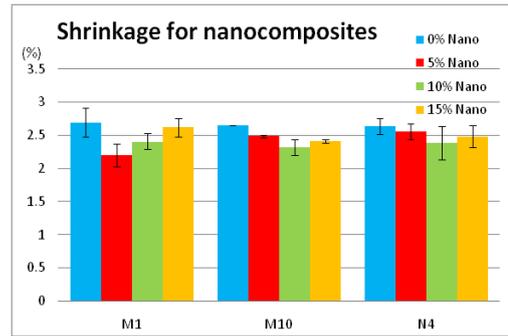


Figure 4 Shrinkage polymerization for Nano composite tested.

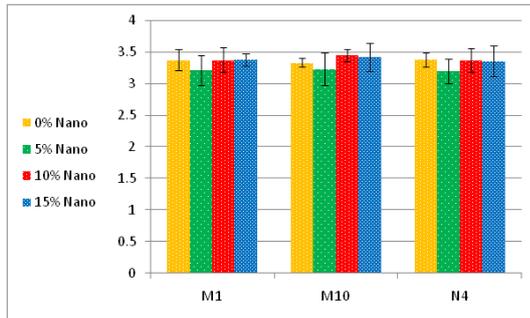


Figure 5 Depth cure for Nano composites tested.

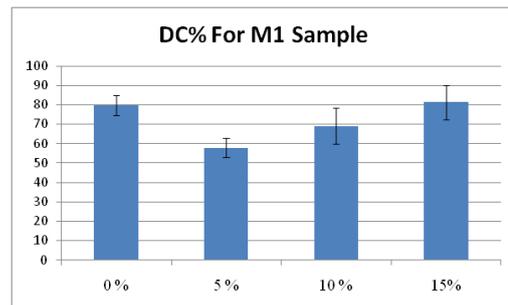


Figure 6 Degree of conversion for Nano composite tested.

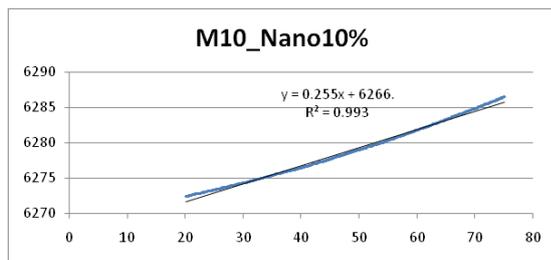


Figure 7 Shrinkage curves and rate of polymerization for M2 composite tested.

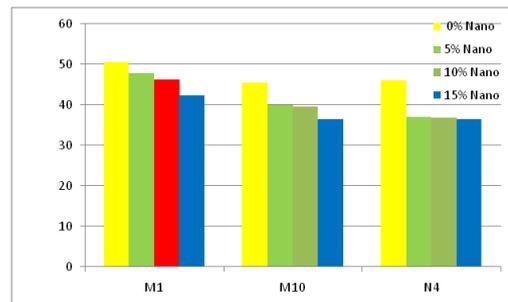


Figure 8 Mean of CTE for Nano composite tested.

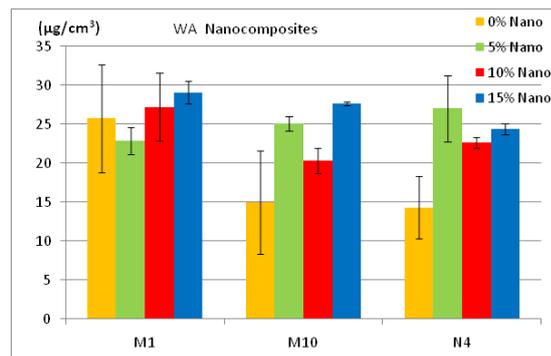


Figure 9 Water sorption for Nano composite tested

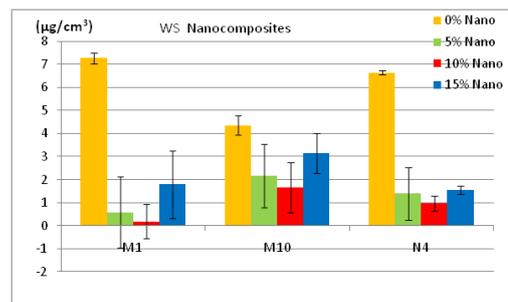


Figure 10 Water solubility for Nano composite tested.

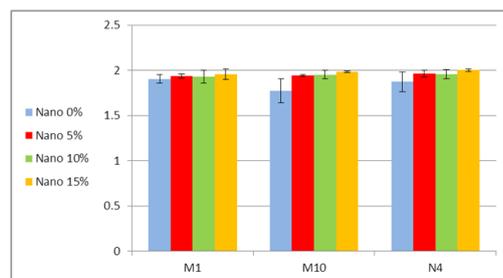


Figure 11 Water solubility for Nano composite tested.

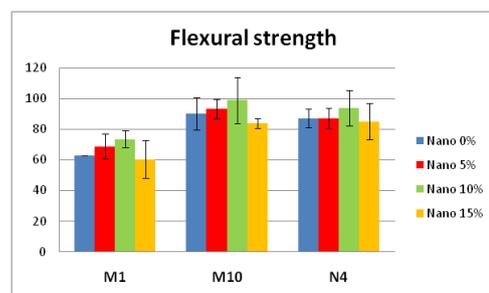


Figure 12 Mean and stand flexural strength (MPa) of Nano composites.

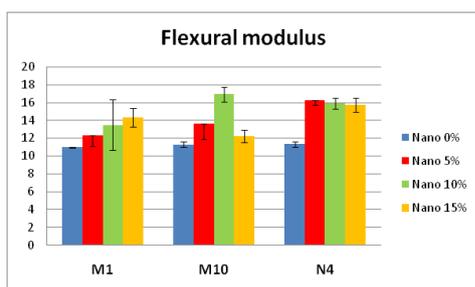


Figure 13 Mean and stand flexural modulus (GPa) of Nano composites.

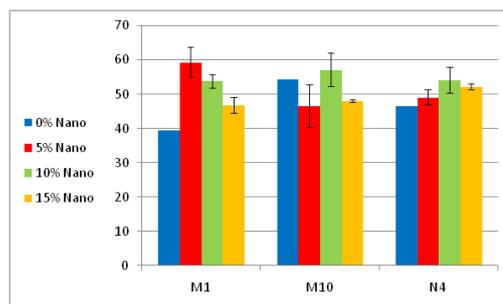


Figure 14 Mean and stand DTS (MPa) of Nano composites.

Table 2 Mass loss determined by TGA for CaF₂NPs

Filler	Temperature °C	Mass loss (%)
CaF ₂	20 -250	1.3
	250-600	1.4

Table 3 Mean values, standard deviation shrinkage and rate of polymerization for nanocomposite materials tested

Sample	Ratio Vol%	Mean 40s (%)	Mean 400s (%)	Stnd	Rate of shrinkage
M1	0	2.69653	0.447545	0.224337	0.36256
	5	2.202877	0.329378	0.171501	0.10197
	10	2.405737	0.358783	0.11901	0.14729
	15	2.619673	0.371447	0.136026	0.13596
M10	0	2.65122	0.402225	0	0.402215
	5	2.488823	0.332347	0.017307	0.23793
	10	2.32265	0.287027	0.119905	0.211493
	15	2.41329	0.366337	0.03399	0.151067
N4	0	2.63989	0.37839	0.128184	0.43054
	5	2.556803	0.381443	0.116282	0.162397
	10	2.386853	0.30591	0.251397	0.143513
	15	2.485047	0.324793	0.163926	0.12463

Table 4 Mean values, standard deviation depth of cure for Nano composite tested

Composites	Ratio Vol%	Mean (mm)	STND
M1	0	3.378667	0.169362
	5	3.218333	0.236012
	10	3.376	0.195768
	15	3.381667	0.092036
M10	0	3.335333	0.068975
	5	3.230333	0.257313
	10	3.4545	0.099514
	15	3.426	0.219674
N4	0	3.381667	0.112934
	5	3.2005	0.197011
	10	3.375333	0.189579
	15	3.365333	0.242501

Table 5 Degree of conversion for Nano composite tested.

Composites	Ratio Vol%	Mean (%)	STND
MI	0	79.57675	5.199894
	5	57.83266	4.872907
	10	69.09447	9.180454
	15	81.26278	8.716959

Table 6 Thermal expansion coefficient for Nano composite tested

Sample	Ratio Vol%	α ($^{\circ}\text{C}^{-1}$) $\times 10^{-6}$
MI	0	50.55786
	5	47.81328
	10	46.30656
	15	42.28836
M10	0	45.50218
	5	39.90676
	10	39.521
	15	36.47236
N4	0	46.04658
	5	36.98827
	10	36.89852
	15	36.4032

Table 7 Mean and stnd water sorption ($\mu\text{g}/\text{mm}^3$) of nanocomposites

Composites	Ratio Vol%	WA		WS	
		Mean ($\mu\text{g}/\text{cm}^3$)	Stnd	Mean ($\mu\text{g}/\text{cm}^3$)	Stnd
MI	0	25.77887	1.466872	7.270188	0.243169
	5	22.8953	4.364397	0.582336	1.539856
	10	27.2515	1.767654	0.186585	0.753892
	15	29.11806	6.922581	1.793822	1.466621
M10	0	14.98267	0.224258	4.348899	0.415229
	5	25.09069	1.672969	2.172158	1.388488
	10	20.32313	0.975839	1.661679	1.083563
	15	27.70239	6.652069	3.148318	0.868841
N4	0	14.32436	0.700863	6.640988	0.0994
	5	27.03722	0.727628	1.390702	1.130795
	10	22.66344	4.220939	0.978282	0.325707
	15	24.41149	4.010647	1.556729	0.171209

Table 8 Mean and stnd Density (g/cm^3) of Nano composites

Sample	Ratio Vol%	Mean (g/cm^3)	Stnd
MI	0	1.903757	0.048574
	5	1.936276	0.027142
	10	1.927614	0.070136
	15	1.9571	0.05487

Table Continued

Sample	Ratio Vol%	Mean (g/cm ³)	Stnd
M10	0	1.772326	0.133672
	5	1.943233	0.007637
	10	1.952311	0.046726
	15	1.983795	0.006894
N4	0	1.873287	0.110015
	5	1.964389	0.037213
	10	1.95734	0.049236
	15	2.001096	0.012715

Table 9 Flexural strength and flexural modulus of Nano composites tested

Composites	Ratio Vol%	Flexural strength		Flexural modulus	
		Mean (MPa)	Stnd	Mean (GPa)	Stnd
M1	0	62.93596	0.15309	10.981	0.057983
	5	68.71951	8.233859	12.28425	1.168859
	10	73.57332	5.469343	13.478	2.820669
	15	60.37538	12.22762	14.291	1.044986
M10	0	90.359	10.50998	11.2945	0.316077
	5	93.12621	6.278888	13.5995	1.714606
	10	98.97776	14.98424	16.92925	0.812253
	15	83.94602	3.285471	15.2065	0.681596
N4	0	88.93967	6.062721	11.311	0.271529
	5	87.15236	6.494254	16.24675	0.496409
	10	93.65408	11.58008	16.9045	0.578345
	15	85.13067	11.89042	16.967	0.789995

Table 10 Mean values and standard deviation of the DTS of the tested materials

Sample	Ratio Vol%	DTS	Stnd
M1	0	39.4435	
	5	59.37527	4.334703
	10	53.86682	1.933219
	15	46.8025	2.269279
M10	0	54.2754	
	5	46.63958	6.169905
	10	57.15533	4.831871
	15	47.98071	0.381999
N4	0	46.58681	
	5	49.12546	2.231517
	10	54.19722	3.696052
	15	52.20782	0.931917

Conclusion

Adding Nano technology caused to a decrease in the liner thermal coefficient of expansion to drop from $50 \times 10^{-6} \text{C}$ to $36 \times 10^{-6} \text{C}$ while using the ratio of 15%, it is gradually decreased. The employment of Nano particles is also cause to increase in the flexural strength and achieved a 10% higher strength while it decreased in using 15% ratio. As a conclusion, Using 10% of Nano filler of Nano composites showed potential for use as dental restoratives and present a promising approach to achieve novel low shrinkage and water sorption, high flexural strength for all Nano composites tested and also higher depth of curve (more than 3mm) which is novel result compared with the conventional value of just 2mm.

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Conflict of interest

The author declares that there is no conflict of interest.

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