Evaluation of Thermal Conductivity and Some Other Properties of Heat Cured Denture Soft Liner Reinforced By Halloysite Nanotubes

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This study aimed to assess the effect of halloysite nanotubes(HNT_S) addition into soft denture lining material on thermal conductivity and thermal diffusivity, shear bond strength, tear strength, and surface roughness of the lining material. HNT_S with 0.75% and 1% concentration by weight (according to the pilot study) were added into acrylic-based heat cured soft denture liner. One hundred and twenty different specimens were prepared and divided into four groups according to the test to be performed. The thermal conductivity and thermal diffusivity of the soft liner/ HNT_S composite were evaluated, shear bond strength, tear strength, and surface roughness were also measured, the results showed that there was a highly significant increase in thermal conductivity of the experimental specimens in comparison with the control specimens and a non-significant change in the thermal diffusivity of the experimental specimens. The shear bond strength between the soft liner and the acrylic denture base and tear strength showed a highly significant increase, but a non- significant difference in the surface roughness test was observed in all experimental specimens. Thus it can be concluded that the addition of HNT_S can provide soft liner material with improved thermal conductivity, shear bond strength and tear strength while thermal diffusivity and surface roughness were non-significantly changed when the concentration of HNTs nanoparticles increased.

Keywords: Soft denture liner, Thermal conductivity, Shear bond strength,
tear strength, Halloysite Nanotubes.

Soft denture liners are materials used to distribute functional loads homogenously on the denture-bearing tissues in complete and partial removable dentures [1].

The denture should be relined when the underlying residual ridge resorbed and the denture will lose its accurate adaptation on this resorbed ridge, so the soft liner is utilized to improve denture's fitting to the underlying supporting tissues, occlusion, retention, stability and patient's appearance [2].

The resilient lining material can be divided into plasticized acrylic resin or silicone elastomers. The plasticized acrylic resin involves of acrylic polymers and copolymers, a liquid containing an acrylic monomer and plasticizers that is responsible for the protection of the material softness. The silicone liner comprises of dimethyl siloxane polymers which devoid of leachable plasticizers and preserve their elasticity for long period [1,3].

Soft denture liners should be nontoxic, odorless, non-irritant, easily processed, no change in color, acceptable aesthetics, no dimensional changes should occur during processing, have low water absorption and solubility, should have sufficient mechanical strength, abrasion resistance and tear resistance, inhibit fungal growth and should bond sufficiently well to polymethyl methacrylate(PMMA) to avoid separation during use [1-4].

A number of problems accompanied with the use of resilient denture liners, including bond failure between the liner and denture base, colonization by *Candida albicans*, loss of softness, porosity and poor tear strength [1,5].

The polymers including polymethyl methacrylate(PMMA) and polyethyl methacrylate(PEMA) have low thermal conductivity compared with cobalt or any other metal alloys that used as a denture base material and this can prevent any sensation of heat which can lead to scald the back of the throat and possibly even the whole esophagus as the patient consuming hot drink without realizing it [6,7].

Several modifications have been done recently to overcome these problems and improve the thermal properties, tear strength and bonding of the polymer. These methods included the addition of Nano particles such as zirconia, glass fiber, alumina and silver nanoparticles [6-8].

To improve the properties of polymer nanocomposites that result from incorporation inorganic nanoparticles are depend on the type of incorporating nanoparticles, their shape and size, also their concentration and interaction with the polymer matrix [6].

Halloysite nanotubes (HNT$_s$) are natural Nano sized tubulars clay mineral that has many potentially important applications uses in different industrial fields [9-11] .The multilayer tubular structure of halloysite results from the wrapping of the 1:1 clay mineral layers under favorable geological conditions. HNTs have different composition of inner and outer surfaces that allow for different modification methods [12,13].

In the present study HNT$_s$ were incorporated into acrylic-based heat cured soft denture lining material in an attempt to improve thermal conductivity and thermal diffusivity and some of mechanical properties.

MATERIALS AND METHODS

A pilot study of thermal conductivity , thermal diffusivity and shear bond strength tests were performed and four concentrations of the nanotubes material were used (0.5%,0.75%,1% and 1.5%) to select the most appropriate and effective concentration of HNT$_s$ for each test and according to the results of this pilot study for the previously mentioned tests, 0.75% and 1% of HNT$_s$ were the most appropriate concentrations because these concentrations showed favorable improvement in thermal conductivity and shear bond strength of the soft liner material. Moreover, according to the pilot study 0.5% and 1.5% concentrations were canceled because 0.5% had minimum effect on the properties while deterioration might be occurred with 1.5% concentration. Therefore; the main study was conducted by addition of halloysite nanotubes powder (Nano Shel, USA) with concentration of 0.75% and 1% by weight into polyethyl methacrylate soft denture liner (PEMA) (Vertex™ Soft, Vertex-Dental, Netherlands). One hundred and twenty different specimens were prepared and divided into four groups according to the tests to be performed. Each group was then subdivided into three subgroups according to weight percentage of HNTs which was added, (a control group without HNTs, and experimental groups with0.75 and 1% HNTs). For each percentage 10 specimens were fabricated, totally 30 specimens for each test.

Scanning electron microscope (AIS2300C, Angstrom Advanced Inc., USA) was taken for both control (PEMA) and experimental (containing 0.75% and 1% HNT$_S$) specimens to show the degree of HNT$_S$ dispersion within the PEMA matrix. As well as energy dispersive X-ray spectroscopy(EDS) used in conjunction with scanning electron microscopy to show the percentages of composite filler of both weight and atoms.

Fourier transform infrared spectroscopy (FTIR) analysis (Tensor 27, Bruker, Germany) was conducted to investigate the chemical interaction between HNT$_S$ and PEMA.

Furthermore; X-ray diffractometer (XRD-6000, Shimadzu, Japan) was used to study crystal structures of nanoparticles.

Thermal properties tests

Ten disc specimens were prepared for each

group:(A) control i.e., PEMA without HNTs, (B) experimental i.e., PEMA with 0.75% HNTs and (C) experimental i.e., PEMA with1%HNTs (Total: 30 specimens). The discs were with dimensions of 40 mm in diameter and 2.5 mm in thickness according to instrument's specifications were prepared for thermal properties tests. For experimental specimens HNTs were weighed by a digital balance with accuracy of (0.0001g),then added into the liner monomer and dispersed by using probe sonication apparatus (Soniprep-150, England) for 3 minutes to break them into individual nanoparticles, then the mixture was cooled down by placing the container in a cooling bath[14]. After that ,the powder of the soft lining material was added into proportion of (Powder/Liquid ratio: for each 1.2g of powder/1ml of liquid monomer)and then mixed, packed and cured according to manufacturer's instructions.

Later after complete curing, all the specimens were finished, polished and immersed in distilled water and kept in the incubator at 37°C for (48) hours before testing. The specimen's thermal conductivity and diffusivity were measured with the hot disk thermal constant analyzer (Tps-500, Kiteley, Sweden) (Figure 1), which consist of an electrically conducting pattern in the shape of double spiral extend out of a thin sheet of Nickel foil that was chosen because of its high and well known temperature coefficient of resistivity.

The equipment connected to computer that are programmed for the test and the hot disk must be turned on about 1 hour prior to making experiment, then the studied specimens will be placed between stainless steel sample on the sensor of the hot disk after chosen the parameter for polymer, later the reading could be taken from the computer after 15 minutes which had the thermal conductivity and thermal diffusivity[6].

Shear bond strength test

Thirty acrylic blocks with specified dimensions (75mm × 25mm × 5 mm length, width, depth respectively) with stopper of depth about 3mm were made to evaluate shear bond strength test, then according to manufacturer's instructions heat cured acrylic resin (Acrosun, Turkey) blocks were made[15].

After that each specimen of shear bond test was consisting of two blocks of acrylic base set over each other forming a space between them measured (25mm × 25mm × 3mm length, width,

depth respectively) to be filled with wax .Then the whole specimen was invested into silicone material inside a custom fabricated metal flask to fabricate a mold for final specimen curing .Wax elimination procedure was done and the empty space was filled with proper amount of soft liner material, then curing was carried out according to manufacturer's instructions[16].

Ten specimens were made for each group as previously mentioned in thermal properties test. Then by using instron testing machine (WDW-20, Laryee Technology Co., Ltd., China) the specimens were tested and the maximum load required for failure was recorded to count up the value of bond strength for each specimen according to the formula:

Shear Bond strength(N/mm2) =F/A[17].

Where:

F=is the maximum load at failure (N)

A= is the cross section area of the sample (mm2).

Tear Strength Test

According to (ASTM specification D-624, 2013),thirty specimens for tear strength test were fabricated with dimension illustrated in the (Figure 2).

The test method measures the force per unit thickness required to initiate a tear using Instron universal testing machine (WDW-20, Laryee Technology Co., Ltd., China).

The following equation was used to determine the tear strength:

Tear strength =F/d [18].

Where:

F is the maximum force required to break the sample (N)

d is the median thickness of each sample (mm).

Surface roughness test

Thirty specimens with dimension of (65mm x 10 mm x 2.5 mm) were prepared to be used for surface roughness test. All specimens were immersed in distilled water at 37°C for 48 hours before being tested. The profilometer device (Time3200/TR200, China) was used to study the effect of halloysite Nano tubes reinforcement into soft liner on the surface roughness of the specimens, three measurements were done for each sample and the average value was calculated [6,19].

Statistical analysis

SPSS (statistical package for social science) computer software (version 21) was used

for analyzing the results of the study, descriptive statistic and inferential statistics were employed. Also, One-way ANOVA (analysis of variance)test was performed, "P" value of > 0.05 was considered statically a non-significant,d" 0.05 was considered a significant and d" 0.01 was considered as a highly significant.

RESULTS

FTIR Analysis

FTIR results showed that there was no chemical reaction between acrylic soft-liner powder and HNTs powder as shown in (Figure 3).

XRD Analysis

XRD patterns of halloysite nanotubes nanoclay(HNTs) and Acrylic-based resilient liners before and after addition of 0.75% and 1% of HNTs nanoclay are shown in (Figure 4).

SEM Examination

The morphology of samples in cross-section and mapping of samples with PEMA soft liner before and after addition of HNTs nanoclay are investigated (Figure 5).

Energy-Dispersive Spectroscopy(EDS)

It signalized the presence of ratio of elements in the liners before and after addition of 0.75% and 1% of HNTs nanoclay as shown in (figure 6,7).

Thermal Conductivity Test

The experimental group (C) showed highest mean value (0.853 w/m.c) followed by the experimental group (B) with (0.732 w/m.c) mean value while the lowest mean value was for the control group (A) with (0.260 w/m.c) (Figure 8).
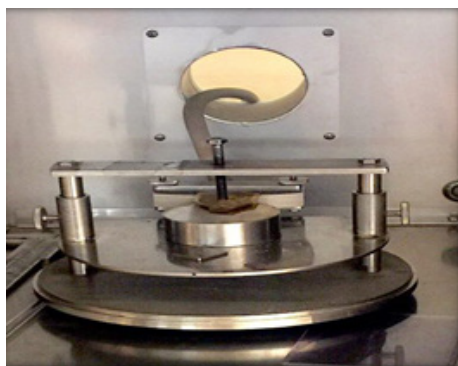
Descriptive statistics and One-way ANOVA for thermal conductivity test results showed a highly significant difference among all the tested groups, while to compare the significance of difference between two independent means, Dunnett's T3 test was applied that presented a highly significant difference among all the tested groups as listed in table 1.

Thermal Diffusivity Test

The experimental group (C) showed highest mean value (0.277mm2/sec) followed by the experimental group (B) with (0.244 mm2/sec) mean value while the lowest mean value was for the control group (A) with (0.210 mm2/sec) (Figure 9).

Descriptive statistics and one-way ANOVA that shown in table 2 were noticed a non-significant difference among all the tested groups as shown in table 2.

Shear Bond Strength Test

The experimental group (C) showed the highest mean value (0.662 N/mm²) while both groups (A) and (B) have nearly the same mean value(0.561 N/mm²),(0.568 N/mm²)respectively (Figure 10).

One-way ANOVA for shear bond strength test results recorded a highly significant difference among all tested groups. The Tukey Honestly Significant Difference (Tukey HSD)test showed that there was a significant difference between the experimental groups, a non-significant difference between control and 0.75% tested groups and a highly significant difference between control and 1 % tested groups as shown in table 3.

Tear Strength Test

The experimental group (C) showed the highest mean value (13.254 N/mm) followed by
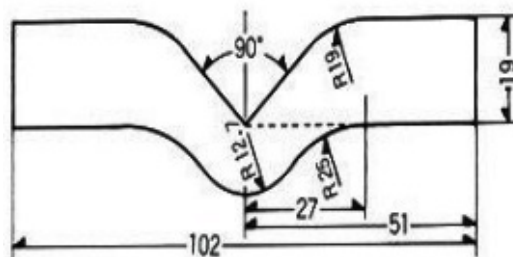

Fig. 1. Hot Disk

Fig. 2. Pattern of tear strength test specimens

the experimental group (B) with (12.155 N/mm) mean value while the lowest mean value was for the control group (A) with (11.300 N/mm) (Figure 11).

One-way ANOVA illustrated a highly significant difference among the tested groups and Tukey HSD was also recorded a highly significant
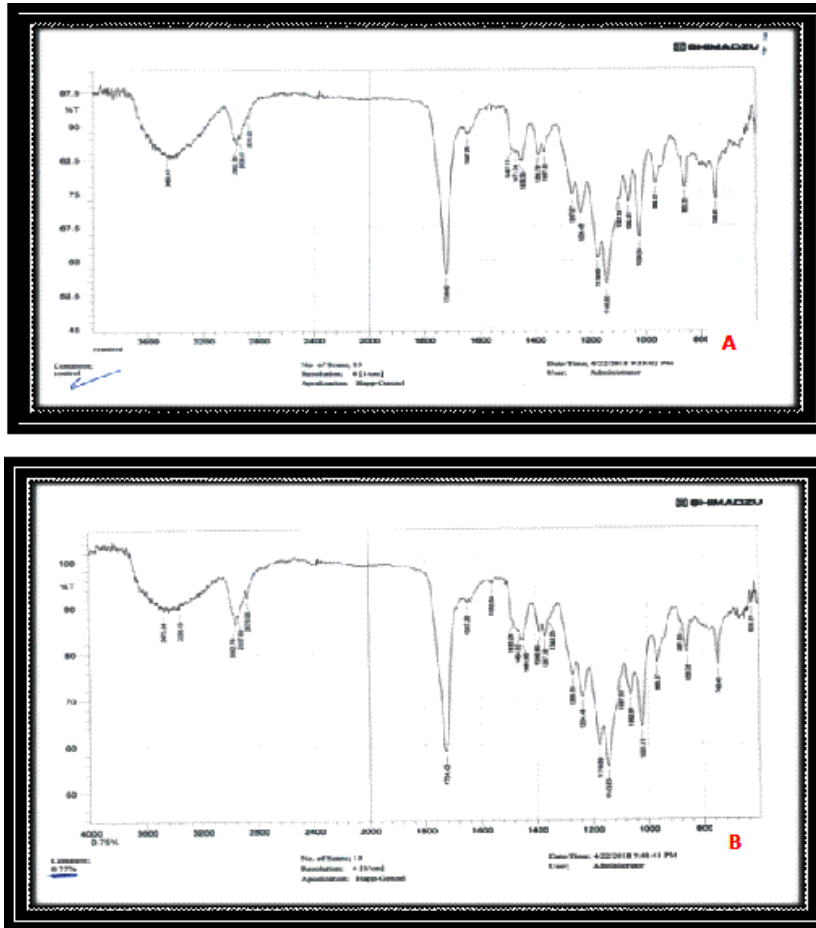

Fig. 3. FTIR of (A)soft liner without addition and (B) soft liner with addition of 0.75%HNTs
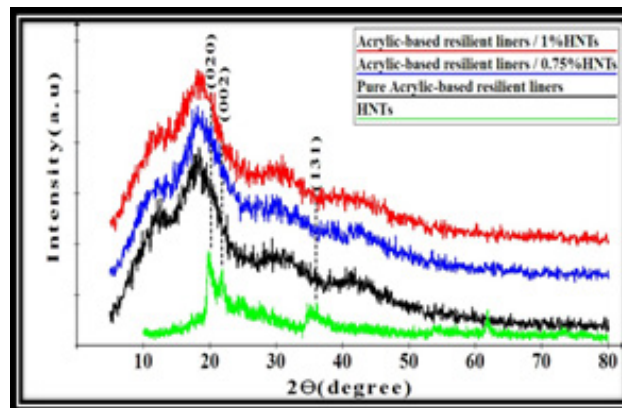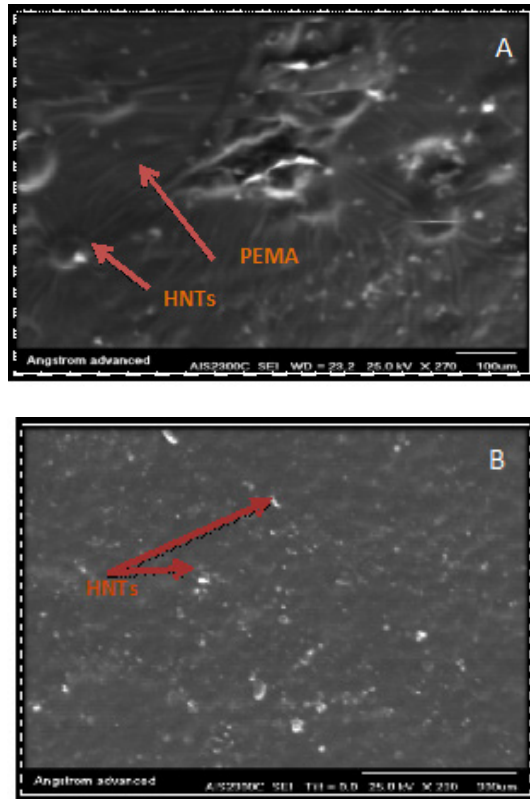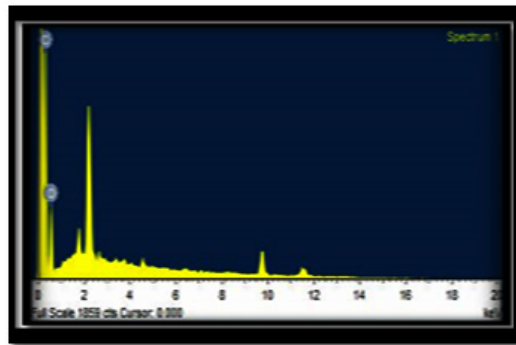

Fig. 4. XRD patterns of pure HNTs, pure Acrylic-base resilient liners and Acrylic-based resilient liners / HNTs mixtures

Fig. 5. (A) SEM image of experimental specimen (0.75%HNTs-PEMA) at 100um and (B)SEM image of experimental specimen (1%HNTs-PEMA) at 300um

difference between the control group and 1% group and between both of the experimental groups, but a significant increase for 0.75% group compared to control group as displayed in table 4.

Surface roughness test

The experimental group (C) showed the mean value of (1.314 μm) nearly the same for the experimental group (B) with (1.313μm) mean value and for the control group (A) with (1.311 μm) (Figure 12).
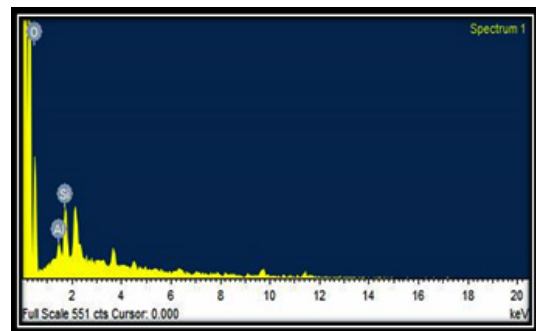
Descriptive statistics and One-way ANOVA for surface roughness test results were recorded a non-significant difference among all tested groups as shown in table 5 **.**

DISCUSSION

In this study an attempt was made to investigate the effect of incorporating HNTs into PEMA. The resin's thermal and some mechanical properties were examined such as shear bond strength, tear strength and surface roughness.

Chemically, FTIR spectral could not reveal any chemical reaction between the soft liner and HNTs nanoparticles even the coordinated bonds which expected to occur between Alumina ($A_{l2} O_3$) and Carbonyl ester were not happened because of Alumina in HNTs was saturated with other oxygen atoms.

XRD spectra of the polymers (including PMMA and PEMA) are amorphous in nature,

Element	Weight%	Atomic%
O K	83.77	89.97
Al K	4.12	2.62
Si K	12.11	7.41
Totals	100.00	

Fig. 6. EDS analysis plot for PEMA soft liner before the addition of HNTs nanoparticles

Element	Weight%	Atomic%
C K	59.06	65.77
O K	40.94	34.23
Totals	100.00	

Fig. 7. EDS analysis plot for PEMA after addition of 1%HNTs nanoparticles

whereas for HNTs are highly crystalline in nature .When HNTs added into PEMA , the characteristic peaks of the polymer have not been changed and this mean the matrix remained amorphous due to low content of nanofillers. Similar trend has also been observed in some previous work [20].

The results of SEM images are clearly indicated that the halloysite nanotubes have a rolled tubular structure and had fair dispersion and little aggregation within the PEMA matrix.

EDS analysis of the control and the two experimental groups revealed that the main elements in the surface of the all groups were (O). However, both 0.75% and 1% groups showed a markedly increase in the oxygen percentages, as compared with control group, this increase in oxygen percentages occurred because the presence of –OH groups on the non-treated outer surface of HNTs (silica) that help to absorb water into the polymer matrix led to increase in oxygen percentage.

Thermal conductivity is the ability to determine the rate at which heat can be transmitted through a given cross sectional area of the specimens of material during a given time interval [21].

A highly significant increase in the rates of thermal conductivity with the addition of HNTs into PEMA was occurred due to the overlapping of

Table 1. Descriptive statistics, one-way ANOVA and Dunnett's T3 of thermal conductivity test

	0%	0.75%	1%	ANOVA F-test	P-value	Compared Groups		Dunnett'sT3 p-value	Sig
N	10	10	10	255.965	0.000 HS	0%	0.75%	0.000	HS
Mean	0.260	0.732	0.853				1%	0.000	HS
SD	0.015	0.060	0.088						
						0.75%	1%	0.005	HS
Min.	0.234	0.683	0.730						
Max.	0.276	0.840	0.966						
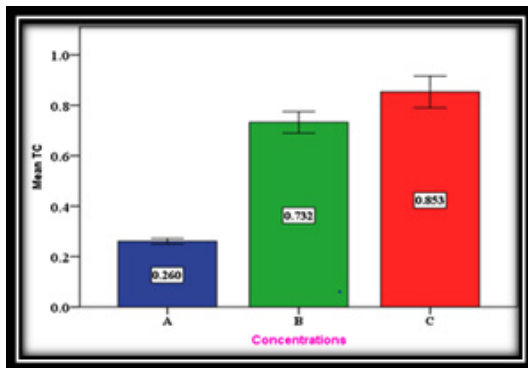
Fig. 8. Bar chart illustration of mean value and standard deviation of thermal conductivity test of all study groups
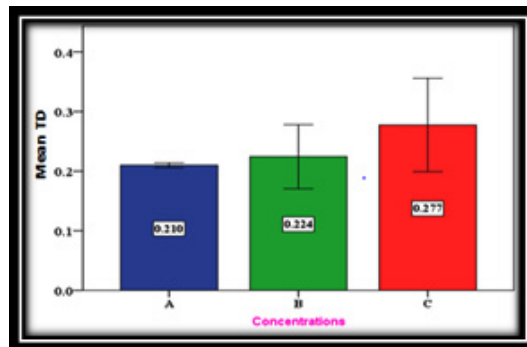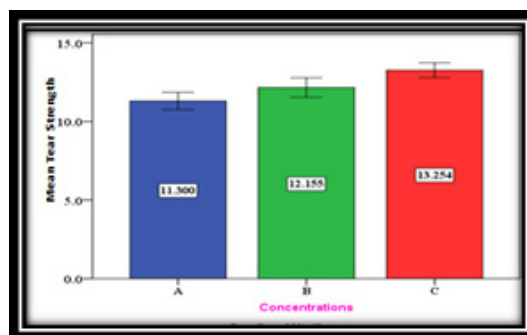

Fig. 9. Bar chart illustration of mean value and standard deviation of thermal diffusivity test of all study groups
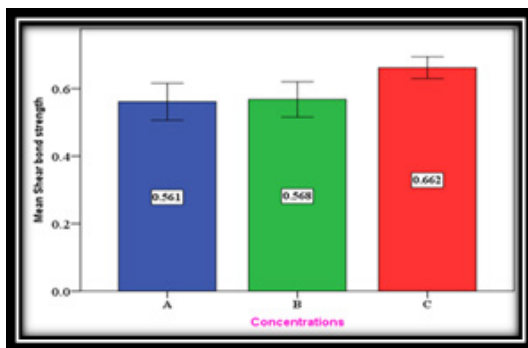
Fig. 10. Bar chart illustration of mean value and standard deviation of shear bond strength test of all study groups

Fig. 11. Bar chart illustration of mean value and standard deviation of tear strength test of all study groups

thermal conductive nanotubes inside the polymer matrix to bridge the insulating effect of PEMA matrix. Whenever the amount of fillers increase, the overlapping of thermal conductive particles will increase make the nanoparticles approximate from each other form pathway that permit transition of heat from one side of specimens to another side [6]. This study coincide with Yadav *etal.* [22].

The improvement in the thermal conductivity also might be attributed to the thermal conductivity property of nanoclay containing silicon (Si), the type of nanoparticles filler and its distribution within the resin matrix [23].

Thermal diffusivity is the rate at which a body with nonuniform temperature reaches

Fig. 12. Bar chart illustration of mean value and standard deviation of surface roughness test of all study groups
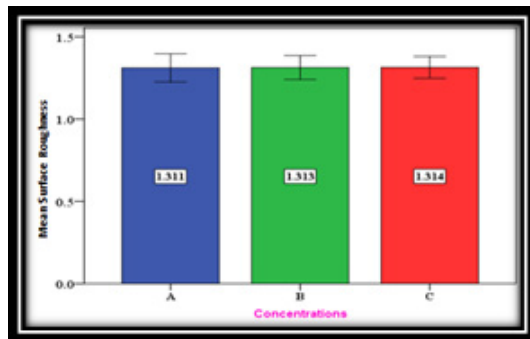
equilibrium, it's related to thermal conductivity [21]. It's the ability of a material to respond to transient temperature changes like those existing in the oral cavity during food and liquid intake [24].

The results of this study showed that there was a non- significant increase in the value of thermal diffusivity with the increase in the percentage of HNTs nanoparticles compared to the control group. This might be interpreted by formation of thermally conducting pathway within the polymer matrix of PEMA from addition of the halloysite nanoparticles within the matrix .This come in agreement with Ellakwa et al. 2008[24] and Atla et al. 2013 [25].

The improved mechanical properties of the soft liner are always attributed to the halloysite nanotube loading, dispersion, and interfacial interactions in the systems. This is related to the fact that the external load is efficiently transferred from the polymer matrix to the HNTs[26].

The statistical analysis showed that there was a non-significant change in the shear bond strength of adding 0.75% of HNTs into soft liner, this could be attributed to the chemical bonding between denture base material and soft liner which both of them have the same compatibility and high degree of similarity in chemical structure [16].

While the highly significant increase by adding 1% concentration of HNTs into soft lining

Table 2. Descriptive statistics and one-way ANOVA for thermal diffusivity test results

	0%	0.75%	1%	ANOVA F-test	P-value
N	10	10	10	2.148	0.136
Mean	0.210	0.224	0.277		NS
SD	0.006	0.075	0.110		
Min.	0.203	0.165	0.141		
Max.	0.217	0.363	0.449		

Table 3. Descriptive statistics, one-way ANOVA and Tukey HSD of shear bond strength test

	0%	0.75%	1%	ANOVA F-test	P-value	Compared Groups		Tukey HSD p-value	Sig
N	10	10	10	7.186	0.003 HS	0%	0.75%	0.971	NS
Mean	0.561	0.568	0.662				1%	0.006	HS
SD	0.077	0.073	0.045			0.75%	1%	0.010	Sig
Min.	0.429	0.461	0.586						
Max.	0.688	0.686	0.742						

Table 4. Descriptive statistics, one-way ANOVA and Tukey HSD of Tear strength test

	0%	0.75%	1%	ANOVA F-test	P-value	Compared Groups		Tukey HSD p-value	Sig
N	10	10	10	16.150	0.000 HS	0%	0.75%	0.0498	Sig
Mean	11.300	12.155	13.254				1%	0.000	HS
SD	0.771	0.872	0.655			0.75%	1%	0.004	HS
Min.	10.290	10.550	12.350						
Max.	12.630	13.140	14.250						

Table 5. Descriptive statistics, one-way ANOVA of surface roughness test

	0%	0.75%	1%	ANOVA F-test	P-value
N	10	10	10	0.002	0.998
Mean	1.311	1.313	1.314		NS
SD	0.119	0.102	0.093		
Min.	1.048	1.073	1.158		
Max.	1.436	1.419	1.440		

materials interpreted to the supramolecular bonds of the van der Waals forces and hydrogen bonds which will increase both the stiffness and the shear strength and decrease the critical length required for load transfer, which will contribute to the energy dissipation [27].

As the silica particles on the outer surface of HNTs have the ability to form hydrogen bonds between its surface hydroxyl group and the oxygen in the polymer chain, this will increase resistance of the polymer chains for rupturing when faced tearing forces due to high shear strength between the nano filler and the polymer chains and this might explain the highly significant increase in tear strength in this study [28,29].

The situ polymerization techniques, hydrogen bonds between the HNTs and the polymer matrix, as well as the high aspect ratio of HNTs and their nanoscale dimensions with low load into high polar PEMA polymer, all these led to 2D homogenization of the nano fillers in polymer matrix that means increase overall stiffness of the polymer and increase its resistance to tearing [26,30].

The results of surface roughness of this study were not significantly increased with the addition of HNTs .When small percentages of Halloysite nanotubes were added to acrylic resin soft liner only ,few particles will be involved with the surface of the specimen which didn't effect on the surface roughness as the surface roughness test is concerned with outer surface and not with inner surface of composite ,this also happened because HNTs have very small size and well dispersion within the matrix [6,31].

CONCLUSIONS

The incorporation of HNTs powder into acrylic soft lining material results in a statistically highly significant improvement of thermal conductivity. Also, this incorporation improves both shear bond strength and tear strength while a non-significant effect on the surface roughness and thermal diffusivity was observed.

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