

## ENHANCEMENT OF DENTURE-BASED MATERIAL PMMA BY INCORPORATION OF SILANIZED HALLOYSITE NANOTUBES

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### ABSTRACT

**The aim:** This study evaluates the effect of adding silanized halloysite nanotubes to the polymethylmethacrylate (PMMA) resin on its hardness, impact strength, transverse strength.

**Materials and methods:** Three groups of acrylic resin were prepared, one group without HNTs, was used as a control group (A). The other two groups contained 0.3% (B), 0.6% wt of silanized halloysite nanotubes (C). For each one, hardness, impact strength and transverse strength were measured. One-way ANOVA and Tukey's test were used for comparison.

**Results:** Regarding to the impact test, there was no significant difference between 0.3% concentration and the pure (control) group while 0.6% concentration had significant decrease compared to the pure group and so between the 0.3% group 0.6% group. For the hardness test, the 0.3% group had no significant difference with the pure group and a significant difference between group 0.6% group and the pure group while there was a no significant decrease between the 0.3% and 0.6% group with the higher hardness mean in the 0.3% compared to 0.6% group. For the transverse strength, both 0.3% wt concentration and 0.6% concentration showed significant difference compared to the pure group and also between each other with the lowest impact strength in 0.6% group followed by 0.3% group with the highest transverse strength in the pure group.

**Conclusions:** The silanation of halloysite nanotubes reduces the mechanical properties of the heat-cured acrylic denture base material. The more concentration of silanized halloysite nanotubes is added, the more weakening occurs in the acrylic material relating to the hardness, transverse strength and impact strength.

**KEY WORDS:** polymethylmethacrylate (PMMA), silanized halloysite nanotubes, denture-based, enhancement

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### INTRODUCTION

Several studies have been conducted to improve the properties of PMMA based acrylic by either changing the curing strategies or adding different components. Halloysite nanotubes (HNTs) are nano materials composed of two layers of aluminosilicate with a predominantly hollow-tubular structure at submicron level beside it, considered as biocompatible material which is safe to incorporate with dental products. Meanwhile, Poly methyl meth acrylate (PMMA) had been used as a main component in denture acrylics. Despite it has good properties, yet there are some deficits in the flexural fatigue under repeated masticatory forces and its brittleness that mainly causes dentures failure [1]. Adding of Nano-materials to the dental resins has introduced an innovative field to upgrade dental materials, the nano size of halloysite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_5 \cdot 2\text{H}_2\text{O}$ ) and its hollow tubular structure give advantages over many other nano-sized fillers such as (carbon nano tubes / nano finer). The chemical properties of the outer surface of HNTs are close to  $\text{SiO}_2$ , which those of the inner surface are close to  $\text{Al}_2\text{O}_3$  [2-3]. Nano sized HNTs have superior mechanical properties. According to Li X et al, 2014 the mixing of HNTs with the resin material considered simple as they dispersed evenly and the presence of rich SiOH group on the outer layer of the HNTs keeps a superior bonding force between the resin and the Halloysite nanotubes which is kept still under masticatory forces and polar solvents [4].

### THE AIM

This study evaluates the effect of adding silanized halloysite nanotubes to the polymethylmethacrylate (PMMA) resin on its hardness, impact strength, transverse strength.

### MATERIALS AND METHODS

A conventional heat-cured resin was used with halloysite powder nanotubes ( $\text{CAI}_2\text{SI}_2\text{D}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ ). Purity: 99.9%, stock No: NSb130-090917, CAS:1332-58-7 as reinforcing agent and silane coupling agent. For each test 30 specimens were prepared, the specimens were categorized into 3 groups coded A to C: group A was the control group (unmodified acrylic resin),

The specimens for the remaining two groups (B, C) were modified with addition of silanized halloysite nanotubes with ratio of 0.3% wt., 0.6% wt consequently with the addition of 96% ethanol for each group.

### SILANATION OF HALLOYSITE NANOTUBES

For the silanation of HNT, 20 gm. of HNTs was mixed in 120 ml of 96% ethanol solution and thoroughly stirred. The HNT with silane ratio of 1:0.2 w.v was stirred for two hours using Soniprep 150 device. The modified samples were dried at room temperature for 24 hours and in a vacuum C for 8 hours under  $70^\circ\text{C}$ . Then silanized Halloysite

nanotubes were added to the monomer by using a probe sonication apparatus 120 W – 60 KH2 for 3 minute for dispersion about 3 minutes; the salinated (HNTs) powder with the monomer were immediately added to the acrylic powder so that the acrylic mixture would not cluster or cause phase separation. The powder/liquid ratio of the acrylic mixture was 2.5:1 wt./vol.6.

### TEST MOULDS PREPARATION

Preparation of the test specimens was done by cutting plastic plates of different thickness, using highly accurate laser cutting machine. For the transverse strength test and hardness test, standardized bar shaped specimens with dimension of 65mm length, 10 width and 2.5mm thickness were prepared according to (ANSI/ADA specification No. 12, 1999). For the impact strength test, standardized bar shaped specimens

with dimensions of 80mm, 10mm, 4mm length width and thickness consequently were used (ISO179 specification).

### ACRYLIC SPECIMENS' PREPARATION

The conventional processing techniques for complete dentures was followed during the mould preparation, after setting of the stone, the flask was opened carefully to separate two halves of the flask and the plastic patterns then were removed from the mould carefully so it became ready for the packing of acrylic. An electronic scale with accuracy of 0.0001gm was used for calibration [5-6].

### ACRYLIC CURING

During the dough stage of the acrylic mixture, it was placed in the molds and the flasks were clamped, then they were

**Table I.** Descriptive Analysis of impact strength

	N	Mean	Std. Deviation	Minimum	Maximum
1	5	.3100	.02236	.30	.35
2	5	.2540	.02881	.22	.30
3	5	.1140	.02191	.10	.15
Total	15	.2260	.08830	.10	.35

**Table II.** Multiple Comparisons of the impact strength

	(I) VAR00002	(J) VAR00002	Mean Difference (I-J)	Sig.
Tukey HSD	A	B	.05600*	.009
		C	.19600*	.000
	B	A	-.05600-*	.009
		C	.14000*	.000
	C	A	-.19600-*	.000
		B	-.14000-*	.000

The mean difference is significant at the 0.05 level.  
Dependent Variable: group A

**Table III.** Descriptive Analysis of hardness strength

	N	Mean	Std. Deviation	Minimum	Maximum
1	3	85.6667	.57735	85.00	86.00
2	3	84.3333	1.15470	83.00	85.00
3	3	79.6667	1.52753	78.00	81.00
Total	9	83.2222	2.90593	78.00	86.00

**Table IV.** Multiple Comparisons of the hardness strength

	(I) VAR00002	(J) VAR00002	Mean Difference (I-J)	Sig.
Tukey HSD	A	B	1.33333	.392
		C	6.00000*	.002
	B	A	-1.33333-	.392
		C	4.66667*	.006
	C	A	-6.00000-*	.002
		B	-4.66667-*	.006

\* The mean difference is significant at the 0.05 level.

**Table V.** Descriptive Analysis of transverse strength

	N	Mean	Std. Deviation	Minimum	Maximum
A	5	.13060	.018257	.120	.163
B	5	.09800	.019235	.080	.130
C	5	.05800	.008367	.050	.070
Total	15	.09553	.034138	.050	.163

**Table VI.** Multiple Comparisons of the transverse strength

	(I) VAR00002	(J) VAR00002	Mean Difference (I-J)	Sig.
Tukey HSD	A	B	.032600*	.019
		C	.072600*	.000
	B	A	-.032600-*	.019
		C	.040000*	.005
	C	A	-.072600-*	.000
		B	-.040000-*	.005

\*The mean difference is significant at the 0.05 level.  
Dependent Variable: group A

placed in a water bath (74 C°, 90 minutes, then in boiling temperature for 30 minutes) for curing. Afterwards, the flasks were cooled in room temperature, acrylic specimens were collected, finished, polished and kept in distilled water at 37 C° for one week [7-8].

**TESTING PROCEDURES**

These tests were: impact strength test, transverse strength test and surface hardness test, for the impact strength test, an impact testing machine used the following formula:

$$\text{Impact strength} = \text{impact strength} = \frac{\text{energy} \cdot 10^3}{D \cdot B} \text{ kj/m}^2$$

D: thickness of the specimen, B: width of the specimen.

Transverse strength test was performed using a universal Instron testing machine

$$\text{transverse strength} = \frac{3 \cdot \text{load} \cdot \text{spanlength}}{2 \cdot \text{width} \cdot (\text{thickness})^2}$$

For the surface hardness test, the durometer hardness tester (shore D hardness) was used.

While the intender pressed the samples, direct measuring from the digital scale was taken from five different spots on the sample then the average of these five measurements was recorded [6].

**RESULTS AND DISCUSSION**

For each test the descriptive analyses of the results in three groups are shown in tables (I,III,IV) including the mean, standard deviation and both maximum and minimum reading. Tukey’s HSD test was chosen for statistical analysis between the groups for each test. For the impact strength the mean value of the modified groups (B, C) was both lower than group A with group C having the lowest mean as in table I; the difference between group A and B

was non-significant while difference between and group A and C was significant and so in between groups B and C as shown in table II.

There was decreasing in the mean value of hardness in group B as compared with pure group which is statistically not significant, while group C showed higher decreasing in hardness which is statistically significant compared to group A; decreasing of the hardness in group C was not significant from that in group B as seen in table IV.

For the transverse strength there was also decreasing in the mean value for the modified groups compared to the controlled group; group C also had the lowest mean as shown in table V. After addition of salinized HNTs to the PMMA, this regression in traverse strength was noticeable in all groups even between group B and C, as illustrated in tables V, VI.

Different researches studied the effect of incorporating nanotubes and nano-fillers to both composite and acrylic resin. This study investigated the addition of halloysite nanotubes to denture base acrylic but with a different approach: by salinating the HNTs in two different concentrations before its addition to the monomer. Reham, 2016 8 added HNTs nanotube to acrylic powder using pestle and mortar without any coupling aging, resulting the improvement of mechanical strength, while the salinated HNTs caused decreasing in the hardness, impact strength and transverse strength. Thus, it ca be concluded the more the concentration of HNTs is, the more decreasing in the modified acrylic occurs.

Although different reports describe using the nanofiber and nanotubes in dental composite, few studies have evaluated the reinforcements potential of Nano fiber and Nano tubes in PMMA denture base resin.

**CONCLUSIONS**

Our study aimed to investigate whether the incorporation of salinized HNTs to the PMMA enhances some me-

chanical and physical properties, especially the hardness, impact strength and transverse strength. It was shown that incorporating of 0.3/ wt of silanized HNTS doesn't improve the mechanical properties as hardness. This decreasing becomes more significant when we increase the value of silanized HNTS to the 0.6/ wt. These results illustrate that the efficient strengthening would not be obtained at higher percentage of silanized HNTS.

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## Contributionship:

Rafah Habib Abdul Amir <sup>A-F</sup>

## Conflict of interest:

The Author declare no conflict of interest.

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**A** – Work concept and design, **B** – Data collection and analysis, **C** – Responsibility for statistical analysis, **D** – Writing the article, **E** – Critical review, **F** – Final approval of the article