

.

**EFFECT OF ADDING CHITOSAN NANOPARTICLES ON FLEXURAL** STRENGTH AND HARDNESS OF HEAT CURED ACRYLIC RESIN **BEFORE AND AFTER THERMO CYCLING** 

Ali Sayed<sup>\*</sup> *and* Mohamed Mahmoud El Sokkary<sup>\*\*</sup>

### ABSTRACT

Objective: The aim of this study was to evaluate the effect of two concentrations of chitosan nanoparticles on the mechanical properties of heat polymerized acrylic resin before and after thermocycling. The tested parameters were flexural strength and hardness.

Material and Methods: 120 specimens were prepared according to the specific dimension for each test (flexural strength and micro hardness) and distributed into:

- Before thermocycling (control, chitosan nanoparticles with concentration 0.3% and 0.5%)

- After thermocycling (control, chitosan nanoparticles with concentration 0.3% and 0.5%)

Results: Flexural strength and micro hardness were tested for both groups. The data was collected and statistically analyzed. Flexural strength was non-significantly increased for ratio of 0.3% chitosan nanoparticles in comparison to control before and after thermo cycling and significantly decreased for 0.5% chitosan nanoparticles before thermocycling and non-significant decrease after thermocycling in comparison to control. For hardness showed non-significant decrease for both concentrations and significant decrease for control after thermocycling

Conclusion: Adding chitosan nanoparticles to heat cured acrylic resin increased the flexural strength for 0.3% ratio and non-significantly decreased for 0.5, while decreased non-significantly micro hardness for both concentrations.

KEYWORDS: Acrylic ,Nano chitosan, , flexural strength, hardness

Lecturer of Dental Materials, Faculty of Dentistry, Assiut University

<sup>\*\*</sup> Lecturer of Prosthodontics, Faculty of Dentistry, Assiut University

# INTRODUCTION

An ideal denture base material should have some mechanical, physical, and biological properties which are required for dental applications <sup>(1)</sup>. Poly methyl methacrylate (PMMA) acrylic resin is usually used as a denture base material due to its reasonable cost, good adaptation, ease of use in different purposes such as in complete denture base, denture teeth, implant-supported dentures, and orthodontic applications <sup>(2)</sup>. However, the main disadvantage of acrylic resin is the liability to fracture during mastication or by sudden drop <sup>(3)</sup>.

Many techniques have been suggested to improve the mechanical properties of the acrylic resin material and to increase its service time, including modifying or reinforcing the resin. A lot of techniques have been used for strengthening (PMMA) such as the use of different forms of metal to be embedded in the acrylic polymer powder <sup>(4)</sup>. Fibers, minerals, metal oxides, ceramics, nano materials and composite materials have been used successfully in different shapes and sizes to improve the properties of acrylic <sup>(5)</sup>.

Nanotechnology has been used successfully in improving the mechanical, physical and biological properties of the prosthetic dental materials especially in removable prosthesis and orthodontic appliances (6). Nano clusters, nanotubes, Nano fibers, and nanoparticles were used in different sizes and concentrations for improving the mechanical properties of acrylic resin denture base materials<sup>(7)</sup>. It was found that the effect of nanoparticles on the properties of acrylic resin depends on multiple factors such as polymer- particle interface, concentration, manufacturing technique, and particle dispersion in the acrylic resin matrix<sup>(8)</sup>. Nano fillers of aluminum dioxide, silver, zinc oxide, zirconia and titanium dioxide have been used to improve mechanical properties of acrylic denture base<sup>(9)</sup>.

Some polymers like Chitosan were used to improve the mechanical, chemical and biological properties of acrylic denture base materials <sup>(10)</sup>.

Chitosan is polymer of glucosamine and N-acetyl glucosamine, which has numerous favourable properties such as biocompatibility, hydrophilicity, biodegradability, bioactivity, and a broad antibacterial spectrum (covering gram-negative and gram-positive bacteria as well as fungi). multiple biological properties such as; biodegradable, biocompatible, and bioactive (10,11). Chitosan also has a high resistance to heat due to its intermolecular hydrogen bonds (11). This property of heat resisting is important for denture base materials because, in the oral cavity, the denture prostheses are usually subjected to thermal variations due to the ingestion of hot and cold liquids, such thermal cycling in a wet environment may affect adversely the mechanical properties of the denture polymers <sup>(12)</sup>. The heat stress may increase water sorption because of increasing the distance between the polymer chains, so absorbed water can act as a plasticizer and soften the denture decreasing strength and hardness, thus reducing the mechanical properties of the material<sup>(14)</sup>. Chitosan nanoparticles can be added to acrylic resins to improve their antibacterial properties, but it is important to ensure that the incorporation of these nanoparticles into acrylic resins does not affect their mechanical properties adversely. (15)

Therefore, the present study was carried out to investigate the effect of adding chitosan nanoparticles on the flexural strength and hardness of heat-cured acrylic resin before and after thermocycling.

#### MATERIAL AND METHODS

An in vitro study was conducted to evaluate the effect of adding chitosan nanoparticles (CSNPs) with concentration (0.3% and 0.5) by weight to the acrylic resin polymer powder on the flexural strength, and hardness of heat-polymerized acrylic resin.

### **Preparation of PMMA + CSNPs**

The dried powder of CSNPs was mixed with polymethyl methacrylate (PMMA) powder at two ratios 0.3 and 0.5w/w, typically for 0.5%, 0.5 gm. of CSNPs mixed with 99.5 gm. of PMMA by meaning of ball milling for 2h to get homogenous mixing. As well, for 0.3% 0.3gm CSNPs was mixed with 99.7 gm. PMMA following the same procedure.

TABLE (1) Materials used in the current study.

Material	Specification	Manufacturer			
Idobase	PMMA heat cured acrylic resin	Paseo de La Estacion (Madrid, Spain)			
Chitosan	Chitosan nano	Nano-gate			
	particles	Company, Egypt			

Sample grouping:

TABLE (2) Specimens were prepared according to the specific dimension for each test (flexural strength and micro hardness) and distributed according to the following table.

		Control		T1		T2	
Flexural strength	No thermocycling	10	10	10	10	10	10
	thermocycling	10	10	10	10	10	10
Micro- hardness	No thermocycling	10	10	10	10	10	10
	thermocycling	10	10	10	10	10	10

The sample dimensions were selected according to specific dimension of each test,  $(65 \times 10 \times 2.5 \text{ mm})$  for flexural strength, the specimens were fabricated according to ADA specification no. 12 (measuring  $65 \times 10 \times 2.5 \text{ mm}$ )<sup>(16)</sup>.

Wax pattern with these dimensions was used to form the mold. The samples were processed according to manufacture instructions (3:1 by volume or 2.5:1 by weight) until reaching the dough stage. Conventional packing method for 1.5 hours at 74°C, then boiling for 1h. After polymerization, the flasks were bench cooled at room temperature for 30 minutes and then placed for 15 minutes under running water before opening. The samples were dried then finished and polished till obtaining smooth surface using the sand paper and polishing chalk. The specimens were inspected for any irregularity as defective specimens were discarded. For micro hardness specimens, the same technique was followed to fabricate the specimens of hardness with the same dimensions ( $65 \times 10 \times 2.5 \text{mm}$ ).

# Thermocycling

Thermal cycles were performed using a thermocycling machine (SD mechatronic thermocycler D-83620 Feldkirchen-Westerham GERMANY) and consisted of 5000 cycles at 5°C and 55°C with a 30-second dwell time.

#### Flexural strength

Specimens were tested by 3-point bending test on Instron universal testing machine (Model 3366, UK) the specimens were loaded -till fracture at a crosshead speed of 5 mm/min.

## Micro hardness

Surface micro-hardness of the specimens was determined using digital display Vickers micro hardness tester (Wilson Tukon 1102, Buhler, Germany) with a Vickers diamond indenter and a 10X objective lens. A 200g was applied to the surface of the specimens. Three indentations were equally done, and not closer than 0.5 mm to the adjacent indentations, were made on the surface of each specimen. The diagonals lengths of the indentations were measured by built in scaled microscope and Vickers micro hardness values were recorded.

#### Statistical analysis

Data presented as mean and standard deviation (SD). Data explored for normality using Kolmogorov-Smirnov and Shapiro-Wilk tests. Oneway ANOVA used to compare between tested groups followed by Tukey's HSD test for pair wise comparison. Independent t-test used to compare between thermocycling (TC) in each group.

The significance level was set at  $P \le 0.05$ .

Statistical analysis was performed with IBM SPSS Statistics for Windows, Version 26.0. Armonk, NY: IBM Corp.



Fig. (1) Thermocycler.



Fig. (2) Specimen in Universal testing machine for measuring flexural strength



Fig. (3) Specimen in hardness tester for measuring micro hardness.

# RESULTS

TABLE (3) The mean values, standard deviations change percent and P values of flexural strength of heat cured acrylic resin and heat cured acrylic resin with chitosan nano particles with and without thermocycling.

Mean		Control		Chitosan (0.3%)		Chitosan (0.5%)		,
		SD	Mean	SD	Mean	SD		– p-value
Flexural	No thermocycling	118.7 <sup>b</sup>	15.9	148.7ª	28.9	105.9 <sup>b</sup>	26.3	0.045*
Strength	thermocycling	106.6	23.8	126.1	10.2	105.7	6.8	0.102 NS
p-value		0.357 NS		0.138 NS		0.984 NS		

- Statistical analysis results revealed that Flexural strength was significantly increased for ratio of 0.3% chitosan nanoparticles before thermo-cycling and non-significant increase after thermocycling in comparison to control.
- Significant decreased for 0.5% chitosan nanoparticles before thermocycling and nonsignificant decrease after thermo-cycling in comparison to control.
- TABLE (4) The mean values, standard deviations change percent and P values of micro hardness of heat cured acrylic resin and heat cured acrylic resin reinforced with chitosan nano particles with and without thermocycling

Mean -		Control		Chitosan (0. 3%)		Chitosan (0.5%)		1
		SD	Mean	SD	Mean	SD		- p-value
Micro- hardness	No thermocycling	36.6	3.1	36.1	2.5	34.7	4.0	0.641 NS
	Thermocycling	34.9	1.5	34.5	2.3	32.5	2.6	0.354 NS
p-value		0.042*		0.330 NS		0.351 NS		

- Statistical analysis results revealed that microhardness strength was non-significantly increased for the ratio of 0.3% chitosan nanoparticles either before or after thermo-cycling in comparison to control group.
- However, non-Significant decrease for 0.5% chitosan nanoparticles either before or after thermocycling in comparison to control group.

# DISCUSSION

Although acrylic resin is the most common used denture base material, but still has some disadvantages such as low mechanical properties, water sorption and liability to bacterial infection<sup>(17)</sup>. Several authors have been indicated that the acrylic resin properties can be improved by adding different materials such as carbon graphite fibers, polyethylene polymer, glass fiber, silver particles and nano particles of different concentrations <sup>(18)</sup>.

Chitosan is a polycationic polymer that has active "amino" and "hydroxyl" functional groups, also has a high resistance to heat due to hydrogen bonds so it can use safely with the thermoplastic resin <sup>(19)</sup>. In this study the authors directed to assess the effect of adding chitosan nano particles in two different concentrations (0.3% and 0.5%) on the flexural strength and micro-hardness, of acrylic resin denture base material

The results of this study showed that the incorporation of chitosan nano particles at concentrations of 0.3% into acrylic resin increases significantly its flexural strength, without thermocycling and nonsignificantly with thermocycling

The increased in strength can be due to the dispersion of chitosan in the resin matrix, so interaction between chitosan and denture base resin leads to strong bonding between chitosan and carbonyl groups of heat polymerized denture base resin. The physical or mechanical bond that can occur due to size difference between the chitosan and denture base resin could have improved the strength <sup>(20)</sup>.

The results of this study also showed that the incorporation of chitosan nano particles at concentrations of 0.5% into acrylic resin decreases significantly its flexural strength, without thermocycling and non-significantly with thermocycling.

This may be due to incomplete wetting of the chitosan Nanofillers due to increase percentage (0.5%) by insufficient amount of liquid monomer, which may prevent the chitosan-polymer from forming covalent bonds with the linear chains of resin as dispersed phase within the matrix that might interrupt the polymer network matrix <sup>(21-22)</sup>.

Hardness is an important indicator for expecting the wear acrylic resins denture base materials. A low surface hardness increases the surface roughness and causes an increase in the plaque accumulation, pigmentation, and eventually weakness of the denture, affecting its durability aesthetics <sup>(23)</sup>.

The results of this study also showed that the incorporation of chitosan nano particles at concentrations of 0.3% and 0.5 into acrylic resin decreases non-significantly its micro-hardness with and without thermocycling as chitosan may have adverse effects on the degree of conversion in polymerization and lead to an increase in the amount of residual monomer that acts as plasticizers, decreasing the microhardness <sup>(24)</sup>.

# CONCLUSIONS

The addition of CSNPs to PMMA in 0.3% w/w enhanced the flexural strength and did not affect the microhardness. Whereas the addition of CSNPs to PMMA in 0.5% w/w did not affect the mechanical properties negatively: either flexural strength or hardness.

## REFERENCES

- Rachmadi P, Firdaus WAK, Sukmana BI, et al. The effect of immersion of 12.5% basil leaves and 25% mauli banana stem mixture extracts on surface hardness, surface roughness and discoloration of acrylic resin. Syst. Rev. Pharm. 2020;11(05):281–287
- Maji P, Choudhary RB, Majhi M , Structural, optical and dielectric properties of ZrO2 reinforced polymeric nanocomposite films of polymethylmethacrylate (PMMA). Optik . 2016;127, 4848-4853.
- Rad F, Ghaffar T, Rezaii F, Ramazan A. Effect of nanosilver on thermal and mechanical properties of acrylic base complete denture. J Dent (Tehran) 2014; 11:495-505.

- Somani M, Khandelwal M, Punia V, Sharma V. The effect of incorporating various reinforcement materials on flexural strength and impact strength of polymethylmethacrylate: A meta-analysis. J Indian Prosthodont Soc.2019; 19:101–12.
- Gad M, Fouda S, Al-Harbi F, Napankangas R, Raustia A. PMMA denture base material enhancement: a review of fiber, filler, and nanofiller addition. Int J Nanomedicine. 2017;12:3801–12.
- Topouzi M, Kontonasaki E, Bikiaris D, Papadopoulou Paraskevopoulos KM, Koidis P Reinforcement of PMMA resin for interim fixed prostheses with silica nanoparticles. J Mech Behav Biomed Mater .2017;69; 213-222.
- Kareem S, Moudhaffer M. The effect of zirconium silicate nanopowder reinforcement on some mechanical and physical properties of heat cured poly (methyl methacrylate) denture base materials. J Baghdad Coll Dent .2015; 27, 37-43.
- Gad M, ArRejaie AS, Abdel-Halim MS, Rahoma A (2016) The reinforcement effect of nano-zirconia on the transverse strength of repaired acrylic denture base. Int J Dent 2016; 7094056.
- Cierech M, Osica I, Kolenda A, Wojnarowicz J, Szmigiel D, Łojkowski W, et al. Mechanical and physicochemical properties of newly formed ZnO-PMMA nanocomposites for denture bases. Nanomaterials (Basel). 2018; 8:305.
- Husain S, Al-Samadani KH, Najeeb S, Zafar MS, Khurshid Z, Zohaib S, et al. Chitosan Biomaterials for Current and Potential Dental Applications. Materials (Basel). 2017;10:602.
- Sha B, Liu Q, Cheng L, Yin X. Preparation and Application of Core-shell PMMA/Chitosan Nanoparticle. Advance Mater Res. 2012; 535: 271-74.
- Nam K-Y, Shin Y-M. Antifungal effect and characterization of denture PMMA impregnated with chitosan. Polym J. 2017; 44: 87-94.
- Franklin P, Wood DJ, Bubb NL. Reinforcement of poly (methyl methacrylate) denture base with glass flake. Dent Mater. 2005; 21:365-70.
- Durkan RK, Özdemir T, Pamir AD, Usanmaz A. Water absorption of two different denture base resins reinforced with dental fibers systems. J Appl Polym Sci. 2010;117:1750-3.
- Chandrasekaran, M.; Moussaoui, Y.; Chun, S.C. Antibacterial Activity of Chitosan Nanoparticles: A Review. Processes 2020,8, 1173.

- SWANEY AC, PAFFENBARGER GC, CAUL HJ, SWEENEY WT. American Dental Association specification No. 12 for denture base resin: second revision. J Am Dent Assoc. 1953 Jan;46(1):54-66. doi: 10.14219/jada.archive.1953.0007. PMID: 13022237).
- UR1 D, R H, A. H. Denture fracture-a survey. Br Dent J. 1994;176(9):342-5.
- Sodagar, A.; Bahador, A.; Khalil, S.; Shahroudi, A.S.; Kassaee, M.Z. The effect of TiO2 and SiO2 nanoparticles on flexural strength of poly (methyl methacrylate) acrylic resins. J. Prosthodont. Res. 2013, 57, 15–19.
- Sodagar, A.; Kassaee, M.Z.; Akhavan, A.; Javadi, N.; Arab, S.; Kharazifard, M.J. Effect of silver nano particles on flexural strength of acrylic resins. J. Prosthodont. Res. 2012; 56, 120–124.
- Wieckiewicz M, Boening KW, Grychowska N, Stolarz P. A Clinical application of chitosan in dental specialties. Mini Rev Med Chem. 2017; 17:401-09.

- Biswas SK, Shams I, Das AK, Islam N, Nazhad MM. Flexible and Transparent Chitin/Acrylic Nanocomposite Films with High Mechanical Strength. Fiber Polym. 2015; 16: 774-81.
- Kundie F, Azhari CH, Ahmad ZA. Effect of nano-and micro-alumina fillers on some properties of poly (methyl methacrylate) denture base composites. J Serb Chem Soc. 2018; 83: 75-91.
- Farina, A.P.; Cecchin, D.; Soares, R.G.; Botelho, A.L.; Takahashi, J.M.F.K.; Mazzetto, M.O.; Mesquita, M.F. Evaluation of Vickers hardness of different types of acrylic denture base resins with and without glass fibre reinforcement. Gerodontology 2012, 29, e155–e160.
- (Naveen Gopi Chander a,, Jayaraman Venkatraman.Mechanical properties and surface roughness of chitosan reinforced heat polymerized denture base resin J Prosthodont Res. 2022; 66(1): 101–108