

Original Article

# Dispersion of Zinc Oxide Nanoparticles in Maxillofacial Silicone Elastomer by Ultrasonication: A Morphological Study

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## Abstract

**Objective:** Aggregation and agglomeration of nanoparticles in silicone elastomer is a common problem that adversely affects the mechanical properties of the silicone because the aggregations act as a weak and stress concentrating point within the silicone elastomer matrix. The objective of this study was to evaluate the effect of sonication on the dispersion of ZnO nanoparticles in M-511 heat vulcanized maxillofacial silicone.

**Methods:** Nano-ZnO was added in concentrations of 1%, 2%, 3%, and 5% by weight to Cosmesil M-511 heat vulcanized maxillofacial silicone elastomer, after sonication of ZnO nanoparticles in ethanol for 30 minutes at room temperature, and 1%, 2%, 3%, and 5% were added by weight without sonication of ZnO nanoparticles. Then field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD) tests were used to assess the efficiency of the dispersion method and to monitor the particle size of nano-ZnO.

**Results:** FESEM test showed a reduction in cluster size of nano-ZnO as a result of sonication. XRD and FESEM showed a homogenous dispersion of ZnO nanoparticles within the silicone matrix.

**Conclusions:** Based on the results of this morphological study, sonication of nano-ZnO in ethanol represented an effective and easy way to disperse nano-ZnO in a silicone elastomer matrix. This led to a superior quality nanocomposite without affecting the base material and without the need for a coupling agent or addition of any third material.

**Keywords:** Maxillofacial Silicone, Nanoparticles, Ultrasonication, Zinc Oxide.

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## Introduction

Silicone elastomeric materials chemically known as polydimethylsiloxane (PDMS), possess some undesirable properties; most important are low tensile and tear strength, insufficient elasticity, and degradation of colour and physical properties<sup>(1)</sup>. Zinc oxide (ZnO) nanoparticles are identified by their small size, active function, large surface area, and high interfacial interaction with the organic polymer. Therefore, the properties of the polymer could be improved by nano-ZnO, which gives resistance to ageing and environmental stress-related cracking<sup>(2)</sup>.

The main challenge lies in maintaining the nanofiller's content at an appropriate level and providing homogenous dispersion. Otherwise, due to their chemical reactivity and higher surface energy, the nanoparticles may agglomerate. The agglomerated nanoparticles act as stress-concentrating centres when the silicone elastomer is under pressure from external forces, thereby decreasing the mechanical strength of the silicone elastomer<sup>(3)</sup>. To achieve beneficial physical and mechanical properties and exploit the advantages of the nanoparticles, controlling the aggregation and mixing well-dispersed nanoparticles into the polymer is essential<sup>(4,5)</sup>. There have been many efforts to prevent the aggregation and agglomeration of nanofillers, such as the application of silane coupling agents between the polymer and nanoparticles<sup>(6-8)</sup>.

Sonication can be defined by the application of sound energy to promote the disruption of agglomerate particles at frequencies higher than 20 kHz, which are largely inaudible to the human ear, through a procedure called cavitation<sup>(9,10)</sup>. Nowadays, ultrasonication is well recognized as an effective, convenient, simple, and inexpensive way to break up cluster formation, dispersing nanoparticles homogeneously, and help scatter the nanoparticles into the base fluids. Sonication techniques are commonly used for preparing nanofluids<sup>(11-13)</sup>.

However, no standard has been established for the preparation of nanofluids especially about what type and duration of modes should be used (pulse mode or continuous mode), duration of sonication, and amplitude of sonication. The National Institute of Standards and Technology (NIST, Gaithersburg, MD) and the Center for the Environmental Implications of Nanotechnology (CEINT of Duke University) have started to develop some standardized and validated protocols for nanoparticles dispersion. The use of pulse mode operation, cooling ice-bath, and flat-bottom cylindrical-shaped beakers are some proposed guidelines, and those guidelines were used in this study<sup>(14)</sup>.

To date, no efforts incorporating both in-vitro and in-vivo study have been made to improve dispersion of nanoparticles within the silicone elastomer matrix without chemical treatment of the nanoparticles. In this study, sonication of ZnO nanoparticles in ethanol is revealed to present an applicable and cost-effective method for dispersing nanoparticles within the silicone elastomers, thereby reducing agglomeration and aggregation of the nanoparticles. The results are supported by field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD). The purpose was to study the effect of sonication on the dispersion of ZnO nanoparticles in Cosmesil M-511 heat vulcanized maxillofacial silicone elastomer. The null hypothesis is that the dispersion of ZnO nanoparticles within the M-511 maxillofacial silicone will not be affected by sonication.

## Materials and methods

M-511 heat vulcanized maxillofacial silicone elastomer (part A and B) was purchased from Technovent Ltd. (South Wales, UK). ZnO nanoparticles (99.8% purity, white-light yellow, 10–30 nm, SSA 30–50 m<sup>2</sup>/g) were purchased from SkySpring Nanomaterials, Inc. (Houston, TX, USA). Ethanol absolute 99.5% (EMPARTA® ACS) was purchased from Merck-KgaA (Darmstadt, Germany).

### Dispersion of ZnO nanoparticle in ethanol

The different weight percentages of nano-ZnO were added to 25 mL and 50 mL ethanol according to the amount of silicone prepared (for each gm of silicone used, add 1 mL of ethanol). The mixture of ethanol and nano-ZnO was then kept under sonication (Q700 sonicator, Newtown, CT, USA) as shown in Figure 1 for 30 minutes at room temperature with continuous cooling. ZnO nanoparticles treated with ethanol are presented as (treated) t-ZnO, and those without treatment are presented as (untreated) u-ZnO. Finally, an FESEM test was used for the analysis of the nanoparticles' size and size distribution.

### Preparation of silicone nanocomposite

Nano-ZnO was added in different concentrations of 1%, 2%, 3%, and 5% by weight to Cosmesil M-511 HTV silicone elastomer. For preparing specimens with u-ZnO (control group), part A of M-511 silicone and u-ZnO nanoparticles were weighted first and mixed according to manufacturer instructions by a vacuum mixer (AX-2000, Aixin Medical Equipment Co., Ltd, China) as shown in Figure 1 for 10 minutes at a speed of 360 rpm and under the vacuum of -0.9 bar. The vacuum was turned off for the first three minutes to avoid suction of the nanofillers, and then it was turned on for the

remaining 7 minutes. The mixing bowl was put aside to cool to room temperature as the heat was generated during mixing, then part B was weighed and added to the mixture and mixed in the vacuum mixer for an additional five minutes.

To prepare specimens with t-ZnO (study group), the mixture of t-ZnO with ethanol was added to part A of M-511 and mixed by the vacuum mixer for 10 minutes. It was then placed over the magnetic hotplate stirrer (Daihan Labtech Co., Ltd., Korea) and connected with the vacuum rotary pump (Euro-Vac, Thompson-CSF, Antwerp, Belgium) as shown in Figure 3 to evaporate the ethanol over 120 minutes, before being mixed every three minutes for one minute by the vacuum mixer to obtain homogenous dispersion of ZnO within the M-511 silicone. The mixture was then cooled to room temperature before part B was added and mixed for an additional 5 minutes by the vacuum mixer.

The mixture was then loaded into the metal moulds with a thickness of 2 mm by a stainless-steel metallic spatula (Klardent AB, Turbingatan, Arlandastad, Sweden) and transferred to a vacuum chamber for 2 minutes to eliminate all air bubbles incorporated during moulding. The moulds were then placed in a pressure pot (Pentola A pressione leone, Lecce, Italy) for two minutes under the pressure of two bars to smooth the surface of the mixture and rupture superficial air bubbles. The mould was closed and placed under hydraulic pressure of 3 tons/m<sup>2</sup> for 5 minutes. Afterwards, the moulds were closed and pressed with G-clamps, and the material was cured in a hot air oven (Mettmert, Memmert GmbH+Co. KG, Schwabach, Germany) at 100°C for one hour. Finally, eight samples were used for FESEM test for u-ZnO and t-ZnO. While two samples used for XRD test for 3%u-ZnO and 3%t-ZnO.

### Characterization

The t-ZnO nanoparticles and u-ZnO nanoparticles were analyzed using an FESEM (Zeiss Sigma VP, Germany). After the specimens were demoulded, they were cut and cleaned with nitrogen and coated with gold before the FESEM test, which was used to observe the dispersion of nano-ZnO within the silicone matrix. The XRD test was used to monitor the dispersion of nano-ZnO within the silicone matrix.

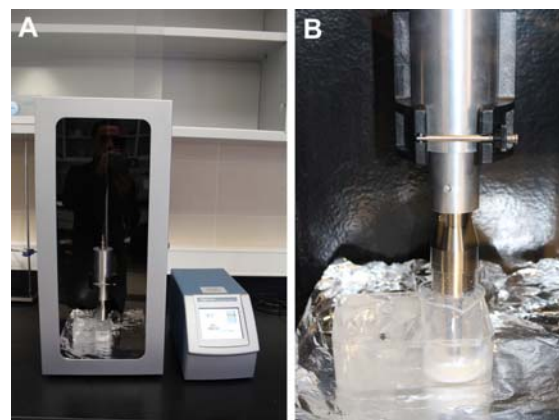


Figure 1: (A) Ultrasonic homogenizer (Q700 sonicator) for dispersing nano-ZnO in ethanol, (B) Flat-bottom cylindrical-shaped beaker placed in ice-bath for continuous cooling.

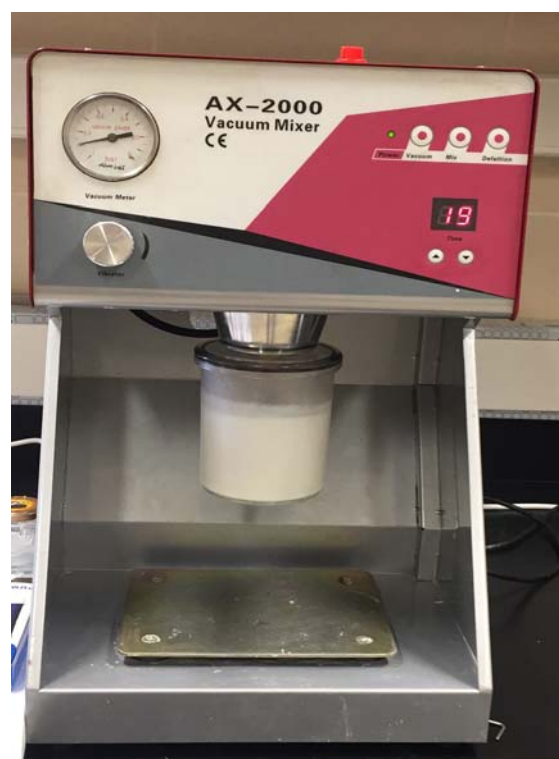


Figure 2: Vacuum mixer for mixing and vacuuming M-511 silicone and nano-ZnO.



Figure 3: Bowl of the vacuum mixer connected to rotary pump and placed over magnetic hotplate stirrer to fasten the evaporation of the ethanol.

## Results

The morphologies of u-ZnO and t-ZnO nanoparticles were inspected using the FESEM (Figure 4). The u-ZnO nanoparticles have a strong clustering property that will not easily disrupt and exhibited aggregation and agglomeration (Figure 4 A and B) at 1  $\mu\text{m}$  and 200 nm scale with different magnification. Meanwhile, the t-ZnO nanoparticles had smaller clusters after being treated, and all aggregation was disrupted and homogeneously dispersed (Figure 4 C and D) at 1  $\mu\text{m}$  and 200 nm scale with different magnification.

The XRD test (Figure 5) for specimens with 3% u-ZnO and 3% t-ZnO showed that u-ZnO had a higher agglomeration rate, while the sonicated nanoparticles of t-ZnO exhibited a smaller size. Specimens with 3% t-ZnO showed higher peaks in the XRD which mean it has more crystallinity, due to the more highly dispersed particles, while 3% u-ZnO has less crystallinity due to aggregation and agglomeration of nano-ZnO.

FESEM images of t-ZnO nanoparticles within the silicone matrix showed a homogenous dispersion, while u-ZnO without ethanol treatment showed aggregation and agglomeration of nanoparticles within the silicone matrix (Figures 6 and 7). FESEM images of cross-sectioned silicone elastomers with different concentration of ZnO nanoparticles are shown in 1  $\mu\text{m}$  scale. Figure 6 panel (A) shows 1% u-ZnO, panel (B) shows 1% t-ZnO, panel (C) shows 2% u-ZnO and panel (D) shows 2% t-ZnO. Figure 7 part (A) shows 3% u-ZnO, part (B) shows 3% t-ZnO, part (C) shows 5% u-ZnO and part (D) shows 5% t-ZnO.

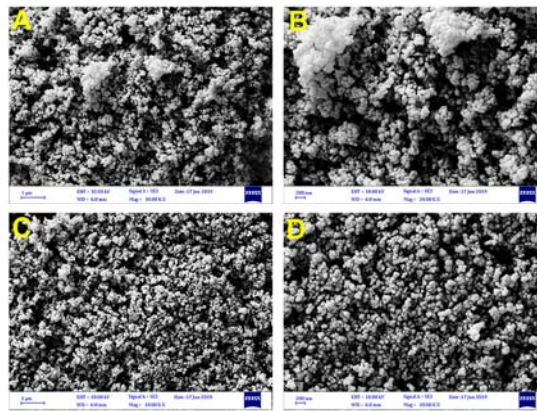


Figure 4: FESEM images of ZnO nanoparticles: (A) and (B) u-ZnO at 1  $\mu\text{m}$  with 10.00 KX magnification, and 200 nm with 20.00 KX magnification, (C) and (D) t-ZnO at 1  $\mu\text{m}$  with 10.00 KX magnification, and 200 nm with 20.00 KX magnification.

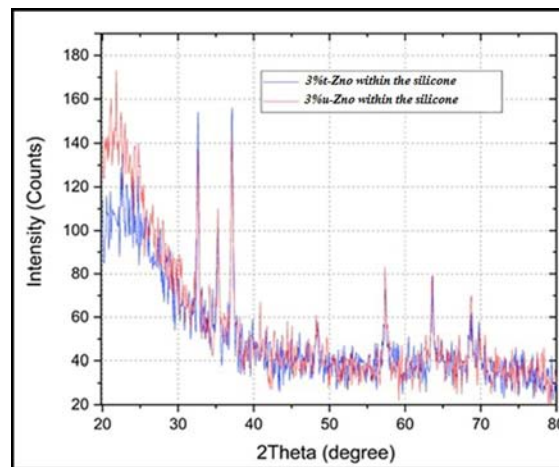


Figure 5: The X-ray diffraction (XRD) patterns of both 3% u-ZnO and t-ZnO within the silicone elastomer matrix.

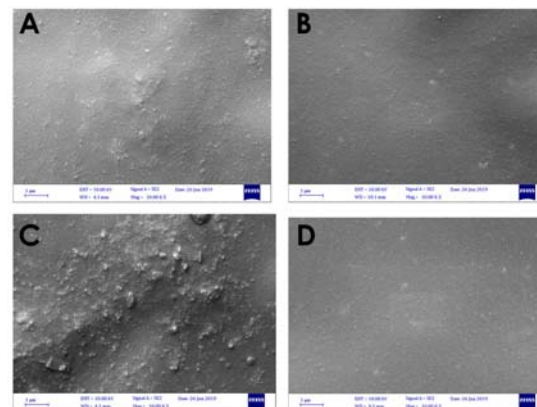


Figure 6: FESEM images of (A) 1%u-ZnO within M-511 silicone, (B) 1%t-ZnO within M-511 silicone, (C) 2%u-ZnO within M-511 silicone, (D) 2%t-ZnO within M-511 silicone.

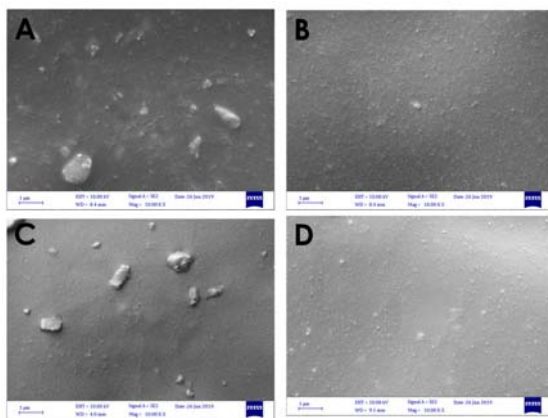


Figure 7: FESEM images of (A) 3%u-ZnO within M-511 silicone, (B) 3%t-ZnO within M-511 silicone, (C) 5%u-ZnO within M-511 silicone, (D) 5%t-ZnO within M-511 silicone.

## Discussion

The purpose of this study was to develop an enhanced material for maxillofacial prostheses with optimal dispersion. The main focus was on dispersing ZnO nanoparticles homogenously within the silicone elastomer matrix. To achieve this, a new technique was used to disperse different concentrations of ZnO nanoparticles within the silicone matrix. Sonication of ZnO nanoparticles affected its dispersion within the silicone, so the null hypothesis was rejected.

The challenge lies in dispersing the fine nanoparticles into the polymer matrix homogeneously to allow the full benefit of the potentially high interface area of the nanofiller-polymer. Uniform nanoparticle dispersion and reducing the size of nanoclusters are of great importance to producing high-quality materials and improving the mechanical properties of the material. Large clusters of nanoparticles result in areas of stress concentration, subsequent crack formation and propagation throughout the matrix of the polymer, and, finally, failure of the polymer<sup>(4,12,15)</sup>.

Dry nanoparticle powders consist of particles that are bound together into macroscopic structures by both particle fusion, which is a strong chemical bond, and by Van der Waals forces which are a weak physical bond<sup>(10,16,17)</sup>. Over time, these particles usually tend to agglomerate by the inter-particle adhesion forces. The ultrasonication techniques act as repulsive forces and affect the surface of nanoparticles which prevent the agglomeration of particles to achieve stable nanofluids<sup>(18)</sup>.

During sonication, the principal responsible waves for powder breakage are the shock waves from cavitation collapse. In fact, the particles act as nuclei to begin the process of cavitation, which partially clarifies why sonication is so effective. When ultrasound energy is applied to the nano-powder suspension, fragmentation of clusters can occur either through erosion or fracture. Detachment of particles from the surface of the large or parent agglomerates refers to erosion, while smaller agglomerates or aggregates separated from agglomerates by the propagation of cracks initiated at surface defects refers to fracture<sup>(11)</sup>.

The most important parameter affecting the deagglomeration is the specific energy, which is a parameter combining both time and power. Sonication can give specific energy to each nanoparticle, which helps it to stay alone in the suspension and not tend to aggregate<sup>(19)</sup>.

During sonication, due to cavitation, extreme local heating takes place and will result in bulk heating of the liquid over time. Excessive bulk heating can lead to changes in the sample volume after ultrasonication, evaporative loss of liquid, and degradation of the nanoparticles or other medium components if proper precautions are not employed. Operating in pulsed mode and immersing the sample in an ice-water bath can retard the rate of temperature increase, allowing better temperature control and minimizing unwanted side effects. These precautions were used in this study<sup>(11,20)</sup>.

Ultrasonication has been accepted as a fundamental step in the preparation of nanofluids, and it is an effective method to break up cluster formation and to facilitate dispersion of the nanoparticles. The FESEM and XRD results revealed a homogenous dispersion of ZnO nanoparticles within the silicone elastomers. The size of nanoclusters decreased through ultrasonication; this agrees with findings from other works<sup>(12,13,21-29)</sup>.

A previous study performed by Han et al.<sup>(3)</sup> incorporated three different nano-oxides of Ti, Zn, and Ce (non-surface treated) to A-2186 maxillofacial silicone elastomer. The SEM result revealed that at concentration of 2%, there were a well-distributed of particles of all the three nano-oxides in the silicone matrix, but all the three nano-oxides showed agglomeration and aggregation when the concentration was increased to 3%, whereas results from the present study, showed homogenous dispersion even in concentration of 5%ZnO as this revealed from the FESEM results.

## Conclusions

Preparing silicone nanocomposite using sonication led to superior quality nanocomposite without requiring nanoparticle modification with coupling agents or any third material addition. Nanocluster size reduction using ultrasonic homogenizer in ethanol allows greater incorporation of fillers than in the previous methods with homogenous dispersion, and without adversely affecting the silicone, and revealed that ultrasonication is an effective and easy way to decrease and reduce cluster size and to disperse ZnO nanoparticles. The practicability of this method reveals a basis for future clinical approaches without using sophisticated techniques.

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