Hybrid effects of zirconia nanoparticles with aluminum borate whiskers on mechanical properties of denture base resin PMMA

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The aim of this study was to investigate the hybrid effects of ZrO₂ nanoparticles (nano-ZrO₂) and aluminum borate whiskers (ABWs) on flexural strength and surface hardness of denture base resin, polymethyl methacrylate (PMMA). Both nano-ZrO₂ and ABWs were modified by silane coupling agent (Z6030) before being mixed with PMMA. Various amounts of silanized nano-ZrO₂ and ABWs were mixed with PMMA to prepare ZrO₂-ABW/PMMA composites. Flexural strength and surface hardness were evaluated using three-point bending test and Vickers hardness test respectively. Fractured surfaces were also observed by scanning electron microscopy (SEM). The mechanical behaviors of silanized ZrO₂-ABW/PMMA composites were significantly improved. Flexural strength reached a maximum value of 108.01±5.54 MPa when 2 wt% of nano-ZrO₂ was mixed with ABWs at a ZrO₂/ABW ratio of 1:2, amounting to an increase of 52% when compared with pure PMMA. Surface hardness achieved a maximum value of 22.50±0.86 MPa when 3 wt% of nano-ZrO₂ was mixed with ABWs at the same ZrO₂/ABW ratio, which was an increase of 27% when compared with pure PMMA.

Keywords: Zirconia nanoparticles, Aluminum borate whiskers, PMMA, Flexural strength, Surface hardness

INTRODUCTION

Polymethyl methacrylate, PMMA, is still widely used as denture base material due to its satisfactory esthetics, easy operation, low cost, and favorable stability in the oral environment^{1,2}. However, poor mechanical property is one of the major shortcomings of PMMA denture base composites, which limits their potential use^{3,4}. To facilitate more clinical uses, various micro- or nano-sized fillers have been incorporated into PMMA⁴⁻⁷. Although this area has seen significant progress⁸⁻¹⁰, the fracture of dentures remains an unresolved clinical problem.

Recent reviews of nanocomposites have highlighted filler materials in the form of whiskers or fibers¹¹⁻¹⁴, due to the latter's high mechanical performance^{15,16}. Whiskers are a highly pure and acicular material with a single crystal structure fabricated under well controlled conditions. Their large length-diameter ratio effectively prevents the matrix from crack development, while their highly ordered arrangement of atoms results in low brittleness, thus enhancing the mechanical properties¹⁷. Among the whisker reinforcement materials, aluminum borate (Al₁₈B₄O₃₃) whiskers offer superior mechanical properties at a low cost. Our previous study showed that flexural strength, surface hardness, and thermal stability were significantly increased by adding an optimum amount of aluminum borate whiskers (ABWs) to the PMMA matrix¹⁸.

Nowadays, numerous investigations have focused on nanomaterials to enhance the mechanical properties of PMMA, because of their special characteristics¹¹⁻¹⁵. In recent years, bioceramic nanoparticles have been used to enhance the mechanical properties of PMMA^{3,19}.

ZrO₂, being a typical bioceramic, shows great biocompatibility and bioactivity. ZrO₂ improves mechanical properties and is suggested to be relatively suitable for dental restorations²⁰.

Mixing very short fillers of less than 1 µm (microfillers) with larger fillers of more than 1 µm (macrofillers) has been shown to produce homogenous structures and improve the mechanical properties of PMMA composites. This is because the microfillers prevented the settling of macrofillers when mixing with monomers²¹. Lin *et al.*¹⁵ found a significant increase in the mechanical properties of polyether ether ketone (PEEK) composites which were reinforced with carbon fibers (microfillers) and ZrO₂ nanoparticles (nanofillers). However, research on reinforcing PMMA denture base composites by compounding nanofillers together with microfillers remains scarce. The aim of this study was to evaluate the hybrid effects of PMMA-based composites with different amounts of silanized ZrO₂ nanoparticles (nano-ZrO₂) and ABWs on flexural strength and surface hardness.

MATERIALS AND METHODS

Materials

Type 2 denture base resin powder and liquid were supplied by Second Medical Zhangjiang Biological Material Co., Ltd. (Shanghai, PR China). ZrO₂ nanoparticles (Tosoh Corp., Japan) had an average granularity of 90 nm and an average surface area of 7±2 m²/g. Aluminum borate whiskers (Shanghai Whisker Composites Manufacturing Co., Ltd., Shanghai, PR China) were of 5–30 µm length and a diameter of less than 1.5 nm, with a surface area of 2.0–2.5 m²/g. Silane

coupling agent was Z-6030 supplied by Dow Chemical Company (USA).

Methods

1. Modification of ZrO_2 nanoparticles

1.5 wt% of Z-6030 was mixed with 10 g of acetone for 10 min by ultrasonic oscillation. Nano- ZrO_2 particles were dispersed into the mixture at room temperature and mixed again ultrasonically for 30 min. Temperature was raised to 80°C for coupling reaction to occur. After nano- ZrO_2 was dried for 24 h, silanized ZrO_2 nanoparticles were thus obtained.

2. Modification of aluminum borate whiskers

Pure ethanol and distilled water were mixed at 9:1 (wt) ratio, and pH value was adjusted to 4–5 using glacial acetic acid. Z-6030 of 2 wt% was added to the mixture and mixed using a magnetic stirring apparatus for 1 h to pre-hydrolyze Z-6030. Meanwhile, ABWs were ultrasonically mixed with distilled water (ABW/water ratio of 1:5) for 5 min to obtain the ABWs solution. Pre-hydrolyzed Z-6030 was slowly added to the ABWs solution and stirred for 10 min. After 30 min, the mixture was filtered by vacuum filtration at room temperature. Coupling reaction continued to occur in the remaining slurry. After drying at 120°C for 24 h, silanized aluminum borate whiskers were thus obtained.

3. Preparation of standardized specimens

Silanized nano- ZrO_2 and ABWs were ball-milled with PMMA powder at a speed of 180 rev/min for 10 min every other alternate way to run the mixed powder for dry grinding for 120 min using a ball mill apparatus (XQM, PR China). Mixed powder was dispersed in mono-MMA liquid at a powder/liquid mass ratio of 2:1. Polymerization of denture base resin was initiated, and silanized ZrO_2 -ABW/PMMA nanocomposites were thus obtained.

The nanocomposites were divided into four groups according to different amounts of nano- ZrO_2 at 1, 2, 3, and 4 wt%. Each group was subdivided according to ZrO_2 /ABW mass ratios of 2:1, 1:1, 1:2, and 1:3. Unsilanized ZrO_2 -ABW/PMMA nanocomposites were prepared in the same way by admixing unsilanized nano- ZrO_2 and ABWs, and were regarded as the control groups. Pure PMMA was used as the blank group.

Based on the recommendations of ISO 20795-1:2008, all specimens in this study had the standardized dimensions of 64 mm length, 10.0 ± 0.2 mm width, and 3.3 ± 0.2 mm height²². Six standardized specimens were used in each group.

4. Vickers hardness test

One specimen, randomly chosen from each group, was polished by waterproof abrasive paper (240 to 2000 CW) to mirror-like smoothness. Six points were randomly selected from each mirror-polished specimen to be subjected to Vickers hardness testing using a microhardness tester (HX-1000TM, Shanghai Taiming Optical Instruments Co., Ltd., PR China). Loading was

50 gf (0.490 N) at a speed of 0.05 mm/s for 10 s.

5. Three-point bending test

Three-point bending test, according to ISO 1566:1999³, was carried out on all groups in a constant-temperature water bath of 37°C for 48 ± 2 h. Using a universal testing machine (EZ20, Lloyd Instruments Ltd., UK), loading was carried out on each test specimen with a span of 50 mm and at a crosshead speed of 5 mm/min until fracture occurred.

6. Scanning electron microscope (SEM) observation

One specimen was randomly selected from each group. Fractured surface was coated with gold and observed by field emission scanning electron microscopy (Sirion 200, FEI Co., USA).

7. Statistical analysis

Data were analyzed using three-level nested ANOVA by SAS 6.12 statistical software (SAS Institute Inc., USA).

RESULTS

Flexural strength

Flexural strength was significantly reinforced by nano- ZrO_2 and ABWs, and silanized ZrO_2 -ABW/PMMA nanocomposites exhibited apparently higher flexural strength than the unsilanized composites (control groups) (Table 1). With an increase in the amount of fillers, the flexural strength of silanized ZrO_2 -ABW/PMMA nanocomposites increased when the amount of nano- ZrO_2 was increased from 1% to 2%, but decreased when it was increased from 2% to 4% (Fig. 1). Flexural strength achieved the highest value when 2% of nano- ZrO_2 was added, and which was significantly different from the other groups ($p < 0.001$).

The ZrO_2 /ABW ratio also played an important role in reinforcing the composites. Flexural strength showed an increase at first, followed by a decrease, with an increase in ZrO_2 /ABW ratio (*i.e.*, amount of ABWs increased while the amount of nano- ZrO_2 remained constant) (Fig. 1). At nano- ZrO_2 of 2%, flexural strength achieved the maximum value of 108.01 ± 5.54 MPa with ZrO_2 /ABW ratio of 1:2, an increase of 52% when compared with the blank group (70.88 ± 7.73 MPa). It was significantly different from the other groups at the same nano- ZrO_2 amount ($p < 0.05$) and from the control group ($p < 0.01$).

SEM observation

The morphology of fractured surfaces of different groups was observed by SEM. Figure 2 shows the representative photographs of ZrO_2 /ABW ratios of 2:1, 1:1, 1:2, 1:3 at ZrO_2 amount of 2% and ZrO_2 /ABW ratio of 1:3 at ZrO_2 amount of 4%. At ZrO_2 /ABW ratio of 2:1, the fracture surface was relatively smooth (Fig. 2(a1)). At a higher magnification, it could be seen that nano- ZrO_2 dispersed evenly in the matrix, while ABWs were not found since its amount was low (Fig. 2(a2)). At ZrO_2 /ABW ratio of 1:1, ABWs could be found at lower

Table 1 Flexural strength of each group (The values with the same mark have no significant difference)

Flexural strength (MPa)			
ZrO ₂	ZrO ₂ /ABW	Experimental group	Control group
1%	2:1	77.9±5.1 ^a	77.5±2.7 ^a
	1:1	81.6±7.2 ^a	81.3±5.0 ^a
	1:2	90.1±3.1 ^a	84.5±3.4 ^a
	1:3	86.9±6.3 ^a	83.9±4.8 ^a
2%	2:1	92.1±4.5 ^a	78.5±3.1 ^a
	1:1	96.2±4.9 ^b	84.8±6.8 ^a
	1:2	108.0±5.5 ^c	81.3±5.8 ^a
	1:3	97.1±3.6 ^b	81.4±7.6 ^a
3%	2:1	82.6±7.2 ^a	74.2±3.6
	1:1	86.6±4.8 ^a	75.7±6.4
	1:2	82.5±5.4 ^a	74.1±4.2
	1:3	82.3±6.4 ^a	81.4±6.9 ^a
4%	2:1	73.1±4.2	68.5±3.7
	1:1	78.3±4.8 ^a	76.7±5.9 ^a
	1:2	77.2±4.6 ^a	73.3±7.7
	1:3	73.3±5.8	73.4±6.4
Blank group (pure PMMA)		70.9±7.7

Fig. 1 Flexural strengths of silanized ZrO₂-ABW/PMMA nanocomposites.

magnification and the fracture surface was irregular (Fig. 2(b1)). The ABWs blended well with the resin matrix, and fracture fossa was found at higher magnification (Fig. 2(b2)). As the amount of ABWs increased, more and more whiskers were seen to be well dispersed in the matrix at lower magnification, with

Fig. 2 SEM images of ZrO₂-ABW/PMMA nanocomposites at different ZrO₂/ABW ratios of: (a) 2:1 with 2% of nano-ZrO₂; (b) 1:1 with 2% of nano-ZrO₂; (c) 1:2 with 2% of nano-ZrO₂; (d) 1:3 with 2% of nano-ZrO₂; and (e) 1:3 with 4% of ZrO₂. (1) Lower magnification at ×4,000; (2) Higher magnification at ×20,000.

nano-ZrO₂ uniformly distributed in the matrix (Fig. 2(c1)). The ABWs were impregnated with resin and well embedded in the resin matrix (Fig. 2(c2)).

When the filler content exceeded its optimal amount, entanglement and agglomeration of fillers occurred. In Fig. 2(d2), the smooth surfaces of ABWs and poor

Table 2 Surface hardness of each group (The values with the same mark have no significant difference)

Surface Hardness (MPa)			
ZrO ₂	ZrO ₂ /ABW	Experimental group	Control group
1%	2:1	18.5±0.6	18.3±0.4
	1:1	19.5±1.1 ^a	18.4±0.3
	1:2	18.8±1.0	19.2±0.9 ^a
	1:3	18.4±0.6	18.5±0.8
2%	2:1	17.9±0.8	18.4±0.6
	1:1	19.6±1.1 ^a	19.2±0.7 ^a
	1:2	21.8±1.3 ^b	19.6±1.1 ^a
	1:3	19.3±0.5 ^a	18.4±1.0
3%	2:1	19.4±0.5 ^a	18.0±1.3
	1:1	21.2±0.4 ^b	18.6±0.9
	1:2	22.5±0.9 ^c	20.1±1.1 ^b
	1:3	21.3±1.5 ^b	19.5±1.0 ^a
4%	2:1	19.5±0.6 ^a	18.0±0.7
	1:1	19.8±1.4 ^b	18.6±0.9
	1:2	18.7±0.8	19.2±1.2 ^a
	1:3	18.3±1.2	18.5±1.5
Blank group (pure PMMA)		17.8±0.5	

adhesion to the resin matrix were manifested. At ZrO₂/ABW ratio of 1:3 and nano-ZrO₂ amount of 4%, the fillers tended toward agglomeration, and the fracture surface demonstrated characteristics of brittle fracture at lower magnification (Fig. 2(e1)). At higher magnification, nano-ZrO₂ and ABWs were unevenly dispersed in the matrix and gathered into clusters (Fig. 2(e2)).

Surface hardness

Silanized ZrO₂-ABW/PMMA nanocomposites showed higher surface hardness than the control groups and the blank group (Table 2). The surface hardness of reinforced groups ran a similar changing pattern as flexural strength (Fig. 3). Silanized ZrO₂-ABW/PMMA nanocomposites showed the highest surface hardness when amount of nano-ZrO₂ was 3% (Fig. 3). It was significantly higher than the other groups ($p < 0.001$). At 3% of nano-ZrO₂, surface hardness achieved the maximum value of 22.50±0.86 MPa when ZrO₂/ABW ratio was 1:2, which was significantly different from the other groups and the control group ($p < 0.05$). This was an increase of 27% when compared with the blank group (17.78±0.50 MPa).

DISCUSSION

Many researches have shown that PMMA could be reinforced by the addition of rigid particles^{3,5,23,24}. The toughening effect of the particles has been explained in terms of certain fracture mechanisms, the most

Fig. 3 Surface hardness values of silanized ZrO₂-ABW/PMMA nanocomposites.

recognized being crack pinning, crack deflection, and plastic deformation²³. Although the existence of crack deflection and pinning was questioned, the definite improvement in mechanical properties of PMMA resins filled with nano-ZrO₂ was unquestionable²⁴. In a previous study, the effects of nano-ZrO₂ on the flexural strength and surface hardness of PMMA were evaluated²⁵. Results showed that ZrO₂/PMMA nanocomposites reached the highest flexural strength (87.37±4.48 MPa) and surface hardness (19.97±1.62 MPa) when nano-ZrO₂ was added at 1.5 wt%, which were increases of 23% and 12% when respectively compared with the pure PMMA. For ABWs, the toughening mechanisms included crack deflection, crack bridging, and frictional pullout²⁶. Our previous study¹⁸ found that the flexural strength and surface hardness of PMMA resin reinforced with ABWs increased by 30%.

In the present study, the flexural strength and surface hardness of silanized ZrO₂-ABW/PMMA nanocomposites were raised by 52% and 27% respectively when compared with pure PMMA. The surface hardness of ZrO₂-ABW/PMMA nanocomposites was not significantly different from that of ABW/PMMA nanocomposites¹⁸. However, the highest surface hardness value of ABW/PMMA nanocomposites was achieved at an ABW amount of 15%¹⁸, while ZrO₂-ABW/PMMA nanocomposites achieved the highest value at a ABW amount of 4% in the present study. Therefore, the reinforcing effect of ZrO₂-ABW/PMMA nanocomposites was more effective, being more economical in the amount of fillers used. This was possible because of the synergistic effect of nano-ZrO₂ and ABWs in enhancing the mechanical properties of PMMA. By compounding the two fillers together, nano-ZrO₂ suppressed the grain growth of ABWs during polymerization. At the same

time, ABWs acted as seeds for the grain growth of nano-ZrO₂ to form large elongated grains around the whiskers, thus resulting in a good grain microstructure²⁷⁻²⁹.

Due to the enormous specific surface area, high surface energy, and active chemical properties, nanoparticles have a strong tendency to aggregate and decrease particle-polymer interactions, thus lowering the reinforcement of PMMA^{9,30}. In the present study, the strategy to modulate the dispersion of fillers and particle-polymer interactions was to surface-treat nano-ZrO₂ and ABWs with a silane coupling agent (γ -MPTS). It is a bi-functional monomer, with the hydroxymethyl groups substituted by hydroxyl groups for attachment to the fillers. This decreased the surface tension of the particles and influenced the spatial distribution of fillers. On the other hand, γ -MPTS contained C=C bonds which reacted with PMMA matrix during the curing process, thereby acting as a “molecular bridge” to establish chemical bonding between PMMA matrix and the particles. Silanized ZrO₂-ABW/PMMA nanocomposites exhibited remarkably higher flexural strength and surface hardness than unsilanized nanocomposites in this study. Another way to control the dispersion of fillers and particle-polymer interactions was to manipulate the ZrO₂-ABW/PMMA nanocomposites preparation procedure. Mechanical attrition, such as bead ball milling and ultrasonication, was used to temporarily resist the agglomeration tendency during the modification step.

Results of this study revealed that PMMA reinforcement was obviously related to the filler amount present in the composites, a claim substantiated by SEM images of their morphologies. The flexural strength and surface hardness of ZrO₂-ABW/PMMA nanocomposites increased gradually at first. At this stage, SEM showed an increase in filler amount with homogeneous dispersion (Figs. 2(a) and (b)). At ZrO₂/ABW ratio of 1:2, ABWs were impregnated with resin and well embedded in the resin matrix, and nano-ZrO₂ distributed evenly (Fig. 2(c)). At this ratio, highest mechanical properties were achieved. However, as the amount of fillers increased, the surfaces of ABWs remained clear and smooth with poor adhesion to the resin matrix, together with the emergence of clusters (Figs. 2(d) and (e)). As a result, the flexural strength and surface hardness deteriorated.

For denture base materials, flexural strength is of prime importance amongst a host of properties. For this reason, 2% of nano-ZrO₂ at ZrO₂/ABW ratio of 1:2 was determined as the optimum amount to reinforce ZrO₂-ABW/PMMA nanocomposites so as to provide enhanced mechanical properties for removable partial dentures.

Besides mechanical properties, thermal property, dimension stability, and biocompatibility are also critical properties of a denture base material. More studies should be conducted to evaluate these properties to prove that ZrO₂-ABW/PMMA nanocomposites are clinically satisfactory.

CONCLUSIONS

The amounts of nano-ZrO₂ and ABWs added to PMMA and their ratio significantly affected the flexural strength and surface hardness of ZrO₂-ABW/PMMA nanocomposite material. To achieve maximum flexural strength, the optimum amount of nano-ZrO₂ and ABWs to reinforce PMMA was 2% of nano-ZrO₂ at ZrO₂/ABW ratio of 1:2, causing flexural strength to increase by 52% when compared with pure PMMA. To achieve maximum surface hardness, the optimum amount was at 3% of nano-ZrO₂ with the same ZrO₂/ABW ratio, causing surface hardness to increase by 27% when compared with pure PMMA.

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