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ZnO-AlBw-reinforced dental resin composites:Effect of pH level on mechanical properties

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Abstract: The aim of the present study was to investigate the pH level on the reinforcement of Zn-fused ceramic whisker composites. zixc oxide (ZnO)-fused aluminum borate whisker (AlBw) were used to strengthen dental resin composites, and the pH level was found to be a pivotal parameter that determined the composite strength. And the purpose of this study was to investigate the effects of pH level on the bending strength, elastic modulus, compressive strength and hardness of the composites at pH=6.0, pH=6.2, pH=6.4, pH=6.6 and pH=6.8, respectively. Each mixture was thermally fused originally, then silanized and combined with a dental resin at a filler mass percentage of 50%. X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) were employed to characterize and analyze the AlBw, ZnO-AlBw and fracture surface of the resin composites. The highest bending strength (Mpa) was the group of pH=6. 4 (140.58±12.86, n=5), and the minimal bending strength was the group of unmodified AlBw (73.20±6.12, n=5). Compressive strength and bending strength were just the opposite, the group of unmodified AlBw was highest (332±40, n=5), and the group of pH=6.4 was lowest (298±20, n=5). Reinforcement

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with ZnO-fused AlBw resulted in novel dental resin composites that possessed bending strength higher than numodified whiskers.

Keywords: ZnO-AlBw; pH level; Resin composites; Bending strength; Fracture surface

Introduction

Extensive research has been engaged in improving and reinforcing the microstructure and properties of dental resin composites[1-3] Reinforcement with networked fibers [4], chopped glass fibers [5] , optimization in filler level and degree of conversion [6, 7] are used to enhance the mechanical properties of dental resin composites. Some studies have discussed the effects of thermal treatment on the enhancement of resin composites toughness and strength [8-10] .However, in order to extend the use of resin composites, stress-bearing applications are needed to improve significantly such as indirect crown and multiple-unit restorations, and direct posterior restorations involving cusps, etc. Because the using of dental resin composites is restricted by the relatively high brittleness and low fracture resistance of current dental composites still limit their uses [11, 12] . For example, a heat-cured and pressure-cured inlay or onlay dental resin composite had a properly low flexural strength [13,14]. An indirect resin composite was not recommended to restore full crown owing to its brittleness. Even incluing inlay and onlay applications, while the clinical failure rate of dental resin composites was brought about[15, 16].

Recently, a novel ceramic whisker filler system was developed to reinforce dental composites [17-19]. The whiskers which were short fiber-shaped single crystals possessed high strength and stiffness. Silica glass particles were fused onto the whisker surface, which could roughen the whisker surface and facilitate silanization for improved retention in the matrix. This approach had greatly enhanced the mechanical properties of the dental resin composites [20, 21]. Xu et al [22] found that the ratio of silica and whisker was a significant microstructural parameter which determined the strength of resin composites. However, then only focused on the processing of filler levels and different silica : whisker ratio without studying the changes in the fracture toughness of the resin composites. Furthermore, the elastic modulus and hardness, that were vital properties for dental resin composites werechanged induced by silica : whisker ratio, which could be measured with a AG – IS universal material testing machine [23-25].

As a kind of extremely significant and strategic material, nano-zinc oxide (ZnO) had received extensive attention in recent years [26]. Due to the direct wide band-gap of 3.37 ev, a large exciton binding energy of 60 Mev at room temperature, also exhibit near-ultraviolet emission, optical transparent, electric conductivity [27], magnetic, piezoelectric. and antibacterial properties [28] etc. Regardless of application, the morphology and particle size of ZnO played important roles, thus calling for novel routes for fabricating ultrafine ZnO particles with special morphologies. Such as nanotube, nanowire, nanorod and nanopaticle. They had elicited considerable attention in the electronics industry and optoelectronic devices. At last, numerous methods and techniques emerged. For instance, pyrolysis [29], hydrothermal method [30], evaporation at high temperature [31], template method [32, 33] etc. However, most of the methods created ZnO nanostructures by using a catalyst, e.g., gold, but it was not desirable due to its high cost. So, sol-gel [34] method was proposed. Such as, Jiang et al [35] researched that the Rod-like ZnO particles were synthesized via sol–gel method by adding ethylene diamine (EDA) to the reaction system of $Zn(Ac)_2 \cdot 2H_2O$ and $H_2C_2O_4 \cdot 2H_2O$. The crystal phase and morphology of the products were characterized by XRD (X-ray diffraction) and TEM (transmission electron microscope). Rod-like ZnO belonged to the hexagonal Wurtzite system, with diameters and lengths of about 20–200nm and 0.2–1.5μm, respectively. Experimental results showed that the morphology of nano-ZnO could be controlled by modulating the quantities of EDA. And EDA played an important role in the formation of rod-like ZnO particles. In addition, the antibacterial activity of nano ZnO had been investigated and presented in recent years. Such as Amornpitoksuk et al [36] revealed that the prepared ZnO particles showed antibacterial effect against E. coli and S. aureus.

Therefore, the aim of the present study was to investigate the pH level on the reinforcement of Zn-fused AlBw surface. It was hypothesized that the different pH value would significantly influence the distribution of ZnO particles on the AlBw surface. And it was further hypothesized that the whisker-reinforced composites would possess significantly higher bending strength and elastic modulus of matching than the unmodified whisker control composites.

Materials and methods

Aluminum borate whisker: modification, high temperature fusion, and silanization

In the first type of modification, the sol of zinc acetate (Chian,AR) and polyethylene glycol (PEG_{6000}, Chian,AR) was dropped by drop into the miscible liquid of AlBw (Haixing, Qinghai, China) having diameter ranging from 0.5 μm to 1 μm with a mean of approximately 0.8 μm. And ethanol solution (Chian, AR) by the constant flow pump. The pH of mixed solution was adjusted to 6.0, 6.2, 6.4, 6.6, 6.8 with aqueous ammonia (Chian, AR), respectively. Secondly, it was stirred at 70℃ for 6 hours, after the solvent was evaporated at 78℃~80℃ until dry. And the dried mixture was sintered at 2℃ per minute to 800℃ [37], then it was maintained for 30 min at 800℃. Lastly the heat-treated powder were silanized. The filler powders from each of the three types of treatment were silanized by being mixed with γ-MPS in cyclohexane with n-propylamine as a catalyst in a rotary evaporator until dry.

Specimen fabrication

Each of the five silanized powders was manually mixed by spatulation with a dental resin monomer consisting of mass percentages of 49.75% of UDMA (Sigma Aldrich - company, USA), 49.75% TEGDMA (Tokyo, Japan), 0.3% CQ (Shymax Chemical Co., LTD, USA) and 0.2% DMAEMA (The Alfa Aesar Chemical Co., LTD, USA). The paste was placed into a steel mold of 2mm*2mm*25mm dimensions (fig. 1 (A) and (B)), and the specimens were cured by light (LITEXTM682, DENTAMERICA, USA) at a room atmospheric pressure to make flexural specimens. As the Fig. 1 showed. Specimens of Filtek™ Z350 Universal Restorative (3M, lot number: 7CH, A3, USA) were cured following the same procedures. Five specimens were made at each filler level for each of the three powders.

X-ray diffraction analyses

XRD analysis was performed with an X-ray diffractometer (M/max 2200, Rigaku Corporation, Japan), which measured by Cu-Ka (λ = 0.15406 Å) radiation in the 2θ range from 0° to 90° with a scanning speed of 4° per min at 36 KV and 30 mA.

Testing

All the cured specimens were immersed in distilled water at 37 ℃ for 24hrs prior to being tested. The test condition at a relative humidity of about 40% in air with 22 ℃ room temperature. A standard three-point flexural test with a fixture span of 20 mm was used to fracture the specimens at a crosshead speed of 0.75 mm/min using a computer-controlled Universal Testing Machine (AG-IS, Shimadzu, Japan). The selected filler powder was sputter-coated with Pt and examined under a scanning electron microscope (SEM, XL30ESEM-TMP, Philips-FEI, Holland).

Statistical analysis

The acquired data of bending strength, elastic modulus, compressive strength and hardness were analyzed with one-way ANOVA ($\alpha = 0.05$) of SPSS software (version 17.0). SNK-q test was used at a family confidence coefficient of 0.95.

Results

Fig. 3. showed the diffraction peaks of AlBw and ZnO-AlBw. It revealed that typical peaks of impurities were observed in the group of AlBw, and there was $KAl_3(SO_4)_2(OH)_6$. The diffraction peaks of ZnO-AlBw at pH=6.0 showed that there were 5 kinds of compounds which were ZnO, $ZnAl_2O_4$, $Al_8B_4O_3$, $Zn_3(BO_3)_2$, $Zn(BO_2)_2$, respectively. When the pH value was 6.2, 6.4 and 6.6, the compounds were ZnO, Al_2ZnO_4, $Al_5(BO_3)O_6$, $Zn_3(BO_2)_2$. In addition, when the pH value was 6.8, the main compounds were Al_2ZnO_4, $Al_5(BO_3)O_6$, $Zn_3(BO_2)_2$, $Zn_4Al_{22}O_{37}$, ZnB_4O_7.

SEM micrographs in fig. 4 showed (A/a) AlBw, which were relatively straight, smooth and larger aspect ratio. (B/b, C/c, D/d, E/e, F/f) the surface of the whisker fused with ZnO particles that were observed on the AlBw surface after fusing at 800 ℃ [44] for 30 min. B/b, C/c, D/d, E/e, F/f corresponded to the pH of 6.0, 6.2, 6.4, 6.6, 6.8, respectively. There was obvious agglomeration on the surface of AlBw at pH=6.0. When the pH was 6.2 and 6.4, ZnO particles were distributed uniformly on the AlBw surface. With the increasing of pH, particle size distribution was less, and even reunion.

Table. 1 and fig. 5 (A) plotted the bending strength whisker composites as a function of the different pH level. Increasing the pH from 6.0 to 6.8 resulted in a significant increase (one-way ANOVA; $p<0.001$) in the measured bending strength which then reduced when the pH value was 6.6 and 6.8. The bending strength values (mean±SD; n=5) at pH=6.0, 6.2, 6.4, 6.6 and 6.8 were 109.64±7.62 Mpa, 121.26±8.92 Mpa, 140.58±12.86 Mpa, 105.18±7.34 Mpa, and 87.38±6.42 Mpa, respectively. In addition, they were significantly different from each other except group of pH=6. 0 and group of pH=6. 6 (P=0. 343), group of pH=6. 2 and group of Filtek^{TM} Z350 (P=0. 705). The composite elastic modulus measured by the computer-controlled Universal Testing Machine were plotted in fig. 5 (B). The 7 groups were significant difference by statistical analysis (one-way ANOVA; p<0.001). But there were not significantly different from each other, including group of unmodified AlBw and group of pH=6.8 (P=0.115), group of pH=6.0 and groups of pH=6.2, pH=6.6, Filtek^{TM} Z350 (P=0.270, 0.245, 0.115), group of pH=6.2 and group of Filtek^{TM} Z350 (P=0.621), group of pH=6.6 and group of pH=6.8 (P=0.389). On the other hand, the composite elastic modulus of pH=6.0 (7.50±0.62 Gpa), pH=6.2 (7.86±0.70 Gpa), pH=6.4 (8.74±0.80 Gpa), pH=6.6 (7.12±0.22 Gpa), and the group of pH=6.8 (6.84±0.54 Gpa) were higher than group of unmodified AlBw (6.32±0.38), The compressive strength values (Fig. 5 (C)) were not statistical significance, except group of unmodified AlBw and groups of pH=6. 4, Filtek^{TM} (P=0. 020). The hardness values (Fig. 5 (D)) were not statistical significance (F=1. 084, P=0. 396).

SEM micrographs of fracture surfaces were shown in fig. 6 for (a_1, a_2) group of pH=6. 0, (b_1, b_2) group of pH=6. 2, (c_1, c_2) group of pH=6. 4, (d_1, d_2) group of pH=6. 6, and (e_1, e_2) group of pH=6. 8. There were a lot of whiskers in the fracture surfaces. Fig. 5 (c_2) showed that there were pulled-out whiskers (blue arrow) and large fracture steps (yellow arrow). In addition, there were lots of ZnO particles on the surface of AlBw (red arrow). The fracture surfaces contained many elements, including C, O, S, Si, Ca, Al, Zn and Zr. In order to observe the internal structure of fracture surface clearly, backscattered electron image was used (Fig. 7. (A)). Many irregular arrangements of whiskers were observed (yellow arrows), and there were many ZnO particles on the whisker surface (red arrow) and in resin matrix (asterisk). In addition, the EDX profile (Fig. 7 (B)) of fracture surface showed that there were 5 elements, including C, O, Ca, Zn and Zr.

Discussion

Reinforcement of resin composites with ZnO-fused AlBw surface brought about a twofold increase in bending strength. The different pH value which producing the ZnO-fused AlBw surface fillers played a significant role in determining the properties of composites. The whiskers were blended into composites that were a typical conventional composite filled with glass particles, and had a mean fracture toughness value similar to those of the commercial control composites. Higher ratios of nanometer particles : ceramic whisker and more whiskers content in the composites would rapidly increase the fracture toughness. During composite cracking, ceramic whiskers in the composite have been observed to pin and deflect the crack propagation, thus it was important to increase the roughness of fracture surface by creating steps and tortuous topographies [21,38].

As shown in Fig. 6, the tortuous topographies were not observed. But whiskers were observed to pin in the composite. These features that consumed energy in creating new surface made up a high surface area [39]. Therefore, the toughening mechanisms was enhanced when proper whisker content was added into the composites. Also it might explain the subjects when the ratio of silica particle and whisker was increased from 1 : 0 to 1 : 2. However, the toughness of resin composites plateaued when the ratio of silica and whisker was further increased to 0 : 1. That was likely likely because the increasing toughness might be offsetted due to whiskers agglomeration and entanglement at a high whiskers content, especially when the ratio of silica and whisker was 0 : 1. A major problem which was confronted with in the whisker reinforcement technology was that the whiskers easily agglomerated and entangled during mixing [40-42]. The results of SEM revealed that the whiskers agglomerated and entangled each other in the resin composites, which was consistent with Xu ' s [40]observations that the whiskers easily agglomerated and entangled,using only whiskers without mixing with nanometer particles. In addition, they were difficult to separate and disperse from each other in the matrix [41]. The fine particles which made whiskers to separate from each other appeared to get in between whiskers, and minimizing whiskers agglomeration and entanglement. Such as silica, ZnO and so on. Therefore, fusing and mixing ZnO particles with AlBw not only improved AlBw distribution in the matrix, also enhanced she AlBw silanization and bonding to the resin matrix. The two factors were important to contribute to the measured substantial increase in the resin composites fracture toughness (Fig. 4 B/b, C/c, D/d, E/e, F/f). So nanometer ZnO particles were introduced and used.

In order to make ZnO particles fused uniformly on the whiskers surface. The pH value played an important role. It was interesting to compare with the different pH value on the ZnO-fused whiskers with that of the flexural strength [22].

The crystal structures of AlBw and ZnO-AlBw were investigated using XRD. As Fig. 3 showed. When the zinc acetate solution mixed into AlBw solution, after reacting, drying and calcinating, ZnO-AlBw was produced. Beyond that, $ZnAl_2O_4$, $Al_8B_4O_3$, $Zn_3(BO_3)_2$, Al_2ZnO_4, $Al_5(BO_3)O_6$, $Zn_4Al_{22}O_{37}$ and ZnB_4O_7 were obtained. It revealed that there was a chemical bond between ZnO and AlBw. In addition, when the pH value was 6.0, 6.2, 6.4 and 6.6, there were still ZnO, But there was no ZnO at pH=6. 8. And there were some different forms of zinc, which showed that different pH level affected on the forms of chemical combination between ZnO and AlBw.

Ceramic Whiskers which combined high stiffness and strength were the attractive enhanced materials for dental resin composites. The small size and nearly free of internal defects of whiskers had been used extensively in thermoplastic matrix composites [43,44] . Yield strength predicted by the theory of elasticity closed to the maximum theoretical value. In addition, whisker was very stable at room temperature. Therefore, in order to make the whisker surface activity to increase, the pH value was put forward [45]. The SEM micrographs showed that under different pH value, the morphologies of ZnO-fused whisker surface were different. Nano ZnO particles fused uniformly on the whiskers surface (Fig. 4 C/c, D/d), at pH=6.2 and 6.4. But when the pH was 6.4, ZnO particles were more well-distributed than pH=6.2. With the increase of pH value, The fusion effect happened to big change. Whisker surface had less particles at pH=6.6 (Fig. 4 E/e). Nevertheless, when the pH value of reaction solution was 6.8, there were hardly ZnO particles on the whisker surface, and the particles happened serious reunion phenomenon (Fig. 4 F/f). The one factor that the whiskers surface had different negative charge under different pH value. In other words, the number of O^{2-} was different on the whiskers surface. So that the combination of Zn^{2+} and O^{2+} was imparity. Eventually it led to the difference among bending strength, elasticity modulus, compressive strength and hardness. In addition, the binding force of Zn^{2+} and O^{2+} was stronger when the pH value was 6.4 than pH=6.2.

While the bending strength and elastic modulus altered with the pH value. The bending strength was the material' s resistance to local plastic deformation, and the modulus was the material' s resistance to elastic deformation. The mean modulus of the ZnO-AlBw composite at pH=6.4 was 8.74 Gpa, slightly higher than 6.32 Gpa, 7.50 Gpa, 7.86 Gpa, 7.12 Gpa, 6.84 Gpa and 8.02 Gpa of other 6 groups, but there were still lower than 22 Gpa of human tooth dentin [46]. The bending strength value change was large. It enabled the calculation of the ZnO-AlBw composite brittleness, or the ratio of compressive strength and hardness, which served as a significant parameter in comparing the brittleness of resin materials [38]. So looking for ways to reduce material brittleness became targets.

As shown in Fig. 5, ZnO-AlBw fillers significantly influenced bending strength, elasticity modulus, compressive strength and hardness of the resin composites compared to unmodified AlBw filler. At the pH=6.4, the values of those were increased to (140.58±12.86) Mpa, (8.74±0.80) Gpa, (298±20) Mpa and (0.60±0.12) Gpa, respectively. These results indicated that ZnO-AlBw fillers could substantially enhance the mechanical properties of the dental resin composites. The suggested reasons might be that ZnO-AlBw had a rougher surface that would increase ZnO-AlBw-matrix interfacial friction force. In addition, the incorporation of appropriate amount of ZnO nanopatricles in the resin matrix was capable to improve the mechanical properties. The values of group of pH=6. 4 were better than other groups. The possible reason was that ZnO particles were more distribution on the AlBw surface, which increased the contact area of ZnO and AlBw. The results were similar with Liu et al [47].

Fig. 5 shown the SEM images of fracture surfaces of the dental resin composites with ZnO-AlBw fillers. The fracture surface of ZnO-AlBw filled resin composites (pH=6. 0, 6.2, 6.4 6.6 and 6.8) had rougher and larger fracture surfaces (Fig. 6. a-e) which indicated that more energy was consumed during fracture. ZnO-AlBw which embedded in the resin composites had a favorable combination with matrix. The optimized interfacial adhesion allowed more effective stress transfer from the matrix to the reinforcement. However, typical AlBws toughening and reinforcing mechanisms were observed, such as AlBw pulling-out (Fig. 6 b_2), crack bridging and deflection (Fig. 6 c_2), break (Fig. 6 e_2) [42], which could absorb more energy to improve the ability of dental resin composites to resist fracture. In addition, ZnO particles which filled in the matrix were likely to increase the filler packing density (Fig. 7. A), which made the dental resin composites stronger and harder.

The EDX profiles (Fig. 6 a_3, b_3, c_3, d_3, e_3) indicated that the fracture surface contained some elements. Zn, Al and Si elements were from ZnO, AlBw and γ-MPS, respectively. And C, O, S, Ca and Zr were likely to come from air or matrin and so on. Fig. 7 B shown that elements distribution were same as Fig. 6 except S, Si and Al.

Conclusion

Reinforcement with ZnO-fused AlBw surface resulted in novel dental resin composites. When the pH was 6.4, ZnO particles were uniformly distribution on the whiskers surface. And when it was blended into resin matrix, the bending strength was significantly higher than other groups and available indirect dental composites. The SEM results of fracture surfaces were shown how the ZnO particles scattered on the whiskers surface and in the resin matrix. In summary, the fusion of ZnO particles onto the AlBw surface not only facilitated the AlBws silanization and bonding with the resin matrix, but also increased the AlBw retention in the matrix by providing rougher whisker surfaces. These factors together produced dental resin composites with superior bending strength..

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Table 1 The different pH of filler on the bending performance of composite resin (mean±SD，n=5)

Groups	Bending strength(Mpa)	Elastic modulus(Gpa)	Compressive Strength(Mpa)	Hardness (Gpa)
unmodified AlBw	73.20±6.12	6.32±0.38	332±40	0.82±0.28
6.0	109.64±7.62	7.50±0.62	316±28	0.70±0.18
6.2	121.26±8.92	7.86±0.70	310±26	0.68±0.20
6.4	140.58±12.86	8.74±0.80	298±20	0.60±0.12
6.6	105.18±7.34	7.12±0.22	318±30	0.74±0.22
6.8	87.38±6.42	6.84±0.54	326±34	0.80±0.24
Filtek^{TM} Z350	123.02±13.04	8.02±0.48	300±22	0.64±0.14

FIGURE CAPTIONS

Fig. 1. (A) steel mold of 2mm*2mm*25mm dimensions and (B) five specimens

Fig. 2. Schematic representation of the preparation of dental resin composite with ZnO-AlBw hybrid fillers

Fig. 3. XRD patterns of AlBw and ZnO-AlBw at pH=6.0, pH=6.2, pH=6.4, pH=6.6 and pH=6.8, respectively.

Fig. 4. SEM images of the surface of the whiskers (A, a) and the ZnO-AlBw (B, b), (C, c), (D, d), (E, e) and (F, f), the pH value of which are 6.0, 6.2, 6.4, 6.6 and 6.8, respectively.

Fig. 5. Mechanical properties of ZnO-AlBw filled resin composites: (A) bending strength, (B) elastic modulus, (C) compressive strength, and (D) hardness.

Fig. 6. SEM images and EDX profiles of fracture surface of the resin composites with the filler of ZnO-AlBw at pH=6.0 (a_1, a_2, a_3), pH=6.2 (b_1, b_2, b_3), pH=6.4 (c_1, c_2, c_3), pH=6.6 (d_1, d_2, d_3) and pH=6.8 (e_1, e_2, e_3), respectively.

Fig. 7. Back scattered electron image (A) and EDX profile (B) of fracture surface of the resin composites with the filler of ZnO-AlBw at pH=6.4.

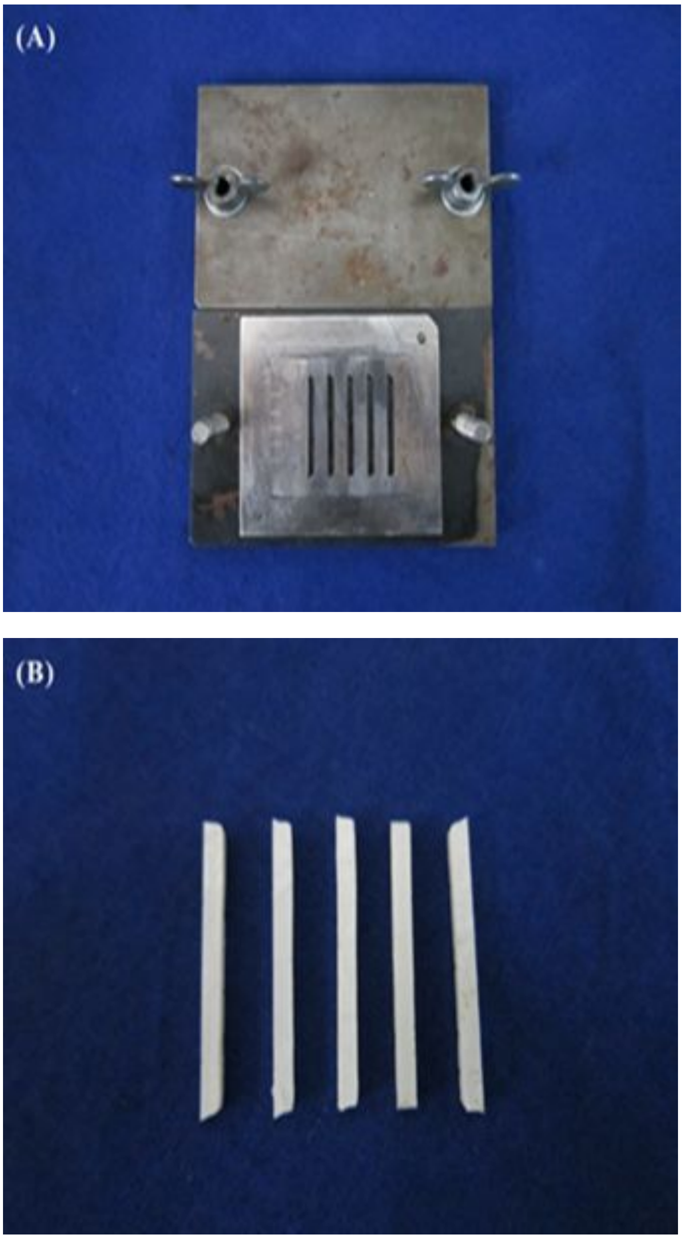


Fig. 1. (A) steel mold of 2mm*2mm*25mm dimensions and (B) five specimens

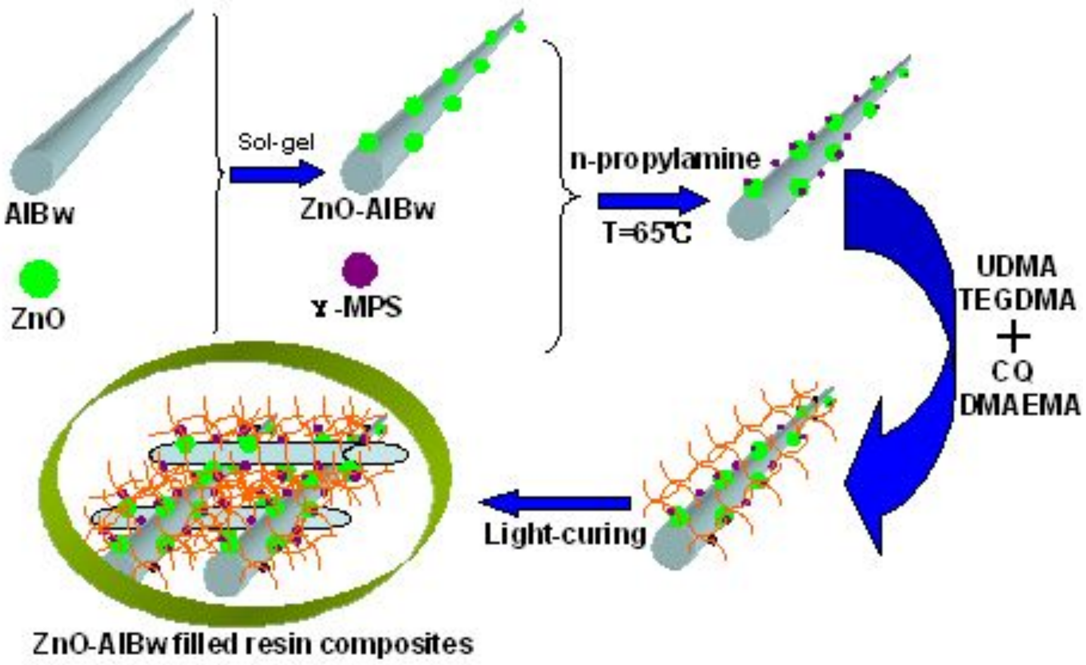


Fig. 2. Schematic representation of the preparation of dental resin composite with ZnO-AlBw hybrid fillers

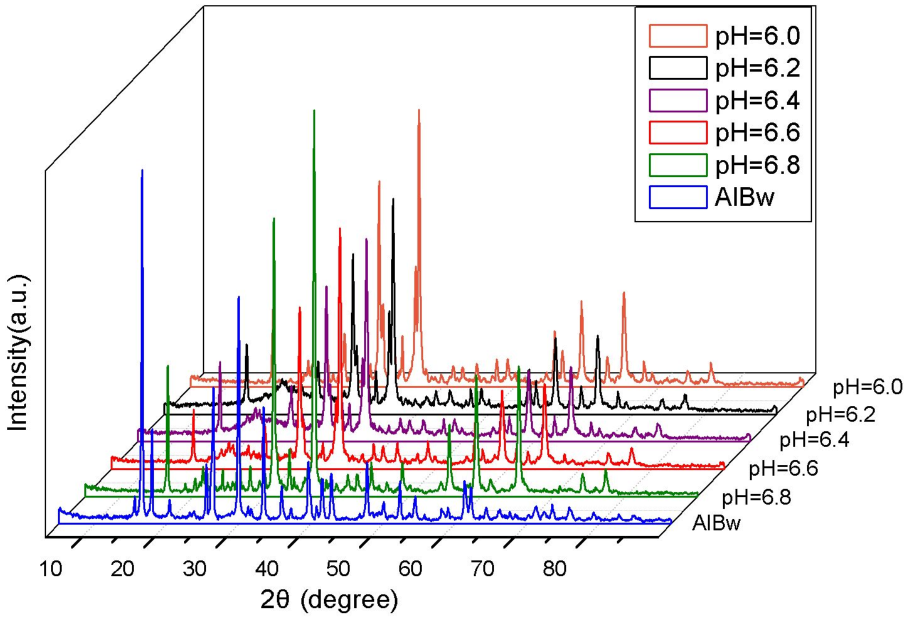
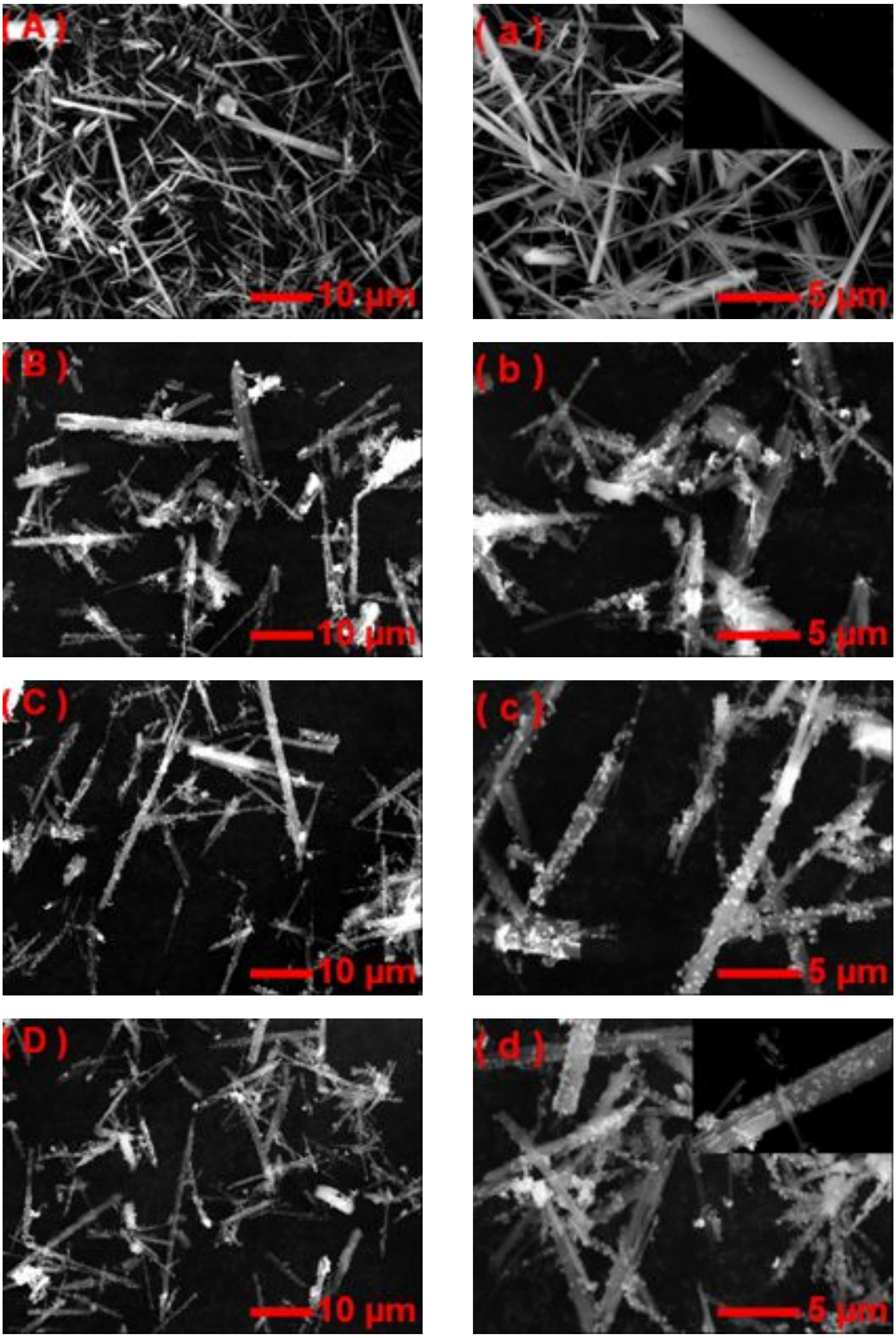


Fig. 3. XRD patterns of AlBw and ZnO-AlBw at pH=6.0, pH=6.2, pH=6.4, pH=6.6 and pH=6.8, respectively.


(A)
10 µm
(a)
5 µm
(B)
10 µm
(b)
5 µm
(C)
10 µm
(c)
5 µm
(D)
10 µm
(d)
5 µm

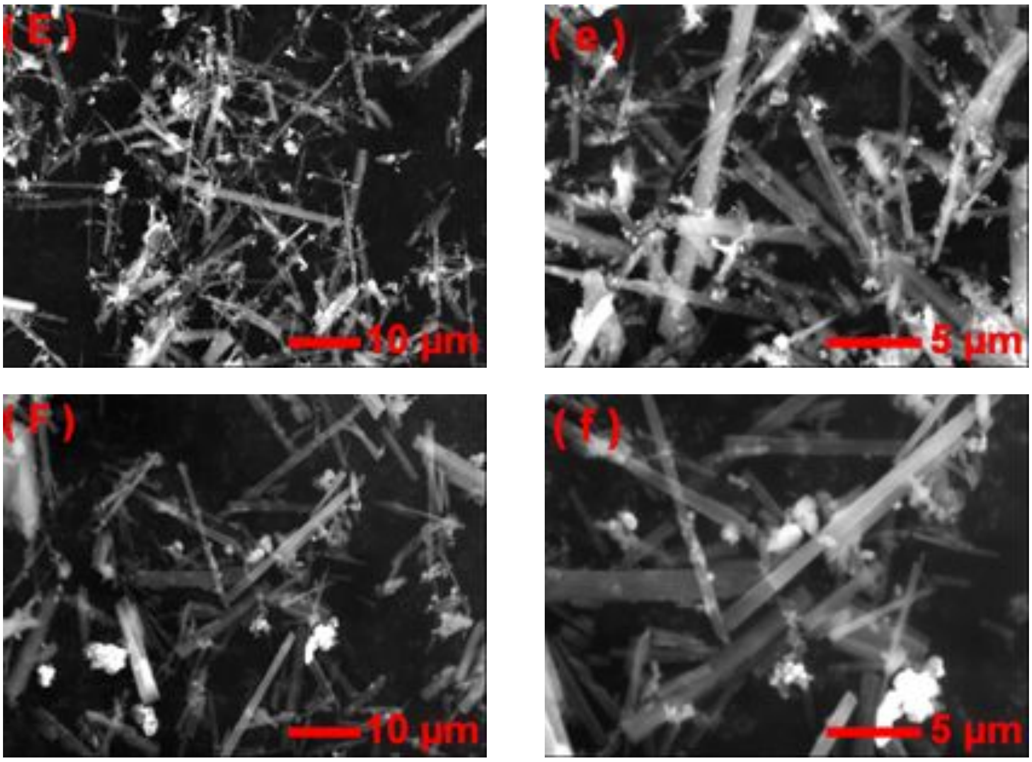


Fig. 4 SEM micrographs of AlBw and ZnO-AlBw

Fig. 4. SEM images of the surface of the whiskers (A, a) and the ZnO-AlBw (B, b), (C, c), (D, d), (E, e) and (F, f), the pH value of which are 6.0, 6.2, 6.4, 6.6 and 6.8, respectively.

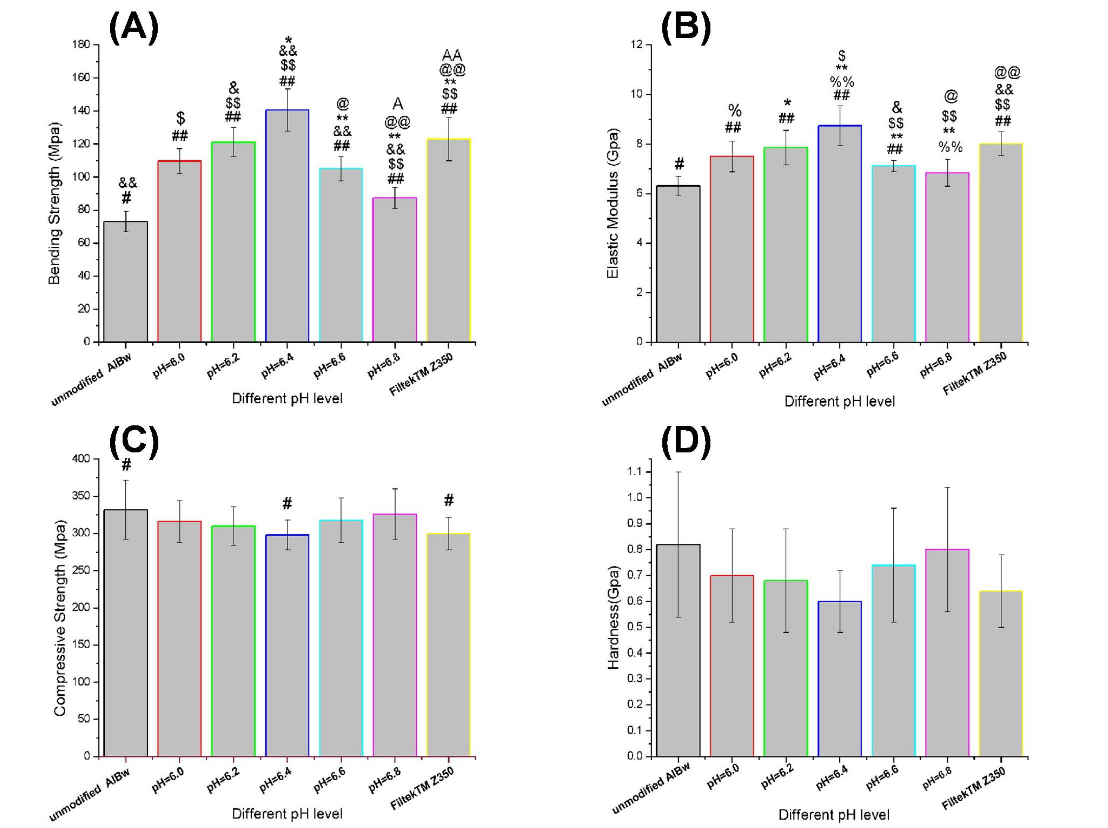


Fig. 5. Mechanical properties of ZnO-AlBw filled resin composites: (A) bending strength, (B) elastic modulus, (C) compressive strength, and (D) hardness.

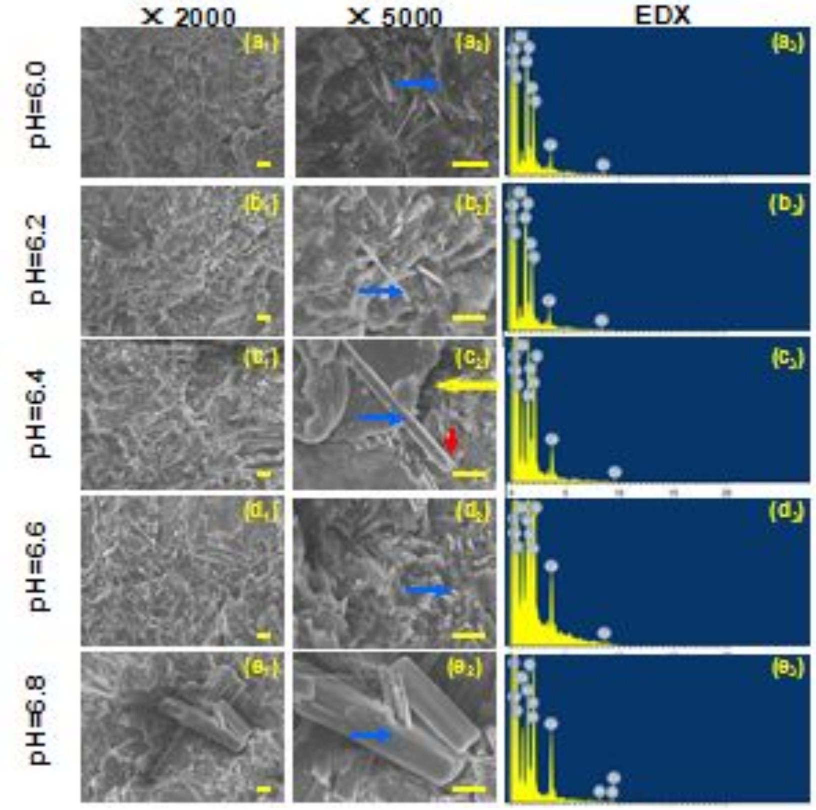


Fig. 6. SEM images and EDX profiles of fracture surface of the resin composites with the filler of ZnO-AlBw at pH=6.0 (a_1, a_2, a_3), pH=6.2 (b_1, b_2, b_3), pH=6.4 (c_1, c_2, c_3), pH=6.6 (d_1, d_2, d_3) and pH=6.8 (e_1, e_2, e_3), respectively.

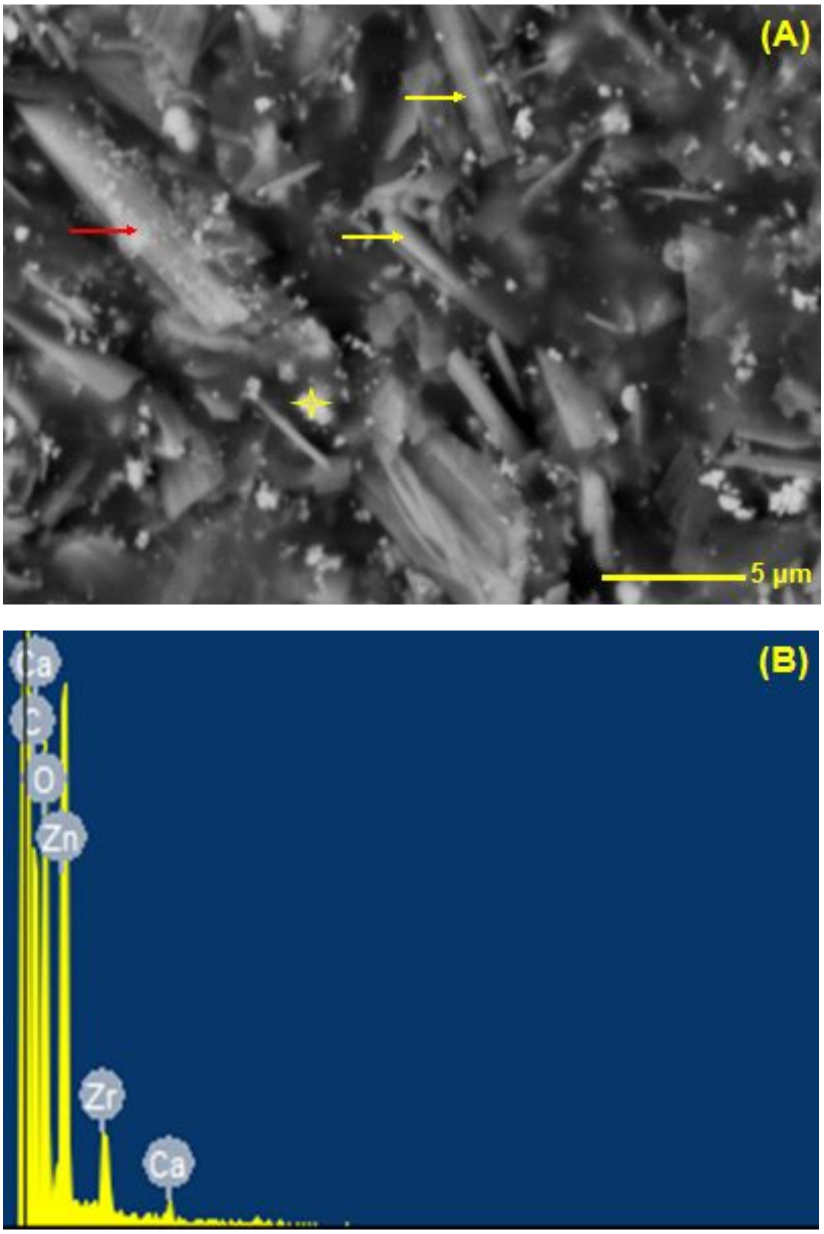


Fig. 7. Back scattered electron image (A) and EDX profile (B) of fracture surface of the resin composites with the filler of ZnO-AlBw at pH=6.4.