Synthesis and Characterization of Nanoparticles and Nanocomposite of ZnO and MgO by Sonochemical Method and their Application for Zinc Polycarboxylate Dental Cement Preparation

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This paper discusses the synthesis of nanoparticles of ZnO and MgO and ZnO/MgO nanocomposite by the sonochemical method. At first, nanoparticles were synthesized by the reaction of $Zn(CHCOO_3)_2$ and $Mg(CHCOO_3)_2$ with tetramethylammonium hydroxide (TMAH) in the presence of polyvinyl pyrrolidone (PVP) and constant frequency ultrasonic waves (sonochemical method). Then, ZnO/MgO nanocomposite was prepared through reaction of magnesium acetate with TMAH in the presence of ZnO nanoparticles and PVP as structure director using ultrasonic-assisted method. After filtration, the synthesized solution was obtained containing magnesium hydroxide in the presence of ZnO nanoparticles. It was calcinated at the temperature of 550 ºC, so that ZnO/MgO nanocomposite could be produced. The effects of different parameters on particle size and morphology of final ZnO and MgO powders and ZnO/MgO nanocomposite were optimized by ''one at a time'' method. Under optimum conditions, spongy shaped, uniformed and homogeneous nanostructured zinc oxide and magnesium oxide powders were obtained with particle sizes of 25–50 and 30-60 nm, respectively. ZnO/MgO nanocomposite was also obtained with more spongy morphology and particle size about 65 nm. Both synthesized ZnO and MgO nanoparticles and ZnO/MgO nanocomposite were successfully applied to the preparation of zinc polycarboxylate dental cement.

Keywords: Nanoparticles, Nanocomposite, Zinc polycarboxylate dental cement, Sonochemical

Introduction

During the last few years, synthesis of nanostructured oxide materials have been attracted considerable attention [1–5]. The metal oxides are extremely important technological materials for use in electronic and photonic devices and as catalysts in chemical industries. They are also often used as active materials of dental cements. In recent years, researchers have focused more on the synthesis of both nanoparticles and nanocomposite of ZnO and MgO due to their application in advanced technologies. Various physicochemical techniques

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have been employed to construct nano-sized ZnO and MgO particles [6-17]. Several techniques have been also developed to prepare nanocomposite of ZnO/MgO. This nanocomposite has attracted much attention because it has a larger band gap than ZnO [18-23]. However, most of the techniques need high temperatures and perform under a costly inert atmosphere. Our goal in this research is to suggest an easy method to synthesize more porous and spongy nanostructured zinc oxide and magnesium oxide and their nanocomposite. Such structures can be useful in active materials of dental cements.

A number of commercially available dental cements differ in chemical composition and therefore possess significantly different physical, mechanical and biological properties [24]. Although all of these materials are used in small extent, they are the most important materials in clinical dentistry because of their application as luting agents, orthodontic attachments, cavity linings and bases, and restorations for teeth. During the last four decades, several new types of dental cements have been developed including: zinc phosphate, zinc polycarboxylate, glass ionomer and resin composite cements that resulted in significant clinical usage. Many researches show that the biological and adhesive properties of polycarboxylate cements are better than those of other luting or base materials but several mechanical properties such as compressive hardness, compressive strength, tensile strength etc. are inferior to those of the other luting materials [25]. Furthermore, recent works on the polycarboxylate cements have shown several improvements of their mechanical properties [26,27]. One of the first chemically adhesive dental materials is zinc polycarboxylate cement. Zinc polycarboxylate cement is a water-based material that hardens following an acid-base reaction between zinc-rich powder and an aqueous solution of polyacrylic acid [28]. The main advantage of this cement lies in its strong adhesion to dentin. However, its low working time (~1-2 min) and relatively low compressive strength (40-70 N/mm^2) [29], causes the cement to be used only as a base or cementing restorative. Some attempts have been made to overcome these disadvantages by modifying polycarboxylic acid using copolymers of acrylic acid [11], adding polyvinyl phosphonic acid [30] or incorporating various fillers into the zinc-containing powder using aluminium compounds [25,31], silicon dioxide [32], magnesium oxide [33], etc.

The present work was intended to use a new and easy method for preparation of homogeneous porous nano-sized ZnO and MgO particles. For this purpose, single frequency ultrasonic waves were applied to prevent growth and help formation of nanoparticles. In addition, polyvinyl pyrrolidone (PVP) was used as a structure director additive. This is the first report on application of ZnO and MgO nano-powders and ZnO/MgO nanocomposite to the preparation of zinc polycarboxylate dental cement. The mechanical strength property of this cement is more than two commercially available polycarboxylate cements.

Experimental

Materials and apparatus

Analytical reagent grade of magnesium acetate tetrahydrate, zinc acetate dehydrate, tetramethylammonium hydroxide (TMAH), ammonia, and polyvinyl pyrrolidone (PVP) were obtained from Merck. NaOH and Na_2CO_3 were obtained from Loba Chem., India and used without any purification. Ethanol (Bidestan Co., Iran) was distilled before being used. For preparation of dental cements, mixture of zinc polycarboxylate (Harvard and Adhesor, Germany), Al_2O_3 (Merck), SiO_2 (Merck) and synthesized ZnO and MgO nanoparticles were used. All solutions were prepared with double-distilled water.

Ultrasonic experiments were carried out by an Elma S60H model (Ultrasonic Instrument Co. Ltd., 40 kHz). The X-ray analysis of the samples were carried out by Brake-AXS D8 Advance Diffractometer (with DIFFRAC plus software) using Cu K_α radiation at 55 kV tube voltage and 11 mA tube current. The crystallite sizes of selected samples were estimated using the Sherrer method. SEM studies were performed using a Philips XL30 model. FT-IR spectra were recorded on a SHIMADZU–IR PRESTIGE 21 spectrometer in a

KBr matrix. The prepared paste was poured into a mold of 6 mm diameter and 12 mm depth. The mechanical strength of the cement specimens was measured using a universal testing machine (Zwick Z250 model) with a crosshead speed of 1 mm/min.

Synthesis of ZnO nanoparticles

All of the experiments were performed under atmosphere conditions. First, 50 mL zinc acetate solution (0.10 M) including PVP (10 g L^{-1}) as structure director additive was sonicated for 30 min and then, enough volume of TMAH solution (0.28 M) was slowly added. In this step, nano-structured zinc hydroxide was formed during the following reaction (1):
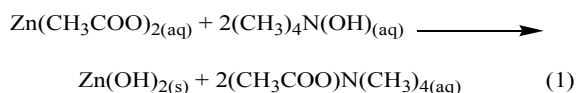
$$Zn(CH_3COO)_{2(aq)} + 2(CH_3)_4N(OH)_{(aq)} \longrightarrow$$

$$Zn(OH)_{2(s)} + 2(CH_3COO)N(CH_3)_{4(aq)} \qquad (1)$$

At the end of the process of adding TMAH solution, the mixture was additionally sonicated for 30 min. The precipitated zinc hydroxide was filtered and washed with distilled water and ethanol for three times. 50 mL ethanol was added to the obtained precipitate and the mixture was sonicated for 30 min and then, the sonicated mixture was filtered. The final obtained precipitate was dehydrated at 320 $^{\circ}$C for 2 h. The following reaction (2) took place in the dehydration phase:

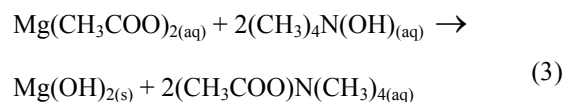$$Zn(OH)_{2(s)} \rightarrow ZnO_{(s)} + H_2O_{(g)} \qquad (2)$$
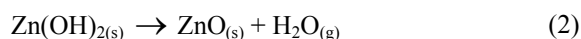
At dehydration phase, nanostructured zinc oxide was formed. The nanoparticles were sonicated in ethanol for 30 min to eliminate agglomeration. At final step, the mixture was filtered and dried at 110 $^{\circ}$C. The final product was obtained in powder form. The nanostructured zinc oxide powder was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), and FT-IR spectroscopy.

Synthesis of MgO nanoparticles

First, 50 mL magnesium acetate solution (0.14 M) including PVP (10 gL^{-1}) as structure director additive was sonicated for 30 min and then, enough volume of TMAH solution (0.34 M) was slowly added. In this step, nano-structured magnesium

hydroxide was formed during the following reaction (3):

$$Mg(CH_3COO)_{2(aq)} + 2(CH_3)_4N(OH)_{(aq)} \rightarrow$$

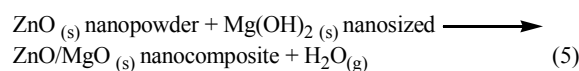$$Mg(OH)_{2(s)} + 2(CH_3COO)N(CH_3)_{4(aq)} \qquad (3)$$

At the end of the process of adding TMAH solution, the mixture was additionally sonicated for 30 min. The precipitated magnesium hydroxide was filtered and washed with distilled water and ethanol for three times. 50 mL ethanol was added to the obtained precipitate and the mixture was sonicated for 30 min and then, the sonicated mixture was filtered. The final obtained precipitate was dehydrated at 550 $^{\circ}$C for 4 h. The following reaction (4) took place during the dehydration phase:

$$Mg(OH)_{2(s)} \rightarrow MgO_{(s)} + H_2O_{(g)} \qquad (4)$$
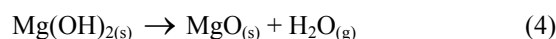
The MgO nanoparticles were sonicated in ethanol for 30 min to eliminate agglomeration. At final step, the mixture was filtered and dried at 110 $^{\circ}$C. The final product was obtained in nano-powder form. The nanostructured magnesium oxide powder was characterized by SEM, XRD, and FT-IR spectroscopy.

Synthesis of ZnO/MgO nanocomposite

First, a 50 mL aliquot containing magnesium acetate solution (0.17 M) and 3.44 g of ZnO nano-powder and PVP (10 gL^{-1}) were sonicated for 30 min and then, 7.5 mL of TMAH solution (0.28 M) was slowly added. In this step, nano-structured magnesium hydroxide was formed. At the end of the process of adding TMAH solution, the mixture was additionally sonicated for 30 min. To form the ZnO/MgO nanocomposite (5), the obtained precipitate was dehydrated at 550 $^{\circ}$C for 4 h.

$$ZnO_{(s)} \text{ nanopowder} + Mg(OH)_{2\,(s)} \text{ nanosized} \longrightarrow$$
$$ZnO/MgO_{(s)} \text{ nanocomposite} + H_2O_{(g)} \qquad (5)$$

The ZnO/MgO nanocomposite was sonicated in ethanol for 30 min to eliminate agglomeration. For evaporation of solvent, nano-powder was heated to 110 $^{\circ}$C. The ZnO/MgO nanocomposite powder was

characterized by SEM, XRD and FT-IR spectroscopy.

Dental cement preparation

The formulations of prepared zinc polycarboxylate dental cements are shown in Table 1. Required amounts of ZnO and MgO nanoparticles and/or ZnO/MgO nanocomposite, fused silica and aluminum oxide were mixed together in a crucible. The mixture was heated to 1050 $^{\circ}$C in the furnace for 5 h. Then various amounts of liquid of Harvard zinc polycarboxylate dental cement were slowly added to this mixture. After adding liquid, the mixture was additionally mixed for 1 min. The prepared paste was poured into cylindrical mold (6 mm diameter and 12 mm deep).

Results and discussion

From the XRD data, it is evident that the major constituents of the cement powder are present as simple oxides specially zinc oxide. MgO and minor ingredients as Al_2O_3 affect the working characteristics and final properties, e.g. dimensional stability after setting, compressive and tensile strength, and rheological behavior of the mixed cement [34-36]. Additional components act as inactive filler (SiO_2), and ensure fluoride release into dental enamel and dentine (CaF_2). To the best of our knowledge, there is no report on the use of nanostructured zinc and magnesium oxides or their nanocomposite for increasing mechanical strength of dental cements. The aim of this work is to synthesize ZnO and MgO nanoparticles and ZnO/MgO nanocomposite in order to obtain the higher mechanical strength than commercial dental cement of zinc polycarboxylate. The parameters including ultrasonic wave, concentrations of $Zn(CHCOO_3)_2$, $Mg(CHCOO_3)_2$, TMAH and PVP, and synthesis temperature were optimized using "one at a time" method [30].

Table 1. Formulation of the powder for the zinc polycarboxylate dental cement.

No	Compound[a]	Wt (%)	Compound[b]	Wt (%)
1	Zinc oxide	89.0	ZnO/MgO nanocomposite	92.8
2	Magnesium oxide	8.9	Fused silica	4.3
3	Fused silica	1.2	Aluminum oxide	2.9
4	Aluminum oxide	0.9	-	-

[a] Compound percents of ZnO and MgO powders are similar for both commercial powder and synthesized nanopowder.
[b] Compound percent of ZnO/MgO nanocomposite is the best percent that the mechanical strength amount was more than other ratios.

Ultrasonication effect

What effects do ultrasonic waves have on particle size and morphology of ZnO and MgO nanoparticles and their nanocomposite? Two synthesis processes were carried out (i) in the presence and (ii) absence of ultrasonic waves at the same temperature and concentrations of $Zn(CHCOO_3)_2$, $Mg(CHCOO_3)_2$ and TMAH in the absence of structure director additives. SEM images of ZnO and MgO nanoparticles and ZnO/MgO nanocomposite show that the ultrasonic waves make both ZnO and MgO nanoparticles and their nanocomposite smaller and more uniform.

Effect of reagents concentrations on the synthesis of ZnO and MgO nanoparticles and ZnO/MgO nanocomposite

After confirming positive effect of ultrasonication, at 30 $^{\circ}$C and 0.20 M TMAH, the concentration of zinc and magnesium acetate solutions was varied from 0.06 to 0.28 M. Morphology and particle size of each compound was studied by SEM. The SEM results showed that concentrations of 0.10 and 0.14 M zinc acetate and magnesium acetate, respectively, produce more uniform and smaller particles. It can be concluded that at low concentrations of zinc (<0.10 M) and magnesium (<0.14 M) ions, the rate of particle growth is less than the rate of nucleation while at

higher concentrations of zinc (>0.10 M) and magnesium (>0.14 M) ions, growth and agglomeration and other mechanisms involved in the formation of heavy particles are more manifest. Therefore, the concentrations of 0.10 M of zinc acetate and 0.14 M of magnesium acetate were selected as the optimum concentrations.

Different alkaline solutions such as NaOH, Na_2CO_3, NH_4OH and TMAH solutions at various concentrations were investigated to produce smaller and uniform particles of ZnO, MgO and ZnO/MgO nanocomposite. The SEM images of synthesized samples showed that TMAH is a suitable alkaline for our purpose. The effect of TMAH concentration on particle size and morphology was investigated by SEM. The TMAH concentration was varied from 0.17 to 0.50 M. The SEM images of synthesized samples revealed that smaller and uniform nanoparticles of ZnO, MgO and nanocomposite of ZnO/MgO can be formed at TMAH concentrations of 0.28, 0.34, and 0.34 M respectively. Lower concentrations of TMAH make high growth rate for precipitation particles and, at higher concentrations, there are some processes such as coagulation and agglomeration that make bigger precipitation particles. Therefore, the TMAH concentrations of 0.28, 0.34 and 0.34 M were selected as the optimum concentration for synthesis of ZnO, MgO nanoparticles and ZnO/MgO nanocomposite, respectively.

Temperature effect

Six synthetic processes were followed at 20, 30, 50, 60, 70 and 80 °C so that the effect of synthesis temperature on morphology and particle size of ZnO and MgO nanoparticles and ZnO/MgO nanocomposite can be investigated. The SEM images showed that at temperatures of 30, 60 and 60 °C, smaller and more uniform ZnO and MgO nanoparticles and ZnO/MgO nanocomposite samples were synthesized respectively, probably because of the fact that growth rate, nucleation rate and agglomeration rate are suitable for formation of optimum powders at these temperatures. Therefore, the temperatures of 30, 60 and 60 °C were selected as the optimum temperatures for synthesis of ZnO, MgO nanoparticles and ZnO/MgO nanocomposite, respectively.

Structure director

There are some reports on the positive effects of PVP used as structure director additive on the formation of suitable products [36-41]. According to these reports, PVP played an important role in determining the morphology of the products. Zhang et al. [41] report that PVP probably organizes the nanostructures by forming a cation–PVP complex. The suggested complex can prevent particles from growing. The probable mechanism based on the suggested complex can be expressed as Scheme 1. The SEM images of synthesized samples showed that PVP, as a structure director, organizes uniformly the nanostructures of both zinc oxide and magnesium oxide in smaller sizes. Finally, 5 different concentrations of PVP (from 5 to 25 g L^{-1}) in synthesis solution were examined in order to obtain the best structure for the final products (ZnO and MgO nanoparticles and ZnO/MgO nanocomposite). As it is shown in Fig. 1, at PVP concentration of about 10 g L^{-1}, both nanoparticles and nanocomposite can be synthesized in excellent and more porous nanostructure (moss shape). Finally, it can be concluded that using the suggested method, ZnO and MgO nanoparticles in the ranges of 25–50 and 30-60 nm, were synthesized respectively. Also, particle size about 65 nm with more spongy morphology was obtained for ZnO/MgO nanocomposite.
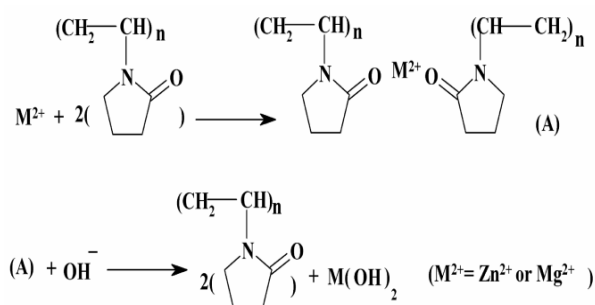
Scheme 1. Structure of the suggested complex for interaction between PVP and metallic ions.

The XRD patterns of three samples (a) ZnO and (b) MgO nanoparticles and (c) ZnO/MgO nanocomposite are shown in Fig. 2. All the peaks in the figures can be indexed to the known Wurtzite structure of ZnO and MgO powders and ZnO/MgO

nanocomposite. The patterns can be indexed according to the hexagonal ZnO (Fm3m225-4-74.6) and cubic MgO (P63mc186-2-47.62). No impurity such as $Zn(CH_3COO)_2$, $Zn(OH)_2$, $Mg(CH_3COO)_2$ and $Mg(OH)_2$ was detected. On comparison with
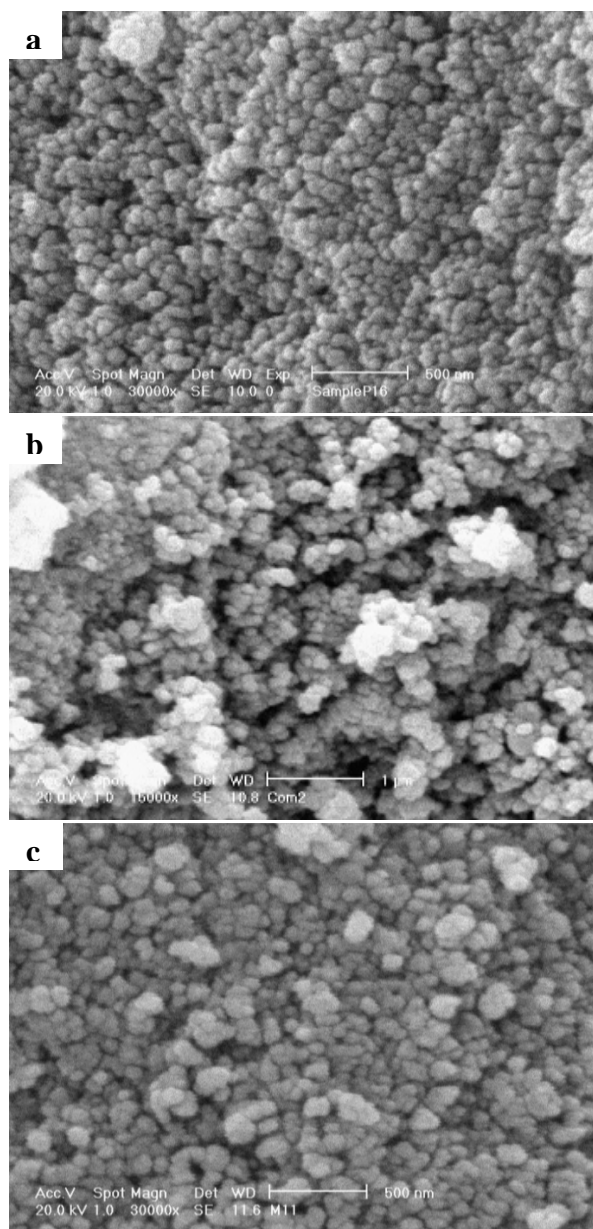

Fig. 1. SEM images of three samples (a) ZnO, and (b) MgO nanoparticles and (c) ZnO/MgO nanocomposite synthesized in optimum conditions: concentration of zinc acetate is 0.10 M, magnesium acetate is 0.14 M, TMAH is 0.28 and ZnO and MgO are 0.34 M, PVP is 10 g L^{-1}. Temperatures are 30, 60 and 60 $°C$ for ZnO and MgO nanoparticles and ZnO/MgO nanocomposite, respectively.

standard XRD cards, the 2θ peaks observed at these patterns show hexagonal and cubic structures of ZnO and MgO, respectively. Peak broadening indicates crystallites smallness in nanometer scale. The grain size was estimated from the Sherrer formula, $D = 0.891\lambda/\beta cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), θ is the diffraction angle and β is full-width at half maximum of an observed peak [41]. The average sizes of the particles are in good agreement with those observed from SEM images.

The FT-IR spectra of the ZnO and MgO nano-powder samples and their commercial powders represented the absorbance characteristic of our high purity ZnO and MgO nanoparticles in comparison with commercial powders (data not shown). The formed ZnO and MgO phases are characterized by intense and very broad IR band which could be assigned to the Zn-O and Mg-O vibrations with poor resolved shoulders at about 500 cm^{-1} [41].

Finally, it can be concluded that while the suggested method is used, ZnO and MgO nanostructured and ZnO/MgO nanocomposite can be synthesized in nanometer scales. In this method, the presence of ultrasonic waves and structure director additive has strongly positive effect on the morphology of the final products.

Dental cement making and tests

Three zinc polycarboxylate dental cements were prepared by combining the same powder formulation (Table 1) with the three different ratios of powder/liquid (gr/gr) of (1) 0.50:0.50, (2) 0.60:0.45 and (3) 0.60:0.40 (Table 2). Then, various amounts of Harvard's liquid zinc polycarboxylate dental cement were slowly added and mixed for 1 min. The mixtures were heated to 1050$°C$ in the furnace for 5 h. The premixed paste was placed into a mold of 6 mm diameter and 12 mm depth, and sandwiched between two porous glass slides (ACE Glass, Vineland, NJ). The mechanical strength magnitude of 6 mm diameter and 12 mm thickness cement specimens were measured on a computer controlled universal testing machine with crosshead speed of 1 mm/min. It was found when the ratio of powder/liquid was increased, the mechanical strength magnitude of cements also increased.

However, by increasing the powder, the compressive strength of zinc polycarboxylate cement prepared from the ZnO and MgO nano- powders were increased. In the powder/liquid ratio of 0.60:0.40 (3) maximum mechanical strength magnitude was observed.
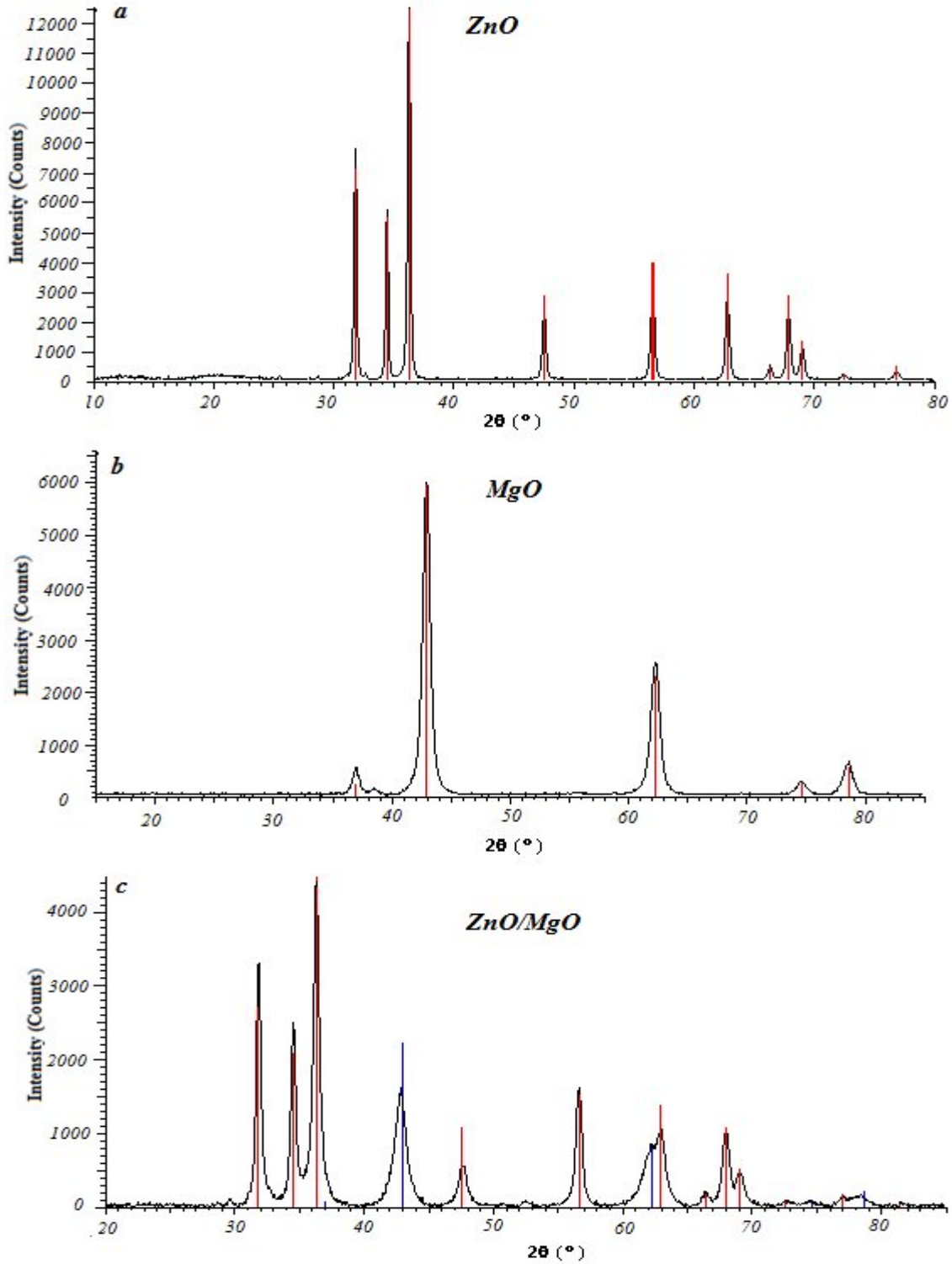

Fig. 2. XRD patterns of three samples (a) ZnO and (b) MgO nanoparticles and (c) ZnO/MgO nanocomposite.

Table 2. Compressive strength values of commercial and formed zinc polycarboxylate dental cements. The results are averaged values. Samples 1, 2 and 3 are three zinc polycarboxylate cements in the present study, containing synthesized nanopowders. Samples 4 and 5 are two commercial zinc polycarboxylate cements of Adhesor and Harvard, respectively, containing commercial ZnO and MgO powders.

No	Powder: Liquid (g/g)	Strength (N/mm^2)
1	0.50/0.50	59.08[a], 48.16[b]
2	0.60/0.45	74.40[a], 66.31[b]
3	0.60/0.40	79.53[a], 73.16[b]
4	1.00/0.50	42.73
5	1.45/0.50	37.84

[a] averaged values of compressive strength for ZnO and MgO nanostructured.
[b] averaged values of compressive strength for ZnO/MgO nanocomposite.

In the ratios higher than 0.60:0.40, the powder is insoluble. Therefore, this ratio was selected as the optimum value. In contrast to the conventional Adhesor and Harvard zinc polycarboxylate cements, the ZnO and MgO nanostructured and ZnO/MgO nanocomposite cements were shown more increased mechanical strength magnitude. In the case of zinc polycarboxylate cement the mechanical strength magnitude were varied from 42.73 and 37.84 N/mm^2 for available commercial sample of Adhesor and Harvard, respectively to 79.53 and 73.16 N/mm^2 for the obtained ZnO and MgO nano-powders and ZnO/MgO nanocomposite, respectively. Furthermore, the setting time of the prepared dental cement from ZnO and MgO nano-powders was assessed 2.5 to 4.5 min, which is acceptable and comparable to those obtained by commercial samples.

Conclusion

Zinc oxide and magnesium oxide can be synthesized in nano-scale in the presence of ultrasonic waves and PVP as a structure director. The uniform small sizes of ZnO and MgO nanostructured and ZnO/MgO nanocomposite can be used as active material in dental cements. The zinc polycarboxylate dental cements obtained by synthesized nano-scale powders revealed excellent mechanical strength. This study showed that mechanical strength of dental cements is dependent on composition size scale. It was found that zinc polycarboxylate dental cement had higher strength than conventional Harvard and Adhesor zinc polycarboxylate cements. The simplicity and low cost of the process would be favorable to high strength zinc polycarboxylate dental cement, and this method may be developed to synthesize other effectiveness dental cements.

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