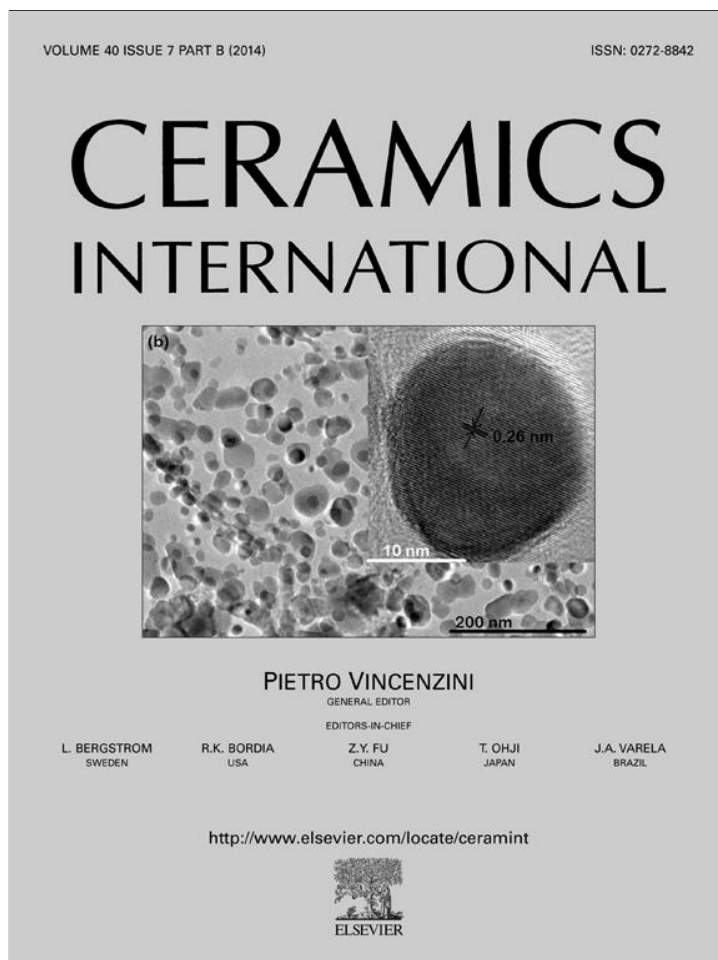


Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/authorsrights>



## Effect of forsterite nanoparticles on mechanical properties of glass ionomer cements

F.S. Sayyed<sup>a,\*</sup>, M.H. Fathi<sup>a,b</sup>, H. Edris<sup>a</sup>, A. Doostmohammadi<sup>c</sup>, V. Mortazavi<sup>d</sup>, A. Hanifi<sup>e</sup>

<sup>a</sup>Biomaterials Research Group, Department of Materials Engineering, Isfahan University of Technology, Isfahan 8415683111, Iran

<sup>b</sup>Dental Materials Research Center, Isfahan University of Medical Science, Isfahan, Iran

<sup>c</sup>Department of Materials Engineering, Shahrekord University, Shahrekord, Iran

<sup>d</sup>Torabinejad Dental Research Center and Department of Operative Dentistry, School of Dentistry, Isfahan University of Medical Science, Isfahan, Iran

<sup>e</sup>Institute of Biomaterials and Biomedical Engineering, University of Toronto, Toronto, ON, Canada

Received 5 February 2014; received in revised form 11 March 2014; accepted 12 March 2014

Available online 24 March 2014

### Abstract

The aim of this study was to assess the effect of forsterite nanoparticles on the mechanical properties of glass ionomer cements (GICs). So, forsterite nanoparticles were produced by a sol–gel process and added to the ceramic component of a commercial glass ionomer cement at 1–4 wt%. An X-ray diffraction (XRD) analysis technique was used to characterize the phase composition and the grain size of forsterite nanoparticles. Compressive strength (CS), three-point flexural strength (FS), and diametral tensile strength (DTS) of the prepared glass ionomer-forsterite nanocomposites were measured. Analysis of variance (ANOVA) was used to compare the obtained results. Scanning electron microscopy (SEM) imaging technique was used to study the morphology of the fractured surface after performing the mechanical tests. XRD analysis confirmed the synthesis of pure nanocrystalline forsterite particles. Statistical analysis showed a significant difference between the results of mechanical properties of the control specimens and the glass ionomer-forsterite nanocomposites. The highest compressive strength, flexural strength and diametral tensile strength were obtained using 3, 1, and 1 wt% of forsterite nanoparticles, respectively. However, at 1 wt% forsterite nanoparticles, all three measures of strength exhibited a significant increase compared to the commercial GIC. Thus, addition of 1 wt% forsterite nanoparticles to the ceramic component of GIC is desired for dental restorations and orthopedic implants applications, where the maximum strength in all three modes of loading would be beneficial.

© 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

**Keywords:** C. Mechanical properties; Glass ionomer cement; Forsterite nanoparticles; Sol–gel

### 1. Introduction

Glass ionomer cements (GICs) are direct tooth-colored restoration materials with many advantages including; anticariogenic properties due to fluoride ion release, thermal compatibility with tooth enamel due to the low thermal expansion coefficient similar to those of tooth structure, the module coefficient similar to dentin, ability of chemical bonding with dentin, biocompatibility, and low cytotoxicity. Nevertheless, weak mechanical properties limit their high-stress applications, such as class I and II restoration [1,2].

Many efforts have been done in order to improve the mechanical properties of GICs over the past few years with their advantages and limitations. The incorporation of amalgam, silver, and metal powders as reinforcements into GIC powder was reported by Irie et al. with inferior esthetic appearance and low bonding strength to the enamel [3]. Mitra and co-workers investigated the light-cured GIC, where resin and a light-curing catalyst were added to stimulate the setting and enhance the mechanical strength of GIC. Light-cured GIC is widely used due to its significant high flexural strength [4]. However, it shows lower compressive strength compared to the conventional GIC [5]. In addition, resin-modified GIC may cause dental pulp irritations, biological side-effects, cytotoxicity, and secondary caries, whereas these negative effects are

\*Corresponding author. Tel.: +98 311 3912750; fax: +98 311 3912752.  
E-mail address: [f.sayyed@yaho.com](mailto:f.sayyed@yaho.com) (F.S. Sayyed).

not caused by conventional GIC [6,7]. Incorporation of SiC whiskers/short fibers into GIC enhances mechanical properties. However, there are health concerns regarding the release of the small fibers and their cytotoxicity to vital organs, similar to the cytotoxicity caused by asbestos fibers [8,9].

Unlike forsterite microparticles, forsterite nanoparticles demonstrate bioactive characteristics due to their high surface energy and reaction tendency that lead to integration with adjacent tissue. They also present higher mechanical properties than forsterite microparticles and hydroxyapatite (HA) [10]. Thus, forsterite nanoparticles might be a good candidate for replacement of HA ceramic in loaded-applications.

Mechanical properties and bioactivity of forsterite nanoparticles and also the possibility of controlled magnesium and silicon ions release that can repair and regenerate bone tissue, make them a desirable candidate to be used as a secondary phase in ceramic matrix. There are several methods to synthesize forsterite nanoparticles including; solid reactions, high temperature and sol–gel. Among them, the sol–gel process provides low working temperature, small size of powder crystals, a narrow particle size distribution, and chemical homogeneity [11].

Kharaziha et al. synthesized forsterite nanoparticles calcined at 800 °C. Fig. 1 shows the transmission electron microscopy image of the nanoparticles with the average size of 25–45 nm [12].

Our previous study showed that adding forsterite ( $Mg_2SiO_4$ ) nanoparticles to the ceramic component of GIC increases the bioactivity of the nanocomposite and decreases fluoride release [13]. In the present study, the aim is to synthesize glass ionomer–forsterite nanocomposites with different amounts of forsterite nanoparticles composition and assesses their mechanical properties including; compressive strength (CS), three-point flexural strength (FS), and diametral tensile strength (DTS).

## 2. Materials and methods

### 2.1. Forsterite nanoparticles

Forsterite nanopowder was synthesized by the sol–gel process according to Kharaziha et al. [12]. Magnesium nitrate hexahydrate

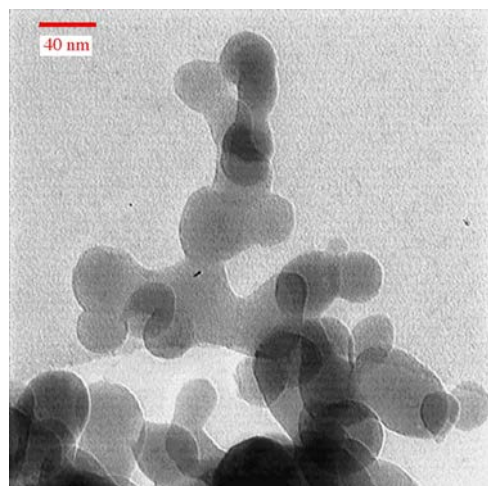


Fig. 1. TEM micrograph of  $Mg_2SiO_4$  nanopowder calcined at 800 °C [12].

( $Mg(NO_3)_2 \cdot 6H_2O$ , Merck, 99.99% purity), colloidal silica ( $SiO_2$ , 34 wt% solid fraction, Sigma), polyvinyl alcohol polymer (PVA) (Merck, molecular weight=72,000), sucrose (Merck, 99.9% purity) and nitric acid were the starting materials. Fuel system combined PVA and sucrose (sucrose-to-metal molar ratio=4:1) was applied to prepare forsterite. Water-based solutions of magnesium salts and colloidal silica were prepared with the stoichiometric molar ratio of forsterite ( $Mg:Si=2:1$  mol) by pouring colloidal silica into the aqueous solution of magnesium nitrate (0.0142 mol magnesium nitrate) dissolved in 50 cc deionized water. The aqueous solution of sucrose (sucrose-to-metal ratio=4:1 mol) in 100 cc deionized water was added dropwise to the precursor solution and two solutions were homogenized together on a warming plate under 2 h continuous stirring. PVA (PVA monomer-to-metal molar ratio=0.8:1) dissolved in 20 cc deionized water was added and the pH was adjusted at 1 using nitric acid and the solution was mixed homogeneously by constant stirring for 2 h with a magnetic stirrer. Subsequent heating at 80 °C for 2 h on a hot plate stirrer, the prepared gel was aged for 24 h. The resulting gel was then heated on a hot plate at 100 °C in air for enough time to complete the dehydration process and change into a voluminous, black, and fluffy gel. To increase the purity of the forsterite nanoparticles, the dried gel was calcined in a furnace at 800 °C for 2 h.

Phase composition analysis of nanoparticles was performed by an X-ray diffractometer (XRD, Philips Xpert) using Ni filtered Cu Ka ( $ICu\ Ka=0.154$  nm, radiation at 40 kV and 30 mA) over the  $2\theta$  range of 20°–80° (time per step: 1.25 s and step size: 0.05°). XRD spectra were compared to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCDPS) [14]. The crystallite size of the forsterite nanoparticles was calculated using the modified Scherrer equation [15].

### 2.2. Glass ionomer–forsterite nanocomposite

Glass ionomer–forsterite nanocomposite was produced by adding forsterite nanoparticles at 1, 2, 3, and 4 wt% to the ceramic component of the GIC, where GIC and forsterite nanoparticles were mixed in the amalgamator for 30 s according to the manufacturer's instruction. Powder/liquid ratio was set at 2.7/1. Then, the specimens were transferred into an aluminum mold. Specimens were removed from the mold after 1 h and prepared for following tests. Commercial GIC (Fuji II, GC International, Tokyo, Japan) was used as the control.

### 2.3. Mechanical properties measurements

Mechanical tests were performed on a screw-driven testing machine (Hounsfield, Model H25KS, England) with a cross-head speed of 0.5 mm/min.

For compressive strength test, cylindrical specimens ( $4 \pm 0.1$  mm diameter and  $6 \pm 0.1$  mm height) were prepared according to ISO 9917-1 standard. The compressive strength was calculated by the equation  $C=4P/\pi d^2$ ; where  $C$  is the compressive strength (MPa),  $P$  is the load at fracture (N), and  $d$  is the diameter of the cylindrical specimen (mm).

Cylindrical specimens ( $9 \pm 0.1$  mm diameter and  $4.5 \pm 0.1$  mm height) were prepared according to ANSI/ADA 66 standard for diametral tensile strength, where  $DT = 2P/\pi dt$  equation was used to calculate the strength. In this equation  $DT$  is the diametral tensile strength (MPa),  $P$  is the load at fracture (N), and  $d$  (mm) and  $t$  (mm) are the diameter and thickness of the cylindrical specimen, respectively.

In order to determinate the flexural strength, specimens were prepared with dimensions of  $(2 \pm 0.1) \times (2 \pm 0.1) \times (25 \pm 2)$  mm<sup>3</sup> according to ISO 4049 standard. The flexural strength in three-point bending was obtained using the equation  $\sigma = 3Fl/2bh^2$ ; where  $\sigma$  is the flexural strength (MPa),  $F$  is the load at fracture (N),  $l$  is the distance between the two supports (mm), and  $b$  (mm) and  $h$  (mm) are the breadth and depth of the specimen, respectively.

Lastly, the morphology of fracture surface was assessed using scanning electron microscopy (SEM, Philips XL30) analysis.

#### 2.4. Statistical analysis

Analysis of variance (One-way ANOVA) with the post hoc Tukey–Kramer HSD multiple range test was used to compare the results, where significant difference was set at  $\alpha = 0.05$ .

### 3. Results and discussion

#### 3.1. Characterization of forsterite nanoparticles

The Xray diffraction pattern of forsterite gel calcined at 800 °C is shown in Fig. 2. The results of the phase analysis of forsterite nanopowder showed that a pure nanocrystalline forsterite with appropriate composition was successfully prepared. Kharaziha et al. [12] demonstrated similar result. The crystallite size of forsterite nanoparticles was calculated using the modified Scherrer equation and was equal to 36 nm.

#### 3.2. Mechanical properties

The average value (standard deviation) of compressive strength (CS), three-point flexural strength (FS), and diametral tensile strength (DTS) are shown in Table 1 and Fig. 3. Statistical analysis showed that the differences between the results of all groups were significant (CS:  $p = 0.005$ , FS:  $p = 0.02$ , and DTS:  $p = 0.0015$ ). Nanocomposite containing 3 wt% forsterite nanoparticles demonstrated the highest compressive strength. Forsterite nanoparticles content less than 3 wt% does not have any significant effect on the compressive strength. Increasing the forsterite nanoparticles content decreases the compressive strength of the cement. However, nanocomposite containing 1 wt% forsterite nanoparticles resulted in the highest flexural strength compared, where forsterite nanoparticles content less than 2 wt% does not have any significant effect on the flexural strength of the cement. The flexural strength of the cement showed a negative correlation with of the forsterite nanoparticles content.

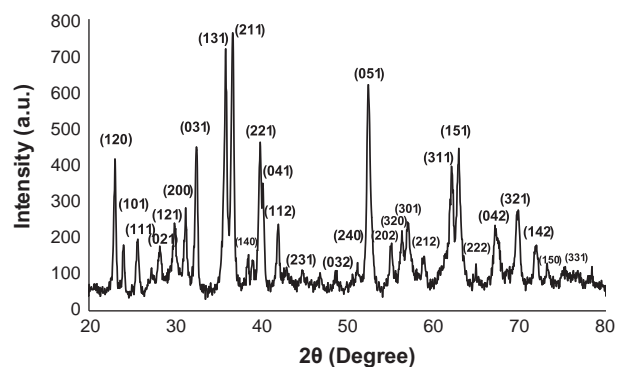


Fig. 2. X-ray diffraction pattern of prepared forsterite nanopowder calcined at 800 °C.

Table 1

The average values (standard deviation) of the mechanical properties of nanocomposite containing different amounts of forsterite nanoparticles.

Forsterite nanoparticles (wt%)	CS (MPa)	FS (MPa)	DTS (MPa)
0	42.4(1.7)	52.4(1.3)	10(0.6)
1	74.4(3.2)	93.7(8.4)	13(0.8)
2	94.1(2.3)	71.1(1.4)	11.7(0.2)
3	106.3(6.9)	31.3(1.5)	9.6(0.1)
4	38(1.8)	–	–

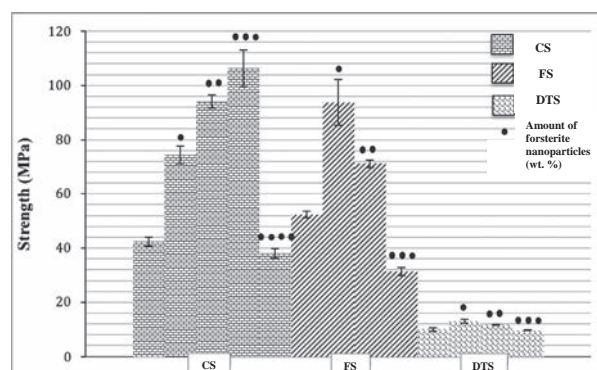


Fig. 3. Mechanical properties of nanocomposite containing different amounts of forsterite nanoparticles (error bars indicate standard deviation).

The results of the DTS measurement showed that the nanocomposite containing 1 wt% forsterite nanoparticles has the largest diametral tensile strength as compared to other samples. No significant variation was seen in the DTS value of nanocomposites containing less than 2 wt% of forsterite nanoparticles. Again, increasing the forsterite nanoparticles composition decreases the diametral tensile strength.

Forsterite nanoparticles demonstrate proper mechanical properties that reinforce the GIC matrix and increase the strength of the cement [10,16]. Forsterite nanoparticles' small size leads to wider particle size distribution which results in higher mechanical properties. Therefore, they can occupy the empty spaces between the glass-ionomer particles and act as a reinforcing material in the composition of the glass-ionomer cement [10,17–19]. In addition, forsterite nanoparticles have



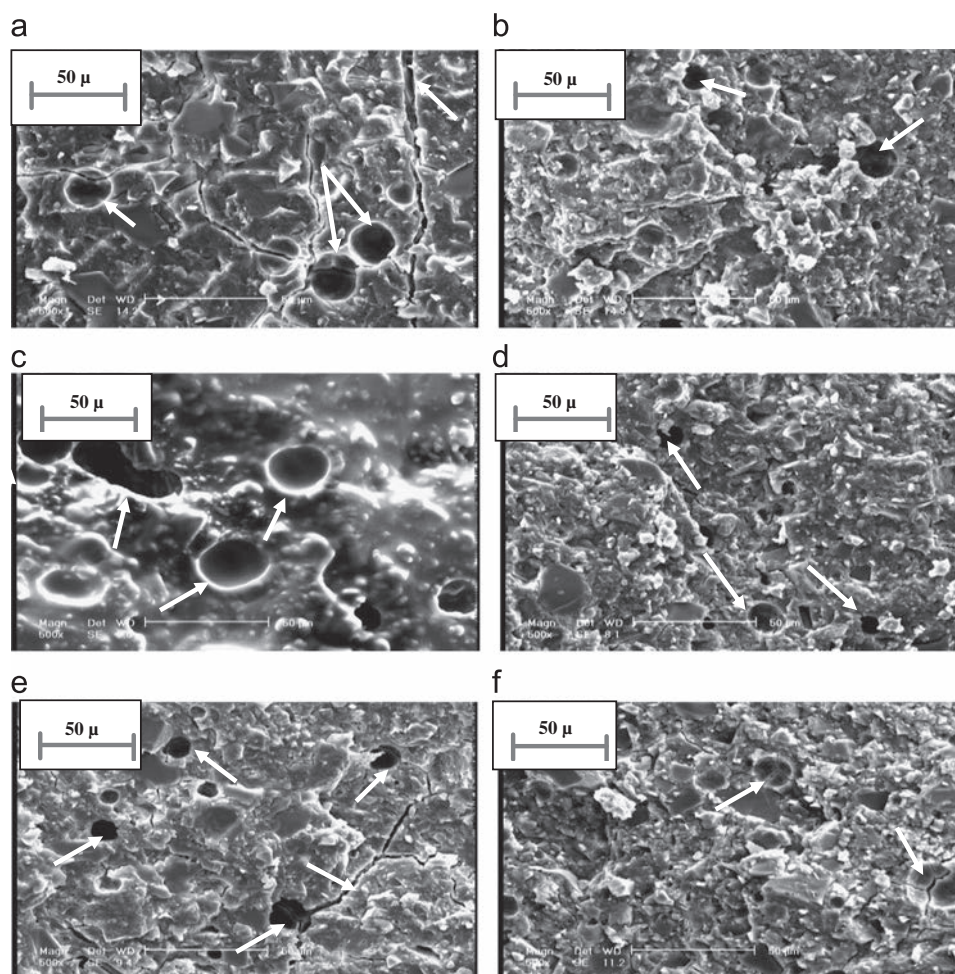


Fig. 4. SEM images of the fracture surface of the specimens after mechanical measurements: (a) Fuji II GIC after CS measurement, (b) nanocomposite containing 3 wt% forsterite nanoparticles after CS measurement, (c) Fuji II GIC after FS measurement, (d) nanocomposite containing 1 wt% forsterite nanoparticles after FS measurement, (e) Fuji II GIC after DTS measurement and (f) nanocomposite containing 1 wt% forsterite nanoparticles after DTS measurement (500 $\times$ ). White arrows show the cracks and voids.

crystalline structure that causes the formation of crystalline phases at the amorphous matrix of the cement and increases CS, FS and DTS [19].

Reduction in strength of the cement caused by the addition of extra forsterite nanoparticles indicates that there is a pronounced interference of the forsterite nanoparticles with the normal glass-ionomer reaction [20]. Strength reduction of the composites containing forsterite nanoparticles more than 3 wt% for CS, 1 wt% for FS, and 1 wt% for DTS is caused by the reduction of bond forces between ceramic and polymeric components of the GIC, where, extra forsterite nanoparticles act as a barrier and prevent perfect juncture of the GIC components [18,19]. On the other hand, reduction in strength of the cement caused by the addition of extra forsterite nanoparticles might indicate unsuitable wettability at the interface of matrix and filler. In this case, cracks are formed around the forsterite nanoparticles, where the number of cracks is directly correlated to the forsterite nanoparticles content. These cracks act as stress concentration centers and decrease mechanical strength. The effect of different amounts of forsterite nanoparticles on mechanical properties of GIC can

be also related to the aforementioned fact. Hence, the mechanism of bonding and debonding between nanocomposite components varies and the maximum effect of forsterite nanoparticles on CS, FS, and DTS occurs at different forsterite nanoparticles contents.

According to the mechanical properties measured in this study (Table 1), the optimum composition of the forsterite nanoparticles for simultaneous enhancement of CS, FS and DTS is 1 wt%. By addition of 1 wt% forsterite nanoparticles to the ceramic component of GIC, mechanical properties including CS, FS and DTS increase up to 75%, 80% and 30%, respectively.

Yap et al. [21] reported Fuji IX glass ionomer containing 4 vol% hydroxyapatite with higher compressive strength but lower diametral tensile strength (CS up to 27% and DTS up to 1.3%) as compared to the commercial GIC. In addition, Moshaverinia et al. [19] reported Fuji II glass ionomer containing 5 wt% fluorapatite nanoparticles with higher compressive and diametral tensile strength (CS up to 14% and DTS up to 70%) as compared to commercial product. In another study, Fuji IX glass ionomer containing 8 wt% hydroxyapatite

nanoparticles demonstrated higher compressive and flexural strength (CS up to 6% and FS up to 83%) [22]. Comparing results of aforementioned studies and the present study shows that the addition of forsterite nanoparticles to the ceramic component of GIC increases the CS, FS and DTS simultaneously to the acceptable values for dentistry and orthopedic applications.

Scanning electron micrographs of the fractured surface of Fuji II GIC as the control, nanocomposite containing 3 wt% forsterite nanoparticles after CS measurement, and nanocomposite containing 1 wt% forsterite nanoparticles after FS and DTS measurements are shown in Fig. 4. It can be concluded that there are more cracks and voids in the fractured surface of control groups compared to the nanocomposite samples.

The control sample exhibits an irregular fracture surface containing many voids. These voids are formed following the release of glass particles from the GIC fractured surface. In fact, there is not strong bond strength between glass particles and polymeric matrix. Also, in the SEM micrograph of the fractured surfaces of the control samples, there are more glass particles and more glass–matrix debonded sites visible due to the weakness of the glass–matrix interface compared to nanocomposite sample. The glass particle–matrix interface is considered to be the weakest component of GIC which may act as a stress concentration center and decreases mechanical properties of the cement [23]. Therefore, fracture is primarily occurred in the glass particle–matrix interface. Forsterite nanoparticles fill the spaces among glass ionomer particles, thus, the fracture surface of the GICs containing forsterite nanoparticles look smoother than control group and have less voids. It has been shown that brittle dental materials such as cements fail by crack propagation. Crack propagation can be prohibited or controlled if there are fewer voids in the structure [2,10,12,16,19].

Forsterite nanoparticles in the structure of GIC decreases glass particles and debonded sites in the glass–matrix interface. Therefore, the fractured surface of the cement looks smoother. In this case, fracture has mainly occurred in the matrix, instead of glass–matrix interface. Crack in the matrix is as the result of strong bond strength in the fillers–matrix interface. More integration in the structure causes better bonding between particles and matrix and better mechanical properties of the cement [2,22].

#### 4. Conclusions

Glass ionomer–forsterite nanocomposite was synthesized and characterized. The effect of forsterite nanoparticles on mechanical properties of the nanocomposite was evaluated quantitatively. It was shown that 3 wt% forsterite nanoparticles increase the compressive strength up to 150%, and 1 wt% forsterite nanoparticles increase the flexural strength, and the diametral tensile strength up to 80% and 30%, respectively. We suggest that the nanocomposite containing 1 wt% forsterite nanoparticles is a good candidate for high stress dental and orthopedic application due to its proper mechanical properties

including; the increase of CS up to around 75%, FS up to 80%, and DTS up to 30% as compared to the commercial product.

#### Acknowledgment

The authors are grateful to Dr. Farzaneh Shirani from Torabinejad Dental Research Center and Department of Operative Dentistry for her assistance in the specimen preparation. Also, we greatly appreciate Isfahan University of Technology support.

#### References

- [1] P. Sasanaluckit, K.R. Albustany, P.J. Doherty, D.F. William, Biocompatibility of glass ionomer cements, *Biomaterials* 14 (1993) 906–916.
- [2] D. Xie, W.A. Brantley, B.M. Culbertson, G. Wang, Mechanical properties and microstructures of glass-ionomer cements, *Dent. Mater.* 16 (2000) 129–138.
- [3] M. Irie, H. Nakai, Mechanical properties of silver-added glass ionomers and their bond strength to human tooth, *Dent. Mater. J.* 7 (1988) 87–93.
- [4] S.B. Mitra, Adhesion to dentin and physical properties of light-cured glass-ionomer liner/base, *J. Dent. Res.* 70 (1991) 72–74.
- [5] X. Xu, J.O. Burgess, Compressive strength, fluoride ion release and recharge of fluoride-releasing materials, *Biomaterials* 24 (2003) 2451–2461.
- [6] C.A. Costa, J. Hebling, G.F. Garcia, C.T. Hanks, In vitro cytotoxicity of five glass-ionomer cements, *Biomaterials* 24 (2003) 3853–3858.
- [7] P.P.C. Souza, A.M.F. Aranha, J. Hebling, E.M.A. Giro, C.A. Costa, In vitro cytotoxicity and in vivo biocompatibility of contemporary resin-modified glass-ionomer cements, *Dent. Mater.* 22 (2006) 838–844.
- [8] M. Kobayashi, M. Kon, K. Miyai, K. Asaoka, Strengthening of glass-ionomer cement by compounding short fibers with CaOP<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> glass, *Biomaterials* 21 (2000) 2051–2058.
- [9] K. Arita, H. Nakajima, M. Nishino, T. Okabe, Effect of reinforcements on mechanical properties of glass ionomer, *J. Dent. Res.* 72 (1992) 631.
- [10] M.H. Fathi, M. Kharaziha, Two-step sintering of dense, nanostructural forsterite, *Mat. Lett.* 63 (2009) 1455–1458.
- [11] K.P. Sanosh, A. Balakrishnan, L. Francis, T.N. Kim, Sol–gel synthesis of forsterite nanopowders with narrow particle size distribution, *J. Alloys Compd.* 495 (2010) 113–115.
- [12] M. Kharaziha, M.H. Fathi, Synthesis and characterization of bioactive forsterite nanopowder, *Ceram. Int.* 35 (2009) 2449–2454.
- [13] F.S. Sayyedani, M.H. Fathi, H. Edris, A. Doostmohammadi, V. Mortazavi, F. Shirani, Fluoride release and bioactivity evaluation of glass ionomer:forsterite nanocomposite, *Dent. Res. J.* 10 (2013) 452–459.
- [14] JCPDS Card No. 34-0189, 1984.
- [15] A. Monshi, M.R. Foroughi, M.R. Monshi, Modified scherrer equation to estimate more accurately nano-crystallite size using XRD, *World, J. NanoSci. Eng.* 2 (2012) 154–160.
- [16] M. Kharaziha, M.H. Fathi, Improvement of mechanical properties and biocompatibility of forsterite bioceramic addressed to bone tissue engineering materials, *J. Mech. Behavior. Biomed. Mater.* 3 (2010) 530–537.
- [17] A. Moshaverinia, S. Ansari, Z. Movasaghi, R.W. Billington, J.A. Darr, I.U. Rehman, Modification of conventional glass-ionomer cements with N-vinylpyrrolidone containing polyacids, nano-hydroxy and fluoroapatite to improve mechanical properties, *Dent. Mater.* 24 (2008) 1381–1390.
- [18] Y.W. Gu, A.U.J. Yap, P. Cheang, K.A. Khor, Effects of incorporation of HA/ZrO<sub>2</sub> into glass ionomer cement (GIC), *Biomaterials* 26 (2005) 713–720.
- [19] A. Moshaverinia, S. Ansari, M. Moshaverinia, N. Roohpour, J. Darr, I.U. Rehman, Effects of incorporation of hydroxyapatite and fluoroapatite nanobioceramics into conventional glass ionomer cements (GIC), *Acta Biomater.* 4 (2008) 432–440.
- [20] H. Prentice, J. Tyas, F. Burrow, The effect of ytterbium fluoride and barium sulphate nanoparticles on the reactivity and strength of a glass-ionomer cement, *Dent. Mater.* 22 (2006) 746–751.

- [21] U.J. Yap, Y.S. Pek, R.A. Kumar, P. Cheang, K.A. Khor, Experimental studies on a new bioactive material: HA/Ionomer cements, *Biomaterials* 23 (2002) 955–962.
- [22] A. Kenji, Y. Aimi, S.h. Yukari, H. Keiko, A. Yoko, N. Keizo, S. Shigeru, Hydroxyapatite particle characteristics influence the enhancement of the mechanical and chemical properties of conventional restorative glass ionomer cement, *Dent. Mater.* 30 (2011) 672–683.
- [23] H. Nakajima, J.H. Watkins, K. Arita, K. Hanaoka, T. Okabe, Mechanical properties of glass ionomers under static and dynamic loading, *Dent. Mater.* 12 (1996) 30–37.