

ENHANCING THE MECHANICAL PROPERTIES OF THE SOL-GEL GLASS IONOMER CEMENT BY TREATED CHITOSAN FIBER REINFORCEMENT

Rawee Dangviriyakul, Oranich Thongsri, Paritat Thaitalay, Sawitri Srisuwan, and Sirirat Tubsungnoen Rattanachan*

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Abstract

Glass ionomer cement (GIC) is commonly used for a restorative dental material which has good physical, biological and mainly anti-caries properties. The sol-gel method is a candidate method for low temperature and controlling glass composition. In this study, the glass ionomer for $4.5\text{SiO}_2\text{-}4\text{Al}_2\text{O}_3\text{-}0.45\text{P}_2\text{O}_5\text{-}2\text{CaO-}2\text{F}_2$ composition was synthesized by the sol-gel method and the treated chitosan fibers were added to reinforce the mechanical properties of the sol-gel GIC. The chitosan fibers were cut randomly with the average length of 1 mm and treated by acetic acid at concentrations of 0.3 M and 0.5 M. After treatment, chemical analysis of chitosan fibers was characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and the morphology of chitosan fiber was observed by scanning electron microscope (SEM). The sol-gel GIC was reinforced with chitosan fibers at the different amount of 0.1, 0.5, and 1 wt%. The compressive strength of GIC reinforced with 0.1 wt% treated chitosan fiber in 0.5 M acetic acid was significantly improved as compared to the GIC without reinforcement. The setting time of GIC was slightly decrease when increasing the fibers. This study successfully improved the compressive strength of the sol-gel GIC by reinforcing with 0.1 wt% chitosan fiber treated in 0.5 M acetic acid.

Keywords: Glass ionomer cement, sol-gel, treatment fiber, chitosan fiber, reinforcement

Introduction

Glass ionomer cement (GIC) is frequently used in restorative dentistry because of several advantage properties such as biocompatibility, the ability to adhere to bone and teeth and antimicrobial (Sidhu and Schmalz, 2001; Sidhu and Nicholson, 2016). GIC material is formed by the acid-based reaction of weak polymeric acid in aqueous solution and an ion-leachable glass powder (Lohbauer, 2010).

Conventional GIC is prepared by the melt quenching method at high temperatures ranging from 1,200 to 1,600°C. In this process, fluorine is lost from the melt by volatilization resulting in variable composition between batches. Nowadays, the alternative sol-gel method became more interesting for synthesis of ionomer glass due to obtaining high homogeneous particle, lower

School of Ceramic Engineering, Institute of Engineering, Suranaree University of Technology, 111 University Avenue, Muang, Nakhon Ratchasima 30000, Thailand. E-mail: sirirat.b@g.sut.ac.th

* Corresponding author

processing temperatures and repeatability (Cestari *et al.*, 2009; Wren *et al.*, 2009).

The reinforcement of fiber or filler is an effective way to increase the mechanical properties of GIC such as glass fiber (Lohbauer *et al.*, 2003), cellulose fiber (Menezes-Silva *et al.*, 2019), flax fiber (Abou Neel and Young, 2017), silk fiber (Bahrami-Abadi *et al.*, 2016) and chitosan (Bao, Liu *et al.*, 2020; Petri *et al.*, 2007). Chitosan is a natural linear biopolyaminosaccharide that obtained by alkaline deacetylation of chitin which derived from crustacean shell such as crabs, shrimps and lobsters. The chitosan present properties such as biocompatibility, antibacterial properties, biodegradability which can be advantage for GIC. (Petri *et al.*, 2007). studied the effect of chitosan into commercial GIC on to flexural strength their result present that flexural strength was increased by reduced of interfacial tension among the components (Petri *et al.*, 2007). However, the reaction between chitosan and GIC is only a hydrogen bond which is not as strong as covalent bonds or ionic bonds. So, the treatment of chitosan fiber by adding functional group of carboxyl (-COOH) was interested by used acetic acid. Normally, chitosan fiber is dissolved in acid solution (pH<6.5) but, (Qin *et al.*, 2006) showed that could be treated chitosan fiber by used acetic acid in isopropanol solution without dissolving chitosan fiber (Qin *et al.*, 2006).

In this study the treated chitosan fiber by acetic acid was added into the sol-gel GIC composite. The chemical structure and morphology of treated chitosan fiber were evaluated. The compressive strength of GIC reinforced by treated chitosan fiber was investigated and compared with the sol-gel GIC without treated chitosan fiber. This study was designed by 2^k factorial design (Minitab 16 statically software).

Design of Experimental (DOE)

DOE is technique of investigating all possible condition in an experimental. It includes of a series of experimental by input variable or factors of product that might observe and identify the changed of output response. DOE provides a quick and effective method to optimize process of experimental (Tanco *et al.*, 2007).

The 2^k full factorial DOE was used to investigate the compressive strength of treated chitosan reinforcement the sol-gel GIC. The DOE factors in this experimental are percent of chitosan fiber reinforcement and concentration of acetic acid treatment. The first factor was divided into 4 level, 0, 0.1, 0.5, and 1 wt%. The second factor was divided into 3 level Untreated, 0.3 and 0.5 M. This experiment design was 12 runs with 6 replicates, that provided total of 72 experiments.

Materials and Methods

Synthesis of the Sol-Gel Ionomer Glass Powder

The glass ionomer powder composition based on 4.5SiO₂-4Al₂O₃-0.45P₂O₅-2CaO-2F₂ in molar ratio was synthesized by the sol-gel method. Firstly, tetraethyl orthosilicate (TEOS, 98%, Acros) dissolved in mixed solution of ethanol absolute (EtOH, Carlo) and DI-water. After that, aluminum nitrate (Al(NO₃)₃·9H₂O, 98%, Kemaus), triethylphosphate (TEP, 99%, Acros), calcium nitrate (Ca(NO₃)₂·4H₂O, 98%, Kemaus) and fluorosilicic acid (H₂SiF₆, 25%, Acros) were added to the solution, respectively. Each step of adding chemical compound was mixed by magnetic stirrer for 30 minutes. After the solution was aged, the obtained gel was calcined at 700°C for 2 h the glass powder was grinded by planetary mills for 2 h to obtain average particle size 10 µm.

Treatment of Chitosan Fiber

The chitosan fiber was purchased from G.T.C. UNION GROUP (HK). Chitosan fiber was cut randomly for 1 mm in length. Acetic acid was purchased from Merck in 100% purity was prepared in isopropanol (99.9%, Carlo) for concentrations of 0.1, 0.3, 0.5, and 0.7 M. Chitosan fiber were soaked in the acetic acid solution for 10 min. and then rinsed by acetone (99.8%, Carlo) for 3 times after that drying at 60°C for 3 h.

Preparation of the Sol-Gel GIC Reinforced by the Treated Chitosan Fiber

The treated chitosan fiber and the sol-gel GI powder were mixed by polypropylene bottle for 1 h with shaking every 15 min until a homogeneous mixture was obtained. The untreated chitosan fiber and chitosan fiber treated with acetic acid concentration 0.3 and 0.5 M were chosen due to the functional group and surface after the treatment. Fibers were added at 0, 0.1, 0.5, and 1 wt%. The treated chitosan fiber contained glass powders were the mixed with liquid (modified polyacrylic) at powder/liquid (P/L) ratio of 2:1 at room temperature.

Characterization of the treated chitosan fiber

The chitosan fiber was dispersed into glass microscope slide. The chitosan fiber was photograph with stereo microscopy at a magnification of 50x. The actual length of 303 fibers were obtained by using Image-J processing program.

The spectra of the treated chitosan fiber were obtained with 64 scans in the interval between 400 and 4,000 cm⁻¹, with a resolution of 4 cm⁻¹, by mean of Fourier Transform Infrared Spectrometer (ATR-FTIR German Bruker, Tensor27-Hyperion).

Water absorption test of the chitosan fiber was modified from (Qin *et al.*, 2006). 0.2 g of chitosan fiber was soaked in 100 mL of distilled water. After 1 h, the fiber was screened by using rayon fabric. Next, the wet fiber (W_w) was dried at 105°C overnight to constant weight (W_d). The water absorption of the chitosan fiber (in percentage) was calculated using Equation 1.

$$\%W = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

Where %W is the percent water absorption, W_d and W_w are the dry weight and the weight after soaking in the water, respectively.

Setting Time and Compressive Strength Testing

Setting time of GIC was measured by according to ISO 9917-1:2007. The working times of GIC was recorded from the start mixing until the cement unable to molding. The net setting time of GIC was measured with Gilmore Apparatus (Humboldt, H- 3150F) following the description of ISO 9917-1. After mixing the GIC paste was molded with sized 10 mm in diameter and 2 mm in height. The net setting time was measured when the heavy and thin needle (453.6 g, Ø 1.06 mm) place on the surface of GIC paste until no mark occurred.

Samples were prepared in mold with 6 mm. in diameter and 4 mm. in height for 1 h, all specimens were kept in DI water at 37°C for 23 h. Six samples ($n = 6$) of every condition were prepared for testing. Compressive strength was evaluated by the universal testing machine (UTM, Instron 5565, Instron GmbH, Germany) with 5 kN load cell at cross speed of 0.5 mm/min. The equation for calculated compressive strength is $CS = 4P/\pi d^2$. Where CS was compressive strength (MPa), P was the maximum load (N), and d was the radius of specimen (mm).

Morphology of Fracture Surface

Fracture surface of the GIC samples were observed after failure of the compressive strength test. The sample surface was coated by gold before observation by SEM (Scanning electron microscopy, JEOL-6010LV). The elemental between fiber and the sol-gel matrix were determined by energy dispersive spectroscopy (EDS, Oxford Instruments X-Max^N 20).

Results and Discussion

Fiber Size Distribution

The length and diameter distribution of chitosan fiber were presented in Figure 1(a) and

Figure 1(b), respectively. The chitosan fiber was generally distributed for 1.0-1.2 mm in length with average 1.118 mm and 10-12 µm in diameter with average 11.428 µm, respectively, as shown in Figure 1.

Chemical Structure of Chitosan Fiber Analysis by FT-IR

The FT-IR spectra of chitosan fibers showed its characteristic peaks at 1,660 cm^{-1} and 1,585 cm^{-1} for C-O stretching (amide) and N-H bending (amine), respectively (Kumar Singh Yadav and Shivakumar, 2012). The other peaks of chitosan were present at 2,923-2,867 cm^{-1} (C-H stretch) and 1,122-860 (C-O and C-O-C) (Mobarak and Abdullah, 2010). The peak of acetic acid treated chitosan corresponding at 1,660 cm^{-1} , 1,550 cm^{-1} , and 1,422 cm^{-1} could be assigned to the stretching of -COOH which might overlap with peak of amide (Joshi and Sinha, 2006; Chen *et al.*, 2015). The chitosan treated with 0.5 M and 0.7 M of acetic acid presented that the intensity of the peak at 2,923-2,867 cm^{-1} and 1,122-860 cm^{-1} were increased because of C-H stretch and C-O from acetic acid the cross-link with chitosan (Joshi and Sinha, 2006).

The FT-IR spectra of chitosan fiber in Figure 2. demonstrated that the increasing of acetic acid concentration resulted in increasing of the -COOH functional group on the chitosan fiber. This functional group had benefit on the setting reaction of the GIC by -COOH group on chitosan fiber able to bonding with metal ion in glass particle (Bao *et al.*, 2020). However, the increasing of carboxyl

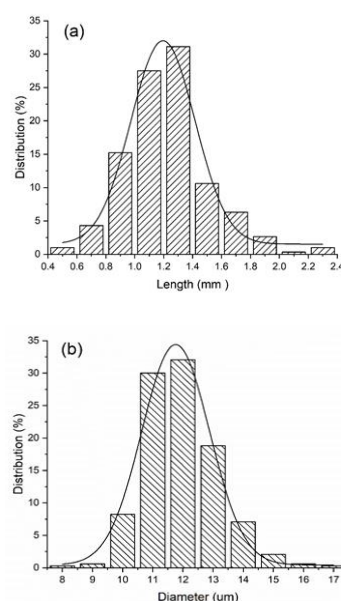


Figure 1. Chitosan fiber size distribution (a) length distribution and (b) diameter distribution

group up to 40% could increase the water solubility to the chitosan fiber (Qin *et al.*, 2006). From our result, the chitosan fiber treated by acetic acid at a concentration of 0.7 M dissolved in water which could be assumed that it had carboxyl group more than 40%. Thus, Next experiment did not select this condition for treatment of chitosan fiber.

Water Absorption

Figure 3 shows the effect of the acetic acid concentration on the water absorption of the treated chitosan fiber. It was found that the water absorption of the chitosan fiber was increased with increasing of acetic acid concentration. The treatment of chitosan fiber with acetic acid resulted in occurrence of the carboxyl group on the surface, which the carboxyl group on the chitosan fiber could improve the water absorption of the fiber (Qin *et al.*, 2006).

Morphology of Chitosan Fiber Analysis by SEM

The surface morphology of chitosan fibers after treatment with different concentrations of acetic acid in comparison with the untreated chitosan fiber were observed by SEM as shown in Figure 4. The acetic acid treated at 0.1 and 0.3 M showed that a smoother surface and cleaner than untreated chitosan fiber as showed in Figure 4(b) and

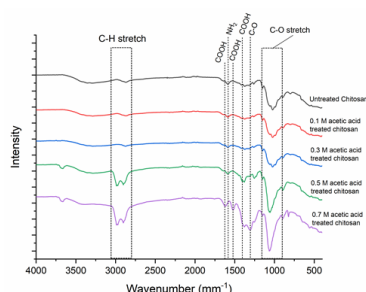


Figure 2. FT-IR spectra of the chitosan fiber treated with different concentrations of acetic acid as comparison with the untreated chitosan fiber

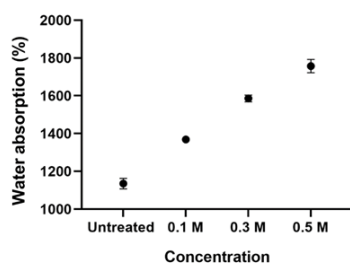


Figure 3. Water absorption of the treated chitosan fiber with the different acetic acid concentrations

Figure 4(c), respectively. Figure 4(d) shows chitosan fiber treated with 0.5 M of acetic acid appeared peeling on surface. The chitosan fiber treated by acetic acid 0.7 M was observed a fiber breakage as shown in Figure 4(e).

Chitosan fiber treated by low concentration of acetic acid (0.1-0.3 M) were removed impurity of insoluble substances such as residual chitin, protein and polysaccharides resulting in smooth and clean surface (Qian and Glanville, 2005). However, the chitosan fiber might be damaged with treatment of high concentration of acetic acid (>0.5 M) occurring peel, tear and breakage of fiber.

Setting Time of the Sol-Gel Glass Ionomer Cement Reinforced by Chitosan Fiber Analysis by Gilmore Apparatus

Figure 5 shows the variation in working and net setting time for the sol-gel GIC reinforced by untreated and treated chitosan fiber. The working

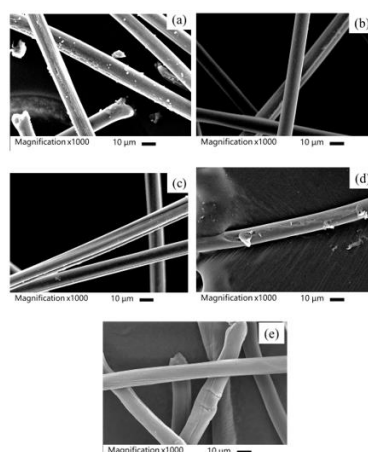


Figure 4. SEM micrographs of (a) untreated chitosan fiber, (b) Treated with 0.1 M acetic acid, (c) Treated with 0.3 M acetic acid, (d) Treated with 0.5 M acetic acid and (e) Treated with 0.7 M acetic acid

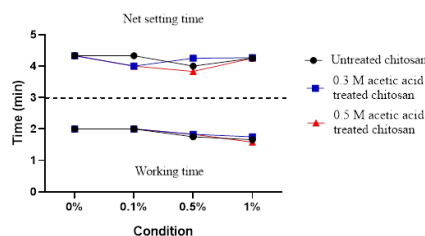


Figure 5. Working time and net setting times of the sol-gel glass ionomer cement reinforced by untreated chitosan fiber, 0.3 M acetic acid treated chitosan fiber and 0.5 M acetic acid treated chitosan fiber

time of the sol-gel GIC was slightly decreased when the amount of chitosan fiber had increased. The net setting times and working time of the sol-gel GIC reinforced by chitosan fiber show no difference between untreated and treated chitosan fibers.

In this study, the chitosan was polysaccharide with high hydrophilicity due to many of hydroxyl group in the structure (Crini, 2005). In addition, this aspect decreased water in system of the GIC paste. This can be assumed that working times of the sol-gel GIC paste were decreased by increasing of viscosity (Prentice *et al.*, 2005).

Design of Experimental Analysis by Minitab 16 Statistically Software

The compressive strength data obtained by the experiment were analyzed using the Minitab release 16 programs. The ANOVA result in Table 1 shows the influence of acetic acid concentrations and chitosan fiber contents on the compressive strength of the sol-gel GIC cements. A factor with a p-value

of less than 0.05 was investigated statistically significant with 95% confidence interval. Therefore, the most significant factor for the compressive strength of the sol-gel GIC was a percent of chitosan fiber.

The main effect plot and interaction plot was shown in Figure 6. The main plot in Figure 6(a). presented that the acetic acid treated chitosan reinforced the sol-gel GIC had compressive strength higher than the sol-gel GIC with untreated chitosan fiber, whereas the percent of chitosan fiber significantly affected the compressive strength. The sol-gel GIC with 0.1 wt% of chitosan fiber showed the highest compressive strength. Figure 6(b) revealed the interaction plot between the concentration and percent of chitosan fiber. Untreated chitosan fiber shown the optimum compressive strength at 0.1 wt%. At concentration of 0.5 M, the compressive strength reached maximum where the percent of chitosan was 0.1 wt%. At concentration of 0.3 M, the maximum compressive strength presented at 0.5 wt% of chitosan fiber.

Since it found carboxyl group on the surface of the treated chitosan, the increasing of acetic acid concentration increased more carboxyl group on the chitosan surface. The carboxyl group on the surface of chitosan fiber was able to interact with ionomer glass particle and poly (acrylic acid) (PAA) (Bao *et al.*, 2020). This interaction reduced the interfacial tension between each components resulting in an increase of compressive strength (Petri *et al.*, 2007). In addition, the surface of untreated chitosan in Figure 4(a) showed the impurity on surface that had an adverse effected on the bonding between chitosan fiber and the sol-gel GIC resulting in reduction of compressive strength.

The compressive strength for chitosan fiber reinforced the sol- gel GIC were presented in Figure 6(b). It showed the different optimum points of the two concentrations acetic acid treated chitosan fibers. Since 0.5 M acetic acid treated chitosan fibers were higher water absorption and

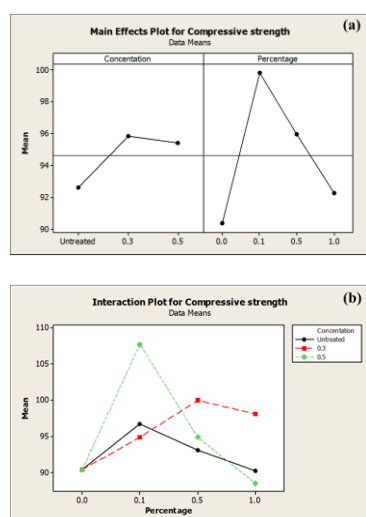


Figure 6. The main effect plot (a) and interaction plot (b) for compressive strength of chitosan fiber reinforcement sol-gel GIC

Table 1. Analysis of variance for compressive strength of the sol-gel GIC reinforced with treated chitosan fibers

Source	DF*	Seq SS**	Adj SS***	Adj MS****	F*****	P*****
Concentration	2	146.81	146.81	73.40	1.80	0.175
Percentage	3	933.60	933.60	311.20	7.63	0.000
Concentration*Percentage	6	896.03	896.03	149.34	3.66	0.004
Error	55	2244.50	2244.50	40.81		
Total	71	4365.50				

* DF = The total degrees of freedom.

** Seq SS = Sequential sums of squares are measures of variation for different components of the model.

***Adj SS = Adjusted sums of squares are measures of variation for different components of the model.

****Adj MS = Adjusted mean squares measure how much variation a term or a model explains.

*****F = The test statistic used to determine whether the term is associated with the response.

*****P = The p-value is a probability that measures the evidence against the null hypothesis

carboxyl functional group than that of 0.3 M acetic acid treated chitosan fibers. The higher water absorption of the treated chitosan required high amount of liquid to handle and setting GIC. In addition, more carboxyl functional groups resulted good bonding between the metallic ions of GIC and the treated chitosan fibers. From EDS result in Table 2, it showed the high Al^{3+} and Ca^{2+} ions concentrations on 0.5 M acetic acid treated chitosan fibers. The ions releasing from the sol-gel glass would be competitive for bonding to the carboxyl groups of the treated chitosan fibers rather than the polyacrylic acid in the GIC matrix.

In this study, the powder to liquid ratio (P/L) was fixed to 2:1, which resulted to the optimum condition for mixing and setting with different composition of GIC. The optimum point for 0.5 M acetic acid treated chitosan fibers reinforced the sol-gel GIC was 0.1 wt% content while the optimum point for 0.3 M acetic acid treated chitosan fibers reinforced the sol-gel GIC was 0.5 wt% content. The compressive strength and properties of the sol-gel GIC should be compromised with the powder to liquid ratio.

Fracture Surface of the Sol-Gel Glass Ionomer Cement Reinforced by Chitosan Fiber Analysis by SEM-EDS

The fracture surface of the sol-gel GIC reinforced by treated chitosan fiber were observed by Scanning electron microscopy as shown in Figure 7. The treated chitosan fiber reinforced the sol-gel GIC showed a good bonding between cement and fiber when compared with untreated chitosan fiber reinforcement that can be observed in Figure 7. The elemental of bonding between chitosan fiber and the sol-gel GIC was randomly determined on the interface bonding of chitosan fiber by EDS analysis.

As shown in Figure 4(a), the untreated chitosan fibers have a lot of impurities, which could weaken the bonds between the fibers and GIC. The chitosan fiber treated with acetic acid resulted in the carboxyl group on the surface of the fiber, which created better bonding with the matrix of GIC Figure 7(d, f), compared to the bonding created by untreated chitosan fiber Figure 7(b). The EDS analysis on the

surface area of the chitosan fibers as shown in Figures 7(b); 7(d), and 7(f). Table 2 shows % atomic of the elements on the surface area of the chitosan fiber in the GIC matrix. It can be found that the concentrations of Al^{3+} and Ca^{2+} ions for the treated chitosan fibers increased as compared to the untreated chitosan fibers. As corresponding to FT-IR result, there are carboxyl functional group, which has an ability to bond with the metal ions (Muzzarelli *et al.*, 1998) on the surface of the treated chitosan fibers. The EDS result showed the chitosan fiber treated with acetic acid 0.5 M have high concentrations of Al^{3+} and Ca^{2+} ions than those of the chitosan fiber treated with acetic acid 0.3 M. It indicated that the chitosan fiber treated with acetic acid 0.5 M modified the carboxyl group higher than that of 0.3 M acetic acid. It can be resulted that the bonding between the treated chitosan fibers and the GIC increased with increasing of the acetic acid concentration.

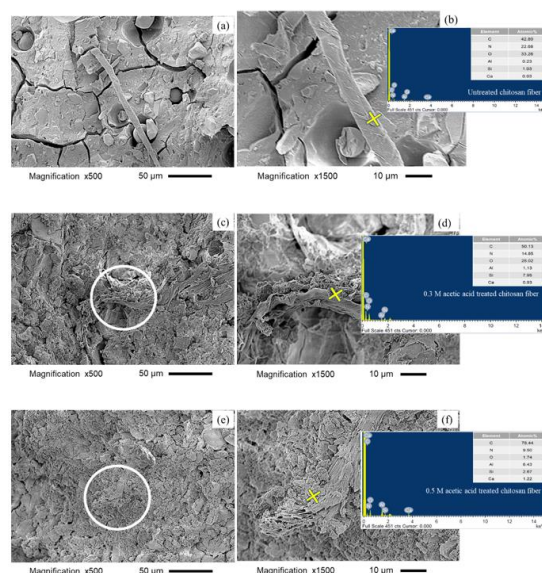


Figure 7. SEM-EDS micrograph of fracture surface of the sol-gel glass ionomer cement reinforced by (a) untreated chitosan fiber at 500x, (b) untreated chitosan fiber at 1,500x, (c) 0.3 M acetic acid treated at 500x, (d) 0.3 M acetic acid treated at 1,500x, (e) 0.5 M acetic acid treated at 500x and (f) 0.5 M acetic acid treated at 1,500x

Table 2. EDS result of %atomic on the surface of the chitosan fibers

Elements	Untreated chitosan fiber	0.3 M acetic acid treated chitosan fiber	0.5 M acetic acid treated chitosan fiber
C	42.60	50.13	78.44
N	22.68	14.85	9.50
O	33.26	25.02	1.74
Al	0.23	1.13	6.43
Si	1.03	7.95	2.67
Ca	0.03	0.93	1.22

Conclusions

This study has been successfully to improve the compressive strength of the sol-gel GIC by reinforcing with treated chitosan fiber. This result presented that there was carboxylic group on the surface of treated chitosan fiber. In addition, the treated chitosan fiber reinforced the sol-gel GIC was increased compressive strength due to the bonding between chitosan fiber and the sol-gel GIC which reduce the interfacial tensile among the sol-gel GIC components. The highest compressive strength was found for the sol-gel GIC with 0.1% wt% treated chitosan fiber by 0.5 M acetic acid. However, the increasing of fiber contained up to 0.5 wt% that resulting in reduced compressive strength except the 0.3 M acetic acid treated chitosan fiber that show high compressive strength at 0.5 wt%.

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