

# Nanoclay addition to a conventional glass ionomer cements

Fareed, Muhammad; Stamboulis, Artemis

DOI:

[10.4103/1305-7456.143619](https://doi.org/10.4103/1305-7456.143619)

License:

Creative Commons: Attribution-NonCommercial-ShareAlike (CC BY-NC-SA)

*Document Version*

Publisher's PDF, also known as Version of record

*Citation for published version (Harvard):*

Fareed, M & Stamboulis, A 2014, 'Nanoclay addition to a conventional glass ionomer cements: Influence on physical properties', *European Journal of Dentistry*, vol. 8, no. 4, pp. 456-463. <https://doi.org/10.4103/1305-7456.143619>

[Link to publication on Research at Birmingham portal](#)

## General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

## Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact [UBIRA@lists.bham.ac.uk](mailto:UBIRA@lists.bham.ac.uk) providing details and we will remove access to the work immediately and investigate.

# Nanoclay addition to a conventional glass ionomer cements: Influence on physical properties

Muhammad A. Fareed<sup>1,2</sup>, Artemis Stamboulis<sup>1</sup>

**Correspondence:** Dr. Muhammad A. Fareed  
Email: docamberfareed@hotmail.com

<sup>1</sup>School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK,  
<sup>2</sup>FMH College of Medicine and Dentistry, University of Health Sciences, Lahore, Pakistan

## ABSTRACT

**Objective:** The objective of the present study is to investigate the reinforcement effect of polymer-grade montmorillonite (PGN nanoclay) on physical properties of glass ionomer cement (GIC). **Materials and Methods:** The PGN nanoclay was dispersed in the liquid portion of GIC (HiFi, Advanced Healthcare, Kent, UK) at 1%, 2% and 4% (w/w). Fourier-transform infrared (FTIR) spectroscopy was used to quantify the polymer liquid of GICs after dispersion of nanoclay. The molecular weight ( $M_w$ ) of HiFi liquid was determined by gel permeation chromatography. The compressive strength (CS), diametral-tensile strength, flexural strength (FS) and flexural modulus ( $E_f$ ) of cements ( $n = 20$ ) were measured after storage for 1 day, 1 week and 1 month. Fractured surface was analyzed by scanning electron microscopy. The working and setting time (WT and ST) of cements was measured by a modified Wilson's rheometer. **Results:** The FTIR results showed a new peak at  $1041\text{ cm}^{-1}$  which increased in intensity with an increase in the nanoclay content and was related to the Si-O stretching mode in PGN nanoclay. The  $M_w$  of poly (acrylic acid) used to form cement was in the range of 53,000 g/mol. The nanoclay reinforced GICs containing <2% nanoclays exhibited higher CS and FS. The  $E_f$  cement with 1% nanoclays was significantly higher. The WT and ST of 1% nanoclay reinforced cement were similar to the control cement but were reduced with 2% and 4% nanoclay addition. **Conclusion:** The dispersion of nanoclays in GICs was achieved, and GIC containing 2 wt% nanoclay is a promising restorative materials with improved physical properties.

**Key words:** Glass ionomer, mechanical properties, nanoclay, setting time, working time

## INTRODUCTION

When a dentist considers the type of restorations to place in the tooth, the decision may be influenced by the variety of available restorative materials and the choice of the patient.<sup>[1]</sup> Glass ionomer cements (GICs) are welcomed in the dental community due to easy manipulation, higher fluoride release and the chemical bonding to base-metals, dentin and enamel.<sup>[2]</sup> They have a similar coefficient of thermal expansion as the tooth structure,<sup>[3]</sup> minimal micro-leakage after setting,<sup>[4]</sup> low toxicity and biological compatibility.<sup>[5,6]</sup> GICs have undergone many developments since emergence<sup>[7]</sup> and several systems are available in the market. However, due to the complexity of these materials no two commercial systems are chemically

or mechanically identical. The modifications in GICs had intermittently been introduced in order to improve the conventional system, for example, miracle mix and cermet,<sup>[8]</sup> resin-modified GICs,<sup>[9]</sup> polyacid-modified composite resins (compomers),<sup>[10]</sup> various new concepts of glass development<sup>[11]</sup> and polymer compositions,<sup>[12]</sup> incorporation of chlorhexidine,<sup>[13]</sup> hydroxyapatite and fluoroapatite,<sup>[14]</sup> nanoclays,<sup>[15]</sup> amino-acids<sup>[16]</sup> and glass fibers.<sup>[17]</sup>

The incorporation of low concentration of montmorillonite nanoclays is a popular strategy to improve polymer materials in the recent years.<sup>[18]</sup> The montmorillonite are aluminosilicate minerals of high purity and are frequently used as additives in hydrophilic polymers such as

**How to cite this article:** Fareed MA, Stamboulis A. Nanoclay addition to a conventional glass ionomer cements: Influence on physical properties. Eur J Dent 2014;8:456-63.

Copyright © 2014 Dental Investigations Society.

DOI: 10.4103/1305-7456.143619

polyvinylalcohols, polysaccharides and poly (acrylic acid) (PAA).<sup>[19]</sup> The high aspect-ratio of nanoclay is ideal for polymer reinforcement. The polymer-grade montmorillonite (PGN) (commonly known nanoclay) was dispersed in the liquid portion of GIC in low concentrations and was mixed with the glass-powder to form GIC. This study aimed to investigate the addition of PGN nanoclay on the physical properties of a conventional glass ionomer restorative. The null hypothesis is that the incorporation of increasing concentrations of nanoclay into GIC does not affect its physical properties.

## MATERIALS AND METHODS

### Experimental materials

The PGN nanoclay was supplied by Nanocor Inc. (Chicago, IL, USA). The structure of nanoclay have a single layer of central alumina octahedral sheet sandwiched between two silica tetrahedral sheets having a thickness of 1 nm. The raw materials of a conventional GIC (HiFi) having HiFi glass powder (alumino-silicate glass) and HiFi PAA powder of commercial grade was obtained from Advanced Healthcare Limited (Kent, UK).

### Dispersion on nanoclay the liquid portion of glass ionomer cement

The polymer solutions were prepared by mixing nanoclay similar to the exfoliation-adsorption method.<sup>[20]</sup> This method involves the shear mixing of nanoclays and water was used as a solvent for dispersion of nanoclay. Approximately, 0.10 g, 0.20 g and 0.40 g (1.0 wt%, 2.0 wt%, 4.0 wt%) PGN nanoclay was added to ionized water and stirred for 2 h at 75°C on a hot plate (Stable Temp Cole-Parmer IL, USA) using a magnetic-stirrer at 100 rpm, followed by the mixing of HiFi PAA powder (4.0 g) and PGN solution for 22 h. The polymer solutions were labeled as PA, PA1, PA2 and PA4 with increase in concentration of nanoclay [Table 1]. GICs were prepared by hand-mixing the HiFi glass powder with the corresponding polymer liquid using a stainless-steel spatula on a paper mixing-pad. A powder to liquid ratio (P: L) of 4.2:1 for HiFi cements was used in accordance with manufacturer's instructions. The schematic presentation of polymer solutions and GICs prepared in this study is given in Table 1.

### Fourier-transform infrared spectroscopy

Fourier-transform infrared (FTIR) spectra of HiFi glass powder and polymer liquids formed after

dispersion of nanoclays were obtained on a Nicolet FTIR spectrometer (FT-Roman Module, MGNA-IR 860) equipped with a mid-infrared source using a deuterated triglycine sulfate detector having a XT-KBr beam-splitter with a Golden Gate Single Reflection Diamond ATR attachment. For each sample, 100 scans were recorded with a 4 cm<sup>-1</sup> resolution in the range of 4000-700 cm<sup>-1</sup>.

### Gel permeation chromatography

Gel permeation chromatography (GPC) was done at Rapra Technology Limited (Shrewsbury, UK) using a Vicotek TDA 301 (Column Oven and Detector System with associated Pump and Auto-sampler) at 30°C and at a flow rate of 1.0 ml/min. The GPC (size exclusion chromatography) system was calibrated with sodium polyacrylates calibrants. Solution for GPC analysis were prepared by dissolving 50 mg PA solution in 10 ml of eluent (0.2 M NaNO<sub>3</sub>, 0.01 M NaH<sub>2</sub>PO<sub>4</sub> pH ~7) and were left overnight to dissolve and then filtered through 0.45 µm polyvinylidene fluoride membrane prior to chromatography. The number-average molecular weight ( $M_w/M_n$ ), the weight-average  $M_w$  and polydispersity ( $M_w/M_n$ ) of PA powder and liquid, were measured. The data were analyzed using Polymer Laboratories Cirrus software.

### Mechanical properties

Cement specimens were prepared using split brass coated with a PTFE dry-film spray (PR Mold release RS-7 Rocol Leeds, UK) to prevent cement adhesion. The cylindrical (6 × 4 mm) specimens for compressive strength (CS), the disk-shaped (2 × 4 mm) specimens for diametral-tensile strength (DTS) and rectangular bar-shaped (25 × 2 × 2 mm) specimens for three-point bend test to measure flexural strength (FS), were

**Table 1: Dispersion of PGN nanoclays in the liquid portion of GIC and cement formation**

Specimen	PGN clay weight %	Liquid	PAA powder
PA	0.0	60% water	40% PAA
PA1	1.0	59% water	40% PAA
PA2	2.0	58% water	40% PAA
PA4	4.0	56% water	40% PAA
Cement specimen	Liquid	Glass powder	Powder: Liquid ratio
HF	PA	HiFi powder	4.2:1
HF1	PA1	HiFi powder	4.2:1
HF2	PA2	HiFi powder	4.2:1
HF4	PA4	HiFi powder	4.2:1

GIC: Glass ionomer cement, PGN: Polymer-grade montmorillonite, PA: Polyacrylic, PAA: Poly (acrylic acid), HF: Hydrofluoric

fabricated. Twenty specimens ( $n = 20$ ) of each cement group and for each storage time were fabricated. Cement was packed in the mold to a slight excess, and the extruded cement was removed to cover the top surface with an acetate sheet. A glass slab was placed on the top surface of the mold and tightened using a C-shaped screw clamp to store for 1 h in a desiccator maintained at 37°C and 95% humidity. Specimens were removed from the mold, conditioned in distilled water maintained at 37°C for 1 day, 1 week and 1 month prior to testing. Mechanical testing was performed on a screw-driven Instron machine (Model 5566, Instron Corporation, High Wycombe, UK) at a cross-head speed of 1.0 mm/min. The CS was calculated from the equation:<sup>[22]</sup>  $CS = 4P/\pi d^2$  where  $P$  is the maximum force applied at fracture and  $d$  is the diameter of the specimen, the DTS was determined from equation  $DTS = 2P/\pi DT$ , where  $P$  is a load at fracture and  $D$  is the diameter, and  $T$  is the thickness of the specimen. FS was obtained from the formula:<sup>[23]</sup>  $FS = 3Fl/2bh^2$ , where  $l$  is the span (20.0 mm) between the two supports,  $b$  the breadth and  $h$  the height of the specimen. The flexural modulus ( $E_f$ ) was calculated according to the ASTM standard<sup>[24]</sup> from the data of three-point bend test at 1 month storage time by drawing a tangent to the steepest initial straight-line portion of the load-deflection curve and calculated by using the formula;  $E_f = l^3m/4bd^3$ ,  $l$  is the distance between the two supports,  $m$  is the slope of the tangent to the initial straight-line portion of the load-deflection curve N/mm of deflection,  $b$  is the width of the beam in mm and  $d$  is the depth (height) in mm of the bar-shaped specimen.

### Working time and setting time

The working time (WT) and the setting times (ST) of the cements were determined at ambient temperature (21-25°C) by a modified Wilson oscillating rheometer having two aluminium platens 1.0 mm apart with 0.50 mm deep groves to hold the cement mass. The WT and ST were calculated by the changes in the oscillatory motion of the lower platen recorded on a software program (RDP Electronics Limited Wolverhampton, UK) using an excel chart and were determined by calculating the time taken to reach 95% and 5% of the initial (maximum) amplitude of oscillation, respectively.<sup>[21]</sup> The values reported are the average of the three traces of each cement group [Figure 1].

### Statistical analysis

The data were analyzed using one-way analysis of variance (ANOVA) and *post-hoc* Tukey's multiple

comparison tests at the associated 95% confidence interval to determine if there were significant differences between the values of experimental GICs and control group.  $P < 0.05$  was used for statistical significance.

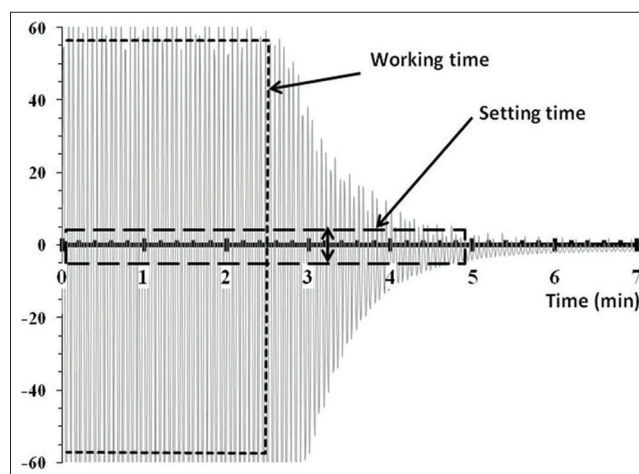
### Scanning electron microscopy

The beam shaped specimens from three-point bend test were used to study the fracture surface of GICs. A JEOL 7000 (Philips Co., Japan) scanning electron microscope (SEM) was used to study the surface of the microstructure of cements. After sputter coating with gold, the sample is transferred into the SEM chamber. The SEM was operated under low-vacuum conditions, in back-scattered electron mode at a voltage of 10 kV.

## RESULTS

### Fourier-transform infrared spectroscopy

The FITR spectra of HiFi liquid (PA) with respective solutions formed after the dispersion of 1.0 wt% (PA1), 2.0 wt% (PA2) and 4.0 wt% (PA4) PGN nanoclay is shown in Figure 2. The peak at 1710  $\text{cm}^{-1}$  was attributed to the C = O stretching vibrations in the carboxylic group and the peak at 1628  $\text{cm}^{-1}$  was associated with -OH bending vibrations in water molecules, which was consistent in all groups after the dispersion of nanoclays. The presence of a new peak at 1041  $\text{cm}^{-1}$  was attributed to the Si-O stretching mode in PGN nanoclay which increased in intensity with an increase in nanoclay contents in PA1, PA2 and PA4 respectively.<sup>[25]</sup> In addition, there was a broad OH stretching band at 3360  $\text{cm}^{-1}$  present in all polymer solutions associated with -OH groups



**Figure 1:** Schematic presentation of a typical glass ionomer cement trace showing working time and setting time obtained from Wilson's oscillating rheometer

in water molecules. The FTIR spectra of the HiFi glass powder used in the preparation of cements is presented in Figure 3 shows the intensive absorption bands in the region of 900-1400  $\text{cm}^{-1}$ , which usually represents a super-position of some bands situated close to each other and assigned to the stretching vibration of  $\text{SiO}_4$  tetrahedral with a different number of bridging oxygen atoms and P-O bonds.<sup>[26]</sup> The main peak in the spectra of HiFi glass powder at 991  $\text{cm}^{-1}$  attributed to the Si-O-Si stretching vibrations and peak at 1740  $\text{cm}^{-1}$  assigned to Si-OH appeared in the HiFi glass.<sup>[27]</sup>

**Gel permeation chromatography analysis**

Figure 4 shows the  $M_w$  distribution of 40% PAA in an aqueous solution PAA powder. The results are summarized as the calculated  $M_w$  averages, polydispersity ( $M_w/M_n$ ) and refractive index peak area in Table 2. The results of GPC analysis show that the PAA powder and 40% PAA aqueous solution have polymer of generally similar  $M_w$ . The polymer content was estimated from the refractive index detector response was 39.2% for PA. The low-peak area for PAA powder implies that it has not fully dissolved and gave a cloudy solution during GPC analysis to prevent any calculation of polymer content estimation. The  $M_w$  of PAA was in the range of 52,000-56,000 g/mol.

**Mechanical properties of cements**

The CS, DTS, FS and  $E_f$  values of PGN nanoclay reinforced GICs at different storage time compared with control group (HF) are shown in Table 3. The CS values at 1 month storage were significantly higher ( $P < 0.05$ ) than at 1 day storage in all cement groups. The HF1 cements resulted in a significant increase ( $P < 0.01$ ) in the mean CS ( $137 \pm 16$  MPa) compared to HF ( $120 \pm 19$  MPa) however, the CS significantly decreased ( $P < 0.05$ ) for HF4 at 1 week storage. Conversely, there was no significant change ( $P > 0.05$ ) in the CS of HF1, HF2 and HF4 was observed at 95% confidence intervals at 1 month

**Table 2: GPC results of the powder polymer used to prepare cement**

Sample	Run number	$M_w$	$M_n$	$M_w/M_n$	Peak area
40% PAA (PA)	1	52,100	11,000	4.7	39,000
	2	52,300	10,700	4.9	39,400
PAA powder	3	56,500	10,100	5.6	4020
	4	55,100	9480	5.8	4020

PA: Polyacrylic, PAA: Poly (acrylic acid), GPC: Gel permeation chromatography, Mw: Molecular weight, Mn: Number-average

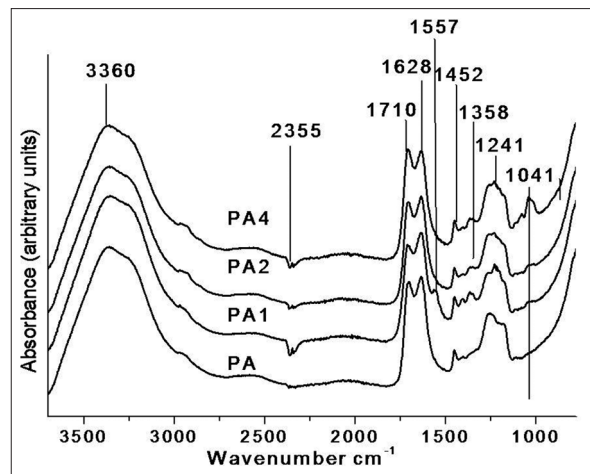


Figure 2: Fourier-transform infrared spectra of the control group (PA) and polymer solutions (PA1, PA2 and PA4) prepared after dispersion of different weight percentages of polymer-grade montmorillonite nanoclay

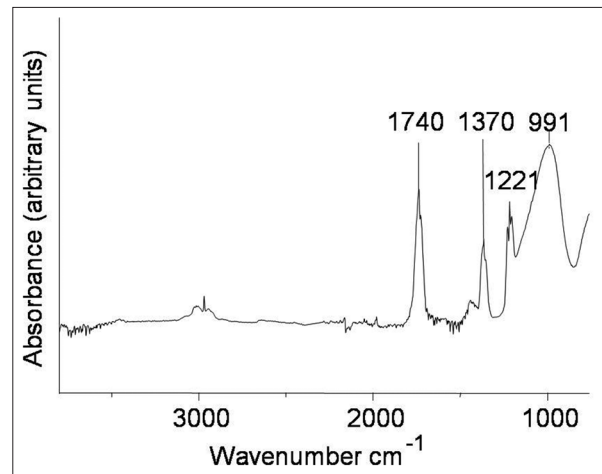


Figure 3: Fourier-transform infrared spectra of HiFi glass powder

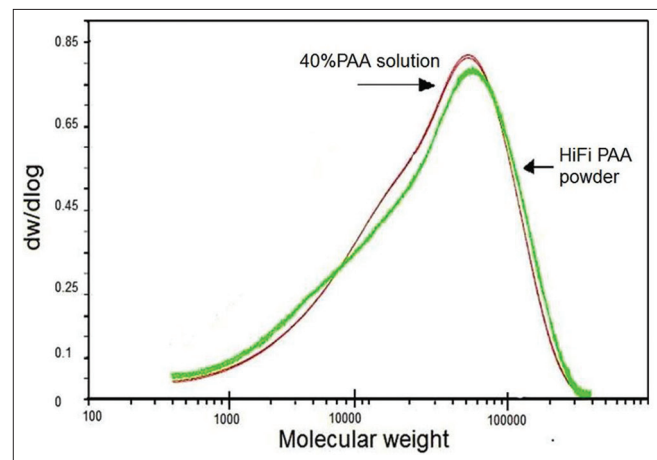


Figure 4: Gel permeation chromatography graph shows an overlay of the computed molecular weight distribution for duplicate run of poly(acrylic acid) (PAA) powder and 40% PAA aqueous solution (HiFi)

storage compared to the control groups. Within each storage time, the mean results of DTS of the cements formed after the dispersion of nanoclays identified no significant difference ( $P > 0.05$ ) in the mean DTS. The average FS values of cements after dispersion of 2.0 wt% PGN nanoclay (HF2) resulted in the highest ( $P < 0.001$ ) FS values at 1 day ( $43 \pm 10$  MPa) and at 1 month ( $43 \pm 9$  MPa) storage time. There was no difference ( $P > 0.01$ ) in FS values of HF, HF1 and HF4 cements at 1 month storage time. The  $E_f$  of cements formed after the dispersion of 1.0 wt% nanoclays (HF1) was significantly higher ( $P < 0.01$ ) and significantly lower ( $P > 0.05$ )  $E_f$  values for HF2 and HF4 when data were analyzed with one-way ANOVA and Tukey's  $t$ -test.

**Working time and setting time**

The result of WT and ST of all cements is presented in Table 3 shows that the cements (HF2 and HF4) formed with HiFi glass powder and polymer liquids after the dispersion of PGN (PA2 and PA4) exhibit lower WT ( $3.05 \pm 0.10, 3.0 \pm 0.15$ ) min and lower STs ( $5.60 \pm 0.10, 5.5 \pm 0.20$ ) min than the control group ( $P < 0.05$ ). The cement with 1.0 wt% nanoclay (HF1) showed similar WT and ST when compared to the control group and was not statistically different ( $P > 0.05$ ).

**Scanning electron microscopy analysis**

Figure 5 show the SEM micrographs of the representative regions of the fractured surface for cements (HF and HF1) after three-point bending at lower magnification as well and higher magnifications. In general, the artifactual cracks were ubiquitously observed when within the GIC matrix when GIC's specimens were examined by conventional SEM due to the dehydration of cement. The presence of some pores and air voids on the surface of GICs can also be observed. The fracture surface contained many small glass particles dispersed in the matrix phase of GIC. The SEM observation of GICs revealed that the fractured surface of cement specimens consists of both large and small glass particles which can readily be distinguished from the polymer matrix. The average size of glass particles was measured under 10-15  $\mu\text{m}$  in the micrograph of the cement, there is a possibility that much smaller glass particles were also be present. However, due to the small weight percentage of nanoclay used, it was difficult to study the dispersion of nanoclays in GICs by SEM and transmission electron microscopy may be useful for this purpose.

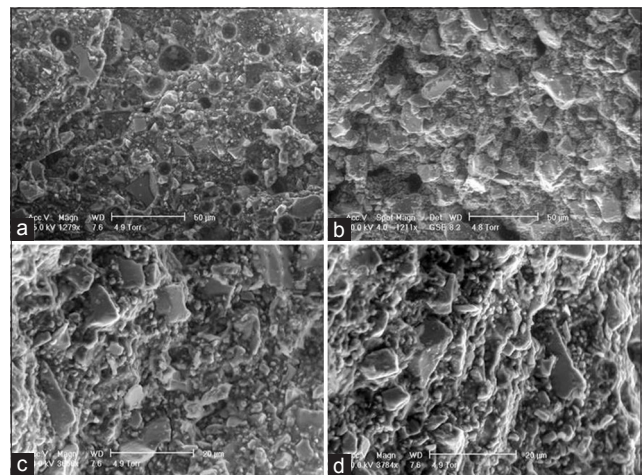
**DISCUSSION**

The FTIR spectra of the PAA-nanoclay suspensions (PA1 PA2 and PA4) were not much dissimilar from the spectrum of PA and small differences were observed in the peak intensities. The presence of a new peak at  $1041\text{ cm}^{-1}$  attributed to the Si-O stretching mode in PGN nanoclays after the addition of nanoclays [Figure 1] suggested the increase

**Table 3: Mean (SD) of the physical properties of GICs with nanoclay incorporation and Tukey's analysis**

Storage	HF	HF1	HF2	HF4
CS (MPa)				
1 day	99 (11) <sup>a</sup>	94 (8) <sup>a</sup>	94 (7) <sup>a</sup>	101 (14) <sup>a</sup>
1 week	120 (19) <sup>b</sup>	137 (16) <sup>c</sup>	127 (14) <sup>b</sup>	107 (15) <sup>d</sup>
1 month	124 (19) <sup>e</sup>	132 (19) <sup>e</sup>	134 (24) <sup>e</sup>	131 (26) <sup>e</sup>
DTS (MPa)				
1 day	20 (3) <sup>f</sup>	19 (4) <sup>f</sup>	20 (4) <sup>f</sup>	17 (4) <sup>f</sup>
1 week	17 (4) <sup>g</sup>	18 (3) <sup>g</sup>	19 (3) <sup>g</sup>	16 (4) <sup>g</sup>
1 month	18 (5) <sup>h</sup>	19 (5) <sup>h</sup>	20 (6) <sup>h</sup>	17 (3) <sup>h</sup>
FS (MPa)				
1 day	27 (4) <sup>j</sup>	33 (4) <sup>j</sup>	43 (10) <sup>k</sup>	35 (4) <sup>j</sup>
1 week	31 (3) <sup>j</sup>	33 (4) <sup>j</sup>	37 (5) <sup>m</sup>	36 (6) <sup>lm</sup>
1 month	36 (6) <sup>n</sup>	39 (5) <sup>no</sup>	43 (9) <sup>o</sup>	38 (10) <sup>no</sup>
$E_f$ (GPa)				
1 month	14 (3) <sup>p</sup>	15 (3) <sup>p</sup>	11 (4) <sup>q</sup>	11 (3) <sup>q</sup>
Working time (min)	3.28 (0.10) <sup>r</sup>	3.35 (0.25) <sup>r</sup>	3.05 (0.10) <sup>s</sup>	3.00 (0.15) <sup>s</sup>
Setting time (min)	6.30 (0.10) <sup>t</sup>	6.50 (0.15) <sup>t</sup>	5.60 (0.10) <sup>u</sup>	5.50 (0.20) <sup>u</sup>

Mean values of each property with the same superscript (row) are not significantly different ( $P > 0.05$ ) and the mean values with different superscript are significantly different ( $P < 0.05$ ). GIC: Glass ionomer cement, SD: Standard deviation, CS: Compressive strength, DTS: Diametral-tensile strength, FS: Flexural strength,  $E_f$ : Flexural modulus, HF: Hydrofluoric



**Figure 5:** Scanning electron microscopy micrographs of the fractured surface of cement at different magnification indicating the presence glass particles and the matrix phase of glass ionomer cement (a and c) HF, (b and d) HF1

in interlayer spacing in nanoclays. Apparently, the Si-O stretching peak which was present at  $973\text{ cm}^{-1}$  in PGN nanoclays moved toward higher intensity at  $1041\text{ cm}^{-1}$  and the absorbance intensity of this peak also increased with increasing the nanoclay content from 1 to 4.0 wt% of PGN nanoclay indicating the strong interaction of nanoclays with the polymer chains.<sup>[20]</sup> The peak at  $1358\text{ cm}^{-1}$  associated with Si-OH became prominent in PA1, PA2 and PA4 with an increase in the nanoclay content. The increase in the nanoclays contents from 1 to 4.0 wt% resulted in the increase in the viscosity and flow resistance of the GICs liquid components due to the adsorption of more random binding of the carboxyl groups to the surface of the nanoclays. The GPC analysis showed that the  $M_w$  of PAA used in the HiFi system was in the range of 52,000-56,000 g/mol. Although the effect of PAA  $M_w$  on the dispersion of nanoclays was not investigated, but Kirwan *et al.* reported that at low pH the attachment of poly-carboxylate molecules on hematite surface was not dependent on the chain length.<sup>[25]</sup> It is expected, however, that the  $M_w$  of PAA would have an effect on the nanoclays exfoliation and specifically on the interlayer spacing as the number of polymer entanglements would have had an effect on the mobility of the chains within the interlayer spacing. The dispersion of different amount of nanoclays in PAA may lead to variations of the flow properties when the weight percentage nanoclay was increased over 2.0 wt%, it resulted in an increase in viscosity and HiFi PAA liquids. At 4 wt% of nanoclays content, the glass powder did not hand-mix easily with the liquid portion due to high viscosity. Therefore, the potential reinforcement of conventional GIC systems with nanoclays at contents more than 2 wt% should be carefully designed. It may become necessary to add certain additives such as surfactants to stabilize the nanoclay particles in the PAA solution or using more dilute PAA solutions. The rheological properties of the Na montmorillonite suspension in an aqueous solution of polyelectrolytes (PAA) were reported by Ramos-Tejada *et al.*<sup>[28]</sup> in order to analyze the changes in the interfacial electric potential of the surface after the dispersion in PAA. Ramos-Tejada *et al.* concluded that the addition of nanoclay can provoke the dramatic changes in the viscoelastic properties of PAA-nanoclay suspensions depending on the pH, polymer charge and concentration.

The mechanical properties (CS, DTS, FS and  $E_f$ ) of GICs with nanoclays reinforcement showed that all the cements became stronger as they matured at 1 month of storage in distilled water. GICs that

contained <2.0 wt% nanoclays, exhibited generally slightly higher CS, similar DTS and FS compared to the control cement groups. An increase in the viscosity of the PAA liquid after the dispersion of nanoclays was not desirable for the successful preparation of cements. The higher nanoclay content in the polymer liquid (4.0 wt% or more) influenced the manipulation and mixing of cements resulted in difficulties in specimen preparation and, therefore, inferior mechanical properties.  $E_f$  results of GICs suggested that the dispersion of 1.0 wt% of nanoclays may be appropriate to achieve better mechanical properties. This suggested that nanoclay addition in the liquid portion of GIC has an effect on polysalt-matrix formation of GIC. Dowling *et al.* reported the addition of nanoclays (Ca-MMT and ADA-MMT) to conventional GIC restoratives and found no significant reinforcement effect or increased performance in the case of Ca-MMT whereas, the addition of organoclays (ADA-MMT) to the powder and liquid elements of the GICs up to 1.0 2.0 wt% had a positive reinforcing effect on the GIC system.<sup>[15]</sup> However, the possibility to achieve the optimum nanoclay dispersion in the polymer liquid established the dispersion of nanoclays in PAA by selecting the most appropriate commercially available clays. Although, the dispersion of nanoclays was successfully achieved, but a small improvement in the mechanical properties of the GIC systems was observed. There are several factors which can affect the improvement of the mechanical properties in cements, for example, the adjustment in the P:L ratio of the GIC systems, the processing technique of nanoclays dispersion in PAA suspensions, the  $M_w$  of PAA and the polymer concentration of the aqueous PAA solutions. The nature of the nanoclay interaction, in particular the bond between the nanoclay and the polymer matrix was an important factor to overall mechanical properties. Thus, it is suggested that the dispersion of nanoclays in lower than 2.0 wt% in GICs may potentially produce cements with better physical properties, however, an understanding of the fundamental aspects of nanoclay dispersion and interactions with the polymer, the choice of suitable handling parameters and the employment of appropriate polymers and glass components is mandatory. The WT and ST of GICs determined by the Wilson's rheometer are presented in Table 3 showed that 1.0 wt% PGN nanoclay dispersion (HF1) is more suitable as it has minimal effect on the WT and ST of cements. Moreover, a significant decrease in the WT and ST of cement after 2 wt% and 4 wt% nanoclay indicates a significant interaction of nanoclay with

the GIC matrix during the initial divalent-mediated gelation stage. An accelerated ST may adversely affect the properties of the cement, therefore, the appropriate rheological characteristics (WT and ST) are one of the prerequisites of dental restorative materials such as GICs.

This study has highlighted the possible potential for improving the performance of GIC when using nanoclay as reinforcement in low concentration. The result of this study reject the null hypothesis since the addition of increasing concentration of nanoclay in experimental GIC affected the test physical properties compared to unmodified GIC. An uniform dispersion and controlled association of nano-particles with the polymer matrix significantly improve the properties. The exfoliation of montmorillonite nanoclays in a polymer matrix provides at least 10 Å thick silicate layers with the high in-plan bond strength and aspect ratios. The reinforcing capability of nanoclays was due to its high modulus, high strength and high-aspect ratio.<sup>[29]</sup> The better the exfoliation of nanoclays in the polymer matrix, the greater is the reinforcing effect resulting in superior polymer nanocomposites. To achieve the maximum reinforcement effects of nanoclays, direct intercalation may be employed. Direct intercalation involves the mixing of the host nanoclay with PAA powder and then pressing the mixture into a pellet and heating at an appropriate temperature. However, the heating temperature will need to be optimized, and it should be above the bulk glass transition temperature of PAA to ensure the presence of polymer melt.<sup>[30]</sup> The resulting product could be used to prepare a PAA solution (35-40% PAA) to make the GIC. Moreover, a comparative study of PAA-nanoclay prepared by solution-blending and melt-intercalation would be very interesting to optimize the most appropriate model for the exfoliation of nanoclays in PAA.<sup>[31]</sup>

## CONCLUSIONS

The dispersion of nanoclays in the liquid portion of GIC was achieved, and the  $M_w$  of PAA used in the HiFi system was suitable for glass ionomer dental restoratives. The reinforcement of 1-2 wt% nanoclay generally resulted in the improved mechanical behavior but statistically it was insignificant for DTS. Working and setting characteristics were not impeded and meet the standard of water-based cements. The nanoclay may be considered as additive for glass ionomer dental restorative however mode of dispersion of nanoclay is a critical measure.

## REFERENCES

- Hickel R. Trends in materials science from the point of view of a practicing dentist. *J Eur Ceram Soc* 2009;29:1283-9.
- Roulet JF. Benefits and disadvantages of tooth-coloured alternatives to amalgam. *J Dent* 1997;25:459-73.
- Sasanaluckit P, Albustany KR, Doherty PJ, Williams DF. Biocompatibility of glass ionomer cements. *Biomaterials* 1993;14:906-16.
- Tyas MJ. Milestones in adhesion: Glass-ionomer cements. *J Adhes Dent* 2003;5:259-66.
- Nicholson JW, Croll TP. Glass-ionomer cements in restorative dentistry. *Quintessence Int* 1997;28:705-14.
- Wiegand A, Buchalla W, Attin T. Review on fluoride-releasing restorative materials-fluoride release and uptake characteristics, antibacterial activity and influence on caries formation. *Dent Mater* 2007;23:343-62.
- Wilson AD, Kent BE. The glass-ionomer cement: A new translucent dental filling material. *J Appl Chem Biotechnol* 1971;21:313-8.
- Williams JA, Billington RW, Pearson G. Silver and fluoride ion release from metal-reinforced glass-ionomer filling materials. *J Oral Rehabil* 1997;24:369-75.
- Mitra SB. Adhesion to dentin and physical properties of a light-cured glass-ionomer liner/base. *J Dent Res* 1991;70:72-4.
- Zhao J, Xie D. A novel hyperbranched poly (acrylic acid) for improved resin-modified glass-ionomer restoratives. *Dent Mater* 2011;27:478-86.
- Bertolini MJ, Zaghete MA, Gimenes R, de Souza RF, Vaz LG. Preparation of new glass systems by the polymeric precursor method for dental applications. *J Non Cryst Solids* 2004;344:170-5.
- Culbertson BM. New polymeric materials for use in glass-ionomer cements. *J Dent* 2006;34:556-65.
- Iz SG, Ertugrul F, Eden E, Gurhan SI. Biocompatibility of glass ionomer cements with and without chlorhexidine. *Eur J Dent* 2013;7:589-93.
- Moshaverinia A, Ansari S, Movasaghi Z, Billington RW, Darr JA, Rehman IU. Modification of conventional glass-ionomer cements with N-vinylpyrrolidone containing polyacids, nano-hydroxy and fluoroapatite to improve mechanical properties. *Dent Mater* 2008;24:1381-90.
- Dowling AH, Stamboulis A, Fleming GJ. The influence of montmorillonite clay reinforcement on the performance of a glass ionomer restorative. *J Dent* 2006;34:802-10.
- Xie D, Chung ID, Wu W, Lemons J, Puckett A, Mays J. An amino acid-modified and non-HEMA containing glass-ionomer cement. *Biomaterials* 2004;25:1825-30.
- Kawano F, Kon M, Kobayashi M, Miyai K. Reinforcement effect of short glass fibers with CaO - P (2) O (5) - SiO (2) - Al (2) O (3) glass on strength of glass-ionomer cement. *J Dent* 2001;29:377-80.
- Alexandre M, Dubois P. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mater Sci Eng R Rep* 2000;28:1-63.
- Ray SS, Okamoto M. Polymer/layered silicate nanocomposites: A review from preparation to processing. *Prog Polym Sci* 2003;28:1539-641.
- Fareed MA, Stamboulis A. Nanoclays reinforced glass ionomer cements: Dispersion and interaction of polymer grade (PG) montmorillonite with poly (acrylic acid). *J Mater Sci Mater Med* 2014;25:91-9.
- Pearson GJ, Atkinson AS. Effects of temperature change on the working and setting characteristics of water-based dental cements. *Dent Mater* 1987;3:275-9.
- ISO 9917-1:2007 Dentistry-Water-Based Cements-Part 1: Powder/liquid Acid-Base Cements. International Organization for Standardisation; 2009.
- ISO 4049:2000 Dentistry, Dentistry-Polymer-Based Filling, Restorative and Luting Materials. International Organization for Standardisation; 2000.
- ASTM D790-07 Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. ASTM; 2007.
- Kirwan LJ, Fawell PD, van Bronswijk W. *In situ* FTIR-ATR Examination of Poly (acrylic acid) Adsorbed onto Hematite at Low pH. *Langmuir* 2003;19:5802-7.



26. MacDonald SA, Schardt CR, Masiello DJ, Simmons JH. Dispersion analysis of FTIR reflection measurements in silicate glasses. *J Non Cryst Solids* 2000;275:72-82.
27. Hwa LG, Hwang SL, Liu LC. Infrared and Raman spectra of calcium alumino-silicate glasses. *J Non Cryst Solids* 1998;238:193-7.
28. Ramos-Tejada MM, Galindo-Gonzalez C, Perea R, Durain JD. Effect of charged polyelectrolytes on the electrophoretic behavior, stability, and viscoelastic properties of montmorillonite suspensions. *J Rheol* 2006;50:995-1007.
29. Kornmann X, Lindberg H, Berglund LA. Synthesis of epoxy-clay nanocomposites. Influence of the nature of the curing agent on structure. *Polymer* 2001;42:4493-9.
30. Vaia RA, Ishii H, Giannelis EP. Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates. *Chem Mater* 1993;5:1694-6.
31. Filippi S, Mameli E, Marazzato C, Magagnini P. Comparison of solution-blending and melt-intercalation for the preparation of

poly (ethylene-co-acrylic acid)/organoclay nanocomposites. *Eur Polym J* 2007;43:1645-59.

Access this article online	
<p><b>Quick Response Code:</b></p> 	<p><b>Website:</b> www.eurjdent.com</p>
<p><b>Source of Support:</b> The authors would like to thank Dr. Neigel Bubb at Leeds Dental Institute for helping with rheological equipment. Financial support from University of Birmingham UK and Higher Education Commission Pakistan is also acknowledged.</p>	
<p><b>Conflict of Interest:</b> None declared</p>	