

Original Article

Effects of incorporating wollastonite and mine-silica by-product to the hardness of glass ionomer cement (GIC)

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Abstract Glass ionomer cement (GIC) has the unique fluoride release property and able to form ionic bond with tooth structure. However, the brittleness of the material results in low hardness. In the present study, a new approach in utilization of local waste materials as fillers for improvement of hardness of GIC is reported. The synthesized wollastonite and mine-silica by-product were individually incorporated into commercial GIC and the Vickers hardness were evaluated. The results shown that the incorporation of 1 % wollastonite into GIC gave ~ 6 % increment in hardness compared to the control GIC (66.53HV \pm 7.37 versus 62.66HV \pm 2.98) but not for the mine-silica. Thus, wollastonite could be a potential material to be utilized as fillers in dental restorative composite.

Keywords: Glass ionomer cement, hardness, mine-silica, wollastonite.

Introduction

Glass ionomer cement (GIC) is basically formulated into powder and liquid, in which the powder is composed of calcium aluminium fluorosilicate glass and the liquid is either a polyacrylic acid or its copolymer (Al-Badry *et al.*, 1994). GIC is commonly used as a restorative material due to its outstanding properties in releasing fluoride, able to form ionic bond with enamel and dentin, and low toxicity (Mousavinasab and Meyers, 2009). However, poor mechanical properties in GIC, which include low fracture strength, low toughness and high wear, remains the major drawbacks that limit its extensive use in dentistry as filling materials in stress-bearing applications (Lohbauer, 2010). As a result, GIC is mostly used in Class III and Class V cavity restorations as it is aesthetically more attractive than metallic restoration and is less technique-sensitive compared to resin composites. In the posterior region as in Class I or Class II cavity restorations, GIC is mainly

used as temporary filling materials. Efforts to improve GIC mechanical properties have been made in several aspects. These include the incorporation of a reinforcing phase such as metal particles, or alumina, zirconia, or glass fibres (Lohbauer *et al.*, 2004; Gu *et al.*, 2005; Yli-Urpo *et al.*, 2005). A reinforcing effect was also observed by compounding hydroxyapatite granules or whiskers into GIC (Lohbauer *et al.*, 2003). However, as far as we are aware, there is no study on incorporation of locally available waste materials as potential fillers in dental restorative composites resin.

Wollastonite (calcium silicate) is naturally available or can be synthesized from mine-silica and lime stone which are largely abundant in Malaysia. Due to its acicular shape, wollastonite is normally used to increase strength, decrease shrinkage and reduce cracks in ceramics processing (Greish and Brown, 2001). Additionally, tensile strength of hydroxyapatite-Ca-polyacrylate composites can also be improved by the addition of

wollastonite fibres (Greish and Brown, 2001). The apatite/wollastonite glass-ceramics has high bioactivity and high mechanical strength compared to other pure glasses and glass-ceramics (Kokubo *et al.*, 1990). Composites of poly(butylene terephthalate)/wollastonite composites were shown as having the physical properties and biocompatibility which deemed it suitable as potential biomaterials (Risbud *et al.*, 2001).

Mine-silica is available as by-product from local mining activities. It is still a question whether the addition of mine-silica would likely to increase the particle-particle interaction with GIC. In the present study, it is envisaged that the wollastonite and mine-silica particles would enhance interaction and packing density of the composites and further improve the hardness of the GIC.

Materials and methods

Materials

The wollastonite and mine-silica was obtained from the Department of Mineral Research and Geoscience Malaysia, Ipoh, Perak. The GIC used in the present study was a commercial product (GC Fuji IX, Japan).

Preparation of wollastonite-GIC and mine-silica-GIC composites

Commercially available GIC was set as the control. The percentage of additives added was according to the weight of GIC. Wollastonite was mixed into the GIC at various percentages (by weight) from 1 to 20 %. Each powder mixture was gently mixed manually with powder/liquid ratio of 1:1 and inserted into a glass plate mould with internal perforation dimension of 5 x 2 mm. Then, the mixture was left to set for 24 hours to complete the setting reaction. Three specimens or three plate moulds were made for each percentage of additives-GIC and control GIC. Surfaces of all the experimented GICs and control GICs were polished with the same amount of strokes which is 50 strokes of 1000 grit silicon carbide paper. The procedure was repeated for mine-silica.

Characterization

Morphology of the samples were examined by using a scanning electron microscope (SEM) (Quanta FEG450, USA), that is equipped with an energy dispersive X-ray (EDX) at 10.00 kV. Fourier transform infrared (FTIR) spectra of wollastonite and mine-silica were obtained by using a FTIR spectrometer (Perkin-Elmer 2000, USA) in the frequency range of 400-4000 cm^{-1} .

Hardness measurement

Vickers hardness (Fuel Inst. Eng. Ltd., India) measurements were taken at 24 hours after the initial setting reaction. The load applied on the sample was 5 kg and the indentation was applied for 15 s. Three indentations were made on the top and the bottom of each specimen's surface. The measurements were made as triplicates for each percentage of materials. The mean of these measurements were then converted into Vickers hardness values.

Results

Characterization by scanning electron microscope (SEM)

SEM of mine-silica (Fig. 1) revealed the particles as having relatively smoothed surface, spherical-like and agglomerated. The particles size varies from ~ 950 to ~ 380 nm. On the other hand, SEM of wollastonite (Fig. 2) revealed its particles as having irregular surface and flake-like shape. The diameter of particles is ~1.18 μm .

FTIR Analysis

FTIR of mine-silica and wollastonite were also analysed (Fig. 3). In mine-silica, the broad absorbance peaks at 3421 cm^{-1} which is due to the Si-OH asymmetry stretching vibration and bending vibration. The peak as observed at 1617 cm^{-1} was attributed to the stretching vibration of -OH group of water molecule on the silica surface. The band located at 1095 cm^{-1} belongs to the asymmetric vibration of Si-O-Si bond. Finally, the band at 800 cm^{-1} and 473 cm^{-1} was ascribed to the Si-O symmetry stretching vibration and bending vibration (Rahman *et al.*, 2007).

In wollastonite, a broad band at 3419 cm^{-1} corresponded to the stretching vibration of $-\text{OH}$ functional group. The band at 1633 cm^{-1} was presented by $-\text{OH}$ bending vibration while the band located at 964 cm^{-1} belonged to the stretching modes of O-Si-O and Si-O-Ca containing non-bridging oxygen. The peak of 1418 cm^{-1} , was ascribed to the symmetric stretching vibration of Si-O-Si bonds. Meanwhile, the band at 470 cm^{-1} was attributed to the bending modes of siloxane bond, Si-O-Si and O-Si-O (Wang *et al.*, 2010).

Vickers hardness of mine-silica-GIC and wollastonite-GIC

The mean Vickers hardness for conventional GIC under the load of 5 kg for 15 s is $62.66\text{HV} (\pm 2.98)$. Table 1 summarized the Vickers hardness mean values and standard deviations (SD) for each group of mine-silica-GIC and wollastonite-GIC at different percentages. The mean values are also represented graphically in Fig. 4 in order to compare the Vickers hardness of different groups of mine-silica-GIC and wollastonite-GIC with control GIC.

In Fig. 4, it is shown that the optimum result is at 1% wollastonite-GIC ($66.53\text{HV} \pm 7.37$) with $\sim 6\%$ increment compared to the control GIC ($62.66\text{HV} \pm 2.98$). At 3% wollastonite-GIC, the hardness decreased to ($64.92\text{HV} \pm 4.86$). Further adding up of wollastonite ($> 5\%$) resulted in the decrease of hardness to the values lower than the control GIC. On the other hand, the mine-silica-GIC did not show any considerable increment in hardness value compared to the control GIC.

Discussion

Hardness provides an indication of the resistance of the material to scratching or abrasion (van Noort, 2007). Surface hardness tests appear to be appropriate for evaluating the degradation and durability of dental materials; to observe the effect of storage mediums on the surface; as indicative of resistance to wear and durability; and also to monitor the hardening process of cements (Shintome *et al.*, 2009). Large hardness means greater resistance to plastic deformation or cracking in compression and contributes to better wear properties.

Table 1 The mean and standard deviation (SD) of Vickers hardness values for each group of mine-silica-GIC and wollastonite-GIC composites.

| % added | Mine-silica | | Wollastonite | |
|---------|-------------|------|--------------|------|
| | Mean | SD | Mean | SD |
| 0 | 62.66 | 2.98 | 62.66 | 2.98 |
| 1 | 60.68 | 6.27 | 66.53 | 7.37 |
| 3 | 57.87 | 4.50 | 64.92 | 4.86 |
| 5 | 62.62 | 5.80 | 48.40 | 7.25 |
| 7 | 57.94 | 7.42 | 42.49 | 5.79 |
| 9 | 57.54 | 6.13 | 44.63 | 5.28 |

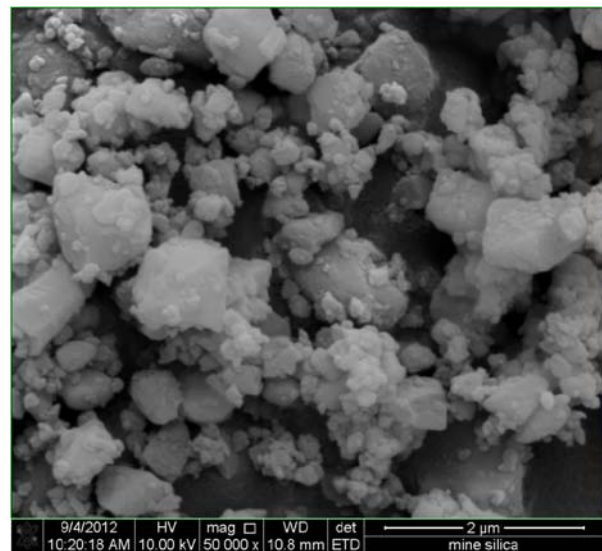


Fig. 1 SEM of mine-silica powder.

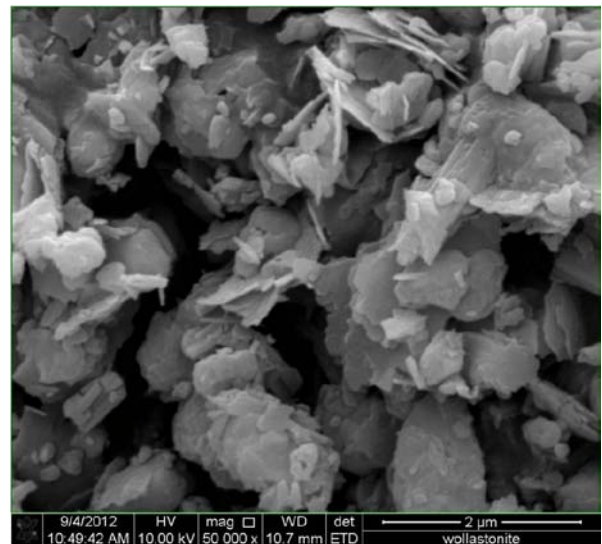


Fig. 2 SEM of wollastonite powder.

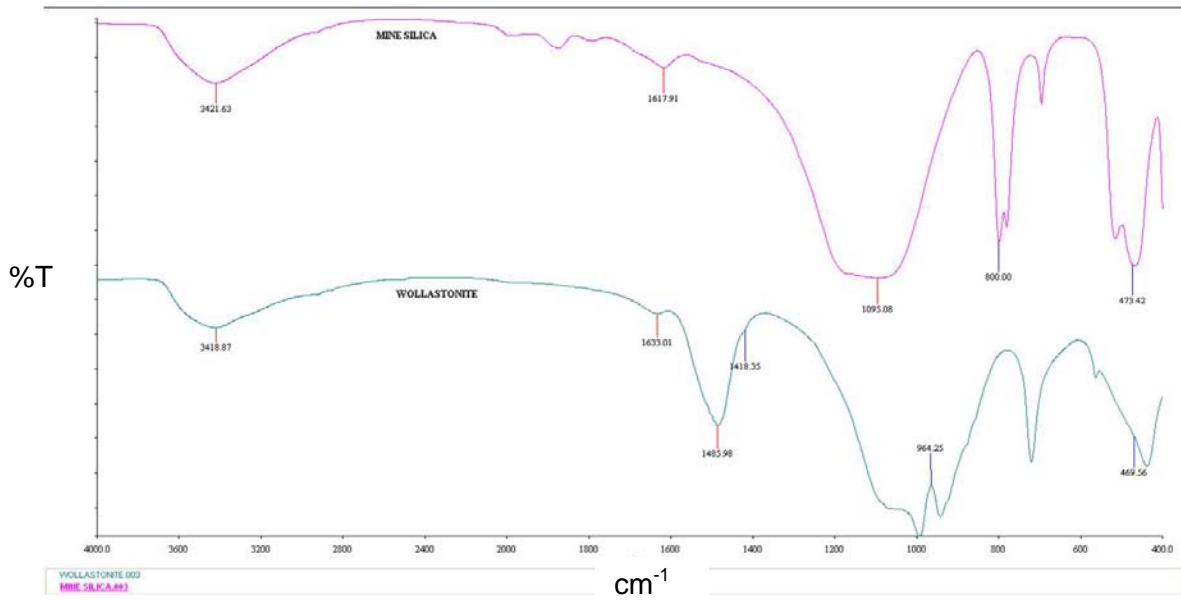


Fig. 3 FTIR spectra of mine-silica and wollastonite.

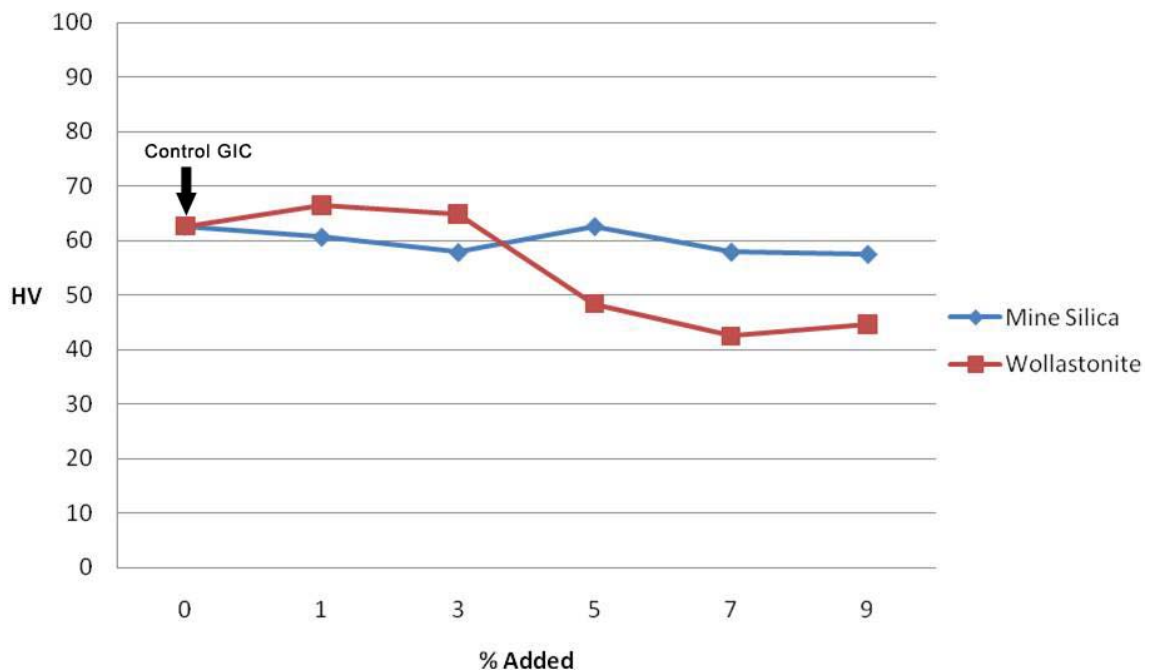


Fig. 4 Comparison of Vickers hardness between mine-silica-GIC, wollastonite-GIC and control GIC (62.66HV).

In the present study, Vickers hardness of the different groups of mine-silica-GIC and wollastonite-GIC composites were evaluated and compared with control GIC, acting as a control. Silva *et al.* (2007) reported that the mean Vickers hardness of Fuji IX as 41.0HV (± 4.03) with the loading force of 100 g for 30 s. Yap *et al.* (2002) who used 5 g load with a dwell time of 15 s, had demonstrated a Vickers hardness of GIC as 54.4HV (± 7.88). The present study, applied a load of 5 kg and a dwell time of 15 s which resulted with a mean Vickers hardness of control GIC (Fuji IX) as 62.66HV (± 2.98).

In the present study, the optimal value of Vickers hardness was at 1 % wollastonite-GIC (66.53HV ± 7.37) with ~ 6 % increment compared to control GIC (62.66HV ± 2.98). SEM of the wollastonite shows that it has irregular surface and flake-like shape. This morphology may provides a better physical bonding with the GIC, thus improves the hardness. However, the Vickers hardness value was only optimum at 1% addition of wollastonite and then decrease with further increase of wollastonite. This is maybe due to uneven phase distribution of wollastonite.

Mine-silica-GIC showed no improvement of hardness compared to the control GIC. Through SEM, mine-silica has smooth surface, spherical like and agglomerate. This feature is very different, compare to the wollastonite. Thus, lack of physical bonding with the GIC. In addition, the aggregation of particles might depress performances of nanomaterials (Fu *et al.*, 2009).

Conclusion

In the present study, the SEM revealed that the morphology of the fillers affect the hardness of commercially available GIC acted as a control. Incorporation of wollastonite with flake-like structure into control GIC do enhance the hardness but were only optimum at the Vickers hardness values of 1 % wollastonite-GIC (66.53HV ± 7.37), and 3 % (64.92HV ± 4.86) compared to the value of control GIC (62.66HV ± 2.98). No considerable improvement was

observed for mine-silica incorporation. Thus, wollastonite could be a potential material to be utilized as filler in dental restorative composite.

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