# Adhesion of glass to steel using a geopolymer

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Many potential and actual uses for geopolymers (GPs) have been listed, such as waste encapsulation, refractories, fire resistant paneling, sewer pipes, building products, and acid-resistant coatings [1]. Other proposed technical uses include fire protection coatings as applied to concrete [2]. Understanding the nature of bonding of GPs to other materials is desirable if GPs are to be applied as protective coatings or adhesives.

Two common methods of making GPs are to add fly ash or metakaolinite (MK: kaolinite heated to ∼750 °C to render it amorphous) to concentrated alkali solutions for reaction and subsequent polymerization to take place. The GPs produced consist of amorphous to semi-crystalline three-dimensional aluminosilicate networks [3]. For industrial applications, the use of fly ash as a precursor gives a cost advantage over MK. However to understand the science of the polymerization process, the use of the latter is preferred.

It has been reported that ball milling the aluminosilicate precursors up to 4 hr improves the compressive strength of GPs [4]. In the present work, we attrition-milled the MK, which is a more effective method of milling than ball milling, to determine the effect on the compressive strength. Furthermore, we examined the adhesion of stainless steel to glass using GPs derived from the milled MK and determined the interfacial fracture energy by a fracture mechanics approach.

The MK was produced by heating kaolinite (Kingwhite 80, Unimin, Australia) at 750 °C for 15 hr in air. An MK-water slurry was attrition-milled at 300 rpm with 5 mm zirconia balls for 30, 60 and 120 min. The milled slurry was dried in a stainless steel pan at 40 °C for 5 days. The particle size distributions of each batch, including the unmilled sample were determined using laser diffraction techniques (Mastersizer 2000, Malvern Instruments Ltd., UK) and are shown in Fig. 1. The MK exhibits a bimodal distribution and the amount of fines (∼0.18 $\mu$m) increased with milling time. The 30 min milling time reduced the coarse particle size from 8.7 to 4.4 $\mu$m and doubled the volumes of fines. A further 30 min again reduced the coarse particles to 2.9 $\mu$m and increased the fines. Additional milling for 60 min did not have the same effects as the previous milling cycles, although it increased the fines and reduced volume of coarse particles with minimal effect on their size. The resulting powder, following the milling, contained a fine fraction with particle size ∼0.18 and ∼2.2 $\mu$m hard agglomerate.

An MK GP of Si/Al molar ratio of 2.0 and Na/Al ratio of 1.0 was prepared. This composition was chosen because other studies showed it gave higher compressive strength and the absence of zeolite formation [1, 5]. The batch composition consisted of (wt%) MK: 33.7; sodium silicate D (PQ Corporation, Australia): 63.0, and demineralized water: 3.3. Each batch consisted of 20–40 g of material. Four different batches were made, using the unmilled MK and the three milled MK powders. The MK was added to the silicate solution, mixed for 5 min and poured into a polycarbonate jar and sealed with a screw cap. For compression testing, solid cylindrical specimens of 25 mm diameter × 30 mm length were cast. Minimum of four specimens were used for each test. All the samples were cured for 24 hr at 22 °C and 24 hr at 40 °C, then for a further 5 days at 22 °C before removing from the container. Samples were then machined flat and parallel.

For interfacial toughness measurements, samples of stainless steel 316 and glass (Corning Glass, no. 2947) were bonded together using the GPs. The glass specimens were cut from soda lime glass microscope slides (thickness = 0.9 mm) and the steel specimens from rolled sheet (thickness = 1 mm) into bars of width 2.5 mm and length 25 mm. The steel specimens were then lapped and polished to a 1 $\mu$m diamond finish on the prospective bonding face. Just prior to bonding, the steel and glass surfaces were cleaned using acetone and then rinsed with ethanol.

GP slurry was then spread evenly and generously over the metal piece, and the glass piece was placed on top in alignment with the metal and pressed down firmly with a 90 g weight. These specimens were cured as before and then polished on either side with a 1200 grit silicon carbide paper to allow the observation of crack propagation. The thickness of the GP interlayer ranged from 50 to 200 $\mu$m.

Compression tests were carried out using a servo-electric universal testing machine (Instron 8562, Instron, UK). A crosshead speed of 0.005 mm/s was used, with a

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preload of ~0.5 kN. Maximum load after destructive failure was measured and used to calculate the compressive strength.

The bond toughness was measured by utilizing a fully-articulated 4-point bending test jig mounted on a small scale tester [6] placed under an optical microscope (Zeiss AxioTech vario 100, Germany). For these tests, a 0.003 mm/s crosshead speed was used, with a 200 N load cell. The load, $P$, and displacement, $\delta$, were continuously monitored. The outer rollers were spaced 20 mm apart and the inner 10 mm apart. The surface of the glass was notched in the centre using a diamond glass-cutter to a depth close to the GP interlayer. The specimen was then loaded, with the glass surface in tension and the metal surface in compression, until the glass cracked. The crack would then propagate from the base of the notch toward the bonded surfaces and extend on both sides along the interface. Load as a function of displacement was measured, and the plateau for stable crack propagation was used to calculate the interfacial fracture energy.

The compression test results are listed in Table I. There is no statistical significance between the values for different milling times. The mean value for all the specimens is 85 ± 11 MPa, which is slightly better than the highest strength (74 MPa) obtained previously [4] for an MK GP.

The strain energy release rate, $G$, or interfacial fracture energy from the bend tests was calculated using the following formula [7]:

$$G = \frac{21P_c^2 l^2\left(1-\nu_{ss}^2\right)}{16E_{ss}b^2h^3} \quad (1)$$

where $b$ is the specimen width, $h$ is the total thickness, $l$ is the moment arm ($l = 5$ mm), $P_c$ is the critical load for stable crack propagation, as deduced from the load-displacement curve for each specimen. $\nu_{\sigma\sigma}$ and $E_{ss}$ are Poisson's ratio and the elastic modulus of the stainless steel substrate, respectively. The elastic properties of the stainless steel were determined by the impulse-excitation method [8] yielding $E_{ss} = 210$ GPa and $\nu_{\sigma\sigma} = 0.29$. The assumption made here is that the crack propagates near equilibrium, so that $G$ approximates the critical strain energy, $G_c$, which is used in this work. A typical load-displacement curve for the GP bonded material is shown in Fig. 2 and the results are listed in Table II along with the fracture energy values for bonding with epoxy

TABLE I Compressive strength of GPs with the milling time of MK

| Milling time (min) | Compressive strength (MPa) |
|---|---|
| 0 | 93 ± 5 |
| 30 | 77 ± 15 |
| 60 | 90 ± 11 |
| 120 | 79 ± 6 |

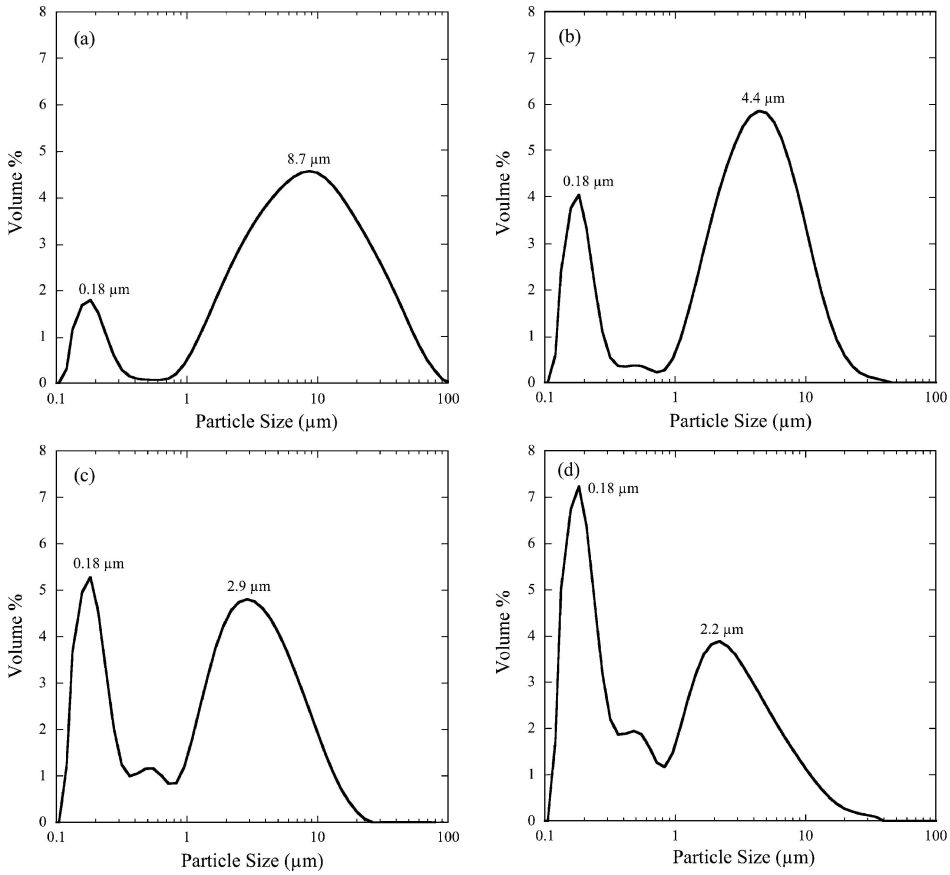


*Figure 1* Particle size distribution of MK: (a) unmilled, (b) 30 min milled, (c) 60 min milled, and (d) 120 min milled.

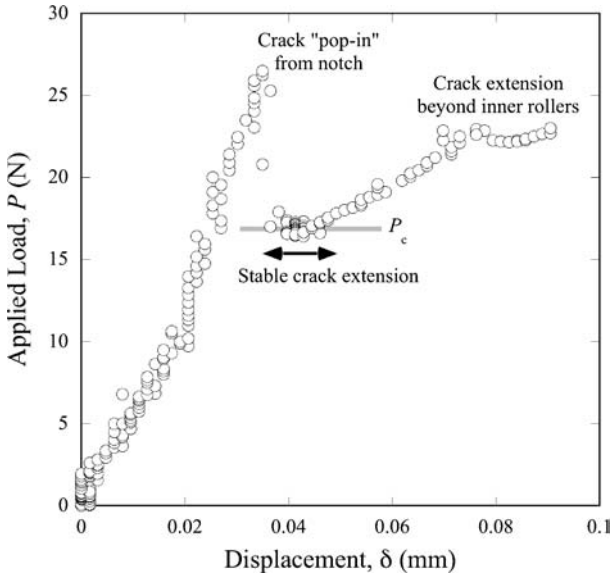


*Figure 2* Typical load–displacement data for the geopolymer bonded system.

resin (Araldite, Selley's, Australia) and a cyanoacrylate-based superglue (QuickTite, Selley's, Australia). Fig. 3 shows representative images of the interface during 4-point bending. Fig. 3(a) corresponds to the load drop when the crack initiates from the notch, propagates towards the interface, and begins to deviate within the GP interlayer. Fig. 3(b) shows at a later point in time, the crack pathway corresponding to a load plateau in the load-displacement curve (stable crack extension as in Fig. 2) where interface delamination has occurred mainly at the interface between glass and GP. The crack has also propagated through the GP layer on the right and caused debonding at the GP/metal interface. The tendency was for the cracks to propagate along the glass–GP interface, although in several instances we observed a mixture as shown in Fig. 3.

The results in Table II show that the 30 min milled MK containing samples gave the highest $G_c$, whilst the unmilled exhibited intermediate behavior and the 120 min milled sample had the lowest $G_c$ (nearly a factor of 3). The reasons for these differences in adhesion performance may be due the better overall coverage of the bonding surfaces that the finer GP provides and subject of further investigation. Interestingly, the highest $G_c$ obtained for the GP-bonded system is slightly greater than that obtained using a two-part epoxy resin and three times that of the superglue bonded system.

TABLE II Strain energy release rate ($G_c$) of steel/glass bonded samples

| Material | $G_c$ (J/m$^2$) |
|---|---|
| Bonded with GP using unmilled MK | $0.7 \pm 0.08$ |
| Bonded with GP using 30 min milled MK | $1.02 \pm 0.06$ |
| Bonded with GP using 60 min milled MK | $0.66 \pm 0.06$ |
| Bonded with GP using 120 min milled MK | $0.38 \pm 0.08$ |
| Bonded with epoxy resin | $0.85 \pm 0.13$ |
| Bonded with superglue | $0.33 \pm 0.12$ |

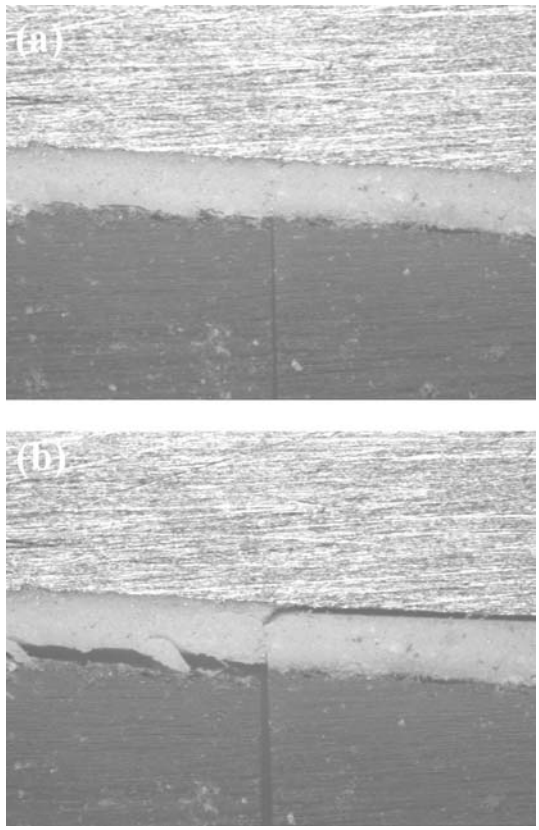


*Figure 3* Optical micrographs showing crack propagation in the geopolymer bonded system during 4-point bending: (a) immediately after crack initiation from notch and (b) during stable crack extension. Glass layer (*bottom*), GP (*middle*), and metal layer (*top*). Horizontal field of view = 1.6 mm.

Energy dispersive spectroscopy under the scanning electron microscope showed that the GP did not chemically react with the glass or steel as far as could be determined on a scale of $\sim$1 $\mu$m and the bonding appears to be purely mechanical rather than chemical. The surface roughness of the steel was $\sim$1 $\mu$m. Surface roughening is a means by which the mechanical bonding may be enhanced by facilitating anchoring.

We have shown that premilling the MK by attritor method did not have an appreciable influence ($\leq$10%) on the compressive strength of the GPs produced. The 4-point bend delamination test method has been applied successfully to study the fracture behavior and crack-driving force in glass–metal bonding with a GP "glue" interlayer. The GP has been shown to be an effective adhesive to bond the glass to metal with fracture energies ranging from 0.4 to 1 J/m$^2$, equivalent to epoxy adhesives.

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