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Effect of plant-derived organic binders on fracture toughness and fatigue of kaolin-based refractories

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Abstract The fracture properties of kaolin-based refractories prepared using plant-derived binders from okra and "mrenda" have been investigated and compared. It was observed that the MOR of fired samples improved from 37.5 ± 0.1 MPa (for binder-free samples) to 69.6 ± 0.1 MPa, and to 120.0 ± 0.1 MPa for okra- and 'mrenda'-plasticized samples, respectively, while the fracture toughness increased from 3.9 ± 0.1 MPa (for binder-free samples) to 5.6 ± 0.1 and 5.7 ± 0.1 MPa for okra and 'mrenda'-plasticized samples, respectively. It is concluded that the use of organic binders enhances the reliability and service life of kaolin refractories used in thermally fluctuating environments.

Introduction

To tap the potential of using ceramics as thermal insulators in devices subjected to temperature fluctuations, ceramics with good thermal shock resistance and long service lifetime need to be developed. Studies over the years have established that brittleness, degree of damage and strength degradation of ceramics subjected to severe fluctuating mechanical and thermal environments (between room temperature of 25.0 and 1,500.0 °C) are major limiting factors in relation to their service requirement and lifetime performance [1].

The addition of organic binders to ceramic powders during plasticizing has been found to enhance the green and fired strength and breakage resistance during handling of green bodies [2]. Most organic binders frequently reported in open literature, which have so far been investigated, are synthetic in nature and they include polyethylene glycol (PEG) [2–4], polyvinyl alcohol (PVA) [5] and acrylic-based polymers [6]. The influence of "mrenda" (*Corchorus olitorius*), a natural organic binder, on the modulus of rupture [7], thermal and mechanical properties of kaolin-based refractories has recently been investigated [8]. However, the effects of this binder on the fracture toughness and behaviour of refractories subjected to thermal fluctuating conditions, has not been investigated.

In this study, we investigate/compare the effects of two natural organic binders extracted from edible vegetable plants, okra (*Abelmoschus esculentus*) and "mrenda" (*Corchorus olitorius*), on the fracture strength and toughness, and on the thermal shock behaviour of kaolin-based refractories.

Experimental procedures

Both the okra and "mrenda" binders were separately prepared from their respective vegetables by boiling 5.0 ± 0.1 kg of the vegetable in 5.0 L of water for 40 ± 1 min, respectively. After cooling, each separate mixture was sieved to obtain the syrup (filtrate). Chemical analysis was performed on the binders and the kaolin clay (obtained from Athi River Mining Co. Ltd, Kenya), to determine the organic and inorganic components in these materials. The inorganic analysis was carried out by the wet chemical analysis method, and the atomic absorption spectrometry (AAS) was used to obtain the percentage composition of the constituent element oxides. The percentage composition of the organic compounds (proteins,

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fats, carbohydrates and ash) was obtained using the macro kjedhah method.

The okra- and "mrenda"-derived binders of varying volume concentrations, from 0 (plain water), 0.1, 0.2 …1.0 (undiluted binder) were then prepared by adding varying amounts of distilled water to the filtrate, respectively. These solutions were separately used to plasticize several batches of kaolin clay by mixing a given mass of kaolin clay with 33-wt.% of the binder solution. The dough was kneaded and thereafter left to age overnight at room temperature. Cylindrical samples (15.0 ± 0.1 cm in length and 1.5 ± 0.1 cm in diameter) were then prepared by extrusion, dried at room temperature for 7 days and then oven dried at 120 ± 2 °C for 24 h. Dried samples were fired in an electric furnace at the rate of 5 K min^{-1} to a peak temperature of 1,150 ± 2 °C and soaked at this temperature for 30 ± 1 min. The furnace was then switched off and left to cool to room temperature overnight. The sintered bulk density and porosity of the samples were determined by the Archimedes' immersion technique, which included boiling the test samples in water for 3 h. The modulus of rupture (MOR) measurements were performed in the three-point bent test mode using a universal tensometer (Instron model 1195) at cross head speed of 3 mm min^{-1}.

Cuboid-shaped samples (15.0 ± 0.1cm in length × 3.5 ± 0.1 cm × 3.5 ± 0.1 cm) for fracture toughness measurements were extruded using a mould fabricated in the laboratory. A notch of width 5.0 ± 0.5 mm was introduced in each sample, while still in the green state, by using a blade. The blade remained in the sample as it dried at room temperature and was removed before drying the sample in the oven. Three batches of 20 samples each were prepared: one plasticized with water, the other with okra binder at 0.3 volume concentration and the third with "mrenda" binder at 0.7 volume concentration. These binder concentrations were chosen since they resulted in respective maximum MOR values.

For fatigue analysis, cylindrical samples of diameter 4.6 ± 0.1 cm × 3.0 ± 0.1 cm in length were prepared. Thermal fatigue analysis was performed by repeated thermal-shocking of the samples from temperatures of 230 ± 1, 250 ± 1 and 270 ± 1 °C, respectively, to room temperature until failure. The failure of the sample was determined by observation, with naked eyes, of a crack on the samples' surface. The fracture toughness of the samples was determined from measurements of the critical stress intensity factor (K_{Ic}). K_{Ic} is a measure of the ability of a material to resist the propagation of an existing crack and is evaluated from Eq. 1 [9, 10].

$$K_{Ic} = \frac{LP_c}{bW^{\frac{2}{3}}} f(a, W) \quad (1)$$

where L is the span, P_c is the load at failure determined from three-point bent test, b is the thickness of the sample, W is the width of the sample and a is the crack length (depth of the notch). The reported values are the mean of 10 samples in each category. Scanning Electron Microscopy (SEM) was performed on fractured surfaces of selected samples using a Joel TSM T-330A scanning electron microscope at 10 KV accelerating voltage.

Results and discussions

Bulk density and apparent porosity

Figure 1 shows the variation of sintered bulk density and subsequent porosity of the samples as a function of binder concentration for both okra and "mrenda" binders, respectively. It is observed, that for both binders, the sintered density initially increases with increasing binder concentrations, reaching optimal values and thereafter decreases with further increase in binder concentrations. The trend of variation is reversed in the case of porosity.

The increase in sintered density (decrease in porosity) with increasing binder concentrations in both cases could be attributed to increased particle–particle bonding caused by sintering [7] and a process which is enhanced by the presence of the binders. Elemental analysis results (Table 1) reveal the presence of fluxing oxides (such as K_2O, CaO, etc) which constitute a total of 0.75% in okra and 1.25% in "mrenda". These fluxes (together with those already present in the kaolin clay) act as sintering aids, which favour densification during sintering. Table 1 also shows that the binders contained about 6.4% of total organic components mainly made up of proteins and carbohydrates, with the carbohydrates contributing half of the total organic compounds. These polymeric (carbohydrates and proteins) compounds act as 'cementing' agents of clay particles [11] resulting in increased green density and green

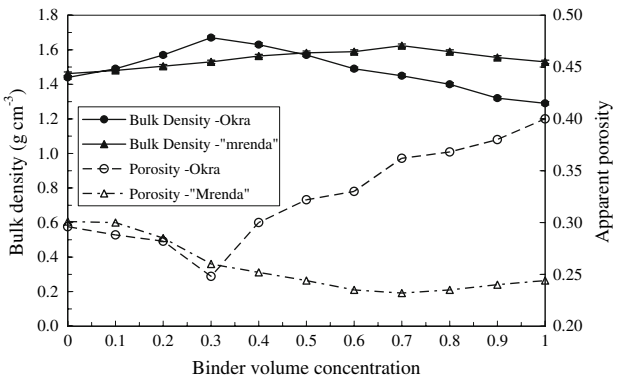

Fig. 1 The variation of sintered bulk density and apparent porosity of kaolin refractories with volume concentration of okra binder. The data on 'mrenda' are obtained from Ref. [8]

Table 1 Inorganic oxides and organic compounds in the binders and kaolin clay

Element	Percentage composition, (%) by mass		
	Okra	"mrenda"	Kaolin
SiO_2	0.02	0.11	51.56
Al_2O_3	0.00	0.03	35.90
Fe_2O_3	0.00	0.01	0.00
CaO	0.10	0.09	0.14
Na_2O	0.05	0.04	0.56
K_2O	0.52	1.00	2.70
MgO	0.14	0.12	0.07
TiO_2	–	–	1.02
Flux content	0.75	1.25	7.49
Proteins	2.20	2.12	
Fats	0.02	0.03	
Carbohydrates	3.10	3.12	
Ash	1.07	1.25	
Total organic compounds	6.39	6.49	

strength which in turn leads to high sintered density and strength.

After the optimal volume concentrations of the binders, the sample bulk density decreases probably due to the increased amount of organic matter which burn out during sintering and subsequently leaves more voids in the samples. The fact that the sintered bulk density begins to decrease (porosity starts to increase) when binder concentration exceeds optimal values shows that the voids created by the burnout of the organic materials outweigh the benefits of the fluxes.

Modulus of rupture (MOR)

Figure 2 shows the variation of MOR for fired samples with volume concentration for both okra and "mrenda" binders, respectively.

The trend of variation in the MOR is similar to that observed for sintered density (Fig. 1). For both sets of samples (samples plasticized with the binders), the MOR initially increases with increasing binder concentrations until some optimal values and thereafter decreases marginally with further increase in binder concentrations. This increase in MOR is a reflection of the trends observed earlier with respect to changes in the bulk density. In effect, therefore, we evoke the same concept of enhanced particle-particle bonding brought about by the binder, which in turn would subsequently require more energy to rupture. Beyond optimal binder concentration, the observed decrease in MOR is attributed to the effect of increased sample porosity earlier observed in Fig. 1. The effect of porosity on MOR is also evident in Fig. 2, where it is

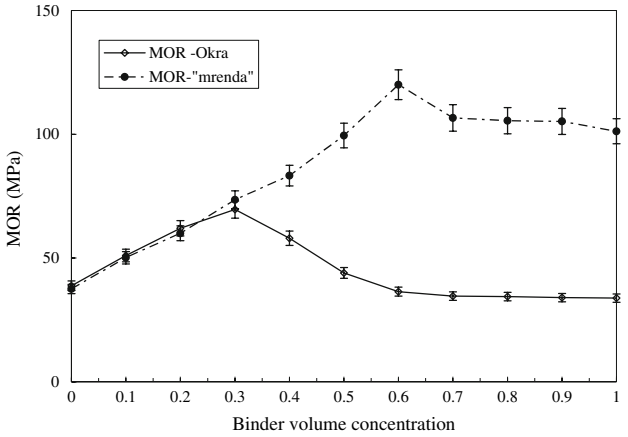

Fig. 2 The variation of MOR for fired samples with okra and "mrenda" binder concentration. The data on "mrenda" are obtained from Ref. [8]

observed that samples plasticized with "mrenda" binder have higher MOR values at higher binder concentrations (due to lower porosity values as observed in Fig. 1) compared to their counterparts plasticized with okra binder.

Fracture toughness

The mean values of the critical stress intensity factor (K_{Ic}) for the group of samples plasticized with okra, "mrenda"; and plain water, respectively, are tabulated in Table 2. We note an improvement in K_{Ic} (of 44.3% for okra binder and 45.8% for mrenda binder, respectively) when organic binders are used to plasticize the kaolin refractory samples as compared to samples plasticized with plain water. The increase in the value of K_{Ic} is an indication that addition of organic binders improves the resistance to the propagation of existing cracks in refractory materials.

The appreciable improvement in fracture toughness of the samples on addition of organic binders may be traced to the superior inter-particle bonding brought about by the binders' added fluxing action as noted earlier. The binders may also have precipitated formation of the Si–Al spinel and/or mullite phases from the kaolinite clay. This formation of the spinel/mullite phases has been reported [12], to be dependent amongst other factors on the presence of impurity oxides present or added externally in the kaolin.

Table 2 Mean values of (K_{Ic}) of kaolinite refractories plasticized with okra, "mrenda" and plain water, respectively

Plasticizer type	Mean fracture toughness (K_{Ic}) ± 0.1 Mpa $m^{1/2}$
Plain water	3.9
Okra	5.6
Mrenda	5.7

We have noted in the preceding paragraphs that the binders provide additional impurity oxides (fluxes) to those already present in the kaolin used in this study. Low-temperature (~1,000 °C) mullitization has been shown to be possible [12]. Furthermore, Chakravorty [13], observed low-temperature (at 980 °C) mullitization which is dependent on the pH in the Al_2O_3–SiO_2 systems. The presence of mullite phase would act as reinforcing phase [14] that inhibits crack growth. Though not specifically investigated, viscoelastic bridging [15] induced by enhanced flux content may not be ruled out. Figure 3a–c is SEM micrographs that seem to corroborate these proposals. As observed in Fig. 3b and c, samples plasticized with binders show some ligament-like grains clearly indicating a high level of inter-granular bonding (between grains) compared to the samples plasticized without the binder (Fig. 3a).

Thermo-cycling (fatigue)

The use of Weibull statistical analysis is a well-established technique to describe the strength distribution of nominally brittle materials, in which the fracture strength is controlled by the most critical defect in the stressed volume of the material. The critical defect is one with the highest stress intensity factor under the given conditions but although it is often, it need not necessarily be the largest inherent defect [16]. Such an approach has been applied classically to ceramic materials and is used in this study to describe the distribution of strength in samples plasticized with plain water, okra and "mrenda" binders, respectively.

The Weibull statistics given by Eq. 2 [16] is used,

$$\ln(-\ln p) = \ln V' + \frac{m}{n}\ln N + m\ln\left(\Delta T_N\right) \tag{2}$$

where p is the survival probability, given as the ratio of number of surviving samples after a given number of thermal cycles (N) to the total number of samples for a given thermal stress severity, (ΔT_N). V' is the stressed volume, m is the Weibull modulus and is a measure of the spread of the strength distribution, while n is the slow crack growth parameter. Both m and n are material properties, independent of sample structure size, geometry and load case. The Weibull fracture probability method allows characterization of strong bonds with good resolution and provides user-independent and comparable results. Thus, it

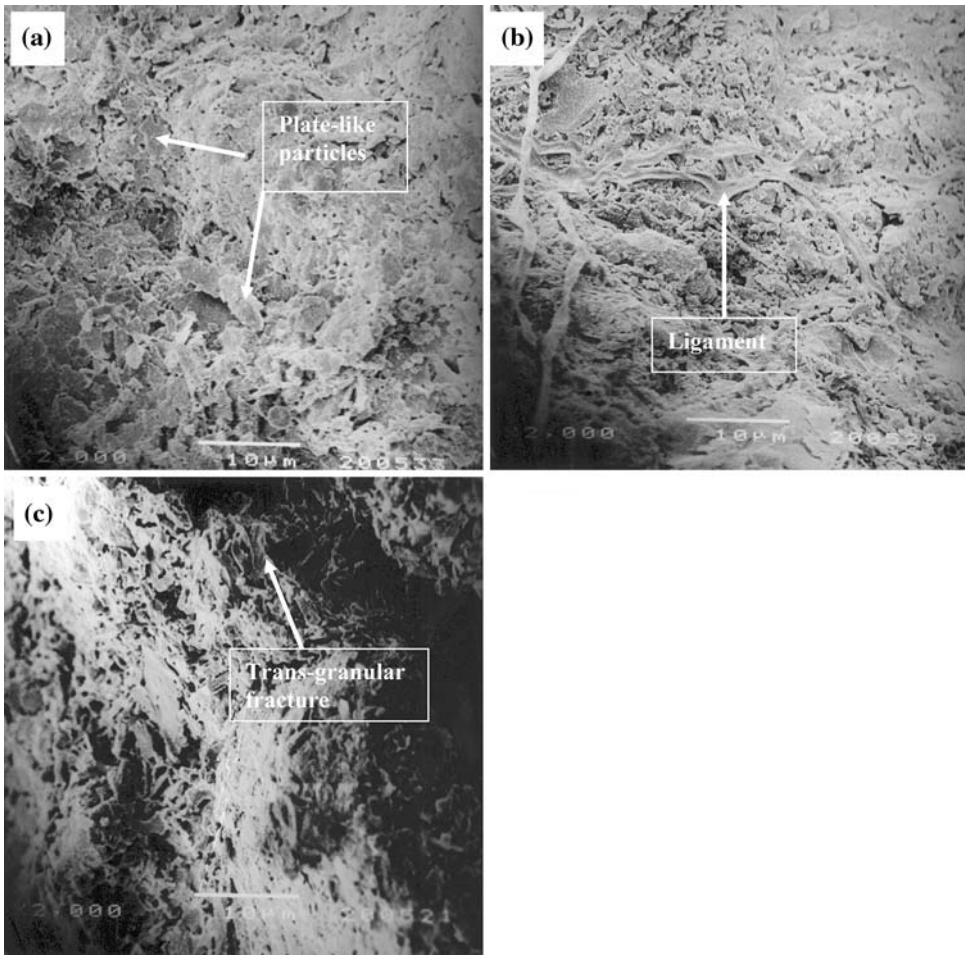

Fig. 3 SEM micrograph of the fractured surface of (**a**) a water-plasticized sample showing plate-like particles of kaolin indicating inter-granular fracture, (**b**) okra-plasticized sample (at optimal concentration) and (**c**) mrenda-plasticized sample (at optimal concentration), both showing ligament-like features that hinder inter-granular fracture but cause the fracture to be trans-granular

is particularly suited for the evaluation of the reliability of the binder-processed refractories.

For a given value of ΔT_N, the ratio of *m/n* was obtained as the slope (Fig. 4) of ln(−ln*P*) versus ln*N* from Eq. 2. The lines in Fig. 4 are linear and have the same gradient of 1.50 (= *m/n*). For a common probability, *p* Eq. 2 yields [16]

$$\frac{N}{N'} = \left(\frac{\Delta T_{N'}}{\Delta T_N}\right)^n \tag{3}$$

Equation (3) implies that $N\Delta T_N^n = \text{constant}$.

The value of *n* was obtained by plotting ln*N* versus lnΔT (shown in Fig. 5) for a common probability $p = 0.7$. The slope of Fig. 5 gives the value of *n* which in this case = 4. Using this value of *n*, together with the value of *m/n* obtained from Fig. 4, the Weibull modulus (*m*) is obtained to be 7. Similar analysis was done for samples plasticized with plain water and okra binder and the respective values of *m* and *n* are tabulated in Table 3. The Weibull modulus (*m*), sometimes called the shape parameter, values obtained are within the accepted range of 5–20 for typical ceramics [17] and shows very marginal increase with the addition of binders. The crack propagation parameter *n* seems to be insensitive to the use of binders. This is contrary to the fracture toughness results obtained above.

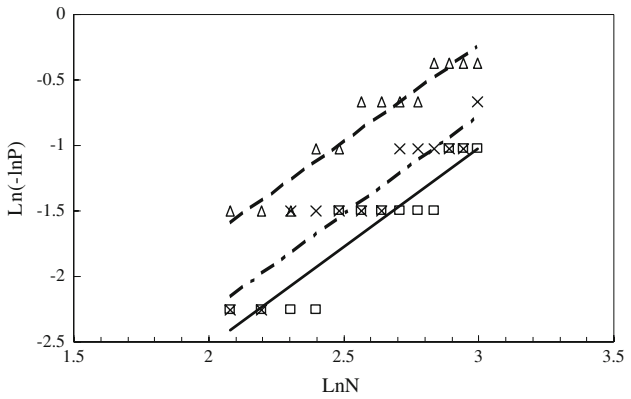

Fig. 4 ln(−ln*P*) versus ln*N* for samples plasticized with "mrenda" binder at optimal plasticization concentration (The samples were quenched from: 270 °C (Δ), 250 °C (x) and 230 °C (□))

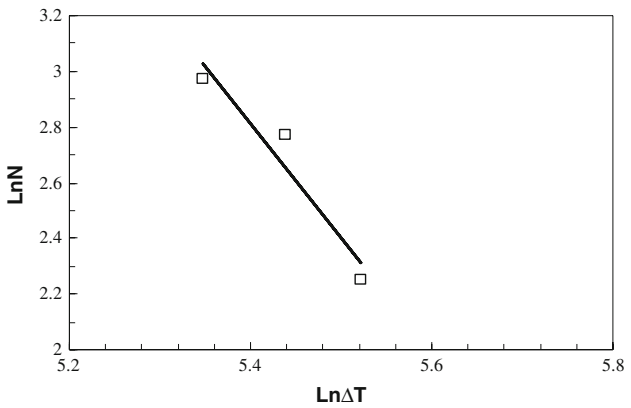

Fig. 5 ln*N* versus lnΔT for samples plasticized with "mrenda" binder

Table 3 Values of *m* and *n* for samples plasticized with different binders

Type of plasticizer (binder)	Binderless-plain water	Okra binder	"mrenda" binder
Weibull modulus $m \pm 1$	5	6	7
Crack propagation Parameter $n \pm 1$	4	4	4

Conclusion

Samples plasticized with plant-derived organic binders depict improved strength and fracture toughness (resistance) values compared to binder-free samples. This was attributed to improved bonding between the kaolin particles and possible low-temperature mullitization due to the binders. From the results obtained in this study, it can be concluded that the use of organic binders enhances the reliability and service life of kaolin samples used in thermal fluctuating environments.

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