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Thermal shock behaviour of a kaolinte refractory prepared using a natural organic binder

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Abstract The thermal shock resistance of a kaolinite-based refractory prepared with a binder derived from a plant (*corchorus olitorius*) was investigated. Thermal shock tests employing water-quenching technique were performed at quench temperature differences of between 80 and 580 °C and then the damage parameter, and thermal shock parameters (R, R', and R'''') evaluated using measured strength and modulus values. The results showed that R and R' parameters increased with increasing binder concentrations, an indication that the damage due to crack initiation was progressively impaired with increased binder concentrations. The R'''' parameter on the other hand decreased with increasing binder concentrations indicating poor resistance of the material to crack propagation. These observations were also matched with thermal shock results which showed that samples plasticized with higher binder concentration had relatively very high strengths before thermal shock, compared to those plasticized with plain water, but they experienced rather large strength losses (over 60% of their initial values) at quench temperature difference (ΔT) exceeding 325 °C. The critical temperature difference (ΔT_C) for the samples tested was in the range 250–325 °C. Scanning electron microscope (SEM) micrographs of samples quenched at temperature difference of 580 °C showed that samples plasticized with high binder concentration (0.68) experienced severe cracking of the matrix compared to their counterparts plasticized with plain water, whose microstructures showed an inhibited crack propagation.

Introduction

Kaolinite clays are used directly or in mixtures with other types of clay in the production of refractories which are employed as thermal insulators in high temperature applications such as in kilns, furnaces, and domestic charcoal stoves (*jikos*). In such applications, these ceramics are often exposed to cyclic thermal stresses and, at times, even severe thermal shocks, resulting in rapid strength degradation or even catastrophic failure of the components. Improving thermal shock resistance of these refractories is hence a key to boosting their durability and reliability in service.

Since thermal shock resistance is not an intrinsic material property, manipulation of material properties such as fracture strength (σ_f), thermal conductivity (K), Young's modulus of elasticity (E), Poisson's ratio (v), and the coefficient of thermal expansion (α) on which it depends, remains the only technique of controlling thermal shock resistance of refractories towards meeting the needs of individual applications.

A number of processing techniques have been suggested and used to manipulate singly or multiply the aforementioned properties. Among those that have been reported widely include better control of sintering temperature and time [1], creation of thermal mismatch between matrix and second phases [2, 3] or addition of polymeric organic binders to ceramic powders during processing [4–6].

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Addition of organic binders is a technique that is widely used in the ceramic industry, because besides improving mechanical properties [6, 7] and/or thermal conductivity [8], it has the additional advantage of minimizing production losses associated with breakage and cracking of ceramic green bodies during manufacture [9].

The binders that have received most attention are poly vinyl alcohol (PVA) and poly ethylene glycol (PEG) [6]. Baklouti et al. [6] used these synthetic based organic binders (PVA and PEG) and observed remarkable tensile strength increase compared to binder-free samples of alumina based ceramics. Recently Aduda et al. [7] studied the effect of a natural organic binder extracted from a plant (*corchorus olitorius*) on the fracture strength of kaolinite refractories and they reported strength (modulus of rupture) improvement of up to 143% in fired bodies compared to similarly fired binder-free samples. Ogacho et al. [10] have reported an initial increase in the effective thermal conductivity, up to an optimal binder concentration followed by a decrease thereafter, of a kaolinite refractory processed using the same binder. The observed enhancement of both the fracture strength and the thermal conductivity of kaolinite refractories by this binder (from *corchorus olitorius*) is a pointer that the binder could influence the thermal shock resistance of refractories.

Two types of parameters have been used to predict thermal shock behavior of refractories: (i) thermal stress resistance, and (ii) thermal shock damage resistance. The first determines the minimum thermal shock required to initiate a crack, and resistance to initiation of fracture by thermal stress. The second expresses the degree of possibility for further damage, that is, further crack propagation or growth caused by thermal shock. The thermo-mechanical (K, α, σ_f), elastic (E, v) properties and thermal shock parameters (R, R' and R''') are related according to the following expressions [3, 11–15]

$$R = \Delta T = \frac{\sigma_f(1-v)}{\alpha} \tag{1}$$

$$R' = \frac{\sigma_f(1-v)K}{\alpha E} \tag{2}$$

$$R''' = \frac{E}{\sigma_f^2(1-v)} \tag{3}$$

$$R'''' = \frac{E\gamma_f}{\sigma_f^2(1-v)} \tag{4}$$

where σ_f is the bend strength (MOR), ΔT is the temperature difference between the sample temperature and the quenchant temperature, and γ_f is the fracture surface energy. R and R' are commonly referred to as thermal stress resistance parameters and represent conditions that are appropriate for resistance to crack initiation. R is relevant to conditions of rapid heat transfer where the surface of the test specimen is assumed to attain the temperature of the quenchant instantaneously, and it defines the minimum temperature difference (ΔT) necessary to produce fracture under conditions of infinite heat transfer coefficient. R' is appropriate under conditions of finite heat transfer. R''' and R'''' are known as the thermal shock damage resistance parameters and they express the ability of the material to resist crack propagation and further damage and loss of strength on thermal shocking. A high value of $E\gamma_f/\sigma_f^2$ is regarded as a good indicator of a good resistance to crack propagation.

Young's modulus determined dynamically is derived from the ultrasonic velocity data using the following relation [16]

$$V_L = \left[\frac{E(1-v)}{\rho(1+v)(1-2v)}\right]^{1/2} \tag{5}$$

where V_L is the measured ultrasonic longitudinal velocity, and ρ is the sample bulk density. Poisson's ratio is calculated using Eq. 6

$$v = (1-2b^2)/(2-2b^2) \tag{6}$$

where $b = V_L/V_s \approx 1.7$ for most materials [17] in which (V_s) is the transverse velocity.

The purpose of this study is to investigate the effects of this *corchorus olitorius* derived binder on thermal shock behaviour of a kaolinite refractory.

Experimental procedure

In the present study, Kaolin clay (supplied by Athi River Mining Company, Athi River Kenya) and fresh leaves of plant (*corchorus olitorius*) were used. The details of extraction of the binder from the plant have been reported elsewhere [7, 10]. Binder concentrations (measured in terms of viscosity η) of the binder were varied by diluting a fixed volume (V_o) of the undiluted syrup of viscosity (η_o) with varying volumes (V), of clean tap water. Finally the concentrations were normalized with respect to the viscosity of the undiluted binder (η_o). Chemical analysis was conducted to determine the organic and inorganic components in the binder. 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 components (proteins, fats, carbohydrates and ash) were obtained using the macro kjedhah method.

Different sets of kaolin pastes were made by mixing a given mass of kaolin clay with 33-wt% of the binder (of different concentrations). This way, the kaolin was plasticized with binders of varying concentrations. For a given binder concentration the mixture was kneaded to obtain a uniform dough, which was left overnight to age, then an extrusion machine was used to make cylindrical specimens 1.50 ± 0.01 cm in diameter and 15.00 ± 0.01 cm long for strength (MOR) measurements, while specimens for elastic modulus (Young's Modulus) were prepared by uniaxially pressing 50 ± 1 g of the paste at pressures of approximately 100 KPa into cylindrical specimens measuring 4.00 ± 0.01 cm in diameter and 4.00 ± 0.01 cm thick [18]. The specimens were left to dry at room temperature for seven (7) days, oven-dried further at 120 ± 5 °C for eight hours and then stored in moisture free chambers. All samples were fired at the rate of 5 K min^{-1} to a peak temperature of 1,150 °C, soaked at this temperature for 30 ± 1min and thereafter allowed to cool to room temperature overnight.

Prior to velocity measurements, the opposite faces of the test samples were polished to 1μ m finish to ensure parallel surfaces; the final polished samples were 3.00 ± 0.01 cm thick and 4.00 ± 0.01 cm in diameter. The ultrasonic longitudinal velocity (V_L) through the samples was then determined using an ultrasonic equipment (PUNDIT) in the through transmission mode as follows. A thin layer of petroleum-based grease was used to couple the specimen and the transducers. Before measuring the ultrasonic times-of-flight in the test specimens, a standard reference block was used to calibrate the unit's time scale. Measurement of thickness (distance covered by ultrasonic pulse) was accomplished with the aid of vernier calipers (±0.0001 m), and the transit time (±0.1 μs) of the ultrasonic pulses were read as displayed by the ultrasonic equipment. The longitudinal velocity V_L, for the sample was then calculated as a ratio of samples' thickness to transit times. For each test piece, V_L was measured three separate times, each time interchanging the faces to which the pulsing and receiving transducers are coupled. The bulk density was determined from dimensions and mass and mass of the samples to an accuracy of ±0.001 Mg/m^3.

The water quenching method was used to assess the thermal shock response of fired samples. To achieve this, thermal gradient ΔT was created relative to water temperature (20 °C) by heating the samples (inside a furnace) to desired temperatures (T) of (100, 200, 270, 300, 345, 400, 500 and 600 °C respectively). On attaining a desired temperature, the specimens were soaked at that temperature for at least 30 min to allow stabilization of the specimen's body temperature. Thereafter, the heated specimens were suddenly removed from the furnace and immersed into a large vessel containing water at 20 °C creating a thermal gradient $\Delta T \approx (T–20)$ °C at the specimens' surfaces. The thermally shocked specimens were then removed, wiped dry and then left to dry further at room temperature for 48 h. To ensure they were completely moisture free, they were further oven dried at 120 °C for 8 (eight) hours, after which, their residual strengths were measured in a three-point flexure test. The modulus of rupture (MOR) was measured using a standard three-point-bend test on an Instron Model 1195 machine at crosshead speed of 3 mm/min. For each binder concentration and temperature differential, ten samples were normally tested to get the mean value of MOR. The decrease in strength (MOR) and increase in damage due to thermal shock was then calculated using a damage parameter, D_{MOR} [19]

$$D_{MOR} = 1 - \frac{\sigma_{\Delta T}}{\sigma_0} \tag{7}$$

where σ_o is the average modulus of rupture of the as-fired samples (specimens not thermally shocked), while $\sigma_{\Delta T}$ is the after-shock strength at temperature difference ΔT.

The morphological characteristics of the thermally shocked specimens were studied using a JEOL TSM T-330A scanning electron microscope (SEM). The SEM specimens were coated with a thin layer (≈ 20–40 nm) of gold to avoid charging effects from non-conductive (electrical) ceramic surface. The coating was done under low-pressure argon gas using Edwards S150B Sputter Coater for four minutes and thereafter, SEM micrographs of fractured surfaces taken.

Results and discussions

Figure 1 shows the variation of the sintered sample bulk density as a function of binder concentration. It is observed that bulk density increases, reaching an optimal value at a binder volume concentration of 0.67 and thereafter, it decreases with further increase in the binder concentration. The increase in the bulk density could be attributed to the improved sintering in the samples brought about by the presence of fluxing oxides in the binder. Results of chemical analysis

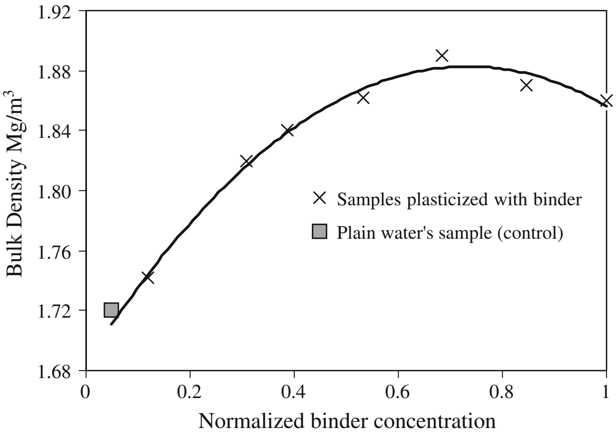

Fig. 1 Variation of sintered sample bulk density with binder concentration

(Fig. 2) shows the presence of fluxing oxides (K_2O with 0.96%, CaO with 0.088% and Na_2O with 0.040%) constituting a total of 1.26% as inorganic components. Despite their total contribution of less than 1.3%, these fluxes act as sintering aids, which favour densification during sintering.

Figure 2 also shows that the binder contained about 6.00% total of organic components (2.12% proteins, 3.15% carbohydrates and 1.25% of the ash). The water component constitute about 94.00% of the binder. The polymeric (carbohydrates and proteins) components are responsible for improving the sample's green density which in turn leads to high sintered density. However, notably, a high binder concentration (high organic component) in the green samples may result in an increased pore volume fraction in sintered samples when the organic components burn out during sintering. This results in decreased sintered sample bulk density and it explains why the sintered density decreases at higher binder concentrations.

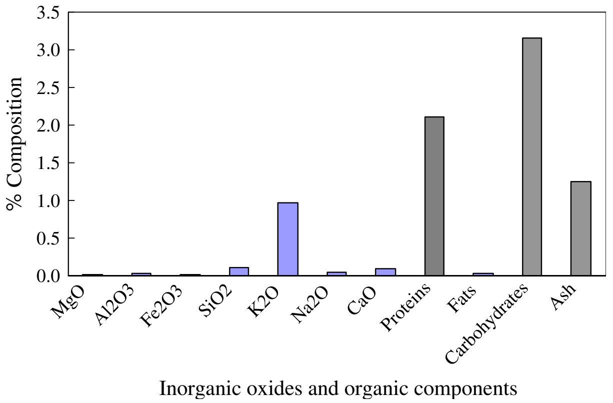

Fig. 2 Percentage composition of inorganic and organic oxides in the binder

Table 1 gives a summary of the measured functional properties (E, K, and σ_f) for data collected at 20 °C. It is observed from the table that the values of fired strength increased, peaking at an optimal binder concentration of 0.67. The trend of behaviour in fired MOR is similar to the trend observed for the fired bulk density indicating that higher densities associated with binder-plasticized samples virtually assume better mechanical properties compared with the binder-free plasticized samples.

Figure 3 shows the variation of the damage parameter as a function of the quench temperature difference. It is observed that the samples suffer precipitous strength degradation at quench temperature difference of between 250–325 °C irrespective of the binder concentrations. This indicates that their critical temperature is within this range of temperature. Notable also from Fig. 3 is the fact that beyond 325 °C the damage parameters attain nearly constant values for each category of specimens with the specimens prepared with plain water exhibiting the least damage parameter. In fact in the higher ΔT ($\geq$ 325 °C) ranges, D_{MOR} increases apparently non-linearly with pre-quench strength (σ_f). That is, the higher the initial strength, the greater is the thermal shock damage. In other words, the retained strength after thermal shock is observed to drop with increasing binder concentrations indicating that samples plasticized with high binder concentrations were weaker after thermal shock compared to binder free samples. Bayuseno et al. [3] have observed a similar trend in base alumina but with ΔT in the 175–200 °C range. The increase in damage parameter and decrease in residual strengths after thermal shock is associated with structural degradation as confirmed from the SEM micrographs shown in Figs. 5–7.

It is important to point out that as the binder concentration used during the plasticization process increased, the porosity of the fired specimens decreased to a minimum at the normalized concentration of 0.68, and thereafter rose slightly (see Table 1). This decrease in porosity is what is responsible for the increase in strength, elastic modulus and effective thermal conductivity.

A comparison of the microstructures (Figs. 4, 5 of samples thermally shocked at a temperature difference of 180 °C with and the microstructures (see Aduda et al. [7]) of samples not thermal shocked shows that no pronounced structural differences are discernable. This indicates that at this quenching temperature difference (ΔT = 180 °C) the thermal-shocked samples did not experience any discernable strength degradation irrespective of the binder concentrations.

Table 1 Summary of functional properties of a kaolinite refractory with corresponding calculated thermal shock parameters

Normalised binder Concentration	Porosity (%)	Thermal conductivity at 20 °C (±0.01 W/m/°C)	Measured material properties.		Calculated figures of merit (*R*-values)		
			E±5% (GPa)	MOR (σ_f)± 5% (MPa)	R± 10% (°C)	R'±10% (W/m)	$R'''x\ 10^{-6}$ $(\mathrm{Pa})^{-1}$
Control sample*	30.1	2.26	17.39	37.50	77	175	16.3
0.12	29.3	2.34	19.46	50.10	93	216	10.2
0.31	26.0	2.43	25.10	73.48	105	256	6.1
0.39	25.2	2.52	28.42	83.30	105	265	5.4
0.53	24.4	2.75	29.49	99.50	121	333	3.9
0.68	23.2	2.96	33.07	106.61	116	363	3.8
0.85	24.0	2.85	32.62	105.23	116	330	3.9
1.00	24.4	2.68	32.98	101.23	110	296	4.2

[*] Plain tap water was used to plasticized the control sample

In contrast, the SEM micrograph of a specimen plasticized with optimal binder concentration and thermally shocked at temperature difference of 580 °C (Fig. 6) shows some large and sharp cracks in the matrix. This indicates that samples plasticized with high binder concentrations experienced substantial strength degradation at high quench temperatures differences. Figure 7 shows a microstructure of a sample plasticized in plain water and thermally shocked at 580 °C. Of significance is the apparent lack of sharp cracks running through the grains such as those clearly visible in Fig. 6, and this could be indicative of inhibited crack growth probably due to crack propagation having been arrested through mechanisms such as crack branching or crack nucleation. High densities of micro-cracks, and consequently lower stored elastic energy, have been reported as efficient in restraining crack growth through crack branching [19]. Total stored elastic energy is known to be the driver of crack extension above the critical temperature difference; hence lowering stored elastic energy is a means of improving resistance to crack proliferation [14].

Thermal shock parameters calculated from the data collected at 20 °C are shown in Table 1. In this case, it was assumed that the solid component of the refractories consisted only of crystalline Si_2O_{II} and crystalline Al_2O_3 and the rule of rule of mixture (Eq. 8) was used to estimate the effective thermal expansion coefficient (CTE), α_{eff}. In the rule of mixture (ROM), it is presupposed that the overall physical and mechanical properties of composites are intimately related to individual components [20] and that a composite is a

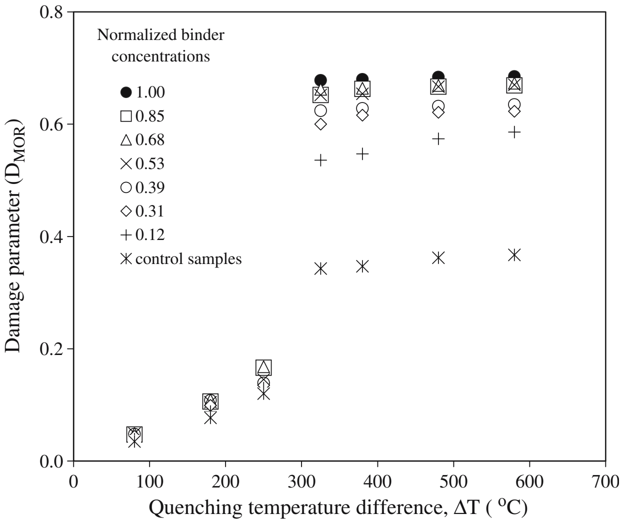

Fig. 3 The variation of damage parameter with quenching temperature difference (Δ*T*) for specimens plasticized with different binder concentrations

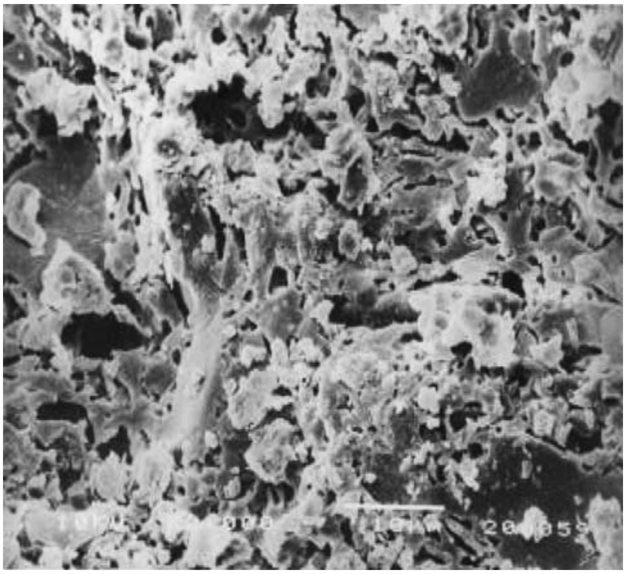

Fig. 4 SEM micrograph of a sample plasticized in a binder concentration of 0.683 after water quenching at a temperature difference (Δ*T*) of 180 °C

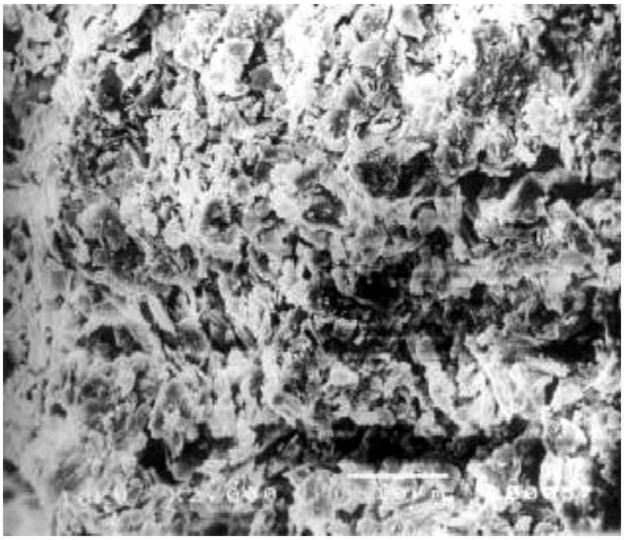

Fig. 5 SEM micrograph of a sample plasticized with plain water after water quenching at a temperature difference (ΔT) of 180 °C

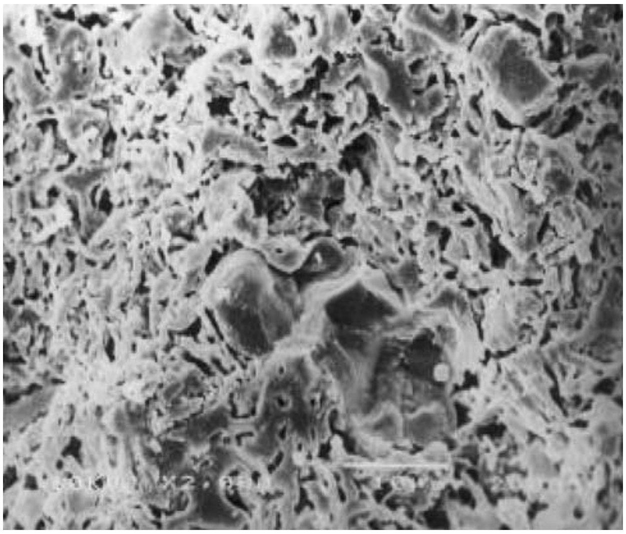

Fig. 7 SEM micrograph of a sample plasticized with plain water after water quenching at temperature difference (ΔT) of 580 °C

mixture of the present phases, with individual phases exhibiting mechanical and thermal behaviors, which are not, influenced by their presence in the mixture. Therefore the effect of microstructural details, plasticity and thermal softening are not accounted for [21]

$$\alpha_{\text{eff.},} = \alpha_1\phi_1 + (\alpha_2)\phi_2 \tag{8}$$

In the above equation α_1 and α_2 are CTE of crystalline Si$_2$O$_{\text{II}}$ = 7.5 × 10^{-6}/°C and crystalline Al$_2$O$_3$ = 4.0 × 10^{-5}/°C respectively [22], while ϕ_1, ϕ_2 are their respective volume fractions.

The thermal shock parameters were eventually calculated using the effective coefficient of thermal expansion value of (α_{eff} = 2.115 × 10^{-5}/°C) and Poisson's ratio, v = 0.24 (calculated using Eq. 6). It was assumed that these two values remained invariant with binder concentrations.

Figure 8 gives a graphical illustration of the (normalized to illustrate the trend) thermal shock parameters as a function of the binder concentrations.

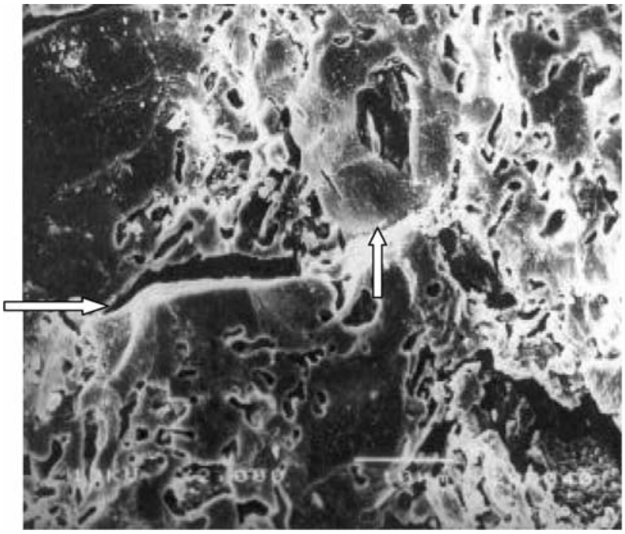

Fig. 6 SEM micrographs of a sample plasticized with optimal binder concentration (0.68) after water quenching at temperature difference (ΔT) of 580 °C. Cracks in the matrix are marked with arrows

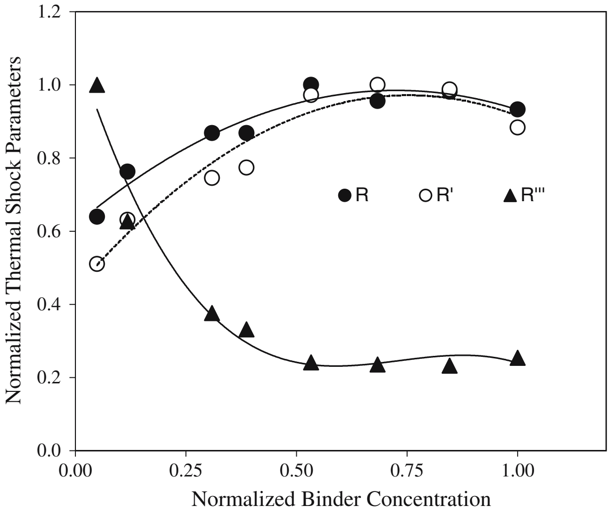

Fig. 8 The variation of normalized thermal shock parameters with binder concentration. (The lines are just to a guide to the eye)

It is observed from Fig. 8 that the thermal shock parameters R, and R', both indicators of resistance to crack initiation, increase with binder concentrations. This is indicative that though both (σ_f) and E increased with increasing binder concentration, the rate of increase in (σ_f) was more sensitive to the presence of the binder than E was. Coupled with the fact that K_{eff} also initially increased with binder concentration, the observed trend in both R, and R' are therefore explained. Thus, it is evident that the use of the binder during plasticization enhanced the resistance to fracture initiation of the refractory of interest.

When the calculated R-values (Table 1) and the experimentally determined ΔT (250–325 °C) values are compared, we note that the former underestimates the latter. We point out that in this comparison we have not taken into account the shape factor of the test specimens, which were cylindrical.

The third parameter R'''' that provides a measure of resistance to crack propagation [13, 15], initially decreased rapidly with increase in binder concentration of up to about 0.3, and then remained fairly constant in broad agreement with thermal shock test results (Fig. 3) and confirmed by SEM micrographs (Fig. 7) results, which showed long and sharp cracks through the grains of samples plasticized with binder of higher concentrations. That these long cracks as observed in the SEM micrographs in samples made with higher binder concentrations were not arrested or deviated indicates that kaolinite refractories made with higher binder concentration had poor resistance to crack propagation particularly at temperature differentials exceeding 325 °C (Fig. 3), probably as a result of the absence of microcracks in the larger grains of the matrix.

It is known that the criteria for maximizing resistance to crack initiation, and crack propagation are contradictory [11, 23], we would propose, from Fig. 8, that the binder concentration range (~0.1–0.2) at which the R, R' and R'''' curves intersect probably would give values of the thermo-mechanical properties that maximizes thermal shock resistance for this material when the plant (*corchorus olitorius*) derived binder is used in the dough plasticization process.

Conclusions

The results of thermal shock behavior revealed that the critical temperature difference of fired samples plasticized with plain water and those plasticized with this binder lie between 250 and 325 °C. It was noted that during the thermal shock, the samples plasticized with the binder experienced the largest strength degradation as evidenced by larger values of the damage parameter especially, above temperature difference (ΔT) exceeding 325 °C. The samples plasticized in high binder concentrations, which initially had higher strengths, suffered the severest strength losses (lost over 60% of their initial strengths). The results of calculated thermal shock parameters (or figures of merit) showed that high binder concentration samples had better resistance to crack initiation but lower resistance to crack propagation, while samples plasticized with water had lower resistance to crack initiation but enhanced resistance to crack propagation associated with their higher porosities. Considering other results reported [7, 10] we recommend the use, though in small quantities, of this*corchorus olitorius* derived binder in the processing of kaolinite refractories to be used as thermal insulators especially in areas characterized by high mechanical stresses but experiencing mild thermal shocks (ΔT <250 °C). However in applications where the components may be exposed to severe thermal fluctuations (ΔT >325 °C) the use of this binder in kaolinite refractories processing may not be advisable.

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