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Rheo-viscoelastic behaviour of fresh cement-based materials: Cement paste, mortar and concrete

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HIGHLIGHTS

- Viscoelasticity of cement paste containing aggregates was investigated.
- Aggregates influences viscoelasticity and rheology modifiers varied the influence.
- Viscoelasticity of concrete/mortar may not be approximate-able from cement paste.
- Aggregate reduces flocculation-driven structuration of cement paste.
- Cement-based materials exhibits viscoelastic pseudo-strain hardening.

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ABSTRACT

The viscoelasticity of fresh fine cement-based material can be investigated by rheological means using dynamic shear rheometry, hence, the term rheo-viscoelasticity. However, readily available classical rheometers are limited to the study of paste due to the aggregate size associated with mortar and concrete. This study, therefore, sets out to experimentally investigate the rheo-viscoelastic behaviour of cement-based materials containing rheology modifiers, by progressively evaluating the viscoelasticity of cement paste-mortar-concrete. The tests carried out include strain sweep, shear rate sweep, creep and creep recovery, stress relaxation and three interval thixotropy test (3ITT). The results show a trend of improved linear viscoelastic properties of the control fresh cement-based materials due to progressive inclusion of aggregate (increasing volume fraction and size). However, the rheology modifiers widely varied this trend, tending to make it difficult to approximate the rheo-viscoelastic behaviour of mortar and concrete from that of the cement paste as generally suggested in literature. The increase in the coarse volume fraction improved the stability of the cement-based materials microstructure to varying shearing rates. The study suggests that the liquid phase has a role in improving the creep recovery and stress relaxation of the mixes. Furthermore, pseudo-strain hardening was observed for the cement-based materials and flocculation-driven structuration was found to be reduced for the cement paste due to the progressive inclusion of aggregates leaving hydration as the main driving source of concrete's structuration.

1. Introduction

Dynamic shear rheometry (DSR), sometimes referred to as small amplitude oscillatory shearing (SAOS), is a test method that can be used to characterize viscoelastic (VE) materials by linking rheology to viscoelasticity [1–3], hence, the term "rheo-viscoelasticity". It involves applying a sinusoidal oscillatory shear strain/stress (stimulus) to a VE sample while monitoring the response of the sample. Viscoelastic materials possess both viscous and elastic properties, hence, the response of the VE sample has a phase lag (δ) to the stimulus [4]. In terms of rheology of fresh cement-based materials, dynamic/oscillatory shear rheometry is considered advantageous over static/rotational shear rheometry because the latter causes the de-structuration of the microstructure [5–8] due to irreversible continuously increasing shearing. Therefore, the rotational shear rheometry does not give insights into the microstructure but rather the overall structure's macroscopic response while SAOS allows the understanding of the microstructural behaviour of VE materials.

Characterisation of VE materials via shear rheometry often starts from an amplitude sweep (strain amplitude, in the case of

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this study) in order to determine the microstructural response and linear viscoelastic range (LVR). The LVR is the range of strain where the VE material behaves like an elastic material (viscoelastic solid), above this limit, the material's microstructure is disturbed and it behaves like a viscoelastic liquid (Ma *et al.*, 2018; Mezger, 2014; Nachbaur *et al.*, 2001). The viscoelastic liquid regime before flow occurs defines the viscoplastic behaviour of VE materials [3,10,11]. It is believed that within the LVR, the particles are in close contact with one another and their interactions yield a linear elastic behaviour [12–14]. The amplitude sweep is often followed by the frequency sweep to investigate the influence of shearing rate on the linear VE behaviour [9]. Below a certain frequency, the VE material has adequate time to relax and release residual energy within its microstructure and elastically return to equilibrium [2,15]. At certain high frequency, the VE material's microstructure suffers degradation from residual energy. In practical terms, frequency sweep can be used to investigate the time-dependent (short-term and long-term) linear deformation behaviour of VE materials using a range of frequencies [4,16], since frequency is the inverse of time. For example, the response of a VE material to a large but sudden/impact loading (short-term) as well as to a small but extended loading (long-term), respectively. In another application, it can be used to examine the response of cement-based materials to changes in the rate of its shear plastic settlement. Other DSR tests used to characterise viscoelastic materials include creep and creep recovery, stress relaxation and thixotropy tests.

When a steady force is applied to a VE material, it experiences an initial instantaneous deformation, followed by a gradually increasing deformation (delayed response) (Fig. 1a). If the stress is removed, the VE material recovers some strain due to its elastic property while some portion of the strain becomes permanent. This phenomenon is simulated and quantified by the creep and creep recovery test. The stress relaxation test simulates and quantifies the behaviour of a VE material subjected to a sustained strain. A typical VE material relaxes/relieves the associated stress (Fig. 1b). VE behaviours are also time-dependent for most materials [4,17]. Fresh cement-based materials, for example, exhibit a reversible time-dependent VE behaviour mainly due to structuration [2,13,18,19]. This is sometimes referred to as thixotropy/rigidification [6]. Two main forces drive this time-dependency of cement-based materials – flocculation of the particles and hydration. A thixotropy test helps in quantifying the time-dependency of the viscoelasticity. Structuration of cement-based materials has been widely investigated [6,20,21], in particular, using the slotted blade rotational shear rheometry (RSR). As noted earlier, RSR requires discrete measurement that causes destruction of the material's structure after a specified resting time [22,23] which is avoidable with the SAOS that can continuously probe the structural build-up in real-time with negligible interference with the material's structure. Shear thickening and thinning have been reported in concrete's rheology [24,25] as the time-independent increase and decrease (respectively) in the microstructure's resistance under shearing. In polymer engineering and as later obtained in this study, increase and decrease in the structuration under SAOS is referred to as microstructure thickening and softening respectively. These are sometimes referred to as pseudo-strain hardening and yielding, respectively [26].

The initial goal of this study was to investigate the rheo-viscoelasticity of concrete, but it was nearly non-existent in literature. Scaling down to mortar, limited studies are available on cement mortar [10,27,28]. Scaling down further to cement paste, studies abound on SAOS tests of cement paste [2,9,12,15,19,29–33]. However, most of the recent studies are directed towards the structural build-up (thixotropy and early hydration) rather than fully characterising the VE behaviour. It is generally believed that aggregates, which makes up about 60–75% of mortar and concrete, are unreactive/inert components/fillers added to cement paste [34–38] to accentuate its rheo-related properties. Indeed, some studies [8,37,39] have attempted to reveal the influence of non-colloidal particles and model aggregates on the rheo-physical properties (such as yield stress, thixotropy and storage modulus) of cement paste. These studies noted that the aggregates truly accentuate the rheo-physical properties. However, the influence of the aggregates on the rheo-viscoelastic properties of cement paste remains largely unknown and unanswered. For example, does the addition of sand/stone in paste/mortar increase or reduce the creep and stress relaxation ability of the paste? Moreover, most practical applications of fresh cement-based materials are in the form of mortar and concrete whose rheo-related behaviours are different and complicated than cement paste [2,10,40]. Typical sources of this complexity are the paste interfacial transition zone with the aggregate [2] and internal frictional interaction of the aggregate. It is, therefore, necessary to exclusively investigate the rheo-viscoelastic behaviour of fresh cement paste, mortar and concrete to examine the progression of the VE behaviour; hence, this study.

Furthermore, most available studies on rheo-related properties of cement-based materials (such as paste, mortar and concrete) are independent studies leading to vastly varying material

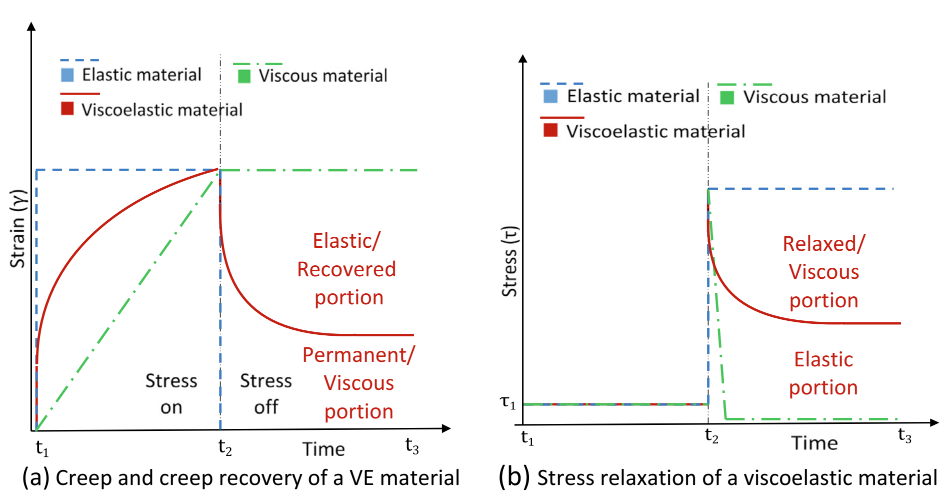


Fig. 1. Viscoelastic behaviour/response to a sustained shear strain and stress.

constituents, instruments' artefacts, and methodology inconsistencies [41]. This doesn't give room to experimentally observe the behavioural progression and links of cement paste-mortar-concrete as the case of this study. For more insights, rheology admixtures were used in this study to systematically reveal the differing influence of the aggregates in the behavioural progression. In addition, admixtures such as the rheology modifiers used in this study influences the rheo-related properties of the cement paste, mortar and concrete [22,42]. While the influence of superplasticiser (SP) and water content on the viscoelastic properties of cement paste has been established by various authors [2,5,12,14,32,43,44], the influence of viscosity modifying agent (VMA) and combined VMA + SP used in this study remains scarce in the literature.

The seemingly big scope of this research emanates from establishing and gaining deeper understanding of the viscoelastic behaviour of fresh concrete, this includes revealing the rheo-mechanical impact of sand and stone on the established viscoelastic behaviour of cement paste. Also, the possible influence of rheology admixtures. This study mainly expatiates on the experimental results and does not focus on the physico-chemical interaction of the paste nor theoretical non-colloidal contribution of the aggregates. Therefore, the novelty of this study lies in improving the body of knowledge and technical data that is scarce in the literature on the viscoelastic behaviour of fresh cement-based materials by progressively incorporating aggregates (fine and coarse, in-order to form mortar and concrete respectively) in rheologically modified cement paste. The resulting 15 mixes were rheologically investigated to establish their viscoelastic behaviour.

2. Experimental framework

2.1. Dynamic shear rheometer

One of the reasons for the scarcity of literature on the rheo-viscoelastic behaviour of cement mortar and concrete is due to the limited availability of sophisticated instruments capable of handling the coarse and heterogeneous nature of the cement mortar and concrete. Small amplitude oscillatory shear (SAOS) application require highly accurate and sophisticated kind of measurements [4,32] which is difficult for materials containing large particles [45]. A special building material cell (BMC 90) capable of testing materials of about 5 mm particles with a modular vane in cup geometry (Fig. 2) [46] was attempted for use. The BMC 90 consists of a cup with a modular insert cage with serrations during testing and a two hollow blades vane (modular stirrer model ST59-2V-44.3/120) with flow breakers to enhance mix-up effects (Fig. 2). The BMC 90 was attached to a Physica MCR 501 rheometer from Anton Paar [47].

The Physica MCR 501 rheometer is capable of both shear stress and strain controlled oscillation while it allows for samples' temperature control via a Peltier temperature device [48]. Although the BMC 90 is advised as a means for relative measurement by the manufacturer, using it is argued as an important step towards closing the gap in knowledge on fresh mortar and concrete's rheo-viscoelastic behaviour. Moreover, conventional geometries (such as parallel plates, concentric cylinders, and cone-plate) associated with SAOS tests of polymer-related researches have been shown to yield imprecise data and cause errors in dispersed/suspension systems [1,49] such as cement-related researches [9,41,50]. In the case of plastic flow tests, these conventional geometries have high sensitivity to sample segregation, sedimentation and friction between particles which are associated with cement-based materials [51]. Furthermore, [9,50,52] using impellers in cylindrical bowls obtained similar rheological information/signature to those of conventional geometries and with lesser variance between replicate samples of the same cement paste materials/mixes. Therefore, it may be concluded that the BMC 90 geometry is a good option for coarse suspension samples, compared to other geometries of rheometers.

In the case of the BMC 90, the slots in the blades of the stirrer prevent progressive migration of particles away from the axis of rotation which is similar in principle to the slotted vane geometry used by [42] to ensure homogeneity during viscosity measurement of cement grouts. The effectiveness of the slots in the BMC 90 is enhanced by the slight edge bend at the end of the blades close to the wall to serve as flow breakers that enhance mix-up effects. The use of slots has also been proposed and shown by studies to effectively reduce wall-sample interactions [23,42,53] which is complemented by the BMC 90′s serrated modular insert cage that prevents wall slippage of samples [54]. It should be noted that while these cited studies are focused on the plastic flow and rotational shearing of cement-based materials where internal friction and migration are pronounced, this current study is mainly focused on the linear viscoelastic range and SAOS. Internal friction and particle migration are minimal/insignificant for SAOS (and LVR) [55]. Attempts made to minimise exogenous error and enhance reproducibility are highlighted in the next section.

2.2. Material properties and mix design

The mix proportions and constituent materials of the mixes are shown in Table 1 while the chemical properties of the cement are

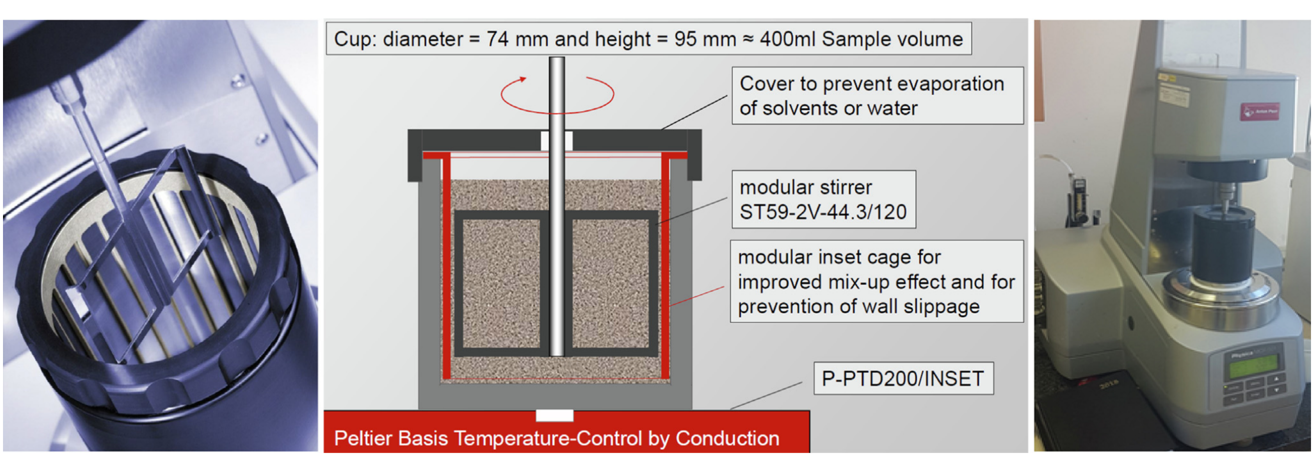


Fig. 2. Special building material cell (BMC 90) [46] and MCR 501 rheometer.

Table 1
Material constituents and properties.

Mixes	Material constituent (kg/m^3)				
	C	CV	CS	CVS	CW
Paste					
Water	217	217	217	217	223
Cement – CEM II 52.5N	395	395	395	395	374
Specific surface area	1.336 m^2/g				
VMA	–	0.6%	–	0.4%	–
Superplasticiser	–	–	0.6%	0.4%	–
w/c ratio	0.55	0.55	0.55	0.55	0.6
Static yield stress (Pa)	27.08	25.69	10.66	8.93	17.30
Mortar					
Water	217	217	217	217	223
Cement - CEM II 52.5N	395	395	395	395	374
VMA	–	0.6%	–	0.4%	–
Superplasticiser	–	–	0.6%	0.4%	–
w/c ratio	0.55	0.55	0.55	0.55	0.6
Malmesbury fine sand	774	774	774	774	796
Water absorption	8.57%				
Specific gravity	2.60				
Static yield stress (Pa)	111.72	78.34	54.18	44.44	85.37
Concrete					
Water	217	217	217	217	223
Cement - CEM II 52.5N	395	395	395	395	374
VMA	–	0.6%	–	0.4%	–
Superplasticiser	–	–	0.6%	0.4%	–
w/c ratio	0.55	0.55	0.55	0.55	0.6
Malmesbury fine sand	774	774	774	774	796
6 mm Greywacke stone	412	412	412	412	407
Water absorption	1.65%				
Specific gravity	2.75				
Static yield stress (Pa)	315.17	304.50	108.55	162.71	161.31
Slump	180	190	240	230	250

C – control; CV – control + VMA; CS – control + SP.
CVS – control + VMA + SP; CW – control + water.

shown in Table 2. Since particle size and distribution are known to influence the rheological properties of suspensions [56–58], the particle size distributions of the dry constituent materials are shown in Fig. 3. A fine natural aggregate/sand (average particle diameter of 0.3 mm) and coarse aggregate/stone (nominal size of 6 mm) were used for the cement-based materials to obtain cement mortar and concrete respectively. The 6 mm nominal size (Table 1 and Fig. 3b) used for the concrete is 1 mm above the size recommended for the BMC 90 (5 mm – Section 2.1). To mitigate the possible effects of the larger stone size, less quantity of stone (cement, sand and stone ratio of approximately 1:2:1) was used in the concrete mixes. That is, the rheometer's torque capacity (maximum normal force and torque of the BMC 90's spindle) was found to adequately handle the ensuing concrete's stiffness for at least 2 h. Satisfactorily, similar test results of initiation of plastic flow of the concrete mixes (in a companion study [59]) were obtained between the established vane-type Germann ICAR rheometer [60] and the BMC 90 as shown in Fig. 4.

The control mix was rheologically modified using polysaccharide-based liquid viscosity modifying agent (VMA), polycarboxylate ester liquid superplasticiser (SP) and water to yield five mixes labelled as C, CV, CS, CVS and CW (see Table 1). The VMA has a specific gravity of 1.0, pH of 9.5, chloride content of less than 0.1% and sodium oxide content of less than 1% while the SP has a specific gravity of 1.05, pH of 7, chloride content of less than 0.1% and sodium oxide content of less than 1%. The admixtures were added by weight of the cement to the mixing water before adding the mixing water to the dried-mixed cement-based constituents in a pan mixer. The dry materials were initially mixed for one minute before adding the mixing water and thereafter mixed for two minutes. The mixes were placed in the BMC 90 without vibration. The end of mixing was taken as time zero for all the tests and it took about 5 min from the end of mixing to the start of each test. This time was maintained for all tests to minimise exogenous error from varying preparation times [12]. After inserting the vane, the samples were allowed to rest for three minutes to reach substantial equilibration from the sampling and inlet of the modular vane disturbance [39]. Fresh samples were prepared for each test (including duplicates) since the viscoelastic and rheological behaviours of cement-based materials are known to be time and shear pre-history dependent [12,19]. At least three fresh samples were tested for the amplitude sweep and at least two for the other tests, the average were reported. All the tests were carried out at a temperature of 23 °C. All these improves the reproducibility of results [61].

2.3. Rheo-viscoelastic behaviour tests

As noted earlier, when a viscoelastic (VE) material is subjected to an oscillating strain, the response stress has a phase lag/angle (δ) which is one of the parameters that define the viscoelasticity. Some other rheo-viscoelastic parameters used to define

Table 2
Chemical properties of the cement.

Oxides	CaO	Al_2O_3	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2	LOI
%	62.7	3.45	2.86	0.51	1.13	0.05	0.26	0.15	19.28	0.18	6.39

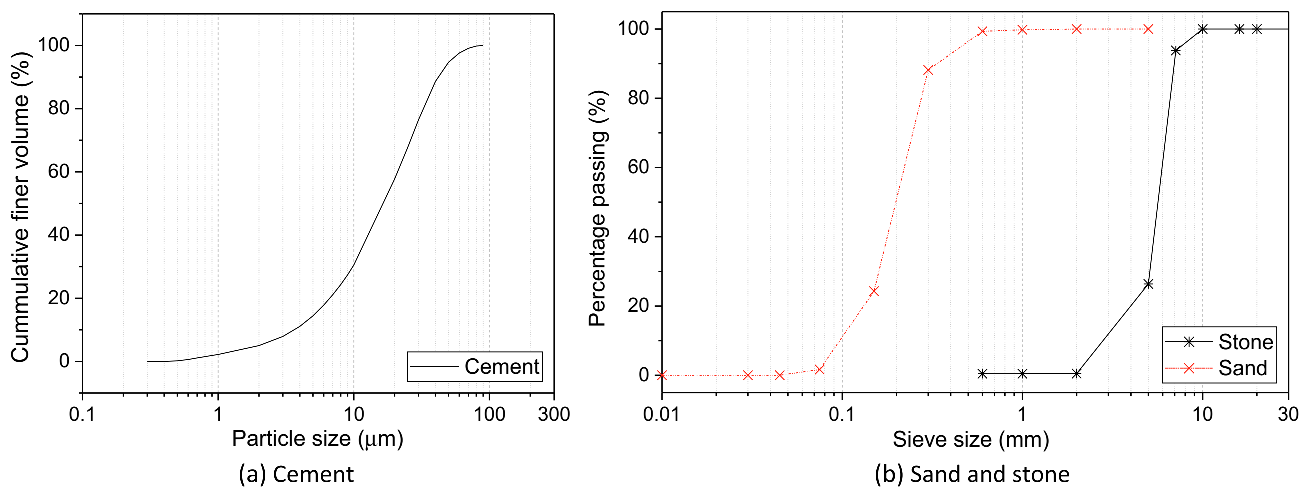


Fig. 3. Particle size distribution of the dry constituents.

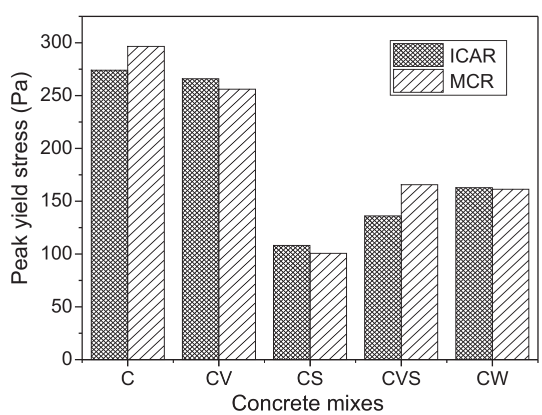


Fig. 4. Comparative results between the Germann ICiAR rheometer and Physical MCR501 rheometer [59].

viscoelasticity include complex shear modulus (G*), storage/elastic modulus (G'), loss/viscous modulus (G"), critical stress/strain (τ_c/γ_c), creep compliance (J), relaxation modulus (G), and thixotropic restructuration [9]. The processing equations [4,5,9,10,12–14] are shown as Eq. (1)–(5). These parameters are obtainable from the tests highlighted in the subsequent sections and indicate the nature, state and microstructure of the test material as shown in Table 3. All the tests were carried out on the cement paste, mortar and concrete respectively.

$$\gamma_t = \gamma_A . \sin(\omega t) \tag{1}$$

$$\tau_t = \tau_A . \sin(\omega t + \delta) \tag{2}$$

$$G^* = \frac{\tau}{\gamma} \tag{3}$$

Table 3
Viscoelastic parameters of various material states (Adapted from [4,9]).

Ideally viscous material	Viscoelastic liquid	Viscoelastic suspension or solid	Ideally elastic material
Viscous	Less viscous	Less solid	Solid
$\delta = 90°$	$90° > \delta > 45°$	$45° > \delta > 0°$	$\delta = 0°$
$\tan\delta \to \infty$	$\tan\delta > 1$	$\tan\delta < 1$	$\tan\delta$ » 0
G'→ 0	G" > G'	G' > G"	G" → 0
$G^* = iG''$	$G^* = G' + iG''$	$G^* = G' + iG''$	$G^* = G'$

$$G^* = G' + iG'' = |G^*|\cos\delta + i|G^*|\sin\delta = \sqrt{\left|G'\right|^2 + \left|G''\right|^2} \tag{4}$$

$$\tan\delta = \frac{G''}{G'} \tag{5}$$

γ_t and τ_t are the oscillating strain and stress respectively, γ_A and τ_A are the strain and stress amplitude, ω is the angular frequency, t is the time, G^*, G' and G'' are the complex, storage and loss modulus respectively, δ is the phase lag between the shear strain and stress, $i^2 = -1$.

2.3.1. Amplitude sweep test

This test yields some of the viscoelastic parameters of the cement-based materials, such as G*, G', G", γ_c (LVR limit), and δ. It involved the application of an increasing strain/stress (amplitude) at a constant shearing rate (frequency). For the purpose of this study, a controlled strain sweep was done from 10^{-4}% to 10^2% at a logarithm ramp of 10 points/decade and a frequency of 10 rad/s. The amplitude sweep testing protocol is shown in Fig. 5a. The choice frequency value was preliminarily determined to be adequate for linear VE response. The LVR is taken as the range of strain where G' remains constant (on a logarithm scale), that is, the sample behaves as an elastic material. The limit of this range defines the γ_c and is taken as the strain associated with a 10% reduction in G' [4,62]. This method is preferable because not all tests (e.g. Fig. 8a) show an easily identifiable deflection/reduction in G' [5]. The G* defines the stiffness of the VE material (Eq. (3)) to shearing, which has elastic (G') and viscous components (G") [1]. G' is the storage modulus which accounts for the elastic energy stored by the VE material and reflects the crosslinking and interactions between the particles while G" is the loss modulus that accounts for the dissipated/consumed energy due to the viscous component of the viscoelasticity [10,16].

2.3.2. Frequency sweep test

This involved the application of an increasing shearing rate at a constant amplitude (shear strain) within the LVR to monitor the VE response. A sweep from 100 rad/s to 0.1 rad/s at a logarithm ramp of 15 points/decade at an amplitude strain of 10^{-2}% was carried out on all the cement-based materials. The frequency sweep testing protocol is shown in Fig. 5b. The selected amplitude strain for the frequency sweep was based on the earlier determined LVR from the amplitude sweep.

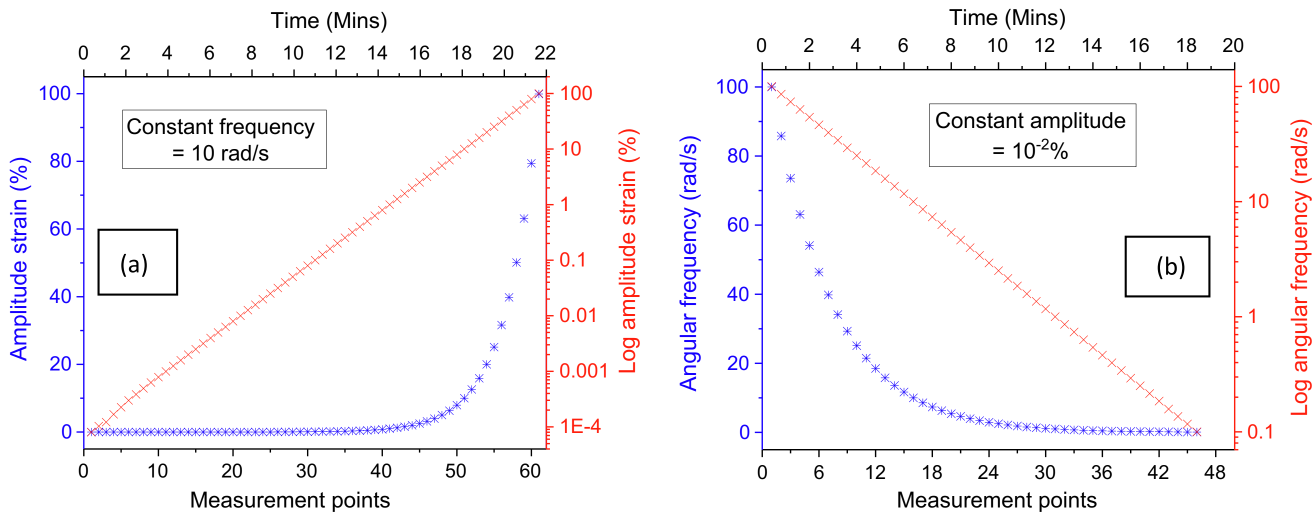


Fig. 5. Test protocol for the (a) amplitude sweep (b) frequency sweep.

2.3.3. Creep and creep recovery test

This test involved the application of an instant and constant shear stress (τ_0) from time t_1 to t_2 (Fig. 6a) while measuring the deformation of the sample between the time interval (Fig. 1a). The shear stress is then removed at time t_2 while the deformation recovery with time is measured up to time t_3 [4]. For this study, 10 min and 30 min intervals ($t_1 - t_2$ and $t_2 - t_3$) were used. The time intervals were found to be sufficient for all the mixes to reach steady strain values. The creep and creep recovery testing protocol is shown in Fig. 6a. $\tau_0$values used for each mix are shown in Table 4 and were taken as approximately 50% of the yield value [63,64]. The measured deformation and recovery can be expressed as creep compliance and creep recovery compliance (J) as shown in Equation (6) [4,29]. This makes the result material-dependent and independent of the applied shear stress [4]. The percentage creep recovery of the mixes was also evaluated according to Equation (7).

$$J(t) = \frac{\gamma(t)}{\tau_0} \quad (6)$$

$$\text{Percentage recovery} = \frac{J_m - J_e}{J_m} x100\% \quad (7)$$

where $J(t)$ is the creep compliance, $\gamma(t)$ is the measured strain, t is the time, τ_0 is the constant applied stress, J_m is the maximum creep compliance, and J_e is the equilibrium creep compliance after recovery.

2.3.4. Stress relaxation test

For this study, a pre-strain (γ_1) of 2% of the relaxation strain was applied from time t_1 to t_2 (Fig. 6b) to level-out the possible effects of pre-stresses due to sampling [4]. Thereafter, an instant strain (γ_0) was applied at time t_2 and kept constant up to time t_3 while recording the stress response with time (Fig. 1b). The stress relaxation testing protocol is shown in Fig. 6b. The value of γ_0 was taken as approximately 50% of the yield strain (Table 5) [63,65]. The results can be expressed as relaxation modulus (Equation (8)) to yield a material-dependent property that is independent of the applied strain [4]. The percentage of stress relaxation was also evaluated using Equation (9).

$$G(t) = \frac{\tau(t)}{\gamma_0} \quad (8)$$

$$\text{Percentage relaxation} = \frac{G_0 - G_e}{G_0} x100\% \quad (9)$$

where $G(t)$ is the relaxation modulus, $\tau(t)$ is the measured stress, t is the time, γ_0 is the constant applied strain, G_0 is the instantaneous relaxation modulus, and G_e is the equilibrium relaxation modulus.

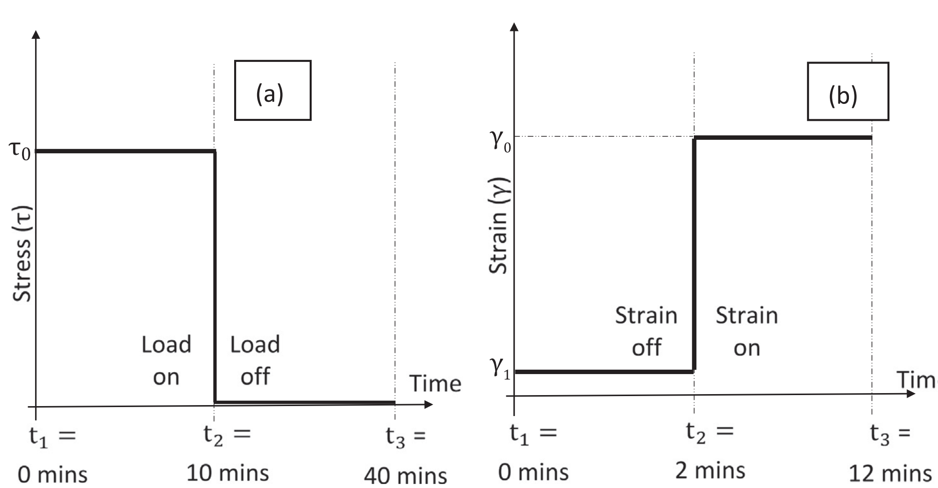


Fig. 6. Schematic test protocol for the (a) creep and creep recovery (b) stress relaxation.

Table 4
Shear stress values (τ_0) for the creep and creep recovery test.

	C (Pa)	CV (Pa)	CS (Pa)	CVS (Pa)	CW (Pa)
Paste	12	10	4	4	8
Mortar	55	40	26	21	40
Concrete	148	148	194	80	80

Table 5
Shear strain values (γ_0) for the stress relaxation test.

	C (%)	CV (%)	CS (%)	CVS (%)	CW (%)
Paste	0.1	0.1	0.05	0.08	0.12
Mortar	0.3	0.2	0.2	0.2	0.2
Concrete	0.8	0.8	0.8	0.8	0.5

2.3.5. 3ITT thixotropy test

The three interval thixotropy test (3ITT) consists of three intervals of test, the first is a test of constant amplitude and frequency within the LVR to measure the reference state of the sample without interrupting the microstructure. This is followed by the second interval, where a high amplitude and frequency is applied to destroy the sample's microstructure. The third interval is the same test as the first, which measures the reversible restructuration (degree and speed of recovery) of the sample. An amplitude strain of 0.01% at 10 rad/s was used for the first and third intervals. The 3ITT testing protocol is shown in Fig. 7 The parameter of interest examined during the intervals to give insights into the microstructure was G' since it is accepted to measure the structure's rigidification [66]. The time-dependent nature of the cement-based materials was examined by the thixotropy test.

3. Results and discussion

Generally, for the rheo-viscoelastic measurements, the cement paste and mortar mixes have a smooth response (torque measurements) to the instrument's induced strains (from the vane) while the concrete mixes results have more noise due to increased stiffness from the coarse aggregate. To evaluate the repeatability of results, three to five new samples of fresh concrete mixes were tested for the amplitude sweep and the variation in the storage modulus reported in Table 6. The coefficient of variations show that the results are reasonably repeatable.

3.1. Viscoelastic parameters of the cement-based materials

Fig. 8 shows the response of the cement-based materials to the strain sweeps. Fig. 8a reveals that the cement paste Mixes C and CV have similar VE behaviour with more elastic tendencies than the other mixes. That is, the inclusion of viscosity modifying agent (VMA) in cement paste did not significantly influence the VE behaviour while the inclusion of superplasticizer (SP), VMA and SP (VMA + SP), and increased water did reduce the elastic component of the VE properties while increasing the viscous component. This can be deduced from the trends of the storage/loss modulus and phase angle of the paste mixes vis-à-vis Table 3. However, the addition of aggregates in the mixes remarkably dampened these effects of the rheology modifiers. Explicitly, the addition of sand to the cement paste caused an average increase of 9% in G' for Mixes C/CV and 49% for Mixes CS/CVS/CW which resulted in similar G' for all the mortar mixes while the addition of stones to the mortar caused an average increase of 26% in Mixes C/CV and 24% in Mixes CS/CVS/CW. The rheology modifiers also influenced the G" values of the concrete mixes with no significant influence on the G' (Fig. 8c). That is, the rheology modifiers caused the concrete to exhibit more flowability and energy consumption/dissipation (G") with good stability/stiffness (G*) [10]. These results suggest that satisfiable conclusions about concrete's VE behaviour may not be approximate-able from that of cement paste as generally suggested in literature, since the rheology modifiers diversified the trend of behaviour. This is because authors [8,37,38] often specify that sand and stone are unreactive solid components in mortar and concrete and therefore, may only magnify the rheo-related properties and not diversely influence it as obtained in this study. However, as observed, the behavioural trend of the mortar is closer to that of concrete than that of the paste. Also, the increase of coarse solid volume fraction can potentially reduce the effects of rheology admixtures in cement-based materials.

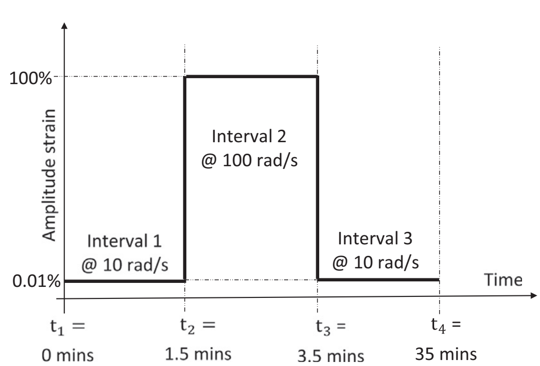


Fig. 7. Schematic test protocol for the 3ITT thixotropy test.

Fig. 8d shows the G' and critical strain (γ_c) obtained from the amplitude sweep of the cement-based materials. Some of the factors that influence G' include particle interaction/adhesion/bridges/linking, particle packing density and level of particle dispersion [2,10,12,13,19]. The rheology modifiers are known to influence these factors [22]. VMA is known to cause microstructure thickening by polymer entanglement [67,68], thereby, improving the particles' bridging that can nullify its negative impact on G' due to dilution. The possible reason for the reduction of G' of the cement paste by SP, VMA + SP, and increased water is their increased contribution to particle dispersion (evident in the lower static yield stress in Table 1). In the same vein, the increased particle packing of mortar and concrete caused the increased progression in G' with reduced effects of the rheology admixtures. The LVR of cement paste in this study is in the order of 10^4 Pa and 10^{-2}% for the G' and γ_c respectively, which is also the general consensus in the literature [5,9,10,12,14,15]. The sand/stone in mortar/concrete increased the γ_c to the order of 10^{-1}% but the stone generally reduced the absolute value compared to that of mortar. That is, the inclusion of sand in cement paste yielded a more ductile

Table 6
Evaluation of repeatability of test results.

Mixes	C	CV	CS	CVS	CW
Average G' (kPa)	30.26	28.63	25.37	27.53	27.70
Number of samples	3	4	5	4	3
COV (%)	0.4	2.4	5.6	4.2	3.0

G' – storage modulus, COV – coefficient of variation.

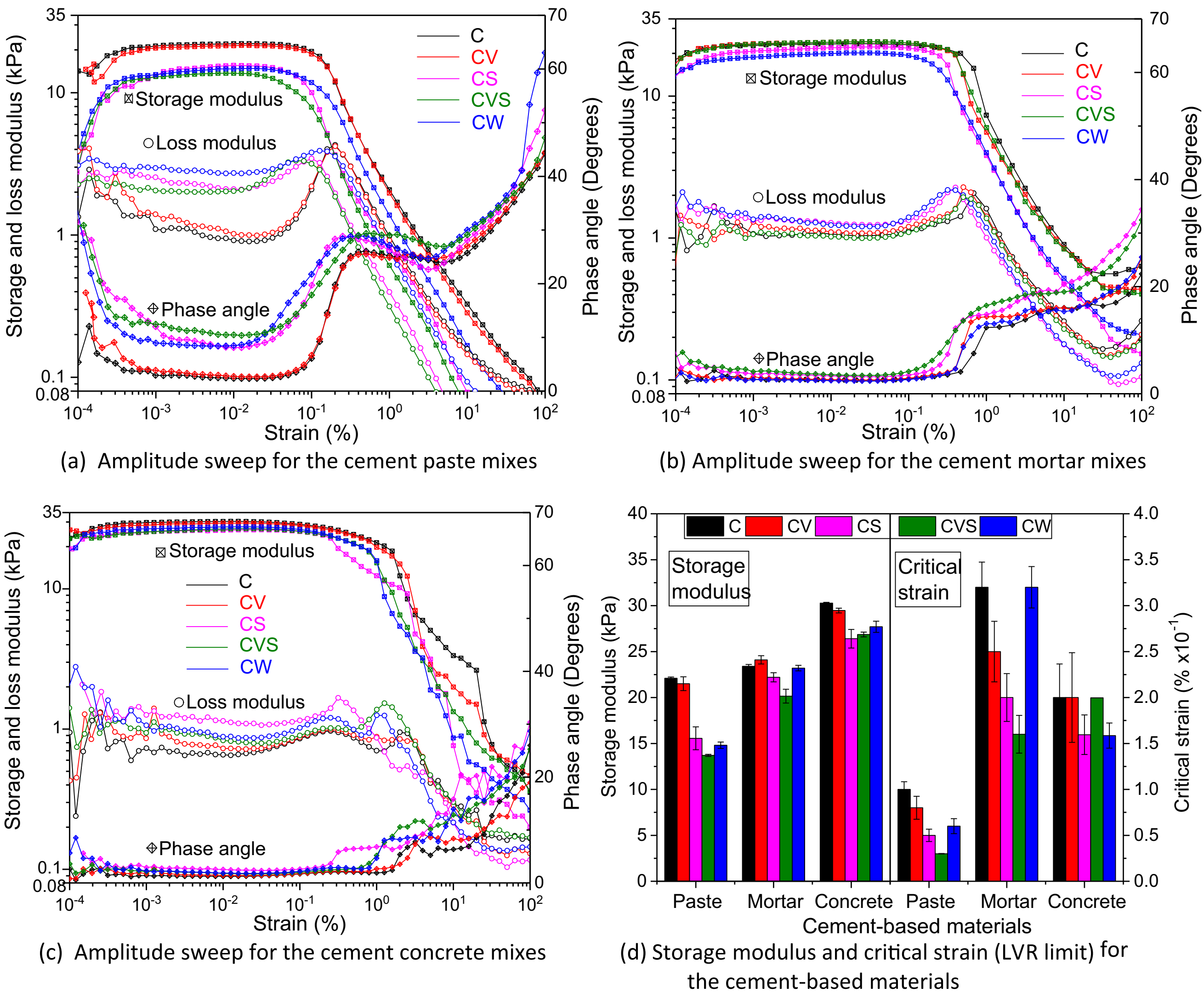


Fig. 8. Results of the amplitude sweep for all mixes.

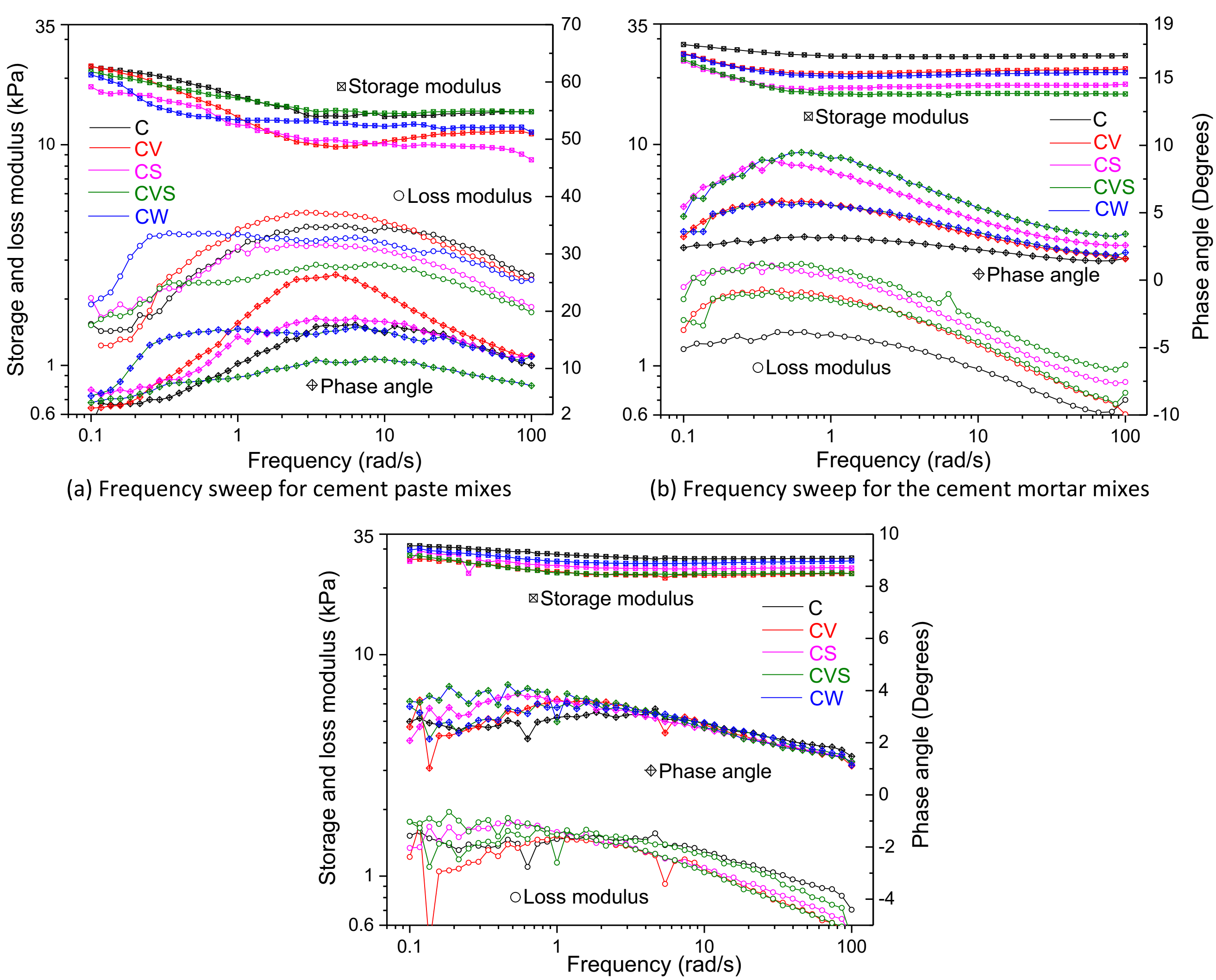
cement-based material while the addition of both sand and stone yielded a more brittle cement-based material. Ideally, wet cement paste has higher bond area and better lubricating effects around fine sand than larger sized stones [34] which could lead to the more ductile cement mortar. Furthermore, the bigger the size of aggregates, the weaker the interfacial transition zone between the aggregates and the bulk paste [69] leading to a more brittle cement-based material. The rheology modifiers generally reduced the γ_c (that is, the linear viscoelastic range – LVR) of cement-based materials.

As noted earlier, the VE response of the cement-based materials beyond the LVR is synonymous to that of large amplitude oscillatory shear (LAOS) tests that gives insight into the viscoplastic response [10,13] and is notable on Fig. 8a-c as the reduction of the G'/G" and increase in δ. For the cement paste (Fig. 8a), Mixes C/CV have similar response and Mixes CS/CVS/CW behaved similarly while for the mortar (Fig. 8b), the observable pattern was C/CV/CVS and CS/CW. This response pattern for the mortar was also obtained for the concrete in the δ plot while the G'/G" plots of the concrete mixes have too many fluctuations to deduce patterns. These patterns of the cement paste, mortar and concrete can be associated to the envisaged viscoplastic behaviour of the mixes, confirming the earlier conclusion regarding the differing progressive influence of aggregates on rheo-related properties of cement-based materials due to the presence of admixtures.

3.2. Influence of shearing rate on the viscoelastic response

Fig. 9a shows the response of the cement paste to the frequency sweep, it should be noted that the sweep was done decreasingly from 100 rad/s to 0.1 rad/s within the LVR. The pastes' microstructures were generally stable for the simulated short-term deformation, that is, a linear response was observed from 100 rad/s down to about 4 rad/s where there was an increase in the storage modulus (G') of the mixes. The increase in the storage modulus at lower frequencies can be due to shear thickening (that is, pseudo-strain hardening [26]) which emanates from the continuous strain oscillations. That is, the paste microstructure can be said to have reached a response peak where the reducing rate of shearing allows for particle flocculate [16]. Starting the sweep test for the fresh sample at a high shear rate of 100 rad/s, the cement paste couldn't relax the stress at each repetition of strain leading to residual stress [2]. Hence, there's an increase in δ/G" down to 4 rad/s where the stress becomes adequately relaxed which then allows for flocculation. Expectedly, there ought to be a microstructure destruction (decrease in G') during this period [10] (slightly shown by Mix CV). Therefore, the relatively stable G' signifies that an inherent simultaneously occurring thickening due to the straining was occurring. This form of thickening for similar concrete mixes due to long term shearing (deformation) was qualitatively reported in a companion paper [22] as rheopexy. Furthermore, He *et al.* and Nachbaur *et al.* [9,10] stated that if the frequency sweep shows no influence on G', then, no structural changes are occurring while Sun *et al.* [2] reported that hydration has no substantial influence on G' of cement paste with similar w/c ratio until about 1 h (dormant period). In essence, the long-term linear deformation behaviour of the cement paste, without the substantial influence of hydration, may be in the form of a shear thickening (pseudo-strain hardening).

Increased water content (Mix CW) caused the thickening to start occurring only at a shear rate of approximately 0.3 rad/s while the viscosity modifying agent (VMA in Mix CV) magnifies the thickening. This could be due to the liquid phase thickening by VMA's polymer entanglement [67,68]. Saasen *et al.* (1991) also reported similar influence of a propanesulfonate-based copolymer on oilfield cement slurries. The response of the cement mortar mixes shown in Fig. 9b is similar to that of the cement paste but at a lesser magnitude and the thickening starts at a lower shearing rate of about 0.6 rad/s down to about 0.1 rad/s. This implies that the inclusion of sand in cement paste reduces the variation/instability of the microstructure to extended (but low) linear deformation. The addition of stones to the mortar to make concrete (Fig. 9c)



(a) Frequency sweep for cement paste mixes

(b) Frequency sweep for the cement mortar mixes

(c) Frequency sweep for the cement concrete mixes

Fig. 9. Frequency sweep results of the cement-based materials.

further reduces the variation/instability. The comparative reduction due to the increasing volume fraction of the aggregates is also evident from the decreasing plot scale of the phase angle (cement-mortar-concrete) of Fig. 9a-c.

It can, therefore, be concluded that increase in the coarse solid volume fraction of cement-based materials tends to improve the microstructure stability to varying shearing rate and extended linear deformation. In addition, the different frequencies (4 rad/s for paste and 0.6 rad/s for mortar) where stability initiates underscores the differing influence of the aggregates.

3.3. Creep and creep recovery

The creep and creep recovery compliance of the cement-based materials shown in Fig. 10 reveals the viscoelastic response of the microstructure to steady stress application and removal. Compliance is the corresponding strain due to the application of unit stress. Note that 50% of the yield stresses were adopted for each of the mixes (Table 4) which allows for equitable comparison. Furthermore, the viscosity and angular velocity were monitored to ensure there was no bifurcation that signifies the start of transient flow [13,19,29,70]. The rheology modifiers influenced the creep of the cement-based materials with the greatest influence on the cement paste (Fig. 10a) while increase in the coarse aggregate volume and size reduced the creep ability (significantly reducing y-axis scale of Fig. 10a, b, c). Viscosity modifying agent (VMA) reduced the creep of the cement paste by 81% while superplasticiser (SP), VMA and SP (VMA + SP), and water increased the creep compliance by 976%, 1728%, and 219% respectively. Although the paste Mix CVS showed significant creep, it still recovered substantially more than the control mix (see Fig. 11a).

Fig. 10a shows further that the paste mixes experienced a reduction in strain after the peak value which is before the recovery phase, and pastes with higher creep showed more this reduction. This implies that a sudden application of stress could cause a corresponding thickening in the microstructure of cement paste. Fig. 10b shows that only the inclusion of SP in the mortar mixes caused the pseudo-strain hardening/thickening while only concrete Mixes C/CW in Fig. 10c slightly exhibited the thickening. It should be noted that unlike the paste mixes, the mortar and concrete mixes showed more instantaneous recovery before the viscous delayed recovery (see Fig. 1a) showing that the increased coarse solid volume fraction caused more elastic behaviour. Likewise, the increased elastic behaviour can be deduced from the reduced values of creep compliance due to the increased coarse solid volume fraction. These highlighted differing influences of the rheology modifiers in the paste-mortar-concrete progression of the creep and recovery behaviour reiterates that accurate conclusions should not be made about the VE behaviour of concrete/-mortar from that of the paste.

From Fig. 10c, Mixes C/CW showed a creep recovery slightly below zero, that is, the rheometer's vane (after stress removal) returned beyond the initial position at the application of the stress. The reason for this observation is unknown and not found in the literature. However, it is suggested that the sudden relieve of the liquid-filled micropores due to the stress removal may have caused some microscopic softening/yielding of the liquid in the micropores, thereby, diffusing through the micropores to assist recovery. Evidently, Mix CW with more water and liquid phase showed more of the negative creep recovery. Moreover, for hardened concrete, the presence of free water (including some adsorbent solids) is believed to be responsible for creep [71–73] by diffusing through the pores under a continuously applied load. Some studies [74–76] have also shown that more capillary water and pore humidity caused a higher rate of creep in cement-based materials. Undeniably, the roles of water redistribution (within the microstructure) in the behaviour of cement-based material under loading has been the focus of recent studies such as [74,77,78]. It should be noted that this suggested phenomenon for the negative creep compliance values is dissimilar from the reduction in the creep/strain of the cement paste mixes after the peak values (Fig. 10a). Notably cement paste and mortar did not show this behaviour highlighting the VE behavioural progress.

Fig. 11a shows the percentage recovery of the cement-based materials, the more the recovery, the more elastic the mix (viscoelastic solid). The viscoelastic solid kind of recovery in Fig. 11a (that is, above 35%) shows the fact that the creep phase did not cause transient damage to the samples' microstructure [19,29] which can potentially cause a viscoelastic liquid recovery (<5%). Though Jayasree *et al.* (2011) reported that SP reduced creep recovery of cement paste, the rheology modifiers (including SP) in this study generally improved the recovery of the cement paste. The earlier suggested phenomenon on micropore liquid yielding could also be responsible here, especially for Mixes CS, CVS and CW with higher dispersed structure (evident in their lower static yield stress - Table 1) while the VMA polymer entanglement could help Mix CV's elastic recovery. The figure also reveals that Mixes CV/CVS consistently showed less recovery from the deformation as the

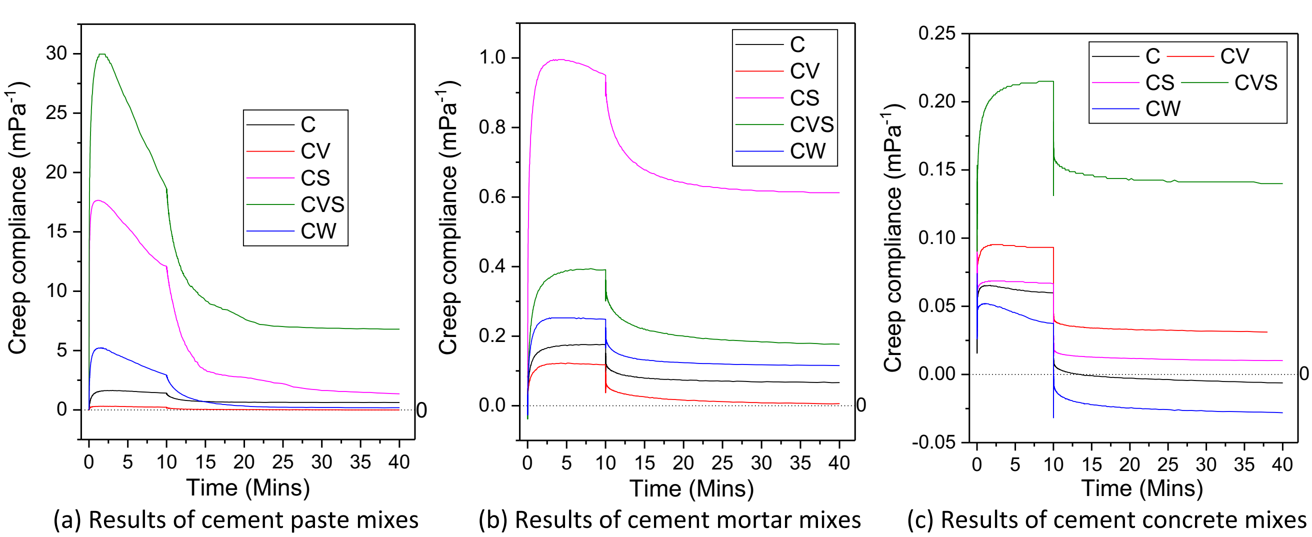


Fig. 10. Creep and creep recovery test results for the cement-based materials.

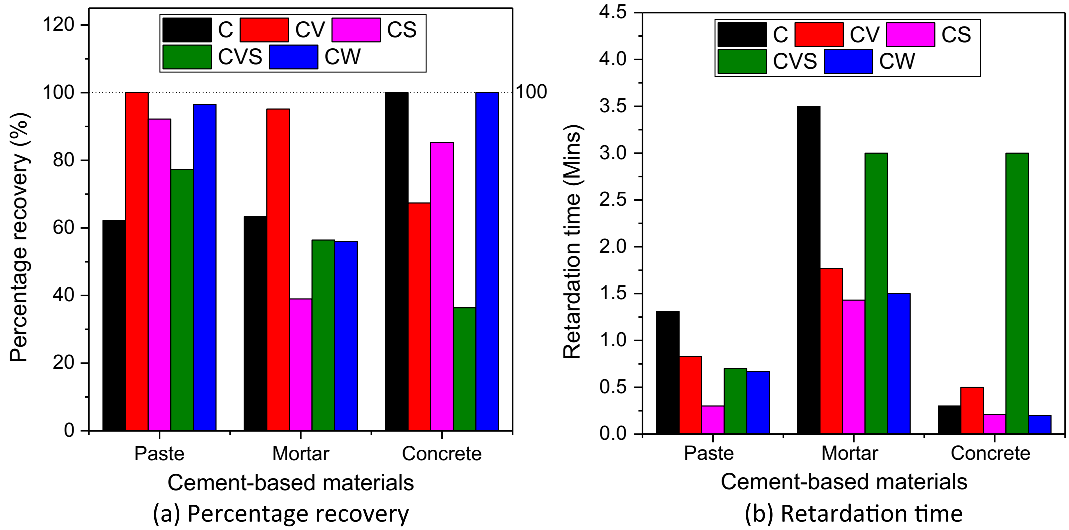


Fig. 11. Percentage recovery and retardation time of the cement-based materials.

aggregate volume increased. That is, increased aggregate reduced the ability of the VMA's polymer entanglement to contribute to elastic deformation behaviour. While the rheology modifiers improved the cement paste recovery (elastic behaviour), they tend to reduce the recovery of the mortar and concrete highlighting the differing influence of the aggregates.

Fig. 11b shows the retardation time of the cement-based materials. It quantifies the delayed response of the cement-based material (in terms of time) to the applied stress and can be referred to as delayed deformation or elasticity [4]. It is the time taken for a VE material to reach the maximum creep/strain (which is taken as 95% of the peak compliance value for this study [4]), an ideally elastic material will have an instantaneous creep (response) with zero-time delay as shown in Fig. 1a. It can be observed from the results that the sand in the mortar mixes tends to cause an increased delay while the stones in the concrete mixes reduced the delay. This reiterates the ductile tendency of the cement-based materials due to the inclusion of sand and the ductility reduction due to the additional inclusion of stones, as observed for the critical strain in Section 3.1.

3.4. Stress relaxation

Fig. 12 shows the stress relaxation modulus of the cement-based materials. Stress relaxation modulus is the stress due to the application of unit strain. Note that 50% of the yield strains were adopted for each of the mixes (Table 5) which allows for equitable comparison. The instantaneous stress relaxation modulus (G_0) values of the mixes are shown in the legends of Fig. 12 and the points marked on the plots. The figure reveals that the cement paste (Fig. 12a) exhibited higher instantaneous stress than that of the mortar (Fig. 12b) while that of the mortar is similar to that of the concrete (Fig. 12c). This is because the G_0 is a function of the solid-like properties of a sample [79]. That is, for both the mortar and concrete, a unit strain causes similar instantaneous stresses though the equilibrium relaxed stresses of the concrete mixes are higher than that of the mortar due to concrete's increased elastic properties due to increased aggregate volume fraction. Moreover, the influence of the rheology modifiers on the instantaneous modulus became dampened due to sand and stones (cement-mortar-concrete) as similarly obtained for the storage modulus in Section 3.1.

Similar observations as that of the creep compliance are also visible in Fig. 12a. That is, there is an increase in stress after the maximum relaxation (plot trough) for mixes containing the rheology modifiers while there was a decrease in strain after the maximum creep (plot peak) for the creep test. Some authors have argued that relaxation and creep are inverse of each other for hardened concrete [71,80–82] and that creep is responsible for stress relaxation of hardened concrete [83,84]. The noted similar observations between the creep and relaxation results of fresh cement-based materials, therefore, tend to support this argument. That is, the application of the step strain by the rheometer's vane can inherently cause creep in the direction of the vane's movement, leading to stress relieve. The increase in stress after the maximum relaxation can be due to the microstructure thickening as explained for the creep behaviour. The progression of cement paste-mortar-concrete (that is, increasing aggregate volume) generally reduced this microstructure thickening. While well dispersed paste and mortar mixes (yield stress in Table 1) consistently showed this phenomenon, only Mix CW (containing more water content) slightly exhibited this phenomenon for the concrete mixes which reiterates the underlining cause of stress relaxation (movement of the liquid phase of concrete through its pores [71]). In fact, a completely dry hardened concrete practically exhibits no relaxation [71].

Fig. 13a shows the percentage relaxation of the cement-based materials and reveals that Mixes C/CV consistently showed a reduction in their ability to relax stress due to aggregate inclusion (paste-mortar-concrete) while the other mixes only showed significant reduction due to the inclusion of stones. The lesser the relaxation ability, the more the elastic component of the response [4]. Fig. 13b shows the time needed for the cement-based materials to relax the applied stress which is taken as 95% of the equilibrium modulus and referred to as relaxation time [4]. Paste Mix C and mortar Mixes C/CV have very high relaxation times (compared to the other paste/mortar mixes) because they did not exhibit the increase in modulus after relaxation. However, a general increase in relaxation time was obtained in the sequence of cement paste-mortar-concrete showing the progressive influence of increased aggregate volume fraction and size.

3.5. Time dependency of viscoelastic behaviour – structuration

Fig. 14 shows the results of the three interval thixotropy test (3ITT), note that measurements were not recorded in the second interval where the samples' microstructure were destroyed. The low and rapidly increasing values of the storage modulus (G') at

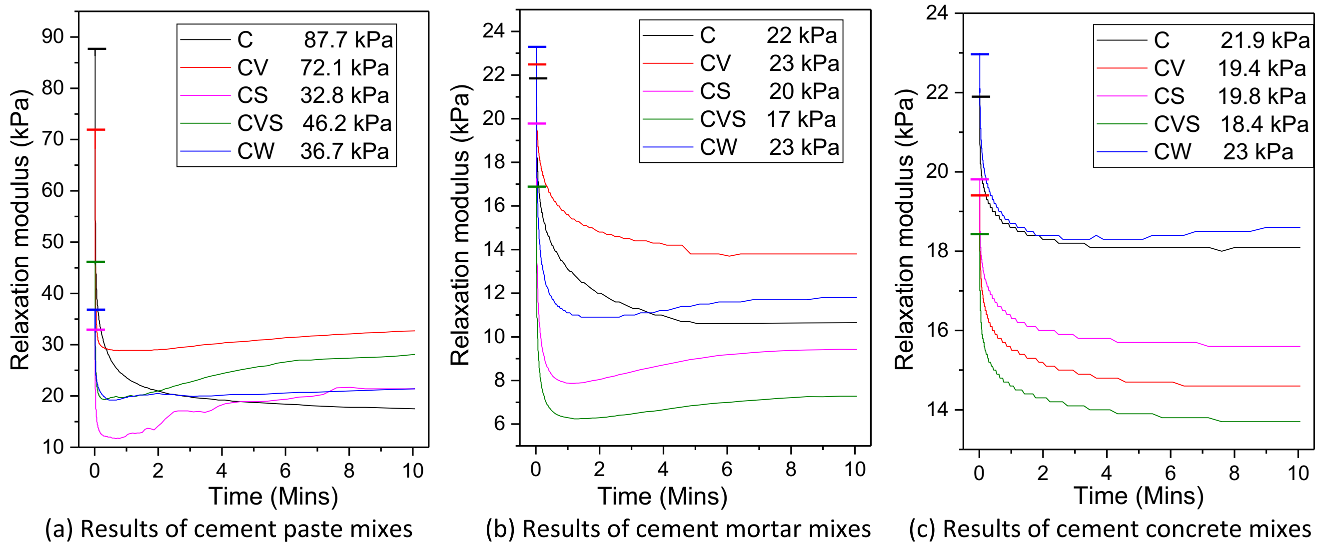


Fig. 12. Stress relaxation test results for the cement-based materials.

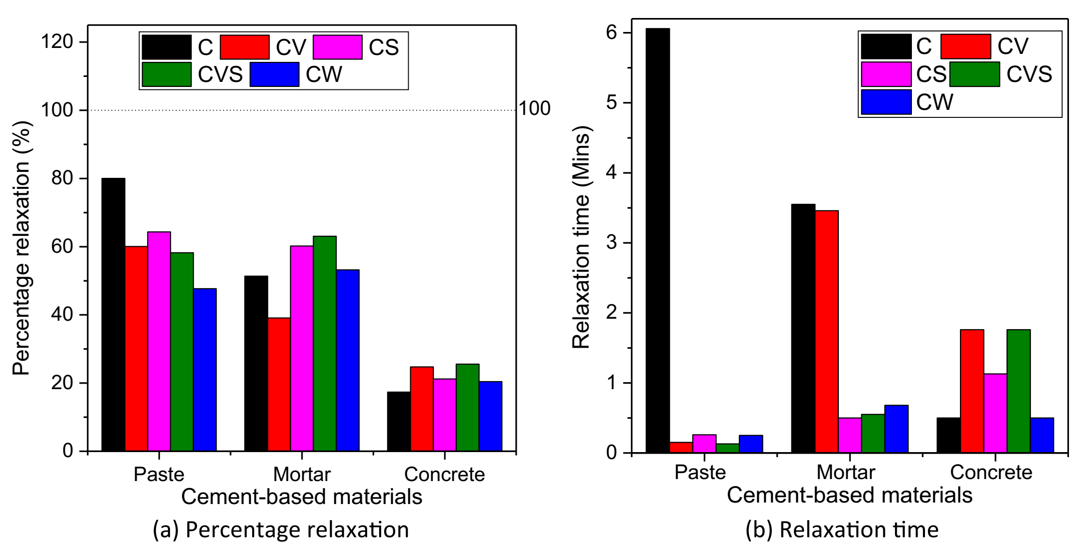


Fig. 13. Percentage relaxation and relaxation time of the cement-based materials.

the first interval for the cement paste Mix CS may be due to sampling disturbance. This rapidly increasing values are similar to that obtained at the lowest strains of the amplitude sweep (Fig. 8a) and reported by some authors as an initial fast flocculation of cement paste after mixing [9,14,85,86]. It should be noted that leaving the paste sample to rest more than three minutes (as stated in Section 2.3) causes the cement particles to settle over time and gather water on top due to the relatively high water-cement ratio (0.55). It is, however, believed that comparable results to other mixes are obtainable since the first interval serves as a reference for the same sample (this is evident with CS having the lowest G' at the start of the third interval). The third interval of the cement-based materials, which shows the recovery/restructuration of the cement-based materials, has two stages, an initial rapid restructuration and a later steady structuration [6,9,87,88]. The initial rapid restructuration is linkable to the flocculation of the cement-based particles [5,9,18,86] and the later structuration is mainly due to hydration [18,32,89]. This phenomenon has also been recently supported by [90].

Fig. 15 shows the rate of restructuration at the third interval of 3ITT test with emphasis on the initial stage of rapid recovery (using log scale). As expected, the cement paste mixes (Fig. 15a) have an initial increasing rate of recovery (except for Mix CV) due to the ability of cement particle to quickly coagulate/flocculate as noted earlier. The initially high but decreasing rate of Mix CV can be due to the liquid thickening of the viscosity modifying agent (VMA) while the lowest flocculation rate of Mix CS can be due to the repulsive dispersion of the superplasticiser (SP). The inclusion of sand and stones in the mortar and concrete mixes limited the initial increasing rate of restructuration. By implication, the inclusion of aggregate (increase in coarse solid volume fraction and size) in cement-based materials inhibits flocculation that translates to an initial fast structure recovery, thereby, reduces the ability for flocculation-driven structuration/thixotropy. The bar chart insets in Fig. 15a-c show the recovery time for the mixes to reach their reference structure at the first interval of the 3ITT test. The increase in aggregate volume fraction generally delayed the recovery since the cement content is the main source of the restructuration. In

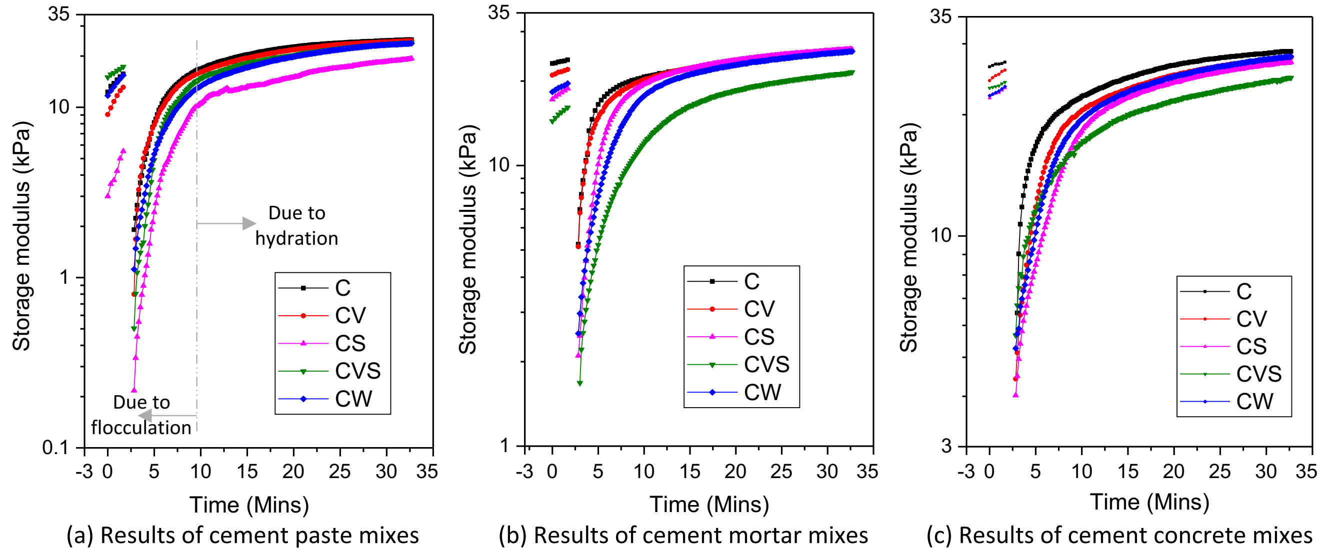


Fig. 14. Three interval thixotropy test results for the cement-based materials.

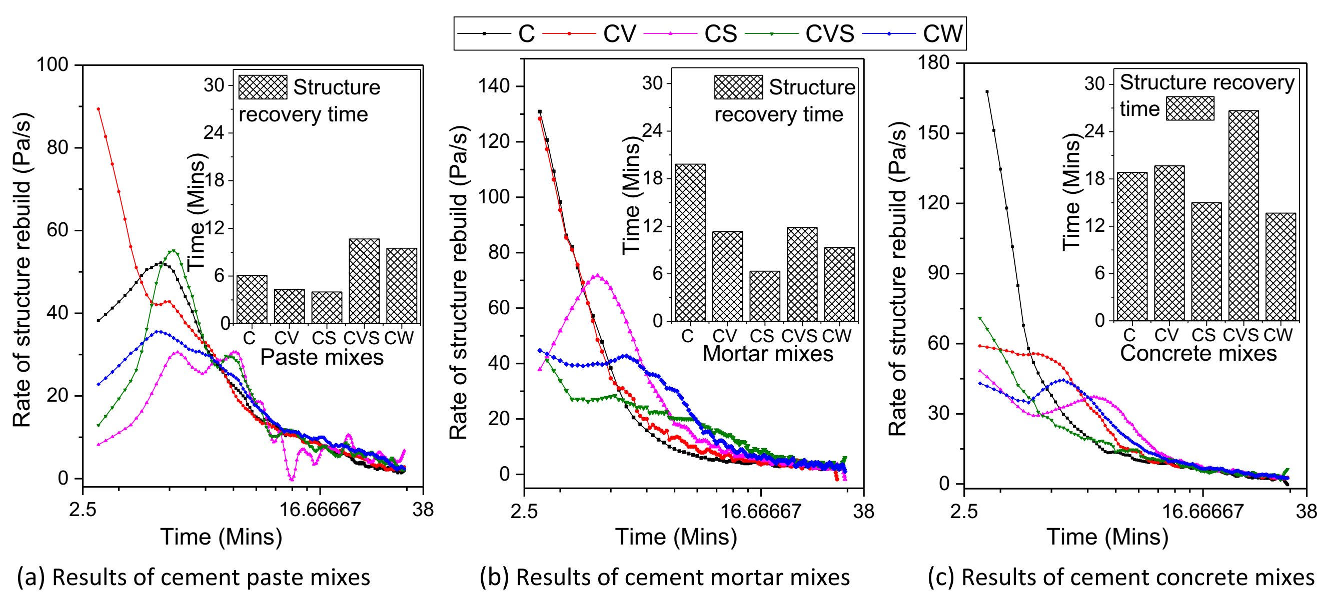


Fig. 15. Rate of restructuration and structure recovery time.

fact, the recovery of all the cement paste mixes were within the flocculation-driven period highlighted in Fig. 14a.

All the cement paste mixes (Fig. 14a) showed similar structures (G') (at about 27 min) at the later stage of restructuration except for Mix CS which is due to its initial low G' at the first interval. The mortar mixes (Fig. 14b) achieved similar structures (at about 17 min) quicker than the cement paste while the concrete mixes could not achieve similar structures by the end of the test. This implies that aggregate in cement-based materials tends to diversify how the rheology modifiers influence hydration-driven structuration. From the previous paragraph and earlier statement, it can be said that early structuration/thixotropy after mixing associated with flocculation/coagulation/agglomeration [5,9,18] of cement paste particles becomes reduced and less-pronounced for concrete (due to aggregates) in which hydration (CSH bridges) becomes the major source of structuration/thixotropy [18]. Oftentimes, studies [5,32,91] suggesting flocculation as source of structuration/thixotropy made use of cement paste.

4. Conclusion

This study experimentally evaluated the rheo-viscoelastic behaviour of rheologically modified fresh cement-based materials. The cement-based materials are paste, mortar, and concrete which progressively allow for examining the trend in the viscoelastic (VE) behaviour and the influence of rheology modifiers. This was carried out using dynamic shear rheometry towards understanding and establishing the viscoelastic behaviour of concrete. The following inferences and conclusions can be made.

- The general trend of behaviour of the control cement paste, mortar and concrete is that, the more the coarse solid volume fraction and size, the more the linear elastic behaviour and vice-versa. However, the rheology modifiers diversified this trend of VE behaviour.
- The addition of aggregates remarkably dampens the effects of the rheology modifiers on the VE behaviour of the cement-based materials.
- Satisfactory conclusions on the VE behaviour of mortar and concrete may not be approximate-able from that of cement paste as generally suggested by in literature, especially, those containing admixtures such as rheology modifiers. The aggregates progressively diversified both the rheo-viscoelastic and viscoplastic behaviour rather than just accentuating the behaviour. The rheo-viscoelastic properties of the cement mortar are, as shown in this study, closer to that of the concrete than that of the paste.
- The inclusion of sand in the cement paste tends to yield a more ductile cement-based material (mortar) in the fresh state while including both the sand and stone tend to make the ensuing concrete more brittle. All the rheology modifiers generally decreased the critical strain of the cement-based material in the fresh state.
- Without the substantial influence of hydration, fresh cement-based materials tend to have a stable VE response to quick/impact linear deformation while the microstructure tends to thicken (pseudo-strain hardening) due to low and extended linear deformation because of the particles' structuration. Progressive addition of the aggregates tends to reduce the structuration and improve the microstructure stability to varying shearing rates.
- Similarly, sudden application of step stress/force can cause the microstructure of fresh cement-based material to thicken. The aggregates reduce this thickening effect. Furthermore, the sudden relieve of the stress/force can cause the yielding/softening of the micropore liquid which can further assist in the creep recovery.
- Quick stress relaxation from a step strain application can also be followed by microstructure thickening. Increased aggregate volume fraction reduced this effect.
- Increasing aggregate solid volume fraction and size reduce the flocculation-driven time-dependent VE behaviour (structuration) of the fresh cement-based material, making hydration as the main driving source of structuration/thixotropy for fresh cement concrete.

CRediT authorship contribution statement

John Temitope Kolawole: Methodology, Validation, Formal analysis, Writing - original draft, Conceptualization. **Riaan Combrinck:** Conceptualization, Writing - review & editing, Supervision, Project administration. **William Peter Boshoff:** Conceptualization, Writing - review & editing, Supervision, Project administration, Funding acquisition.

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