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Viscoelastic – non-Newtonian Transitory Response of Cement Paste and Superplasticizer Combinations

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ABSTRACT

Cement paste exhibits mechanical response similar to a viscoelastic fluid. When superplasticizers are added, the viscoelastic effects diminishes and the mixture exhibits non-Newtonian response. Under complete dispersion, the mixture exhibits a Newtonian response. To develop an understanding on the choice of superplasticizer (dosage and type), it is necessary that one understands the transitory response of cement paste and superplasticizer combinations. This investigation is related to developing such understanding.

Ordinary 53 grade Portland cement was used with superplasticizers from the naphthalene, melamine and polycarboxylate family of products. Creep and recovery and stress relaxation experimental data was collected under different loading combinations at room temperature. It was seen that as the dosage increased, the response varied from a viscoelastic fluid to a non-Newtonian fluid. The experimental data was modelled using an upper convected Burgers' model. The polycarboxylate based superplasticizer exhibited interesting trends in terms of the viscoelastic – non-Newtonian transition.

Keywords: Viscoelasticity; Cement paste; Superplasticizer; Burgers' model; non-Newtonian

INTRODUCTION

The mineral and chemical admixtures have become the essential components of modern sustainable concrete to improve its performance. The concept of strength through better durability can be achieved with less cement and water by incorporating superplasticizers leading to sustainable concrete construction. It is also well known that the use of self consolidating concrete lowers the placing energy by avoiding the vibration. Also, high workability concrete reduces the construction time. However, the compatibility between different admixtures and the influence of type and dosage of admixtures on properties of concrete needs special attention.

Superplasticizers are commonly used during the production of high quality concrete due to their multifunctional properties. Even though the addition of superplasticizers influences the hardening and hardened state properties of concrete, their major influence is on the fresh state properties of concrete and this in turn is governed by the rheology of concrete. Superplasticizers are incorporated in concrete either to maintain the same workability at reduced water cement ratio (w/c) or to increase the workability by maintaining constant w/c ratio (Ramachandran 2002).

When superplasticizers are added, organic molecules of the superplasticizer having charged groups (SO_3^-, COO^-) adsorbs on the surface of cement particle of positive charge by electrostatic forces (Flatt and Houst 2001). These adsorbed particles give negative charge (Zeta potential) to cement particles and the resulting electrostatic repulsive forces causes dispersion of cement particles. Van der Waals attraction between the cement particles causes coagulation whereas the electrostatic repulsion and steric hindrance produced due to the addition of superplasticizer causes energy barrier against coagulation. The function of superplasticizer is to ensure that dispersion is more easily achieved and coagulation is more difficult (Wallevik 2005).

Also, addition of superplasticizers drastically changes the manner in which the reversible and irreversible reactions take place in cement paste. It is also possible for some of the superplasticizer-cement combination to exhibit incompatible behaviour due to short duration of dispersion effect. To overcome this, in some instances excessive amount of superplasticizer is added. However this can result in possible shear thickening. This shear thickening may be due to high concentration of solids in non-flocculated suspensions as the hydration process is accelerated during shearing (Cyr et al. 2000).

To develop an understanding of the cement paste – superplasticizers mixtures, constitutive models depicting the shear stress – shear rate relationship comes in handy. Ultimately such models lead to optimizing the dosages and help to sustain the influence of superplasticizers on concrete. A variety of models such as Bingham, Herschel-Bulkley and power law models are used for characterizing the response of the material. The main intent of most of these investigations have been to study the influence of these admixtures on some of these model based parameters such as plastic viscosity, yield stress, consistency and flow index. For instance, the influence of the dosage of superplasticizer on the Bingham model parameters such as yield stress and plastic viscosity shows that both of these parameters decrease with increase in dosage of superplasticizer up to saturation dosage and remains constant thereafter and similar is the case with Herschel-Bulkley parameters (Nehdi and Rahman 2004). There are also contradictory observations reported in the literature for the same mixture of materials. For instance, while the Bingham model reports negative yield stress for high dosage of superplasticizers, Herschel-Bulkley model reports a non–negative yield stress and the reason for this is normally ascribed to the so called non-linearity between shear stress and shear rate of Herschel-Bulkley model (De Larrard et al. 1998).

One can visualize the cement paste as a dense assembly of deformable or rigid objects close to a jamming density. These dense assemblies are lubricated by the hydrodynamic or physical-chemical interactions of the interstitial fluid, a mixture of water and superplasticizer. Such mixture can exhibit diverse response characteristics depending on the magnitude of dispersion. For instance, it is possible for the material to exhibit elastic response when subjected to constant strain rate. Subsequent increase of shearing can lead to these materials exhibiting what is commonly referred in cement paste rheology as ‘yield stress’ beyond which there can be continuous increase of deformation. It is interesting to note that classification of such response into ‘gel-like’ and ‘paste-like’ have been provided depending on the type of mechanical behaviour the material exhibits during steady shear (Van Damme et al. 2002).

The superplasticized cement paste exhibits a transition from non-Newtonian-viscoelastic characteristics to non-Newtonian and subsequently to linearly viscous behavior depending the type and dosage of the superplasticizer (Jayasree et al., 2011). The optimum dosages of the superplasticizer which affects these rheological characteristics are usually determined through empirical tests such as Marsh cone and mini slump. However, in a complex system of cement, mineral and chemical admixtures for the development of high performance concrete such as self consolidating concrete usually requires a better understanding about the dispersibility achieved with the type and dosage of the superplasticizer. This requires the use of more fundamental tests to understand the transitional nature of the cement paste at different dosages. Therefore, the determination of the optimum dosage of the superplasticizer based on more fundamental tests such as creep and recovery and stress relaxation will lead to the production of economical and sustainable concrete.

A proper constitutive model taking into account all the internal structural changes taking place during the hydration process is lacking currently. This is not surprising as the cement paste-superplasticizer mixture exhibits the most diverse and complex responses one can think of. In this investigation, a first attempt is made by modeling the mixture as an upper convected Burgers’ fluid. Creep and recovery and stress relaxation experimental data collected using a dynamic shear rheometer are used to validate the predictions of the model. The experimental observations used in this paper are from Jayasree et al., 2011.

EXPERIMENTAL INVESTIGATION

To understand the effect of different plasticizers, three superplasticizers belonging to different families such as naphthalenes (SNF), melamines (SMF) and polycarboxylates (PCE) were chosen in this study. The base cement used was an Ordinary Portland Cement of 53 grade conforming to the Indian Standard IS 12269-2004. A constant water cement ratio of 0.35 was maintained for all cement pastes. Details of the mix used for testing is given in Table 1.

Table 1. Mix details for cement paste with different plasticizers (Jayasree et al., 2011)

Type of mix	w/c	Dosage of superplasticizer (sp/c %)
Plain cement paste	0.35	Nil
Cement paste with SNF-S1		0.05
Cement paste with SNF-D2		0.05
Cement paste with SMF-S1		0.05
Cement paste with PCE-D1		0.01, 0.025, 0.05, 0.1

Jayasree et al., 2011 detail the experimental procedure related to the preparation of the mixture. A dynamic shear rheometer was used to study the stress relaxation and creep and recovery behavior of the cement pastes. A parallel plate attachment of 25 mm diameter and 1 mm gap was used for conducting the experiments. All the tests were performed at ambient conditions and before performing the tests, the materials were conditioned at 27 ^{o}C for 24 hours. The details of the test for creep and recovery and stress relaxation experiments are given in Table 2.

Table 2. Details of test for stress relaxation and creep and recovery (Jayasree et al., 2011)

Test	Details	Data acquisition
Stress relaxation	Ramping of strain - 0.5 sec Stress Relaxation - 33 sec	0.05 sec 0.05-5 sec varied linearly during 100 sec
Creep and Recovery	Creep - 10 sec Recovery - 100 sec	5×10^{-3} sec 5×10^{-3} sec to 20 sec varied logarithmically during 33 sec

CONSTITUTIVE MODEL AND NUMERICAL PROCEDURE

Taking into account the complex interactions expected in the cement paste – superplasticizer combinations, an upper convected Burgers' model derived within the framework of multiple natural configurations is used here. Strictly speaking one should model these systems within the purview of continuum theory of mixtures; however, we take a different approach here. We assume that each of the constituents of the mixture can have different relaxation mechanism corresponding to different natural configurations. We refer the reader to Krishnan and Rajagopal (2004) for complete details related to the model development. Here we state only the essential equations.

The velocity field related to shearing in a parallel plate is given as follows,

$$\boldsymbol{v_R} = 0, \boldsymbol{v}_\theta = rZ\frac{d\Omega}{dt}, \boldsymbol{v}_Z = 0. \tag{1}$$

Here (R, θ, Z) are the cylindrical polar coordinates of the particle in the reference configuration, t denotes time and $\frac{d\Omega}{dt}$ represents angular velocity.

The constitutive model chosen in this study is as follows:

$$\boldsymbol{\sigma} = -p\mathbf{I} + \mu_1\mathbf{B}_{\mathrm{kp1}} + \mu_2\mathbf{B}_{\mathrm{kp2}} \tag{2}$$

$$\frac{1}{2}\overset{\nabla}{\mathbf{B}}_{\mathrm{kpi}} = \frac{\mu}{\eta}\left(\frac{3}{\mathrm{tr}(\mathbf{B}_{\mathrm{kpi}}^{-1})}\mathbf{I} - \mathbf{B}_{\mathrm{kpi}}\right) \tag{3}$$

Here, $\boldsymbol{\sigma}$ is the Cauchy stress tensor, p is the Lagrange multiplier. $\boldsymbol{B}_{kpi}$ is the left Cauchy-Green stretch tensor. The Oldroyd derivative of $\boldsymbol{B}_{kpi}$ is given by,

$$\overset{\nabla}{\boldsymbol{B}} = \frac{D\boldsymbol{B}}{Dt} - \boldsymbol{lB} - \boldsymbol{lB}^t. \tag{4}$$

Here, $\boldsymbol{l}$ represents the velocity gradient and $\frac{D}{Dt}$ represents the material time derivative.

Now the velocity gradient is given by,

$$\boldsymbol{l} = \begin{pmatrix} 0 & -Z\dot{\Omega} & 0 \\ Z\dot{\Omega} & 0 & R\dot{\Omega} \\ 0 & 0 & 0 \end{pmatrix}. \tag{5}$$

We assume $\mathbf{B}_{kpi}$ of the following form (Krishnan and Rajagopal 2004))

$$\boldsymbol{B}_{kpi} = \begin{pmatrix} B_{rr} & 0 & 0 \\ 0 & B_{\theta\theta} & B_{\theta z} \\ 0 & B_{\theta z} & B_{zz} \end{pmatrix} \tag{6}$$

The Oldroyd derivative of the left Cauchy-Green stretch tensor is given as

$$\overset{\nabla}{\boldsymbol{B}} = \begin{pmatrix} \dot{B}_{rr} & 0 & 0 \\ 0 & \dot{B}_{\theta\theta} - 2r\dot{\Omega}B_{\theta z} & \dot{B}_{\theta z} - r\dot{\Omega}B_{zz} \\ 0 & \dot{B}_{\theta z} - r\dot{\Omega}B_{zz} & \dot{B}_{zz} \end{pmatrix} \tag{7}$$

Substituting the Oldroyd derivative of the left Cauchy-Green stretch tensor in equation (3), the following set of differential equations can be obtained.

$$\dot{B}_{rr} = \frac{2\mu}{\eta}\left(\lambda - B_{rr}\right), \tag{8}$$

$$\dot{B}_{\theta\theta} = \frac{2\mu}{\eta}\left(\lambda - B_{\theta\theta}\right) + 2r\dot{\Omega}B_{\theta z}, \tag{9}$$

$$\dot{B}_{zz} = \frac{2\mu}{\eta}\left(\lambda - B_{zz}\right), \tag{10}$$

$$\dot{B}_{z\theta} = \frac{2\mu}{\eta}\left(-B_{z\theta}\right) + r\dot{\Omega}B_{zz} \;. \tag{11}$$

Also for an incompressible material,

$$B_{rr}\left[B_{\theta\theta}B_{zz} - B_{\theta z}^2\right] = 1 \tag{12}$$

For stress relaxation experiments, the torque can be calculated as follows

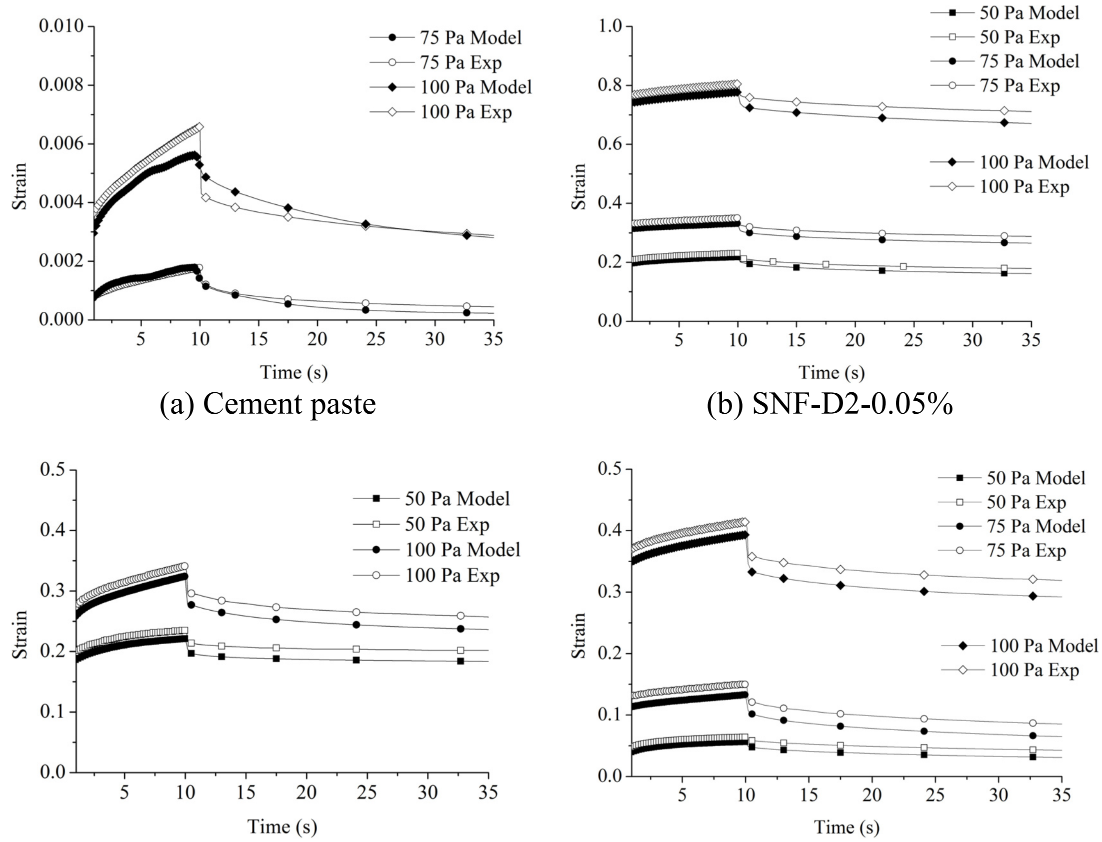
$$M = 2\pi\int_0^R \sigma_{\theta z} r^2 dr = 2\pi\int_0^R (\mu_1 B_{\theta z1} + \mu_2 B_{\theta z2})\, r^2 dr. \tag{13}$$

For creep and recovery experiment, the predicted $B_{\theta z1} + B_{\theta z2}$ was compared with the experimental strain.

The material parameters were determined through a trial and error procedure so that the root mean square error between predicted and experimental results is minimized. The MATLAB ODE solver was used for the solution of all the equations. Ideally, the parameters should be determined through an optimization algorithm such that the set of parameters with the least root mean square error is chosen, however such attempt was not carried out in this investigation.

RESULTS

Creep and Recovery:

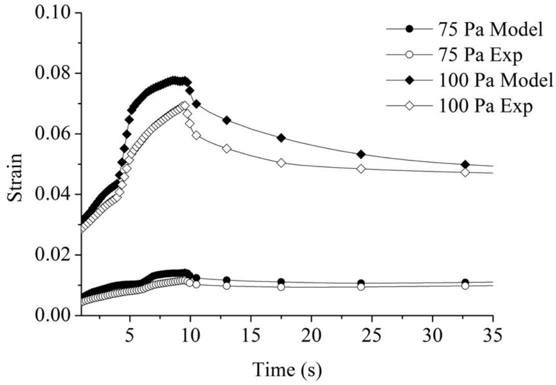


(a) Cement paste (b) SNF-D2-0.05%

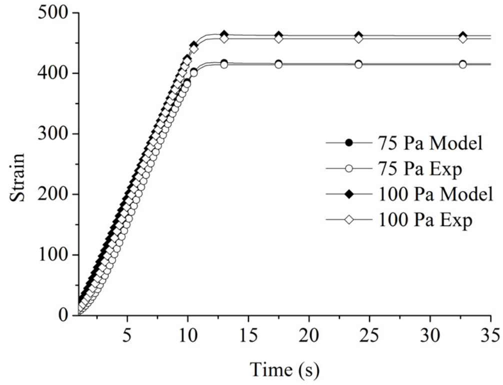
(c) SNF-S1-0.05% (d) SMF-S1-0.05%

Figure 1. Experiment and model comparison for creep and recovery of cement paste and superplasticizers combinations

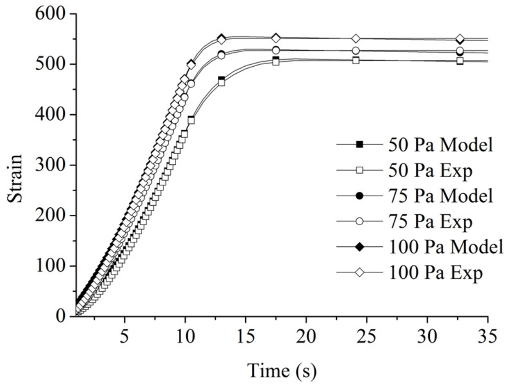
Figure 1 shows the experimental creep and recovery and the model predictions for cement paste and the three superplasticizer combinations. The model predictions are close to the experimental data collected. While modelling the response of the data, some of the experimental data were not considered since they were considered suspect. Figure 2 shows the creep and recovery response of PCE based superplasticizers. The difference in the response of the material can be clearly seen especially when one compares the 0.05% dosage rate response of Figure 2-C with Figure 1-B, 1-C and 1-D. The model is able to predict the response of the material for all the strains level recorded. It is to be noted that for such strain levels, it is necessary that one uses the non-linear models of the form described here. One needs to compare the response of the material as the dosage rate is increased. While for a dosage of 0.01% (Figure 2-a), one sees the creep and recovery similar to that of a viscoelastic fluid, for higher dosages (Figures 2-b through 2-d), the expected elastic jump and recovery is not seen and it is interesting to note that the model has clearly captured such change in response.



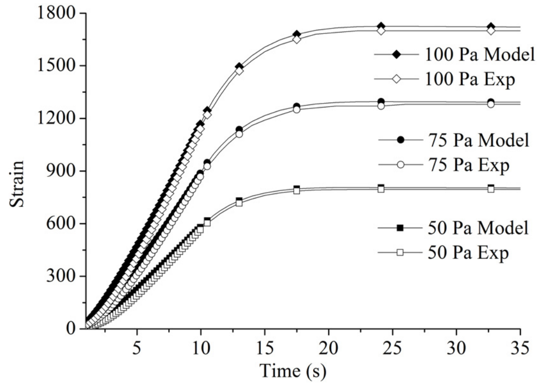
(a) PCE-D1-0.01%



(b) PCE-D1-0.025%



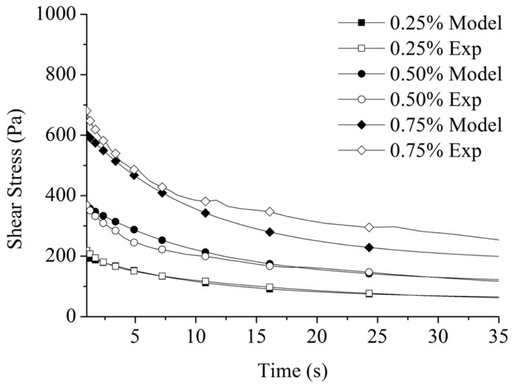
(c) PCE-D1-0.05%



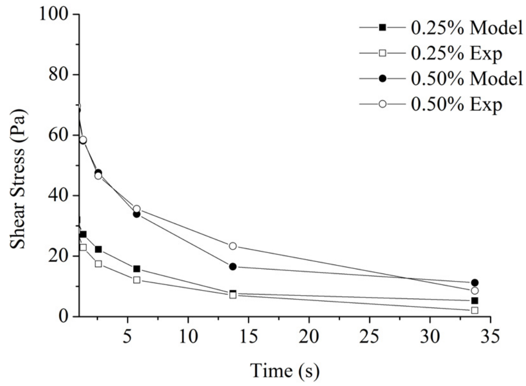
(d) PCE-D1-0.1%

Figure 2. Experiment and model comparison for creep and recovery of cement paste with PCE superplasticizers of different dosages

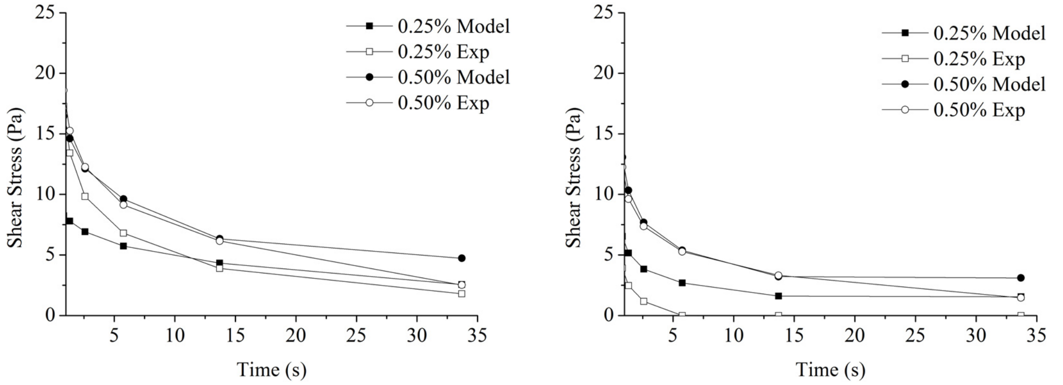
Stress relaxation:



(a) Cement Paste

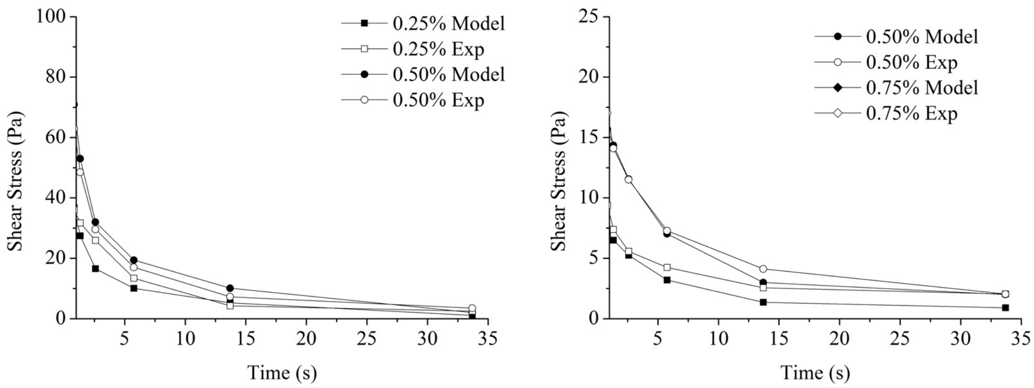


(b) SNF-D2-0.05%

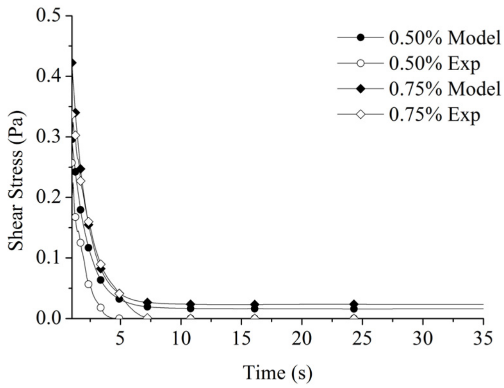


(c) SNF-S1-0.05% (d) SMF-S1-0.05%

Figure 3. Experiment and model comparison for stress relaxation of cement paste and paste with different superplasticizers



(a) PCE-D1-0.01% (b) PCE-D1-0.025%



(c) PCE-D1-0.05%

Figure 4. Experiment and model comparison for stress relaxation of cement paste with PCE of different dosages

Figure 3 shows the stress relaxation response of the cement paste and superplasticizers of the SNF and SMF families whereas Figure 4 shows the response of PCE based superplasticizers. For the SNF and SMF superplasticizers within the experimental time scale, the material did not completely stress relax whereas the PCE based superplasticizers for the same dosage stress relaxed completely. The model results are also reasonably closer.

Table 3 shows the model parameters and Table 4 shows the root mean square error calculated between experimental data and model predictions. A careful purview of the model parameters indicates that the nature of the internal structural response of the material during creep and recovery and stress relaxation is completely different. If one is interested in modelling the response of this material, it is desirable that the model parameters are identical for both the experiments. However, as discussed in the introduction, it is possible that the hydrodynamic or physical-chemical interactions of the interstitial fluid plays a different role in each of these testing conditions leading to different response characteristics and thus resulting in different material parameters. Ideally, a model capable of capturing all the response should be arrived at by appropriately appealing to the energy storage and dissipation mechanism of the material for all the testing conditions. To the best of the knowledge of these authors, such modelling attempts for these materials are not available in the literature.

Table 3: Model parameters for stress relaxation and creep experiments

Cement Paste/ Plasticizer	Stress Relaxation × 10^3				Creep and Recovery × 10^3			
	μ_1 (Pa)	η_1 (Pa-s)	μ_2 (Pa)	η_2 (Pa-s)	μ_1 (Pa)	η_1 (Pa-s)	μ_2 (Pa)	η_2 (Pa-s)
Cement paste	51.786	974.790	25.893	15231.091	70.063	670.168	3.046	15231.091
SNF-D2	15.231	97.479	2.132	15231.091	15.231	0.975	2.132	15231.091
SNF-S1	3.046	24.370	0.914	15231.091	3.046	0.244	0.914	15231.091
SMF-S1	3.046	9.139	0.609	15231.091	3.046	0.091	0.609	15231.091
PCE-0.01	15.231	30.462	6.092	152.311	15.231	152.311	6.092	15231.091
PCE-0.025	3.046	30.462	0.396	15.231	9.139	30.462	0.396	15231.091
PCE-0.05	0.091	0.228	0.003	15.231	0.091	0.228	0.259	761.55
PCE-0.1	-	-	-	-	0.030	0.152	0.015	152.311

Table 4: RMSE estimate for stress relaxation and creep experiments

Cement Paste/ Plasticizer	Stress Relaxation			Creep and Recovery		
	0.25%	0.50%	0.75%	50 Pa	75 Pa	100 Pa
Cement paste	7.066	22.313	46.542	-	0.000	0.001
SNF-D2	4.227	3.639	-	0.013	-	0.028
SNF-S1	2.897	1.055	-	0.014	0.015	0.017
SMF-S1	1.702	1.027	-	0.008	0.018	0.021
PCE-0.01	1.305	1.013	-	-	0.002	0.010
PCE-0.025	0.127	0.022	0.099	24.428	37.581	48.556
PCE-0.05	-	0.043	0.029	5.141	6.404	6.859
PCE-0.1	-	-	-	0.022	9.553	11.490

CONCLUSION

In this investigation, the creep and recovery and stress relaxation experimental data of cement paste and superplasticizers were used for modelling. These experiments were predicted using a proper non-linear, frame invariant viscoelastic fluid model of the Burgers' type. From the careful analysis of the experimental data and the modelling results, it is clearly seen that plain cement paste exhibits viscoelastic response. Addition of superplasticizer changes the behaviour of the material substantially. As can be seen from the experimental data and model predictions, PCE based superplasticizer resulted in considerable dispersibility and the material parameters captured such trends. It will be interesting to use such framework to arrive at the optimal dosage rates of superplasticizers and it is possible that one can get different dosage rates based on different testing regimes and modeling strategies. Taking into account the influence of the dosage of superplasticizers on the subsequent mechanical response of fresh cement concrete, such investigations are currently required.

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