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The role of C_3S and C_3A in the early-age structural build-up of model pastes

O papel das fases C_3S e C_3A na evolução estrutural em idades iniciais de pastas modelo

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ABSTRACT

This study investigates the role of C_3A and C_3S phases in the early-age structural build-up of model Portland cement pastes. Pastes containing only C_3S, C_3A + gypsum, and hybrid systems were evaluated using oscillatory rheometry, providing valuable insights into the evolution of viscoelastic parameters, such as the storage modulus (G') and loss modulus (G"), under varying strain conditions. The results show that systems with only C_3A and gypsum exhibited a more pronounced structural build-up and a marked increase in G' over time, accompanied by sharp stress peaks upon strain application. In contrast, the inclusion of C_3S in these systems diminished this behavior. Pastes containing only C_3S, and limestone demonstrated a slower structural build-up. The observed competition between C_3A and C_3S for available water molecules may explain these differences, suggesting the need for further investigation into the underlying mechanisms driving this behavior.

Keywords: Structural build-up; C_3A; C_3S; Rheology; Hydration.

RESUMO

Este estudo investiga o papel das fases C_3A e C_3S na estruturação inicial de pastas modelo de cimento Portland. Pastas contendo apenas C_3S, C_3A + gipsita e sistemas híbridos foram avaliadas usando reometria oscilatória, fornecendo insights valiosos sobre a evolução de parâmetros viscoelásticos, como o módulo de armazenamento (G') e o módulo de perda (G"), sob condições de deformação variáveis. Os resultados mostram que sistemas com apenas C_3A e gipsita exibiram uma estruturação mais pronunciada e um aumento acentuado no G' ao longo do tempo, acompanhados por picos de tensão acentuados após a aplicação de deformação. O C_3S nesses sistemas diminuiu esse comportamento. Pastas contendo apenas C_3S e calcário demonstraram uma estruturação mais lenta. A competição observada entre C_3A e C_3S por moléculas de água disponíveis pode explicar essas diferenças, sugerindo a necessidade de mais investigação sobre os mecanismos subjacentes que impulsionam esse comportamento.

Palavras-chave: Estruturação; C_3A; C_3S; Reologia; Hidratação.

1 INTRODUCTION

Concrete rheology has recently gained increased attention from both industry and academia due to the emergence of novel technologies, such as 3D printing of concrete, which rely heavily on these properties due to the variety of processes involved (e.g., extrudability, pumping, buildability) (Han et al., 2024; John et al., 2019). This focus on cement rheology highlights the importance of early hydration and its effect on the rheological properties of cement mixtures, which are directly related to the structural build-up of pastes (Carvalho et al., 2024). The rheological behavior of cement pastes is primarily characterized by the evolution of viscoelastic parameters, particularly the storage modulus (G'), which reflects the elastic component, and the loss modulus (G"), which is associated with the viscous component of the material (Alnahhal et al., 2021).

The structural build-up of cement pastes is commonly attributed to colloidal interactions and the formation of links between early hydration products, particularly C-S-H (Roussel et al., 2019). Colloidal interactions and hydrate linkages develop over time, leading to a flocculated structure that progressively strengthens, forming a rigid network at later stages (Han et al., 2024). However, Portland cement phases react at different ratios, and the distinct roles of the C_3S and C_3A phases in this process have not been sufficiently explored. In particular, the early hydration of C_3A, including the precipitation of hydrates such as ettringite (AFt), may play a crucial role in the early-age structural development of the paste. This paper aims to investigate the individual contributions of C_3S and C_3A to the early-age structural build-up of model Portland cement pastes, employing oscillatory rheometry to assess the evolution of rheological properties.

2 EXPERIMENTAL PROGRAM

2.1 MATERIALS AND SAMPLE PREPARATION

Considering the raw materials used, cement phases of C_3S (MRPC, France, 98.7 wt% purity, 1.14 m²/g BET SSA and D_{50} = 7 µm) and cubic and orthorhombic C_3A (MRPC, France, 97.8 wt% purity) were used. A limestone filler with similar BET SSA (1.18 m²/g), density of 2.714 g/cm³, and D_{50} of 16 µm was also adopted. Furthermore, gypsum (Dinâmica™, 1.98 m²/g BET SSA, density of 2.306 g/cm³ and D_{50} = 43 µm) served as the calcium sulfate source for the model pastes production. A total of five systems were produced, with details provided in Table 1. All the evaluated systems contained typical proportions of C_3S and C_3A + gypsum commonly found in ordinary Portland cement (OPC), *i.e.*, 70% C_3S, 6% C_3A, and 4% gypsum. To complete the 100% content, limestone filler was used, as it is typically included in OPC production and does not significantly influence early-age hydration (in terms of ion release), allowing to focus on the effects of C_3S and C_3A + gypsum. The inclusion of limestone also enabled the production of C_3A pastes with realistic w/c ratios, as 100% C_3A pastes typically require higher w/c ratios to achieve sufficient workability. A constant water/solid ratio of 0.5 was maintained. For paste preparation, the materials were hand-mixed with a spatula for 30 seconds, followed by a 90-second mix at 650 rpm using a hand shear mixer.

Table 1: Mix proportions adopted for the model pastes production

Mix ID	C_3S (wt.%)	ort-C_3A (wt.%)	cb-C_3A (wt.%)	Limestone filler (wt.%)	Gypsum (wt.%)
C_3S	70	-	-	30	-
ort-C_3A	-	6	-	90	4
cb-C_3A	-	-	6	90	4
C_3S_C_3Aort	70	6	-	20	4
C_3S_C_3Acub	70	-	6	20	4

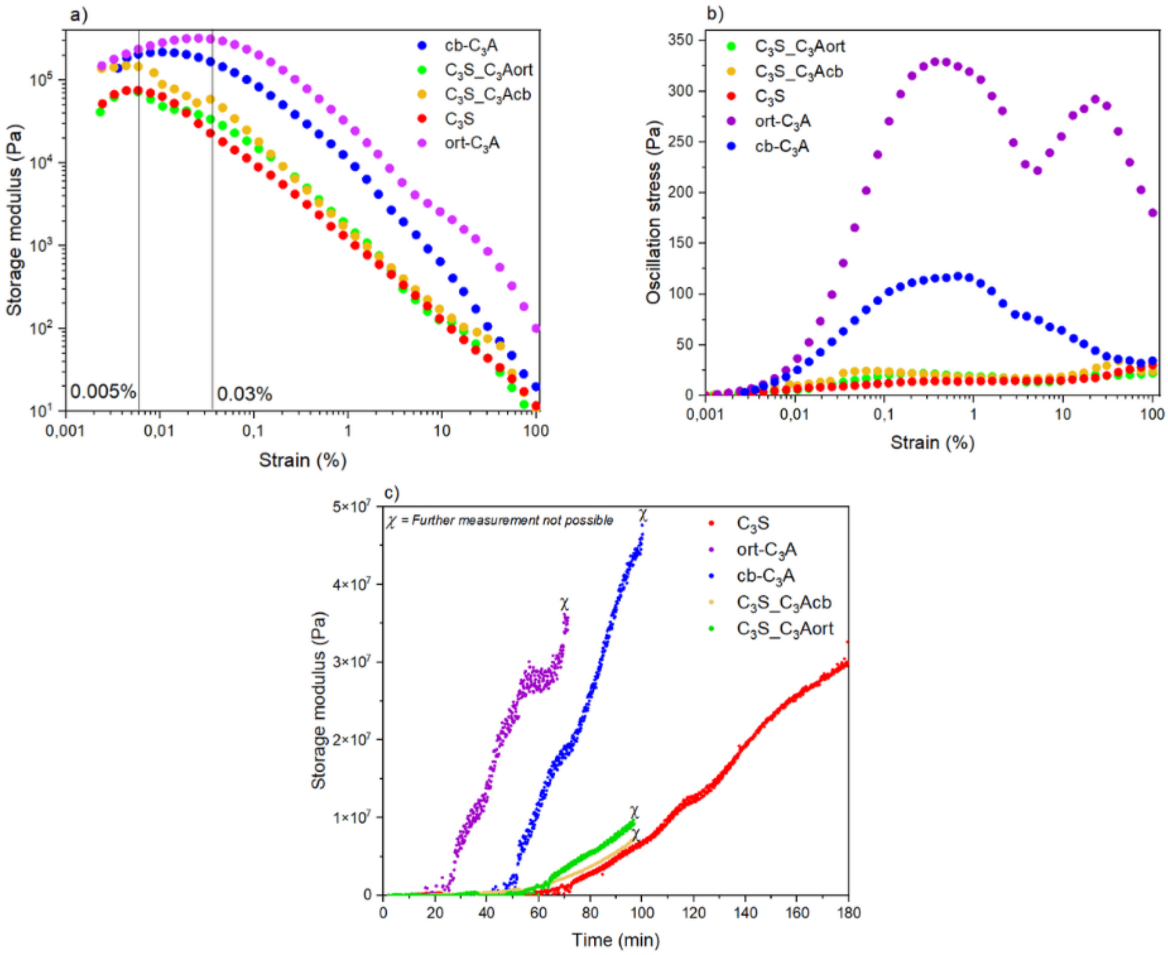
2.2 TEST METHODS

Oscillatory rheological analysis was employed to evaluate the early-age structural build-up of the model pastes by monitoring viscoelastic parameters in response to strain and time. Each measurement was conducted in a parallel-plate geometry with a pre-shear at 30 s^{-1} for 30 seconds, followed by a 60-second resting period to eliminate prior shear history. An oscillatory strain sweep test was first performed, with strain varying from 0.001% to 100%, to identify the critical strain that kept the pastes within the linear viscoelastic region (LVR). Furthermore, a small amplitude oscillatory shear (SAOS) test was conducted to track the evolution of the storage modulus (G'), loss modulus (G"), and phase angle over time. A strain of 0.002% was selected for the SAOS test based on the strain sweep results, ensuring the paste remained within the LVR. The test was carried out over 180 minutes, with an insulation tool used to prevent water evaporation, and an oscillatory frequency of 1 Hz was applied.

3 RESULTS AND DISCUSSION

The strain sweep test is essential for identifying the critical strain and the linear viscoelastic region of the model pastes. As shown in Fig. 1a, two distinct critical strains were observed across the different model systems. For pastes containing C_3S, the critical strain was lower, around 0.005%, while pastes with only C_3A and gypsum exhibited a higher critical strain of 0.03%, *i.e.*, 6 times higher. This may be related to the quick reaction of C_3A even in the presence of calcium sulfate, forming an appreciable amount of AFt within the first minutes (e.g. 10 minutes or so) (Andrade Neto et al., 2022b) and partially consuming the free water. To ensure all pastes remained within the LVR during subsequent SAOS measurements, a fixed strain of 0.002% was selected.

Figure 1: a) Critical strain determination, b) stress vs strain curves and c) storage modulus evolution obtained from oscillatory rheometry tests.



Source: Authors (2024)

Fig. 1b presents the oscillation stress results obtained from the strain sweep tests, where stress was measured over the applied strain variation. Notably, stress peaks were observed in the C_3A systems, with the orthorhombic C_3A exhibiting two distinct sharp peaks, while the cubic polymorph (cb-C_3A) produced a first broader peak and a second but not well-defined small peak. In contrast, systems containing C_3S, regardless of the presence of C_3A, did not exhibit any stress peaks. This behavior may be attributed to the early precipitation of calcium sulfoaluminate hydrates (AFt and AFm phases) during C_3A + gypsum hydration, which generates stress peaks as these bonds are broken. The higher reactivity of orthorhombic C_3A, as reported by Andrade Neto et al. (2024), likely explains the more pronounced stress measurements observed compared to the cubic polymorph. In OPC systems, similar peaks have been linked to both colloidal interactions and C-S-H linkages, as discussed by Roussel et al. (2012). In the current systems without C_3S, the precipitation of AFt and AFm products may play an analogous role.

A similar trend was observed in the SAOS test, where the evolution of the storage modulus (G’) was tracked over 180 minutes (Fig. 1c). For the orthorhombic C_3A paste, a sharp increase in G’ was observed after 20 minutes of hydration. The cubic polymorph displayed a comparable response but with a slightly delayed onset, starting after 50 minutes. As extensively discussed by Andrade Neto et al. (2022a), the orthorhombic polymorph of C_3A exhibits significantly higher reactivity compared to the cubic form, leading to faster consumption of gypsum and anticipating its subsequent depletion. This increased gypsum consumption, i.e., the higher reaction rate between C_3A and gypsum, facilitates the rapid formation of AFt in the initial minutes of hydration. This early-phase reaction significantly influences the viscoelastic properties, as evidenced by the reported measurements and findings.

In the other hand, as seen in Fig. 1c, the inclusion of C_3S slowed down the structural build-up in the pastes containing C_3A, with the stiffening evolution of the binary systems progressing much more slowly than the C_3A-only systems. For instance, at 95 min, the C_3S_C_3Acub and C_3S_C_3Aort pastes had a G’ of 7.32 and 9.67 MPa, respectively, while the C_3S paste had a G’ of 5.96 MPa at this age. This behavior may be linked to a reduced reaction between C_3A and water upon the introduction of C_3S. In this case, alite dissolution releases calcium ions, competing with C_3A dissolution and limiting the reaction rate of the aluminate phase, thus slowing the overall structural build-up of the paste. In the system containing only C_3S and limestone, a delayed but continuous increase in G’ was observed. However, the systems with C_3A could not be accurately measured by the 180-minute mark, likely due to the setting of C_3A, which interfered with the equipment's ability to capture reliable data.

Considering the characteristics of the system, measurements taken over extended periods may yield higher G' values for systems containing C_3S due to the continued precipitation of C-S-H at later stages. However, during the early-age hydration (within the first 3 hours), C_3A played an important role in the structural build-up of the pastes. It is important to note that the direct influence of limestone on the early-age structural build-up of the pastes was not assessed. However, given its inert nature and physical characteristics relative to the other raw materials used, limestone is not expected to significantly affect the viscoelastic behavior of the pastes.

4 CONCLUSIONS

This study analyzed model Portland cement systems to assess the contributions of both C_3A and C_3S phases to the early-age structural build-up of pastes. The results indicate that the precipitation of AFt/AFm products may significantly influence the early-age structural build-up of cement pastes based on results observed from the strain sweep test. However, the introduction of C_3S into the system reduces the dissolution rate of C_3A, thereby diminishing the impact of the aluminates precipitation on the structural build-up. On the other hand, C_3S exhibited a delayed evolution of the storage modulus due to its slower hydration kinetics compared to C_3A. Nevertheless, this evolution may eventually surpass the G' development associated with C_3A alone at later stages (not addressed here). The competition between C_3S and C_3A dissolution during cement hydration is a crucial factor for understanding the role of these phases in early-age structural build-up, and further research on this topic is required.

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