Fiber-reinforced reactive magnesia-based tensile strain-hardening composites

Ruan, Shaoqin; Qiu, Jishen; Yang, En-Hua; Unluer, Cise

2018

Ruan, S., Qiu, J., Yang, E.-H., & Unluer, C. (2018). Fiber-reinforced reactive magnesia-based tensile strain-hardening composites. *Cement and Concrete Composites*, 89, 52-61.
doi:10.1016/j.cemconcomp.2018.03.002

<https://hdl.handle.net/10356/90095>

<https://doi.org/10.1016/j.cemconcomp.2018.03.002>

© 2018 Elsevier Ltd. All rights reserved. This paper was published in *Cement and Concrete Composites* and is made available with permission of Elsevier Ltd.

Downloaded on 26 Apr 2023 18:58:06 SGT

Fiber-reinforced reactive magnesia-based tensile strain-hardening composites

Shaoqin Ruan, Jishen Qiu, En-Hua Yang, Cise Unluer*

School of Civil and Environmental Engineering, Nanyang Technological University,
50 Nanyang Avenue, Singapore 639798, Singapore

* Corresponding author. Tel.: +65 91964970, E-mail address: ucise@ntu.edu.sg

Abstract:

This study focuses on the development of a new strain-hardening composite (SHC) involving carbonated reactive MgO cement (RMC) and fly ash (FA) as the main binder. Rheological properties of the developed composites were investigated by varying FA and water contents to achieve desirable fiber dispersion. A suitable mix design, in which polyvinyl alcohol (PVA) fibers were introduced to provide tensile ductility, was determined. The effect of key parameters such as w/b ratio and curing age on the mechanical properties of carbonated RMC-SHC was evaluated. Adequate binder content and w/b ratio was necessary for desirable fiber dispersion. Lower water contents and longer curing ages contributed to the strength development of RMC-SHC by improving the fiber-matrix interface bond and enhancing the formation of a dense carbonate network.

Keywords: MgO; Rheology; Carbonation; Tensile properties; Fiber reinforcement

1. Introduction

Portland cement (PC)-based concrete is the most frequently used construction material. The annual global production of PC exceeds 4 billion tons [1]. The production of PC is associated with a high energy consumption and ~8% of the total global anthropogenic carbon dioxide (CO₂) emissions [2]. The notable environmental impact of PC production has driven the search for alternative binders with potentially lower environmental footprints. Reactive magnesia (MgO), obtained via the calcination of magnesite (MgCO₃) at a temperature of 700-1000 °C (dry route) [3], magnesium silicates (e.g. serpentine) [4] or extracted from seawater or brine (wet route) [5], is of interest as a new binder.

Several studies have looked into the use of reactive MgO cement (RMC) as the main binder with or without the use of PC, fly ash (FA) or slag [6-12]. Most of these studies reported the strength development of RMC-based mixes via the carbonation of MgO, following its hydration into brucite (Mg(OH)₂). When in the presence of CO₂, these Mg-phases carbonate and form a range of hydrated magnesium carbonates (HMCs), such as nesquehonite (MgCO₃·3H₂O), hydromagnesite (4MgCO₃·Mg(OH)₂·4H₂O), dypingite (4MgCO₃·Mg(OH)₂·5H₂O) and artinite (MgCO₃·Mg(OH)₂·3H₂O). The hardened dense carbonate network reduces sample porosity and provides binding strength within RMC-based samples [13-15].

In addition to laboratory-scale samples reported in many studies, the use of RMC in the production of commercial-scale masonry units has been demonstrated in earlier studies [16, 17], highlighting its feasibility to be utilized in various non-structural applications. Recent studies on the use of RMC as a binder focus on understanding the factors that affect the carbonation and the associated strength development of RMC formulations, including mix design [18], curing conditions [14, 19] and use of additives [10, 11, 13, 19, 20], leading to 28-day concrete strengths as high as ~60 MPa [10]. Although continuous research on RMC formulations has achieved significant improvements in terms of mechanical performance, RMC-based concrete is still considered as a brittle material, which could highly benefit from the use of reinforcement in the development of structural

members. Nevertheless, the relatively low pH (i.e. ~ 10) of carbonated RMC formulations presents a challenge in the use of steel reinforcement [9], which can face a risk of corrosion due to the loss of the passivated surface at such relatively low alkalinities, thereby potentially creating structural safety issues.

To increase the application spectrum of RMC within the construction industry, it is curial to develop alternative methods that will enhance the ductility of RMC-based formulations. The inclusion of a small amount of short polymeric fibers has been proven to be very effective in eliminating the brittleness and enhancing the tensile ductility of PC-based composites [21]. One of the successful derivatives involving the use of fibers is engineered cementitious composites (ECC), which adopt polymeric fibers at a fraction of typically $\sim 2\%$ by volume. Unlike the strain-softening conventional PC, ECC demonstrate strain-hardening behavior as their tensile stress continues to increase even in the presence of cracks. ECC samples can achieve a tensile ductility of 1-5%, enabled by the formation of multiple fine cracks ($< 100 \mu\text{m}$) with very small spacing (1-5 mm) [22-24]. The tensile properties of ECC can be further tailored with micromechanics to achieve multiple attributes such as high impact resistance [25, 26] and fatigue resistance [27-29]. Therefore, to reduce the dependence of RMC-based structural members on steel reinforcement, the use of short polymeric fibers, which can provide similar tensile strain-hardening behavior and high ductility within RMC formulations, can be explored.

One of the key factors to be considered in increasing the ductility of RMC-based strain-hardening composites (SHC) is the provision of desirable fiber dispersion. Previous studies on the rheology of ECC mixtures have shown that a relatively low yield stress (i.e. to ensure the flowability of the mixture) and high plastic viscosity (i.e. to provide sufficient shear force for the separation of the micro-fibers, which are bound together in their original form) are desirable properties [30]. The required yield stress and viscosity can be achieved by adjusting both the water/binder (w/b) ratio and FA content. Specifically, while a lower w/b ratio can lead to a high viscosity, it can also cause an undesirably high yield stress [31]. Alternatively, the replacement of cement by FA can

significantly reduce the yield stress without compromising viscosity due to the distinct spherical shape and similar particle size of FA as ordinary cement. The relationship between the rheology of cement pastes and tensile ductility, assessed via the measurement of the uniformity of fiber dispersion, has revealed that an increase in viscosity can lead to higher ductility [32].

While a desirable fiber dispersion is critical, it does not necessarily guarantee strain-hardening behavior or high ductility. As shown in Fig. 1, the hardened composites must satisfy the two strain-hardening criteria [33]. Specifically, the complementary energy of the fiber-bridging curve, J_b' (i.e. the hatched area), must be larger than the crack tip toughness of the matrix, J_{tip} , as shown in Equation 1. Furthermore, the fiber-bridging strength, σ_0 (i.e. the curve peak), must be higher than the tensile cracking strength of matrix, σ_c , as shown in Equation 2.

$$J_{tip} \leq \sigma_0 \delta_0 - \int_0^{\delta_0} \sigma(\delta) d\delta \equiv J_b' \quad (1)$$

$$\sigma_c < \sigma_0 \quad (2)$$

As the fiber-bridging and matrix crack tip toughness are influenced by factors such as the w/b ratio [13], it is important to study the effect of these factors on the tensile performance of RMC-SHC. Until now, no studies have been reported on the development of RMC-based fiber-reinforced samples. In this respect, this paper presents a pioneering study on the development of RMC-based SHC by investigating the influence of key parameters throughout this process. The first part of the study focuses on the effect of w/b ratio and FA content on the rheological properties of RMC pastes, with the goal of determining a suitable mix design that leads to a desired viscosity and sufficient flowability for good fiber dispersion. The second part focuses on the inclusion of fibers within the mix design determined in the first stage and investigates the effect of certain factors such as the w/b ratio, fiber aspect ratio, fiber surface treatment and curing age on the performance of the developed formulations.

2. Materials and Methodology

2.1. Materials

Reactive MgO cement (RMC), obtained from International Scientific Ltd. (Singapore), was the main binder used in this study. Class F fly ash (FA), obtained from Bisley Asia Ltd. (Malaysia), was used to adjust the rheology of the fresh mixtures and function as a binder via its limited reaction with brucite [34]. The chemical composition and particle size distribution of these two binders are provided in Table 1 and Fig. 2, respectively. Sodium hexametaphosphate ($\text{Na}(\text{PO}_3)_6$), acquired from VWR International Ltd. (Singapore), was added to the prepared formulations as a water reducer at 10% of the water content [35]. Polyvinyl alcohol (PVA) fibers, one of the most common types of fibers used in ECC [36], were obtained from Kuraray Ltd. (Japan) and included in selected RMC-SHC samples. The properties of the PVA fibers used in this study are listed in Table 2.

2.2. Methodology

The experimental program designed in this study consisted of two parts. The first part studied the effect of w/b and FA/b ratios on the rheology of fresh mixtures before the inclusion of fibers. The goal of this part was to determine a suitable mix design (i.e. w/b ratio and FA content) that led to a desired plastic viscosity and flowability for good fiber dispersion. In the second part, during which PVA fibers were introduced into the mix design determined in the first part, the effects of the w/b ratio and curing age, whose increase can lead to a higher degree of carbonation and improve the strength development of RMC mixes [14], on the mechanical properties of RMC-SHC were studied.

The details of the seven different mix proportions prepared in the first part of the study are provided in Table 3. The notation for sample names followed a format of FA(X)-(Y), where X represented the FA content (i.e. as a percentage of the total binder) and Y represented the w/b ratio. A range of w/b (0.47-0.58) and FA/b (0-0.6) ratios were determined from preliminary samples prepared for each formulation. The sample preparation process started with the dissolving of $\text{Na}(\text{PO}_3)_6$ in the pre-determined amount of water. This solution was then added to the dry mix of RMC and FA during the mixing process. A stopwatch was set to notify two minutes from the moment the solution was added to the dry RMC-FA mix. After two minutes of mixing, one spoon of the fresh mixture was placed onto a 39 mm proliferated base plate on the rheometer, equipped with a 39 mm P35 TiL top plate pressed against the mixture at 0.5 N. The rheology measurements were performed via a HAAKE MARS III 379-0400 rheometer, which was used to measure the shear resistance of the fresh mixtures at a designated rotation speed according to the test setup shown in Fig. 3. Three rheology measurements were taken at 6, 12 and 18 minutes. For each measurement, the top plate was first rotated at a relatively high speed (50 /s) for 30 seconds to prevent any agglomeration [37], followed by an increase in the shear rate from 1 to 100 /s within 180 seconds. The shear resistance, τ , was recorded throughout the total 210 seconds. The sample was kept in-situ between measurements. Both the sample preparation and subsequent measurements were conducted under an ambient temperature (25 °C).

As a certain level of plastic viscosity is crucial for good fiber dispersion and tensile ductility [30], results from the first part of the study were used in the selection of w/b and FA/b ratios to be incorporated in the mix designs in the second part. Previous literature [32] has shown that while the fiber dispersion coefficient increased with plastic viscosity, tensile ductility stabilized after a threshold fiber dispersion coefficient. This value corresponded to a plasticity of about 3.5 Pa·s, which was also adopted in this study for the preparation of samples used in the testing of tensile properties. Referring to the results obtained in the first part of the study to identify samples that demonstrated good fiber dispersion (e.g. FA30-0.53), the three mix proportions listed in Table 4 were prepared to assess the tensile performance of RMC-SHC. For all the mix designs, the

FA/b was fixed at 0.3, whereas the w/b ratio was kept at ≤ 0.53 according to the outcomes of the rheology measurements. A constant fiber fraction corresponding to 2% of the binder content was utilized in line with the previous literature on ECC [36].

To initiate sample preparation, RMC and FA were dry mixed in a planetary mixer for over 3 minutes, after which the prepared $\text{Na}(\text{PO}_3)_6$ solution was slowly added to form the fresh mixture. The mixing process continued for an additional 2-3 minutes until a uniformly mixed homogenous mixture was achieved, after which the PVA fibers were slowly added within 2 minutes. During the entire mixing process, the blade rotation speed was kept constant at 6.4 rad/s. The prepared mixture was cast into cubic (50x50x50 mm) and dogbone shaped molds, whose dimensions are shown in Fig. 4(a). The cast samples were stored in a sealed container, where silica gel was used for removing the excess moisture from the pastes to facilitate the penetration of CO_2 within the sample pore structure in the subsequent stage [38]. After 3 days, samples were removed from their molds and cured in a carbonation chamber set at a CO_2 concentration of 10%, temperature of 30 ± 1.5 °C and relative humidity (RH) of $85 \pm 5\%$ (i.e. ambient levels in Singapore) for 7 days [13, 20]. The effect of curing duration was studied by exposing one of the prepared samples (RMC-0.41) to carbonation curing for a total of 28 days under the same conditions.

Once curing was completed, the compressive strength of cubic samples were measured in triplicates in accordance with the specifications of ASTM C109/C109M-13 [39]. The equipment used for compression testing was Landmark 370.25, operated at a loading rate of 0.25 mm/min. The uniaxial tensile tests were conducted on at least three specimens for each mix design by using an Instron 5569, as shown in Fig. 4(b). During this test, the loading rate was set at 0.02 mm/min and two LVDTs were used to determine the extension of the gauged length (60-70 mm). After the uniaxial tensile test, the crack width and spacing (i.e. gauge length/crack number) on each specimen were determined with a Nikon DS-Fi2 high resolution camera equipped with NIS Elements (Nikon) software and an OPTEM Zoom 70XL microscope at a magnification of 420x. For each mix design, three to six samples were analyzed to evaluate their crack

patterns, which involved capturing the image with the camera, and counting and recording the crack number within the gauge length of sample under the microscope.

In addition to their compressive and tensile strengths, the CO₂ uptake of selected samples during carbonation curing were assessed by obtaining representative powders from each sample. These powders were ground to pass through a 75 µm sieve and vacuum dried before analysis. The quantitative measurements were performed via thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) conducted on a Perkin Elmer TGA 4000 equipment. During TGA/DSC, the samples were heated from 40 to 900 °C at a heating rate of 10 °C/min under nitrogen flow.

3. Results and Discussion

3.1. Rheological properties

Fig. 5 illustrates the typical relationship between the shear resistance τ (Pa) and shear rate N (/s) of a fresh RMC mixture at different elapsed times. The curves show that the fresh mixtures were Bingham liquids, in which the shear force exceeded the initial mixture resistance to initiate rotation, after which the shear resistance increased linearly with the rotation speed N (/s), showing no shear thinning or thickening effect. The relationship between τ and N of Bingham liquids is quantitatively described by Equation 3, where g (Pa), the intercept on the y-axis, is the yield stress needed to break the network of interactions between particles and initiate rotation; and h (Pa · s), the slope of the curve, is the plastic viscosity [40]. For any given fresh mixture at a designated time, g and h are constants that represent the rheological properties of that mixture.

$$\tau = g + Nh \quad (3)$$

In regular cement-based fresh mixes, shear resistance, which varies with shear rate (N) and solid volume fraction (V_s), depends on several types of particle interactions (i.e. Van

der Waals forces, direct contact forces between particles and hydrodynamic forces, for which the friction between fluid layers increases with velocity) [41]. At relatively low shear rates (i.e. whose threshold depends on the w/b ratio [42, 43]), the yield stress (g) is mainly determined by Van der Waals or direct contact forces. Previous studies on the yield stress of C_3S pastes [44] showed that a critical V_s existed at 0.38, beyond which the solid particles became so compacted that the dominant particle interaction shifted from Van der Waals to direct contact forces. As C_3S and RMC have a comparable particle size distribution [9], and they both conform to Bingham model, the information on C_3S was used to evaluate the behavior of RMC-based samples. It must be noted that the yield stress can also be related to the surface chemistry of particles, which was not differentiated here. Most of the mix designs presented in this study, except for FA0-0.58 ($V_s = 0.35$) and FA30-0.58 ($V_s = 0.37$), had V_s values that were larger than 0.38, indicating the dominance of direct contact forces. At relatively high shear rates, the yield stress is majorly determined by hydrodynamic forces, while the effects of Van der Waals and direct contact forces still exist.

The measured values of the yield stress (g) and plastic viscosity (h) of all samples at different elapsed times are provided in Table 5. For some mixes, the values of g and h at 12 and 18 minutes were not listed due to the loss of contact between the top plate and the fresh mixture, resulting in the underestimation of shear resistance. A generally increasing trend in g and h was observed with elapsed time. This was possibly associated with the precipitation of brucite ($Mg(OH)_2$) on the surface of RMC particles [45], which increased the direct contact between particles by enlarging the solid particle size and leading to additional drag between fluid layers.

The effects of water and FA contents on the rheological properties of RMC samples are shown in Fig. 6, where a declining trend in g and h was observed with increasing water content at both FA/b ratios of 0.53 and 0.58. The reduction in plastic viscosity and yield stress with increasing w/b ratios could be attributed to the higher liquid content that decreased direct contact amongst particles. Regarding the effect of FA content, the trend in g and h values at different FA contents ranging between 0% and 60% was

shown at a w/b of 0.58. An increase in the FA content from 0 to 30% (i.e. $V_s < 0.38$, Van der Waals forces dominate) led to an increase in plastic viscosity, while it did not have a profound effect on the yield stress. This increase in the plastic viscosity could be due to the enhanced Van der Waals forces via the reduction of the distance between particles as V_s increased from 0.35 to 0.37. The constant yield stress of samples FA0-0.58 and FA30-0.58 could be associated with the loose compaction of particles within these two mixes, thereby limiting the effect of particle shape on Van der Waals forces. A further increase in the FA content from 30% to 60% (i.e. $V_s > 0.38$, direct contact force dominates) resulted in the decline of both g and h at all w/b ratios. Although an increase in the solid volume fraction with an increase in the FA content could be expected due to the lower density of FA than RMC (2400 vs. 3230 kg/m³), the reduction of the yield stress and plastic viscosity with increasing FA content could be attributed to the spherical geometry of FA particles, which reduced the contact force between particles.

3.2. Mechanical performance

Based on the rheological results mentioned in Section 3.1, samples containing 30% FA (i.e. FA/b = 0.3) with different w/b ratios (0.41-0.53) and curing ages (7 and 28 days) were prepared for compression and uniaxial tensile tests. The obtained results are presented in Table 6. The tensile stress recorded at the occurrence of the first crack is referred to as the “first cracking strength”, whereas the tensile stress and tensile strain approaching specimen failure are referred to as the “ultimate tensile strength” and “tensile strain capacity”, respectively. In addition to the first cracking strength, ultimate tensile strength, and tensile strain capacity, crack spacing and average crack width of each sample are also provided in Table 6.

The relationship between the tensile stress and strain within each mix are shown in Fig. 7. Distinct elastic and strain-hardening stages were observed within each sample. In the elastic stage, the tensile stress developed linearly with the strain. The continuous increase in the load led to the introduction of the first crack, which marked the beginning

of the strain-hardening stage. During the strain-hardening stage, tensile stress increased slowly with the strain, accompanied with the progressive generation of multiple fine cracks that indicated ductility. Towards the end of strain-hardening, tensile stress started to drop dramatically due to the deterioration of fiber bridging followed by damage localization with increasing load. At this point, the load was released immediately after specimen failure, leading to the shrinking of a majority of the cracks due to the spring effect of fiber-bridging. Fig. 8 shows the typical crack distribution on a failed specimen after unloading, highlighting the occurrence of multiple cracking in RMC samples. The typical fracture surface can be seen in Fig. 9(a), where the layout of fibers at the location of the crack at failure is revealed. The pulled-out fiber and the leftover fiber tunnel at a fracture point are shown in Fig. 9(b) and (c), respectively. As can be seen from these images, the fiber surface was smooth with a very small amount of matrix debris attached on it, showing that a majority of the fibers were pulled out instead of ruptured. This suggests the fiber strength was not fully utilized in the developed formulations and the limiting phase was the fiber-matrix interface, which may be further strengthened.

3.2.1. Effect of w/b ratio

The results obtained after the mechanical testing of samples RMC-0.53, RMC-0.47 and RMC-0.41 are listed in Table 6. The influence of w/b content on the performance of each sample was observed both in terms of compressive and tensile strengths. As could also be seen in Fig. 7, the mechanical properties were enhanced when the w/b reduced from 0.53 to 0.47, where a less pronounced change was observed as the w/b further reduced to 0.41.

The initial reduction in the w/b from 0.53 to 0.47 led to a compressive strength that was almost four times higher (4.6 vs. 16.3 MPa). This was accompanied with a 50% increase in the first tensile crack strength, which mainly depended on the matrix performance. This improved performance could be associated with the increased

diffusion rate of CO₂ in a less saturated pore system, as well as the higher initial density provided by the lower water content within sample RMC-0.47. The increased diffusion of CO₂ could translate into a higher degree of carbonation and hence the formation of strength providing HMCs [14]. The other tensile properties, such as the ultimate tensile strength and ductility, which were mainly determined by the fiber-bridging, were also improved under lower water contents. The ultimate tensile strength was more than doubled, while the ductility was increased by about 50%. The reduction in crack spacing indicated that strain-hardening became more robust as the w/b ratio decreased. The enhanced fiber bridging, which was clearly indicated by the reduced crack width, could also be attributed to the higher degree of carbonation and denser microstructure at the fiber/matrix interface [46, 47]. When compared to RMC-0.53, the enhanced fiber-bridging of RMC-0.47 also led to a higher complementary energy J'_b , resulting in a more saturated multiple cracking. The reduced crack width would be especially important for any potential crack healing [48].

A further decrease in the w/b ratio from 0.47 to 0.41 (i.e. at 7 days) led to improved mechanical performance, albeit at a lower rate than previously observed. When compared to the increase in performance when the w/b changed from 0.53 to 0.47, the lower rate of increase observed in the transition of the w/b from 0.47 to 0.41 could be explained by the limited hydration of RMC due to the lower availability of water, which could have also hindered the formation of HMCs in the longer term. On the other hand, as the diffusion of CO₂ is faster in drier environments, the relatively low w/b of 0.41 could have provided the right medium for increased carbonation, which can explain the higher compressive strength results of sample RMC-0.41 [14]. Another factor that may have contributed to the relatively higher strength results of this sample was its reduced porosity within the interfacial zone of fiber-matrix under the low water content, thereby resulting in a denser structure than samples RMC-0.47 and RMC-0.53. The reduction in crack spacing and average crack width were also an indicator of improved strain-hardening and fiber bridging.

3.2.2. Effect of curing age

While a robust strain-hardening and ultra-high ductility were achieved in RMC-SHC samples, their mechanical properties were still not at the same level as typical PC-based SHC, whose ultimate tensile strength and ductility can easily reach 5 MPa and 3-5%, respectively [49]. Accordingly, samples with the highest ductility (RMC-0.41) were chosen to be exposed to additional CO₂ curing for up to 28 days to explore the full potential of RMC-SHC samples in terms of tensile strength enhancement. A comparison of samples RMC-0.41-7d and RMC-0.41-28d revealed an increase in the ultimate tensile strength by ~40%, which could be attributed to the continued formation of carbonate phases that strengthened the fiber/matrix interface over the 28-day curing period [14]. On the other hand, there were no notable changes in the tensile ductility, crack spacing and crack width. These results indicated the feasibility of enhancing the ultimate tensile strength of RMC-SHC formulations via the effective use of additional CO₂ curing, during which their strain-hardening robustness was not compromised.

3.3. CO₂ sequestration

The amount of CO₂ sequestered during the curing process was quantified via TGA/DSC, a representative curve for which is shown in Fig. 10. The mass loss < 100 °C due to the loss of hygroscopic water was followed by two distinct endothermic peaks. The first peak at around 320 °C corresponded to the removal of water of crystallization in Mg-carbonates that formed during carbonation curing and the decomposition of uncarbonated hydrates (Mg(OH)₂) into MgO. The second peak at around 460 °C corresponded to the decarbonation of carbonate phases, leaving MgO at the end of the analysis. The quantification of the mass loss at > 460 °C, which was associated with the loss of CO₂ from the carbonated RMC system, revealed an average carbonation degree of around 10%. A similar outcome can be expected under ambient carbonation conditions, albeit at a much slower rate due to the low concentration of CO₂ in the atmosphere (0.04%). These results indicate that the sequestration of CO₂ in the form of

stable carbonates within the prepared formulations can not only provide a safe storage for atmospheric CO₂, but also contribute to the development of a new type of strain-hardening composite that does not necessitate the use of any PC.

4. Conclusions

This study presented a preliminary investigation focusing on the development of ductile carbonated reactive MgO cement (RMC)-based strain-hardening composites (SHC) that did not involve the use of any PC. The effect of key factors such as the mix design (i.e. binder component and water content) on the rheological properties of fresh RMC mixtures was studied. The obtained results revealed the ideal binder composition and w/b ratios that led to a relatively high plastic viscosity and sufficient flowability for desirable fiber dispersion. Compressive and tensile strength tests were conducted to evaluate the effect of water content and curing age on the mechanical performance of the developed formulations. The use of carbonation curing enhanced the strength development of RMC-SHC by improving the fiber-matrix interface bond, but not ductility. Lower water contents led to increased tensile strength and ductility, which was attributed to the strengthening of the bond between the fibers and the matrix. The prepared RMC-SHC samples, which presented a considerable CO₂ sequestration capability during the curing process, achieved an ultimate tensile strength and ductility of up to 3.7 MPa and 3.3%, respectively. The RMC-FA formulations developed in this study, with a potentially lower environmental impact than corresponding PC-based mixes due to their ability to gain strength via carbonation, are considered as a promising candidate for strain-hardening composites that can be used in various building applications.

Acknowledgement

The authors would like to acknowledge the financial support from the Singapore MOE Academic Research Fund Tier 1 (RG 95/16) for the completion of this research project.

References

- [1] Statista-The portal for statistics. United States and world cement production in 2010 and 2016 (in million metric tons), <https://www.statista.com/statistics/219343/cement-production-worldwide/> (2016).
- [2] J.G. Olivier, G. Janssens-Maenhout, M. Muntean, J.A. Peters, PBL Netherlands Environmental Assessment Agency. Trends in global CO₂ emissions 2016 European Commission, Joint Research Centre (2016).
- [3] S. Ruan, C. Unluer, Comparative life cycle assessment of reactive MgO and Portland cement production, *Journal of Cleaner Production* 137 (2016) 258-273.
- [4] A. Fedoročková, M. Hreus, P. Raschman, G. Sučík, Dissolution of magnesium from calcined serpentinite in hydrochloric acid, *Minerals Engineering* 32 (2012) 1-4.
- [5] H. Dong, C. Unluer, E.-H. Yang, A. Al-Tabbaa, Synthesis of reactive MgO from reject brine via the addition of NH₄OH, *Hydrometallurgy* 169 (2017) 165-172.
- [6] M. Liska, A. Al-Tabbaa, Ultra-green construction: reactive magnesia masonry products, *Proceedings of the ICE-Waste and Resource Management* 162(4) (2009) 185-196.
- [7] F. Jin, K. Gu, A. Al-Tabbaa, Strength and drying shrinkage of reactive MgO modified alkali-activated slag paste, *Construction and Building Materials* 51 (2014) 395-404.
- [8] F. Jin, K. Gu, A. Al-Tabbaa, Strength and hydration properties of reactive MgO-activated ground granulated blastfurnace slag paste, *Cement and Concrete Composites* 57 (2015) 8-16.
- [9] L. Pu, C. Unluer, Investigation of carbonation depth and its influence on the performance and microstructure of MgO cement and PC mixes, *Construction and Building Materials* 120 (2016) 349-363.

- [10] N. Dung, C. Unluer, Sequestration of CO₂ in reactive MgO cement-based mixes with enhanced hydration mechanisms, *Construction and Building Materials* 143 (2017) 71-82.
- [11] N. Dung, C. Unluer, Improving the performance of reactive MgO cement-based concrete mixes, *Construction and Building Materials* 126 (2016) 747-758.
- [12] L. Vandeperre, A. Al-Tabbaa, Accelerated carbonation of reactive MgO cements, *Advances in Cement Research* 19(2) (2007) 67-79.
- [13] C. Unluer, A. Al-Tabbaa, Impact of hydrated magnesium carbonate additives on the carbonation of reactive MgO cements, *Cement and Concrete Research* 54 (2013) 87-97.
- [14] C. Unluer, A. Al-Tabbaa, Enhancing the carbonation of MgO cement porous blocks through improved curing conditions, *Cement and Concrete Research* 59 (2014) 55-65.
- [15] C. Unluer, A. Al-Tabbaa, Characterization of light and heavy hydrated magnesium carbonates using thermal analysis, *Journal of Thermal Analysis and Calorimetry* 115(1) (2014) 595-607.
- [16] M. Liska, A. Al-Tabbaa, K. Carter, J. Fifield, Scaled-up commercial production of reactive magnesium cement pressed masonry units. Part I: Production, *Proceedings of the Institution of Civil Engineers-Construction Materials* 165(4) (2012) 211-223.
- [17] M. Liska, A. Al-Tabbaa, K. Carter, J. Fifield, Scaled-up commercial production of reactive magnesia cement pressed masonry units. Part II: Performance, *Proceedings of the ICE-Construction Materials* 165(4) (2012) 225-243.
- [18] S. Ruan, C. Unluer, Influence of mix design on the carbonation, mechanical properties and microstructure of reactive MgO cement-based concrete, *Cement and Concrete Composites* 80 (2017) 104-114.
- [19] L. Vandeperre, M. Liska, A. Al-Tabbaa, Hydration and mechanical properties of magnesia, pulverized fuel ash, and portland cement blends, *Journal of Materials in Civil Engineering* 20(5) (2008) 375-383.
- [20] C. Unluer, A. Al-Tabbaa, The role of brucite, ground granulated blastfurnace slag, and magnesium silicates in the carbonation and performance of MgO cements, *Construction and Building Materials* 94 (2015) 629-643.
- [21] A.M. Brandt, Fibre reinforced cement-based (FRC) composites after over 40 years of development in building and civil engineering, *Composite Structures* 86(1) (2008) 3-9.

- [22] V. Li, D. Mishra, H.-C. Wu, Matrix design for pseudo-strain-hardening fibre reinforced cementitious composites, *Materials and Structures* 28(10) (1995) 586-595.
- [23] V.C. Li, S. Wang, C. Wu, Tensile strain-hardening behavior of polyvinyl alcohol engineered cementitious composite (PVA-ECC), *ACI Materials Journal* 98(6) (2001) 483-492.
- [24] E.-H. Yang, Y. Yang, V.C. Li, Use of high volumes of fly ash to improve ECC mechanical properties and material greenness, *ACI Materials Journal* 104(6) (2007) 620-628.
- [25] E.-H. Yang, V.C. Li, Tailoring engineered cementitious composites for impact resistance, *Cement and Concrete Research* 42(8) (2012) 1066-1071.
- [26] E.-H. Yang, V.C. Li, Strain-rate effects on the tensile behavior of strain-hardening cementitious composites, *Construction and Building Materials* 52 (2014) 96-104.
- [27] J. Qiu, E.-H. Yang, A micromechanics-based fatigue dependent fiber-bridging constitutive model, *Cement and Concrete Research* 90 (2016) 117-126.
- [28] J. Qiu, X.-N. Lim, E.-H. Yang, Fatigue-induced deterioration of the interface between micro-polyvinyl alcohol (PVA) fiber and cement matrix, *Cement and Concrete Research* 90 (2016) 127-136.
- [29] T. Tecoco Pty Ltd. Australia, US Patent 7347896 (2008).
- [30] E.-H. Yang, M. Sahmaran, Y. Yingzi, V.C. Li, Rheological control in production of engineered cementitious composites, *ACI Materials Journal* 106(4) (2009) 357-366.
- [31] B. Felekoğlu, S. Türkel, B. Baradan, Effect of water/cement ratio on the fresh and hardened properties of self-compacting concrete, *Building and Environment* 42(4) (2007) 1795-1802.
- [32] M. Li, V.C. Li, Rheology, fiber dispersion, and robust properties of Engineered Cementitious Composites, *Materials and Structures* 46(3) (2013) 405-420.
- [33] E.-H. Yang, S. Wang, Y. Yang, V.C. Li, Fiber-bridging constitutive law of engineered cementitious composites, *Journal of Advanced Concrete Technology* 6(1) (2008) 181-193.
- [34] A.F. Abdalqader, F. Jin, A. Al-Tabbaa, Characterisation of reactive magnesia and sodium carbonate-activated fly ash/slag paste blends, *Construction and Building Materials* 93 (2015) 506-513.

- [35] T. Zhang, C. Cheeseman, L. Vandeperre, Development of low pH cement systems forming magnesium silicate hydrate (MSH), *Cement and Concrete Research* 41(4) (2011) 439-442.
- [36] V.C. Li, On engineered cementitious composites (ECC), *Journal of Advanced Concrete Technology* 1(3) (2003) 215-230.
- [37] D.A. Williams, A.W. Saak, H.M. Jennings, The influence of mixing on the rheology of fresh cement paste, *Cement and Concrete Research* 29(9) (1999) 1491-1496.
- [38] L. Mo, D.K. Panesar, Effects of accelerated carbonation on the microstructure of Portland cement pastes containing reactive MgO, *Cement and Concrete Research* 42(6) (2012) 769-777.
- [39] ASTM, C109-16A, Standard test method for compressive strength of hydraulic cement mortars, ASTM, Philadelphia, PA, USA (2016).
- [40] C.F. Ferraris, N.S. Martys, W.L. George, Development of standard reference materials for rheological measurements of cement-based materials, *Cement and Concrete Composites* 54 (2014) 29-33.
- [41] N. Roussel, A. Lemaître, R.J. Flatt, P. Coussot, Steady state flow of cement suspensions: a micromechanical state of the art, *Cement and Concrete Research* 40(1) (2010) 77-84.
- [42] D. Lootens, H. Van Damme, P. Hébraud, Giant stress fluctuations at the jamming transition, *Physical Review Letters* 90(17) (2003) 178301.
- [43] T.H. Phan, M. Chaouche, M. Moranville, Influence of organic admixtures on the rheological behaviour of cement pastes, *Cement and Concrete Research* 36(10) (2006) 1807-1813.
- [44] S. Mansoutre, P. Colombet, H. Van Damme, Water retention and granular rheological behavior of fresh C_3S paste as a function of concentration, *Cement and Concrete Research* 29(9) (1999) 1441-1453.
- [45] S.D. Rocha, M.B. Mansur, V.S. Ciminelli, Kinetics and mechanistic analysis of caustic magnesia hydration, *Journal of Chemical Technology and Biotechnology* 79(8) (2004) 816-821.

- 548 [46] J. Li, J. Qiu, S. He, E.-H. Yang, Micromechanics-Based Design of Strain Hardening
549 Cementitious Composites (SHCC), International Conference on Strain-Hardening
550 Cement-Based Composites, Springer, 2017, pp. 12-27.
- 551 [47] T. Kanda, V.C. Li, Interface property and apparent strength of high-strength
552 hydrophilic fiber in cement matrix, Journal of Materials in Civil Engineering 10(1) (1998)
553 5-13.
- 554 [48] Y. Yang, M.D. Lepech, E.-H. Yang, V.C. Li, Autogenous healing of engineered
555 cementitious composites under wet–dry cycles, Cement and Concrete Research 39(5)
556 (2009) 382-390.
- 557 [49] E.-H. Yang, Y. Yang, V.C. Li, Use of high volumes of fly ash to improve ECC
558 mechanical properties and material greenness, ACI Materials Journal 104(6) (2007).

559

List of Tables:

Table 1 Chemical composition of RMC and FA.

Material	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	K ₂ O	TiO ₂	Others
RMC	97%	1.3%	1.3%	0.2%	0.2%	-	-	-
FA	0.8%	1.2%	58.6%	4.7%	30.4%	1.5%	2.0%	0.8%

Table 2 Properties of the PVA fibers used in this study.

Length (mm)	Diameter (μm)	Fiber aspect ratio, i.e. length/diameter	Density (kg/m^3)	Nominal tensile strength (MPa)	Surface oil- content (%)
12	39	307	1300	1600	0

Table 3 Mix proportions of fiber-free RMC mixtures prepared for rheology measurements.

*Sample	RMC (kg/m ³)	FA (kg/m ³)	Water (kg/m ³)	Na(PO ₃) ₆ (kg/m ³)	FA (%)	w/b	Solid (RMC+FA) volume fraction
FA0-0.58	1102	0	639	64	0	0.58	0.35
FA30-0.47	840	360	570	57	30	0.47	0.42
FA30-0.53	789	338	595	59	30	0.53	0.39
FA30-0.58	744	319	617	62	30	0.58	0.37
FA60-0.47	462	693	548	55	60	0.47	0.44
FA60-0.53	435	653	573	57	60	0.53	0.42
FA60-0.58	411	616	596	60	60	0.58	0.39

* The rheology measurements performed on samples FA0-0.47 and FA0-0.53 were not presented as these fresh mixtures hardened too fast, resulting in incorrect results. Specifically, once the plate-to-plate spinning started, these samples immediately dislodged and were no longer in full contact with the upper plate.

Table 4 Mix proportions prepared for testing hardened tensile properties.

Sample	RMC (kg/m ³)	FA (kg/m ³)	Water (kg/m ³)	Na(PO ₃) ₆ (kg/m ³)	PVA fiber (kg/m ³)	w/b	Curing duration (days)
RMC-0.53	799	342	601	59	26	0.53	7
RMC-0.47	853	365	573	53	26	0.47	7
RMC-0.41	864	370	510	51	26	0.41	7 and 28

Table 5 Rheological test results.

Sample	Elapsed time = 6 min		Elapsed time = 12 min		Elapsed time = 18 min	
	g (Pa)	h (Pa·s)	g (Pa)	h (Pa·s)	g (Pa)	h (Pa·s)
FA0-0.58	60.6	1.15	-	-	-	-
FA30-0.47	153.1	5.55	-	-	-	-
FA30-0.53	172.8	3.66	183.3	4.79	-	-
FA30-0.58	48.0	2.59	76.0	3.29	94.8	4.66
FA60-0.47	26.2	2.24	40.3	2.66	54.8	3.14
FA60-0.53	6.1	1.13	11.0	1.93	31.0	3.41
FA60-0.58	2.1	0.43	1.6	0.44	5.5	1.17

* “-“ indicates g and h were underestimated due to the loss of contact between the top plate and the fresh mixture.

Table 6 Mechanical test results.

Sample	Curing age (days)	Compressive strength (MPa)	Results of uniaxial tensile test				
			First cracking strength (MPa)	Ultimate tensile strength (MPa)	Tensile strain capacity (%)	Crack spacing* (mm)	Average crack width (μ m)
RMC-0.53	7	4.60 ± 0.07	1.09 ± 0.11	1.32 ± 0.09	1.40 ± 0.66	12.80 ± 3.50	146.80 ± 22.90
RMC-0.47	7	16.27 ± 0.47	1.60 ± 0.13	2.89 ± 0.26	2.13 ± 1.02	2.66 ± 1.10	49.74 ± 12.88
RMC-0.41	7	18.97 ± 0.48	2.19 ± 0.48	2.61 ± 0.48	2.64 ± 1.22	1.45 ± 0.14	47.21 ± 15.08
	28	-	2.38 ± 0.24	3.67 ± 0.35	2.70 ± 0.96	1.74 ± 0.27	63.77 ± 10.38

*Crack spacing (mm) = Gauged length extension/crack number; a smaller crack spacing is usually associated with a higher degree of strain-hardening.

List of Figures:

Fig. 1 Illustration of the fiber-bridging constitutive law, showing the tensile stress-crack opening displacement $\sigma(\delta)$ curve and strain-hardening criteria [33]

Fig. 2 Particle size distribution of RMC and FA

(a)

(b)

Fig. 3 Measurement of sample rheology, showing (a) rheometer used and (b) test setup

Fig. 4 Illustration of uniaxial tensile test, showing (a) dimensions of the dogbone specimen and (b) test setup

(a)

(b)

Fig. 5 τ - N curve of sample FA60-0.53 at 6, 12 and 18 minutes, showing (a) overall test results and (b) section selected in (a)

(a)

(b)

Fig. 6 Effects of the water and FA contents on the (a) plastic viscosity and (b) yield stress of RMC samples

Fig. 7 Tensile stress vs. strain curves of samples (a) RMC-0.53-7d, (b) RMC-0.47-7d, (c) RMC-0.41-7d and (d) RMC-0.41-28d

Fig. 8 Crack pattern of a typical sample (RMC-0.41 at 7 days)

(a)

(b)

(c)

Fig. 9 Illustration of a typical failed specimen (RMC-0.41 at 7 days), showing the (a) fracture surface with several pulled fibers, (b) FESEM image of a pulled-out fiber and (c) FESEM image of a left-over tunnel from the pulled fiber

Fig. 10 A typical TGA/DSC curve of a RMC-SHC sample (RMC-0.53)