OBSERVATION OF THE SETTING PROCESS OF UNSHAPED REFRACTORY MATERIALS BY DYNAMIC-MECHANICAL ANALYSIS

V. Hopp*, A. Masoudi Alavi, A. Sax and P. Quirmbach
University of Koblenz-Landau, Germany

ABSTRACT

The investigation of the stiffening behavior of unshaped refractories is essential for an adequate lining process. The most common method to monitor the stiffening is to observe the propagation of ultrasonic waves in the material over time. However, this method is not applicable for every refractory system. In some cases, it could be shown that the propagation of the ultrasonic waves does not directly correlate with the increase of the mechanical strength and thus the real hardening of the mixture. Therefore, an alternative measuring method is presented. The so-called Dynamic-Mechanical Analysis (DMA) provides a new approach for the observation of setting processes. Although originated in the plastics research area, this method can be adapted for inorganic systems as for example unshaped refractories. It allows monitoring the evaluation of the viscoelastic properties of a material as a function of time and temperature, thus representing a powerful tool for time-dependent tracking of the strength-development during setting processes. In addition, frequency-dependent measurements offer the possibility to determine characteristic points in the setting process as for example the gel and the glass point in sol-gel-bonded systems. The suitability of the Dynamic-Mechanical Analysis for the class of unshaped refractories is shown by means of hydraulic and chemically bonded materials.

INTRODUCTION

For unshaped refractories different binder systems are used to shape the loose basic materials and allow its processing. For the selection of the optimal binder composition, the setting behavior, particularly the setting time, is of special interest as the processing latitude is crucial for an adequate lining.

The most common method to monitor the stiffening of unshaped materials is to observe the propagation of ultrasonic waves in the material over time[1-4]. During the propagation, the ultrasonic field interacts with the sample material due to the varying transfer of vibrational energy between unequal coupled particles, which leads to changes e.g. in the running time, damping and frequency. This method is therefore suitable to show changes in the materials stiffness and thus, time-dependent observation of these parameters by continuous ultrasonic velocity measurements can obtain information about the setting progress.

The runtime of the ultrasonic waves represents the average stiffness of the whole material, which is usually composed of very hard aggregates and the much less strong binding phase. The strength of the material during the setting process, however, depends mostly on the weakest part of the structure, which means the binding phase and its adhesion to the grains[3]. Thus, the results obtained by the ultrasonic wave propagation do not always represent the real strength development of the mixtures[3,4]. Another approach to

determine the strength development during setting processes is the execution of strength tests after different time periods[5]. However, the suitability of those methods is limited especially in the early setting stage of pasty mixtures with very low stiffness.

In a current research project, the early setting stage is of special interest for the development of mixtures for additive manufacturing (AM) of refractories. AM technologies require challenging setting properties, which are realized by tailored additive systems. Due to the restrictions of other methods, the Dynamic-Mechanical Analysis (DMA) was chosen for an alternative approach to investigate the influence of different additives and its combinations on the workability of AM refractory mixtures.

DMA allows time-dependent tracking of the strength development during setting as it measures the viscoelastic properties of a material as a function of temperature, frequency and time. By application of an oscillating mechanical force (exciter signal), the elastic part (storage modulus E‘) and the plastic part (loss modulus E‘‘) of the viscoelastic properties can be determined from the response signal of the sample. The ratio between E‘‘ and E‘ is defined as the loss factor tanδ[6].

In preceding work[7], DMA was used to determine the setting behavior of sol-gel bonded materials. On this basis, the aim was to investigate, if the developed test procedure is applicable for other sol-gel systems too. In addition, the adaption of the test method to the class of hydraulic bonded systems was considered.

EXPERIMENTAL

To investigate the suitability of the DMA for describing the early setting processes, measurements of mixtures based on varying binder systems were carried out.

For the class of sol-gel-based binder systems, sample mixtures of sodium water glass and different inorganic hardeners were prepared. After the addition of the powder hardeners to the water glass sol, the mixture was stirred manually for 3 minutes. In the present work, the results of the setting of water glass Betol47T (Wöllner) with 20 wt.% of a phosphate hardener ($AlPO_4$, synth.) are shown. A focus was the detection of the characteristic gel point and its reproducibility by DMA.

Concerning the hydraulic binder systems, measurements of mixtures of calcium aluminate cements with different accelerators (e.g. based on silicates, carbonates) were carried out. In this test series, additional focus was set on the comparison of the pure binding phase and the binding phase combined with typical refractory aggregates (e.g. Al_2O_3, SiO_2, mullite). In the presented part of the study, the findings are exemplified by measurements of pure mixtures of a calcium aluminate cement (Secar 71) with water (water to cement ratio w/c = 0.4) and an alkali silicate accelerator (1 wt.%) compared to its combination with an Al_2O_3 (Tabular Alumina T 60, Almatis) aggregate (amount of cement in the combined mixture = 10 wt.%).

Preparation and mixing of the samples were conducted according to the following scheme:

- Mixing and stirring of the dry powder components for 1 minute.
- Addition of processing water under further stirring for 2 minutes.

Due to the time-dependence of the measurement the preparation procedure was exactly determined with regard to its duration to ensure that every DMA measurement starts five minutes after mixing the components (mixing and stirring: 3 minutes + preparation of DMA measurement: 2 minutes). In all of

the shown diagrams this 5-minute time slot was added to the pure measuring time.

DMA Measurements

For the determination of the stiffening behavior, time-dependent DMA measurements were carried out using a DMA 242C from Netzsch. With regard to the consistency of the mixtures a compression mode and a stress-controlled (maximum dynamic force = 7 N) measuring principle were chosen. The influence of the frequency is determined using cyclic frequency sweeps at f = 1, 2, 5, 10 Hz. Both the frequencies and the mechanical parameters were selected with regard to the above mentioned preceded studies[8].

Due to its low viscosity the measurements of the pasty samples were carried out in a crucible. Stress is put into the system using a spherical feeler stamp (Fig. 1). The mixtures are filled in the crucible up to a height of h = 11 mm and the feeler stamp is immersed completely in the material. To prevent deeper invasion of the stamp during the measurement, further contact pressing is avoided by choosing a proportional factor (relation of dynamic to static force) of zero. During the measurements, a temperature chamber was used to ensure a constant temperature of T = 25°C.

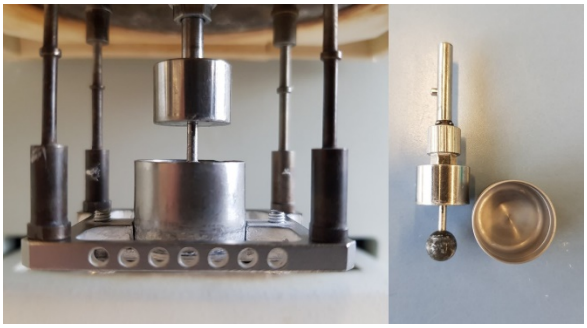

Fig. 1: Experimental set-up Dynamic-Mechanical Analysis

RESULTS AND DISCUSSION

The different approaches to investigate the suitability of the DMA are exemplified by the previously described mixtures. With regard to the presented figures it should be noticed, that the geometry of the feeler stamp hinders the mathematical determination of absolute values of the mechanical parameters. Therefore, the maximum achieved storage or loss modulus in every test series was normalized.

Sol-gel based binder systems

The strength development and setting progress of the sol-gel-bonded samples are represented by a sigmoid increase of the storage modulus (Fig. 2) which is typical for setting processes: After only small changes in an initiation phase, the storage modulus increases significantly, which goes along with a peak in the tanδ. Although the increase in the storage modulus slows down, it does not reach a plateau that would represent a complete hardening after the measuring time of 24 hours. The development of the storage modulus during DMA measurements matches with a macroscopic observation of comparative samples.

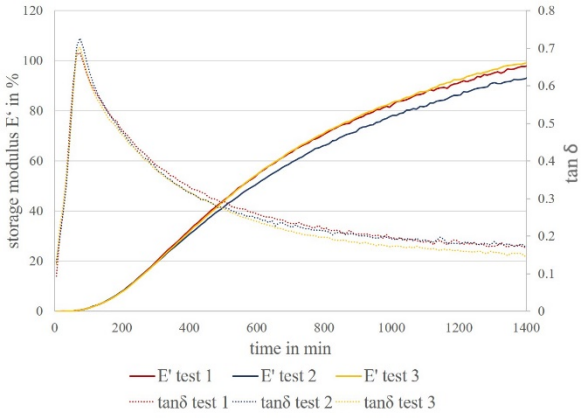

Fig. 2: DMA measurements of 3 comparative test series of the water glass phosphate mix: Development of storage modulus E‘ and tanδ at a frequency of 1 Hz as a function of time.

The consideration of the three comparative test series in Fig. 2 shows a high reproducibility, both in the storage modulus and tanδ. More detailed insights in the reproducibility can be gained by the comparison of the gel points. Gel points were determined as the point in time when the frequency dependence of tanδ disappeared[7] (Fig. 3). These characteristic points are reached after 51.5 minutes (test 1), 55 minutes (test 2) and 55.5 minutes (test 3).

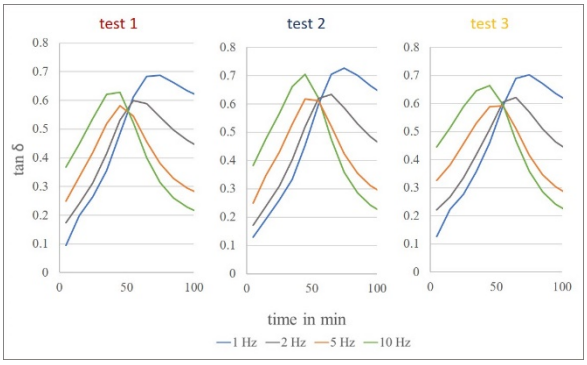

Fig. 3: DMA measurements of 3 comparative test series of the water glass phosphate mixtures: Point of intersection of the loss factor tanδ for a multi-frequency measurement in dependence of the hardening time.

The good accordance of the gel points and in the progress of storage modulus and tanδ as well as the transferability of the method to different types of water glasses support the suitability of the DMA for the investigation of sol-gel systems.

Hydraulic binder systems

Even in the case of hydraulic binder systems the setting is represented by the progress of the storage modulus. Fig. 4 shows a direct increase of E‘ for two comparative measurements. From a macroscopic view it corresponds to a slight thickening of the mixture. In the further progress an abrupt and strong decrease of the storage modulus can be observed. It can be explained by the formation of cracks in the sample material due to the movement and the pressure of the feeler stamp. At this point the elastic portion of the mixture is too low to compensate the input of the mechanical energy and brittle cracking occurs. Nevertheless, ongoing stiffening can be observed by a further increase in the storage modulus until the formation of other cracks. After a certain time, a critical number of cracks is reached, and the inserted energy is more or less completely lost over the cracks. From this point, no further determination of the stiffening is possible, represented by a plateau in the storage modulus that is in conflict to the macroscopic observed ongoing stiffening. Further investigations are focused on avoiding this effect e.g. by varying the geometry of the feeler stamp. Anyway, the contemporaneous crack formation in the two comparative samples highlights again the high reproducibility of the method.

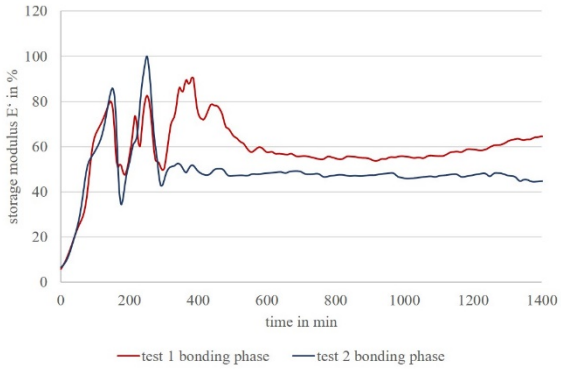

Fig. 4: DMA measurements of 2 comparative test series of the cement-water mixtures: Development of storage modulus E‘ at a frequency of 1 Hz as a function of time.

The problem of crack formation cannot be observed in the DMA measurements of samples with aggregate addition (Fig. 5), due to its overall higher strength. The storage modulus increases quickly until it reaches a plateau that is in good accordance to the macroscopically detected hardening.

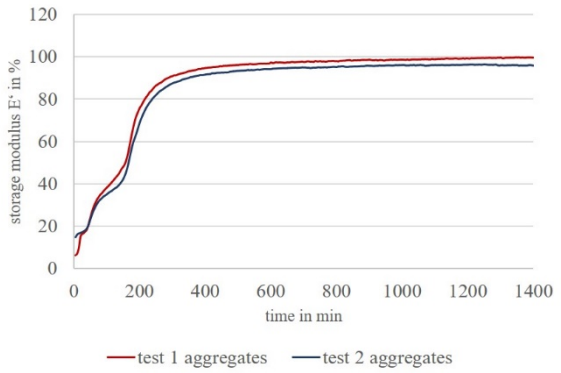

Fig. 5: DMA measurements of 2 comparative test series of the cement binding system with aggregate addition: Development of storage modulus E‘ at a frequency of 1 Hz as a function of time.

During the interval of fast increase of the storage modulus a kind of step, formed due to a decline of the setting velocity, followed by an anew rise can be seen. When coupling these measurements with the results of the pure binding phase as it is shown in Fig. 6, a correlation between the steps in the storage modulus’ increase can be determined. Even if the setting of the pure binding phase is slower, the step in the progress of E‘ is quite similar. This is a good evidence that the DMA does not only reflect an average stiffness of the system as in the case of ultrasonic velocity measurements, but reflects the real strength development even in presence of very hard aggregates.

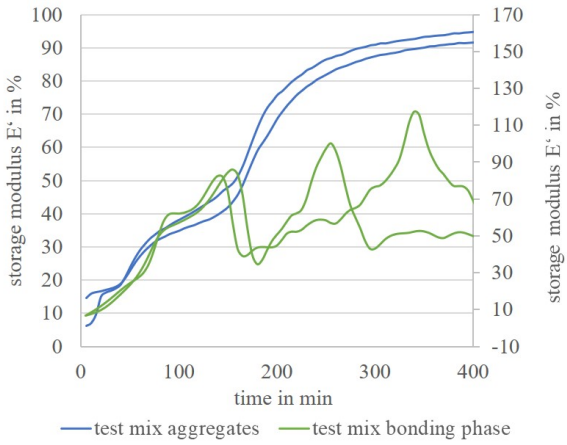

Fig. 6: Combination of the DMA measurements of the pure binding phase and the binding phase with aggregate addition.

CONCLUSIONS

DMA measurements were conducted to investigate the suitability of this method for determining the setting process of varying binder systems. First main aspects of the ongoing study are exemplified by the results of a phosphate hardened sol-gel system and a cement-accelerator mixture. From the presented parts of the study the following conclusions can be drawn:

- DMA measurements of all binder systems investigated show a high reproducibility and a good accordance of the progress in the storage modulus to the macroscopic observed stiffening.
- The only exception can be seen in DMA measurements of the pure cement binding phase. Crack formation due to the mechanical impact of the feeler stamp results in a loss of the validity of the progress in the storage modulus. Ongoing research is actually done to avoid these effects.
- The comparison of DMA measurements of the pure cement binding phase and the cement-aggregate mixtures show analogous

steps in the storage modulus' increase, indicating the suitability of the method to describe strength development during setting processes even in presence of hard aggregates.

ACKNOWLEDGEMENTS

This research was financially supported by the European Union (European Regional Development Fund, project: competence center for additive manufacturing of inorganic non-metallic materials), and the funding line "Investment for Growth and Jobs", of the Ministry of Economic Affairs, Transport, Agriculture and Viticulture of Rhineland Palatinate.

REFERENCES

1. R. Demirboga, I. Türkmen and M. B. Karakoc, "Relationship between ultrasonic velocity and compressive strength for high-volume mineral-admixtured concrete" Cement and Concrete Research 34 2329–2336 (2004), doi:10.1016/j.cemconres.2004.04.017

2. C. Große, „Quantitative zerstörungsfreie Prüfung von Baustoffen mittels Schallemissionsanalyse und Ultraschall", Ph.D. Thesis, University of Stuttgart, Germany (1996)

3.W. Erfurt, „Erfassung von Gefügeveränderungen in Beton durch Anwendung zerstörungsfreier Prüfverfahren zur Einschätzung der Dauerhaftigkeit", Ph.D. Thesis, Bauhaus University, Weimar, Germany (2002)

4. D.-Y. Yoo, H.-O. Shin, 2 and Y.-S. Yoon, "Ultrasonic Monitoring of Setting and Strength Development of Ultra-High-Performance Concrete", Materials, 9, [294] (2016), doi:10.3390/ma9040294

5. C. Lee, S. Lee and N. Nguyen, "Modeling of Compressive Strength Development of High-EarlyStrength-Concrete at Different Curing Temperatures", Int. J. Concr. Struct. Mater., 10 [2] 205–219 (2016)
doi: 10.1007/s40069-016-0147-6

6. K. P. Menard, "Dynamic Mechanical Analysis - A Practical Introduction", 2nd ed. Taylor and Francis Group, Boca Raton, FL, USA (2008)

7. V. Hopp, A. Sax, D. Helmus and P. Quirmbach, "Adaptation of the dynamic mechanical analysis to determine the gel point during the setting of liquid alkali silicates" Int. J. Appl. Ceram. Technol., 16, 2331–2341 (2019)
doi: 10.1111/ijac.13334

8. V. Hopp, A. Masoudi Alavi, A. Sax and P. Quirmbach, "Influence of Aluminium and Boron Orthophosphate on the Setting and the Resulting Structure of Alkali Silicate Binders for Refractory Application", Ceramics, 3, [1] 1–11 (2020)
doi:10.3390/ceramics3010001