

# Rheological Lab Testing of Building Formulations

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Rheology is the science of flow and deformation of matter. It concerns the relationships between shear stress  $T$ , shear strain  $\lambda$  and time  $t$ . Ideal systems are described by simple, linear equations as, e.g., Hooke's Law for ideal solids or Newton's Law for ideal liquids. Reality is more complicated than ideal and therefore ideal systems are rather the exception than the rule. This is true for food, cosmetics, coatings, plastics and building formulations just to mention a few. Under building formulations we mean a blend of binders which could be cement or plaster with aggregates like silica sand or limestone and last, but not least, additives to improve performance. After addition of water, mortars result which, depending on the composition, are used as machine plasters, tile cements, masonry mortars, joint fillers, grouts, self-levelling compounds etc.

The requirements for a mortar are manifold and often set by local habits and traditions. Yet, generally speaking, they should be easy to apply, provide smooth workability, high efficiency and meet certain requirements on final strength. And, of course, production costs should be reasonable. Some of these properties can be linked to rheology [1,2,3] as, e.g., the mortar consistency and the set of plaster.

Consistency probably could be best described as mortar structure and mortar flow. Structure and flow means absence or presence of a yield point; and if a yield point exists, the yield stress value to overcome the yield point as well as the corresponding viscosity. Once flow starts, the resulting viscosity at a given shear rate can describe the smoothness of the mortar. Rotational viscometry is a suitable tool to generate the rheological information. It has to be kept in mind that the existence of a yield point value means the destruction of a structure to induce flow into the system. Today, commercial rheometers are available that can apply a lower shear stress than the existing yield stress. The approach enables the operator to study the intact system - how it performs on increase of shear stress that finally leads to destruction of the mortar structure. This method is preferred over the one which determines yield stress by extrapolation of shear stress values to a shear rate of zero. Inherent in the latter procedure is the fact that shear values are recorded in an already broken-down system in order to calculate conditions for an intact structure. Our approach is demonstrated with a bentonite gel as an example.

The rheometer operates in such a way that shear stress is gradually increased in a controlled fashion and with simultaneous recording of the material deformation. The apparent viscosity (defined as the ratio of shear stress to shear rate) will increase and then drop dramatically once the structure is destroyed and the matter flows. Yield stress is defined as the shear stress at maximum viscosity. Both values are useful to characterize a system. Besides these values, we also used the mortar viscosity, once flow has started, to judge consistency.

The crucial question is how to rate the data and correlate them with the statement of a craftsman judging mortar consistency by experience. Well-known sagging tests were used to adjust mortar from sagging to firm stand-up. Determination of yield stress and yield viscosity of these mortars by rotational viscometry led to a minimum yield value that has to be met to prevent sagging. This is shown in the next chart. The correct water factor was adjusted by an established sagging test to a point of just preventing sliding of tiles. The rotational evaluation gives a yield value of 350 Pa. The technique we use provides even more information, as can be shown.

For the very same mortar, a defined stress is applied in the creep test and the system monitors if there is any flow over time. As can be seen, the mortar withstands a stress of 300 yet flows at 400 Pa. By mathematical conversion, these values can be expressed as the force of a certain tile weight that acts upon the mortar. A statement can then be given at where tile weight sagging occurs and even how fast sagging is.

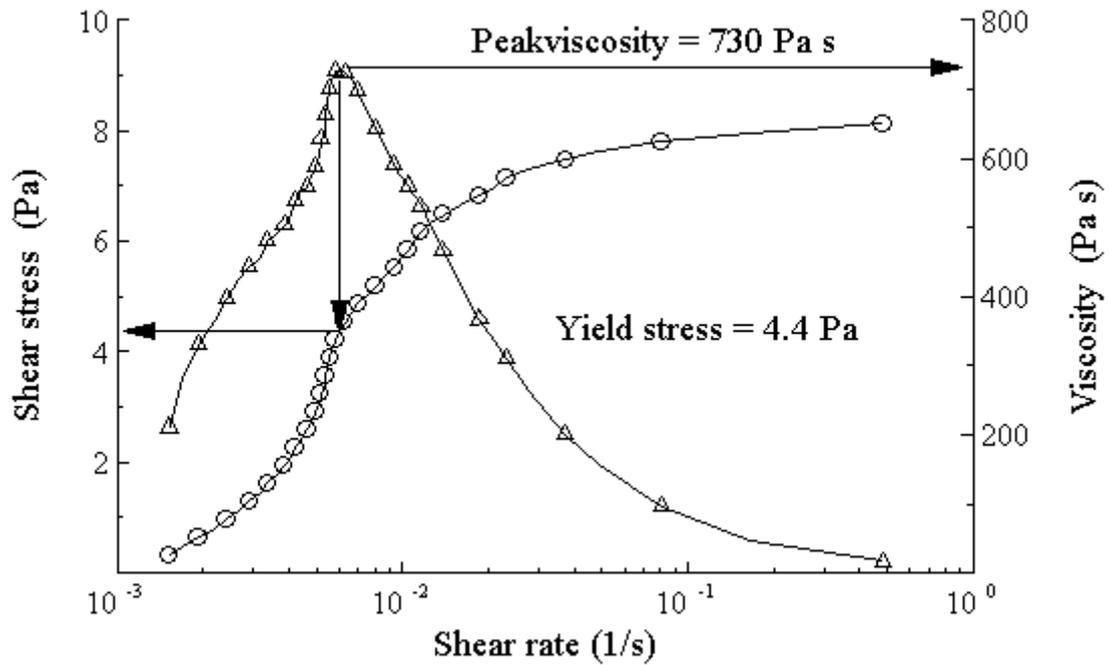


Fig. 1: Measurement of yield stress and yield stress viscosity of a bentonite gel

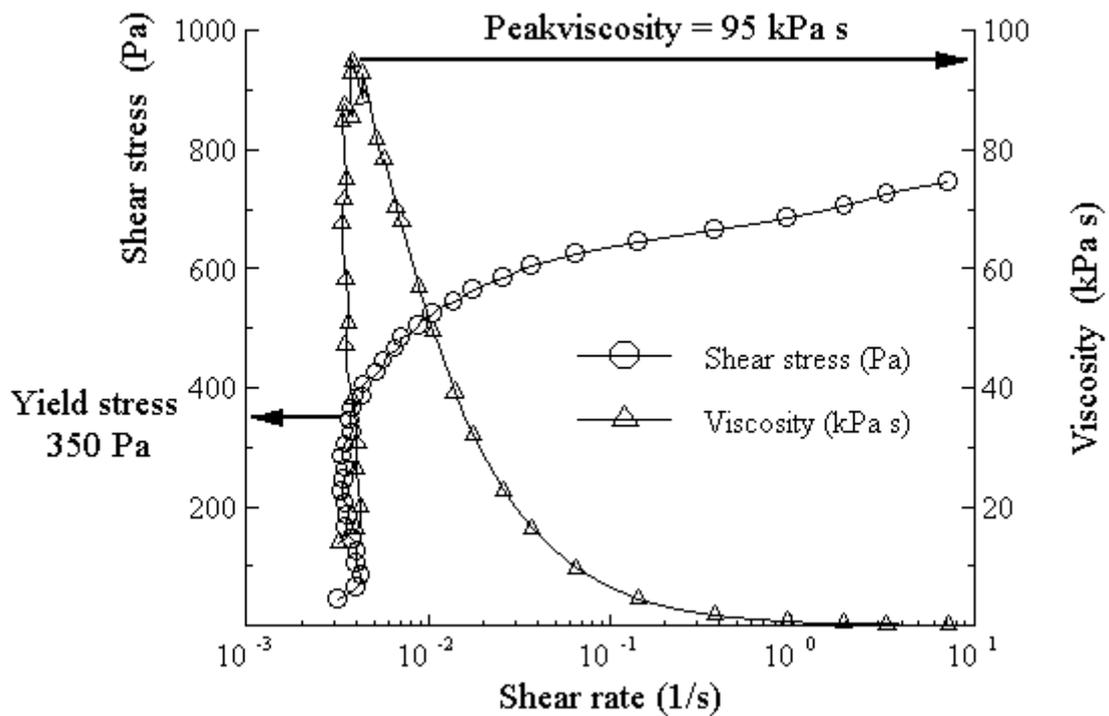


Fig. 2: Yield stress and viscosity of a tile cement mortar

While we need to meet a minimum yield stress, too high a value is detrimental. If for a given application a very high yield value was present, the craftsmen evaluated the mortar as heavy and sticky.

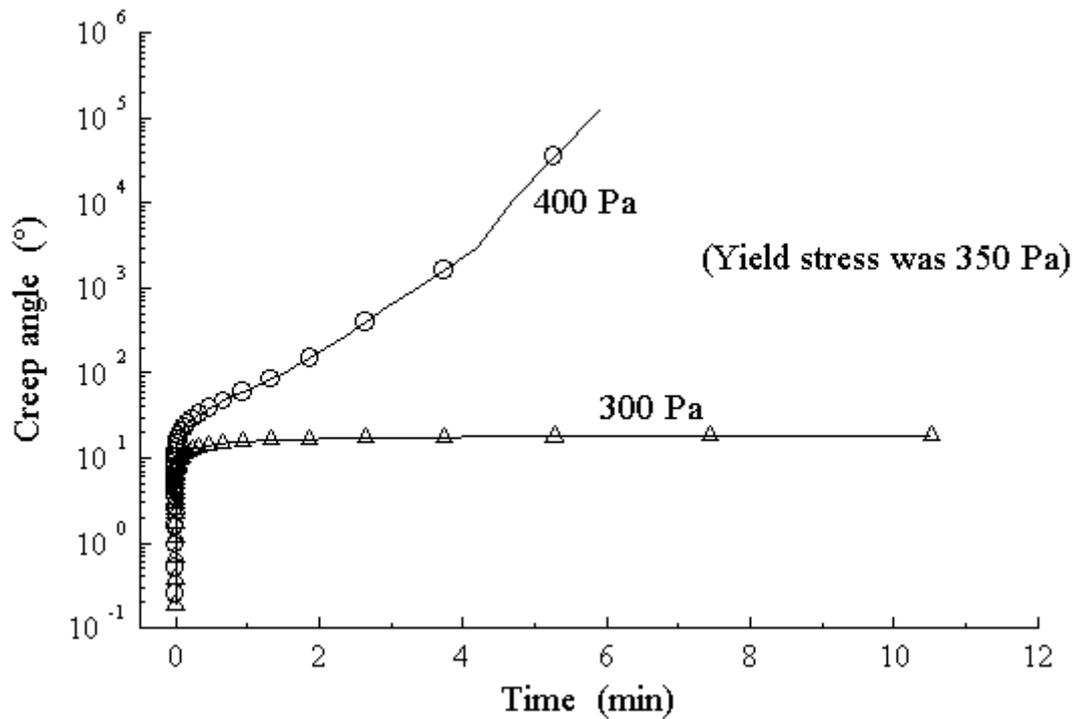


Fig. 3: Creep test with tile cement mortar applying different stress to simulate sagging

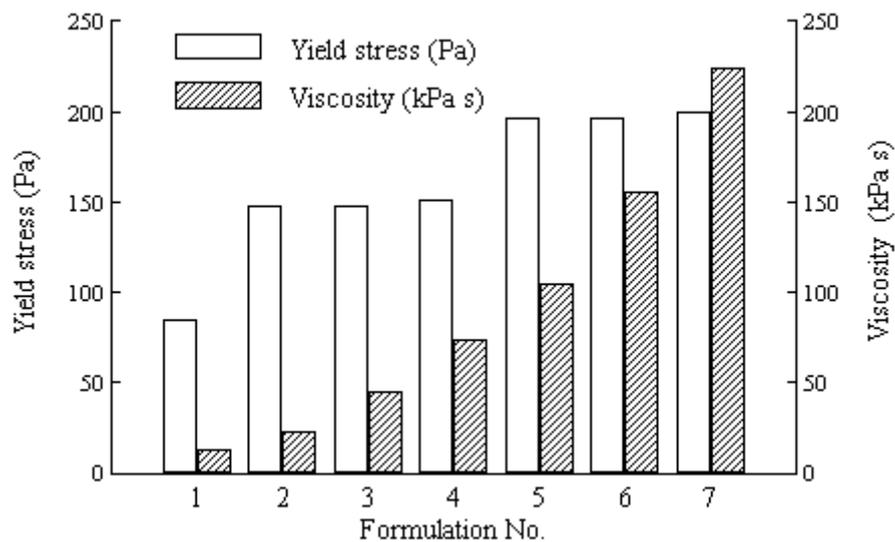


Fig. 4: Adjustment of yield stress and viscosity of a mortar by chemical modification

The example shows mortars with different yield stress. By chemical modification we could also adjust the corresponding yield stress viscosity. As it was said, too high a yield stress was unfavourably rated. Interestingly for mortars having the same yield stress, the one with lower yield stress viscosity was judged to provide smooth workability in contrast to the other that was rated as cloggy.

Once a rating system was established, it was of interest to check the influence of cellulose ether and modifying agent on mortar consistency. As an example, tile cement was used. The cellulose ether is a straight methyl cellulose MC, having a 2% aqueous viscosity of 4000 mPa·s. The yield stress is 240 Pa for a water ratio of 0.25. Adding modifier to the MC results in a yield stress of 320 Pa at the considerably higher water ratio of 0.28. What can be demonstrated is the pronounced influence of modifying agent on mortar consistency even at very low use levels, overruling completely the effect of cellulose ether on consistency. Of course, the phenomenon is well known to the expert yet, to the best of our knowledge, no quantification was known up to now.

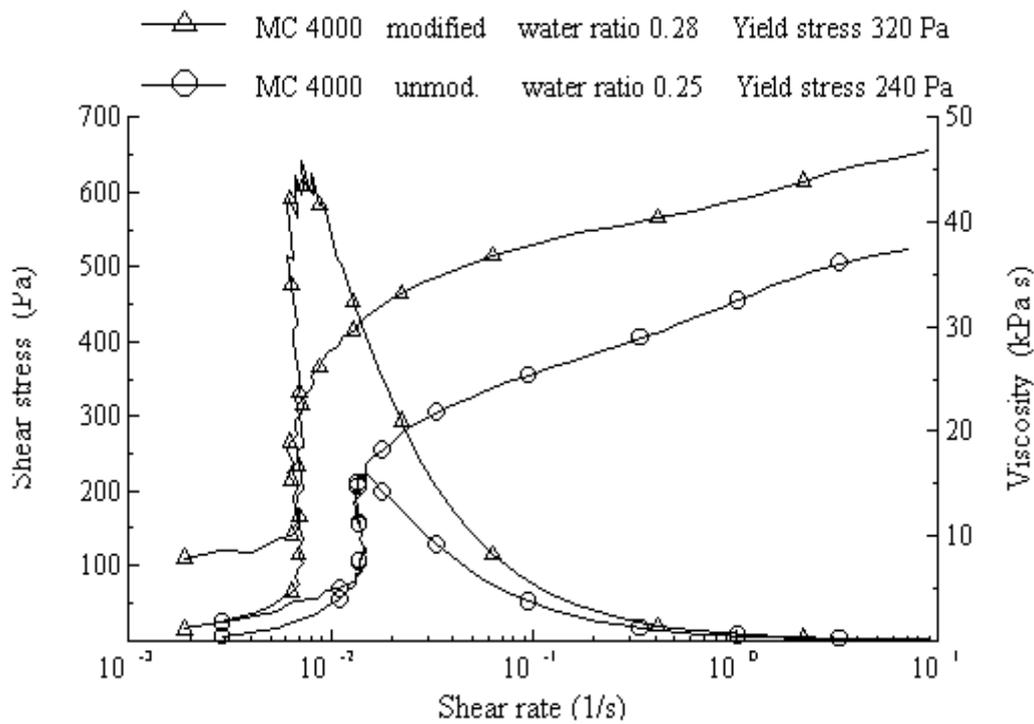


Fig. 5: Influence of cellulose ether and modifier on tile cement consistency

The same effect is also demonstrated in the next experiment.

Again, it shows how by modification the consistency of a tile cement gets stiffer to give more anti-sagging. The unmodified cellulose ether provides a yield stress of 170 Pa at a water factor of 0.25. By modification, yield stress increases to 340 Pa with an 0.28 water factor. If one wants to produce the same yield stress as with the unmodified cellulose ether, the water factor has to be raised to 0.31. Comparison of the viscosity values after flow, e.g., at a shear rate of 1 or 10 s<sup>-1</sup> showed a lower viscosity for the modified tile cement. The experts rated the consistency as smoother compared to the one for the non-modified mortar.

To check if the influence of the modifying agent on mortar consistency is limited to tile cement only, we included gypsum-based machine plasters in the investigation. On top of that, the question was addressed as to how cellulose ether viscosity influences mortar properties. For the test, methyl hydroxypropyl cellulose MHPC of the same substitution yet with a viscosity of 5000 or 32000 mPa·s was added at the same use level, either.

As can be seen from the yield stress data, only the modified MHPC provides high values irrespective of the cellulose ether viscosity. There is no significant difference in yield stress, yield stress viscosity and flow viscosity between the two modified MHPC products. For the straight MHPC types, yield stress and viscosity are not the same. Interestingly, the medium viscous MHPC provides a higher yield stress than the highly viscous 32000 mPa·s type. But again, the overriding effect of adding a modifying agent is obvious as it totally eliminates the subtle differences between the two cellulose ethers.

In that aspect, it is important to add a word of caution. These data could lead to the impression that a modified medium viscous MHPC performs as well as a high viscous modified species. While this is true for mortar consistency, it is most certainly false for other vital properties. A highly viscous cellulose ether will always provide a better water retention and also better adhesion. The mortar with the medium viscous MHPC is a likely candidate to have insufficient water retention and therefore "burn" on the substrate although it has a proper consistency. It has to be kept in mind for any optimization of mortar properties that the total performance profile has to be met.

modified or straight.

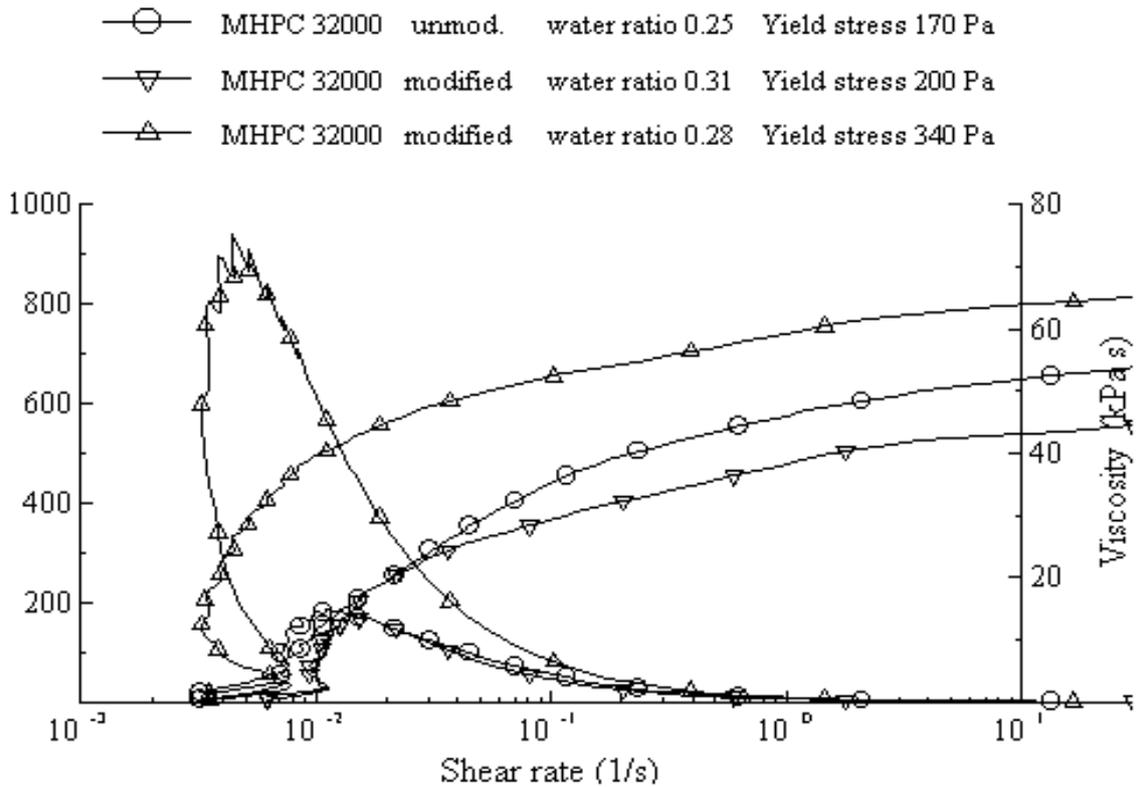


Fig. 6: Influence of cellulose ether, modifier and water ratio on consistency

All the examples shown deal with freshly prepared mortars and the rating and correlation of their properties deduced from the results of rotational rheology. During application, the plaster will set and harden, and set time is an important criterion. Methods exist to determine set, e.g., DIN 1168 [4] mentions the considered use of a Vicat cone. Set starts once the penetration depth of the cone in the mortar is reduced to a certain value. The same DIN also mentions the knife-cut method. On setting, the cuts remain intact because the mortar is already too stiff for healing. Recently, a paper [5] described an entirely new approach using the measurement of surface gloss reflection as a tool to determine set time. The method is based on the property that the surface is rich in water and reflects light well, so long as there is no set. Set time is determined by change of reflectance over time. It correlates well with the one generated calorimetrically.

Rheologically speaking, set is the formation of a rigid three-dimensional network originating from a flocculated system. Therefore, setting should show up in rheological measurements.

The technique we used is low-amplitude oscillatory shear. Polymer solutions as well as flocculated systems show viscoelastic behaviour. By applying oscillatory shear and measuring the output, i.e., level of stress and the phase shift, information may be obtained about the viscoelastic nature of the system. Monitoring the parameters over time indicates changes in structure. The relevant oscillatory shear parameters are shown in table 1.

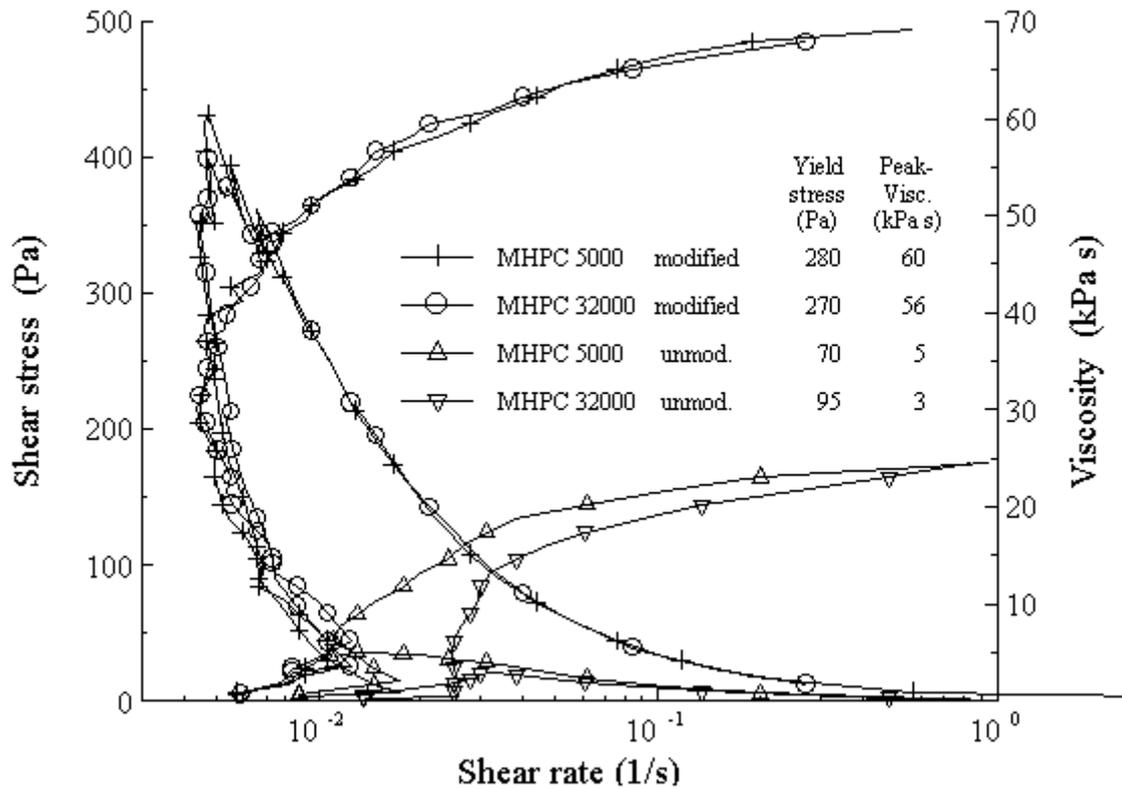


Fig. 7: Yield stress tests with gypsum machine plaster

Table 1: Oscillatory shear parameters

parameters		ideal solid system	ideal liquid system
complex dynamic modulus	$G^*$	$G^* = G'$	$G^* = G''$
storage modulus	$G'$	$G' = G^*$	$G' = \text{zero}$
loss modulus	$G''$	$G'' = \text{zero}$	$G'' = G^*$
phase angle	$\delta$	$\delta = 0^\circ$	$\delta = 90^\circ$

$G'$  is the storage modulus, which represents the elastic or in-phase component of the applied stress.  $G''$  is the loss modulus and stands for the out-of-phase stress component. In ideal solids  $G'$  equals  $G^*$ , with  $G''$  being zero. For ideal liquids, the picture is reversed:  $G^*$  equals  $G''$ , with  $G'$  being zero.

Viscoelastic systems reveal a rheology that is in between a liquid and a solid state and closer to the one whose modulus dominates.

Important in oscillatory rheology is the linear viscoelastic region (LVR). It defines the maximum deformation that can be applied to the sample without destroying the structure. Below the limit, the particles stay in close contact with each other and recover elastically to any applied deformation. The sample acts as a solid and the micro structure remains intact. Beyond the maximum, the structure is destroyed and the liquid character will increase. It should be mentioned that the theory on oscillatory shear and the equations are only valid for the LVR. Once the LVR is established, set time can be measured.

At first it was of interest how the type and use level of set retarder affects set time.

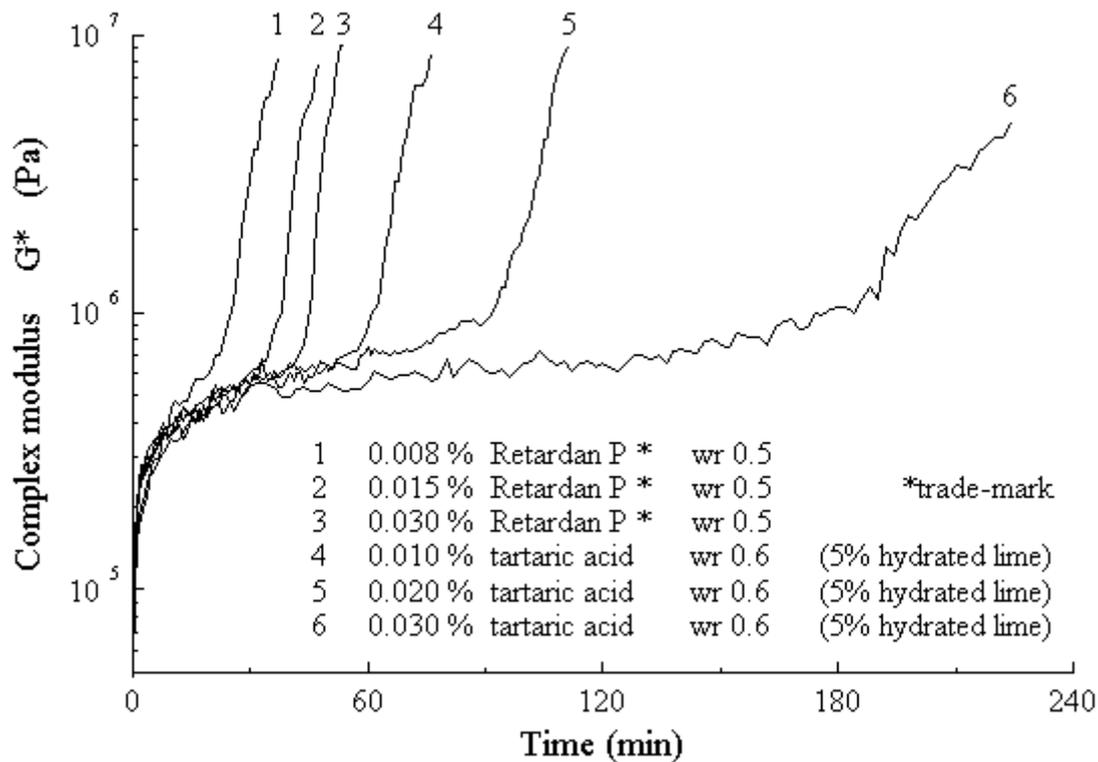


Fig. 8: Plaster set time as a function of the retarder

The set retarder in example 1 - 3 is Retardan P®, in contrast to tartaric acid used in tests 4 - 6. For tartaric acid, lime has to be added and the water ratio was increased from 0.5 to 0.6.

The setting of plaster is based on the dissolution of calcium sulphate hemihydrate in the make-up water followed by precipitation as the dihydrate which forms long needles. Once a certain amount of dihydrate is available, a felt-like system is formed due to the entanglement of the long needles. This change becomes macroscopically noticeable by the change of the paste to a stiff mass. Recording  $G^*$  over time, one notices for all examples a fast increase of  $G^*$  followed by levelling off to a plateau. The shape is independent of the retarder type and use level. During that phase hemihydrate dissolves. Once an oversaturated solution is obtained, precipitation of dihydrate starts. Precipitation and needle entanglement are influenced by the retarder and show up as a strong increase in  $G^*$  again.

One explanation how gypsum set retarders work is by complexing calcium ions and the precipitation of amorphous instead of needle forms of calcium sulphate. One might speculate that, by such a theory, it takes longer to finally form the needles and that such a behaviour should show up in longer plateau times. The oscillatory data provide much more information than the traditional methods used to determine beginning set. As one can see, the slope of the second  $G^*$  increase is not as steep for higher use levels of retarders, indicating a smoother set, whereas with low levels one would expect spontaneous setting. Setting time can also be conveniently defined as the intersection of the straight lines fitted to the  $G^*$  slope of plateau and second increase. How do the set time values compare with the one generated by Vicat cone method described in DIN 1168?

As can be seen, there is very good agreement among the data. For setting times between 30 and 60 min, discrepancy is within 2 min; for longer set time, the Vicat cone seems to give slightly higher values.

It is known from the literature that set time is influenced by the mixing intensity after soaking of the plaster. Intensive agitation leads to a shorter set time. The explanation offered is the formation of more crystal seeds due to high shear. This speeds up the whole process of crystal needle interaction. To check

the influence of agitation, paste 1 (made by hand stirring) was compared with pastes 2 - 4. Those were made by stirring 30s with a kitchen mixer with increasing speed.

As can be seen, set time indeed is a function of agitation, yet the structure of the plaster is not influenced by differences in shear, otherwise the increase in the slope of  $G^*$  increase after the plateau time would be different for the four pastes.

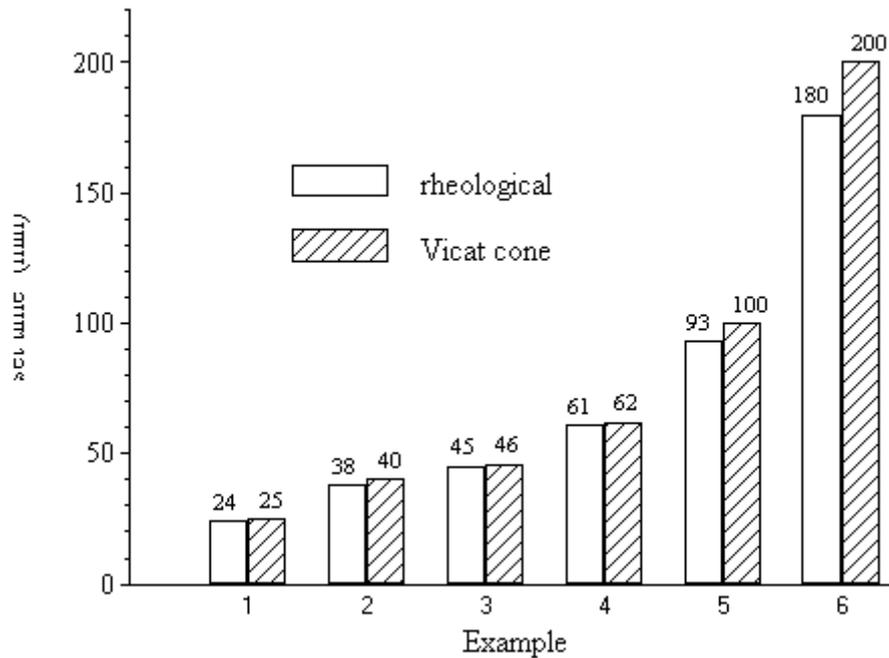


Fig. 9: Comparison of set time

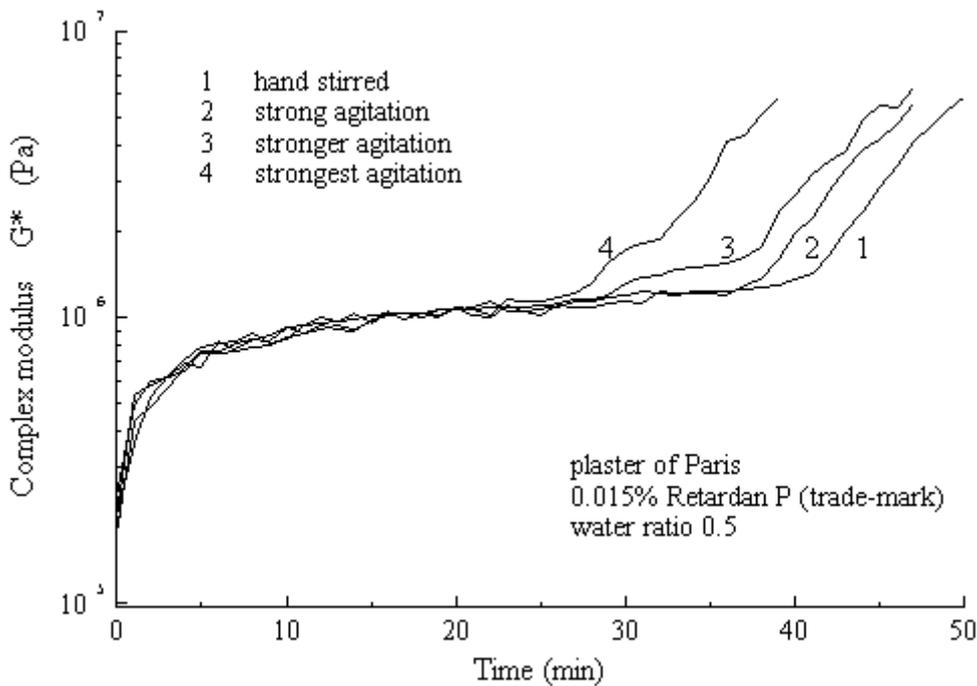


Fig. 10: Influence of agitation rate on plaster set time

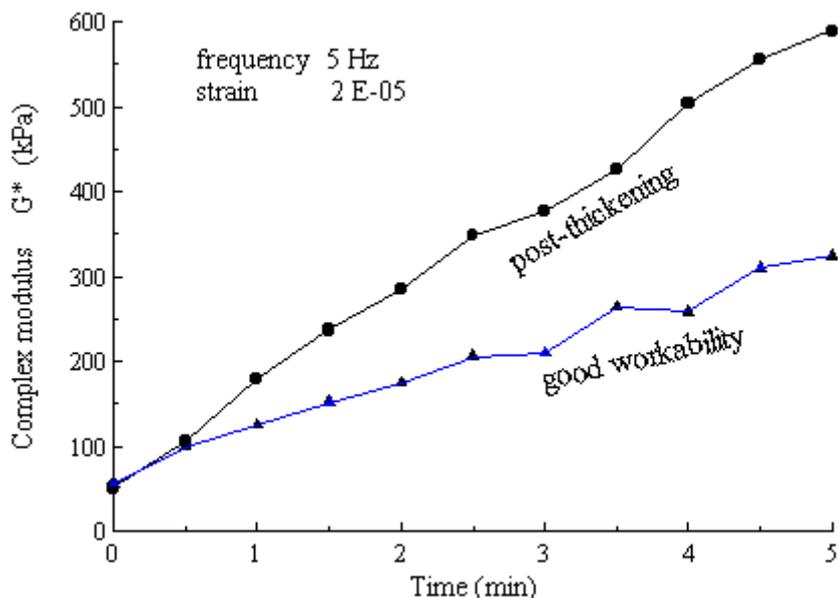


Fig. 11: Post thickening of gypsum machine plaster

The last example deals with gypsum machine plaster. This application demands a fast-dissolving cellulose ether. If the hydration rate is too slow, the plaster will post-thicken on the substrate. It leads to an unacceptable workability and requires a tremendous effort to smooth the surface. The situation was simulated by using a cellulose ether of the same viscosity, yet one was a very fine powder compared to a coarser material.

Both plasters start from the same dynamic modulus  $G^*$  value, yet the increase of  $G^*$  over time is more pronounced for the plaster which was rated by the craftsmen as post-thickened. It is the one with the slower hydrating, coarser cellulose ether.

It was our intention to demonstrate that rheological measurements can be useful to characterize mortar consistency and set time without substantially interfering with the system. Depending on the formulation in question, rotational or oscillatory rheometry can provide information. Care must be taken to select the proper test conditions. In addition, the results should be compared with the judgement of the craftsmen. If these conditions are met, the new method could be a valuable tool to characterize and optimize mortar formulations.

## Quellenverzeichnis:

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