EFFECT OF CMC AND STPP ADDITION ON RHEOLOGICAL BEHAVIOR OF FLOOR TILE GLAZES

Mohsen ZAMANI[(1),(3)], Pervin GENÇOĞLU[(1)], Alpagut KARA[(1),(3)], Arife ÇIRPIN[(2)], Yıldız YILDIRIM[(2)], Kağan KAYACI[(2)]

(1)Ceramic Research Center, Eskişehir, Turkey
(2)Kaleseramik Research and Development Center, Çan, Turkey
(3)Eskisehir Technical University, Department of Materials Science and Engineering, Eskişehir, Turkey

The performance of ceramic tiles is highly affected by the quality of the glaze layer. This study focuses on the rheological characterization of floor tile glazes. For this purpose, rotational and oscillational analyzing methods, which provide extensive information on deformation and rheological behavior of glaze suspensions, were used to promote the chances of achieving perfect surfaces. In the study, keeping other variables constant, the influence of the addition of two additives, commonly employed for optimizing the rheological behavior of the glaze suspensions, was investigated.

These additives were sodium tripolyphosphate (STPP) as a dispersing agent and sodium carboxymethylcellulose (CMC) as a plasticizer agent. As known, dispersants modify the rheological behavior of glaze suspensions by reducing the attractive forces among ceramic particles, which prevents the slurry from agglomerating. Plasticizers or adhesion agents act as the binder and play their role in water retention. Moreover, they increase the uniformity of the suspensions and prevent application and drying cracks. Adopting both rotational and oscillational techniques we were able to characterize different aspects of rheological behaviors of glaze suspensions such as dynamic viscosity, thixotropy, viscoelastic, and settling behaviors, coping with increasing ratio of CMC or STPP content. The results showed that the rheological behavior of floor tile glazes was highly dependent on the ratio of the rheology modifier agents. Moreover, flow behavior can be affected by both CMC and STPP content of floor tile glazes, where higher ratios of STPP content can alter pseudoplastic flow (or shear-thinning) behavior to dilatant flow (or shear-thickening) behavior. Furthermore, the viscoelastic region, yield point, and settling behavior of glaze suspensions were highly influenced by the type and ratio of rheology modifier agents.

INTRODUCTION

Ceramic glazes which are a thin glassy layer that covers the ceramic bodies are important for both aesthetic and functional matters [1-3]. Regarding both decorative and functional properties of ceramic glazes, many variables should be considered as main topics: these are raw materials, particle size distribution, microstructure, sintering parameters, rheological aspects, etc. The performance of final ceramic products is highly affected by the quality of the surface (glaze) layer. Thus, there are many studies in the relevant literature based on modifications of the surface properties of ceramic glazes. Different aspects of performance improvement were studied in these papers, which can be summarized as follows: the effects of sintering and process parameters [4,5], raw materials [6-8], glaze rheology [9,10], microstructure [11,12], and environmental interactions [13,14].

The rheological behavior of glaze suspensions plays an important role in ceramic glazes. An unstable suspension can cause significant difficulties during production and lower the quality of the final product [9]. Glaze suspensions generally contain silica, combined with mixtures of metal oxides, dispersed in water. Considering that most of the components in the formulation of the ceramic glazes are heavy components, it is almost necessary to include at least one rheology modifier agent in the process to control the rheological properties of the raw glazes [15].

Except for the formulation and characteristic properties of raw materials, the rheological behavior of a glaze suspension is usually adjusted by the addition of deflocculants, plasticizers/binders, and suspension agents.

Sodium carboxymethylcellulose (Na-CMC or CMC), known for its capability to control the rheology and viscosity of aqueous systems, is a water-soluble cellulose ether. CMC is chosen as a plasticizer in the production of sanitary ceramics and/or ceramic glazes, due to its superior properties such as good adhesion, deagglomeration, and water retention effects. It also increases the strength and reduces the drying shrinkage of the glaze at the same time. It makes the glaze suspension firmly combine and prevents it from precipitation. Moreover, it also improves water retention behavior of the glaze which leads to uniform drying and dense glazed surfaces [16].

The sodium tripolyphosphate (STPP) anion consists of triply condensed PO_4 tetrahedra. STPP is used as a deflocculant for solid slurries to reduce the amount of water needed as in the cases of cement manufacturing, kaolin clay mining, and oil well drilling mud formulations, as well as ceramic body and glaze formulations. In the case of ceramic glazes, STPP plays significant roles: STPP adjusts water retention, viscosity, and density of the glaze suspension, which improves the quality of the glaze layer eventually [17].

This work focuses on the influence of the addition of different ratios of CMC (as a binder or plasticizer agent) and STPP (as a dispersing agent) on the rheological behavior of the prepared floor tile glaze.

MATERIALS AND METHODS

A floor tile glaze was prepared by wet milling from commercial grade raw materials. The oxide composition of the prepared glaze is represented in Table 1.

SiO_2	Al_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	ZnO	B2O3
57.50	13.00	0.20	13.51	2.19	1.27	2.13	4.10	2.61

Table 1. *Oxide composition range for the experimental glazes (wt.%).*

The grinding was continued to obtain a raw glaze with d50≤15µm and d90≤50 µm. The final particle size distribution was measured by laser diffraction using Malvern Mastersizer 2000 model equipment. Figure 1 and Table 2 illustrate the particle size distribution and the average values of the particle size distributions (d_{10}, d_{50}, d_{90}, d_{99}) obtained after five measurements.

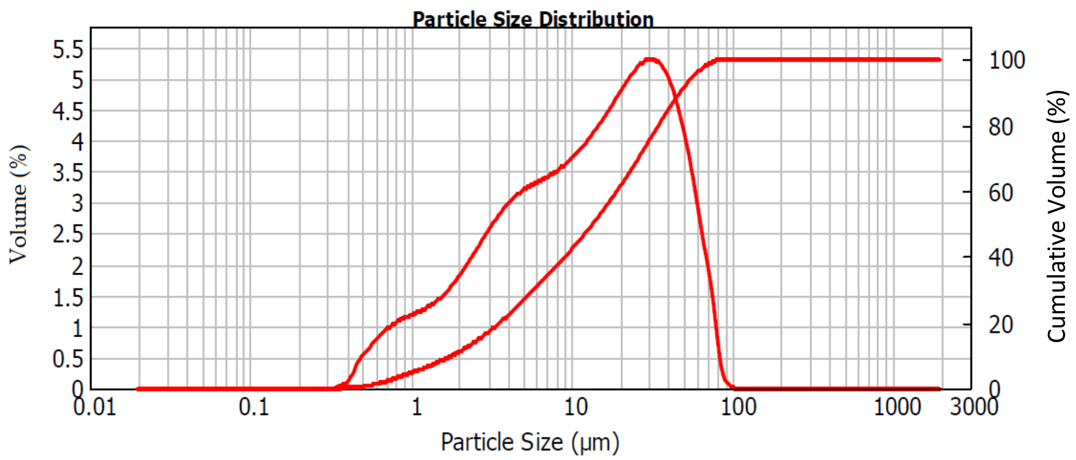

Figure 1*. Particle size distribution of the experimental glaze.*

d_{10}	d_{50}	d_{90}	d_{99}
1.789	13.489	47.320	74.799

Table 2*. Numerical values of particle size distribution of the experimental glaze in % by volume (µm).*

The final density of the raw glaze was measured and adjusted to 1800±3 g/L at 25 ºC, using a glass pycnometer. Water with a pH of 6.8 was used in the experiment. 0.08 wt.% Reotan D50 as a liquid deflocculant was used to assure the fluidity of the raw glaze. To study the influence of rheology modifiers on the rheological behavior of floor tile glazes, two setups (***S***; *to study the influence of the addition of different ratios of dispersing agent (STPP)*, ***C***: *to study the influence of the addition of different ratios of plasticizer agent (CMC)*) were prepared. For this purpose, a commercially available CMC and STPP were chosen. The detailed information of these two setups is provided in Table 3.

Sample Code	STPP (wt.%)	CMC (wt.%)	Reotan (wt.%)	Density (g/L)
S1	0.05	0.0	0.08	1800±3
S2	0.10			
S3	0.20			
S4	0.30			
C1	0.0	0.05		
C2		0.1		
C3		0.15		
C4		0.20		
C5		0.25		

Table 3. *Samples to examine the influence of increasing content of STPP and CMC on floor tile glaze rheology.*

The rheological characterization was performed by an Anton Paar Modular compact rheometer: MCR 102 with a torque range from 2 nNm to 200 mNm. The temperature of the suspension was kept constant at 25 °C during rheological analysis.

RHEOLOGICAL CHARACTERIZATION

In this work, a modular compact rheometer was used to characterize the rheological behavior of the samples, using five different measurements:

i. *Shear Rate-Viscosity Measurement (Dynamic viscosity).*

In this measurement, a force of up to 500 s^{-1} shear rates was applied to the suspension at a shear rate of 0.01 s^{-1}. Viscosity measurement was carried out by continuously reducing the applied force from 500 s^{-1} to 0.01 s^{-1}.

ii. *Thixotropy Measurement using the (Rotation-Rotation-Rotation) Method (Rotational Recovery).*

This measurement includes three different intervals. In the first one (rest interval), almost no force is applied to the suspension for a certain time. In the second interval (load-interval), a relatively high force is applied to the suspension over a fixed period to simulate glazing application. In the last stage (recovery interval), a force equal to which was applied in the rest (first) interval, is applied again to observe the thixotropic behavior of the suspension. The recovery ratio at the 2^{nd} second of the recovery interval was selected to compare the thixotropic behavior of the samples.

iii. *Determination of Viscoelastic Region and yielding point using the Oscillation Method (Amplitude sweeps).*

In this measurement, continuously increasing deformation force (0.01%-100% Shear Strain (γ)) at a fixed angular frequency (ω=10 s^{-1}) is applied to the suspensions. As a result of this measurement, the elastic region and yield point of different glazes can be determined.

iv. *Determination of Settling Behavior using the Oscillation Method (Frequency sweeps).*

In this measurement, a continuously increasing frequency force is applied to the suspension under a constant shear strain. At the end of this measurement, a diagram would be the outcome; the one that illustrates angular frequency versus the storage modulus (G') and loss modulus (G'') and Loss factor ($\tan(\delta)=G''/G'$).

v. *Thixotropy measurement using the Oscillation-Rotation-Oscillation method (ORO).*

This measurement is a mixture of both the rotation and oscillation methods. The purpose here is to observe/simulate the particle packaging behavior during the recovery stage of thixotropy measurement of the rotational method.

RESULTS AND DISCUSSION

Firstly, the results of the addition of a different ratio of STPP are discussed. Later the results of the addition of a different ratio of CMC are examined.

I. STPP ADDITION (S-CODED SAMPLES)

In this section, rheological measurement of continuously increasing ratio of STPP content and its effects on the rheological behavior of the floor tile glaze was monitored. The numeric values of these measurements are represented in Appendix 1 and 2.

According to viscosity curves (Fig.2), it is seen that up to 1 wt.% suspension shows pseudoplastic flow behavior. This is a fundamental property essential in floor tile glazes, where a decreasing viscosity behavior with increasing shear rates is required. After that point, dilatant flow behavior is observed where an increasing viscosity behavior with decreasing shear rates takes place. The viscosity measurement of S-coded samples shows that STPP addition decreases viscosity values in general, but it reduces the viscosity values of lower shear rates more than higher shear rates.

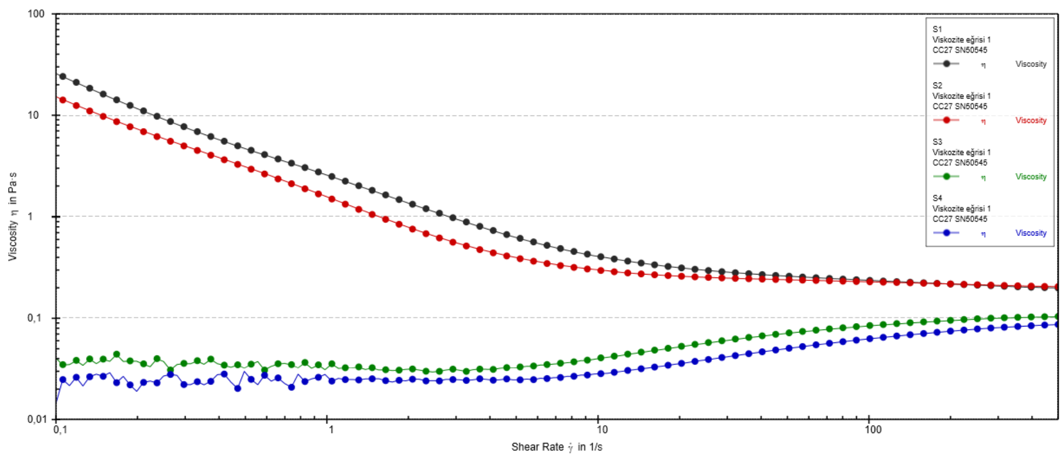

Figure 2. *Viscosity curves of S-coded samples measured by Modular Compact Rheometer*

With regard to the rotational recovery behavior of the samples, it can be observed that STPP addition diminishes the thixotropic behavior of the floor tile glazes (Fig.3). Taking the 2^{nd} second of the recovery interval as a reference point demonstrates that 43.8% recovery ratio in S1 coded sample dropped to 35.9% in the S2 sample. The other samples (i.e., S3 and S4) show inverted recovery curves due to their dilatant behavior.

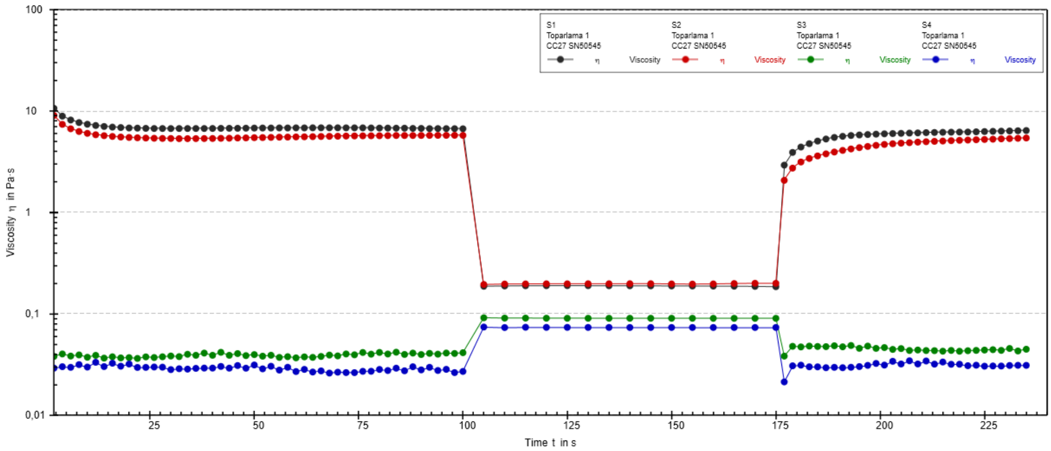

Figure 3*. Recovery behavior of S-coded samples measured by Modular Compact Rheometer*

The amplitude sweep test is used to describe the slurry deformation behavior of the samples. Characterizing the deformation behavior of the glaze is crucial to counterbalance the process parameters. Using this method, the upper limit for non-destructive deformation range and yielding point of the slurry can be determined. According to Figure 4, both the upper limit for the non-destructive deformation range and yield point of the glaze samples decreases as STPP content increases. Increasing STPP addition makes the loss modulus of the suspension more dominant than the storage modulus, which is undesirable rheological behavior.

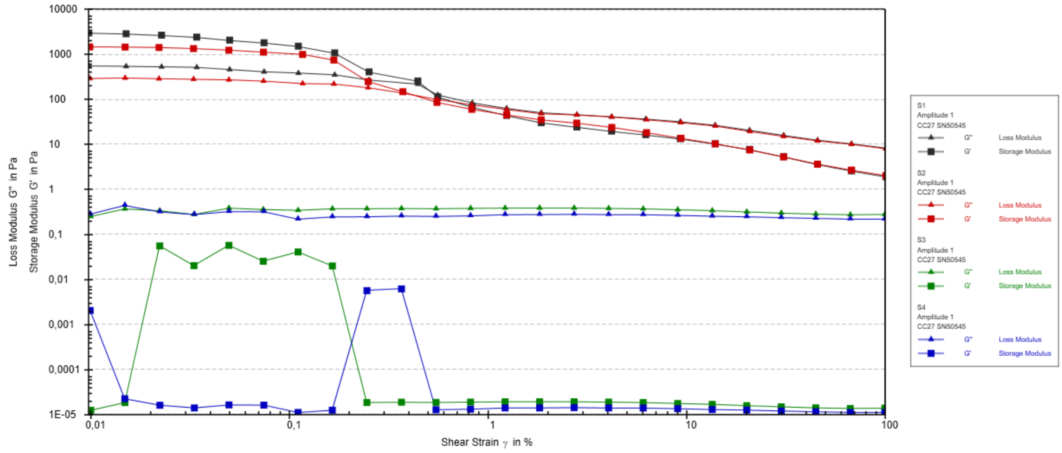

Figure 4. *Amplitude sweep test of S-coded samples measured by Modular Compact Rheometer*

According to frequency sweep analysis of S-coded samples, the increasing amount of STPP content triggers the settling behavior of the glaze at low shear strain values. Figure 5 illustrates that when STPP content exceeds a certain ratio (1 wt.% in this case) the suspension tends to be unstable, and its components separate. In the case of S1 and S2 coded samples, increasing content of STPP increases complex viscosity, and reduces the loss factor. It means that STPP addition dominates the elastic behavior of the glaze, as the loss factor approaches the loss factor of ideally elastic materials ($\tan \delta < 1/\infty = 0$). Regarding S3 and S4 coded samples it can be seen that passing a particular frequency rate leads to an instant increase in loss factor impending to those of ideally viscous materials ($\tan \delta > \infty/1 = \infty$).

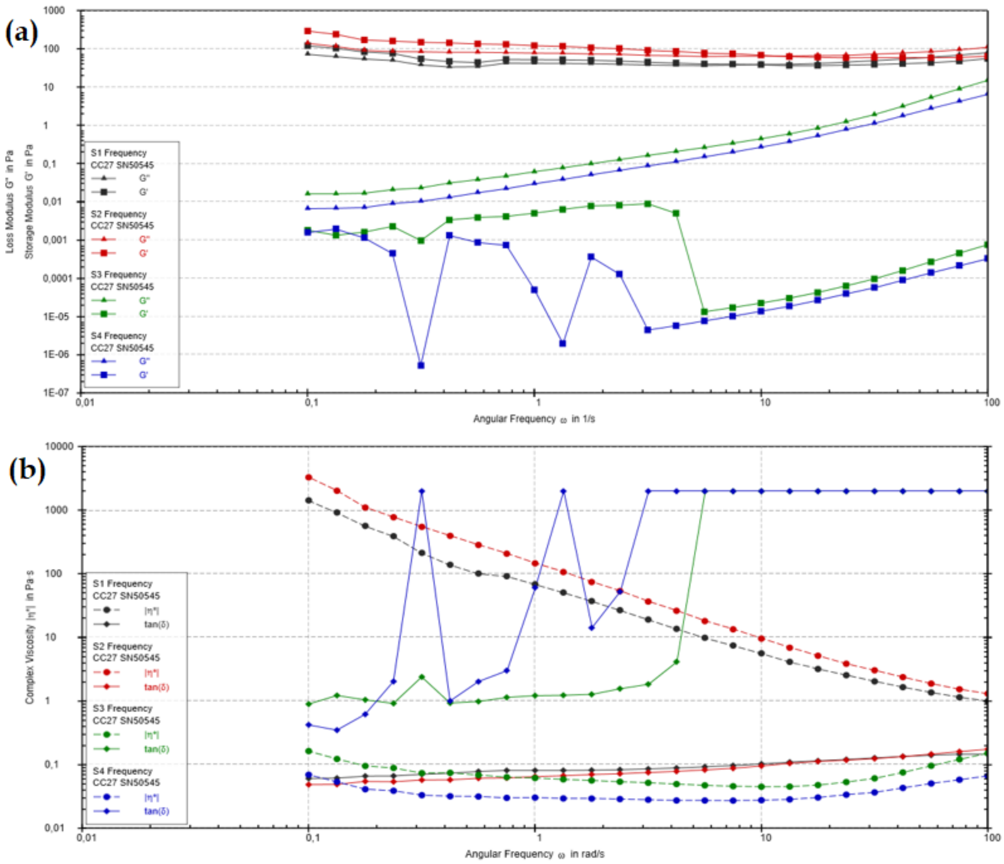

Figure 5*. Frequency sweep tests of S-coded samples measured by Modular Compact Rheometer. [a: angular frequency versus the storage modulus (G') and loss modulus (G''), b: angular frequency versus complex viscosity (|η^*|) and Loss factor (tan(δ))].*

Using the thixotropy measurement by the Oscillation-Rotation-Oscillation method, particle repackaging behavior during the recovery stage was simulated to minimize the risk of unperfect surfaces. This analysis was designed to observe the behavior of the storage and loss modulus during the recovery interval. The analysis shows that increasing STPP content postpones the repacking behavior of the floor tile glazes. It takes almost 5 seconds in the S1 coded sample, till the elastic modulus overlies the loss modulus and repacking occurs once more, where this cycle is about 7 seconds in the S2 coded sample.

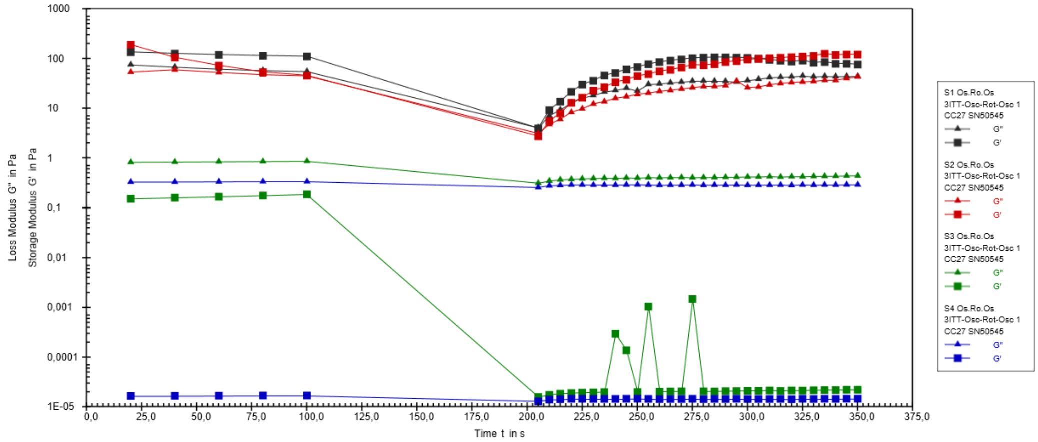

Figure 6*. Oscillation-Rotation-Oscillation measurements of S-coded samples measured by Modular Compact Rheometer.*

II. CMC ADDITION (C-CODED SAMPLES)

In this part of the study, the rheological measurement of continuously increasing ratio of CMC content and its effects on rheological behavior of floor tile glaze was monitored. The numeric values of these measurements are also represented in Appendix 1 and 2.

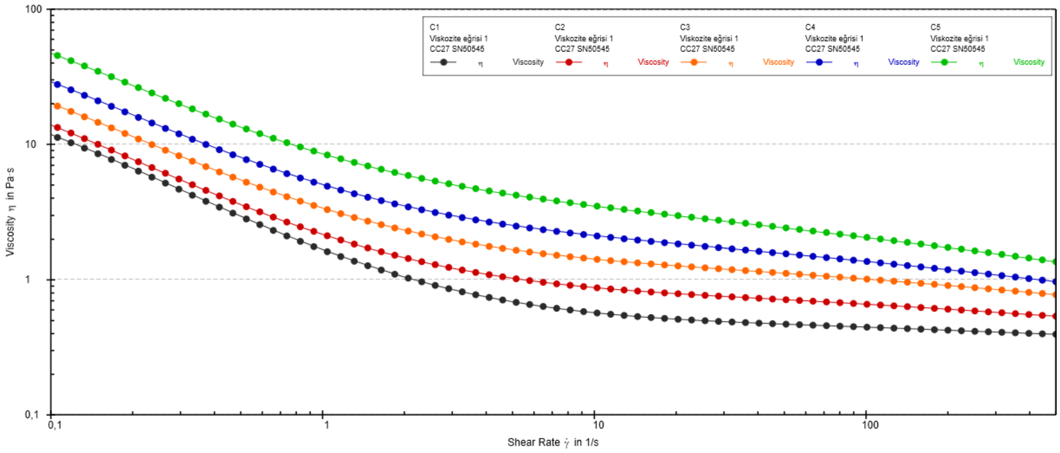

Figure 7. *Viscosity curves of C-coded samples measured by Modular Compact Rheometer*

Regarding the dynamic viscosity of C-coded samples (Fig.7), it can be seen that increasing the ratio of CMC content leads to an increase in viscosity values where all samples exhibit pseudoplastic behavior. Moreover, increasing CMC ratio increases the viscosity curve slope, where the absolute slope value (see eq.1) was calculated as 0.023, 0.027, 0.039, 0.056, and 0.093 for C1:C5 samples, respectively. The higher the slope the faster viscosity changes, which is an indication of enhanced thixotropic behavior.

$$slope = \left|\frac{Change\ in\ viscosity}{Change\ in\ shear\ rate}\right| = \left|\frac{\eta_{500} - \eta_{0.1}}{500 - 0.1}\right| \qquad (1)$$

Regarding the rotational recovery behavior of the samples, it can be observed that even 0.05 wt.% of CMC addition as a plasticizer agent, enhances the thixotropy behavior and recovery ratio of the raw glaze (Fig.8). Considering the recovery percentages at the 2nd second, the recovery ratio increases by 54.4%, 65.6%, 82.0%, 97.2%, and 100% for C1:C5 samples, respectively. It seems that the recovery ratio is directly associated with the CMC ratio.

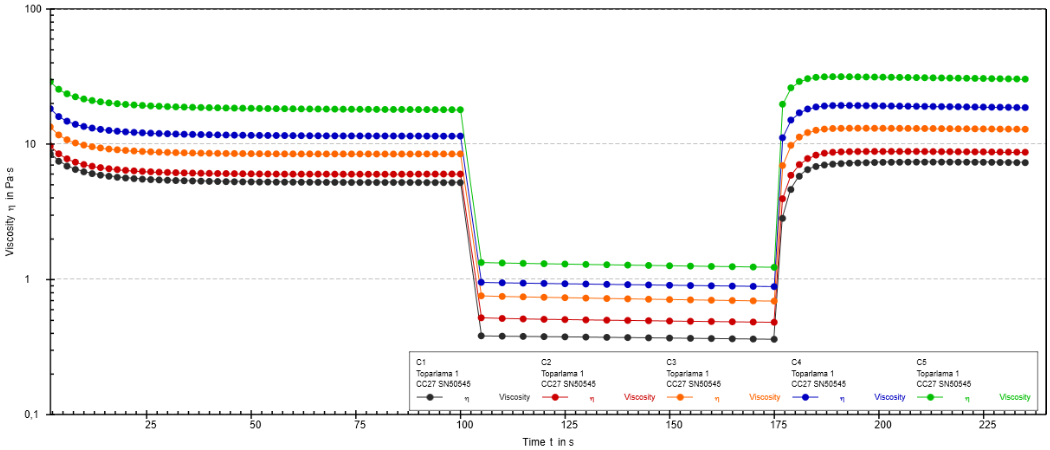

Figure 8. *Recovery behavior of C-coded samples measured by Modular Compact Rheometer*

For deformation behavior of the C-coded samples, it is perceived that the stability of the samples increases as both non-destructive deformation range and yield point increases by increasing ratios of CMC content (Fig.9). Using amplitude sweep analysis, the upper limit for the non-destructive deformation range is observed to increase from about 65 Pa in the C1 sample to almost 360 Pa in the C5. Likewise, the yield point values increase from about 14 to 63 Pa.

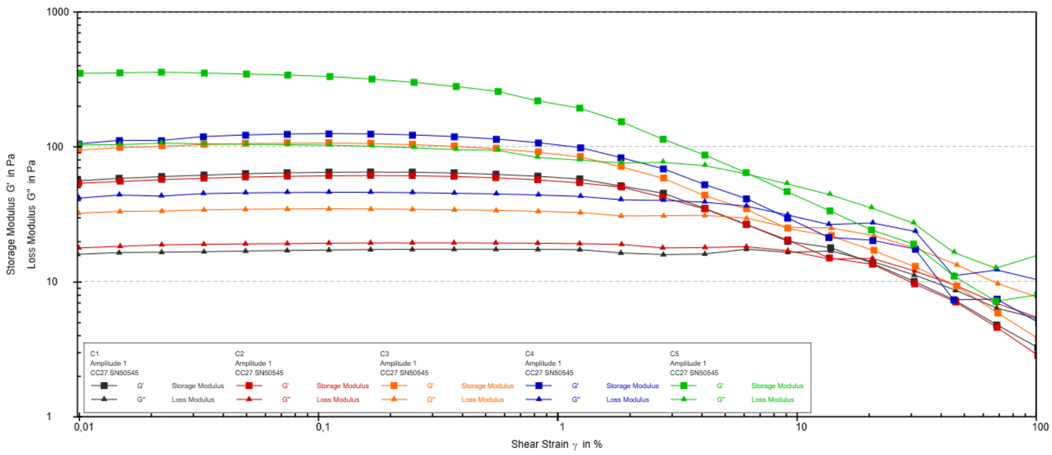

Figure 9. *Amplitude sweep tests of C-coded glazes measured by Modular Compact Rheometer.*

Frequency sweep analysis of C-coded samples (Fig.10) shows that CMC addition enhances the settling behavior of floor tile glazes. Apart from the C1 coded sample that shows a modest instant increase in loss factor value, the other samples display a stable manner during frequency sweep analysis.

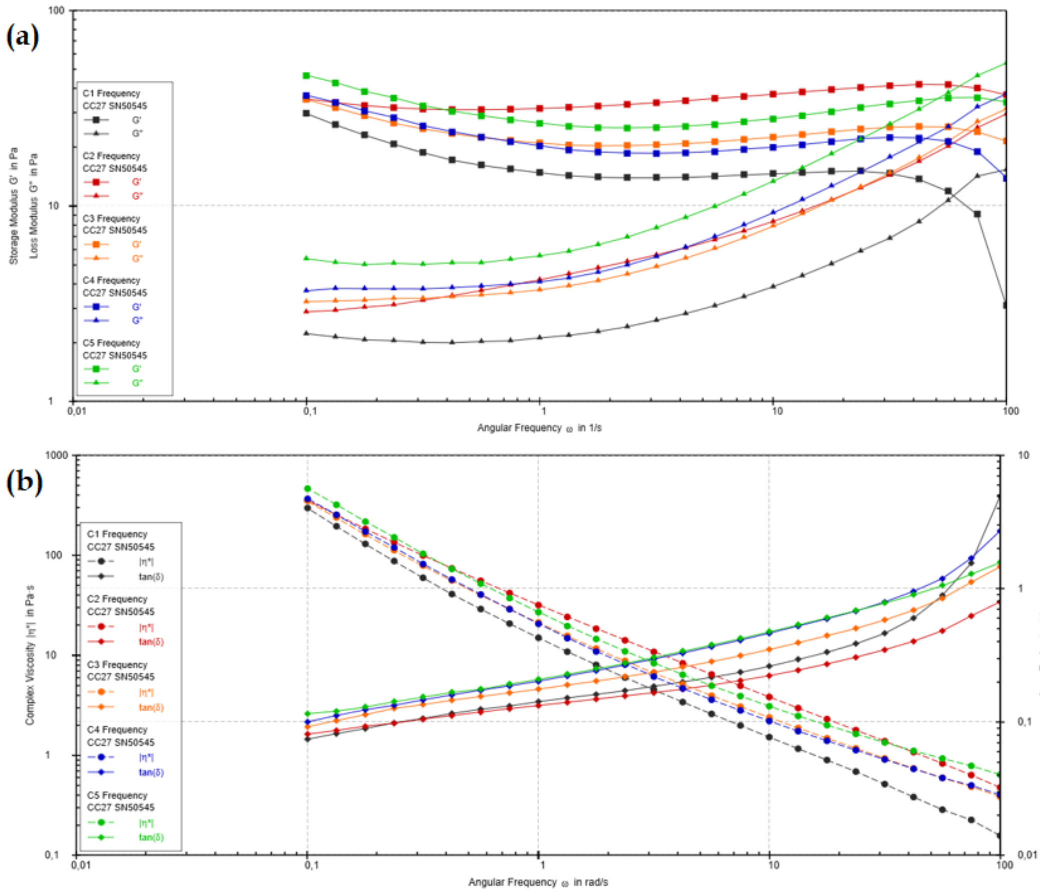

Figure 10. *Frequency sweep tests of C-coded samples measured by Modular Compact Rheometer. [a: angular frequency versus the storage modulus (G') and loss modulus (G''), b: angular frequency versus complex viscosity (|η^*|) and Loss factor (tan(δ)].*

Oscillation-Rotation-Oscillation analysis of C-coded samples shows that increasing CMC content accelerates the repacking behavior of the floor tile glazes. The increasing ratio of CMC content enlarges the difference between the storage modulus (G') and the loss modulus (G'') at the zero point of recovery interval (Fig.11), which indicates an accelerated repacking process.

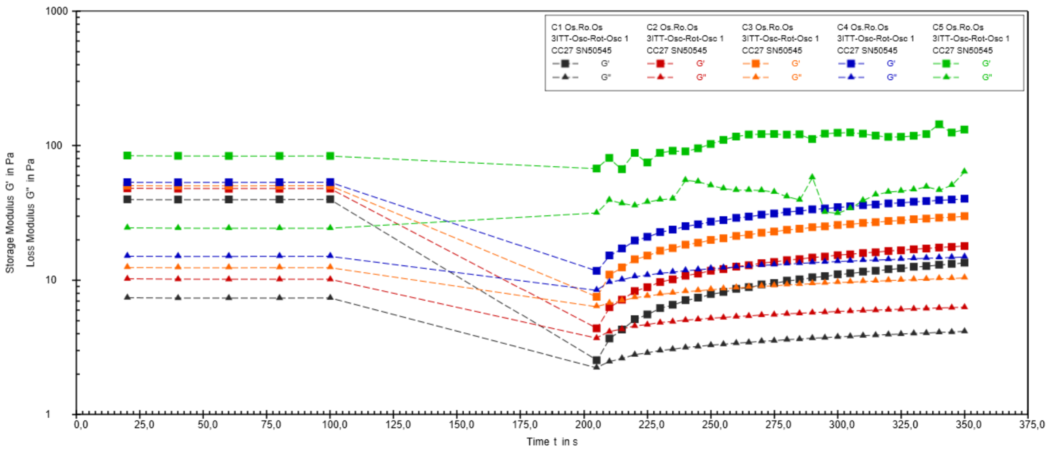

Figure 11. *Oscillation-Rotation-Oscillation measurements of C-coded samples measured by Modular Compact Rheometer.*

CONCLUSION

In this work, the effects of two important rheology modifiers on the rheological behaviors of floor tile glazes were studied. These were.

- the influence of dispersing agent content (i.e., STPP)
- the influence of plasticizer content (i.e., CMC)

The effects of these two parameters on rheological behavior were measured by five different analyses, where all the other parameters were kept constant. These measurements were dynamic viscosity, recovery ratio or thixotropy behavior, amplitude sweeps (to determine the viscoelastic behavior of the glaze), frequency sweep (to determine the settling behavior), and Oscillation-Rotation-Oscillation measurements (to simulate the repacking process at the recovery stage).

Based on the rheological measurements, conclusions are as follows:

(1) The STPP addition decreases the viscosity of floor tile glazes. Further STPP addition alters the pseudoplastic behavior of the glaze to dilatant behavior.

(2) Increasing STPP ratios decreases the recovery ratio and postpones the repacking process.

(3) STPP decreases the viscous and elastic yield point and accelerates settling behavior. Further STPP addition makes loss modulus dominant over the storage modulus.

(4) The CMC addition increases the viscosity of floor tile glazes. It also leads to an increase in the slope of the viscosity curve.

(5) Increasing CMC ratios increases the recovery ratio and accelerates the repacking process.

(6) Increasing CMC content increases the viscous and elastic yield point and prevents settling behavior.

To sum up, the results show that optimizing the ratio of rheology modifier content could improve the rheological behavior of the glaze suspensions. This will lead us to benefit from the advantages of an optimal glaze suspension such as maximum recovery ratio, more resistance to yield and settling, and enhanced repacking behavior.

REFERENCES:

[1] Bernasconi, V. Diella, N. Marinoni, A. Pavese, and F. Francescon, Influence of Composition on Some Industrially Relevant Properties of Traditional Sanitary-Ware Glaze, *Ceram. Int.*, Elsevier Ltd and Techna Group S.r.l., 38(7), 5859–5870 (2012). http://dx.doi.org/10.1016/j.ceramint.2012.04.037

[2] J. Partyka and J. Lis, The Influence of the Grain Size Distribution of Raw Materials on the Selected Surface Properties of Sanitary Glazes, *Ceram. Int.*, Elsevier Ltd and Techna Group S.r.l., 37(4), 1285–1292 (2011). http://dx.doi.org/10.1016/j.ceramint.2010.12.006

[3] J. Li, J. Liang, F. Wang, and L. Wang, The Role of Firing Process on Bubble Formation in a Glaze Layer of Sanitary Ware, *Thermochim. Acta*, Elsevier B.V., 588, 75–80 (2014). http://dx.doi.org/10.1016/j.tca.2014.03.024

[4] L. Fröberg, T. Kronberg, and L. Hupa, Effect of Soaking Time on Phase Composition and Topography and Surface Microstructure in Vitrocrystalline Whiteware Glazes, *J. Eur. Ceram. Soc.*, 29(11), 2153–2161 (2009). https://doi.org/10.1016/j.jeurceramsoc.2009.01.012

[5] L. Fröberg, T. Kronberg, L. Hupa, and M. Hupa, Influence of Firing Parameters on Phase Composition of Raw Glazes, *J. Eur. Ceram. Soc.*, 27(2–3), 1671–1675 (2007). https://doi.org/10.1016/j.jeurceramsoc.2009.01.012

[6] Karasu, E. Dölekçekiç, and B. Özdemir, Compositional Modifications to Floor Tile Glazes Opacified with Zircon, *Br. Ceram. Trans.*, 100(2), 81–85 (2001). https://doi.org/10.1179/096797801681251

[7] E. Bou, A. Moreno, A. Escardino, and A. Gozalbo, Microstructural Study of Opaque Glazes Obtained from Frits of the System: SiO2-Al2O3-B2O3-(P2O5)-CaO-K2O-TiO2, *J. Eur. Ceram. Soc.*, 27(2–3), 1791–1796 (2007). https://doi.org/10.1016/j.jeurceramsoc.2006.04.148

[8] B.E. Yekta, P. Alizadeh, and L. Rezazadeh, Synthesis of Glass-Ceramic Glazes in the ZnO-Al2O3-SiO2-ZrO2 System, *J. Eur. Ceram. Soc.*, 27(5), 2311–2315 (2007). https://doi.org/10.1016/j.jeurceramsoc.2006.08.009

[9] M.G. Rasteiro, E. Simões, A. Jorge, and T. Gassman, Effect of Aging on Glaze Suspensions Rheology, *J. Am. Ceram. Soc.*, 90(6), 1693–1702 (2007). https://doi.org/10.1111/j.1551-2916.2007.01536.x

[10] M. Da Graça Rasteiro and A. Jorge, The Influence of Particle Size Distribution on the Performance of Ceramic Particulate Suspensions, *Part. Part. Syst. Charact.*, 24(2), 101–107 (2007). https://doi.org/10.1002/ppsc.200601042

[11] M. Leśniak, J. Partyka, K. Pasiut, and M. Sitarz, Microstructure Study of Opaque Glazes from SiO2–Al2O3–MgO–K2O–Na2O System by Variable Molar Ratio of SiO2/Al2O3 by FTIR and Raman Spectroscopy, *J. Mol. Struct.*, 1126, 240–250 (2016). https://doi.org/10.1016/j.molstruc.2015.12.072

[12] K.A. Langworthy, D.H. Krinsley, and R.I. Dorn, High Resolution Transmission Electron Microscopy Evaluation of Silica Glaze Reveals New Textures, *Earth Surf. Process. Landforms*, 35(13), 1615–1620 (2010). https://doi.org/10.1002/esp.2061

[13] X. Yin, T.J. Huang, and H. Gong, Chemical Evolution of Lead in Ancient Artifacts -A Case Study of Early Chinese Lead-Silicate Glaze, *J. Eur. Ceram. Soc.*, Elsevier, 40(5), 2222–2228,(2020). doi:10.1016/j.jeurceramsoc.2020.01.002. https://doi.org/10.1016/j.jeurceramsoc.2020.01.002

[14] M. Piispanen, T. Kronberg, S. Areva, and L. Hupa, Effect of Mechanical and Chemical Wear on Soil Attachment and Cleanability of Sanitary Ware with Additional Coatings, *J. Am. Ceram. Soc.*, 94(3), 951–958 (2011). https://doi.org/10.1111/j.1551-2916.2010.04120.x

[15] I. Crespi, Stefano (Busto Arsizio, IT), Antoniotti, Marco (Novara, IT), Li Bassi, Giuseppe (Gavirate, IT), Floridi, Giovanni (Novara, "RHEOLOGY MODIFIER FOR CERAMIC GLAZES," United States, (2013). https://www.freepatentsonline.com/y2013/0150229.html

[16] R.L. Feddersen and S.N. Thorp, "Sodium Carboxymethylcellulose," Industrial Gums: Polysaccharides and Their Derivatives: Third Edition, ACADEMIC PRESS, INC., 2012, doi:10.1016/B978-0-08-092654-4.50024-3.

[17] A.D.F. Toy, Tripolyphosphates, Chem. Phosphorus, 1973, 112 (May), p 514–519.

APPENDIX 1

Numerical values and additional information about rheological measurements.

Sample	Viscosity at different shear rates [Pa.s]					Recovery (%)		Amplitude (yield point)		Frequency
	0.1 (1/s)	*10 (1/s)*	*100 (1/s)*	*300 (1/s)*	*500 (1/s)*	*2nd sec*	*10th sec*	*Shear strain (%)*	*G'=G" (Pa)*	*Settling behavior (Yes/No)*
S1	26.18	0.40	0.24	0.21	0.20	43.8	75.6	0.52	148.37	No
S2	15.20	0.30	0.23	0.21	0.20	35.9	62.6	0.43	123.32	No
S3	0.04	0.04	0.08	0.1	0.1	-	-	-	-	Yes
S4	0.005	0.03	0.06	0.08	0.09	-	-	-	-	Yes
C1	11.83	0.57	0.45	0.41	0.39	54.4	100	18.43	14.80	Yes
C2	14.04	7.99	0.66	0.57	0.54	65.4	100	14.80	14.49	No
C3	20.19	1.41	1.01	0.85	0.77	82.0	100	9.05	25.34	No
C4	29.16	2.11	1.36	1.09	0.98	97.2	100	8.06	33.03	No
C5	47.78	3.51	2.06	1.56	1.36	100	100	6.33	63.04	No

APPENDIX 2

Numerical values and additional information of Oscillation-Rotation-Oscillation method.

Sample	Recovery time for specific recovery ratio in recovery interval (sec)				Recovery ratio at a specific time in recovery interval (%)				Time until G' = G" in recovery interval (sec)
	(25%)	*(50%)*	*(75%)*	*(100%)*	*10th sec*	*20th sec*	*60th sec*	*150th sec*	
S1	234	42	56	N.R*	8	19	77	69	5.0
S2	18	30	41	52	12	28	100	100	7.0
S3	-	-	-	-	-	-	-	-	-
S4	-	-	-	-	-	-	-	-	-
C1	82	N.R	N.R	N.R	9	13	21,5	34	-
C2	53	N.R	N.R	N.R	13	17	26	37	-
C3	16	96	N.R	N.R	22	28	42	59	-
C4	7	48	149	N.R	28	37	74	75	-
C5	-	-	-	19	96	100	100	100	-

*N.R: Not Reached