INFLUENCE OF CALCIUM SULFATE ON DEVELOPMENT OF EARLY-AGE RHEOLOGICAL PROPERTIES IN SELF-LEVELING UNDERLAYMENTS BASED ON ETTRINGITE BINDER

Nguyen Ngoc Lam[1*]

Summary: The aim of this study is to evaluate the effect of the types and the amount of calcium sulfate (C$Hx) replacing calcium aluminate cement (CAC) in ettringite binder on the early-age rheological properties of self - leveling underlayment. The evolution of rheological properties such as yield stress, plastic viscosity, rheological dynamic modulus (storage modulus and loss modulus) was determined by a rheometer with the rotation mode and the oscillation mode. The use of these technics is considered as a method to monitor the development of structure in cementitious materials. Increasing the yield stress, plastic viscosity and dynamic modulus of the self - leveling underlayment during hydration was identified from just 5 minutes after mixing to the period where the transition from a fluid state to a solid state where the development of elastic properties in the self - leveling underlayment takes place. The result shows that the structuration of compositions based on anhydrite (C$ - $CaSO_4$) or compositions containing 90CAC/10C$Hx is faster than that of the composition 75CAC/25C$Hx or the compositions based on hemihydrate (C$H_{0.5}$ or $CaSO_4 0.5H_2O$).

Keywords: Self - leveling underlayment; calcium aluminate cement; calcium sulfate; ettringite binder; rheological properties.

1. Introduction

In recent years, self-leveling underlayment (SLU) has been studied for concrete floors in various fields such as office buildings, apartments, stores, schools, hospitals, factories, parking lots, vessels and repairing works because of its high flow ability and self-smoothing properties [1]. Besides the strength, other characteristics of SLU such as workability, rapid drying, rapid hardening, shrinkage compensation, smooth nature... are required. One of the innovative binders for SLUs is ettringite binder. This binder includes calcium aluminate cement (CAC), different sources of calcium sulfate (C$Hx) and Portland cement (PC). The combination of this binder with special additives produces rapid setting and hardening, shrinkage compensation of autodessiccation and desiccation [2,3].

The hydration of an ettringite binder containing calcium aluminate cement (CAC) and calcium sulfate (C$Hx) induces ettringite ($C_6A\$_3H_{32}$) and aluminum hydroxide (AH_3) as follows:

$$3CA + 3C\$H_x + (38-3x)H \rightarrow C_6A\$_3H_{32} + 2AH_3 \qquad (1)$$

$$3CA_2 + 3C\$H_x + (47-3x)H \rightarrow C_6A\$_3H_{32} + 5AH_3 \qquad (2)$$

$$C_{12}A_7 + 12C\$H_x + (137-12_x)H \rightarrow 4C_6A\$_3H_{32} + 3AH_3 \qquad (3)$$

The rate of the reactions in the fresh mixture depends on the CAC/CH_x ratio, the type of the calcium sulfate and admixtures [4,5]. There are three types of CH_x: anhydrite, hemihydrate and dihydrate. Alpha-hemihydrate and beta-hemihydrate are two forms of hemihydrate calcium sulfate, which are normally used for different SLU compositions. The hydration of the anhydrite and dihydrate products is slower than that of hemihydrate products. And the hydration of the beta-hemihydrate is quicker than that of the alpha-hemihydrate form [1,6]. Thus, the characteristics of SLUs strongly depend on the used sulfate calcium form.

Gradually, as the microstructure evolves and causes the change of the macrostructure, the material transition from the liquid state to the solid state leads to the setting and increases mechanical strength [7-10].

[1] Dr, Faculty of Building Materials. National University of Civil Engineering (NUCE).
* Corresponding author. E-mail:lamnn@nuce.edu.vn.

Onshi [1] investigated the influence of calcium sulfate on workability, setting time, compressive strength, dimensional stability, hydration kinetics of SLU produced from the ternary system of CAC-OPC-C$Hx. The results showed that in both ettringite system and CAH-CSH system, the maximum of heat evolution is related to flow value. The flow value increases with a decrease in max of heat evolution, conversely flow value decreases with an increase in max of heat evolution. The hemihydrate formulations showed strong expansion and the hardened mortar for those formulations showed pronounced cracking while the dimensional stability of the anhydrite formulations showed shrinkage. In both Ettringite system and CAH-CSH system, the compressive strength starts to increase significantly once a plateau is reached in the dimensional stability curve. Kighelman [11] has reported for self-leveling flooring compounds applied in thin layers that the CAC dominated formulations react faster and more ettringite is formed because of the higher $CaO.Al_2O_3$ (CA) content. The porosity is lower, the chemical shrinkage is larger but the autogenous expansion is lower than that of the observed PC dominated formulations. In the other study, Radek Magrla [12] investigated the influence of plasticizing admixtures depending on technological properties of self-leveling screed produced by ternary binder system composing Portland cement - calcium aluminate cement - gypsum; and it is concluded that the ettringite binder is a suitable binder for SLU.

However, the number of researches on ettringite binder, especially on the rheological characteristics development at an early age of SLUs is very limited. It is difficult to define clearly the term of the "early age", because this period may be associated with a rapid hydration process after mixing the binder with water, which leads to the development of the microstructure relating to structuration and macroscopic property evolution. Generally, it is considered that in the case of ettringite binders, structuration ends 24 hours after mixing [11]. But it depends on the mineral composition (or chemical) of binder, the water/binder ratio, the temperature and the nature of the chemical adjuvantation... The beginning of the structuration can begin within a few minutes to a few hours. The aim of this study is to evaluate the rheological properties of self - leveling compound based on ettringite binder at early-age. In this study, the influence of C$Hx on yield stress, plastic viscosity, rheological dynamic modulus (storage modulus and loss modulus) of SLUs has been investigated.

2. Experimental methods and materials

2.1 Rheological properties

Rheological properties can be determined in rotation mode or oscillatory mode.

2.1.1 Rotation mode

In rotation method, rheometer allows measuring the rheological parameters, namely yield stress and plastic viscosity, using different deformation rates. Fresh mortar or cement paste can be considered as a fluid material, where the yield stress represents the initial resistance to the flow, caused by contacts between particles, while the plastic viscosity controls the behavior once the required torque was achieved to initiate the movement [14]. The rheological behavior of cement paste, mortars could be presented by the Bingham model as follows:

$$\tau = \tau_o + \mu_p \cdot \dot{\gamma} \qquad (4)$$

where τ (Pa) is the shear stress, τ_o (Pa) is the yield stress, μ_p (Pa.s) is the plastic viscosity and $\dot{\gamma}$ (s^{-1}) is the shear rate.

The yield point of a material described in Fig.1 is the point at which the material will start to flow caused by that the external forces acting on the material are larger than the internal structural forces. The transition from elastic behavior to viscous behavior of materials gives information about its structuration versus times.

2.1.2 Oscillation mode

The principle of the rheometer in dynamic mode is to apply the material a sinusoidal deformation with frequency ω:

$$\gamma(t) = \gamma_o \cdot \cos(\omega t) \qquad (5)$$
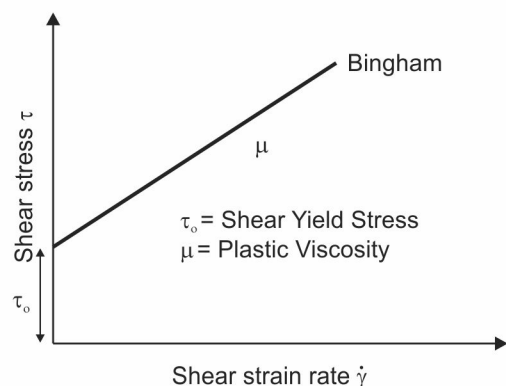

Figure 1. Rheological Bingham model [14]

In the case where the applied strain belongs to the linear viscoelastic region, the resulting shear stress is also sinusoidal and out of phase by a time δ with respect to deformation:

$$\tau(t) = \tau_0 . \cos(\omega t + \delta) \tag{6}$$

where: γ_0 and τ_0 are the shear strain and shear stress amplitude of oscillation respectively.

These modulus can also be used to describe the complex modulus, G*, by the relation:

$$G^* = \tau_o / \gamma_o \tag{7}$$

Recall that the oscillating stress of a viscoelastic material is in phase opposite with the phase of strain. The conservation modulus or storage modulus (G') and loss modulus (G") then can be written:

$$G' = G^* \cos\delta \tag{8}$$

$$G'' = G^* \sin\delta \tag{9}$$

A real material has a viscoelastic behavior, G' and G" are finite. The material can exhibit a solid-like behavior, with G' >> G", liquid gold-like one, with G' << G" (in low frequency range).

Dynamic mode rheology has also been used to study the mechanical properties of cement pastes from mixing until setting [17]. The ability to realize nondestructive measurements in the linear viscoelastic domain (LVD) presented in Fig.2 is especially interesting and it provides useful information concerning structure or forces acting inside the paste.

Monitoring the evolution of rheology characteristics gives the information about structuration of cement paste, mortars or concrete at early age.
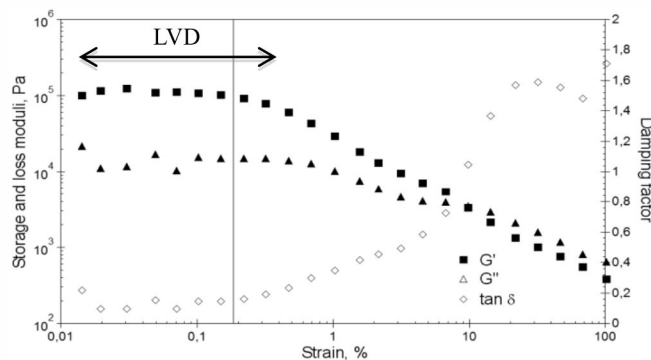

Figure 2. *Strain sweep of the modulus G' and G" [14]*

2.2 Apparatus

A parallel plate rheometer was used in experimental testing (Fig. 3). The rheometer was equipped with serrated test plates (35 mm diameter) to measure the rheological properties of the materials. A gap between the two plates must be larger than the size of a particle in cement paste or mortars (normally the selected gap is 10 times larger than the maximum particle size) [13,14]. This ensures the flow of particles does not present disturbances induced by blockages between the two plates, thus the gap between the plates was fixed at 1.5 mm. The specimen was enclosed by a box to limit the evaporation of water from the sample. The mixing operation lasted 3 min and another minute was needed to transfer the material from the mixer to the rheometer and begin measurements. Consequently, the first test was started approximately 5 min after mixing of water with cement.

Figure 3. *Parallel plate rheometer equipped with a box to reduce evaporation [15]*

Testing protocols

- In rotation mode: To obtain the flow curve, four mixtures were sheared by an increasing gradient from 0.1 s^{-1} to 50 s^{-1} with a step of 10 s^{-1}. Rheometer records shear strain as a function of shear rate, then the plastic viscosity and yield stress were calculated from the Bingham model.

- In oscillation mode: To characterize the rheological behavior of a material, several test parameters must be defined to find out the linear viscoelastic domain: the critical strain γ_c and the rotation frequency f [14]. However, in order to observe the structuration, which takes place during the first minutes, the selected frequency in this research is 1Hz which is similar as that of Portland cement [16]. Then, the storage modulus G' and loss modulus G" were measured as a function of strain amplitude.
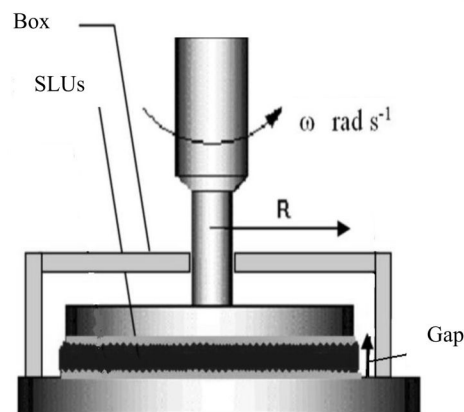
2.3 Characterization of raw materials

The binder of SLU consists of calcium aluminate cement (CAC), white Portland cement (PC) and calcium sulfate such as anhydrite (A) or α-hemihydrate (P). The chemical composition of these raw materials is shown in Table 1:

Table 1. *Chemical composition of different binders*

Raw materials	Principal oxides, wt%										
	Al_2O_3	CaO	SiO_2	Fe_2O_3	MgO	TiO_2	K_2O	Na_2O	SO_3	MnO	L.O.I
CAC	69,68	29,78	0,26	0,16	0,15	0,04	-	0,23	0,27	0,01	-
CEM I – 42,5	5,30	67,28	20,22	0,20	1,02	0,18	0,26	0,20	2,63	0,06	-
α-Hemihydrate	-	38,70	0,27	0,03	0,1	0.003	-	-	52,40	-	8,4
Anhydrite	-	42,69	-	0,07	0,05	0,002	-	-	56,83	0,006	3,9

The mineral composition of CAC and PC is presented in Table 2. The CAC composes mainly of calcium aluminate CA and CA_2 kind. The main composition of PC is C_3S, C_2S and C_3A.

Table 2. *Mineralogical compositions of CAC and PC*

Cement type	Percentage of phases, by weight %				
CAC	CA	CA_2	$C_{12}A_7$	C_2AS	$C_4A_3\$$
	57,70	37,50	0,35	0,65	1,07
CEM	C_3S	C_2S	C_3A	C_4AF	SO_3
	71,5	14,05	11,6	-	2,4

The skeleton of SLU composes of silica sand, slag and limestone fillers. The average diameter are presented in Table 3:

Table 3. *Average diameter of materials used in study*

Raw materials	Average diameter, D50/μm
Silica sand	88,19
Slag	11,95
Limestone filler	1,38 -24,96

2.4 Composition of self - leveling underlayment

The formulation of SLU based on ettringite binder is presented in Table 4:

Table 4. *Composition of self - leveling underlayment compound*

Raw materials		SLU mixtures	
		75CAC/25C\$H$_x$	90CAC/10C\$H$_x$
		%	%
BINDER + SKELETON	CAC	24.26	29.11
	C\$H$_x$	8.09	3.23
	CEM I - 42,5	3.97	3.97
	Silica Limestone filler Slag	33.41	33.41
ADMIXTURES	Superplasticizer Viscosity Modifying Admixture Shrinkage reducing admixture	5.46	5.46
	Retarder Accelerator	0.238	0.238
Water		24.57	24.57
Water/solid		0.326	
Total (%)		100	100

2 types of calcium sulfate: α-hemihydrate-$CaSO_4 0.5H_2O$ (P) and anhydrite-$CaSO_4$ (A) were used in the search. Thus the 4 compositions of 75CAC/25P; 75CAC/25A ; 90CAC/10P ; 90CAC/10A were studied.

3. Results and discussion

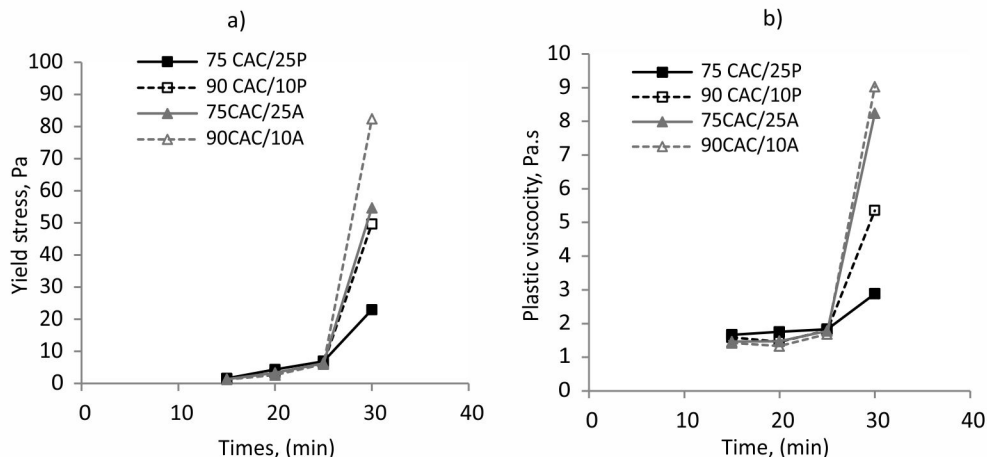### 3.1 Evolution of the yield stress and plastic viscosity

As mentioned above, SLUs can be considered as a fluid material, the Bingham model can describe rheological behavior of SLUs as equation (4):

$$\tau = \tau_o + \mu_p \cdot \dot{\gamma} \tag{4}$$

The results on the influence of the type and content of calcium sulfate to the development SLUs structuration versus time (yield stress and plastic viscosity) is shown in table 5 and Fig. 4:

Table 5. Yield stress and plastic viscosity of four mixtures versus time

Mixture	Time after mixing (minute)	τ_o (Pa)	μ_p (Pa.s)	R^2
75 CAC/25P	15	1.5876	1.666	0.9633
	20	4.38	1.7547	0.9756
	25	6.9335	1.8331	0.9683
	30	22.957	2.8844	0.8821
90 CAC/10P	15	1.5085	1.5866	0.9718
	20	3.2378	1.458	0.9800
	25	6.2366	1.7935	0.9692
	30	49.65	5.3531	0.9393
75CAC/25A	15	1.3419	1.4652	0.9760
	20	3.3197	1.4781	0.9792
	25	6.3211	1.7784	0.9682
	30	54.697	9.2385	0.907
90CAC/10A	15	1.2992	1.4206	0.9767
	20	2.6092	1.3302	0.9820
	25	6.0017	1.6873	0.9688
	30	82.418	9.0275	0.9035

Figure 4. Augmentation of yield stress and plastic viscosity versus time of SLU
a) Yield stress   b) Plastic viscosity

In these figures, two points could be clearly observed:

- From 15 to 25 minutes after mixing: the yield stress and plastic viscosity increase slightly and no difference for the four mixtures.

- From 25 to 30 minutes: the rapid increase in yield stress and plastic viscosity indicates suddenly changes in SLU structuration that increases inter-granular friction and strengthen the cohesion in ettringite binder system. At the same amount of calcium sulfate in the SLUs, the mixtures based on anhydrite seem to form structuration faster than the ones based on hemihydrate regardless of the calcium sulfate dosage. For the 75CAC/25C$Hx mixtures, a slower evolution of plastic viscosity and yield stress were observed.

After 30 minutes, these SLUs start the transition from the liquid state to the solid state and a setting period, the rheometer cannot apply shear rate as desired. Thus, the determination of viscosity and yield stress was stopped after 30 minutes from mixing the SLUs with water.

3.2 Monitoring structuration in dynamic mode

Before performing an oscillation test versus time, the determination of linear viscoelastic domain is required:

- The storage modulus G' of the four compositions were monitored by sweeping the deformation ranging from 2.10^{-5} (0.002%) to 1.10^{-4} (0.01%) at constant frequency f = 1Hz. The results of the evolution of dynamic rheological modulus (G', G'') are presented in Fig.5:
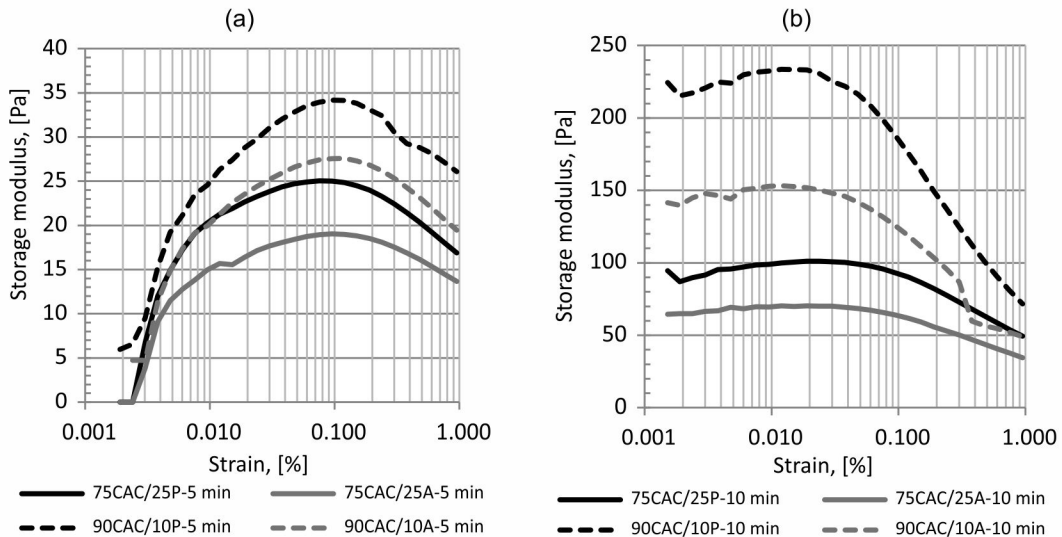
Figure 5. *Evolution of storage modulus depending on the deformation at the frequency f = 1Hz*
(a) 5 minutes after mixing; (b) 10 minutes after mixing

In Fig. 5, the storage modulus G' changes very fast with time. After 5 minutes of mixing, the results show the difficulty in determining the linear viscoelastic region. The value of the critical strain when the modulus G' starts to decrease is about 0.1%. This value is too large to follow the structuration of SLUs versus time. A second deformation sweep test is initiated 10 minutes after mixing. In this case, Fig. 5 (b) shows that the value of storage modulus G' is better established. The critical strain is about 0.02%, so the deformation of 0.01% (10^{-4}) is retained to monitor the structuration.

The storage modulus G' and loss modulus G'' of four compositions were followed by imposing a shear strain of 0.01% at a constant frequency f = 1Hz. The results relating to kinetics of these rheological modulus (G', G'') are shown in Fig 6.a, Fig 6.b and Fig 6.c:

Differences in kinetics of rheological modulus evolution are identifiable according to the nature of the calcium sulfate and its contents; these results are compatible with the results of rheology measurements (plastic viscosity and yield stress) mentioned above. The mixtures based on anhydrite seem harden faster than the compositions based on the hemihydrate regardless of the dosage of calcium sulfate. It is also noted that regardless of the nature of the calcium sulfate, the structuration is prolonged with increasing amount of calcium sulfate.

- The results in Fig 6.a and 6.b show that the evolution of storage modulus G', which describes the SLUs structuration, in oscillatory mode is similar to that of yield stress and plastic viscosity in rotation mode before 30 minutes of mixing. Afterwards, the storage modulus G' begins to increase rapidly after 30 minutes of mixing, then no longer increases with time (G' is about 3 MPa). While the loss modulus G'' in Fig 6.c from the beginning increases to a critical value, then it starts to go down. The peak of the loss modulus G'' indicates the maximum consumption energy and therefore, the maximum of the lost deformation energy.

- In Fig 6.d, the peak of the curve tan(δ) = G''/G' indicates the maximum ratio G''/G' and therefore the maximum value of lost energy and storage energy in the deformation. It is found that the peak of tan(δ) occurs at the moment where appears a sharp augmentation in the evolution of the loss modulus G'' and the storage modulus G' in about 30 minutes. Therefore, we can consider this peak tan(δ) as the initial signal related to the structuration. Before 20 minutes, the SLU remains in the liquid state. The cohesion between the particles is not important, the energy dissipated due to friction between particles is always low. Therefore, the plastic viscosity and yield stress of SLU increase quite slowly during the first 20 minutes. However, when the degree of hydration increases, the hydrates were formed the more and more as a function of time and strengthened the cohesion in the mixture of self-leveling compound, thus the viscosity of the matrix increases and results in a loss energy which becomes more and more important and reaches a maximum. Then this peak tan(δ) starts to decline after 30 minutes when the SLU becomes more elastic due to increasing amount of solid phases. We can deduce that the tan(δ) also provides us the hydration kinetics of the self-leveling underlayments and the transition of SLU from the liquid state to the solid state.

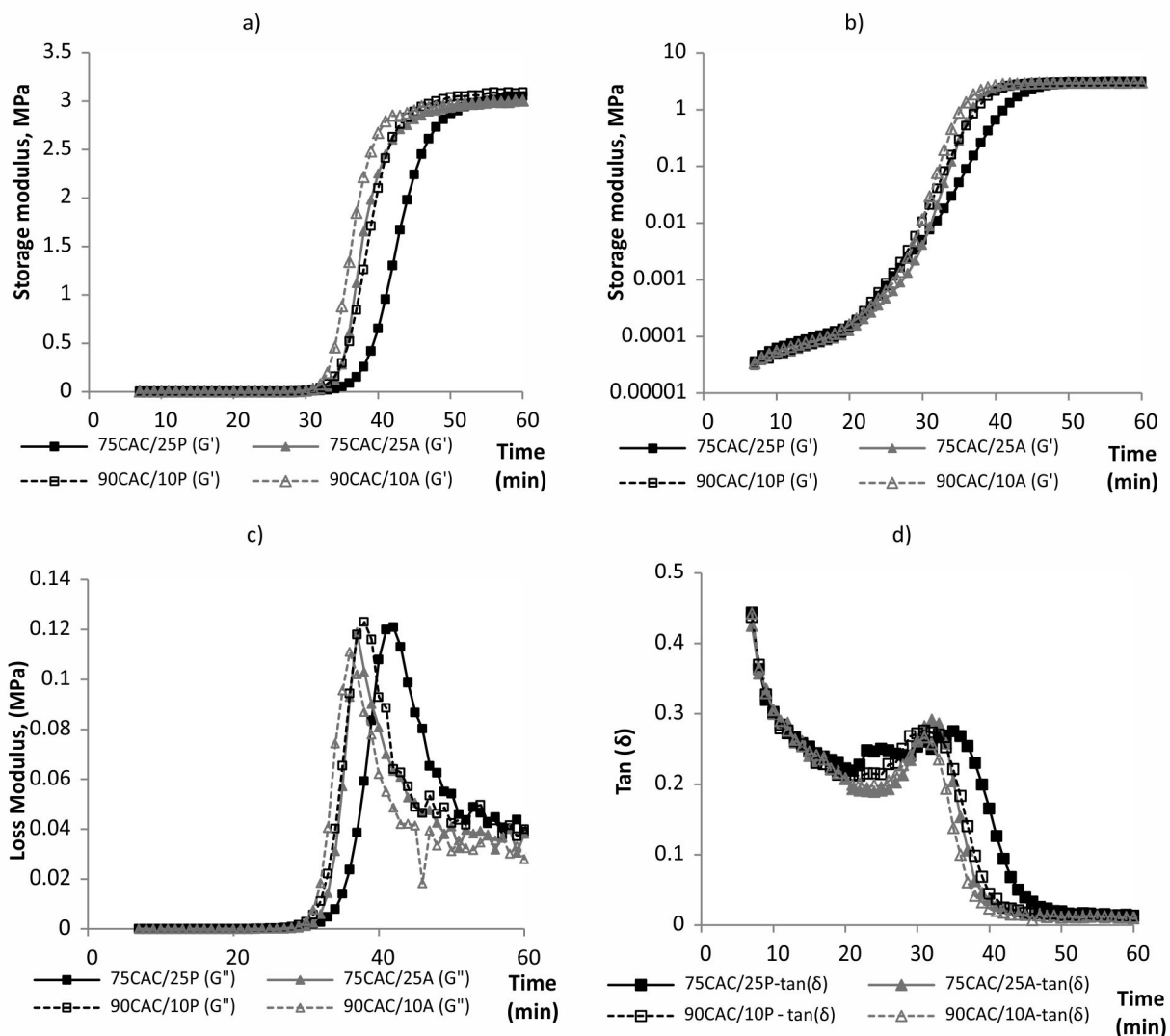**Figure 6.** *Evolution of rheological modulus versus time*
a)Storage modulus G' on a linear scale   b) Storage modulus G' on a log scale
c) Loss modulus G"   d) Tan (δ))=G"/G'

4. Conclusions

The evolution of the rheological properties at early age of self - leveling underlayment until setting by detecting continually the changes in the structuration was studied, some conclusions can be withdrawn as follows:

- At the same amount of calcium sulfate in the SLUs, the rheological parameters such as yield stress, plastic viscosity, storage modulus G' and loss modulus G" of the mixtures based on anhydrite develop faster than the ones based on hemihydrate regardless of the calcium sulfate content. For the 75CAC/25C\$H$_x$ mixtures, a slower evolution of plastic viscosity and yield stress were observed.

- Structuration of the mixtures based on anhydrite or compositions 90CAC/10C\$H$_x$ takes place faster than the composition 75CAC/25C\$H$_x$ or the compositions containing hemihydrate.

- By using rheometer in rotation mode, the transition from liquid state to solid state of SLU was determined, that was the moment after 30 minutes of mixing. This result is suitable to the result achieved by oscillation mode. The peak of tan(δ) after mixing 30 minutes begins to decrease, this moment corresponds to a increasing amount of solid phases and a simultaneous increase in the storage modulus G' and the loss modulus G" which reflects the hardening of the SLU.

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